Hydrogeochemical quality and suitability studies of groundwater in northern Bangladesh

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Abstract

Agriculture, rapid urbanization and geochemical processes have direct or indirect effects on the chemical composition of groundwater and aquifer geochemistry. Hydro-chemical investigations, which are significant for assessment of water quality, were carried out to study the sources of dissolved ions in groundwater of Dinajpur district, northern Bangladesh. The groundwater samplish were analyzed for physico-chemical properties like pH, electrical conductance, hardness, alkalinity, total dissolved solids and Ca^{2+}, Mg^{2+}, Na^+, K^+, CO_3^{2-}, HCO_3^-, SO_4^{2-} and Cl^- ions, respectively. Based on the analyses, certain parameters like sodium adsorption ratio, soluble sodium percentage, potential salinity, residual sodium carbonate, Kelly's ratio, permeability index and Gibbs ratio were also calculated. The results showed that the groundwater of study area was fresh, slightly acidic (pH 5.3-6.4) and low in TDS (35-275 mg l^{-1}). Ground water of the study area was found suitable for irrigation, drinking and domestic purposes, since most of the parameters analyzed were within the WHO recommended values for drinking water. High concentration of NO_3^- and Cl^- was reported in areas with extensive agriculture and rapid urbanization. Ion-exchange, weathering, oxidation and dissolution of minerals were major geochemical processes governing the groundwater evolution in study area. Gibb's diagram showed that all the samples fell in the rock dominance field. Based on evaluation, it is clear that groundwater quality of the study area was suitable for both domestic and irrigation purposes.

Introduction

Groundwater is the most essential prerequisite for increasing crop production as well as for sustainable agricultural development. Availability of groundwater for irrigation has contributed to manifold increase in crop productivity in Bangladesh. Increasing population, food insecurity, growing economy and poor water management are exerting unprecedented pressure on the world's freshwater resources (UNCSD, 2012). The use of groundwater to surface water is much higher in northwestern districts of Bangladesh as compared to other parts of the country. All rivers and cannels of the area dry up during dry season and force the people to completely depend on groundwater (Shahid, 2008; Shahid and Behrawan, 2008). As per Barind Multipurpose Development Authority (BMDA), the ground water level has declined substantially during the last decade threatening the sustainability of water use for irrigation and in other sectors in the region (Jahan *et al*., 2010). Although, ground water dominates the total irrigated area, its sustainability is at risk in terms of quantity in the northwest region (Simonovic, 1997; Shahid, 2011). Frequent shortage of water in the region has adversely affected the economic, social and environmental sphere (Sajjan *et al*., 2002). Availability of water is also decreasing owing to variation in rainfall (climate change), rapid

increase in population , increased environmental degradation, pollution of rivers and draining of wetlands (WRC, 2008; Ackah *et al*., 2011).

The rapid and unplanned expansion of groundwater-based irrigation has resulted in a complex set of drawdown externalities including aquifer depletion, migration of low quality water, land subsidence and loss of environmental services (Burke and Moench, 2000; Morris *et al*., 2003). The recharge rates in some regions are lower than abstraction rates. This limits future carrying capacity, economic potential and overall human development, and negatively affects the overall ecosystem. In addition, contamination of aquifers by percolation and accumulation of agro-chemicals can prove irreversible. Exploitation of groundwater over years for municipal, industrial and agricultural purposes, without proper attention to its management and protection is cause for concern. While there have been economic gains from groundwater consumption, it is evident that current withdrawals are not sustainable, and could in fact jeopardize the productivity benefits thus far achieved. Abstraction of shallow fresh groundwater leaves a residual of inferior water quality. This could be due to chemical percolation from land surface, confining aquifers, or adjacent aquifers that contain saline or contaminated water.

Hydrologic interactions between groundwater and surface water are forcing us to examine these two resources in a more integrated manner. For example, groundwater is recharged by surface water percolation, and the baseflow of perennial streams is maintained by groundwater discharge. Groundwater storage further changes diurnally due to evaporation via vadoze zone, and transpiration by phreatophytes (Sophocleous, 2010). Contamination of shallow groundwater, particularly through irrigation, has been well documented and studied for many decades (George, 1987). Recently, there has been widespread public health concern about the contamination of wells and drinking supplies by heavy metals occurring either through mobilization in the parent geologic materials, or through leachate percolation from landfill sites. The extent and severity of arsenic poisoning of well water in countries such as China, Bangladesh, India and Nepal has been reported by several researchers (Smith *et al*., 2000; Harvey *et al.*, 2002; Chakraborti *et al*., 2003; Safiullah, 2006; Johnston and Sarker, 2007; Neumann *et al*., 2010;). Abu Fazal *et al*. (2001) hypothesized that enhanced irrigation is perhaps one of the cause of arsenic contamination of shallow groundwater, through the process of pyrite oxidation. As water table is lowered by irrigation tubewells, arseno-pyrite oxidized in the vadoze zone releases arsenic. In subsequent recharge, iron hydroxide releases arsenic into the groundwater. The disastrous effect of arsenic on human from such contaminated wells is well documented (Smith *et al*., 2000; Chiou *et al*., 2001; Milton *et al*., 2005). Therefore, the present research was undertaken to assess the natural hydro-geological and geochemical processes of groundwater resource, important for a

comprehensive understanding of vulnerability of aquifers to pollution as well as the suitability of groundwater for different uses.

Materials and Methods

Location, climate and geological setting : The study area is located (25° 48' to 26° 04'N, 88° 30' to 88° 42' E) in Birgonj Upazilla in the northern part of Bangladesh, covering approximately 413 km^2 (Fig.1). Bangladesh has a tropical monsoon climate characterized by heavy seasonal rainfall, high temperature and humidity. The average rainfall during monsoon ranges from 1194 mm to 3454 mm. The lithology of most northern region of Bangladesh, especially the 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 upper aquifer, main aquifer and deep aquifer
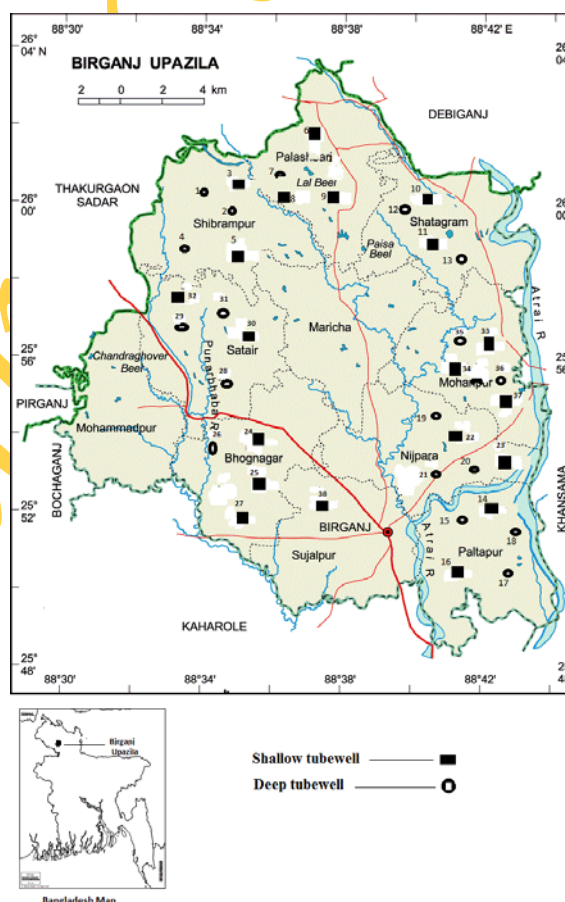

Fig. 1 : Map of the sampling sites of the Birgonj Upazilla (20 shallow tubewell and 18 deep tubewell; total 38) under the District of Dinajpur along with the map of Bangladesh. Map used here is available in Google software program (Coutesy: Google.com)

(UNDP, 1982). The water samples were collected from main aquifer. It is the main water bearing zone and occurs at depths ranging less than 5 m in northwest region of Bangladesh. This aquifer is either semi-confined or leaky, and consists of stratified interconnected, unconfined water bearing zones. The aquifer comprises of medium and coarse grained sediments, at places inter-bedded with gravel (UNDP, 1982). These sediments occur upto 140 m depth, below ground surface.

Collection of water samples and sampling techniques : Well water samples were collected in March and April 2012 during the time period when groundwater level is generally low relative to other seasons of the year. A total of thirty eight (18 deep tubewell and 20 shallow tubewell) samples were collected from various locations (Table 1). Samples were collected in 2 l sterilized plastic bottles and analyzed in the Department of Agricultural Chemistry, Hajee Mohammad Danesh Science and Technology University, Dinajpur.

Most the wells were being used for irrigation, industrial and domestic water supply, and were being pumped during the sampling period therefore purging mostly lasted for 5-10 minute.

Table 1 : Information regarding of sampling sites of the Birgonj Upazilla under the District of Dinajpur, Bangladesh; location, well type, depth, and the duration of uses

Sample No.	Sampling sites Location	Union (Small administrative unit)	Depth of sink (m)	Type of Well	Duration of use (year)
1	Deuli	Shibrumpur	70	DTW	8
2	Dhanga	Shibrumpur	85	DTW	13
3	Gonopoit	Shibrumpur	35	STW	5
4	Milanpur	Shibrumpur	95	DTW	9
5	Modonshekho	Shibrumpur	60	STW	6
6	Brammonvita	Polashbari	55	STW	3
7	Dhulauri	Polashbari	100	DTW	9
8	Polashbari	Polashbari	45	STW	6
9	Jhuljhuli	Polashbari	40	STW	4
10	Rangalipara	Shotogram	42	STW	6
11	Jharbari	Shotogram	48	STW	4
12	Proshadhpara	Shotogram	90	DTW	10
13	Fekadhangi	Shotogram	110	DTW	8
14	Shadulahpara	Paltapur	36	STW	5
15	Raghunathpur	Paltapur	120	DTW	10
16	Kajal	Paltapur	40	STW	3
17	Vogdoma	Paltapur	110	DTW	15
18	Shatalpara	Paltapur	105	DTW	8
19	Nokhapara	Nijapara	86	DTW	11
20	Dariapur	Nijapara	105	DTW	6
21	Jaliapara	Nijapara	95	DTW	12
22	prembazar	Nijapara	36	STW	5
23	Kollani	Nijapara	45	STW	4
24	Chokropur	Vognogor	25	STW	7
25	Doulotpur	Vognogor	45	STW	6
26	Kalitola	Vognogor	84	DTW	9
27	Mashboil	Vognogor	45	STW	5
28	Shealkhedha	Shatar	100	DTW	11
29	Shingodhani	Shatar	75	DTW	10
30	Dakeshshori	Shatar	34	STW	7
31	Chopokoria	Shatar	65	DTW	13
32	Shatar	Shatar	45	STW	4
33	Tulshipur	Mohonpur	40	STW	7
34	Matiakhura	Mohonpur	35	STW	7
35	Laterhat	Mohonpur	80	DTW	10
36	Krishnonogor	Mohonpur	95	DTW	11
37	Kashipur	Mohonpur	45	STW	5
38	Badiapara	Shujalpur	35	STW	8

STW=Shallow tubewell, DTW= Deep tubewell

The samples earmarked for ion analysis were filtered at site through 0.45 µm cellulose filters by a hand operated vacuum pump. The bottles and caps meant for collecting major ions were rinsed three times with filtered water after which they were filled to the brim and caped. Samples for cations analysis were preserved with few drops of nitric acid to maintain pH < 2. All the samples were kept in an ice chest containing ice blocks and transported to the laboratory for further analysis.

Analytical procedures : Groundwater samples collected were analyzed for pH, EC, TDS, Ca^{2+}, Mg^{2+}, Na^+, K^+, Zn^{2+}, Cu^{2+}, Mn^{2+}, Fe^{3+}, PO_4^{3-}, As^{3+}, CO_3^{2-}, HCO_3^-, SO_4^{2-}, NO_3^- and Cl^- ions following the standard methods of APHA (2005). The pH and electrical conductivity (EC) were measured electrometrically (APHA, 2005) while TDS was measured by drying and weighing method. Ca^{2+} and Mg^{2+} ions were analyzed by complexometric titration. Alkalinity was measured by measuring the amount of acid (hydrochloric acid) required to bring the sample to pH 4.5. K^+ and Na^+ ions were estimated by flame emission spectrophotometry. SO_4^{2-} was determined turbidimetrically. CO_3^{2-} and HCO_3^- were analyzed titrimetrically. Chloride was estimated by argentometric titration and PO_4^{3-} and NO_3^- were determined colorimetrically (APHA, 2005). Zn^{2+}, Cu^{2+}, Mn^{2+} and Fe^{3+} ions present in the groundwater were analyzed by atomic absorption spectrophotometer in the Soil Resources Development Institute, Dinajpur, Bangladesh. Arsenic was determined by atomic absorption spectrophotometer equipped with hydride generator. A Perkin–Elmer Analyst 100 atomic absorption spectro photometer equipped with FIAS-100-flow injection hydride generation system was used for estimation of arsenic. All samples for arsenic determination were pre-reduced with concentrated HCl (1 ml), 5 % KI and ascorbic acid mixture prior to hydride generation. The ion-balance-error was computed, taking the relationship between total cation (Ca^{2+}, Mg^{2+}, Na^+ and K^+) and total anions (HCO_3^-, Cl^-, SO_4^{2-}) for each set of complete analysis of water samples. Only samples which fell within ±5% were reported in this work.

Equations used in calculating water class rating parameters : The suitability of groundwater for specific purpose depends on the criteria or standard set for that purpose. The following formulae related to irrigation water classes rating were used to classify water samples using chemical data.

Sodium Adsorption Ratio (SAR)

$$SAR = \frac{Na^+}{\sqrt{\dfrac{Ca^{2+} + Mg^{2+}}{2}}}$$

Soluble Sodium Percentage (SSP)

$$SSP = \frac{\text{Soluble Na concentration (meq l}^{-1})}{\text{Total cation concentration (meq l}^{-1})} \times 100$$

Residual Sodium Carbonate (RSC)

$$RSC = (CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+})$$

Hardness or Total Hardness (H_T)

$$H_T = 2.5 \times Ca^{2+} + 4.1 \times Mg^{2+} \text{ (Freeze and Cherry, 1979)}$$

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

$$\text{Permeability Index (P.I.)} = \frac{Na^+ + \sqrt{HCO_3^-}}{Ca^{2+} + Mg^{2+} + Na^+}$$

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

Gibbs Ratio I (for anion) = $Cl^- / (Cl^- + HCO_3^-)$

Gibbs Ratio II (for cation) = $Na^+ + K^+ / (Na^+ + K^+ + Ca^{2+})$

where concentrations of ionic constituents for calculating all parameters are in meq l^{-1} except hardness (mg l^{-1}).

Results and Discussion

Ionic composition of water samples : The result of physico-chemical composition of groundwater samples analyzed is presented in Table 2 and 3. The pH of water samples ranged between 5.3 to 6.4 revealing acidic nature of groundwater. Several important properties of water such as suitability of groundwater for domestic and commercial use and the ability of water to transport potentially harmful chemicals are determined by pH. The EC and TDS values ranged between 60 to 430 µS cm^{-1} and 35 to 275 mg l^{-1}, respectively. The EC values differed distinctly in groundwater samples collected from different sampling sites. Electrical conductivity is one of the most indirect and convenient method used to test water. Hardness varied between 52 to 428 mg l^{-1} in groundwater samples analyzed. Most of the natural water contain substantial amount of dissolved carbon dioxide, which is the principal source of alkalinity. An increase in temperature or decrease in the pressure reduces the solubility of CO_2 in water. In the present study, alkalinity ranged between 12 and 58 mg l^{-1}. High level of alkalinity in water samples may also be due to the presence of carbonaceous stuff and dolomites, while high TDS level in groundwater might be due to the presence of dissolved bicarbonate, chloride and sulfate compounds containing Ca^{2+}, Mg^{2+}, Na^+ and K^+ ions (Karanth, 1994). The order of abundance of major ions in groundwater samples was found in the following order: $Mg^{2+} > Ca^{2+} > Na^+ > K^+ = Cl^- > HCO_3^- > NO_3^- > SO_4^{2-}$ (Table 2). Ca^{2+} and Mg^{2+} were major cations present in groundwater samples ranging between 0.38 to 1.46 meq l^{-1} and 0.65 to 2.45 meq l^{-1}, respectively. Na^+ and K^+ ions ranged between 0.35 to 1.15 meq l^{-1} and 0.035 to 0.65 meq l^{-1}, whereas K^+ ions were found in lower concentration than Na^+ concentration. Comparing the relative concentration of major cations in water samples, Na has always been found to be in high concentration than K due to its more

abundance in the host rocks, and K-minerals in primary volcanic parageneses are more resistant to weathering than Na-minerals; moreover K^+ is easily stabilized in neo-formation minerals (clay minerals). The abundance of Mg^{2+} over Ca^{2+} may probably be due to its presence in the outcropping rocks. The agricultural application of fertilizer may be a possible source of Cl^- level in groundwater which ranged between 0.20 to 3.30 meq l^{-1}, respectively. An appreciable amount of HCO_3^- ranging between 0.80 to 2.60 meq l^{-1} was present in all the water samples, though CO_3^{2-} was negligible in most cases. NO_3^- and SO_4^{2-} concentration ranged between 3.68 to 7.00 mg l^{-1} and 0.005 to 0.35 meq l^{-1}, respectively. The concentration of Fe^{3+}, Mn^{2+} and As^{+5} in water samples varied from 0.001 to 0.384 mg l^{-1}, 0.1 to 0.62 mg l^{-1} and 0.01 to 0.042 mg l^{-1}, respectively. Kelly's ratio, potential salinity and permeability index calculated for the groundwater samples varied between 0.12 to 0.49, 0.21 to 3.30 and 0.52 to 0.91, respectively (Table 3).

Compositional relations of groundwater : The compositional relation among dissolved ions can be used to assess the origin of solutes and the processes that results in water compositions. Since Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, Cl^-, SO_4^{2-} and NO_3^- ions were major ions analyzed in groundwater samples, an examination of their stoichiometric relation could account for their source of origin. The Na-Cl relationship has often been used to identify the mechanisms for acquiring salinity and saline intrusions (Jalali, 2007). Most of the groundwater samples in the present study had Na^+:Cl^- ratio <1, while few had Na^+:Cl^- ratio equal to one (Fig. 2c). A ratio equal to one is sometimes attributed to dissolution of NaCl while Na^+:Cl^- ratio greater than one might reflect release of Na^+ from silicate weathering (Meyback, 1987). A non-significant correlation ($r=0.69$) existed between Na^+ and Cl^- indicating similar source of origin (Table 5). Low concentration of Cl^- in groundwater suggests that dissolution of halite is not important for regulating Na^+ level in groundwater (Jalali, 2007); while increase in alkali metals with simultaneous increase in Cl^- ion reflect a common source of origin for these ions (Datta and Tyagi, 1996).

Among anions, HCO_3^- and Cl^- are often dominant anions present in groundwater. Precipitation of salts can decrease HCO_3^- level and thereby anions in groundwater are dominated by Cl^-. Precipitation of $CaCO_3$ might decrease Ca^{2+} concentration, supporting the present findings of high Na^+ level in groundwater. As a result, Mg^{2+}:Ca^{2+} ratio was found to be > 1 in the groundwater as seen in Fig. 2e. Krishna *et al.* (2009) proposed that source of major cations such as Ca^{2+} and Mg^{2+} in groundwater may result due to weathering of calcium and magnesium minerals. Yousaf *et al*. (1987) reported that Na^+ hazard can be high, where groundwater is dominated by $Na^+ + Mg^{2+}$ ions rather $Na^+ + Ca^{2+}$ ions. High concentration of Na decreases the hydraulic conductivity of soil/weathered materials, thus reducing the drainage conditions. HCO_3^- : Na^+ ratio can also be used to assess the weathering process (Krishna *et al.,* 2009; Suba Rao, 2008) that occurs in groundwater. HCO_3^- : Na^+ ratio >1 (Fig. 2d) results in carbonate weathering, while a ratio <1 indicate occurrence of silicate weathering. In the present study, all the groundwater samples had a ratio of Ca^{2+}: $HCO_3^- + CO_3^{2-}$ and Mg^{2+}: $HCO_3^- + CO_3^{2-}$ > 1, while Na^+: $HCO_3^- + CO_3^{2-}$ ratio was equal to 1 suggesting the predominance of Ca and Mg containing minerals over Na-containing minerals at study sites (Fig. 2f and Fig. 2d). As a result, $Ca^{2+} + Mg^{2+}$: total cation ratio in most of the water samples were >1 or approaching unity while $Na^+ + K^+$: total cations ratio was far below unity (Fig. 2a, b). $Ca^{2+} + Mg^{2+}$ versus HCO_3^- plot (Fig. 2f) fell above the equiline (1:1), suggesting that excess alkalinity in water was balanced by alkali ($Na^+ + K^+$) metals. Furthermore, all the sampling points were found approaching equiline in $Ca^{2+} + Mg^{2+}$: TC (total cations) plot**.** This emphasized a low contribution of alkalis metals to major ions chemistry. In $Na^+ + K^+$: TC plot (Fig. 2a), most of the samples fell far below the equiline. This infers that the supply of cations via silicate weathering and/or soil minerals

Table 2 : pH, EC, TDS, hardness, and anionic constituents of groundwater during the study period

	pH	EC μScm^{-1}	TDS mgl^{-1}	Hardness mgl^{-1}	Alkalinity (mgl^{-1} as $CaCO_3$)	HCO_3^- $meql^{-1}$	Cl^- $meql^{-1}$	SO_4^{-2} $meql^{-1}$	NO_3^- mgl^{-1}	PO_4^{3-} mgl^{-1}
Min	5.3	60	35	52	12	0.80	0.20	0.005	3.68	0.008
Max	6.4	430	275	428	58	2.60	3.30	0.35	7.00	0.087
Mean	5.7	135	86	122	26	1.50	0.66	0.09	6.09	0.031
SD	0.20	93	62	79	11	0.44	0.59	0.08	0.80	0.016

Table 3 : Potential salinity (PS), permeability index (PI), Kelly's ratio and cationic constituents of groundwater during the study period

0	Ca^{2+} $meql^{-1}$	Mg^{2+} $meql^{-1}$	Na^+ $meql^{-1}$	K^+ $meql^{-1}$	Cu^{2+} mgl^{-1}	Zn^{2+} mgl^{-1}	Mn^{2+} mgl^{-1}	Fe^{3+} mgl^{-1}	As^{5+} mgl^{-1}	PS $meql^{-1}$	PI	Kelly's ratio
Min	0.38	0.65	0.35	0.035	0.001	0.021	0.10	0.001	0.010	0.21	0.52	0.12
Max	1.46	2.45	1.15	0.65	0.099	0.042	0.62	0.384	0.042	3.30	0.91	0.49
Mean	0.62	1.30	0.56	0.175	0.017	0.031	0.28	0.128	0.021	0.71	0.73	0.31
SD	0.21	0.47	0.15	0.12	0.02	0.01	0.12	0.11	0.008	0.58	0.10	0.09

dissolution is not significant.

Excess of Na$^+$ ion over K$^+$ ion observed in the present study was due to greater resistance of K$^+$ ions to chemical weathering and its adsorption on clay minerals. Climatic conditions affect the rate of evapotranspiration, hence, it is important to examine the contribution of evaporation as an effective indicator of concentration for further enrichment of dissolved ions in groundwater. Groundwater samples were plotted in Na$^+$/ Cl$^-$ ratio vs EC diagram, the points were found to spreads vertically (Fig. 3a). This means that the Na$^+$/ Cl$^-$ ratio might change significantly with increase in EC. Therefore, the

process of evapotranspiration, as suggested by Jankowski and Acworth (1997) might be the main cause of increase of Na$^+$ and Cl$^-$ ions concentration in groundwater. As study area has high rate of evapotranspiration characterized by tropical climate and restricted fresh water exchange, salt layers may form near the evaporating surface (Karanth, 1994). On the other hand, ongoing human activities in the adjoining areas of groundwater withdrawal might lead to change in the chemical composition of groundwater. For instance, intensive and long-term irrigation can leach salts from soil/weathered rock zone due to availability of water. Gibbs (1970) proposed a diagram to establish a relationship between water composition and aquifer lithological characteristics. Three

Table 4 : Quality classification of water samples for irrigation

SI No	EC μScm^{-1}	TDS mgl^{-1}	SAR	SSP	RSC	Water class based on					Alkalinity-salinity class
						EC	TDS	SAR	SSP	RSC	
1	130	72	0.70	28	-0.25	Ex	Fre	Ex	Good	Suit	C1-S1
2	230	150	0.69	24	-0.61	Ex	Fre	Ex	Good	Suit	C1-S1
3	110	77	0.35	24	-4.12	Ex	Fre	Ex	Good	Suit	C1-S1
4	110	64	0.71	26	-0.50	Ex	Fre	Ex	Good	Suit	C1-S1
5	90	55	0.51	21	-0.28	Ex	Fre	Ex	Good	Suit	C1-S1
6	350	217	0.58	23	0.02	Good	Fre	Ex	Good	Suit	C2-S1
7	375	263	0.53	21	0.03	Good	Fre	Ex	Good	Suit	C2-S1
8	70	39	0.42	17	-0.62	Ex	Fre	Ex	Ex	Suit	C1-S1
9	110	75	0.74	27	-0.15	Ex	Fre	Ex	Good	Suit	C1-S1
10	110	68	0.81	31	-0.31	Ex	Fre	Ex	Good	Suit	C1-S1
11	90	54	0.68	26	-0.62	Ex	Fre	Ex	Good	Suit	C1-S1
12	80	47	0.82	27	-0.55	Ex	Fre	Ex	Good	Suit	C1-S1
13	330	221	0.88	22	-1.81	Good	Fre	Ex	Good	Suit	C2-S1
14	60	38	0.44	14	-1.01	Ex	Fre	Ex	Ex	Suit	C1-S1
15	80	50	0.50	19	-0.46	Ex	Fre	Ex	Ex	Suit	C1-S1
16	70	41	0.63	26	-0.11	Ex	Fre	Ex	Good	Suit	C1-S1
17	110	63	0.38	15	-0.17	Ex	Fre	Ex	Ex	Suit	C1-S1
18	430	275	0.68	25	-0.03	Good	Fre	Ex	Good	Suit	C2-S1
19	100	70	0.48	20	-0.18	Ex	Fre	Ex	Ex	Suit	C1-S1
20	275	176	0.60	18	-1.55	Good	Fre	Ex	Ex	Suit	C2-S1
21	90	62	0.42	14	-0.71	Ex	Fre	Ex	Ex	Suit	C1-S1
22	80	51	0.38	14	0.00	Ex	Fre	Ex	Ex	Suit	C1-S1
23	90	51	0.58	19	-0.33	Ex	Fre	Ex	Ex	Suit	C1-S1
24	110	74	0.45	17	-0.63	Ex	Fre	Ex	Ex	Suit	C1-S1
25	150	102	0.38	14	-0.19	Ex	Fre	Ex	Ex	Suit	C1-S1
26	80	55	0.52	22	-0.17	Ex	Fre	Ex	Good	Suit	C1-S1
27	80	56	0.46	20	-0.56	Ex	Fre	Ex	Ex	Suit	C1-S1
28	90	58	0.67	25	-0.31	Ex	Fre	Ex	Good	Suit	C1-S1
29	60	35	0.42	15	-0.24	Ex	Fre	Ex	Ex	Suit	C1-S1
30	150	89	0.59	21	-0.41	Ex	Fre	Ex	Good	Suit	C1-S1
31	160	107	0.31	11	-0.67	Ex	Fre	Ex	Ex	Suit	C1-S1
32	90	60	0.77	29	-0.11	Ex	Fre	Ex	Good	Suit	C1-S1
33	120	70	0.78	30	-0.61	Ex	Fre	Ex	Good	Suit	C1-S1
34	110	75	0.41	18	-0.66	Ex	Fre	Ex	Ex	Suit	C1-S1
35	80	47	0.69	28	-0.47	Ex	Fre	Ex	Good	Suit	C1-S1
36	80	51	0.50	19	-0.44	Ex	Fre	Ex	Ex	Suit	C1-S1
37	110	74	0.78	32	-0.27	Ex	Fre	Ex	Good	Suit	C1-S1
38	80	49	0.60	24	0.17	Ex	Fre	Ex	Good	Suit	C2-S1

Ex = Excellent, Fre = Fresh, Suit = Suitable

distinct fields, namely precipitation dominance, evaporation dominance and rock dominance areas are shown in Gibbs diagram (Fig. 4). In the present study, Gibbs ratios for groundwater samples were plotted against their respective total dissolved solids to find out whether the ground water chemistry was due to rock dominance, evaporation dominance or precipitation dominance and it was observed that the samples fell into precipitation dominance area.

Cation-exchange : Several chemical processes, such as oxidation of ammonium and/or organic matters also influence the groundwater chemistry. Gimenez and Morell (1997) stated that cation exchange is a regulating factor of ionic concentration in water that play a role of temporary buffer when the ionic contents are variable, causing non-steady-state conditions. The exchangeable cations on exchange sites tend to compensate for variation in the chemical composition of waters, modifying considerably the cationic concentrations (Appelo and Postma, 1993). Increase in Na^+ concentration without an associated increase in Cl^- concentration can be explained by this process (Andre *et al.*, 2005). The evidence of ion exchange in development of salinization can lead to release of Na^+ ions from clay products replacing Ca^{2+} ions present in groundwater (Gibrilla *et al.*, 2010). Fig. 2h shows a plot between Na^+ and Ca^{2+} ions, the data plot on or above 1:1 line signified excess of Na^+ over Ca^{2+} ion, which might be due to the proximity of wells in clay horizons. Ion exchange process therefore may be responsible for higher concentration of Na^+ in groundwater. A graph was plotted between $Ca^{2+} + Mg^{2+} - HCO_3^- - SO_4^{2-}$ and $Na^+ - Cl^-$ in order to test the possibility that cation exchange significantly affects groundwater composition. $Na^+ - Cl^-$ represents the amount of Na^+ gained or lost relative to that provided by chloride salt dissolution (mostly halite dissolution), while $Ca^{2+} + Mg^{2+} - HCO_3^- - SO_4^{2-}$ represents the amount of Ca^{2+} and Mg^{2+} gained or lost relative to that provided by gypsum, calcite and dolomite dissolution. If these processes were

significant composition controlling process, relationship between these two parameters should be linear with a slope of -1. Fig. 3f shows an increase in Na^+ related to a decrease in $Ca^{2+} + Mg^{2+}$ or an increase in $HCO_3^- + SO_4^{2-}$. Data plots were found close to straight line ($r^2 = 0.91$) with a slope of -0.81 indicating that Na^+, Ca^{2+} and Mg^{2+} participated in the ion exchange reaction (Andre *et al.*, 2005).

Weathering : Kim *et al.* (2004) reported that mineral weathering is the major process affecting groundwater chemistry if 1:1 ratio is maintained between total cation and alkalinity. Feldspar and carbonates are important minerals regulating the chemistry of natural waters from the standpoint of reactivity and abundance in the earth's crust (Bowser and Jones, 1993). Carbonate minerals, such as calcite and dolomite, also influence the water chemistry if present in the geological material because their dissolution rates are up to six orders of magnitude faster than those of alumino-silicate minerals (Lasaga, 1984). As a result, 1:1 relationship between total cation and alkalinity indicates the influence of mineral weathering on water chemistry. Relationship between total cation and alkalinity is shown in Fig. 3b. The samples were far away to the 1:1 mineral dissolution lines with $r^2 = 0.82$, indicating that dissolution of minerals in groundwater is not an important geochemical process governing the chemistry of the groundwater in the study area.

Oxidation process : Several chemical processes, such as oxidation of ammonium and/or organic matters also influence the groundwater chemistry. Oxidation process is one of the suggested reasons for deviation from the mineral dissolution lines. Oxidation of ammonium and organic matter increases NO_3^- concentration by decreasing alkalinity and therefore, the concentration of total cation becomes unbalanced due to alkalinity. Cl^- salts also causes upward deviation from mineral dissolution line by supplying additional cations without changing alkalinity. Therefore, total cation concentrations were corrected

Table 5 : Correlation matrix of different chemical constituents of groundwater with depth, n=38, units of each parameter are in Table 2 and Table 3

	Depth	EC	TDS	Cl^-	HCO_3^-	SO_4^{2-}	NO_3^-	Ca^{2+}	Mg^{2+}	Na^+	K^+	SAR	SSP	H_T
Depth	1.00													
EC	0.37	1.00												
TDS	0.37	1.00	1.00											
Cl^-	0.31	0.27	0.27	1.00										
HCO_3^-	0.09	0.07	0.07	-0.22	1.00									
SO_4^{2-}	0.00	-0.04	-0.05	-0.20	0.37	1.00								
NO_3^-	-0.47	-0.29	-0.28	-0.09	-0.02	0.16	1.00							
Ca^{2+}	0.24	0.21	0.20	0.56	0.25	-0.06	-0.12	1.00						
Mg^{2+}	0.23	0.09	0.10	0.33	0.70	0.37	0.10	0.23	1.00					
Na^+	0.24	0.30	0.29	0.69	-0.09	0.03	-0.18	0.47	0.12	1.00				
K^+	0.23	0.35	0.37	0.72	0.10	-0.11	-0.15	0.42	0.41	0.36	1.00			
SAR	0.13	0.21	0.19	0.41	-0.43	-0.06	-0.12	0.12	-0.29	0.82	-0.01	1.00		
SSP	-0.09	0.06	0.01	0.05	-0.60	-0.17	-0.13	-0.13	-0.67	0.54	-0.30	0.84	1.00	
H_T	-0.14	-0.03	-0.03	-0.03	0.27	-0.22	-0.01	0.24	0.09	0.08	-0.13	0.05	0.01	1.00

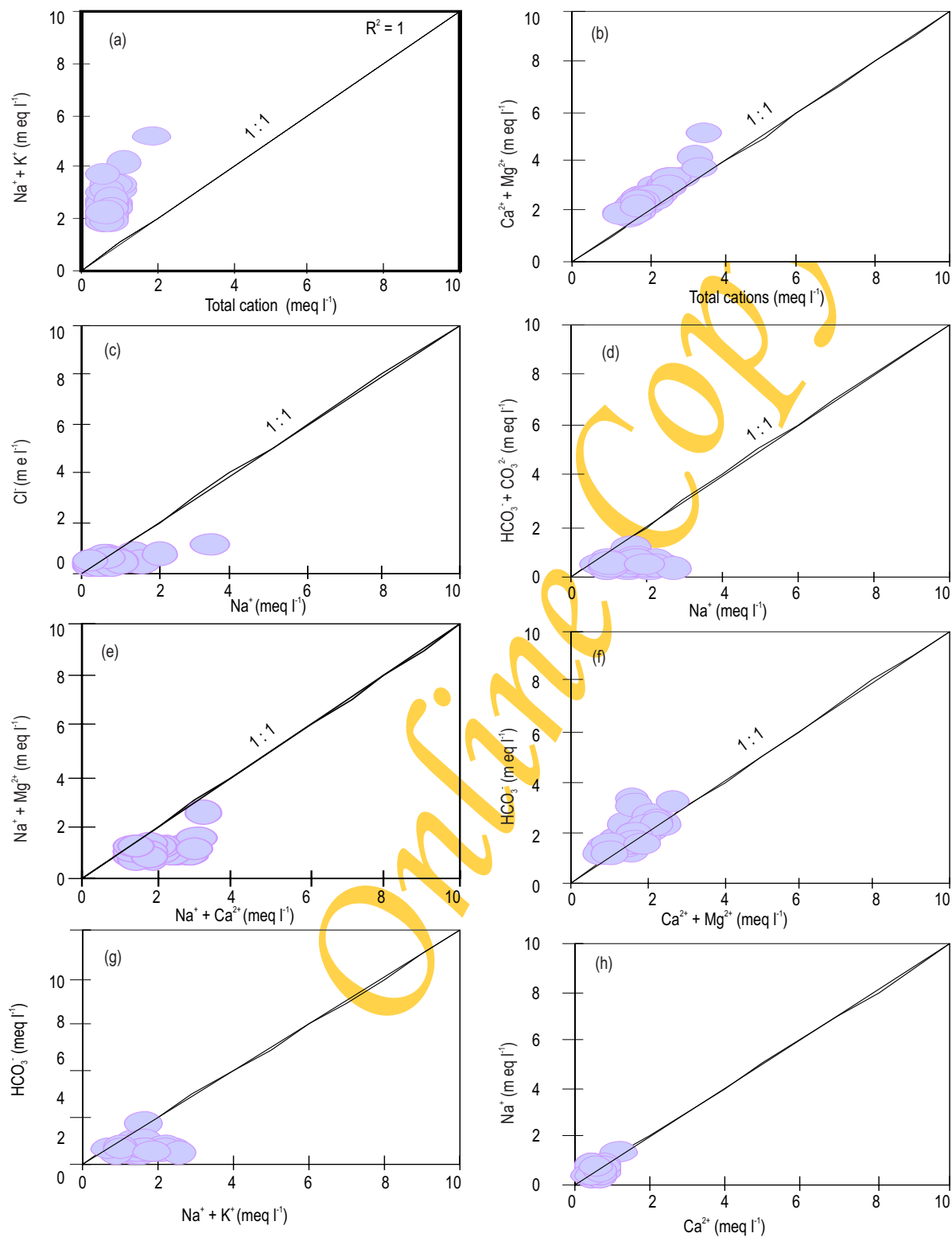Italic values are significant at *p* =0.05 where r e" 0.32

Fig. 2 : Ratios of the major anions and cations in groundwater from Birgonj Upazilla, Bangladesh
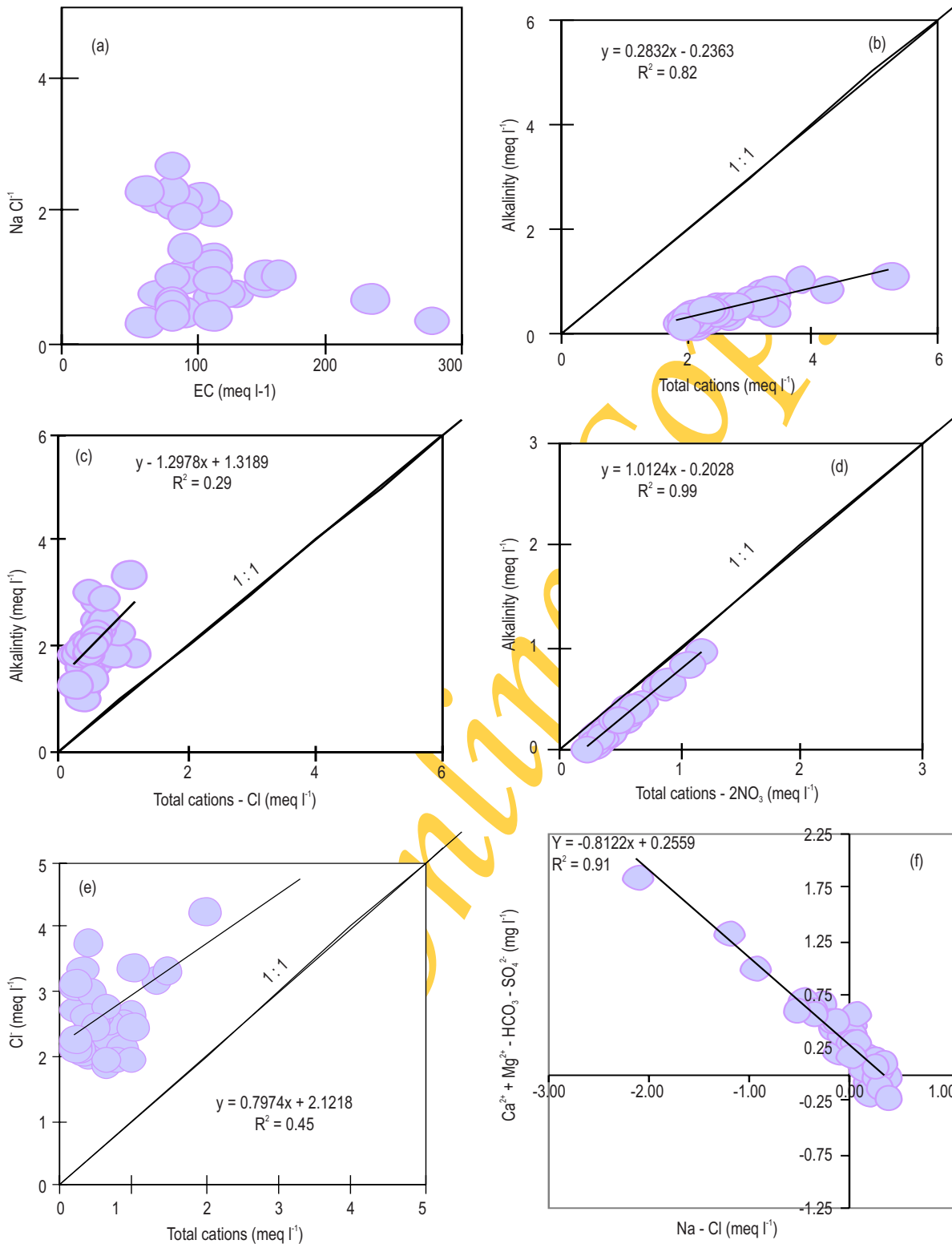
Fig. 3. Scatter plots, correlations and ratios of the major water quality parameters of Birgonj Upazilla, Bangladesh.

for evaluating the effect of ammonium oxidation and Cl⁻salt.

Chloride concentration was subtracted from total cation concentration to correct the influence of Cl-salt (Kim *et al*., 2004). Fig. 3e shows that total cation correction made the relationships more linear with respect to alkalinity and the samples showed a closer relationship to the mineral dissolution lines with r^2 = 0.45. For correction of ammonium oxidation, it was assumed that NO_3^- is derived from ammonium oxidation (nitrification) only. Hence, ammonium oxidation requires two equivalents of alkalinity to generate an equivalent of NO_3^-, so twice the amount of NO_3^- concentration was subtracted from total cation to correct the anthropogenic effect (Kim *et al*., 2004). Results showed that there was a close linearity when NO_3^- correction was made (r^2 = 0.99) indicating that not all the samples were influenced by this factor. It also emphasized that nitrification may not only be the major source of NO_3^- in groundwater, but other sources such as fertilizers may also contribute NO_3^- in agricultural areas.

Suitability for irrigation based on pH, EC, SAR and SSP : The pH of groundwater ranged between 5.3-6.4 with a mean value of 5.7. High acidic condition can be attributed to the activities occurring in unsaturated zone which might affect the groundwater before recharge since these areas are characterized by intensive agricultural activities. Irrigation water quality can have profound impact on crop production. The major factors that influence the substrate solution pH during plant production are as follows: pre-plant materials such as dolomitic limestone used into the substrate and substrate components themselves; alkalinity of irrigation water; acidity / basicity of fertilizers used during production and the growing plant species. With few exceptions, all the groundwater samples were suitable for irrigation, according to the results of pH, as the acceptable pH for agricultural use ranges between 6.0 to 8.5 (Ayers and Westcot, 1985).

High concentration of salts in irrigation water makes the soil saline and also affects the salt uptake capacity of plants through roots. In the present study, a significant variation observed in EC values in groundwater is in confirmation with the EC values reported in groundwater of Nepal (Chapagain *et al*., 2009). Table 4 shows that out of 38 water samples analyzed, 5 were rated as 'good' and 33 as 'excellent' for irrigation purposes based on Wilcox requirement. Accumulation of salts in roots of plant occur in two ways either by the upward movement of shallow saline-water table or left over salts in the soil due to insufficient leaching (Grattan, 2002). According to Richards (1968), irrigation water has been classified as C1S1 with six C2S1 categories. C1 indicates 'low' salinity (EC < 250 μS cm⁻¹), C2 indicates 'medium' salinity (EC= 250-750 μS cm⁻¹) and S1 indicates 'low sodium' with respect to SAR. Irrigation with C1 and C2 class water is unlikely to affect the osmotic pressure of soil solution and cell sap of crop plants. However, irrigating soil with saline water for a longer time may reduce crop yield due to accumulation of salts in plant roots

(Jahidul *et al*., 2010). As total concentration of salts increase into the saline sodic range, concentration of Ca^{2+} is adequate for most plants and osmotic effect begins to predominate. However, some species are susceptible to salinity induced by Ca^{2+} deficiencies. Some cultivars of corn, sorghum, rice, wheat and barley exhibit severe Ca^{2+} deficiency at high $Na^+:Ca^{2+}$ ratio (Grieve and Fujiyama, 1987). Excess Na^+ level in water may change the properties of soil and reduce permeability of soil. Hence, it is essential to assess Na^+ ion concentration in groundwater before using it for irrigation. Plants uptake water from soil by osmosis and the osmotic pressure in roots is proportional to salt content, which affects the growth of plants, soil structure and permeability (Gupta *et al*., 2009). The degree to which irrigation water tends to enter the cation-exchange reactions in soil can be indicated by sodium adsorption ratio. The exchange or replacement of Na+ ions by Ca^{2+} and Mg^{2+} ions is hazardous as it damages the soil structure by making it compact and impervious. SAR is an important parameter studied to determine suitability of irrigation water as it is responsible for sodium hazard (Todd and Mays, 2005). With respect to SAR values, all the groundwater samples were classified as excellent (S1) for irrigating crops and did not produce negative effect on soil quality (Table 4). A low EC value and high SAR means there is a high potential for permeability or water
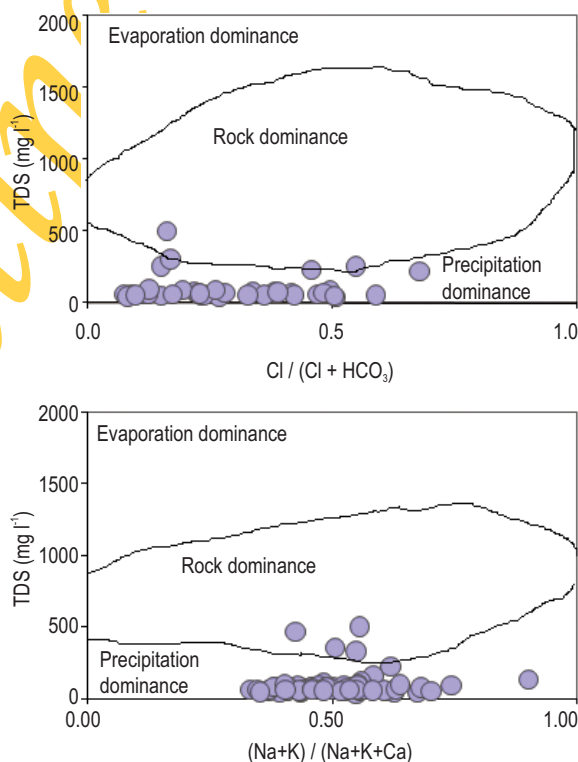

Fig. 4 : Mechanisms controlling the quality of groundwater of Birgonj Upazilla (Gibbs, 1970)

infiltration problems. They can act separately or collectively to disperse soil aggregates, which in turn reduces the number of large pores in the soil. These large pores are hence responsible for aeration and drainage (Grattan, 2002).

Soluble sodium percentage (SSP) is another important criterion for soil physical properties and can affect plant growth. Among the groundwater samples analyzed, 16 were rated as 'excellent' and 22 as 'good' for irrigation purposes according to Wilcox (Wilcox, 1955). Natural occurrence of Na enriched minerals in parent materials and geochemical processes during interaction with groundwater may account for elevated Na concentration. As a result, soil may undergo deterioration due to accumulation of Na, resulting in crust formation and seal development on the soil surface over a long period of time. Sodium toxicity is often modified and reduced if Ca^{2+} and Mg^{2+} are also present. Moderate level of Ca^{+2} and Mg^{+2} ions may reduce sodium damage and higher amounts even prevent it. High concentration of Na^+ ions in irrigation water tend get absorbed by clay particles, displacing Mg^{2+} and Ca^{2+} ions. This exchange process of Na^+ in water for Ca^{2+} and Mg^{2+} in soil reduces its infiltration capacity (Anthony *et al*., 2013).

Suitability for irrigation based on TDS, RSC, H_T, Cl^-, NO_3^- and metals : On the basis of TDS values (35 to 275 mg l^{-1}) reported in the groundwater samples except for one, rest of the samples were rated as 'fresh' and found suitable for growing crops as recommended by Freeze and Cherry (1979). Residual Sodium Carbonate (RSC) index of irrigation / soil water is another important criteria used to indicate alkalinity hazard in soil. RSC index is used to find the suitability of water for irrigation in clay soils which has high cation exchange capacity. A negative RSC value indicate that total CO_3^{2-} and HCO_3^- concentration is lower than sum of Ca^{2+} and Mg^{2+} concentrations, reflecting that there is no residual carbonate present to react with Na^+ to increase sodium hazard in the soil.

Chloride is not adsorbed by soil but moves readily with water and is taken up by the roots and moves upward to accumulate in the leaves. According to Ayers and Westcot (1985), the recommended concentration of chloride in irrigation water is 4.0 meq l^{-1}. In the present study, chloride concentration in the groundwater samples ranged from 0.20 to 3.30 meq l^{-1} and was found suitable for irrigation. Our results showed that NO_3^--N in groundwater (3.68 to 7.00 mg l^{-1}) did not exceed the permissible limit of 30 mg l^{-1}, therefore most crops remained unaffected due to nitrogen hazard. Level of trace metals (Cu^{2+}, Zn^{2+}, Fe^{3+}, As^{3+}, Mn^{2+}) in the groundwater samples were also found to be low and were considered suitable for crop production and soil environment (Ayers and Westcot, 1985).

Correlations among the parameters with depth : Correlation coefficient is commonly used to assess the relationship between two variables. It is a simple measure to exhibit how well one variable predicts the other. The correlation matrix of 14 parameters, for 38 water samples is presented in Table 5. There were few significant relationships observed among the measured concentrations with depth. A high correlation observed between Cl^- and K^+ (r=0.72), Cl^- and Na^+ (r=0.69), HCO_3^- and Mg^{2+} (r=0.70) and between Na+ indicated that were derived from same source of water (Table 5). Similarly a good correlation between EC and Na^+; Cl^- and TDS; TDS and Na^+ and Cl^- and SO_4^{2-} were also observed in the present study. Thus conductivity in the groundwater samples is contributed largely due to the presence of Na^+ and Cl^- ions. However, for most ions no significant correlation was found between them. High correlation between EC and TDS reflects the interdependency of the two parameters as well as the general measures of the amount of total dissolved solutes. A high correlation observed between EC and TDS (r=1.00) was due to the fact that electrical conductivity depends on total dissolved solids. A significant positive correlation (r=0.84) observed between SSP and SAR indicate that sodium adsorption by soil particles may increase with the amount of soluble sodium that may cause alkali hazard in soil hindering successful crop production. However, relationship between EC and TDS indicate that increase of one element will or may increase the concentration of other and synergistic behavior amongst the dissolved ions in water.

Suitability for drinking and domestic uses : In the present study, pH level (range 5.3 to 6.4) in groundwater samples were below the permissible limit for drinking water (6.5-8.5) as recommended by WHO (2004). The permissible limit of TDS in groundwater is 500 mg l^{-1} (WHO, 2004) and TDS level in all the water samples were found below the permissible limit. Hard water leads to high incidence of urolithiosis (WHO, 2004), anencephaly, parental mortality, few types of cancer and cardio-vascular disorders. Such type of water can develop scales in water heaters, distribution pipes and well pumps, boilers and cooking utensils, and require more soap for washing clothes (Todd and Mays, 2005; Karanth, 1994). In drinking water, Na^+ ion should not exceed 200 mg l^{-1}. A sodium-restricted diet is therefore recommended to patients suffering from hypertension, congenial heart diseases or kidney problems. For such people, extra intake of Na^+ through drinking water may prove critical. High Cl^- level in groundwater is indication of organic pollution and may result in heart or kidney disease and may impair human health (Ayeni *et al*., 2011; Ojosipe, 2007). Excessive Cl^- gives salty taste and has a laxative effect in people not accustomed to it (Ayeni *et al.,* 2011; Ojosipe, 2007). High concentration of SO_4^{2-} in drinking water is associated with respiratory problems (Subba Rao, 1993). In the present study, NO_3^- level in groundwater varied from 3.68-7.00 mg l^{-1} with an average of 6.09 mg l^{-1}. It has been observed that igneous rocks contain small amount of NO_3^-, however the main source of NO_3^- in drinking water are fertilizers, nitrification by leguminous plants ,animal excreta, industrial and domestic wastes (Ozoko, 2004; Edet and Okereke, 2005; Alagbe 2006). Excessive intake
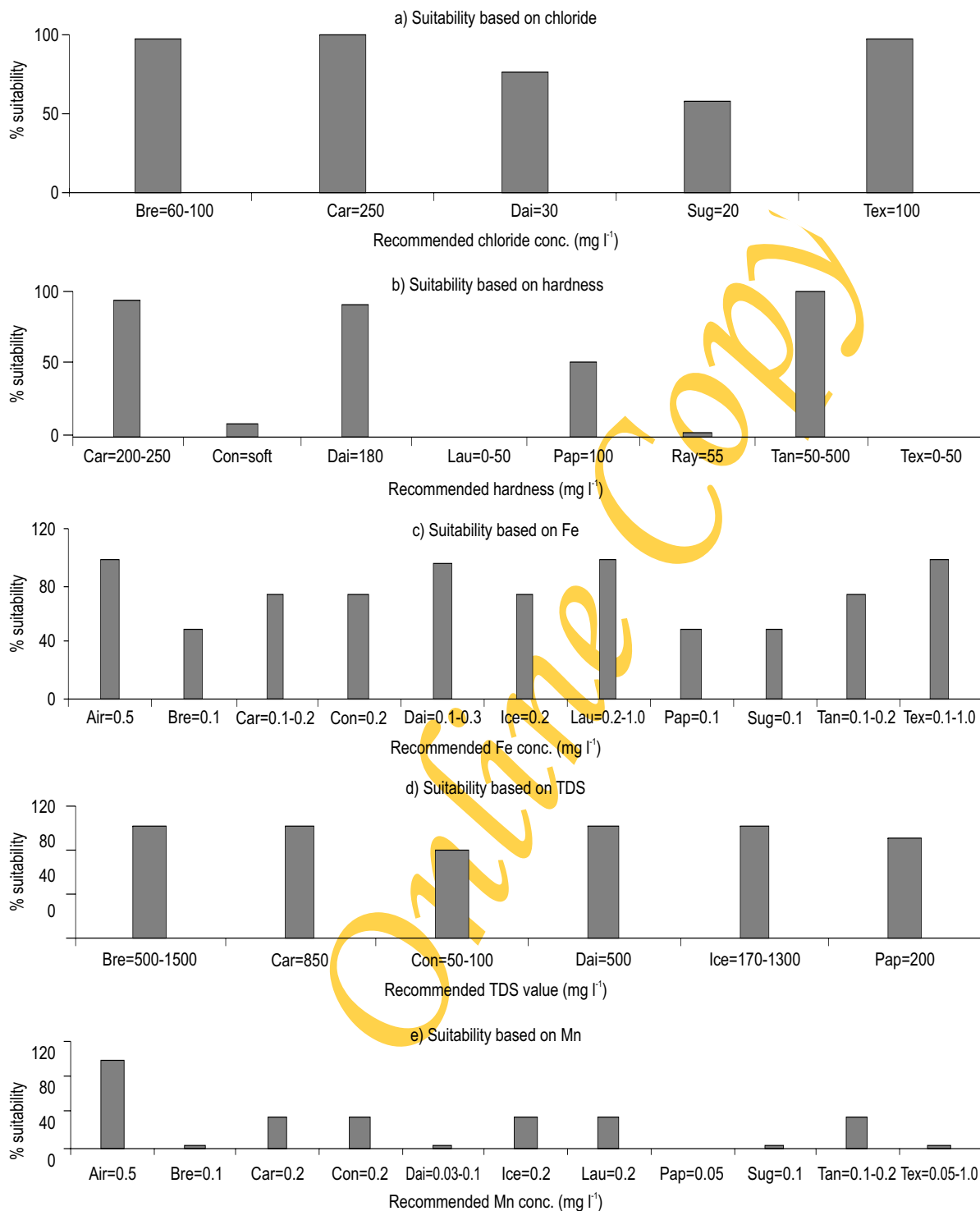
Fig. 5 : Relative suitability of studied water samples for various industries based on a) chloride concentrations, b) hardness, c) Fe, d) TDS, and d) manganese concentrations. X axis shows the recommended concentrations for different industries according to Todd and Mays (2005). Air=Air-conditioning, Bre=Brewing, Car=Carbonated beverage, Con=Confectionary, Dai=Dairy, Ice=Ice manufacture, Lau=Laundering, Pap=Paper & pulp, Sug=Sugar, Tan=Tanning, Tex=Textile, Ray=Rayon manufacture

of NO_3^- via drinking water can cause methemoglobinemia, gastric cancer, birth malformations and hypertension. Elevated concentration (> 5 mg l^{-1}) of nitrate in water indicates water pollution (Atabey, 2005a, b). However, the concentration of Na^+, Cl^-, SO_4^{2-} and NO_3^- in groundwater samples were far below the recommended limits (Na^+= 8.7 meq l^{-1}, Cl^- =7 meq l^{-1}, SO_4^{2-} =3.12 meq l^{-1}, NO_3^-=10 mg l^{-1}) for drinking water according to WHO (2004).

Industrial rating based on Cl^-, Fe^{3+}, SO_4^{2-}, NO_3^-, Mn^{2+}, pH, TDS and hardness : The groundwater samples were found suitable for brewing, laundry and tanning industries as water was acidic in nature(5.3 to 6.4) and within the permissible limit recommended for above mentioned industries(4.5-6.0, 6.0-6.8 and 6.0-8.0) (Todd and Mays, 2005). Total dissolved solids in the water samples ranged from 35 to 275 mg l^{-1} so groundwater was not found suitable for confectionery as per the permissible limit of 50-100 mg l^{-1} (Todd and Mays, 2005). However, all the samples were found suitable for brewing, dairy, carbonated beverage and ice manufacturing industries (Fig. 5) while only 79% water samples were found suitable for confectionary and 92% for paper and pulp industries, respectively. In relation to hardness, all the water samples were found unsuitable for textile, tanning and laundry industry while 92% water samples were suitable for carbonated beverage, 89% for dairy, 11% for confectionary, 53% for paper and pulp industries and only 3% for rayon manufacturing industries, respectively. On the basis of Cl^- level in groundwater, 97% samples were found suitable for brewing and carbonated beverage industry, cent percent for dairy, 76% for sugar and 58% for textile, respectively. The permissible limit of Mn^{2+} in water required for various industries ranged from 0.05 to 1.0 mg l^{-1}, with an exception to sugar manufacturing industry where water should be free from Mn (Todd and Mays, 2005). Concentration of Fe in the ground water samples were within the permissible limit of 0.015 to 0.384 mg l^{-1} and more than 50% of these samples were found nearly suitable for all industrial purposes (Fig. 5).

The major geochemical processes governing groundwater evolution in the study area were ion-exchange, weathering, oxidation and dissolution of minerals. As groundwater of this region is primarily being used for irrigation, agricultural run-off could be one of the reason for groundwater pollution. Accumulation of salts on the surface of irrigated fields could further leach through soil zone by recharge water and reach the water table. Therefore, it can be concluded that water of shallow tube wells and deep tube wells located at Birgonj Upazilla, Dinajpur, Bangladesh were found suitable for irrigation, drinking, domestic and industrial uses; although few samples were found unsuitable for specific industries.

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