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Alkalinity and Hardness of Natural Waters in Chittagong City of Bangladesh

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Abstract

Alkalinity and hardness often used exchangeable when discussing water quality. These collective properties of water share some resemblances but are distinctly different but both has high mineral content. Generally, the water shows alkalinity due to the presence of weak acid and strong base resulting salt, typically as the form of bicarbonate salt and it can create some serious problems in water body. Hard drinking water, carry excess of Ca and Mg salt, may have moderate health benefits but can pose critical problems in domestic and industrial settings. Thus, it is important to assess the water quality with respect to hardness and alkalinity. The objectives of this study to provide an overview of alkalinity and hardness, an understanding of the importance of alkalinity and hardness from ecological perspectives and management, a summary of methods for measuring each, and the current state regulations for each in public waters of Chittagong city. The results obtained for pH, conductivity and alkaline ionic compositions from different surface and ground water samples of Chittagong city presented here with critical observations. For investigations, some related anions and metals examined by UV-visible spectrophotometer and FAAS utilizing Na-tetraborate after the pre-concentration on a column packed with Amberlite XAD-16 resin. The results show that some parameters such as salinity, total alkalinity and hardness; Na^+, Ca^{2+}, Cl^-, and HCO_3^- loaded in both surface and ground water is quite high than slandered value; other parameters like NO_3^-, NO_2^-, SO_4^{2-}, PO_4^{3-}, K^+, NH_4^+, and Mg^{2+} levels are in permissible range. Overall, it may state that the water of studied areas is very hard, saline as well as alkaline and suggesting that water should not uses for household, irrigation, and industrial purposes without proper treatment.

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1. Introduction

The water alkalinity, from Arabic '*al-qali*' means 'saltwort ashes' (Dictionary.com, 2018), is the measurements to resist changes the pH that would make the water more acidic (WRC, 2018) and roughly refers to the amount of bases in a solution that can be changed to uncharged species by a strong acid (Drever, 1988; US-EPA, 2006). Alkalinity is the strength of a buffer-solution composed of weak acid and their conjugated base. It measures the ability of a solution to neutralize acids to the equivalence point of carbonate or bicarbonate. In the natural environment carbonate alkalinity tends to make up most of the total alkalinity due to the common dissolution and occurrence of metal carbonate rocks and presence of atmospheric CO_2. Other common natural components that can contribute to alkalinity include hydroxide, borate, silicate, phosphate, the conjugated base of some organic acid, dissolve NH_3, and sulphate (Reham, 2008). Neither alkalinity nor acidity, have no any known adverse health effects. But, highly alkaline, or acidic water considered distasteful. Knowledge of these parameters may be important because the alkalinity delivers information about how sensorial that water body will be to acid inputs such as by acid rain and waste water. On the other hand, turbidity often removed from drinking water by flocculation or coagulation and this process releases H^+ into the water and alkalinity must be present more than that destroyed by the H^+ released for complete and effective coagulation to occur and hard waters normally softened by precipitation technique; the alkalinity of the water must be known to estimate the Na_2CO_3 and $Ca(OH)_2$) necessities for precipitation. Besides, other importance of the concept on these parameters are to control corrosion in water bearing piping systems the alkalinity of water body, alkaline parameters HCO_3^- and CO_3^{2-} may complex with other elements or compound and altering their toxicity, transport, and fate in the environment; and alkalinity is very significant for fish and aquatic life (function best in pH ranges 6.0 to 9.0) because it protects or buffers against rapid pH changes (WRC, 2018)

Alkalinity in natural waters is mostly due to CO_3^{2+}-species and the following set of chemical equilibria recognized in waters where H_2CO_3 represents the total concentration of dissolved CO_2 and H_2CO_3 (Benjamin, 2015). Traditionally alkalinity conveyed as mg/L of $CaCO_3$ since most alkalinity derived from the weathering of carbonate minerals and rocks. Though, alkalinity is primarily a term invented in oceanography, it also used in hydrology to describe temporary hardness in water (Dickson, 1992). Besides, it is one of the best measures of the sensitivity of the stream to acid inputs which can be long-term changes in the alkalinity of streams and rivers in response to anthropological disturbances (Kaushal et. al., 2013; US-EPA, 2013). On the other hand, among the physical parameters of natural water, total hardness (T_H) is very crucial and significant with respect to both household and industrial purposes. T_H is not caused by single constituent but by a variety of dissolved multivalent metallic ions, dominate Ca and Mg cations, though other cations such as Fe, Al, Zn, Mn, Ba, and Sr also contribute and allied anions are bicarbonate (temporary T_H) and non-carbonate (permanent T_H) (*WHO, 2011*). Water holding $CaCO_3$ (or equivalent value) at concentration bellow 60 mg/L generally considered as soft; 61-120 mg/L, moderately hard; 121-180 mg/L, hard; and more than 180 mg/L, very hard (*McGowan, 2000*). Hardness and alkalinity values are usually like magnitude because Ca, Mg, HCO_3^- and CO_3^{2-} ions in water resulting in equivalent measures from the solution of limestone in sedimental deposits. But in some water's alkalinity may surpass its hardness level and vice versa. If alkalinity is high and hardness low, pH may increase to very high levels (>10.5) throughout periods of quick photosynthesis (DPI, 2018). Alkalinity and hardness are related through common ions formed in aquatic systems. Specifically, the counter-ions associated with the bicarbonate and carbonate fraction of alkalinity are the principal cations responsible for hardness (usually Ca^{++} and Mg^{++}). As a result, the carbonate fraction of hardness (expressed as $CaCO_3$ equivalents) is chemically equivalent to the bicarbonates of alkalinity present in water (Burton Jr. and Pitt, 2002) at specific area where the water interacts with limestone rock (Timmons et al. 2002). Any hardness greater than the alkalinity represents noncarbonate hardness.

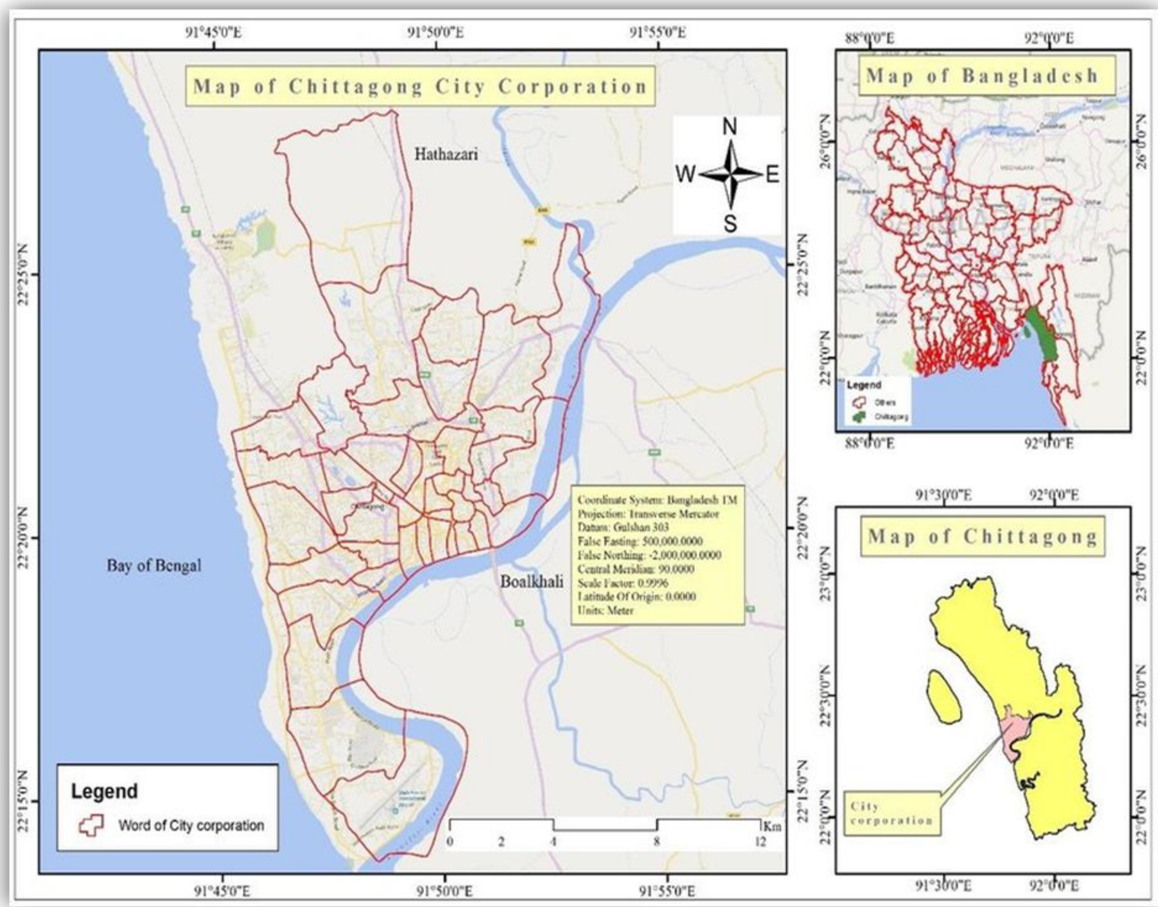

Fig. 1. Map of Chittagong City Corporation (Hredoy et. al., 2018).

Chittagong is one of the most beautiful and densely populated cities in the world gifted with its fascinating geographical location, natural beauty, cultural heritage, and hospitality of its people attracted the travelers from different part of the world. Besides, this city holds all the natural resources. The Karnafuli and Halda river, the Bay of Bengal, a lot of ponds, reservoirs, tanks, estuaries, and lakes; hilly forest etc. are situated in and around this city. Maximum waste discharging industries are located within 30 km from the mouth of the Karnafuli river bank, which originated from the *Lusai* hill of India and falls into the Bay of Bengal. Unrefined wastage effluents from 144 industries of 8 industrial zones, located generally near the bank of this river, fall in the river through drains and canals (Majumder and Shajedul, 1995). Among the discharging materials huge amount of primary alkaline materials like caustic soda, soda ash, ammonia etc., originated from urea, dyeing, pulp and paper, soap and detergent, TSP etc. factories received by this river. Some Secondary alkaline materials that react with water and from primary alkaline substances also mixed. Except these, the alkaline materials may originate from the dissolution and weathering of soils, rocks, minerals etc., as well as from rain, dust, atmospheric pollutants etc. (Rahman et. al., 2012). According to the need water supply authority of government is not a position to meet the demand of pure piped water in this city. A good number of families use unrefined raw ground water, which collected by own-owner hand tub-well, for the drinking and other household purposes. Strictly speaking, various components as ionic form may be infiltrate into soil with water and join the underground water layer (UNICEF, 2009). Those ionic components are the main sources of the alkalinity and hardness of groundwater aquifers. The alkaline features of groundwater depend largely on the mineral composition of the rocks through which the water has moved. The rate of minerals movement and characteristics of water depends on organic and inorganic reactions, industrial effluents, rain fall, soil erosion, weathering of rock etc. (Zahid, 2015). The underground water tends to contain more dissolved materials than those in river or pond water because of their more intimate and longer contact with organic materials of soil and rock particles. Often the anionic composition in subsurface water controlled by organic reaction associated by micro-organisms whereas the cationic composition controlled by inorganic reactions (BWDB-UNDP, 1982).

For the assessment of alkaline and hardness status of ground and surface water in studies areas select some parameters for come to decision and critical observations such as pH, conductivity, ionic compositions like Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, HCO_3^-, Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+} as well as total alkalinity, hardness, salinity and dissolved solid (TDS). Those ionic parameters are mainly responsible for both alkalinity and hardness but not serious toxic to human physiology. Natural water has trace amount of those individual cation and anion and those are consider to "*essential*" if it is present in all healthy tissues in living things and its deficiency, depletion or withdrawal from the body induces reproducible structural and physiological abnormalities irrespective of the species studied (Dara, 1995). But if the concentration of those parameters is higher than threshold or tolerance limits (Rand *et al*., 1976; WHO, 2011) those become harmful to human health that those components which tend distributed abnormally considered as '*nonessential'* components. For example, Ca is essential element and low dose Ca is responsible for rickets but high concentration of Ca becomes goitrogenic, it binds iodine with the thyroid (Taylor, 1954). In this paper, a co-relation between the parameter's concentration and the distance of sampling sites from the sea bank has also shown.

Sampling Site and Detected Parameters

Chittagong is the second largest city and prime sea port and the heart of commercial and business activities in Bangladesh (Ahmed et al., 2014). This city lies within 22°14' and 22°24' N latitude and between 91°46' and 91°53' E longitude (Chittagong city-Banglapedia, 2018). Chittagong City Corporation(*CCC*) area has an area of 160.99 sq. km and it is divided into 41 wards for administrative purpose (*Fig. 1*). Chittagong city is located towards south-east of the capital city of Dhaka on the bank of Karnafuli river and surrounded by rich natural resources like green hilly terrain, lacks, sea etc. (Ahmed et al., 2014). Surface water samples collected from the Karnafuli river (mouth to 30 km distance from sea, 26 points), ponds (from 20 different place), and sea (from 07 different points). Ground water samples collected from hand tube-well (30 region) at different points. The period of sampling was winter-spring season (average temp. 20^0C) and various alkaline parameters, which stated above, investigated. The chemical constituents generally presented in micro and sub-micro quantities in the water body and their determination at these levels requires accurate, precise, and sensitive analytical techniques. In this study very sensitive and modern type pH meter, conductometer, UV-spectrophotometer, FAAS (facilitate from Atomic Energy Center, DU campus, Dhaka) and as well as analytical-reagent grade chemicals (*Merck, Germany*) used. In this study, Na, K and Mg level were determined by FAAS utilizing Na-tetraborate after the pre-concentration on a column packed (Tokalioglu et. al., 2001) and Ca was determined directly by the same. NO_3^-, NO_2^-, SO_4^{2-}, PO_4^{3-} and NH_4^+ investigated by UV-visible spectrophotometer (*Shimadzu, model-160*) with the help of calibration curve for respective standard color developed solution (Kudesia, 1990; Hadi *et al.*, 1991).

2. Sources of Alkalinity and Hardness in Natural Water

Sources of alkalinity

Alkalinity in water system derived from several sources: soil ion-exchange reactions, weathering of minerals and rocks, precipitation and evaporation of minerals, biological reception, reduction of strong acid anions, and atmospheric dust-particle deposition (WHO, 2011).

Cation exchange. Cation exchange may increase alkalinity when H^+ in solution exchange on surface by base cations. This effect is generally reversible and thus the process may not contribute to long-term increases in alkalinity once the cation exchange sites depleted. Basically, cation exchange can act in reverse if base cations added from sea spray or road salt to a soil solution, causing temporary acidification and loss of alkalinity. However, soils with large cation exchange capacities can act as a large buffering reserve against relatively short-term acidification events (WHO, 2011; WRC, 2018).

Weathering of rock and mineral. The large variations in the alkalinity of inland waters can be attributed to the degree of weathering of bedrock material and soils. Rock can divide into three broad classes: slow weathering non-carbonate rock (e.g., gneiss or igneous rock) with resulting thin soils, low cation exchange capacity, and low pH; moderate weathering of rocks with low carbonate content, but deeper soils; and rapid weathering carbonate bedrock (e.g., alluvial limestone), deep soils with high cation exchange and high soil pH (Kaushal et. al., 2013). In areas where bedrock is deeply buried, soils play the major role in alkalinity of surface waters. The weathering of rock provides carbonates and to a lesser extent silicate as weak acid anions along with base cations such as Ca and Mg from the rock which creates hardness in water (UNEP, 1992).

Evaporation and Precipitation. The amount of alkali produced by chemical precipitation reactions depends on the cations and anions involved. Precipitation of $CaCO_3$ as calcite mineral removes two equivalents of alkalinity from solution because the base cation Ca^{2+} removed by a weak acid anion CO_3^{2-} (Wilson, 2010). However, the precipitation of gypsum, $CaSO_4$, has no effect because equal equivalents of base cation and strong acid anion removed together. Just as dilute low alkalinity waters can mix with and reduce alkalinities of surface waters, such as occurs during heavy rainfall or snowmelt events, transpiration and evaporation can concentrate waters, resulting in seasonal and daily fluctuations in alkalinity. Typically, the first minerals to precipitation are Ca and Mg-carbonate (Thomas et. al., 2008). In areas dominated by silicate bedrock weathering, other monovalent cations such as the alkali metals, Na and K may be abundant enough to create alkaline soda lakes as the polyvalent cations quickly precipitate out of solution.

Assimilatory uptake. The uptake of inorganic carbon and other cations and anions during plant growth are generally balanced with little net effect on alkalinity with the general exception of nitrogen uptake. The uptake of NO_3^- during plant growth tends to raise alkalinity of the solution (WRC. 2018; DPI, 2018). Forests, for example, may produce net gains in alkalinity in stream water by the uptake of nitrate found in acid.

Dissimilatory redox reactions. A similar reaction may occur with dissimilatory uptake of acid anions. In this case anaerobic microbes do not use the ions to build cellular material, but instead use the NO_3^- and SO_4^{2-} ions as electron acceptors during anaerobic decomposition of organic matter (WRC. 2018; DPI, 2018). This process strips the oxygen from the acid anions to produce CO_2 and in effect removes the strong acids from solution (Thomas at. al., 2008). The reduced end products from the processes of denitrification and sulfate reduction are N_2 and H_2S respectively. If the reduced product is not re-oxidized, the alkalinity gain is permanent (Wilson, 2010).

Sources of Hardness

Hardness of water not caused by a single substance but by a variety of dissolved polyvalent metallic ions, predominantly Ca and Mg cations(Wilson, 2010). It mostly expressed as mg/L of $CaCO_3$ equivalent. Although hardness caused by cations, it may also discuss in terms of carbonate (temporary) and non-carbonate (permanent) hardness. The principal natural sources of hardness in water dissolved polyvalent metallic ions from sedimentary rocks, seepage, and runoff from soils. Ca and Mg, the two principal ions, are present in many sedimentary rocks, the most common being limestone and chalk (Snoeyink, 1980). Also, they are common essential mineral constituents of food. As mentioned above, a minor contribution to the total hardness of water also made by other polyvalent ions, such as Al, Ba, Fe, Mg, Sr, and Zn (CWSE, 2009).

3. Materials and Methods

Samples collected from surface and ground water sources and then transported to laboratory; preserved by adding 40 mg $HgCl_2$ per liter and refrigerate for NO_3^-, NO_2^-, and PO_4^{3-} level determination (De, 1992). For metal analysis the water samples made acidic with conc. HNO_3 in order to minimize chemisorption and hydrolysis of metal ion and preserved at 4^0C in refrigeration (Lajunan, 1992). pH measurement performed by using an NEL, digital pH-meter with a combination electrode and sp. conductivity investigated by Conductivity Bridge (Type-PW950/01, Philips, Holland). HCO_3^- and Cl^- levels of samples measured by simple acid-base titration and by the titration with standard $AgNO_3$ solution respectively. For UV-spectrophotometer analysis, standard nitrite, nitrate, sulfate, and phosphate solution were prepared (Hadi *et al.,* 1991) from *analar* grade $NaNO_3$, $NaNO_2$, K_2SO_4 and K_3PO_4 salts. Distilled de-ionized water used for standard dilution and necessary preparations. The calibration curves previously constructed by using respective standard solution. For the color development of samples, a usual procedure (Rand *et al.,* 1965) followed. The absorbance of the colored solution measured for nitrite, nitrate, sulfate and phosphate at 520 nm, 410 nm, 500 nm, and 380 nm respectively using a reagent blank referring it to the calibration curve (APHA, AWWA, WEF, 1988). A Perkin Elmer 3110 model Atomic Absorption Spectrometer (AAS) with an air-acetylene burner used in the determination of the metals in the water samples. To determine the metals by using the column filled with Amberlite XAD-16 resin, the column procedure which had previously optimized with model solution used (Tokalioglu *et al.,* 2001). For this purpose, the pH of an aliquot of 450 ml of the water sample adjusted to 9.2 using Na-tetraborate reagent and then the solution obtained passed through the column at a flow rate of 1ml/min. with the aid of a vacuum pump. The metals retained on the column eluted with 1M HCI in acetone and then elute was evaporate to incipient dryness. The residue taken into a volume of 2 ml with 1M HCI. The measurement of the metals performed by FAAS using the injection method. Ca was also determined directly by FAAS after diluting the samples when necessary (Rand *et al.,* 1965).

To determine the alkalinity, a known volume of water sample is titrated with a standard solution of strong acid to a pH value in the range of 4 to 5 and total hardness determined by EDTA titration at pH 10 (Julian et. al., 2008, US-EPA, 1978a, 1978b). Titrations should be distinguishing between three types of alkalinity; carbonate, bicarbonate, and total alkalinity. In this study, only total alkalinity measurement performed. It is determined by titration of the water sample to the endpoint of the methyl orange indicator, or an approximate pH of 4.5 (US-EPA, 2006; APHA, 1998). The higher the total alkalinity, the lower the endpoint will be (Snoeyink and Jenkins,1980). The following endpoints, corresponding to total alkalinity concentrations, suggested in AWWA (1992): pH = 5.1 for total alkalinities of about 50 mg/L, pH = 4.8 for 150 mg/L, and 4.5 for 500 mg/L. Alkalinity measurements often made on-site but sometimes not considered to be as critical as pH, since the loss of CO_2 does not in itself change the alkalinity. However, Smith and Fritz (1988) and Fritz et. al., (1969) found that significant errors introduced using laboratory rather than *in-situ* data because of biological activity that changes the alkalinity or extreme loss of CO_2 may lead to precipitation of $CaCO_3$ in the sample container. For these reason, total alkalinity of collected samples investigated after several hours from collection time.

4. Results and Discussion

The alkaline parameters with total hardness, alkalinity, and salinity level of collected water samples from various sources given in Table 1 and 2. The pH level and sp. Conductivity of all samples found to be somewhat higher, that indicates the basicity and the higher concentration of total salt in natural water. A higher pH-value (7.3 - 8.8) of Karnafuli river in studied areas obtained due to the alkaline materials accumulation by the various industries. The level of total alkalinity, hardness, and salinity presented in same Tables. Result shows that the values of these parameters are very high than threshold level (Table 4). If alkalinity is much less than total hardness it may signify elevated levels of $C1^-$, NO_3^-, or SO_4^{2-}. Water with low levels of alkalinity (<150 mg/L) is more likely to be corrosive; whereas, high alkalinity (>150 mg/L) may contribute to scaling (DPI, 2018). Total hardness in water less than 150 mg/L considered soft water while values greater than 200 mg/L considered hard water. In that view, maximum samples collected from various sources of Chittagong city are very hard. Among the halide, chloride is the most dominant ion in water and is mainly responsible for salinity. The $C1^-$ concentration of ground (80.3 - 710 mg/L) and surface (river: 90 - 18400, pond: 50 – 90, sea: 970-16220 mg/L) water samples is much higher than other region of Bangladesh (Majumder and Shajedul, 1995) and native and international standard also (Table 4). Logically, due to sea attachment, the ground and surface waters are containing higher concentration of chloride salts. It is relatively harmless but a salty taste in water will appear only. Among the cations and anions, the most significant parameter is Ca^{2+} and HCO_3^- and these ion concentrations in ground water found to be higher than that in surface water in the studied areas. The carbonate-rich water dissolves calcium and is, therefore, responsible for the hardness of water and is very favorable for the growth of G-strain bacteria (WHO, 2011). Already a study (Majumder and Shajedul, 2005) has established that both surface and ground water of Chittagong city are very hard, mostly is temporary. Both NO_2^- and NO_3^- found in surface water to be present in low concentration and lower than Rajshahi and Dhaka city (Mostafa et. al., 2015; Hadi *et al.,* 1991) which exceeds the danger level. Probably the inhabitants of the present investigated areas used lower amount of nitrogenous fertilizer than these areas. NO_3^- and NO_2^- found naturally by electrical storm, nitrogen-fixing organism, and the action of bacteria on ammonia. The levels of NO_2^- are far below the level of NO_3^- which usually expected because NH_3 oxidized by nitrifying bacteria to nitrite and then by nitrifying bacteria to nitrate. But the level of these ions are somewhat high in ground water (NO_2^-: 0.3 - 0.92 and NO_3^-: 3.5 - 57.7 mg/L) than surface water (river- NO_2^-: 0.35 - 0.79, NO_3^-: 11.7 - 16.2 mg/L and ponds- NO_2^-: 0.29 - 0.81, 11.9 - 16.1 mg/L) samples. NO_3^- is particularly dangerous to infants less than six-month-old, causing child disease, *methemoglobinemia*.

Table 1: Alkaline parameters concentration determined with standers deviation(±sd) value in the surface water of Chittagong city.

Parameters	Karnafuli River water			Pond water			Sea water		
	No. of samples	*Range, mg/L*	*Mean conc ±sd, mg/L*	*No. of samples*	*Range, mg/L*	*Mean conc ±sd, mg/L*	*No. of samples*	*Range, mg/L*	*Mean conc ±sd, mg/L*
pH	24	7.3-8.8	7.8 ± 0.03	16	7.3-7.9	7.5 ± 0.03	07	8.1-9.4	8.6 ± 0.3
sp. Cond.*	24	0.8-2.9	1.9 ± 0.11	16	0.1-1.1	0.25 ± 0.03	07	28-53.7	39.7 ± 1.2
TDS**	24	7.3-18.2	11.9 ± 0.37	16	11.0-1.6	1.3 ± 0.19	07	18.3-20.1	18.9 ± 0.9
Total salt**	24	0.04-32.7	6.15 ± 5.1	16	0.12-0.17	0.14 ± 0.03	07	17.1-18.9	17.9 ± .02
Alkalinity (Total)	24	30.3-150	72.4 ± 3.9	16	215-267	136.6 ± 1.9	07	125-199	167 ± 1.1
Hardness (Total)	26	65.3-851	402 ± 37.6	16	122-159	136.6 ± 11	07	751-910	789 ± 0.9
Cl^- **	26	0.09-18.4	3.05 ± 2.5	20	0.05-0.09	0.07 ± 0.01	07	9.7-16.22	13 ± 0.5
NO_2^-	24	0.35-0.79	0.51 ± 0.04	20	0.29-0.81	0.53 ± 0.05	07	3.5-7.9	5.1 ± 0.4
NO_3^-	24	11.7-16.2	14.3 ± 0.08	20	11.9-16.1	13.4 ± 0.07	07	1.1-2.9	1.3 ± 1.1
SO_4^{2-}	24	8.9-54.4	20.1 ± 0.20	20	5.8-23.2	12.1 ± 0.08	07	87.5-104	91 ± 1.2
PO_4^{3-}	24	3.7-36.5	13.3 ± 0.30	20	2.7-48.3	13.2 ± 0.21	07	3.5-6.9	4.6 ± 0.3
HCO_3^-	24	70.1-159	90.7 ± 1.30	20	72-192	92.5 ± 0.3	07	221-274	249 ± 0.1
Na^+**	20	0.05-1.23	0.83 ± 0.5	16	0.03-0.056	0.04 ± 0.01	07	1.22-1.432	1.32 ± 0.1
K^+	20	8.3-102.5	29.7 ± 3.08	16	2.1-22.7	13.7 ± 0.2	07	59-109	65 ± 0.8
NH_4^+	20	1.8-40.3	7.6 ± 0.80	16	0.9-3.5	2.1 ± 0.07	07	0.93-1.3	1. 1 ± 0.2
Mg^{2+}	20	2.5-25.7	6.3 ± 0.63	16	0.9-2.9	1.8 ± 0.03	07	22.1-27.3	24.9 ± 0.2
Ca^{2+}	20	31.3-142	82.1 ± 0.2	16	120-149	129 ± 0.3	07	111-187	137 ± 0.3

*in mmho/cm. **in ppt. [a] standard deviation.

Table 2: Alkaline parameters concentration with standard deviation (±sd) determined in groundwater of different location of Chittagong city.

Parameters	No. of samples	Mean Depth, (m)	Range, (mg/L)	Mean conc ± sd, (mg/L)
pH	30	23.6	7.2-8.1	7.5 ± 0.03
sp. Cond.*	30	23.6	0.35-1.89	1.21 ± 0.09
TDS**	30	23.6	0.709-1.979	1.123±0.027
Total salt**	30	23.6	0.19-2.54	1.01±0.3
Alkalinity (Total)	30	23.6	30.8-732.0	123.9±1.8
Hardness (Total)	30	23.6	65.7-1005	289±9.51
Chloride, $C1^-$	24	22.9	80.3-710	337.6 ± 0.4
Nitrite, NO_2^-	24	22.9	0.31-0.92	0.75 ± 0.03
Nitrate, NO_3^-	24	22.9	3.51-57.7	15.42 ± 0.1
Sulphate, SO_4^{2-}	24	22.9	1.15-53.7	16.53 ± 0.1
Phosphate, PO_4^{3-}	24	22.9	0.32-11.8	1.90 ± 0.2
Bicarbonate, HCO_3^-	24	22.9	51.7-737.3	207.8 ± 0.3
Sodium ion, Na^+**	26	23.1	50.1-260.3	150.2 ± 0.2
Potassium ion, K^+	26	23.1	10.3-190.7	42.7 ± 0.2
Ammonium, NH_4^+	26	23.1	0.91-13.6	5.15 ± 0.09
Magnesium ion, Mg^{2+}	26	23.1	5.53-82.1	32.13 ± 0.5
Calcium ion, Ca^{2+}	26	23.1	12.5-290	102.52 ± 0.5

*in mmho/cm. **in ppt.

Table 3: Alkaline parameters mean concentrations (mg/L) of ground water samples at different distances from sea bank.

Parameters	*Distance from sea bank (km)*							Mean value (mg/L)
	0 - 3	*3 - 6*	*6 - 9*	*9 - 12*	*12 - 15*	*15 - 18*	*18 - 21*	
pH	7.9	8.0	7.6	7.6	7.4	7.3	7.3	7.5
sp. Cond.*	1.80	1.29	1.45	1.30	0.90	0.40	0.30	1.21
TDS	1823	1961	1672	1512	963	1011	719	1123
Total salt**	2.5	1.82	1.91	0.78	0.21	0.51	0.20	1.01
Alkalinity (Total)	723	697	327	411	123	87.7	32.1	123.9
Hardness (Total)	823	1050	902	345	408	102	41.5	289
Cl^-	691	655	409	382	190	201	89	337.6
NO_2^-	0.90	0.81	0.89	0.31	0.49	0.35	0.39	0.75
NO_3^-	45.1	39.5	16.9	12.7	18.6	9.9	7.7	15.42
SO_4^{2-}	43.9	37.7	7.3	11.7	3.1	4.8	1.2	16.53
PO_4^{3-}	8.3	10.7	3.1	7.4	0.4	0.7	1.2	1.9
HCO_3^-	532	448	552	212	79	103	192	207.8
Na^{+**}	252	232	182	192	102	59	63	150.2
K^+	139	179	59	64	19	11	13.5	42.7
NH_4^+	13.0	11.2	5.9	8.3	2.9	1.1	3.9	5.15
Mg^{2+}	71.7	69.8	13.7	28.3	29.9	11.7	5.5	32.13
Ca^{2+}	282	192	183	89	109	122.5	15.3	102.52

*in mmho/cm. **in ppt.

The mean concentration of NO_3^- and NO_2^- in studied areas are less than maximum permissible level (Table 4). The concentration range of SO_4^{2-} and $PO_4^{3-}$of surface water is higher than ground water (Table 1&2). Mine drainage waste may contribute sulfates by virtue of pyrite oxidation and the use of phosphate as fertilizer in agriculture as well as binder in detergent is the main cause of phosphorous load in surface water. Most of the laundry detergent contain 35-50% sodium triphosphate, $Na_5P_3O_{10}$ which yield hydro-liquidly $P_3O_{10}^{5-}$ ion along with soluble $[CaP_3O_{10}]^{3-}$and $[MgP_3O_{10}]^{3-}$ ions. These phosphates are not very toxic but in presence of nitrogen compounds accelerate the growth of algae, cause oxygen depletion from the surface water and increase BOD by eutrophication (Kaupi *et al.,* 1986) process. The results show that the SO_4^{2-} and PO_4^{3-} load in surface and ground water are not objectionable in perspective of drinking, fish culture and industrial purpose (Table-4) etc. Ammonia as ammonium ions or as free ammonia is the most commonly occurring nitrogenous pollutant, apart from being a natural breakdown product. Due to industrial waste effluents the NH_3 as well as NH_4^+ load in the Karnafuli river is quite high than the other river Padma (Islam et. al., 2016). Aquatic life exposed to ammonia levels of 1 mg/L in water may suffocated because of a significant reduction in the oxygen combining capacity of blood (Ottawa, 1980).

Table 4: Standard values (mg/L) of alkaline parameters for natural water. ref: DPH, (2016); WHO, (2011), US-EPA, (2018), FAO, (1998).

Parameters	Drinking			Fishing	Industrial	Irrigation	Livestock
	EQSB	*WHO*	*US-EPA*				
pH	6.5-8.5	7.5-8.5	6.5-8.5	6.5-7.5	7.0	7.5	7.0
Total Alkalinity	200	200	-	-	-	250	-
Total Hardness	200-500	500	300	400	200	500	500
TDS	100	600	500	-	-	500-1000	-
Cl^-	150-600	250	250	600	250	600	2000
NO_2^-	0.5	2.0	1.0	0.5	-	-	Nil
NO_3^-	10	44	10	15	-	-	-
SO_4^{2-}	400	500	250	-	15	-	70
PO_4^{3-}	6.0	2.0	-	0.8	0.8	0.2	0.1
HCO_3^-	-	400	-	-	15	-	500
Na^+	200	200	30-60	-	-	45	-
K^+	10-15	-	-	-	-	-	-
NH_4^+	0.2	-	-	5	0.5	10	10
Mg^{2+}	30-40	50	-	-	-	-	-
Ca^{2+}	75	200	-	-	50	-	700

EQSB-Environmental Quality Standard for Bangladesh

The levels of some metal ions determined in the same samples also given in the Table-1 and 2. Result shows that the level of Na^+, K^+, Ca^+, and Mg^{++} are significantly high. The high concentration of Ca and Mg and HCO_3^- indicate the temporary hardness of water. Reports from several countries have shown an inverse statistical association between the hardness of drinking water and the death rate from cardiovascular disease (WHO, 1971). At the same place the higher concentration of Na^+ in drinking water create the complex reaction of hardness of water and cardiovascular disease rate (Kawasaki et al., 1978, Weinberger et al., 1986; Farquhar et al., 2015). The evidence is based solely on circumstantial evidence and statistical association. Further studies are in progress to establish a possible connection between certain water characteristics and the development of cardiovascular diseases.

Table-3 shows a fantastic correlation between the parameter concentrations of ground water and the distance from sea bank to sampling site. Most of the parameter concentrations are decrease with the distance. The samples of 0 - 2 km distance from sea bank contain much more amount of ionic constitution. So, near the bank of sea areas the ground water is very saline, hard, and alkaline also and this water is not safe for drinking purposes.

5. Conclusion

Water's alkalinity and hardness are the significant parameters since both regime the acidity or basicity characteristics of natural water. Ionic parameters concentration in water depend on the rate of mineral dissolution and weathering of rock in aquifers. These processes controlled by the water pH and that be subject to alkalinity as well as hardness of water. Alkalinity and total hardness are usually nearly equal in concentration when they are both reported in mg/L CaCO3 because they form from the same minerals. If alkalinity is much greater or less than total hardness, it may indicate that water has passed through a water softener or it may signify elevated levels of chloride, nitrate, or sulfate. Water with low levels of alkalinity is more likely to be corrosive and high alkaline water may contribute to scaling. This is a test for overall water quality. There are not enough health concerns related to alkalinity and hardness. The level of alkalinity should be roughly 75% to 100% of the total hardness value in an unsoftened sample. In studied area, the alkalinity almost double in concentration of all samples and this indicate the higher level of chloride, nitrate, or sulfate.

Finally, it may conclude that, among the alkaline parameters Na^+, Ca^{2+}, Cl^- and HCO_3^- levels are quite high in both surface and ground water, this indicated that the water of studied areas is very hard, saline and as well as alkaline and it should not use in domestic and industrial purposes without any treatment. Other parameters are, overall, in permissible ranges.

6. References

Ahmed, B., Rahman, M. S., Rahman, S., Huq, F. F. and Ara, S. (2014). *Landslide Inventory Report of Chittagong Metropolitan Area*, Bangladesh, Dhaka-1000.

APHA, AWWA, and WEF. (1988). *Standard Methods for Examinations of Water and Wastewater.* American Public Health Association (APHA), American Water Works Association (AWWA), and Water Environmental Federation (WEF). 20th ed. Baltimore, Maryland: United Book Press.

Benjamin, M.M. (2015). *Water Chemistry*, 2nd ed. Long Grove, Illinois: Waveland Press, Inc.

Burton, G. A. Jr. and Pitt, R. E. (2002). *Storm Effects Handbook: A Toolbox for Watershed Managers, Scientists, and Engineers*, Boca Raton, FL: Lewis Publishers.

BWDB-UNDP, (1982). *Groundwater Survey: The Hydrogeological Conditions of Bangladesh*. Bangladesh Water Development Board (BWDB) and United Nation Development Programme (UNDP), Technical Report, No. DP/UN/BGD-74-009/1, pp. 113.

Chittagong City-Banglapedia, (2018). Retrieved from: http://en.banglapedia.org/

CWSE, (2009). *Interpreting Drinking Water Quality Results: Identifying Problems and Solutions.* Center for Watershed Science and Education, Trainer Natural Resources Building , 800 Reserve St. Stevens Point, WI 54481.

Dara, S.S. (1995). *A Text Book on Environmental Chemistry and Pollution Control*, 5th ed. New Delhi: S. Chand & Co. Ltd.

De, A. K. (1992). *Environmental Chemistry*. New Delhi: Wiley Eastern Ltd.

Dickson, A.G. (1992). Measuring CO_2 in the ocean. Advances earth and space science. *JGOFS*, 73(51), pp. 546-546.

DPH, (2016). *Water Quality Parameters Bangladesh Standards & WHO Guide line*. Department of Public Health, Govt. of Bangladesh. Source: http://old.dphe.gov.bd/

DPI, (2018). *Monitoring alkalinity and hardness*. Department of primary industries, NSW, Australia. Source: https://www.dpi.nsw.gov.au/

Drever, J. I. (1988). *The Geochemistry of Natural Waters*, 2nd Ed., New Jersey 07632: Prentice Hall.

FAO, , (2011). FAO's Information System on Water and Agriculture. AQUASTAT: Food and Agriculture Organization of the United Nations.

Farquhar, W.B., Edward, D,G., Jurkovitz, C.T. and Weintraub, W.S. (2015). Dietary sodium and health: more than just blood pressure. *J. Am. Col. Cardiol*. 65(10), pp. 1042-50.

Fritz, J.S., Sickafoose, J.P. and Schmitt, M.A. (1969). Determination of total hardness in water employing visual and spectrophotometric titration procedures. *Anal. Chem.* 41(14), pp. 1954-1958.

Hadi, D .A., Trafdar, S.A. and Mia, Y. (1991). The Study of Nitrate, Nitrite and Phosphate in Some River Water Around Dhaka City, Bangladesh . *Nuclear Science and Applications,* 3(1), pp. 73-76.

Hredoy, M.S.N., Naim, M. N. H., Sikdar, M. S. and Islam, M. K. (2018). Spatio-temporal Change Analysis of Wetland in Chittagong City Corporation by Remote Sensing and GIS Technique. *4th International Conference on Advances in Civil Engineering (ICACE 2018)*, 19 –21 December 2018, CUET, Chittagong, Bangladesh.

Islam, M.S., Kabir, M.H., Sifat, S.A., Tushera, T.A. and Meghlaa, N.T. (2016). Status of Water Quality from the Padma River at Bheramara Point of Kushtia in Bangladesh. *Int. J. of Sustainable Water & Environmental Systems,* 8(2), pp. 87-92.

Julian, K.T., Stuart, M. and Reeder, S. (2008). Contaminated Groundwater Sampling and Quality Control of Water Analyses. *Environmental Geochemistry*, pp. 29-57.

Kaupi, L., Kenthomines, K. and E. R. Puomido. (1986). Effect of Nitrogen and Phosphorous Removal from Sewage on Eutrophication of Lakes. *Vesientutkomus Laitoksen Julk*, 69, pp. 70-87.

Kaushal, S. S. (2013). Increased river alkalization in the eastern U.S. *Environ Sci Technol*, 47, pp. 10302–10311.

Kawasaki, T., Delea, C.S., Bartter, F.C. and Smith, H. (1978).The effect of high-sodium and low-sodium intakes on blood pressure and other related variables in human subjected with idiopathic hypertension. *Am. J. Med.* 64(2), pp. 193-8.

Kudesia, V. P. (1990). *Water Pollution*, 3rd ed. Meerut: Progoti Prokashon.

Lajune, L.H.J. (1992). *Spectrochemical Analysis by Atomic Absorption and Emission*. Cambridge, London: The Royal Society of Chemistry, XII, 242 S., Brochure 18.50f, ISBN 0-86 186-873-8.

Majumder, S.M.M.Q. and Shajedul, M.I. (1995). Study on water quality parameter of surface and groundwater in Chittagong and Cox's bazar town. *An international workshop proceeding on 'Coastal Aquaculture and Environmental Management,'* Cox's bazar, Bangladesh.

Majumdar, S.M.M.H. and Shajedul, M.I. (2005). An Extensive Study on Water Quality Parameter of Karnafuli River in an Industrial Belt and their Impact on Aquatic Environment. *Pakistan Journal of Water Resources*, 9(2), pp. 17-22.

McGowan, W. (2000). *Water processing: residential, commercial, light-industrial*, 3rd ed. Lisle, IL: Water Quality Association.

Mostafa, M.G., Helal Uddin, S.M. and Hamidul Hoque, A,B.M. (2015). Assessment of hydro-geochemistry and groundwater quality of Rajshahi City in Bangladesh. *Appl Water Sci*, Springer.

Ottaway, J.H. (1980). *The Biochemistry of Pollution*, London: Edward Arnold Ltd.

Rahman, M.M. and Mahbub, A.Q.M. (2012). Lithological study and mapping of Barind Tract using borehole log data with GIS: In the context of Tanore upazila. *J. Geogr. Inf. Syst*. 4, pp. 349–357.

Rand, R., Gigante, A. E. and Taras, M.J. (1976). *Method for the Examination of Water and Waste Water*, 16th ed. New York: American Public Health Association (APHA).

Reham, M.A.S. (2008). *Comprehensive Analytical Chemistry*, Elsevier, Volume 81, ISSN 0166-526X.

Smith, D.L. and Fritz, J.S. (1988). Rapid determination of magnesium and calcium hardness in water by ion chromatography. *Analytica Chimica Acta*. 204, pp. 87-93.

Snoeyink, V.L. and Jenkins, D. (1980). *Water Chemistry*. New York | Chichester: Wiley.

Taylor, S. (1954). Calcium as a goitrogen. *J. Clinical Endocrinol.* 14, pp. 1412-1412.

Thomas, H., Schiettecatte, L-S., Suykens, K., Kone, Y.J.M., Shadwick, E.H., Prowe, A.E.F., Bozec, Y., de Baar, H.J.W. and Borges, A.V. (2008). Enhanced Ocean Carbon Storage from Anaerobic Alkalinity Generation in Coastal Sediments. *Bio-geosciences Discussions*. 5, pp. 3575-3591.

Timmons, M.B., Ebeling, J. M., Wheaton, F. W., Summerfelt, S. T., and Vinci, B. J. (2002). *Recirculating Aquaculture Systems,* 2nd ed. Ithaca, N.Y: CAYUGA AQUA VENTURES.

Tokalioglu, S., S. Ugur, and S. Kartal (2001). Determination of Fluoride and some Metal Ion Levels in the Drinking Waters in Kayseri Province. *Turkey Journal of Chemistry*, 25, pp. 113-121.

UNEP, (1992). Water Quality Assessments - *A Guide to Use of Biota, Sediments and Water in Environmental Monitoring.* 2nd Ed., London: Published on behalf of WHO by F & FN Spon, 11 New Fetter Lane, EC4.

UNICEF, (2009). *Water, Sanitation and Hygiene*. Annual Report-2009, UNICEF WASH Section Programmes, UNICEF, New York.

US-EPA, (2006). *pH and Alkalinity.* Volunteer Estuary Monitoring Manual, A Methods Manual, 2nd Edition, Chapter 11, United State-Environmental Protection Agencies, US-EPA-842-B-06-003.

US-EPA, (2013). *Total Alkalinity. Water: monitoring and assessment,* United State-Environmental Protection Agencies, EPA'S wave archive. https://archive.epa.gov/

US-EPA. (1978a). *Alkalinity (Titrimetric, pH 4.5).* Methods for the Chemical Analysis of Water and Wastes (MCAWW), United State-Environmental Protection Agencies, US-EPA, Method: 310.1, EPA/600/4-79/020.

US-EPA. (1978b). *Hardness, Total (mg/L as $CaCO_3$) (Titrimetric, EDTA).* Methods for the Chemical Analysis of Water and Wastes (MCAWW), United State-Environmental Protection Agencies, US- EPA, EPA Method: 130.2, EPA/600/4-79/020.

US-EPA, (2018), *Drinking Water Standards and Health Advisories Tables*. EPA 822-F-18-001, Office of Water, U.S. Environmental Protection Agency, Washington DC.

Weinberger, D.R., Berman, K.F. and Zec, R.F. (1986). Physiologic dysfunction of dorsolateral prefrontal cortex in schizophrenia. I. Regional cerebral blood flow evidence. *Arch. Gen. Psychiatry*. 43(2), pp. 114-24.

WHO, (1971). *International Standard for* Drinking *Water*. 3rd ed. World Health Organization (WHO), Geneva.

Wilson, P.C. (2010). *Water quality notes: Alkalinity and Hardness*. UF/IFAS Extension, U.S. Department of Agriculture and University of Florida, IFAS, Florida.

WHO, (2011). *Hardness in Drinking-water*. Background document for development of WHO Guidelines for Drinking-water Quality, World Health Organization, Geneva, HSE/WSH/10.01/10/Rev/1.

WRC, (2018). *Hard Water, Hardness, Calcium-Magnesium, Water Corrosion, Mineral Scale.* Water Research Center (WRC), B.F. Environmental Consultants Inc. 15 Hillcrest Drive, Dallas, PA 18612.

Zahid, A. (2015). *Groundwater aspects in Bangladesh*. Technical report, Center for Water and Environment (CWE) and Bangladesh Water Development Board (BWDB), Dhaka.

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