Contamination of Estuary Water of Ship Breaking Activities in Sitakund Region, Bangladesh

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Authors' contributions

This research was performed by all authors. Author ARMTI started the study design, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Authors MSI, NA, MAR and MKR managed the literature searches, field investigation, chemical analysis and managed the experimental result from atomic energy commission. Authors NA and MKR took part of result and discussion. Author MAP reviewed and prepared final version of the manuscript. All authors read and approved the final manuscript.

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ABSTRACT

The present study aimed to investigate hydrogeochemistry and its suitability for drinking and irrigation purposes and to determine the contamination of estuary water of ship breaking activities in Sitakunda region, Chittagong, Bangladesh. The study was carried out by in-situ field measurement of physical parameters while chemical parameters were followed by atomic absorption spectrometry (AAS) methods of laboratory analyses of 12 estuary water samples. The result shows that the P^H value was average 7.08 indicated neutral water while E^h, EC, TDS and TH value was average -24.65 mv, 8586.5 µS/cm, 5495.36 µS/cm and 432.41 mg/l respectively, indicated that the estuary water is not safe

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and suitable for domestic and irrigation purposes. Inferential statistical results were depicted that a strong positive correlation (ρ) between the parameters such as EC, TDS, TH, Ca^{2+}, Na^+, K^+, Cl^-, Br^{2-}, SO_4^{2-}, PO_4^{2-}, NO_3^- while negative correlation (ρ) were existed between Mg^{2+} and HCO_3^-. According to most abundance of major cations were $Na^+>Ca^{2+}>Mg^{2+}>K^+$ whereas major anions were $Cl^->SO_4^{2-}>HCO_3^->Br^->NO_3^->PO_4^-$. The concentration of cations and anions in the study area exceeded drinking standards according to the World Health Organization (WHO) and the Directorate of Environment (DOE), Bangladesh. Irrigation quality index (SAR and PI) indicated that the quality of water is not suitable for irrigation. The origin of solutes in estuary water was influenced by chloride dissolution, although weathering of silicate and cation exchange also added to the water chemistry. This is not conclusive but it may be suggested that the sampled water is not ionically balanced and is highly contaminated due to ship breaking activities.

1. INTRODUCTION

Modern civilization imposes heavy demands on estuary water. Estuary is the mouth of river where mixing of sea water and freshwater. But this water may pollute either from natural or other sources. Currently, ship-breaking activities in Bangladesh are concentrated in Sitakund region of Chittagong city on the eastern coast of the Bay of Bengal. Mehedi [1] reported that comparative pen picture of pollutant status of the coastal belt of Bangladesh with special reference to Halishahar. Hossain and Islam [2] studied in ship breaking activities and its impact for sustainable management on the coastal zone of Chittagong, Bangladesh. In recent years a number of studies have been carried out on the hydro-chemistry of estuarine environments [3-7]. Owing to the micro tidal characteristics, the estuary is facing gross pollution problems following the release of untreated effluents from industries (0.104×10^6 m^3 d^{-1}) and domestic sectors (0.26×10^3 m^3 d^{-1}) over the past five decades resulting in deleterious changes in the estuarine ecosystem [8-9]. The major polluting industries in the coastal region include fertilizer plant, oil refinery, rare earth processing plant, minerals and rutile plant, zinc smelter plant, insecticide factory and organic chemical plant [10].

There are very rare studies on detail hydro-geological investigation related to the study area. Consequently, the present study has an attempt and planned to provide a various hydro-chemical investigation in the small estuarine environment due to ship-breaking activities. The study was aimed to explore detail hydro-geochemical analysis of estuary water in terms of domestic and irrigational quality assessment and to determine the nature and the mechanics of contamination of the estuary water due to ship-breaking activities.

2. METHODOLOGY

2.1 Location of the Study Area

The study area located in between Faujdarhat railway station in south of Sitakund and Kumira, next railway station in north of Sitakund upazila of Chittagong district, Bangladesh. The area is a small estuary (named Dakshin Sonaichhari) lies in between 22º 28′ 18″ N to 22º 30′ 5″ N latitude, and 91º 39′ 29″ E to 91º 43′ 84″ E longitude (Fig. 1). The study was performed in Dakshin Sonaichhari, Sitakund Upazilla, north of the port city of Chittagong,

about 37 km Northwest of the city and 200km southeastern corner of Bangladesh from Dhaka, the capital of Bangladesh.
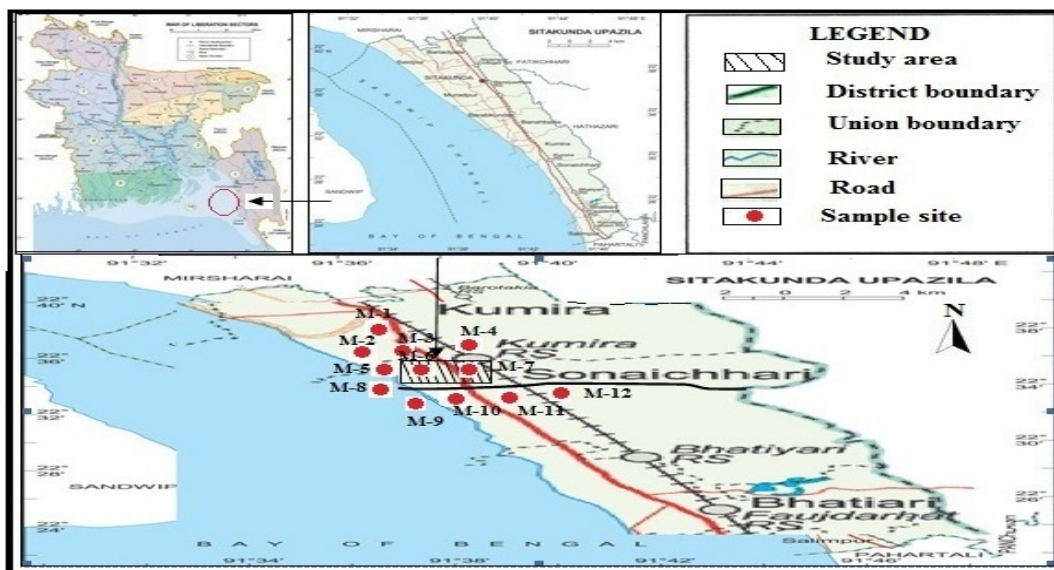

Fig. 1. Location map shows sampling sites in the study area

2.2 Water Sampling and Study Design

Estuary water sample for chemical analysis was obtained during February, 2011. A total of 12 representative estuary water samples were collected from different sites to examine the hydro-geochemistry of the study area (Fig. 1). The procedure stipulated by APHA [11] was pursued for sampling and preservation of samples. After collecting samples of water each sample were packed in a new plastic battle of 500 ml capacity, which was immediately stopper airtight to protect it from air bubbles inside it. Each sample fraction was filtered using 0.45 or 0.20 urn member filter. The determinations of samples were made within 72 hour after collection. One of the achievements of P^H values of 4.0 to avoid any sort precipitation of the dissolved ions. The field parameters such as Hydrogen ion concentration (P^H), Redox potential (E^h), Electric conductivity (EC) and alkalinity were determined during in-situ field investigation by portable instruments. Temperature was measured in the field using scientific thermometer. P^H and E^h were measured by using sension-1, sension-5, sension-6. Chemical analyses of cations and anions were done by ion chromatograph system and atomic absorption spectrometry method which was carried out at hydrogeology laboratory of Atomic Energy Commission (AEC), Savar, Dhaka, Bangladesh. The following equation 1 and 2 which expressed as meq/l were used to calculate irrigation quality indices including Sodium Absorption Ratio (SAR) [12] and Permeability Index (PI) [13].

$$SAR = \frac{Na}{\sqrt{\dfrac{(ca^{2+} + Mg^{2+})}{2}}} \quad (1)$$

$$PI = \left\{ \frac{Na + \sqrt{HCO_3}}{Ca + Mg + Na} \right\} \times 100 \qquad (2)$$

2.3 Data Analysis

Chemical analysis of the estuary water was presented to statistical assessment using SPSS 16 (version). Spearman correlation matrix (ρ) was employed to find out the significance among the physico-chemical parameters of estuary water samples. MS excel (version 7) and Adobe Photoshop and Illustrator were used for preparing map and graphs for the study.

3. RESULTS AND DISCUSSION

3.1 Hydro-chemical Parameters of Estuary Water

Hydro-chemical parameters of the 12 estuary water samples and their statistical result in the study area are presented in the Table 1. The average temperature of 26.21°C of the estuary water was close to the mean atmospheric temperature of 27°C indicating present day climatic influence of water. In general, P^H of estuary water samples was slightly acidic to alkaline in nature [14]. The P^H values of water sample ranged from 6.11 to 7.51 with average 7.08 indicating neutral water. Positive potential (E^h) indicate that the system is relatively oxidizing and negative potential indicate that it is relatively reducing [15]. The redox potential (E^h) values ranged from –o.4 mv to -41.8 mv with average -24.65 mv indicating the estuary system is relatively reducing due to their negative potential values. The EC and TDS values of estuary water samples were very high with ranged of 433 µS/cm to 16740 µS/cm and average 8586.5 µS/cm and ranged of 277.12 mg/L to 10713.6 mg/l with average 5495.36 mg/l respectively both indicates very high contamination of estuary water. Hence, EC and TDS contain very high at the mouth of the 'Chhara' which is one of the most ship breaking units. The values of TH were ranged from 321.5 mg/l to 607 mg/l. There is a health risk attached to hardness depicted by the surface water as very hard categories might lead to pre-mantal mortality and cadio-vuscular diseases [16]. Genetically, estuary water of the study are belongs to "Highly Chloride" and "Highly Sulfate", group According to hardness scale by USGS [15]. The estuary water of the study area is very hard which may cause of health hazard.

On the other hand, major ionic concentrations were high and the order of ionic concentrations in (mg/l) for the cations are $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ and for the anions are $Cl^- > SO_4^{2-} > HCO_3^- > Br^- > NO_3^- > PO_4^{2-}$ (Table 1). All ionic concentrations are above accessible limit [17] standard for domestic purpose. The dissolve ionic species in the surface water are the resultant product of weathering of rock forming minerals with minor contribution from atmospheric precipitation and anthropogenic activities [18]. The contribution of atmospheric sources to the dissolved salts in the water bodies can be assessed by considering the rain water chemistry or by taking the ratios of elements to Cl^- [19-20].

Sodium and chloride are the major ions in the studied water sample. Most of the samples are above the desirable limit of sodium and chloride. The possible reason is due to dissolved salt and weathering and also influence of seawater from coast to land where ship activities are higher. Secondary source of Na+ is the estuary water is agriculture by products and industrial effluents [15]. The highest concentration of Na^+ in the coastal zone is mainly due to the ship breaking activities. Other minor concentration of Mn^+ and As are within reasonable limit except Fe^{total} in the study area samples.

Table 1. Hydro-geochemical parameters result of estuary water samples in the study area

S. No.	Tem°C	pH	Eh (mV)	EC (µS/cm)	TDS (mg/L)	TH (mg/L)	Major cations (mg/L)					Major Anions (mg/L)					Minor and trace elements (mg/L)		
							Ca	Mg	Na	K	HCO_3	Cl	Br	SO_4	PO_4	NO_3	Fe	As	Mn
M_1	26.8	7.40	-35.5	15940	1020.16	584.5	144.43	54.62	4375	80.05	76	6629	17.82	711.23	0.068	1.29	2.21	0.00181	1.01
M_2	24.1	7.26	-27.8	16740	1071.36	607	152.28	55.21	4594	84.07	52	6961	18.71	746.68	0.082	1.30	2.38	0.00173	1.06
M_3	27.0	7.51	-41.8	12500	800	503.5	113.26	53.78	3430	62.77	82	5198	13.97	557.55	0.053	0.750	1.98	0.00175	1.00
M_4	27.1	7.51	-41.8	12180	779.52	485.5	110.36	51.21	3342	61.16	38	5064	13.61	543.28	0.044	0.715	1.73	0.00168	1.05
M_5	26.9	7.42	-36.3	15210	973.4	548	137.00	50.28	4062	76.38	94	6161	16.90	678.43	0.042	1.81	1.64	0.00177	1.00
M_6	26.1	6.76	-0.4	7100	454.4	422	86.53	50.20	1898	35.65	100	2876	7.93	316.68	0.040	0.92	1.79	0.00168	1.02
M_7	26.4	6.94	-9.9	6020	385.28	405	78.21	51.11	1609	30.23	94	2438	6.72	268.51	0.039	0.36	2.01	0.00184	1.03
M_8	26.0	7.30	-29.9	5630	360.32	321.5	46.38	50.11	1504	28.17	104	2240	6.58	251.12	0.039	0.32	1.55	0.00172	1.06
M_9	26.1	6.55	-11.7	3550	227.2	326	45.31	51.88	948	17.82	74	1437	3.97	158.62	0.036	0.029	1.97	0.00165	1.03
M_{10}	26.1	6.87	-16.0	1622	103.80	327	42.11	54.11	432	8.15	92	656	1.81	72.47	0.032	0.024	2.11	0.00179	1.05
M_{11}	26.0	6.11	-35.7	554	35.45	325.5	38.39	55.78	145	6.78	82	220	0.60	34.75	0.031	0.019	2.43	0.00183	1.07
M_{12}	26.0	7.42	-9.1	433	27.71	321.5	38.22	55.12	108	6.17	102	165	0.46	19.37	0.029	0.29	2.21	0.00185	1.08
Range	24.1-27.1	6.11-7.51	-41.8-0.4	433-16740	277.12-10713.6	321.5-607	38.22-152.28	50.11-55.78	108-4594	6.17-84.0	38-104	165-6961	0.46-18.7	19.37-746.68	0.029-0.08	0.019-1.81	1.55-2.43	0.00165-0.00184	1-1.08
Mean	26.21	7.08	-24.6	8586.5	5495.36	431.41	86.04	52.78	2203.91	41.45	82.5	3337.08	9,09	362.22	0.04	0.65	2.00	0.001	1.0380.
STD	0.79	0.44	14.4	6123.62	391.90	110.43	44.21	2.81	1677.75	29.8	20.2	2543.98	6.82	272.01	0.01	0.58	0.28	6.76	0.027

Note- *M_{1-5}: Coast water sample, *M_{6-12}: Sanaichari water sample, *STD- Standard deviation*

3.2 Correlation Matrix Analysis

Correlation matrix analysis is a bivariate method that describes the degree of relationship between two parameters [21]. Spearman's rank correlation coefficient is indicated by suitability for drinking and irrigation purpose ρ (rho) and its values between -1.0 and +1.0. Hydro-chemical parameters of estuary water samples of the study were calculated using Spearman rank correlation. A positive ρ corresponds to an increasing while a negative ρ corresponds to a decreasing monotonic trend between two estuary water sample parameters [14]. A high correlation coefficient (near 1 or -1) means a good relationship between two variables and its value around zero means no relationship between them [22]. Parameters including temperature, P^H, E^H, EC, TDS, TH, Ca, Mg, Na, K, HCO_3, Cl^-, Br^-, SO_4, PO_4, NO_3 were demonstrated a significant correlation among themselves and with other parameters. The correlation result of hydro-chemical parameters were investigated and showed in the Table 2.

In the present study, temperature was shown a positive correlation with P^H and negative correlation with E^h. P^H revealed that weak negative correlation with E^h. The value of EC and TDS were indicated the significance strong positive correlations with most of the parameters while negative correlations were existed between Mg^{+2} and HCO_3. The TH values indicated strong positive correlation with most of the parameters except Mg and HCO_3. The significance positive correlation was observed between Ca^{2+} and Na, K, Cl^-, Br^-, SO_4, PO_4, NO_3 whereas negative correlation was observed between Ca^{2+} and Mg^{2+} and HCO_3. Mg^{2+} shows negative correlation with all the parameters in the study area samples. A positive strong correlation was depicted between Na^+ with K^+, Cl^-, Br^-, SO_4, PO_4, NO_3 except HCO_3. The negative correlation was observed between HCO_3 with Cl^-, Br^-, SO_4, PO_4, NO_3. The values of Cl^- were shown the positive strong correlation with Br^-, SO_4, PO_4, NO_3. Rests of the parameters such as Br^-, SO_4^{2-}, PO_4^{2-}, NO_3^- were shown a significant positive correlation in the study area sample (Table 2).

3.3 Hydrogeochemical Facies Analysis

Pipar Trilinear diagram provides a convenient method to classify and compare water types based on the ionic composition of different water samples [15]. This diagram is very useful to bringing out the chemical relationship among waters in more definite terms [23]. Pipar [24] presented a graphical technique which used to assess the nature of hydro-geochemistry of the estuary waters. It is an effective tool in separating hydrochemical analysis for critical studies with respect to the sources of dissolved constituents (major cations, Ca^{2+}, Mg^{2+}, Na^+, K^+ and major anions; cl^-, Br^-, No_3^-, So_4^-, Co_3^-, HCo_3^-) in waters, modifications in the character of water as it passes through an area and related to geochemical problems. The central plotting field (diamond shape) of the trilinear diagram is divided into nine areas and water is classified into nine types depending upon the area in which the analysis results fall and the alkali cations (Na^+ and K^+) are called primary constituents and the alkaline earth cations (Ca^{2+} and Mg^{2+}) are called secondary constituents. The strong acid cations (So_4^{2-}, Cl^-) are treated as saline constituents and Co_3^{2-} and Hco_3^- are treated as weak acid. Approximate balancing of these cations and anions determine the chemical character of water.

Table 2. Spearman correlation matrix (ρ) analysis for the hydro-geochemical parameters in the study water sample

Parameter	Te-mp	P^H	E^h	EC	TDS	TH	Ca	Mg	Na	K	HCO3	Cl⁻	Br	SO₄	PO₄	NO₃
Temp	1.00	.54*	-.52	.39	.39	.43	.39	-.36	.39	.39	-.27	.39	.39	.39	.39	.34
P^H		1.00	-.53	.42	.42	.35	.42	-.13	.42	.42	-.04	.42	.42	.42	.46	.49
E^h			1.00	-.41	-.41	-.38	-.41	-.08	-.41	-.41	.45	-.41	-.41	-.41	-.45	-.22
EC				1.00	1.00**	.93**	1.00**	-.12	1.00**	1.00**	-.42	1.00**	1.00**	1.00**	.97**	.91**
TDS					1.00	.93**	1.00**	-.12	1.00**	1.00**	-.42	1.00**	1.00**	1.00**	.97**	.91**
TH						1.00	.93**	.08	.93**	.93**	-.54*	.93**	.93**	.93**	.90**	.84**
Ca							1.00	-.12	1.00**	1.00**	-.42	1.00**	1.00**	1.00**	.97**	.91**
Mg								1.00	-.12	-.12	-.44	-.12	-.12	-.12	-.09	-.25
Na									1.00	1.00**	-.42	1.00**	1.00**	1.00**	.97**	.91**
K										1.00	-.42	1.00**	1.00**	1.00**	.97**	.91**
HCO₃											1.00	-.42	-.42	-.42	-.48	-.13
Cl⁻												1.00	1.00**	1.00**	.97**	.91**
Br⁻													1.00	1.00**	.97**	.91**
SO₄														1.00	.97**	.91**
PO₄															1.00	.85**
NO₃																1.00

*Correlation is significant at the 0.05 level (p<0.05)
**Correlation is significant at the 0.01 level (p<0.01)

In the present study, the chemical characteristics of estuarine water from Dakshin Sonaichhari study area fall in different subdivisions of the diamond shaped field of the Piper's Trilinear diagram are shown in Fig. 2. All the samples from estuary fall in the field-2, suggested that Alkalis exceed alkaline earth. All samples fall in field-3, which indicates a weak acid exceeds strong acids. Again 10 samples also fall in the field-8 which indicates carbonate alkali (Primary Salinity) exceeds 50% here plot the estuarine water, which are inordinately soft in proportion to their content of dissolved solids. It is also obvious from Fig. 2. that in case of twelve of the estuarine water samples belonging to field-9 of the piper Trilinear Diagram no cation anion pair exceed 50%.

The facies mapping approach is one of the most significant ways to determine the hydro chemical facies from chemical data [25]. In this case samples are classified according to facies with two templates for the Piper's Trilinear diagram. The cation facies shown that Ca+ Mg versus Na+K representing 90 % of estuary water as dominant Na+K while anion facies depicted that SO_4+Cl versus HCO_3- representing 10 % SO_4+ Cl⁻ as a minor facies in the study (Fig. 3).
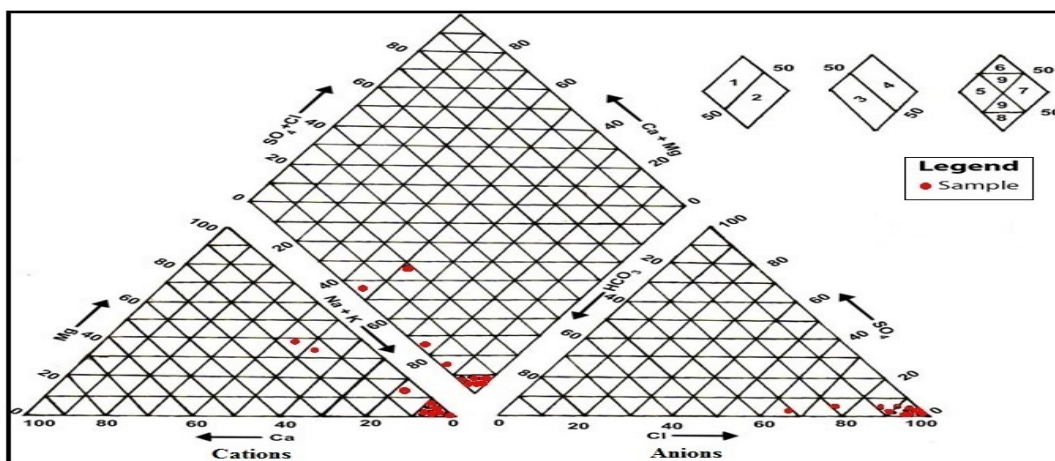
Fig. 2. Piper's trilinear diagram for hydrogeochemical facies of estuary water
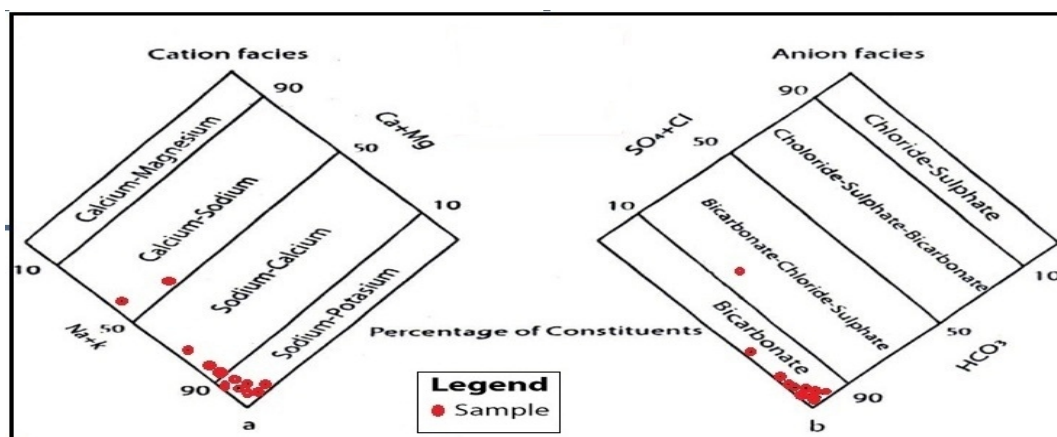
Fig. 3. Facies analysis of estuary water samples in the study area

3.4 Drinking Quality Assessment

The drinking water quality assessment are those which satisfy all of the limitations of water use criteria recommended by World Health Organization and Bangladesh Water Pollution Control Board which gives the guideline values of chemical constituents in water for drinking standard [26-28].The estuarine water of the study area is compared and correlated with WHO and Bangladesh Standard for drinking purposes is given in the Table 3. From this table we can say that all the parameters have been determined systematically are not suitability for drinking and health purposes, because all the samples are not within permissible.

Table 3. Correlation of the quality of estuary water of the study area with WHO, DOE and BWPCB for drinking purpose

Serial No.	Water Quality Parameters	WHO Standard (1983)	DOE Bangladesh Standard(1997)	BWPCB Standard (1976)	Concentration in the Study Area	Remarks
1	pH	6.5-8.5	6.5-8.5	6.5-9	7.08	All samples
2	Tem (°C)	–	20-30	–	24-27	are not
3	TDS(mg/L)	1000	1000	1500	27.71-1071.36	within a
4	TH(mg/L)	500	200-500	–	4667-10374.5	permissible
5	Ca^{+2}(mg/L)	9	75	–	38.22-55.21	limit of the
6	Mg^{+2}(mg/L)	50	30.35	–	50.20-55.21	study area
7	Na^{+}(mg/L)	200	200	–	108-4594	
8	K^{+}(mg/L)	–	12	–	6.17-84.07	
9	HCO^{-3}(mg/L)	–	600	–	38-104	
10	Cl^{-}(mg/L)	250	150-600	600	165-6961	
11	SO_4^{-2}(mg/L)	400	400	400	19.37-746.68	
12	PO_4^{-3}(mg/L)	–	–	–	.032-.082	
13	Fe^{total}(mg/L)	0.01	0.3-1.0	1-5.0	1.64-2.43	

3.5 Irrigation Quality Assessment

Water containing high concentration of chloride and sulphate makes the water salty in taste and indicates contaminated, which might not be suitable for human consumption. High sodium content in irrigation water brings about pudding of soil. The control of salt and alkali in the soil is an important as the supplying of irrigation water for the development and maintenance of successful irrigation projects [29]. In the study area the Na+ content is higher than the permissible limit. The sulphate salts go into solution readily and are rather quickly removed from coarse grained sediments after environmental changes, such as an uplift of land surface or a decline of sea level. In the present study, Sodium Adsorption Ratio (SAR) and Permeability index (PI) were key irrigation water quality parameters which used for deciding the aptness of estuary water for irrigation purposes.

The U.S salinity Laboratory [12] defined the sodium-adsorption ratio (SAR) of water as sodium divided by square of calcium and magnesium ion which divided by two. Where all ion concentrations are expressed in meq/l, SAR predicts reasonably well the degree to which irrigation water tends to enter into cation exchange reactions in soil. High values for SAR imply a hazard of sodium replacing adsorbed calcium and magnesium, a situation ultimately damaging to soil structure. Salinty and toxicity problems of irrigation water are attributed to SAR [30]. The high value of SAR (>18) in any irrigation center implies a hazard of sodium (alkali) replacing Ca^{2+} and Mg^{2+} of the soil through cation exchange process [31]. This is a

situation, which eventually causes damage to a soil structure namely permeability, which ultimately affects fertility status of soil and reduces crop yield. The SAR Values in the surface water of the study area from coast to Chhara ranges from 81.07-2.62 with an average 41.84, which implies that alkali hazard is anticipated in the study area and this water is highly contaminated (Sample M_1 to M_{11}). Salinity classification was done using a quality diagram given by U.S. Salinity Laboratory [32].The US regional salinity laboratory has constructed waters describing 16 classes with reference to SAR as an index for sodium hazard (S) and EC as an index of salinity hazard (C) (Fig. 4). By plotting the calculated results in the diagram fall into the class of very high alkalinity hazard (S_4) and fall in the class of very high salinity hazard (C_4), which implies that the quality for irrigation with very high alkali hazard and very high salinity hazard which might be increased due to ship breaking activities in the area.
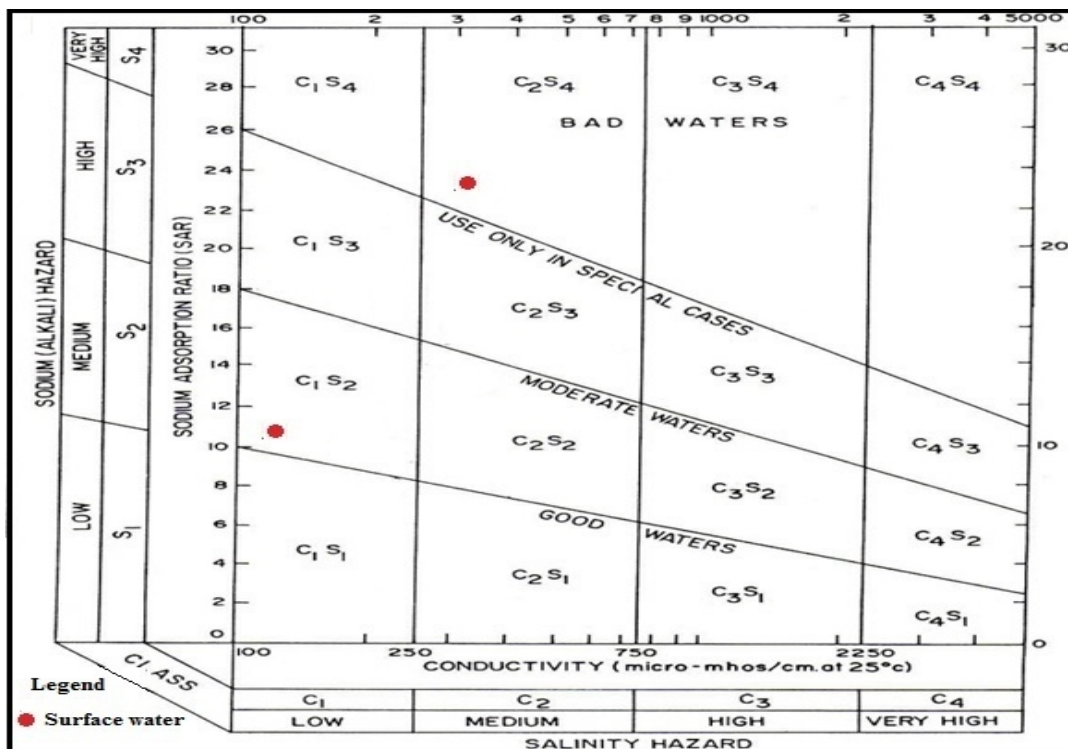
Fig. 4. Salinity classification of estuary water for irrigation purpose of the study area [32]

Doneen [13] evolved a criterion for evaluating the suitability of water for irrigation based on permeability index (PI). Where, all ions are measured in meq/l. According to Doneen chart, the estuary water samples of the study area are all fall in the class-III which implies that the estuarine water quality is not very good for irrigation purposes (Fig. 5).
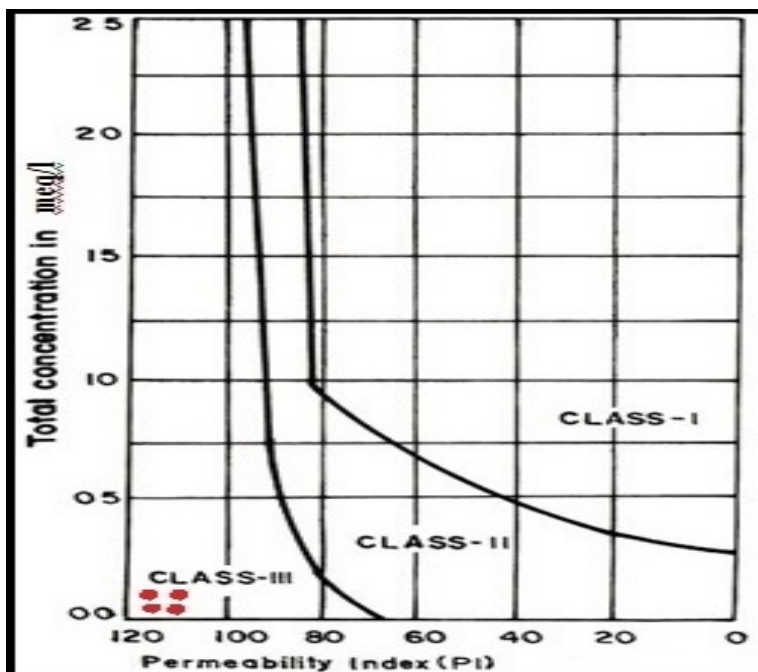
Fig. 5. Classification of estuary water for irrigation use based on PI [13]

3.6 The Origin of Solutes in Estuary Water

Compositional relationships among dissolved ions were revealed the origin of solutes in estuary water and the process that produced the experiential water compositions. The Na^+ vs Cl^- relationship has often been used to identify the mechanisms for acquiring salinity and saline intrusions in semi-arid regions [33-36]. The high Na^+ and Cl^- contents detected in certain samples may suggest the dissolution of chloride salts. A parallel enrichment in both ions indicates dissolution of chloride salts or concentration processes by evaporation. These two mechanisms are those that predominate in the studied region with a distribution of values very close to one in most cases. Fig. 6A shows the plot of Cl^- versus Na^+ (R^2=1) in the estuarine water samples. The dissolution of halite in water release equal concentrations of sodium and chloride into the solution, water sample data deviate from the expected 1:1 relation revealing that a large fraction of sodium is linked with an anion other than chloride. A Na/Cl molar ratio greater than one is typically interpreted as reflecting Na^+ released from silicate weathering reactions [37]. Silicate dissolution can be a probable source for Na^+ in estuarine water in the Dakhsin Sonaichhari area. One potential source of excess Na^+ is weathering of sodium plagioclase in the Neogene rocks of the Sitakund Hill Range. The excess of sodium in these samples may also result from dissolution of sodium sulfate minerals [33]. Those samples with a value of Na/Cl ratio higher than one also show a scarcity of Ca^{2+} and Mg^{2+} and this is consist with a Ca^{2+}- Na^+ cation exchange process which leads to a softening of the water [38]. There are also high positive correlation between K^+ and Cl^- (R^2=0.998) and Ca^{2+} and Cl^- (R^2=0.963) while low correlation coefficient between Cl^-/Br^{2-} and Cl^- (R^2=0.529) indicating geogenic input in the estuary water sample (Figs. 6B and 6C and 6D).
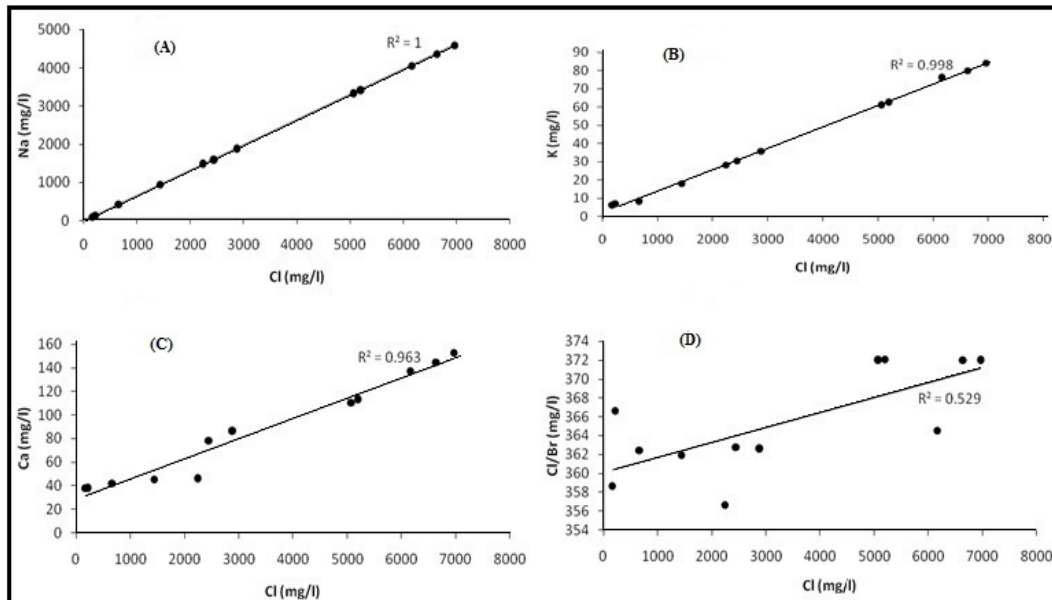
Fig. 6. Shows the relation between different cation and anion in the study samples. A) Cross plot of Cl⁻ versus Na⁺. B) Cl⁻ versus K⁺ plot. C) Cl⁻ versus Ca²⁺. D) Cl⁻ versus Cl/Br⁻

The most common weathering reaction for calcite is simple dissolution giving a ½ Ca: HCO_3 equivalence ratio of 1:1 [39]. The abundance of carbonate and dolomitic rocks in some part of the Sitakund Hill Renge from where the Sonichhari estuary originates, suggest that dissolution of these minerals adds significant amounts of Ca^{2+} and Mg^{2+} to the reservoirs. The relationship between Ca^{2+} and HCO_3^- ($R^2=0.238$) in the estuarine water shows in Fig. 7A. It is observed that there is no relationship between these ions and the correlation coefficient is not significant. So, calcite is not the source of Ca^{2+}. Fig. 7B show that most of the data between Mg^{2+} and HCO_3^- ($R^2=0.044$) deviated from the expected 1:1 situation suggesting in another source of Mg^{2+}. The source of the Mg^{2+} may be linked, at least partially with the dissolution of aluminosilicates in the metamorphic rocks of the southern recharge area. Figs. 7C and 7D shows the cross plot of HCO_3^- versus Na^+ ($R^2=0.257$) and K^+ ($R^2= 0.250$) as in the estuarine water samples both deviated from the 1:1 relation suggesting another source of Na^+ and K^+ . Figs. 8B and 8D indicate a linear regression plot of TDS versus Na^+ and Cl^- with high positive correlation coefficient ($R^2= .936$ and $.935$) compared to Figs. 8A and 8C with relatively low correlation coefficient ($R^2= .588$ and $.760$) which deviated from 1:1 relation signifying that high TDS values are likely to be consequently of ship breaking activities in the study area.

Fig. 9A shows that a cross plot of Ca^{2+} versus SO_4^{2-} indicate that most of the estuarine water samples deviated from the 1:1 line with strong positive correlation coefficient ($R^2 =0.962$). There was also strong correlation between Na^+ and SO_4^{2-} (($R^2= 0.996$) and K^+ and SO_4^{2-} ($R^2= 0.995$) suggesting that most of the SO_4^{2-} originates from dissolution of sodium and potassium minerals (Figs. 9B and 9D). Fig. 9C show a plot of NO_3 and SO_4^{2-} which deviated from 1:1 line most of the samples depicted that positive correlation ($R^2= 0.795$) was existed between them. Therefore the positive correlation between the above mentioned pairs of cations and anions suggest that these ions are part of a buried evaporate body in the estuary, probably of earlier age.
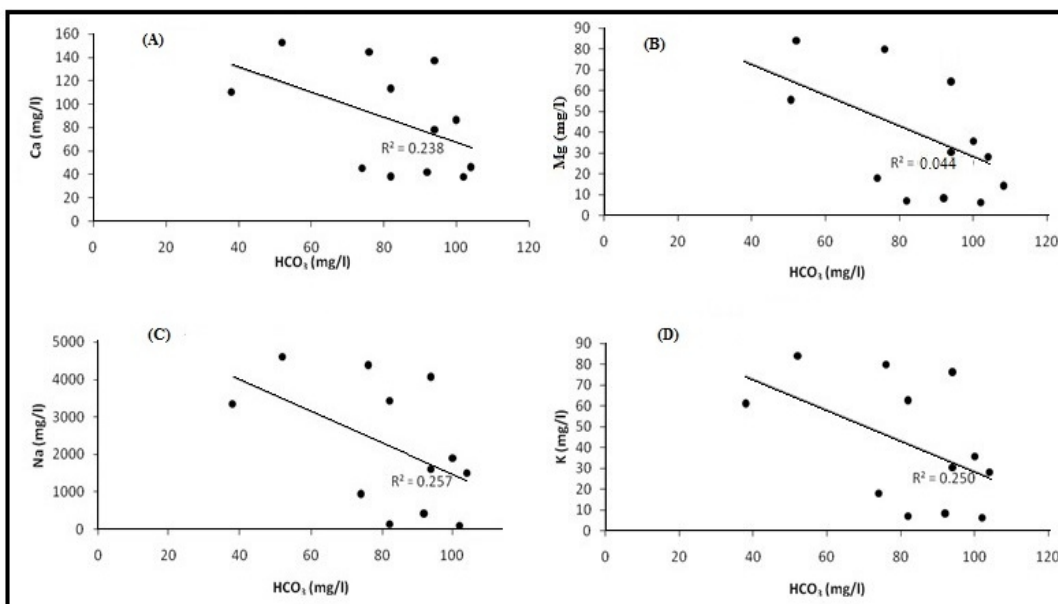
Fig. 7. Show the relation between different cation and anion in the study samples. A) Cross plot of HCO_3^- versus Ca^+. B) HCO_3^- versus Mg^{2+} plot. C) HCO_3^- versus Na^+. D) HCO_3^- versus K^+
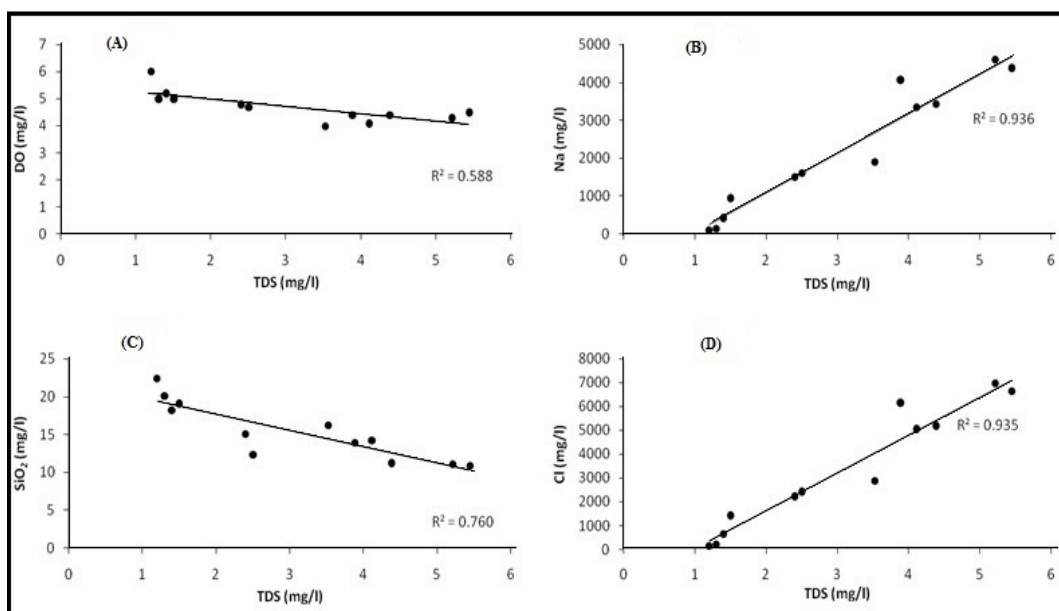

Fig. 8. Show the relation between different cation and anion in the study samples. A) Cross plot of TDS versus DO. B) TDS versus Na^+ plot. C) TDS versus SiO_2. D) TDS versus Cl^-
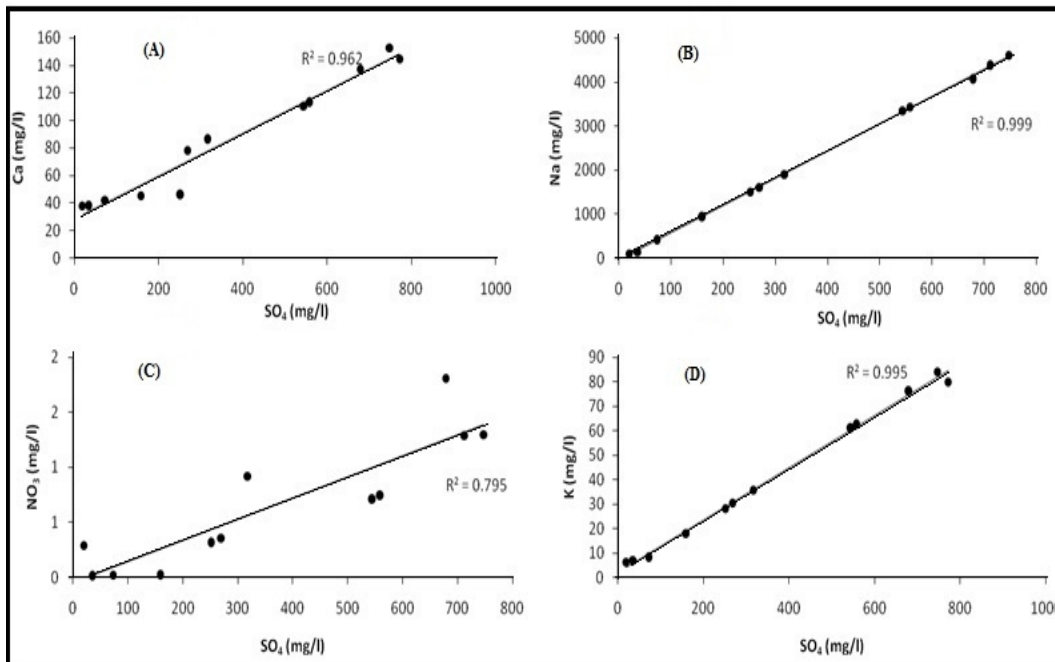
Fig. 9. Show the relation between different cation and anion in the study samples. A) Cross plot of SO_4^- versus Ca^{2+}. B) SO_4^- versus Na^+ plot. C) SO_4^- versus NO_3^-. D) SO_4^- versus K^+

A plot of PO_4 versus SO_4 and NO_3 versus Ca^{2+} show deviation from 1:1 relation with comparative positive correlation (R^2=0.703 and 0.831) suggesting surface anthropogenic activities in the study area (Figs. 10A and 10B). Fig. 10C indicates that a cross plot of Ca^{2+}+ Mg^{2+}, SO_4^{2-} and HCo_3^- are derived from simple dissolution of calcite, dolomite and gypsum, then a charge balance should exist between the cations and anions suggesting a shortage of (HCO_3^-+ SO_4^{2-}) versus (Ca^{2+}+Mg^{2+}) exits in most of the estuarine samples. So, the excess positive charge of Ca^{2+} and Mg^{2+} must be balanced by Cl^- , as a major anion in the study water sample. The evidence for silicate weathering or cation exchange is given by bivariate plots of Ca^{2+}+ Mg^{2+}- HCo_3^- SO_4^{2-} as a function of $Na^++K^+-Cl^-$ (R^2= 0.987) is shown in Fig. 10D. $Na^++K^+-Cl^-$ represents the amount of Na^++K^+ gained or lost relative to that provided by chloride salts dissolution (mostly halite dissolution) while Ca + Mg - HCO3 SO_4 represents the amount of Ca2+ and Mg2+ gained or lost relative to that provided by gypsum, calcite and dolomite dissolution [40]. Indicates an increase in Na^+ + K^+ related to a decrease in Ca^{2+}+ Mg^{2+} or an increase in HCo_3^- + SO_4^{2-}. A cross plot close to a straight line (R^2=0.946) with a slope of -1.007 (Fig. 10C). This indicates that almost all Na^+, Ca^{2+} and Mg^{2+} participate in the ion exchange reaction [41].
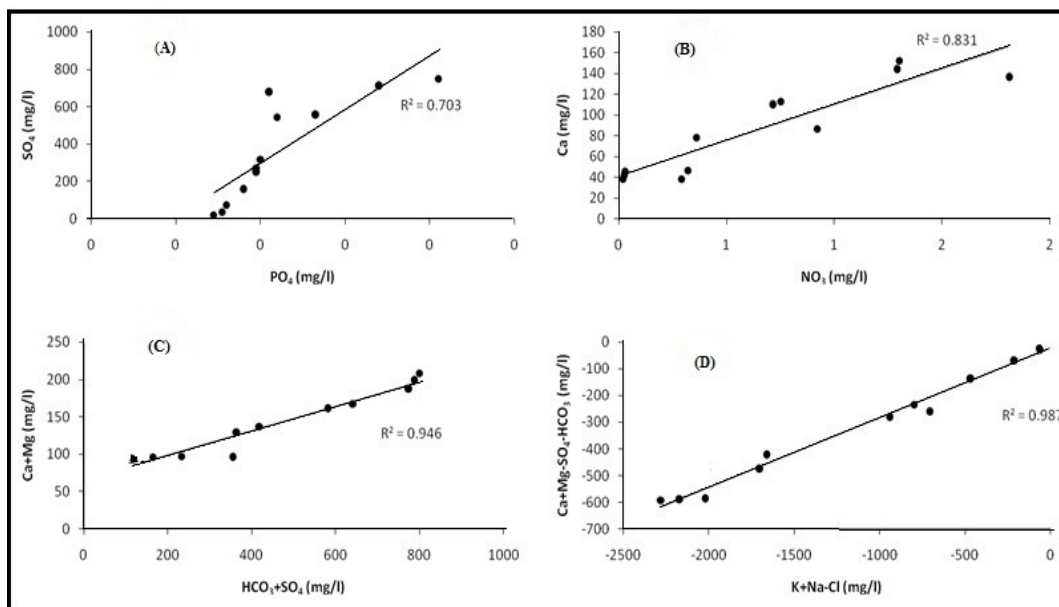
Fig. 10. Show the relation between different cation and anion in the estuary water samples. A) Cross plot of PO_4^- versus SO_4^-. B) NO_3^- versus Ca^{2+} plot. C) HCO_3^- + SO_4^- versus $Ca^{2+}Mg^{2+}$. D) $K^+ + Na^+$ -Cl^- versus Ca^{2+} +Mg^{2+}-SO_4^-- HCO_3^-

4. CONCLUSION

The study was to determine hydro-geochemistry of estuary water for drinking and irrigation purpose and to find out the origin of solutes and the mechanics of contamination of estuary water due to ship breaking activities. In the study area, most of the human health hazards have been caused due to excess limit of Ca^{2+}, Na^+, Cl^-, HCO_3^-, EC, TDS, TH, Fe^{total} concentration in drinking water. Hydrological characteristics reveal that the EC, TDS and TH values are not within allowable limit although P^H value was averaged 7.08 which indicate almost neutral of estuarine water but not enough suitable for drinking and irrigational purpose due to ship breaking activities as it increase towards the coast from the sonaichhari. Major ionic concentrations were high and the order of ionic concentrations in (mg/l) for the cations are Na^+ > Ca^{2+} >Mg^{2+}> K^+ and the anions are Cl^-> SO_4^{2-}>HCO_3^-> Br^-> NO_3^-> PO_4^{2-}. All of the cations and anion of the estuary water are not within an allowable limit due to ship breaking activities or some other causes. Major hydro-geochemical facies were recognized using pipar trilinear diagram. From the facies mapping approach of water quality data revealed that the estuarine water of the region could be classified as Na-Cl, Ca-Mg cation facies and anion facies as Cl-SO_4-HCO_3 type. Based on PI and SAR the estuary water of the study area is highly polluted and is not good quality for irrigation purposes. It can be concluded that the water of the estuary for irrigation and drinking purposes are high alkali hazard and moderate to high salinity hazard. The high Na^+ and Cl^- contents detected in certain samples may suggest the dissolution of chloride salts. The possible dissolution of halite, calcite, gypsum in the sediments results in the Ca^{2+}, Na^+, ,Mg^{2+}, Cl^-, and SO_4^{2-} content in the estuary waters. Although, weathering of silicate mineral and cation exchange were also added to the content of Na^+ and K^+. It may be create laxative effects of higher level and may not be recommended for livestock consumption.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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