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HYDROGEOCHEMICAL PROPERTIES PROVIDING LINKS TO METHANOGENESIS IN DEEP AQUIFER OF BHOLA ISLAND, BANGLADESH

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Abstract

This paper compares the hydrogeochemical signatures between naturally flowing wells with methane (FWs) and non-flowing wells (require pumping) without methane (NFWs) by analyzing a total of 59 groundwater samples to find possible links for methane gas generation. Relatively higher concentration of HCO_3^- indicates oxidation of organic matter (OM) for both the cases which is corroborated by the dominance of Na-Mg-HCO_3 and Na-Mg-HCO_3-Cl water type. Low concentrations of redox sensitive parameters i.e., NO_3^-, SO_4^{2-}, Fe^{2+} and Mn^{2+} are indicating prevalence of extremely reducing condition and relatively lower concentrations of SO_4^{2-} in FWs suggest microbial sulphate reduction reaching final stage of redox ladder i.e., methanogenesis. Comparatively higher temperature and subsequent higher electrical conductivity (EC) in FWs possibly attributed by the chemical reactions of methane generation or vice versa. Low geothermal gradient, presence of OM and distribution of the FWs over a paleo valley in the deep confined aquifer zone refer to the existence of favourable environment for biogenic methane production rather than the upward migration or leakage of thermogenic gas from the reservoir below.

Key words: Methane gas, Deep tubewells, Deep aquifer, Hydrogeochemistry, Methanogenesis

Introduction

Presence of methane gas in the water wells is not uncommon and many parts of the world have been reported to have microbial methane gas in water wells including Canada, United States, Denmark, Gulf of Mexico, Russia, East of China (Ridgeley *et al.* 2001, Molofsky *et al.* 2016, Bernerd *et al.* 1976, Delaune *et al.* 1986, Zhang *et al*. 2008, Kulongoski *et al.* 2018). Biogenic methane is frequently occurred at shallow depth (10 - 100 m) in the recent fluvio-deltaic plains of Bangladesh where extremely reducing condition prevails (Ahmed *et al.* 1998, Hoque *et al*. 2003). Interestingly unlike other parts of the country, Bhola district is unique in the context of water well methane gas occurrence due to its presence in the household deep tube wells specifically in FWs installed between 260 m and 295 m depth of the aquifer zone which sits on the Shahbazpur anticline, a mega-reserve of thermogenic gas (Imam 2015) and non-coexistence with highly saline groundwater (Ahmed *et al.* 1998).

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These deep tube wells are the only source of water which provide quality drinking water to local people (EC<1 mS/cm) (BWDB 2013) as shallow tube wells (depth<35 m) are unusable due to presence of high salinity (EC~8 mS/cm, according to field investigation).

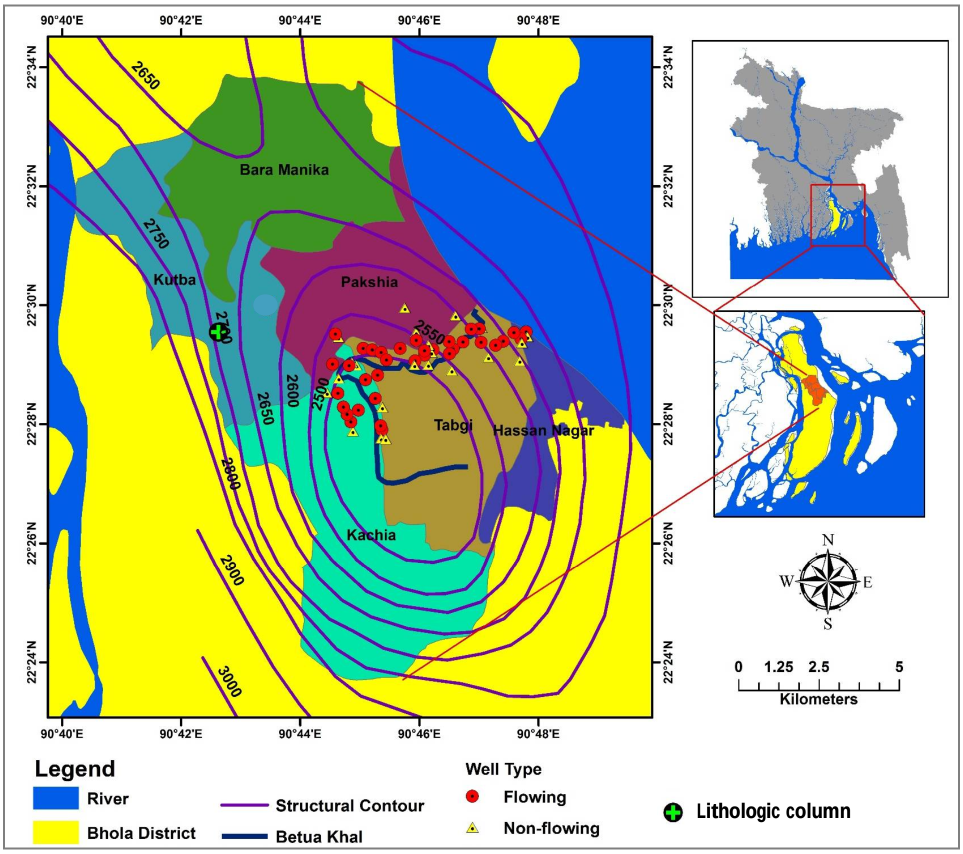


Fig. 1. Map of study area in Burhanuddin Upazilla, Bhola Island showing Shahbazpur anticline in purple contours and water sampling locations; yellow triangle for non-flowing wells (NFWs) and red circle for flowing wells (FWs) and lithologic column location green cross within black circle.

Therefore, the evaluation of hydrogeochemical properties of this strategically important source merits attention. Shallow groundwater in association with methane gas has been studied (Ahmed *et al.* 1998, Hoque *et al.* 2003) and most studies of the deep groundwater is confined to arsenic association (Shamsudduha *et al.* 2018, Hoque 2010, Burgess *et al.* 2010*)* and no study has been done so far on deep groundwater to methane gas association in Bangladesh. At this end, an attempt has been made to assess hydrogeochemistry of the deep groundwater and to compare the hydrogeochemical nature of FWs and NFWs in order to link them with methane gas association.

The study area covered five unions i.e., Kachia, Tabgi, Kutba, Pakshia and Hassan Nagar of Burhanuddin Upazilla of Bhola Island, the largest offshore island in Bangladesh situated in the south eastern part at the mouth of Meghna river (Fig. 1). A natural khal named “Betua” is present nearly at center of the study area is a major geomorphic feature of interest (Fig. 1). In the subsurface of Bhola Island, Shahbazpur anticline is present where fluvio-deltaic sequence of Holocene age composed of fine to medium unconsolidated sand interbedded with clay layers and occasional presence of woody material extended up to 480 m depth (BAPEX 1995), Mondal *et al*. 2009, Rahman *et al*. 2016). This thick fluvio-deltaic sequence forms the aquifers *viz.* shallow, main and deep aquifers (BWDB-UNDP 1982) in the area where the deep zone is the depth of interest in this study. Deep seated gas has been discovered at a depth > 2500 m in Shahbazpur structure being produced commercially since 1995 (Mondal *et al.* 2009). On the other hand, the supply of methane gas through FWs is not limited but rather extensive which are deliberately constructed targeting deep aquifer within 225 to 290 m depth are composed of fine to medium sand and aimed to collect methane gas and water simultaneously. These FWs provide good quality of water as methane gas escapes immediately after reaching surface. The local people have been using this vented gas for household purposes through low tech local method since 1953 (BAPEX 2007) but frequently facing difficulties during well construction due to the presence of high pressure zones in the aquifer. The pressure of the gas in FWs is adequate to serve the households (BAPEX 1995).

Materials and Methods

Fifty nine groundwater samples from deep household tube wells (depth range 260 - 370 m) have been collected for chemical analysis out of which 24 are from NFWs and 35 from FWs. Fig. 1 shows spatial distribution of sampled FWs and NFWs.

The onsite parameters i.e., EC, pH, temperature were recorded in each location using portable EC and pH meter. Filtered acidified and unacidified samples were collected using standard methods and analyzed in the hydrogeochemistry laboratory at the Department of Geology, University of Dhaka. Concentration of cations (major and minor) were measured using Atomic Absorption Spectrophotometry and concentrations of anions i.e., sulphate and nitrate were measured by Ion Chromatography. Titration method was used to measure the concentration of bicarbonate. The quality of the sample analysis was checked by ionic balance and taken as ±10% for hydrochemical assessment. Sediment samples (return wash samples during well drilling) were collected from one borehole installed by Department of Public Health Engineering (DPHE) in Kutuba union which is about 3 - 4 km away from the sampling periphery and lithologs have been produced by visual inspection (Fig. 8b).

Moreover, total organic carbon (TOC) has been analyzed for the aquifer sand and underlying clay between 250 m and 285 m depth by Loss on Ignition (LOI) method. Data were compiled in excel spread sheet and analysis was done using hydrogeochemical software Aquachem 4.0. All the maps were produced using mapping software ArcGIS 10.1.

Results

Variations of temperature and EC: Temperature of groundwater shows relatively higher values in FWs (27 - 32.5°C) than the NFWs (25.5 - 28.4°C) which may be due to chemical reaction during methane gas generation (Fig. 2a) and is not depth controlled. Electrical conductivity (EC) does not vary significantly between the two sampling groups but is shown to be relatively higher in FWs (Fig. 2b) ranging from 0.5 to 1.38 mS/cm whereas it ranges from 0.56 to 1.0 mS/cm in NFWs except one sample having EC of 1.31 mS/cm.

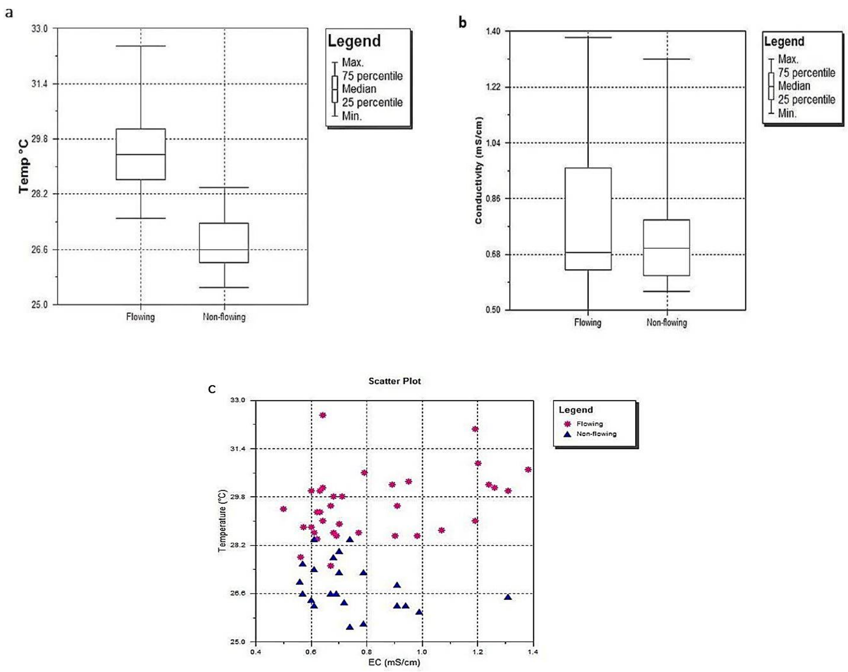


Fig. 2. Box and Whisker plot of temperature (a) and EC (b) in FWs and NFWs; Scatter plot EC and temperature (c) in FWs (shown as pink stars) and NFWs (shown as blue triangles).

Majority of samples from FWs are positively related to the temperature (Fig. 2c) (Freeze and Cherry 1979) and the reason of the counter intuitive relation for many wells in NFWs remains unknown. A noticeable spatial pattern of relatively high temperature and high EC is observed for FWs in eastern part of the sampling zone covering Kachia and Tabgi union (Fig. 3a,b).

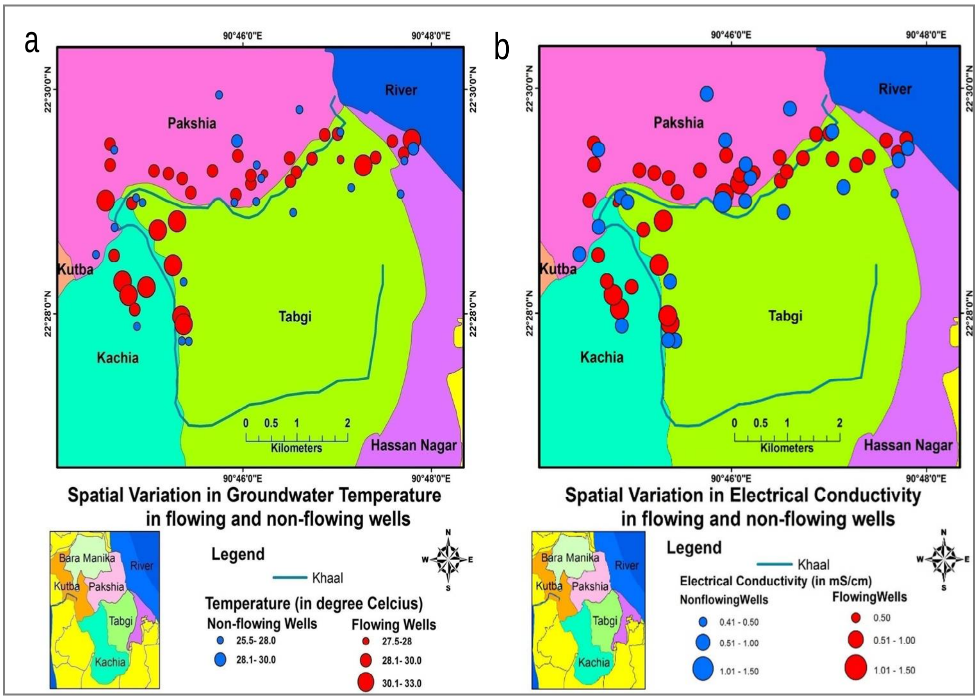


Fig. 3. Map showing spatial variation of temperature (a) and EC (b) in FWs and NFWs.

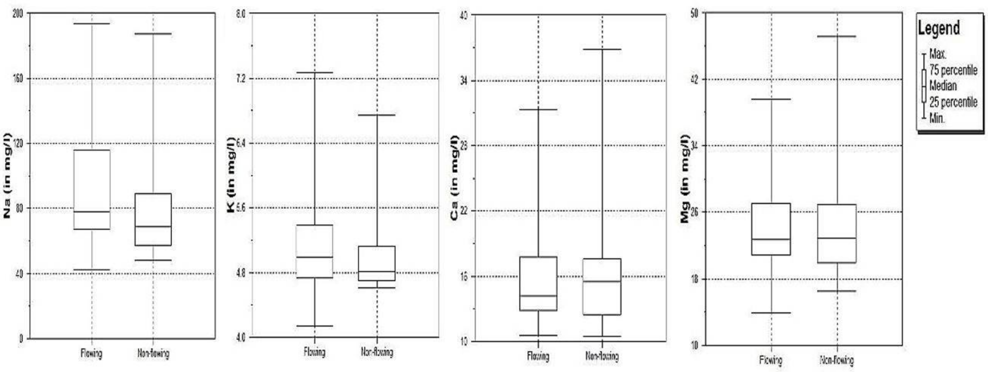
Variation in concentrations of major and minor ions: Relatively high Na^+ and K^+ concentrations of deep groundwater (in both FWs and NFWs) in the study area adjacent to the Shahbazpur gas field pointing to reducing aquifer indicating the water with higher retention time which is further supported by low Ca^{2+} ion concentrations. Concentrations of Mg^{2+} ion in both FWs and NFWs are in similar range and generally are low (Table 1 and Fig. 4). On contrary, the concentrations of HCO_3^- ions in both FWs and NFWs are high suggesting oxidation of organic matter (Table 1). Minor ions like Fe^{2+} and Mn^{2+} play pivotal role in determining groundwater condition and the low concentration of Mn^{2+} concomitant with low concentration of Fe^{2+} both in FWs and NFWs (Table 1 and Fig. 6) indicates reducing condition. Low concentration of Mn^{2+} may be due to prevalence of reduced condition.

Among major cations, sodium and potassium have shown distinguishing variation between FWs and NFWs (Table 1). The median of Na^+ concentrations is 77 mg/l in FWs and is higher than the median of NFWs which is 65 mg/l (Fig. 4) and in both the cases majority of the samples lie above median.

Table 1. Concentrations of major and minor ions in mg/l of FWs and NFWs.

	Ions	FW (mg/l)	NFW (mg/l)
Major ion	Na+	42.47 - 194.53	47.89-187.55
	K^+	4.142 - 7.27	4.27 - 6.75
	Ca^{2+}	10.5 - 31.34	10.44 - 36.84
	Mg^{2+}	13.97 - 39.62	13.97 - 47.17
	HCO_3^-	274.5 - 381.25	289.75 - 373.63
	NO_3^-	0.005- 0.18	0.007-0.30
	SO_4^{2-}	0-0.18	0.00-1.06
	Cl^-	10.27-203.76	3.9-210.98
Minor constituents	Mn^{2+}	0.01-0.091	0.00-0.077
	Fe^{2+}	0.012-1.38	0.017-1.33

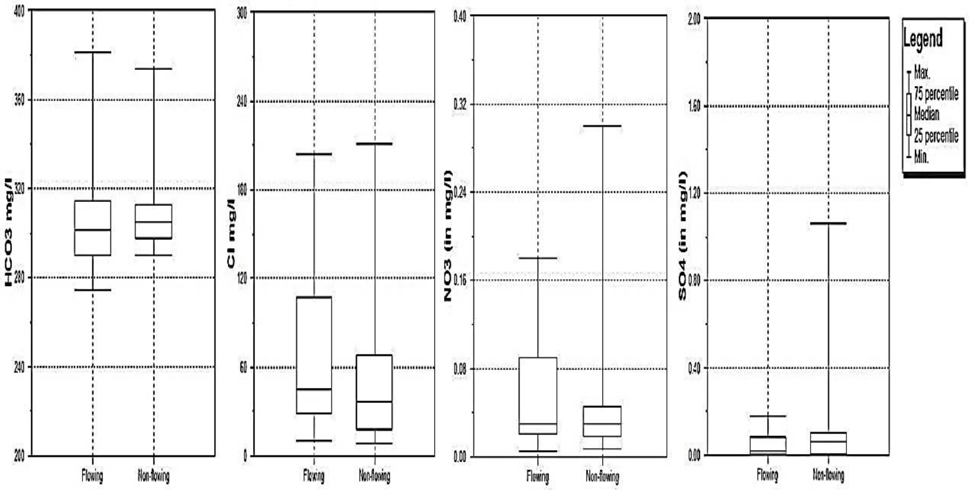
Similar observation applies for the concentration of K. Cl^- concentration of groundwater in most of the FWs vary within a range of 10.27 to 199.02 mg/l with a median value 45.27 mg/l except one sample having higher value (203.76 mg/l) (Fig 5).



Na^+ K^+ Ca^{2+} Mg^{2+}

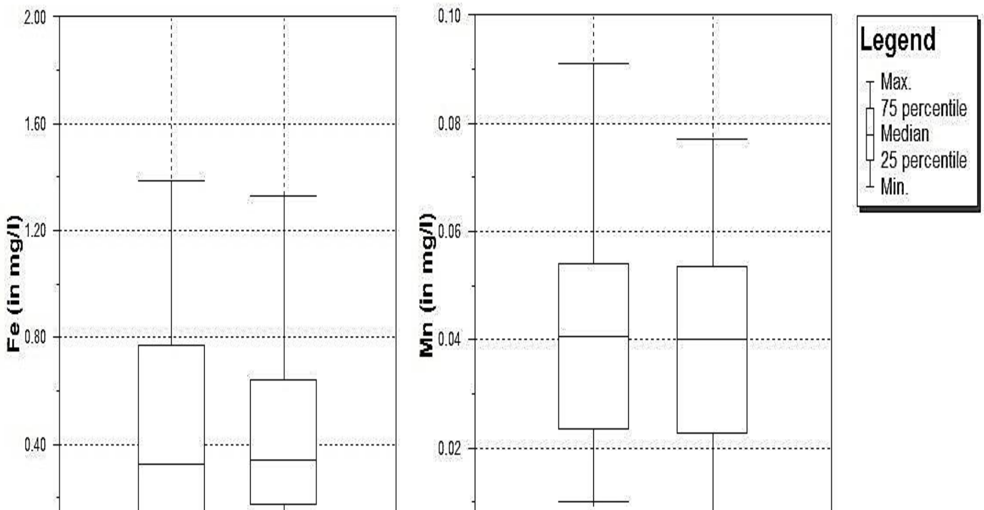
Fig. 4. Comparison of concentrations of major cations in mg/l in FWs and NFWs.

On the other hand, the range is 3.9 to 126 mg/l in most of the NFWs except one sample having concentration 210.98 mg/l with a median value of 42.65 mg/l. $NO_3^-$and SO_4^{2-} ion concentration is below detection level in most of the cases except a few where both of them shows relatively higher concentration in FWs than NFWs. These undetectable and very low $NO_3^-$and SO_4^{2-} concentration in the wells may be due to anaerobic ambience facilitating reduction reactions (Table 1, Fig. 5). The concentration of Fe^{2+} and Mn^{2+} are also very low (Fig. 6).



HCO_3^- Cl^- NO_3^- $SO4^{2-}$

Fig. 5. Comparison of concentrations of major anions in mg/l in FWs and NFWs.



Fe^{2+} Mn^{2+}

Fig. 6. Concentrations of Fe^{2+} and Mn^{2+} in mg/l in FWs and NFWs.

Hydrochemical facies: The chemical compositions of water slightly vary between FWs and NFWs. Na-Mg-HCO_3-Cl type water dominate (~50%) in FWs whereas Na-Mg-HCO_3 type is predominant (~50%) in NFWs (Fig. 7). About 40% samples show Na-Mg-HCO_3 type water in FWs and nearly 40% samples are of Na-Mg-HCO_3-Cl type in NFW. There are a few wells which indicate occurrence of Na-HCO_3-Cl type water. Groundwaters types of Na-Mg-HCO_3-Cl, Na-Mg-HCO_3 and Na-HCO_3-Cl in association with vanishing concentrations of nitrate and sulfate in reducing condition suggesting *in situ* methane formation under methanogenesis (Humez *et al.* 2016).

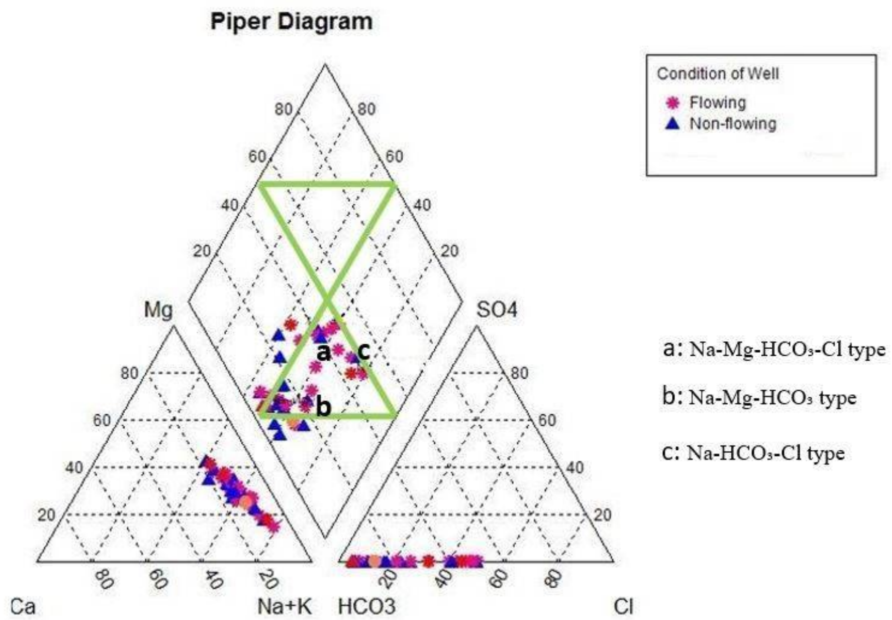


Fig. 7. Piper Diagram showing types of water in FWs and NFWs.

Redox ladder providing links to methanogenesis: It is suggested that enrichment of HCO_3^- took place due to oxidative dissolution of organic matter present in the aquifer. The following reactions are likely to occur there:

$$CH_2O + O_2\,(g) = CO_2\,(g) + H_2O$$

$$CO_2\,(g) + H_2O = H^+ + HCO_3^-$$

Chemical analysis of FWs and NFWs reveals low concentrations of redox sensitive parameters such as NO_3^-, SO_4^{2-}, Fe^{2+} and Mn^{2+} (Table 1) indicate prevalence of highly reducing environment (Fig. 8a). Redox ladder or oxidation-reduction reaction series can be a proxy to identify the origin of methane as microbial methanogenesis where CO_2 reduction as its main formation pathway (Ahmed *et al.* 1998, Kulongoski *et al*. 2018).

Microbial reduction of sulphate and organic matter (OM) in the sediment leads to the suitable environment for methane fermentation (Molofsky *et al.* 2013). The possible reduction reaction of sulphate and organic matter in the anaerobic environment of deep aquifer is as follows:

$CH_2O + SO_4^{2-} = HCO_3^- + HS^- + CO_2 + H_2O$ (I) (Ahmed *et al.* 1998)

$CH_2O = CO_2 + CH_4$ (II) (Zhang *et al.* 1997)

Though concentrations of SO_4^{2-} is low both in FWs and NFWs, relatively lower concentrations of SO_4^{2-} in FWs suggest microbial sulphate reduction reaching final stage of redox ladder i.e., stage of methane fermentation. (Fig. 8a).

The catalyzing action of the anaerobic bacteria was also identified on site of FWs by the rotten egg smell of H_2S gas. The reaction incorporated in generation of H_2S gas is:

$HS^- + H^+ = H_2S$

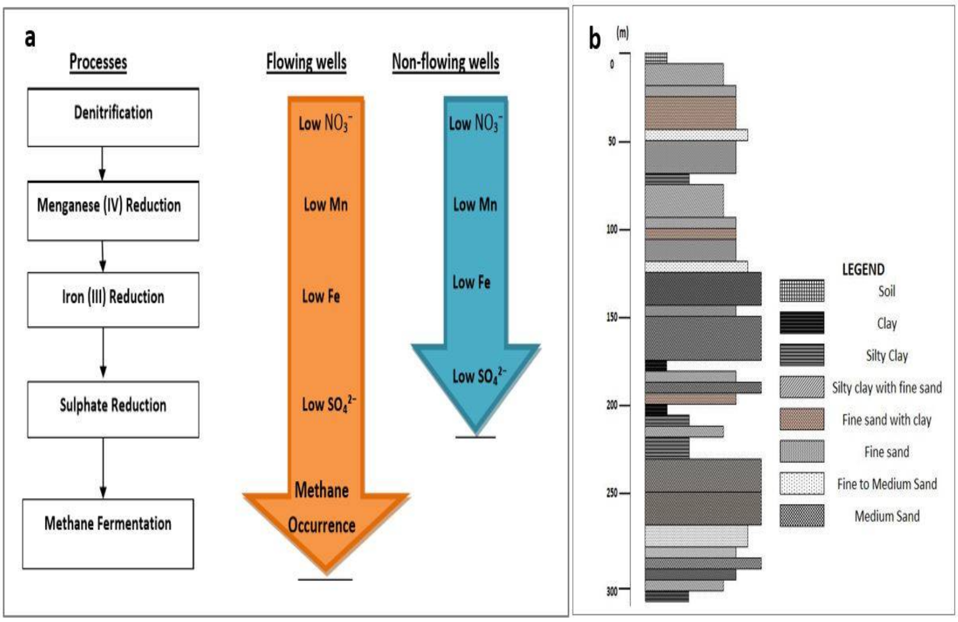


Fig. 8. (a) Redox Ladder showing the stages of reduction reactions in the aquifers for FWs and NFWs and (b) lithologic-column from DPHE test well in Kutuba union, Burhanuddin Upazilla. (Location shown in Fig. 1).

The lithological column (Fig. 8b) indicates a sequence of gray coloured unconsolidated fine to medium sand interbedded with silty clay and clay layers indicating low degree of compaction and forms three cycles of sedimentation (fining upward). No woody material was found as mentioned in literature (BAPEX 1995, Mondal *et al.* 2009, Rahman *et al.* 2016) may be either due to the distant location of the well used for litholog generation from the sampling periphery or due to generation of litholog from wash samples which cannot catch single details of subsurface variation.

Deeper layer of silty clay at 236 m separating the upper sequences from the lower sequences may be acting as the confining layer above the deep aquifer in which all the FWs and NFWs are screened where the presence of FWs themselves are proof of confined and/or artesian aquifer. Lack of oxygen supply by being limited/no vertical recharge in such depth provides this deep confined aquifer zone suitable anaerobic atmosphere for methanogenesis.

Though wood particles were not found, some blackish particles were observed in sand samples at depth between 250 and 285 m. The measured TOC content of these samples is ~0.04 and underlying clay is 0.11 which is almost one order of magnitude lower than the required amount (0.5%) for any hydrocarbon generation (Tissot and Welte 1984).

Most of the FWs are located in the axial region of Shahbazpur gas field along "Betua Khal" a major geomorphic feature indicative of existence of paleo-valley (Molofsky *et al.* 2016) that have been shifted and subsided over the past geologic time. Low geothermal gradient (2 < 2.5 k/100 m) have been reported (Kabir 2007) for the region despite being an area of thermogenic gas reserve. FWs have been tested several times by BAPEX to find any clue about seepage from the thermogenic gas reservoir. No evidence of fracture has been reported so far in 2250m vertical profile of Shahbazpur structure (BAPEX 1995) to validate possibility of thermogenic gas migration from the mega-reserve present at a depth of >2500 m (Mondal *et al.* 2009) to FWs constructed at ≤ 320 m depth. The composition of the gas of FWs as identified by its flammable characteristics is pure methane occasionally associated with little higher hydrocarbons (BAPEX 2007). Generally, biogenic gas contains >98.5% methane and a little ethane gas (Tissot and Welte 1984). The C_1/C_2 ratio of gas samples from FWs of Burhanuddin Upazilla is 1200 - 3500 whereas the ratio is 20-35 for the deep thermogenic gas produced from Shahbazpur Well-1 (Rahman 2015) also supports the biogenic origin of collected methane gas. The dryness of the gas (~1) shows very little possibility of mixing of thermogenic gas as the thermogenic gas tends to have moderate dryness values (Rahman 2015). Moreover, the widespread occurrence of methane in FWs was well known even before the completion of deep thermogenic gas well i.e., Shahbazpur #1 (BAPEX 1995). More study is needed to ascertain the spatial correlation between these two phenomena.

The mechanism responsible for methane gas occurrences in FWs mentioned above “methanogenesis” in deep reducing aquifer zone where it reaches final stage of reduction reaction series sulphate being reduced by microbial activity and consequently produces “biogenic gas” methane. Aquifer type i.e., deep confined aquifer, depth of burial, presence of OM, geothermal gradient and water type i.e., dominancy of Na-Mg-HCO_3 water in FWs being distributed over a paleo valley are referring to the existence of favourable environment to methanogenesis rather than the upward migration or leakage of thermogenic methane concomitant with gas field in the region.

Isotopic study i.e., stable isotopes are highly recommended to deduce the age of the groundwater. $\delta 13C_{CH4}$ study is a good option to ascertain the origin of the gas (biogenic or thermogenic) or deduce C_1/C_2 ratio of FWs otherwise.

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