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Identifying the Influence of Fluoride Mobilization Mechanism on Groundwater Quality Dynamics of Sanghar District, Lower Indus Basin

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Abstract

Groundwater contamination is one of the major concerns of deltaic plain areas of lower Indus basin. Forty ground water samples from hand pumps were geochemically evaluated and investigated to ascertain the quality of water in three union councils of District Sanghar, Sindh. Study was conducted to identify the mobilization mechanism of fluoride and its impact on the concentration trends of groundwater quality. Water quality is assessed for measuring the levels of pH, TDS, Ca, Mg, Na, HCO_3^-, SO_4^{-2}, SAR and Nitrate-Nitrogen. Results revealed that Fluoride concentration was 3.1-9.2 mg/L and Nitrate 0.2-0.8 mg/L as per WHO permissible limits. The value of pH was found 7.0-8.3, which shows a dominancy of alkaline concentrations in groundwater. Chemical analysis revealed sodium chloride is accompanied by the ion pair of $Ca(HCO_3)_2$. Hydrogeochemical classification specifies the mixed-type concentration inclining Na-K-type ionic concentrations. Analytical studies exhibited that the areas rich in Ca^{2+} display a comparatively low concentrations of dissolved fluoride. It is found that alkaline environment is favorable for F^- dissolution in ground water of the study area.

Keywords: Fluoride Mobilization Mechanism; Indus Basin; Hydrogeochemical Classification; Alkaline Environment; Groundwater Quality.

Introduction

Environmental, industrial, drinking and agricultural activities greatly depend on the availability of water resources (Prasanth et al., 2012; Hossain et al., 2016; McMahon et al., 2020; Han et al., 2020). Water scarcity turns into the crises due to the alarming increase in world's population particularly in South Asian countries. Safe drinking water supply is one of the neglected sectors in major cities of the world (Chen et al., 2020; Biddau et al., 2017; Addison et al., 2020; Kausar et al., 2011). The province of Sindh is badly affected by extreme a shortage of water since decades. There is arid climate prevailing in Sindh and low precipitation is observed along with extreme temperatures. Fluoride toxicity is present in higher concentrations in Thar Desert and Indus delta and the quality of ground water get poor in the rural areas (Rafique et al., 2004; Husain et al., 2009). Water quality parameters are distributed in groundwater and soil types by very complex processes.

Groundwater has a variety of chemical composition. Human activities are equally responsible of groundwater quality as of lithology and recharge water type. Water quality evaluation and its geochemistry are influenced by various physicochemical aspects and the mobility patterns of elements (Pi et al., 2015; Bashir et al., 2013; Sundaram et al., 2009; Fuge, 2019)). Ion exchange mechanism has a strong relation with the occurrence of ions in ground water and the elemental composition of an aquifer (Aghazadeh and Mogaddam, 2010; Han et al., 2021; Onipe et al., 2021).

Nitrate as nitrogen is released through manmade and natural sources (Vladeva et al., 2000; Gupta et al., 2000 and Weyer et al., 2001). Preliminary efforts were made to recognize the groundwater contamination due to nitrate irrigated rich areas of Pakistan (Latif et al., 1999). Such studies were executed in Rawalpindi and Islamabad (Tahir et al., 1998; Sajjad et al., 1998). Shallow groundwater is susceptible to nitrate contamination at greater extent in the areas of well drained soils (Tahir and Rasheed, 2008).

Variations in fluoride are very significant even the similar hydrogeological conditions which makes it essential to study the geochemical processes of water responsible for the release of F^- ions (Avtar et al.,2013; Podgorski& Berg,2022; Biddau et al., 2017). Aquifer material has key importance in fluoride accompanying groundwater (Reddy et al. 2010). The effects of excessive amounts of fluoride in groundwater on human beings were considered by many researchers (Qiao et al., 2022; Handa 1988; Jain et al. 1999; Kundu et al. 2001, Saxena and Ahmed 2001; Li et al., 2020).

The study area (Union councils: Jam Nawaz Ali, Nauabad and Hothi Wassan) lies in Southwestern side of Sanghar District, Sindh, Pakistan between 25°47 to 25°52 North latitudes and 68°52 to 68°57 East longitudes as shown in **Fig. 1**. Research area is about 60km from the main city of Sanghar. The objective of this study was to assess the fluoride mobilization mechanism in the study area and the ways in which the concentrations are concerned with different water quality parameters.

Hydro-geological Settings

The Thrust Mountains surround Indus delta in the western side and in the North, there are Himalayan thrust. Indus River and its tributaries are the major surface water resources in Indus deltaic plain. The formation of 150km wide Indus deltaic plain is attributed to the sediments loads of river Indus in Holocene (Giosan et al., 2006). Levees are one the component of the deposits which are present in the meandering belts of deltaic plain (Kazmi and Jan, 1997). In glacial period (Holocene) the alluvium deposited is very fertile (Ansari and Vink, 2007) and is very rich in medium to fine sand and clay deposits as illustrated in Fig. 2. Alluvial sediments are common in the study area having comprising of fine to medium sands, clays and silt covering the rocks of

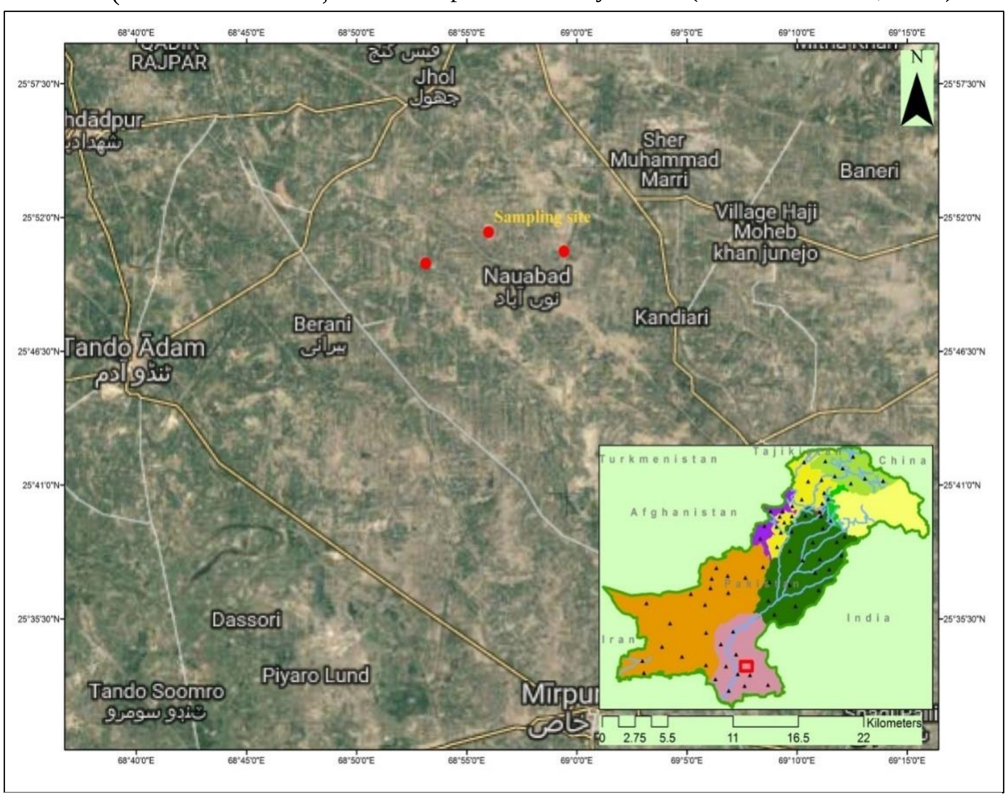

Figure 1. Location map of the study area

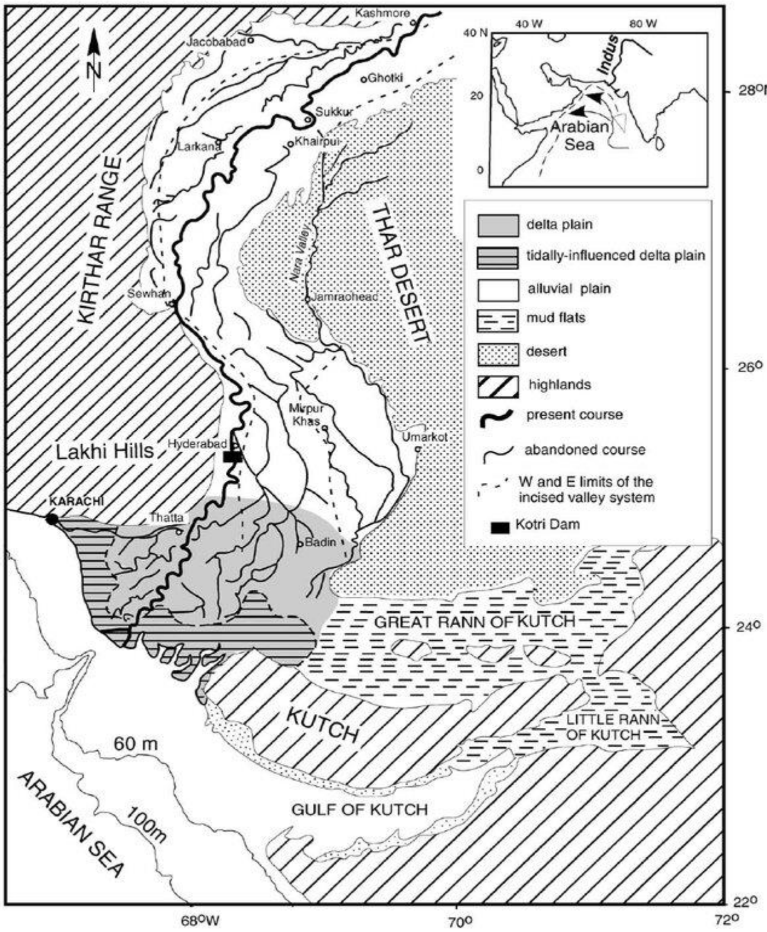

Figure 2. Physiography and Former River courses Lower Indus basin and Indus delta (after Staubwasser et al., 2002)

Tertiary age. Soils of the study area are dominantly heterogonous (Rafique et al., 2009).

MATERIALS AND METHODS

Sampling

A total of forty random groundwater samples from three union councils (8 from Jam Nawaz Ali, 18 from Nauabad and 14 from Hothi Wassan) Sanghar District, Sindh, were collected. Locations of the sample collection sites are plotted on the google image using ArcGIS 9.3 software as given in Fig. 1. The samples were collected in 1.5-liter polyethylene bottles (Akoto and Adiyiah, 2007) after letting the hand pumps to flow for about 10 min for providing the standard environment (Tahir et al., 2010).

Methods

Standard methods of WHO and APHA (2012) were adopted to analyze physicochemical properties of groundwater. Field measurements of TDS, pH was done by using Denver Instrument Model 50. Sulfate concentrations were calculated by using gravimetric method, while the other parameters, namely Cl, Ca, Mg and HCO_3^- were determined by means of volumetric techniques. Flame Photometry was used to estimate the Alkali ion concentrations (K, Na and Li). Fluoride content in the collected groundwater samples was assessed by calorimeter and the Flame photometer in the laboratory.

RESULTS& DISCUSSION

Eight ground water samples collected from Jam Nawaz Ali have cation concentrations: Na^+ (198-223 mg/L), K^+ (6.5-13.4 mg/L), Ca2+ (98-144 mg/L) and Mg2+ (50-71 mg/L) while have anionic concentrations HCO_3^- (130-145 mg/L), Cl^- (84-182 mg/L), F^- (0.4-0.9 mg/L), SO_4^{2-}(67-111 mg/L) and Nitrate is found between 3.1-9.2 mg/L. The pH of these samples ranges from 7.2-7.9 as tabulated in Table 1. As for the 18 samples from Nauabad are concerned, their geochemistry indicates that cation concentrations are bit lower than the observed ones of Jam Nawaz Ali which are Na^+ (170-215 mg/L), K^+(3.5-31 mg/L), Ca^{2+} (73-152 mg/L) and Mg^{2+} (39-51 mg/L). The

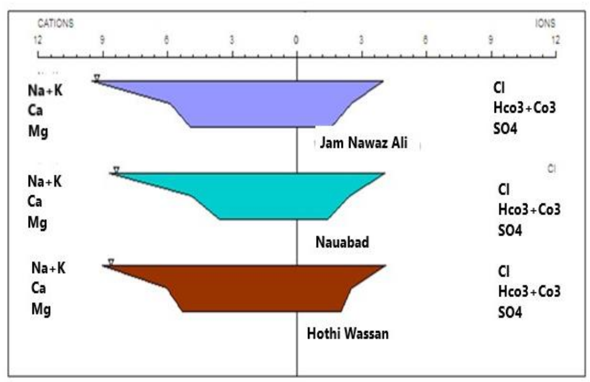

Figure 3. Stiff diagram representing the ion association mechanism

anion concentrations in Nauabad are: HCO_3^- (129-145mg/L), Cl^-(95-185mg/L), F^- (0.2-1.1mg/L), SO_4^{2-} (48-971mg/L) and Nitrate resides between 3.1-7.8 mg/L. pH values in the union council of Nauabad ranges from 7.1-8.2. In Hothi Wassan area geochemistry reveals that: Na^+ was (175-248 mg/L),

K^+ (4-48 mg/L), Ca^{2+} (80-150 mg/L) and Mg^{2+} (54-75 mg/L). The anion concentrations in Nauabad are: HCO_3^- (135-146 mg/L), Cl^- (119-174 mg/L), F^- (0.2-1.1mg/L), SO_4^{2-}.

Table.1 Observed average cation, anion concentrations, TDS and pH in water Samples in Different Union Councils of District Sanghar. N=40

Cations& TDS (mg/L)					**Anions (mg/L) & pH**					
Na^+	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**TDS**	**NO_3.(N)**	**$SO_4{}^{2-}$**	**F^-**	**Cl^-**	**HCO_3^-**	**pH**
199.6	13.0	110.7	54.7	1091.9	5.6	80.5	0.6	145.5	138.6	7.4

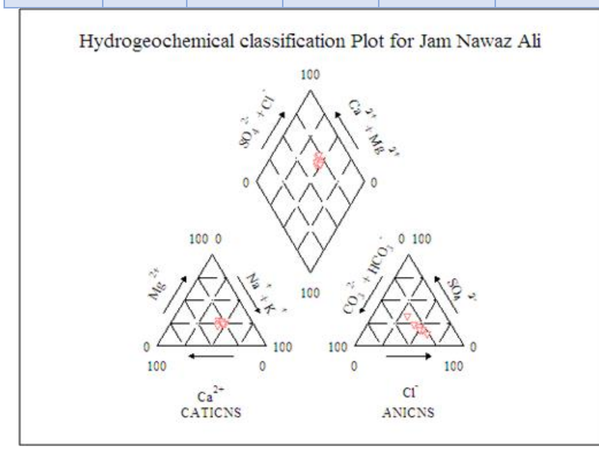

Figure 4. Hydrogeochemical classification of Jam Nawaz Ali

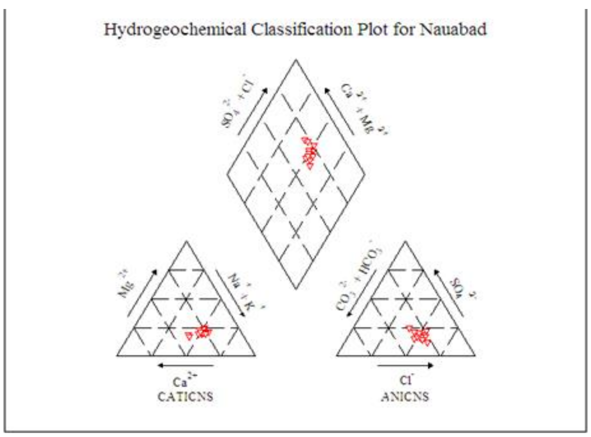

Figure 5. Hydrogeochemical classification for Nauabad.

(145-189 mg/L) and nitrate is about 3.7-7.8. pH of the observed samples ranges 7.1-8.3 which the highest as compares to the other all samples.

Chemical analysis of the observed samples shows that sodium chloride is associated with the concentrations other the ion pair of $CaHCO_3^-$ (Fig.3). Hydrogeochemical classification of the observed geochemistry was made by applying piper diagram method which shows specifies Mixed-Type concentrations. There is an inclination of Cl^- type concentrations in Jam Nawaz Ali area which are also found significantly of Mixed-type as depicted in Fig. 4. As for the geochemistry of the Nawabad union council is concerned the cationic concentrations of sodium and potassium are dominant with ion pair dominancy of sodium chloride as illustrated in. Hothi Wassan is very much of mixed-type anionic and cationic concentrations (Fig.5 & 6).

F^-shows a poor relation with calcium and magnesium which may help exchange with sodium (Farooqi et al.,2007). High concentrations of calcium are considered as a restriction for fluoride solubility (Handa,1975; Hem,1985).

$$Ca + F \rightarrow CaF_2 \quad (1)$$

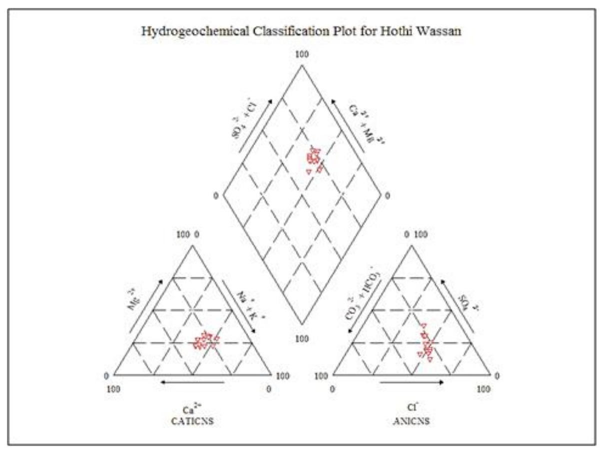

Figure 6. Hydrogeochemical classification for Hothi Wassan

The concentrations of calcium and fluoride found in groundwater samples of the study area are in poor correlation (R^2=0.009) (Fig.7). According to Rao and Devadas (2003) bicarbonate concentrations in groundwater have a direct proportionality with released fluoride at constant pH. Bicarbonate concentrations in many of the groundwater samples have also a poor correlation with fluoride (R^2=0.0002) (Fig.8). There is no significant relationship between NO_3-N and fluoride

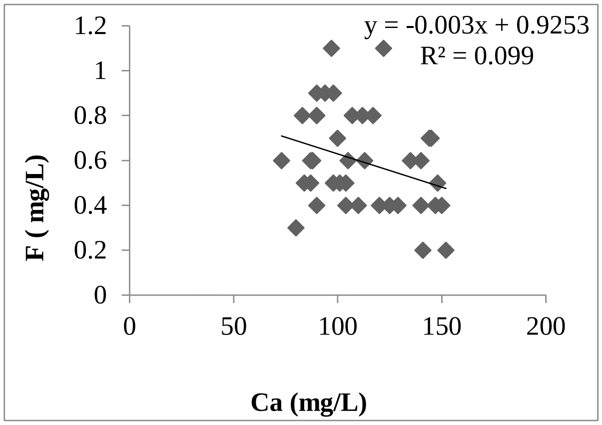

Figure 7. Correlation plot of Fluoride and Calcium concentrations

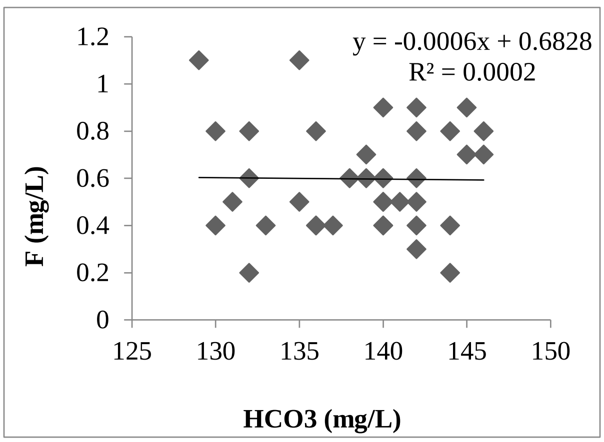

Figure 8. Correlation plot of Fluoride and Bicarbonate concentrations

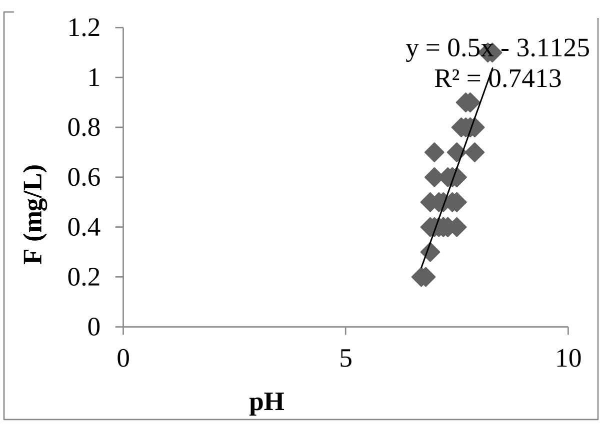

Figure 9. Correlation plot of Fluoride and pH of the Samples

concentration (R^2 = 0.0896) representing a poor influence as well.

The pH of the groundwater has a strong relation with the solubility of fluoride (Sexena and Ahmed, 2013).

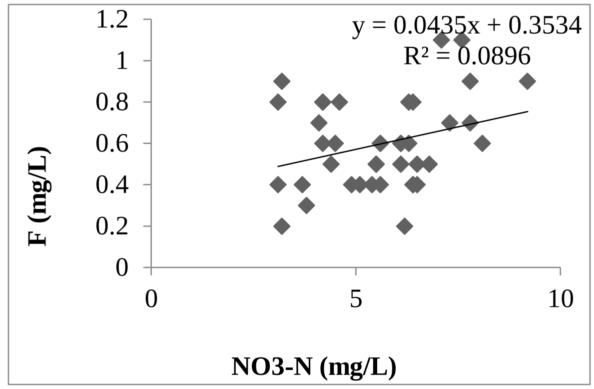

Figure 10. Correlation plot of Fluoride and NO_3-N concentration

In the study area about the 35 percent samples have shown pH inclination towards alkaline behavior (Fig.9). Groundwater receives the released concentrations of Fluoride by the weathering of primary rocks. The concentrations of different components in alkaline soils make them most contaminated by Fluoride concentrations (Kundu et al.,2001). The presence of Fluoride in majority of groundwater samples is found under the permissible limits of WHO. The carbonate and sodium concentrations are also in high which may help to dissolve fluoride-rich minerals in an alkaline environment. It is commonly observed that exchangeable Fluoride is replaced by hydroxyl ions (Fig.10). The study results are comparable with the findings of Gou et al., 2007and Li et al., 2018.

CONCLUSIONS

Fluoride concentrations in south western Sanghar district can be attributed to alkaline soils and the climatic conditions like semi-arid. The values of groundwater pH was noted as 6.8 to 8 that defines a slight alkaline conditions prevailing in the study area which may provide a possibility of fluoride release in groundwater. Fluoride correlation with HCO_3^- does not fully support the alkaline environment. The under saturation of calcite could be considered due to slightly alkaline pH of the study area. Analytical studies exhibited that the areas rich in Ca^{2+} display a comparatively low concentrations of dissolved fluoride. It is found that alkaline environment is favorable for F^- dissolution in groundwater in the study area.

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