Ionic toxicity assessment of groundwater for irrigation in the selected aquifers of Khulna area

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Abstract: An effort was made to evaluate the level of ionic toxicity of groundwater for irrigation collected from the selected aquifers of the district of Khulna. Fifteen samples were collected to explore major ionic constituents for the suitability of groundwater as irrigation usage. All the groundwater samples were slightly alkaline to alkaline in nature (pH=7.77-8.25) and were not problematic for irrigation. EC and SAR indicated that most of the groundwater samples were medium salinity (C2) and low alkalinity (S1) hazards expressing as C2S1. In respect of TDS values, all the samples were categorized as fresh water in quality and were not problematic for irrigation. As regards to SAR values, all the samples were excellent class. Based on SSP, water samples were classified as excellent, good, permissible and doubtful. According to RSC and permeability index (PI), all the samples were suitable for irrigation usage. As per hardness (H_T), 3 samples were hard in quality and the rest 12 samples were very hard. The ionic dominance of groundwater samples were in the order of Cl>Na>SO_4>Ca>Mg>Fe>Mn>K>HCO_3>PO_4. The detected Fe, Mn and Cl ions in the collected water samples were above the permissible limit for long-term irrigation and these ions were considered as toxicants. The contents of Na, K, HCO_3, SO_4 and PO_4 ions were detected below the toxic level and might not pose threat to soil system as irrigation water. The association between chemical parameters and ionic constituents was established. The combinations of pH vs RSC, pH vs H_T, EC vs TDS, EC vs SAR, TDS vs SAR, SAR vs SSP, SAR vs RSC, SAR vs H_T, SAR vs PI, SSP vs RSC, SSP vs H_T, SSP vs PI, RSC vs H_T, RSC vs PI and H_T vs PI exhibited significant relationships and the remarkable significant correlation existed between Ca vs K, Ca vs Na, Ca vs Cl, Mg vs K, Mg vs Na, Mg vs SO_4, Mg vs HCO_3, Mg vs Cl, K vs Na, K vs HCO_3, K vs Cl, Na vs Cl and Fe vs Mn. In the study area, it was noted that the detected ions as toxicants should not be ignored for long-term irrigation.
Key words: Ionic toxicity, groundwater, irrigation, aquifers, Khulna, Bangladesh.

Introduction

Groundwater is a renewable natural resource and a valuable component of the ecosystem as it is vulnerable to natural and human impacts. The uppermost shallow aquifer is extensively used for extraction of water for irrigation purpose almost all over the country (Shahid *et al.*, 2006). Groundwater used for irrigation can vary greatly in chemical quality depending upon type and quantity of dissolved ionic constituents. As because, groundwater contains a wide variety of dissolved ionic constituents in different concentrations. Among the ions, Ca, Mg, Na, B, CO_3 and HCO_3 are of prime importance in assessing the water quality for irrigation (Michael, 2008). The ionic constituent of groundwater as irrigation usage affects plant growth directly through toxicity or deficiency, or indirectly by altering plant availability of nutrients (FAO, 1992). High quality crops can be produced only by using high quality irrigation water keeping other inputs optimal. When the polluted groundwater is applied to soil for long-term irrigation, the dissolved ionic constituents containing toxic ions may accumulate in the soil thus destroying soil qualities (Schwartz and Zhang, 2012). Henceforth, it becomes less suitable for irrigation in relation to soil properties and crop growth. In this aspect, it becomes a prime need to conduct field level investigations of the existing water management. A few studies were conducted in the coastal regions of Bangladesh particularly in Khulna district regarding the ionic contamination of groundwater used for irrigation. There is no systematic investigation to assess the extent of ionic contamination in groundwater at field level. With a view to the above facts, this study was designed to appraise the level of ions in groundwater samples for irrigation purpose in the selected aquifers under the district of Khulna.

Materials and Methods

Water sampling: Groundwater sampling sites were selected from five unions *viz.*, Maguraghona, Kharnia, Dumuria, Shubna and Bhandarpara of Dumuria Upazila under the district of Khulna. Exactly 15 water samples were randomly collected from shallow tubewell to cover most of the investigated area following the sampling techniques as outlined by APHA (2012). The depth of tube wells ranged from 24.0 to 94.0 m and the duration of irrigation usage was from 5 to 26 years. For metal analysis, the collected samples were acidified with HNO_3 (pH<2) to prevent the loss of metal by adsorption and/or ion exchange with the walls of the containers. After collection, all the plastic bottles were sealed tightly to avoid air exposure. Groundwater samples were filtered through filter paper (Whatman No. 42) before ionic analysis. The chemical analysis of groundwater samples were performed as soon as possible on arrival at laboratory.

Water analysis: pH, EC and TDS values were measured electrometrically (Gupta, 2013). The contents of Ca and Mg ions were estimated titrimetrically (Page *et al.*, 1982). The levels of K and Na ions were determined flame photometrically as well as the contents of CO_3 and HCO_3 ions were estimated titrimetrically (Gupta *et al.*, 2012). The concentrations of Fe and Mn ions were analyzed atomic absorption spectrophotometrically and the status of Cl ion was estimated titrimetrically (APHA, 2012). The concentrations of PO_4 and SO_4 ions were determined spectrophotometrically (Jackson, 1973; Tandon, 2013).

Water toxicity rating: To evaluate the ionic toxicity of groundwater and its suitability irrigation, the following chemical parameters were computed using the analytical results of water samples:(i) Sodium adsorption ratio (SAR) = $Na^+ \div [\sqrt{\{(Ca^{2+} + Mg^{2+}) \div 2\}}]$, (ii) Soluble sodium percentage (SSP) = $[\{(Na^+ + K^+) \div (Ca^{2+} + Mg^{2+} + Na^+ + K^+)\} \times 100]$, (iii) Residual sodium carbonate (RSC) = $\{(CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+})\}$, (iv) Hardness ($H_T$) =

($2.5 \times Ca^{2+} + 4.1 \times Mg^{2+}$), (v) Permeability Index (PI) = $[(Na^+ + \sqrt{HCO_3^-}) / (Ca^{2+} + Mg^{2+} + Na^+)] \times 100$, Whereas, all ionic concentrations were expressed as me L^{-1} but in case of hardness, cationic concentrations were expressed as mg L^{-1} (Raghunath, 1987).

Statistical analysis: The statistical analyses of the analytical results obtained from groundwater samples were performed following Gomez and Gomez, 1984. Correlation studies were also done following the standard method of Computer Programme (SPSS).

Results and Discussion

In the study area, ionic constituents such as Ca, Mg, Na, K, Fe, Mn, PO_4, SO_4, HCO_3 and Cl were analyzed and these ionss were present in variable amounts in the collected groundwater samples. Ionic constituent and its contamination rating of groundwater samples for irrigation purpose have been presented in Tables 1-3.

pH, EC and TDS values: Groundwater samples were slightly alkaline to alkaline in nature (pH = 7.77-8.25) (Table 1). These might be due to the presence of major ions in water (Rao *et al*., 1982). According to FAO (1992), the acceptable pH range for irrigation water is from 6.5 to 8.4. As per this limit, these water samples might not be harmful for successful crop production. EC values of all samples were within the limit of 175.0 to 506.0 µS cm^{-1} with the mean value of 356.7 µS cm^{-1} (Table 1). According to Richards (1968), all the samples were classified as medium salinity (C2, EC=250-750 µS cm^{-1}) except two samples (Sample no.: 6 & 7) that were classified as low salinity (C1, EC<250 µS cm^{-1}) classes. Considering EC values, all the groundwater could be safely used for moderate salt tolerance crops growing on soils with moderate level of permeability and leaching. Groundwater samples contained TDS ranging from 117.0 to 339.0 mg L^{-1} having mean value of 239.1 mg L^{-1} (Table 1). A sufficient quality of bicarbonate, sulphate and chloride of Ca, Mg and Na caused high TDS values (Karanth, 1994). According to Freeze and Cherry (1979), all the groundwater samples were classified as fresh water (TDS<1,000 mg L^{-1}) in quality. These water samples would not affect the osmotic pressure of soil solution and cell sap of plants when applied to soil system as irrigation water. Similar results on TDS values in groundwater quality were reported by Islam and Rahman (2014ab) and Rahman *et al*. (2015).

Table 1. pH, EC and TDS values of groundwater samples

Sample ID	Sampling sites		pH	EC µS cm^{-1}	TDS mg L^{-1}
	Union	Village			
1	Maguraghona	Kakurpara	8.21	336.0	225.0
2		Maguraghona	8.08	466.0	312.0
3		Arashnagar	8.05	506.0	339.0
4	Kharnia	Tipna	7.94	294.0	197.0
5		Bahadurpur	7.99	348.0	233.0
6		Mesagona	7.87	213.0	143.0
7	Dumuria	Dumuria	8.05	175.0	117.0
8		Sajiara	8.25	493.0	330.0
9		Hajibunia	8.00	382.0	256.0
10	Shubna	Shubna	7.81	363.0	243.0
11		Gabtali	7.86	363.0	245.0
12		Malmolia	7.94	322.0	216.0
13		Cingra	7.81	378.0	253.0
14	Bhandarpara	Bhandarpara	7.90	309.0	207.0
15		Ula	7.77	403.0	270.0
		Min.	7.77	175.0	117.0
		Max.	8.25	506.0	339.0
		Mean	-	356.7	239.1
		SD	-	91.7	61.4
		CV(%)	-	25.7	25.7
		aFAO value	6.5-8.4	-	-

[a]FAO (1992)

Ca, Mg, K and Na levels: In groundwater samples, the level of Ca existed within the limit of 2.40 to 11.0 me L^{-1} with an average value of 6.33 me L^{-1} (Table 2). The contribution of Ca ion in groundwater was largely dependent on the solubility of $CaCO_3$, $CaSO_4$ and rarely on $CaCl_2$ (Karanth, 1994). Groundwater containing less than 20 me L^{-1} Ca was suitable for irrigating crop plants (FAO, 1992). On the basis of this ion, all the samples could safely be used for irrigation and had no any impact on soil system. The amount of Mg in groundwater samples was detected within the limit of 0.56 to 7.80 me L^{-1} with the average value of 3.36 me L^{-1} (Table 2). According to FAO (1992), water samples containing less than 5.0 me L^{-1} Mg are not problematic for irrigating soils and crops. In the investigated area, 4 samples exceeded this limit (Table 2). Considering Mg content, all the samples except 4 samples were suitable for irrigation. The level of K in all the samples was within the range of 0.02 to 0.42 me L^{-1} with an average value of 0.19 me L^{-1} (Table 2). Karanth (1994) reported that the presence of lower quality of K in some groundwater samples might be due to some potash bearing minerals such as sylvite (KCI) and nitre (KNO_3) in aquifers. The detected limit of K in the collected groundwater samples had no remarkable influence on its quality for irrigation. In groundwater samples, Na content was found within the limit of 0.66 to 22.74 me L^{-1} with the mean value of 14.17 me L^{-1} (Table 2). Water generally contained less than 40 me L^{-1} Na is acceptable for irrigation (FAO, 1992). The detected limit of Na in all the samples under study was below this acceptable limit. Considering this ion, all the samples could safely be used for long-term irrigation without harmful effect on soils and crops.

Fe and Mn levels: Fe content of all samples ranged from 0.39 to 6.56 mg L^{-1} having mean value of 3.06 mg L^{-1} (Table 2). According to FAO (1992), the permissible limit of Fe in water used for irrigation is 5.0 mg L^{-1}. The detected Fe level of 3 samples (Sample no.: 11, 14 & 15) was above the permissible limit and this ion was treated as toxicant in these samples. So, the rest 12 groundwater samples could be safely used for long-term irrigation system. In all the groundwater samples, Mn level was recorded within the range of 0.13 to 4.46 mg L^{-1} with the mean value of 1.05 mg L^{-1} (Table 2). As per FAO (1992), the permissible limit of Mn in water used for irrigation is 0.20 mg L^{-1}. The concentration of Mn in 12 groundwater samples exceeded the acceptable limit and this ion was considered as toxicant. So, all the water sample except 3 samples (Sample no.: 1, 2 & 3) could not be safely applied for long-term irrigation.

Table 2. Ionic constituent of groundwater samples

Sample ID	Ca	Mg	K	Na	Fe	Mn	PO_4	SO_4	HCO_3	Cl
	me L^{-1}				mg L^{-1}		mg L^{-1}		me L^{-1}	
1	3.76	0.56	0.02	0.66	3.01	0.17	BDL	1.71	0.091	0.48
2	4.20	2.60	0.15	2.07	4.03	0.13	0.04	1.10	0.137	0.68
3	5.40	1.20	0.26	4.05	2.88	0.15	0.23	1.00	0.131	0.88
4	7.60	5.60	0.05	19.69	2.83	0.95	0.005	19.17	0.150	22.77
5	10.0	2.00	0.17	21.64	1.18	1.18	BDL	0.69	0.137	19.99
6	8.40	1.60	0.09	15.68	3.32	1.46	0.001	0.84	0.091	26.99
7	3.33	2.00	BDL	15.82	2.00	1.11	0.008	7.70	0.124	18.56
8	2.40	2.40	BDL	12.91	0.81	0.82	0.05	1.30	0.118	11.56
9	5.00	4.20	BDL	13.49	0.39	2.60	0.02	1.96	0.137	17.70
10	6.88	5.68	0.42	18.23	3.46	0.46	0.19	41.86	0.150	29.13
11	6.50	7.80	0.25	22.74	6.56	0.84	BDL	9.42	0.118	23.06
12	5.40	5.60	0.37	17.99	3.82	0.28	0.006	1.45	0.150	29.13
13	8.10	2.10	BDL	14.02	0.54	4.46	BDL	6.58	0.098	24.84
14	11.0	4.20	0.27	22.05	5.64	0.66	BDL	22.06	0.131	23.49
15	7.00	3.00	0.14	11.63	5.53	0.62	0.004	14.85	0.104	15.70
Min.	2.4	0.56	0.02	0.66	0.39	0.13	0.001	0.69	0.091	0.48
Max.	11.0	7.80	0.42	22.74	6.56	4.46	0.23	41.86	0.15	29.13
Mean	6.33	3.36	0.19	14.17	3.06	1.05	0.05	8.77	0.12	17.66
SD	2.45	2.05	0.13	7.05	1.89	1.13	0.08	11.57	0.02	10.01
CV(%)	38.72	60.95	63.98	49.79	61.64	107.13	150.96	131.85	16.57	56.67
[a]FAO value	20.00	5.00	0.05	40.00	5.00	0.20	2.00	20.00	1.50	4.00

[a]FAO (1992); BDL=Below Detection Limit

Table 3. Chemical quality classification of groundwater and its suitability for irrigation usage

Sample ID	SAR		SSP		RSC		Hardness		PI		Alkalinity & salinity hazard classes
	Ratio	Class	%	Class	me L^{-1}	Class	mg L^{-1}	class	%	Class	
1	0.44	Ex	13.59	Ex	-4.22	Suit	216.27	Hard	19.31	Class-II	C2S1
2	1.12	Ex	24.61	Good	-6.66	Suit	339.96	VH	27.50	Class-II	C2S1
3	2.22	Ex	39.50	Good	-6.46	Suit	330.33	VH	41.42	Class-II	C2S1
4	7.66	Ex	59.92	Perm	-13.05	Suit	659.78	VH	61.04	Class-II	C2S1
5	8.83	Ex	64.50	Doub	-11.86	Suit	600.65	VH	65.42	Class-II	C2S1
6	7.01	Ex	61.19	Doub	-9.90	Suit	500.56	VH	62.23	Class-II	C1S1
7	9.68	Ex	74.78	Doub	-5.20	Suit	266.65	Hard	75.15	Class-II	C1S1
8	8.33	Ex	72.89	Doub	-4.68	Suit	239.82	Hard	74.83	Class-II	C2S1
9	6.28	Ex	59.45	Perm	-9.06	Suit	459.76	VH	61.08	Class-II	C2S1
10	7.27	Ex	59.75	Good	-12.41	Suit	627.69	VH	60.46	Class-II	C2S1
11	8.50	Ex	61.64	Doub	-14.18	Suit	714.28	VH	62.31	Class-II	C2S1
12	7.67	Ex	62.53	Doub	-10.85	Suit	549.56	VH	63.38	Class-II	C2S1
13	6.20	Ex	57.88	Perm	-10.10	Suit	510.44	VH	59.17	Class-II	C2S1
14	7.99	Ex	59.48	Perm	-15.06	Suit	760.36	VH	60.16	Class-II	C2S1
15	5.20	Ex	54.06	Perm	-9.89	Suit	500.17	VH	55.25	Class-II	C2S1
Min.	0.44		13.59		-15.06		216.27		19.31		
Max.	9.68		74.78		-4.22		760.36		75.15		
Mean	6.29		55.05		-9.572		485.08		56.66		
SD	2.85		16.72		3.47		173.93		15.71		
CV(%)	45.31		30.37		-36.29		35.85		27.73		

Legend: Ex=Excellent; Perm=Permissible; Doub=Doubtful; Suit=Suitable and VH=Very Hard , C1= Low Salinity; C2 = Medium Salinity and S1=Low Alkalinity

PO_4 and SO_4 levels: Groundwater samples contained PO_4 ion ranging from 0.001 to 0.23 mg L^{-1} with the mean value of 0.05 mg L^{-1} (Table 2). On the basis of FAO (1992), the permissible limit of PO_4 in irrigation water is less than 2.00 mg L^{-1}. Accordingly, all the water samples were not problematic for irrigation without harmful effect on soils and crops grown. In all the groundwater samples, SO_4 content varied from 0.69 to 41.86 mg L^{-1} with the mean value of 8.77 mg L^{-1} (Table 2). According to FAO (1992), 13 samples were suitable for irrigating soils and crops grown in the investigated area except 2 samples (Sample no.: 10 & 14) because these 2 samples contained SO_4 above the acceptable limit (20 mg L^{-1}).

CO_3, HCO_3 and Cl levels: The amount of CO_3 was not detected in all the water samples in the study area. The content of HCO_3 ion in all the samples ranged from 0.09 to 0.15 me L^{-1} with the mean value of 0.12 me L^{-1} (Table 2). According to FAO (1992), the recommended maximum concentration of HCO_3 for irrigation water used continuously on soil is 1.5 me L^{-1}. As per this acceptable range, HCO_3 status of the collected samples was not hazardous for irrigation. Groundwater sample collected from the study area contained Cl ranging from 0.48 to 29.13 me L^{-1} with the mean value of 17.66 me L^{-1} (Table 2). The recorded Cl content in 12 samples was not suitable for irrigation purpose indicating Cl toxicity because these samples contained Cl above the acceptable limit (4.0 me L^{-1}, FAO, 1992). Most of the chloride in water was present as sodium chloride (NaCl) but chloride content exceeds sodium due to the base exchange phenomena (Karanth, 1994).

Table 4. Correlation matrix among chemical parameters of groundwater samples

Parameters	EC	TDS	SAR	SSP	RSC	Hardness	PI
pH	0.271^{NS}	0.269^{NS}	-0.325^{NS}	-0.321^{NS}	0.754**	-0.753**	-0.284^{NS}
EC		0.999**	-0.481^{NS}	-0.348^{NS}	0.241^{NS}	-0.240^{NS}	-0.356^{NS}
TDS			-0.480^{NS}	-0.348^{NS}	0.237^{NS}	-0.237^{NS}	-0.356^{NS}
SAR				0.957**	-0.495^{NS}	0.495^{NS}	0.956**
SSP					-0.371^{NS}	0.372^{NS}	0.998**
RSC						-0.999**	-0.336^{NS}
H_T							0.336^{NS}

Legend: ^{NS} = Not significant; *Significant at 5% level & **Significant at 1% level, Tabulated values of r with 13 df are 0.514 at 5% and 0.641 at 1% level of significance, respectively.

Table 5. Relationship between major ions of groundwater samples

Ions	Mg	K	Na	Fe	Mn	SO_4	HCO_3	Cl
Ca	0.186^{NS}	0.086^{NS}	0.591^{NS}	0.254^{NS}	0.236^{NS}	0.346^{NS}	0.044^{NS}	0.543*
Mg		0.512*	0.643**	0.466^{NS}	-0.094^{NS}	0.506*	0.540*	0.578*
K			0.366^{NS}	0.226^{NS}	-0.283^{NS}	0.439^{NS}	0.582*	0.434^{NS}
Na				0.148^{NS}	0.203^{NS}	0.407^{NS}	0.328^{NS}	0.872**
Fe					-0.556*	0.345^{NS}	-0.007^{NS}	0.080^{NS}
Mn						-0.126^{NS}	-0.302^{NS}	0.360^{NS}
SO_4							0.346^{NS}	0.453^{NS}
HCO_3								0.200^{NS}

Legend: ^{NS} = Not significant; *Significant at 5% level & **Significant at 1% level, Tabulated values of r with 13 df are 0.514 at 5% and 0.641 at 1% level of significance, respectively.

SAR, SSP, RSC, Hardness and PI values: Sodium adsorption ratio of all the groundwater samples was found from 0.44 to 9.68 with the mean value of 6.29 (Table 3). Water used for irrigation having SAR less than 10 might not be harmful for agricultural crops (Todd and Mays, 2004). Considering this classification, all the samples were excellent for irrigation and rated as low alkalinity hazard (S1) class. Soluble sodium percentage (SSP) value of the collected samples varied from 13.59 to 74.78% with the mean value of 55.05% (Table 3). Only 1 samples were classified as excellent (SSP<20%), 3 samples were rated as good class (SSP=20-40%), 5 samples were rated as permissible class (SSP=41-60%) and the rest 6 samples were classified as doubtful (SSP=61-80%) as reported by Todd and Mays (2004). In the study area, only 4 samples could safely be used for irrigating agricultural crops and other samples were not unsuitable for irrigation purpose. RSC value of groundwater samples was from -15.06 to -4.22 me L^{-1} with mean value of -9.57 me L^{-1} (Table 3). According to Schwartz and Zhang (2012), all the samples were found as suitable class (RSC<1.25 me L^{-1}). For this reason, all the groundwater samples were not problematic for irrigation usage. The calculated hardness (H_T) of all the groundwater samples varied from 216.27 to 760.36 mg L^{-1} having mean value of 485.08 mg L^{-1} (Table 3). According to Sawyer and McCarty (1967), 3 samples were hard (H_T=150-300 mg L^{-1}) in quality and the rest 12 samples were classified as very hard (H_T>300 mg L^{-1}). The hardness indicated the presence of higher amounts of Ca and Mg in samples (Todd and Mays, 2004). PI value of the collected water samples was from 19.10 to 75.15% with the average value of 56.66% (Table 3). PI values designated the appropriateness of water for irrigation (Vasanthavigar *et al.,* 2010). All the groundwater samples were under Class-II implying that all samples were suitable for irrigation usage (Domenico and Schwartz, 1990).

Relationship between chemical parameters and ionic constituents: The relationship between chemical parameters *viz*., EC, TDS, SAR, SSP, RSC, harhness (H_T) and PI were studied. Among the combinations, pH vs RSC, EC vs TDS, SAR vs SSP, SAR vs H_T, SAR vs PI, SSP vs H_T, SSP vs PI and H_T vs PI relations showed positive significant correlation (Table 4). The relationship between major ionic constituents like Ca, Mg, K, Na, Fe, Mn, SO_4, HCO_3 and Cl differed significantly as shown in Table 5. Among the major ionic constituents, the remarkable significant correlation existed between Ca vs K, Ca vs Na, Ca vs Cl, Mg vs K, Mg vs Na, Mg vs SO_4, Mg vs HCO_3, Mg vs Cl, K vs Na, K vs HCO_3, K vs Cl, Na vs Cl and Fe vs Mn.

It is concluded from the aforesaid findings that all the groundwater samples could not safely used for long-term irrigation due to the presence of Mn, Fe and Cl ions. These ions as toxicants in groundwater samples would consider its suitability for irrigation purpose demanding suitable water management as well as proper water treatment in the study area.

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