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# Fluoride Contamination in Groundwater of Community Tube Wells, Source Distribution, Associated Health Risk Exposure, and Suitability Analysis for Drinking from Arid Zone

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**Abstract:** Fluoride ($F^-$) pollution in potable groundwater (GW) is a serious environmental concern in Pakistan with substantial human health hazard reports. The research on $F^-$ pollution in GW resources in Sindh Province is still incomplete. To explore the realistic conditions, the present research aimed to investigate the GW quality of community tube wells concerning $F^-$ contamination in Tharparkar, Sindh, Pakistan. A total of 53 samples were collected and examined for $F^-$, along with other physicochemical parameters. The $F^-$ values observed varied from 0.2–4.2 mg/L, with a mean value of 1.63 mg/L. Among the 53 samples, 46% had $F^-$ levels that were higher than the World Health Organization's (WHO) recommended limit (1.5 mg/L). The water type of the studied region was Ca-$HCO_3$ type, which can be attributed to fresh recharged water. The interaction of rock–water contact controls the hydrochemistry of GW. The GW resources of the research zone were highly saturated with fluorite minerals. Human health risk calculation outcomes exposed that 21 samples showed high HQ values for children and 7 samples showed high values for adults in the research zone. Children are at high risk in the study area from drinking $F^-$-contaminated GW. WQI results showed that 31 samples were not suitable for drinking.

**Keywords:** groundwater fluoride; possible sources; non-carcinogenic risk; geochemical modelling

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## 1. Introduction

Groundwater (GW) is a vital resource for domestic, agronomic, and manufacturing use. The exploitation of this vital resource is increasing internationally as a result of the rising population, climate change, and easy access to new and inexpensive extraction technology [1,2]. In recent years, an increasing trend toward underground trash disposal has accelerated the flow of contaminants in GW systems [3]. A wide range of pollutants can contaminate GW throughout regions where industry and agricultural activities have been allocated [4]. The primary contaminant in GW supplies is fluoride ($F^-$), which is produced by mining activities, industrial effluent, mineral fertilizers, insecticides, and landfills [5,6]. The contamination of $F^-$ in GW is a significant problem, especially in rapidly growing urban and commercial areas in which untreated industrial effluent discharge,

heavy pesticides, inadequate landfills, and agricultural runoff are widespread [7–9]. High concentrations of fluoride ($F^-$) in groundwater are deemed a severe health risk. Fluorosis is a prevalent endemic disease rooted in geological factors. There exists a well-established relationship between the severity of fluorosis and the concentrations of fluoride ($F^-$) in groundwater. Regarding the permissible level of fluoride ($F^-$) in groundwater, the World Health Organization (WHO) recommends 1.5 mg/L.

However, excessive $F^-$ consumption, which is common in the drinking GW of Sindh, Pakistan, leads to the disease fluorosis, which damages the teeth and bones [10]. Dental effects can be seen with moderate doses, but long-term consumption can cause significant bone problems [11]. The reproductive, neurological, neuromuscular, hormonal, and nephrotoxicity systems can also experience damage from chronic exposure to $F^-$ toxins, which in some situations can result in genotoxicity [12]. The main inorganic toxicity linked to fluorine is designated ($F^-$), and it prefers an alkaline pH, high levels of $Na^+$, high levels of $HCO_3{}^-$, and low $Ca^{2+}$ ion levels [13]. $F^-$ enrichment exists in a number of environments, such as GW, soil, and rocks [14].

Pakistan is also facing the same problem in terms of GW quality deterioration with ($F^-$) contamination in drinking GW, which is a serious issue in Pakistan, especially in Sindh Province [15]. Many people are exposed to ($F^-$) contamination through drinking GW. The ($F^-$) concentrations in the GW have surpassed the permitted limit of 1.5 mg/L in several parts of Sindh Province, including UmarKot, Dadu, Khairpur, Sanghar, Haider Abad, and Jacob Abad [16–18]. However, the research on GW quality is still inadequate to reveal the realistic situation of $F^-$ pollution in GW resources in Sindh Province, Pakistan [19]. This study, in which we investigated the $F^-$ concentrations in the community tube wells throughout the study area, is the first to be conducted in the study area. The local people of the area use tube well water for domestic and agricultural practices; however, the tube well water samples were observed to have elevated concentrations of $F^-$ contamination.

Keeping in view the aforementioned situation of GW contamination in Sindh Province, this research aimed (i) to explore the physico-chemical profile of tube well water in the studied region, (ii) to investigate the relationship of $F^-$ with other GW parameters, (iii) to evaluate the population's health risk index caused by $F^-$ pollution in the study area, and (iv) to employ the water quality index to determine whether the water from tube wells is suitable for drinking.

## 2. Research Area

*Setting and Weather*

The study area is a desert region and can be found at an elevation of 28 m (92 feet) at 24°74′ N and 69°80′ E, as shown in Figure 1. It is 450 km from Karachi. Toward the south, there is the town of Kertee, which is more established than Mithi, and around 20 KM to the north, the town Amrio is found. Faqeer Muqeem Kunbher Nohto is 40 km to the north. The district experiences mostly semi-arid and arid climates having less than 125 mm of annual average rainfall. Even for drinking, this region has few resources of fresh water. However, precipitation is necessary for crops. The irregular volume and distribution of rainfall exacerbate the circumstances and the dependent nature of the area. As a result of this issue, appropriate management techniques and other resources, such as groundwater, can be utilized for irrigation purposes following quality standards. Almost all bodies of water contain salts. However, the composition and concentration of ions in water determine its quality [20].

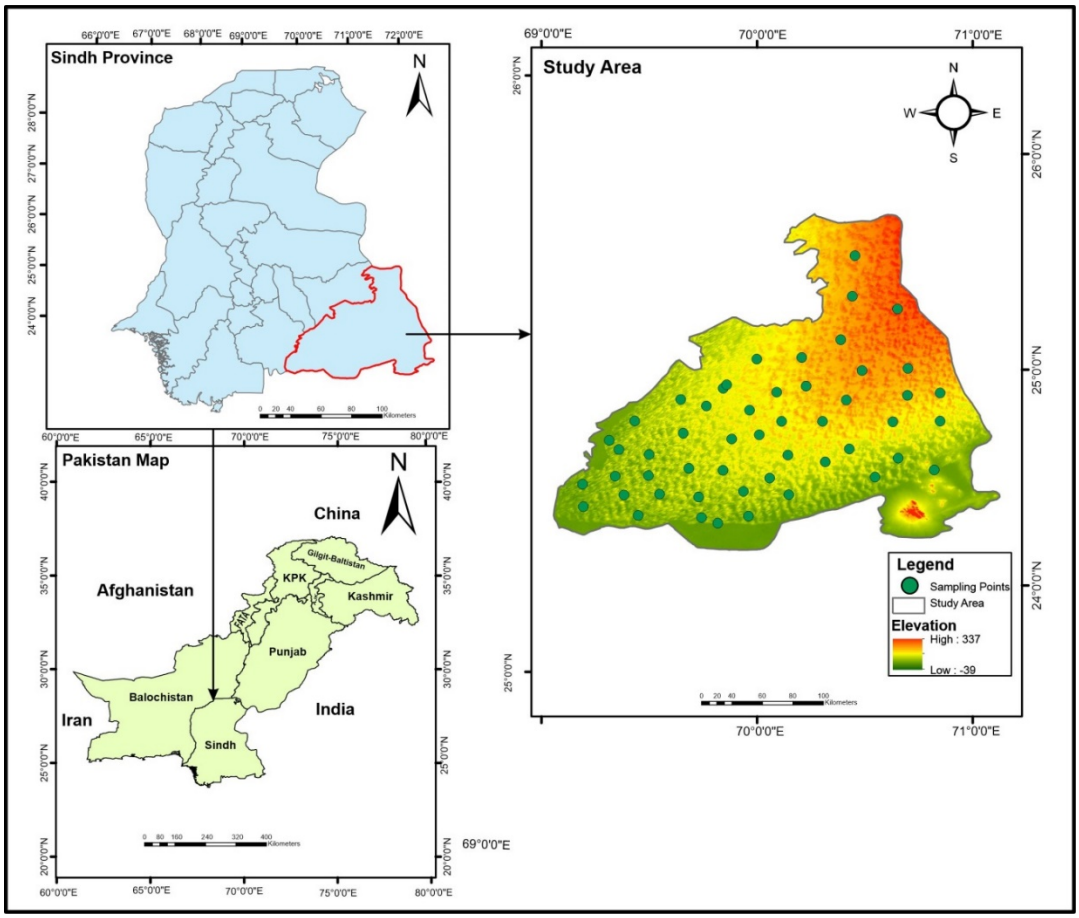



**Figure 1.** Location of the study area and groundwater sample stations.

## 3. Materials and Methods

### *3.1. Sampling and Analysis of Groundwater*

GW samples (n = 53) were obtained individually from community tube wells in the investigated area to assess the quality of the tube wells' water. The sample investigation was carried out in June 2021, and samples were deliberately gathered in the most populated regions of the study area. In order to prevent the effects of steady water and obtain an accurate GW sample, GW sources were pumped for 10 min prior to sampling [21]. The 1.5 L plastic bottles used to collect the GW samples were free of contaminants. In the field, using a multi-parameter analyzer (Hanna HI9829, Smithfield, RI, USA), the following basic water quality characteristics were measured: pH, total dissolved solids (TDS), and electrical conductivity [22]. All the collected GW samples were immediately transferred to a water quality lab for further examination. The concentrations of $SO_4^{2-}$ and $NO_3^-$ were examined using an ultraviolet spectrophotometer. A titration technique was used for the analysis of $Cl^-$ and $HCO_3^-$ following [23]. The main cations $Mg^{2+}$ and $Ca^{2+}$ were examined using titration with ethylene diamine tetraacetic acid (EDTA, 0.05 N) with a 2% analytical error. The $Na^+$ and $K^+$ levels were determined by a flame photometer. Fluoride concentrations in GW samples were analyzed using a Fluoride Analyzer ion-selective electrode (ISE) (HANNA Instruments, Tokyo, Japan) [24].

Analytical accuracy, as well as the precision of the GW data, were evaluated using a calculation of the ionic charge balance of cation and anion errors (ICBE). The ionic charge balance error (ICBE) was used to determine the water quality's consistency and validity using the following equation (Equation (1)).

$$\text{ICBE} = [\sum \text{cations} - \sum \text{anions} / [\sum \text{cations} + \sum \text{anions} \times 100 \quad (1)$$

### *3.2. Geology*

The Thar Desert is mostly covered in sand dunes with limited surface rock exposure. Below the surface, there are granodiorite and granite rocks. The geological history includes metabasites, acidic dykes, and various granite types. Some Mesozoic and Tertiary strata are exposed near the Indo-Pakistan border, but the underlying geology is poorly understood. Seismic data suggests that a granitic basement formed due to pre-Jurassic rifting, with younger strata in the northwest and older formations toward the southeast [19].

### *3.3. Hydrology*

The Thar Desert faces severe groundwater scarcity with mostly brackish to salty water in low-lying interdune playa flats. Perched aquifers exist where older deposits meet sand dunes, found at depths ranging from 52 to 93 m below the surface. The water table above the coal zone is 41.38 to 40 m below sea level, and water-bearing layers consist of 3.35 to 41.27 m of coarse to medium sand. Groundwater is primarily accessed from wells drilled into these aquifers, with the coal zone containing two to three perched aquifers 2.24 to 68.74 m thick located between 43 and 150 m below mean sea level [25]. The coal-bearing formation's aquifers, composed of medium- to coarse-grained quartzitic sand, are consistently found between 94 and 175 m below sea level, with thickness ranging from 5.50 to 47 m. These aquifers are the primary water source for most tube wells in the Thar region.

### *3.4. Eminence Declaration and Excellence Regulator*

To ensure the accuracy of the analytical data results, duplicate analyses, standard calibration, reagent blanks, and routine quality control checks were carried out. Deionized water and a 30% HCl solution were used to thoroughly clean all flasks to eliminate the contaminants. After being washed following a standard procedure, the glassware was oven-dried.

### *3.5. Hydrochemical and Statistical Analysis*

#### 3.5.1. Water Type

Piper figures are frequently used to define the hydrogeochemical categories and comparative levels of major ions in numerous GW samples. They also show the probable geo-chemical progressions that can offer support in considering and assessing the GW type. Grapher (version 14) was used to construct a Piper diagram.

#### 3.5.2. Controlling Mechanism of Groundwater Chemistry

The communal technique for defining the connection between lithology and hydro-chemistry in aquifers is portrayed by the Gibbs diagram. According to Gibbs, there are three dominating zones that influence the hydrochemistry of GW, such as the dominance of rock, precipitation, and evaporation [26].

#### 3.5.3. Mineral Phases

The saturation index can be used to evaluate the conditions of the GW to dissolve a particular mineral. Evaluating the mineral stability makes it simpler to predict the dissolved mineral reaction in water [27]. PHREEQC (Interactive version 3.4), a geo-chemical simulation program, was applied to compute saturation indices following [28].

#### 3.5.4. Statistical Analysis

The descriptive statistics were calculated on the basis of the minimum, maximum, mean, and standard deviation using IBM-SPSS software version 25. Principal component analysis was used to identify pollutant sources. The relationships between water quality parameters were most often assessed using Pearson correlation analysis. By contrast, the inverse distance weightage (IDW) interpolation method with ARC GIS (version 9.3) was utilized to create a water quality map and a fluoride distribution level map.

3.5.5. Assessment of Health Risk

Using USEPA recommendations (1992), the hazard quotient (HQ) and daily intake (EDI) via $F^-$ were estimated [29].

$$EDI_{oral} = \frac{C \times IR \times EF \times ED}{BW \times AT} \quad (2)$$

Here, *C* is the GW dissolved $F^-$ level (measured in mg/L), *IR* represents the quantity of water consumed daily (L Day $^{-1}$), and *EF* represents the rate of exposure (days $y^{-1}$); the length of exposure (y) is represented by *ED*, the average period (days) is represented by *AT*, and body weight is represented by *BW*. Equation (2) can be further simplified to EDI $_{oral}$ = C × IR/BW since the product of EF and ED is equal to AT [3].

$$HQ_{oral} = EDI_{oral}/RfD_{oral} \quad (3)$$

An $HQ_{ORAL}$ of 1 indicates that the water is safe to drink, whereas $HQ_{ORAL} > 1$ denotes the possibility of fluorosis having an adverse impact on human health. The health of individuals is affected by fluorosis. RfD ORAL, the reference oral dose, was computed to be 0.06 mg $F^-$ per kilogram of body weight each day. Adults consumed water at a rate of 2 L/D and had a body weight of 70 kg, whereas children used 0.89 L per day and weighed 15 kg. [3].

3.5.6. Suitability Analysis of Groundwater

Mathematical mean water quality index (WQI) values were employed to determine if the GW was safe for human consumption. The WQI values were calculated using Equation (4) in accordance with the WHO [30] drinking water standard.

$$WQI = \sum_{i=1}^{n} Sli - n \quad (4)$$

## 4. Results and Discussion

### *4.1. Hydrochemistry of Groundwater*

Table 1 shows the hydrochemical analysis of the GW sample parameters collected from the study area. The depth value of the GW resources in the study area ranged between 66 and 117 (feet) with a mean value of 91.6 (feet). The values of the pH of the GW samples differed between 7.3 and 8.6, with a mean value of 7.96, and was below the suggested limit of the WHO. As a main water quality parameter, the determination of pH is necessary due to its dynamic characteristics in the saturation of GW parameters [31,32]. The TDS levels of 237 to 607 samples, with an average value of 391 mg/L, were below the permissible range specified by the WHO. The EC values in the GW samples varied from 312 to 667 µS/cm, with an average value of 484 µS/cm, and were beyond the permitted limit of the WHO. Turbidity values were recorded in the GW samples in the range of 0.5–3.7 NTUs, with a mean value of 194 NTUs, and were below the suggested limit of the WHO for ingestion. The concentration of $HCO_3^-$ in the GW samples was recorded in the range of 137–521 mg/L, with an average value of 270 mg/L, and was beyond the recommended value of the WHO for drinking purposes. Mostly, higher concentrations of $HCO_3^-$ in GW sources are due to dolomite-, calcite-, marble-, and carbonate-bearing rocks, which promote $HCO_3^-$ concentration in GW sources [9,16,33]. The values of $Ca^{2+}$ and $Mg^{2+}$ in the GW samples varied from 19 to 68 mg/L and 17 to 63 mg/L, respectively, with mean values of 43.5 and 32.7 mg/L, respectively; the values of $Ca^{2+}$ and $Mg^{2+}$ in all GW samples were below the permitted limits of the WHO for drinking purposes. The concentration of $Na^+$ in the GW samples varied from 137 to 511 mg/L, with an average value of 258 mg/L, and was beyond the suggested limit of the WHO for drinking purposes. An elevated concentration of $Na^+$ in GW sources is due to the dissolution of sodium-containing minerals, and anthropogenic activities may lead to a higher concentration of $Na^+$ in GW [34]. Sulfate levels in the GW samples ranged from 18 to 82 mg/L, with a mean of 38 mg/L, and were found to be within

the allowed range prescribed by the WHO for drinking purposes. The $NO_3^-$, $K^+$, and $Cl^-$ values in the GW samples were within the proposed WHO limits of 0.1–3.1 mg/L, 0.6–4 mg/L, and 8–52 mg/L, respectively, with mean values of 1.64, 1.93, and 24.2 mg/L, respectively. The concentration of $Fe^{2+}$ in the GW samples varied from 0.01 to 0.2 mg/L, with an average value of 0.03 mg/L; except for a few samples, all of the samples were within the permitted limit suggested by WHO. The elevated concentration of $Fe^{2+}$ in GW sources is linked to adjacent weathering processes, and erosion products contribute to a higher concentration [35].

**Table 1.** Descriptive statistics of selected parameters in groundwater samples.

| Parameters | Min | Max | Mean | SD | WHO |
|---|---|---|---|---|---|
| Depth (feet) | 66 | 117 | 91.6 | 13.4 | - |
| pH | 7.30 | 8.60 | 7.96 | 0.32 | 6.8–8.5 |
| TDS (mg/L) | 237 | 607 | 391 | 84.6 | 1000 |
| EC (µs/cm) | 312 | 667 | 484 | 91.1 | 400 |
| Turbidity (NTU) | 0.50 | 3.70 | 1.94 | 0.72 | 5 |
| $HCO_3^-$ (mg/L) | 137 | 521 | 270 | 111 | 250 |
| $Ca^{2+}$ (mg/L) | 19 | 68 | 43.5 | 14.9 | 200 |
| $Mg^{2+}$ (mg/L) | 17 | 63 | 32.7 | 12.8 | 150 |
| $Na^+$ (mg/L) | 137 | 511 | 258 | 97.2 | 200 |
| $SO_4^{2-}$ (mg/L) | 18 | 82 | 38 | 14.6 | 250 |
| $NO_3^-$ (mg/L) | 0.10 | 3.1 | 1.64 | 0.82 | 10 |
| $K^+$ (mg/L) | 0.60 | 4 | 1.93 | 0.79 | 12 |
| $Cl^-$ (mg/L) | 8.00 | 52 | 24.2 | 10.9 | 250 |
| $Fe^{2+}$ (mg/L) | 0.01 | 0.20 | 0.03 | 0.04 | 0.3 |
| $F^-$ (mg/L) | 0.20 | 4.20 | 1.63 | 0.96 | 1.5 |

### *4.2. Fluoride Concentration in Groundwater*

Table 1 shows the levels of $F^-$ in the GW resource samples, which varied from 0.2 to 4 mg/L with a mean concentration of 1.63 mg/L. Among the samples (n = 53), 46% were beyond the permitted limit of 1.5 mg/L suggested by the WHO for ingestion. The elevated content of $F^-$ in GW is primarily attributable to water–rock interaction, cation exchange, elevated $Na^+$ and $HCO_3^-$ concentrations, and cation exchange [3]. Furthermore, in relation to carbonate minerals, the common ion effect implicitly regulates the hydrochemical behavior of $F^-$. Additionally, the $Na^+$ and $HCO_3^-$ water type saturated with calcite has mostly low levels of $Ca^{2+}$ and elevated concentrations of ($F^-$) [36]. Likely, the rocks contain minerals like mica and fluorite, which promote $F^-$ in GW resources. Figure 2 shows the concentrations of $F^-$ in the GW of the studied zone.

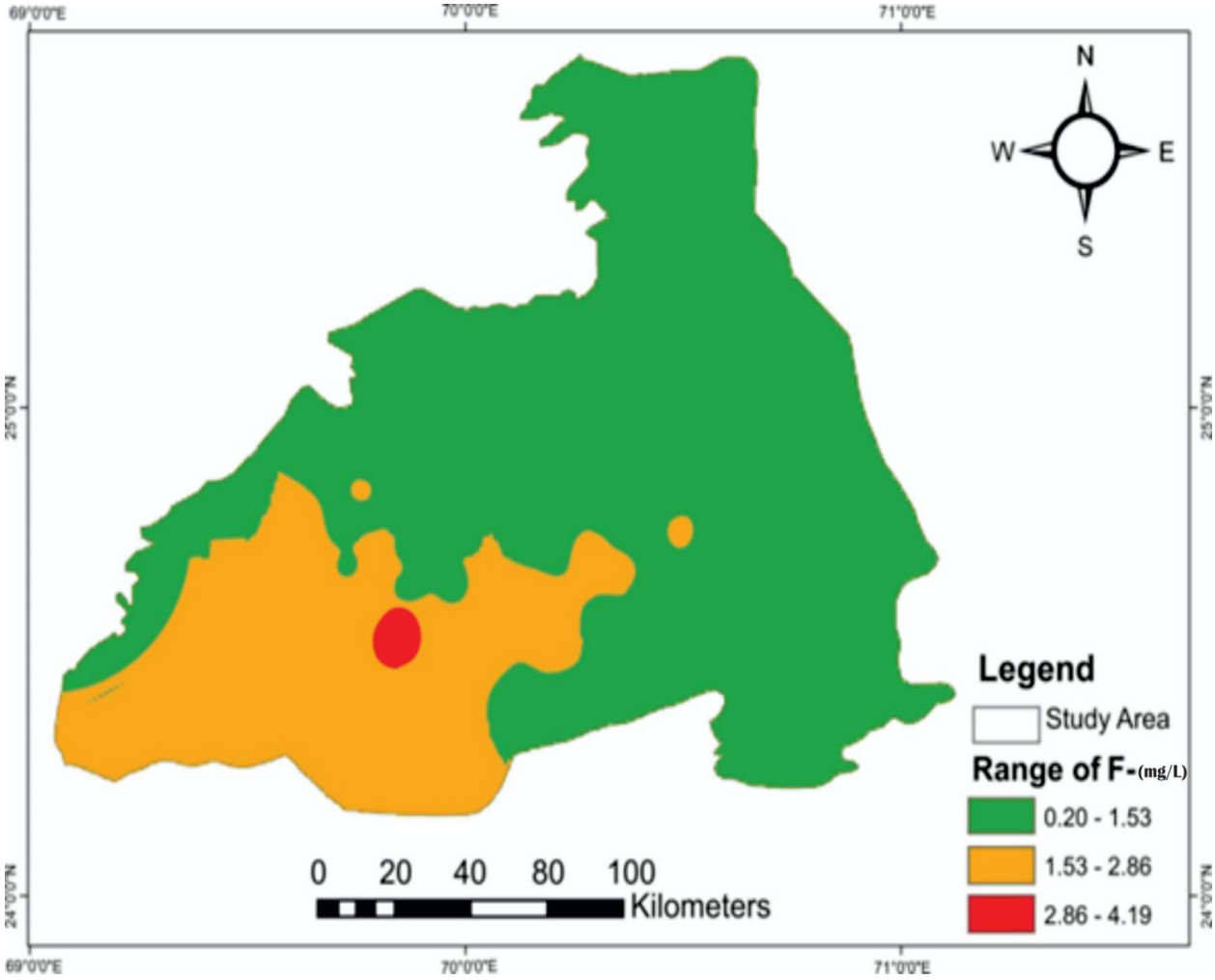



**Figure 2.** Spatial distribution map of fluoride in the study area.

### *4.3. Water Type of Groundwater Samples*

Hydrochemical facies represent the complete GW phase inside a geomorphological configuration. To comprehend the development and flow outline of the GW, a Piper diagram is needed [37]. The hydrochemical profile of the samples and their hydrochemical nature are displayed graphically in the Piper figure. The levels of $F^-$ in GW are mainly determined by the natural characteristics of the region, which are characterized by its hydrochemical facies. The GW samples were plotted on a Piper diagram to show the GW samples' varying chemical compositions (Figure 3). In the present study, the GW samples belonged to the (Ca-$HCO_3$) water type, which can be attributed to fresh recharged water. Concerning cations, all of the samples lay in zone C (Magnesium type), which is directly linked to the evaporation of shallow GW, silicate weathering, and ion exchange [38]. All of the samples were located in zone E (bicarbonate type), which is affected by carbonate erosion, in anions [39]. The authors of [3] found higher fluoride in this water type, supporting the findings of this study.

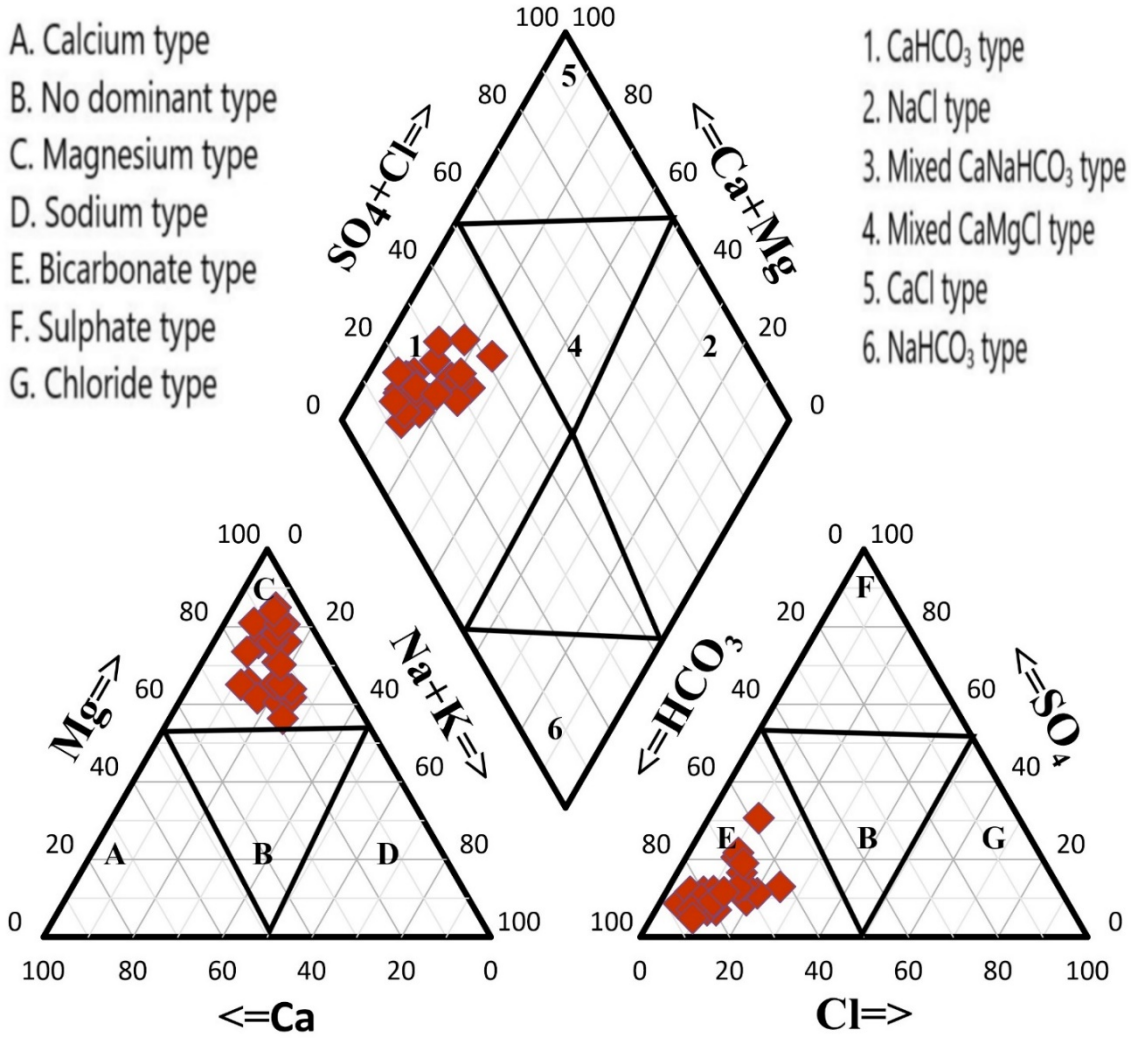



**Figure 3.** Water type of groundwater samples collected from the study area.

### *4.4. Formation Mechanism of Groundwater Chemistry*

The relative influence of evaporation, precipitation, and weathering on groundwater chemistry can be shown using a Gibbs diagram. All of the samples were plotted using the Gibbs diagram, and (Figure 4) shows that every sample was located in the rock dominance zone, showing that the majority of the GW samples were impacted by rock dominance. The weathering of rocks was the primary factor in the enrichment of GW with minerals. The groundwater's process of combining soluble salts and minerals accelerated the parent rock's weathering [34]. Additionally, prolonged rock–water contact residence time allows for the breakdown of minerals [40].

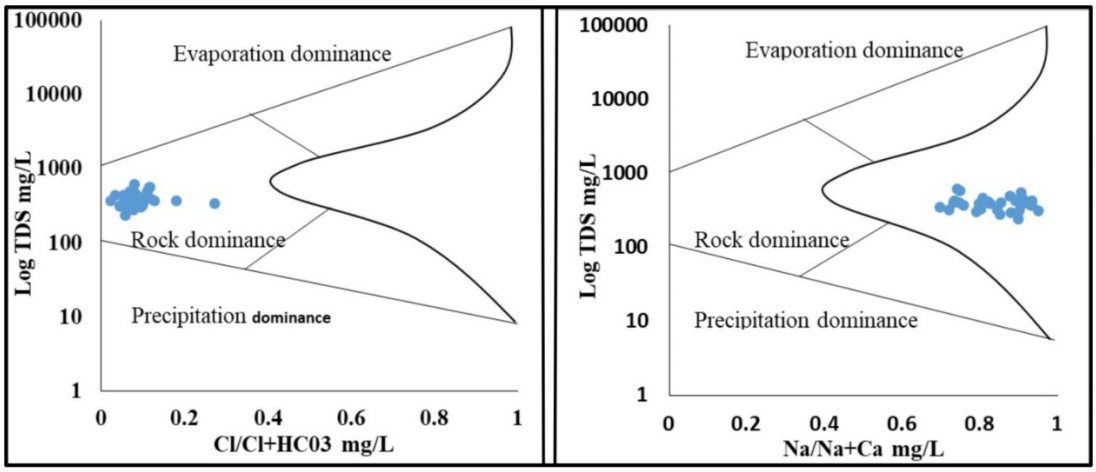



**Figure 4.** Groundwater chemistry formation mechanism in the study area.

### *4.5. Saturation Indices*

The subsurface mineralogy can be estimated using saturation measurements. Both surface and underground water minerals, such as calcite and dolomite, are frequently present in equilibrium [41]. The recent analysis's SI calculations, as shown in Figure 5, revealed that the fluorite minerals had varying saturation levels, gypsum was found in the equilibrium state, and halite minerals were found in the under-saturated state in the aquifers of the study area. The positive SI values of fluorite and gypsum showed that these minerals had dynamic characteristics in the pollution of the GW resources in the research zone.

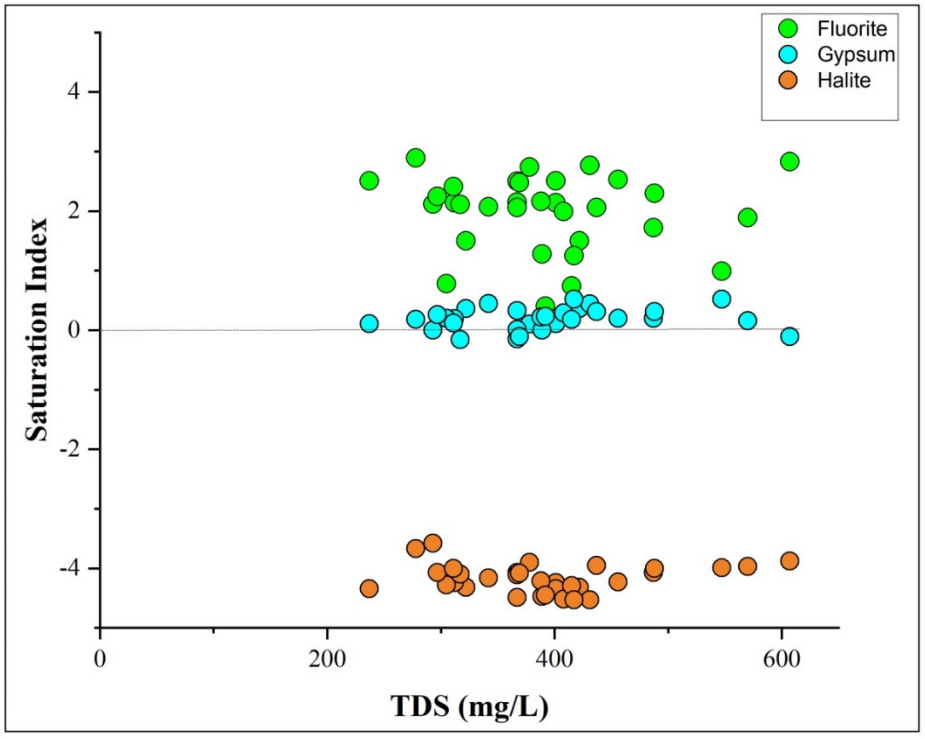



**Figure 5.** Mineral phases of groundwater samples collected from the study area.

### *4.6. Source Identification of Contaminants*

All of the geochemical processes that emerged in the study area were investigated using the principal component analysis (PCA) method for n = 53 GW samples. Table 2 shows the six rotating principal components for the GW variables, F1, F2, F3, F4, F5, and

F6, with a total variance of (75.55%). The variance of each factor was determined to be F1: 22.07%, F2: 14.52%, F3: 13.32%, F4: 9.74%, F5: 8.37%, and F6: 7.53%, with eigenvalues of 3.31, 2.18, 2.0, 1.46, 1.26, and 1.13, respectively.

**Table 2.** Principal component analysis of groundwater sample variables.

| | F1 | F2 | F3 | F4 | F5 | F6 |
|---|---|---|---|---|---|---|
| Depth | 0.27 | −0.09 | 0.40 | −0.73 | 0.24 | 0.12 |
| pH | −0.19 | 0.46 | 0.56 | 0.00 | −0.12 | −0.31 |
| TDS | −0.33 | −0.03 | 0.67 | −0.22 | −0.17 | 0.24 |
| EC | −0.60 | 0.47 | 0.20 | 0.44 | 0.03 | −0.05 |
| Turbidity | −0.48 | 0.53 | −0.07 | 0.09 | 0.12 | 0.51 |
| $HCO_3^-$ | 0.90 | 0.20 | −0.03 | 0.19 | 0.07 | 0.14 |
| $Ca^{2+}$ | −0.58 | −0.13 | −0.14 | 0.40 | 0.03 | −0.16 |
| $Mg^{2+}$ | −0.05 | −0.62 | 0.45 | 0.19 | −0.08 | 0.20 |
| $Na^+$ | 0.62 | 0.48 | −0.06 | 0.12 | 0.25 | 0.39 |
| $SO_4^{2-}$ | 0.16 | −0.48 | 0.52 | 0.44 | 0.25 | 0.15 |
| $NO_3^-$ | 0.04 | 0.36 | 0.08 | −0.12 | 0.67 | −0.47 |
| $K^+$ | 0.40 | 0.18 | −0.02 | −0.12 | −0.65 | −0.31 |
| $Cl^-$ | 0.52 | −0.33 | 0.24 | 0.29 | 0.21 | −0.38 |
| $Fe^{2+}$ | 0.00 | −0.43 | −0.67 | 0.00 | 0.10 | 0.06 |
| $F^-$ | 0.72 | 0.31 | 0.14 | 0.36 | −0.27 | 0.07 |
| Eigenvalues | 3.31 | 2.18 | 2.00 | 1.46 | 1.26 | 1.13 |
| % of Variance | 22.07 | 14.52 | 13.32 | 9.74 | 8.37 | 7.53 |
| Cumulative % | 22.07 | 36.59 | 49.91 | 59.65 | 68.02 | 75.55 |

F1 showed strong loading for $HCO_3^-$, $Na^+$, $Cl^-$, and $F^-$, and their coefficient ($R^2$) values were determined to be 0.90, 0.62, 0.52, and 0.72, respectively. The source of $Na^+$ and $HCO_3^-$ in the GW sources is the weathering and dissolution of carbonate and albite minerals in GW sources. The positive correlation of $Na^+$ and $HCO_3^-$ with $F^-$ shows that a higher concentration of such parameters promotes $F^-$ concentration in GW sources [42]. The sources of $Cl^-$ in GW sources are agrochemical fertilizers and domestic waste, which promote $Cl^-$ concentration in GW [43]. Thus, F1 reflects the geogenic and anthropogenic sources of contamination. F2 showed moderate loading for turbidity with a coefficient ($R^2$) value of 0.53; the source of high turbidity in GW sources is poorly built wells [44]. Furthermore, the high turbidity of GW is also due to erosion, runoff, and wastewater [45]. F2 showed the anthropogenic source of contamination. F3 showed moderate loading for pH, TDS, and $SO_4^{2-}$ with coefficient ($R^2$) values of 0.56, 0.67, and 0.52, respectively. The sources of such parameters in GW sources may include leaching from salt and sulfide strata [46], and the positive correlation of TDS and $SO_4^{2-}$ with pH suggests that pH plays a vital role in the saturation of these parameters [47]. F3 reflected the geogenic source of contamination. F4 had a substantial negative loading for depth with a value of −0.73, indicating that depth had no direct influence on the GW variables in the research area's GW resources. F5 showed moderate positive and negative loading for $NO_3^-$ and $K^+$ with coefficient ($R^2$) values of 0.67 and −0.65, respectively. The source of $NO_3^-$ in GW sources is agricultural pesticides, while the source of $K^+$ is the rocks that contain $K^+$-bearing minerals [48]. The negative correlation between these variables shows that they have no direct effect on each other. F5 showed mixed types of contamination sources. F6 showed moderate loading for turbidity with a coefficient ($R^2$) value of 0.51; the sources of turbidity are runoff, wastewater recharge, and poorly built wells [49], which are anthropogenic sources of contamination.

Therefore, it can be inferred from the PCA findings that the study area's GW sources were contaminated as a result of geogenic and anthropogenic sources of contaminants.

### *4.7. Human Health Risk*

The high levels of hazardous elements in the water that people consume can be harmful to their health [50]. The health risk evaluations in the current investigation included average daily intake (ADI) and hazard quotient (HQ) as non-carcinogenic risk (non-CR). The ADI and HQ values for children and adults in the research area are presented in Table 3.

**Table 3.** Health risk assessment of average daily intake (ADI) and non-carcinogenic risks (HQ) of fluoride ingestion in groundwater samples.

| | | Children | | Adults | |
|---|---|---|---|---|---|
| **GW Samples** | **$F^-$ mg/L** | **ADI** | **HQ** | **ADI** | **HQ** |
| Min | 0.20 | $1.19 \times 10^{-2}$ | $1.98 \times 10^{-1}$ | $5.71 \times 10^{-3}$ | $9.52 \times 10^{-2}$ |
| Max | 4.20 | $2.49 \times 10^{-1}$ | $4.15 \times 10^{0}$ | $1.20 \times 10^{-1}$ | $2.00 \times 10^{0}$ |
| Mean | 1.63 | $8.51 \times 10^{-2}$ | $1.42 \times 10^{0}$ | $4.10 \times 10^{-2}$ | $6.83 \times 10^{-1}$ |

The ADI for children in the GW samples varied from $1.19 \times 10^{-2}$ to $2.49 \times 10^{-1}$, with an average value of $8.51 \times 10^{-2}$. Similarly, the HQ values for children varied from $1.98 \times 10^{-1}$ to $4.15 \times 10^{0}$, with a mean value of $1.42 \times 10^{0}$. Among 32 samples, 21 samples exceeded the HQ value for children in the study area. The ADI value for adults was observed to vary from $5.71 \times 10^{-3}$ to $1.20 \times 10^{-1}$, with a mean value of $4.10 \times 10^{-2}$, while the HQ values of the GW samples for adults varied from $9.52 \times 10^{-2}$ to $2.00 \times 10^{0}$, with a mean value of $6.83 \times 10^{-1}$; among 53 samples, 17 samples showed high HQ values for adults in the study area. As a result, it is concluded that children have a high hazard due to $F^-$ pollution from drinking GW compared with adults, which poses a risk of dental and skeletal fluoresces.

### *4.8. Analysis of Water Quality for Drinking*

One of the most complete measures for addressing the general quality of GW is the water quality index (WQI). The WHO's recommended standards for drinking water are applied to compute the water quality index (WQI), which gives information on the complex relationship between GW chemical characteristics and overall GW quality [51]. According to the WQI values, we classified the GW samples as follows: (0–25) excellent, (26–50) good, (51–75) poor, (76–100) extremely poor, and (>100) inadequate for ingestion [52]. Table 4 shows the category of each GW sample for drinking purposes, and the spatial distribution map of the WQI is shown in Figure 6. The WQI results revealed that 22 samples belonged to the good category, 27 samples belonged to the poor category, and 4 samples belonged to the very poor category. As an outcome, n = 31 samples of GW from the research zone were not suitable for drinking purposes, placing them in the poor and very poor categories (Table 4). No samples were observed with a WQI value of >100 (in the not suitable category). The existence of elevated levels of $F^-$ in drinking water sources may render them unsuitable for human consumption, and they may have an adverse effect on the health of human beings. The occurrence of high $F^-$ concentrations in GW depends on numerous factors, such as the saturation state with respect to fluorite. Moreover, the "common ion effect", with respect to carbonate minerals (e.g., calcite) indirectly controls $F^-$ hydrogeochemical behavior. The Na-HCO3 water type saturated with calcite often has low concentrations of dissolved $Ca^{2+}$ and higher $F^-$ concentrations. Moreover, granite rocks are rich in fluorite, and mica minerals further increase the $F^-$ concentrations in GW wells.

**Table 4.** Classification of groundwater samples based on WQI values.

| Category | WQI | Water Quality | Water Sample |
|---|---|---|---|
| A | 0–25 | Excellent | 0 |
| B | 25–50 | Good | 22 |
| C | 51–75 | Poor | 27 |
| D | 76–100 | Very poor | 4 |
| E | >100 | Not suitable | 0 |

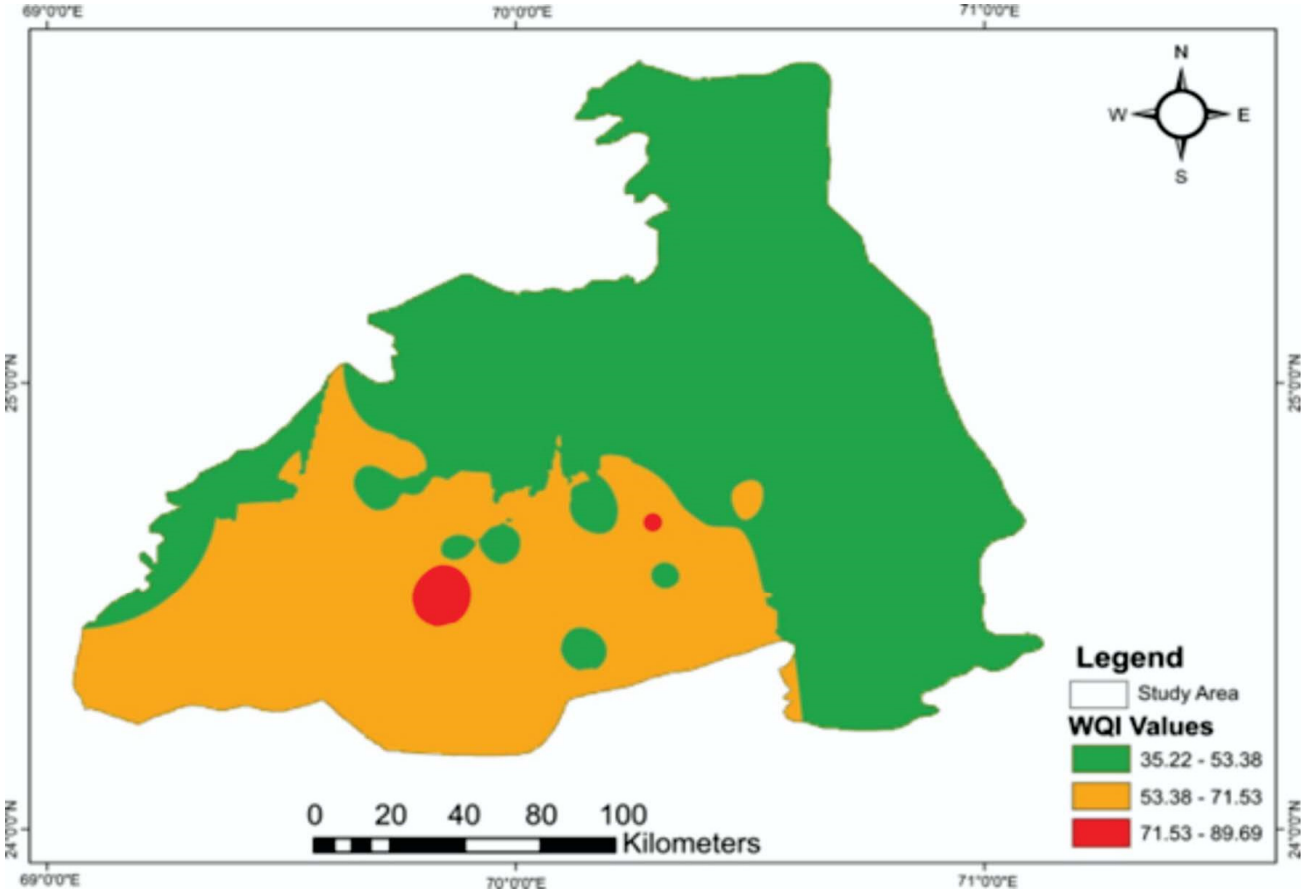



**Figure 6.** Spatial distribution map of groundwater quality for drinking.

## 5. Conclusions

Higher levels of $F^-$ in potable GW may make it unsuitable for drinking purposes and may cause various health disorders. In the present study, in which we evaluated 53 GW samples concerning $F^-$ contamination, 46% of samples had levels beyond the suggested levels of the WHO for ingestion. The $F^-$ levels varied from 0.2 to 4.2 mg/L, with a mean value of 1.63 mg/L. The water type of the studied zone was Ca-$HCO_3$ type, which can be attributed to fresh recharged water. Rock–water interaction controls the hydrochemistry of GW. The aquifers of the study area were highly saturated with fluorite minerals. Factor analysis demonstrated that geological and anthropogenic activity contaminated the studied area's GW resources. The calculation of human health risk revealed that children are at high risk in the study area due to the drinking of $F^-$-contaminated GW. The WQI results showed that 31 samples were not suitable for drinking. According to our findings, groundwater safety management and monitoring are essential for meeting the constantly growing mandate of the people and financial actions without additional harm to humans or deterioration of the GW. Safe drinking water wells and the establishment of a comprehensive groundwater monitoring network should be implemented by local governments.

Public awareness of the safe and sustainable use of groundwater resources must also be increased. Effective groundwater management is essential for safeguarding human health and ensuring a sustainable water supply. It requires a combination of regulatory measures, education, and community involvement. Collaboration among various stakeholders is crucial in addressing these complex issues and protecting this valuable resource.

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