RESEARCH ARTICLE

International Journal of Civil, Environmental and Agricultural Engineering

DOI: 10.34256/ijceae2021

Evaluation of the groundwater quality index (GWQI) and the human health risk (HHR) on fluoride concentration in Namakkal district, South India

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Received: 01-02-2022; Revised: 19-04-2022; Accepted: 23-04-2022; Published: 02-05-2022

Abstract: This research aims to determine the health consequences of fluoride contamination of groundwater in the Namakkal region in south India using the groundwater quality index (GWQI). Study area latitude and longitude: 11° 00' and 11° 30' in the north, and 77° 45' and 78° 15' in the east. Statewide, it is among the largest districts in the state. The study region occupies an area of 3406.37 km2. The geology of the studied area is mainly based on the Archaean crystalline and metamorphic complex. The district's major aquifer systems are composed of crystalline rocks that are weathered and fractured and of colluvial deposits. Alluvium and colluvium are examples of porous formations in the cross-section. Only the main river channels have alluvial deposits. The phreatic properties of groundwater Depending on the topography, these aquifers may reach 5 m saturation thickness. Groundwater samples were obtained from 58 bore well sites across the study area during the North-East Monsoon (NEM) of 2015. pH concentrations in suitable drinking water regions during the seasons assist in limiting the availability of groundwater for drinking purposes. TDS are an important factor in determining water suitability for various purposes. The groundwater sample in the study area shows cation domination in ascending order of Na+ > Ca2+ > Mg2+ > K+ due to the dissolution of aquifer minerals in rainfall in the study area. In the NEM seasons, rock dominance and anthropogenic contributions to higher Na+ > Mg2+ > Ca2+ > K+ values. Fluoride concentration differentiates into three groups such as < 0.5 indicates low risk, 0.5 to 1.5 indicates moderate risk, and > 1.5 means high risk. More than 2 fluoride implies very high risk, whereas fluoride in the range of 1.5 to 2.24 suggests a very high risk. The appraisal of non-carcinogenic risk was done to stress the health issues that succeed due to the intake and dermal contact of drinking water in the Namakkal district. The percentage of risk HQ >1 shows that 48 men groundwater samples, followed by 46 groundwater samples women and 30 groundwater samples children, constitute possible health hazards. Overall, health risk estimation results showed that all the groundwater samples have surpassed the permissible limit of HQ <1 for children.

Keywords: Water Quality Index (WQI), Fluoride Risk, Health Hazards, Groundwater

1. Introduction

The groundwater is essential for food security and drinking water, rendering a good ecosystem and human health [1]. The groundwater is a significant causal factor in climate change because of its proportional steadiness in quantity and quality [2]. There is a freshwater reserve in the groundwater that is susceptible to unmanageable abstraction [3, 4]. Today, the scale of groundwater reduction is unknown across the globe [5]. The groundwater abstraction rate is about 1500 km^3/year for agricultural and drinking water use [6, 7]. Globally, the over-exploitation of fresh water has resulted in a significant fall in the groundwater table [8, 9]. In India, the groundwater abstraction is about 243 $km^{2.}$ and abstraction meets more than 50% of urban water demand, about 62% of irrigation requirements, and about 85% of rural drinking supply [2]. The number of wells, such as diesel and electric pumps, has increased considerably since the 1970s after introducing the green revolution [10-13]. In many parts of India, groundwater resources are decreasing rapidly [14-19] due to irrigation and change in monsoon precipitation pattern [20, 21].

Water is one of the essential things for all living things in the world. And around 780 million people worldwide do not have any source of water that is not polluted, the United Nations estimates [22]. As the world's population grows, so does water usage and groundwater stress Degradation of water quality and quantity due to global climate and land-use changes [23, 24]. Climate change threatens food output, population health, ecology, and many other natural ecosystems in developed and developing nations [25]. Also, determine the causes of the deterioration in groundwater quality. Groundwater scarcity is becoming a significant issue in some parts of India, predominantly in hard rock terrain, due to the country's increasing population and growing demand. Due to its geographical and economic arrangement of accessible water resources. Pollutants impact the water quality of both surface and underground water, resulting in the following changes [26]. Water quality decline is a critical alarm in this day and age, predominantly considering the limited availability of water [27, 28]. Contamination of water and the health risks that come with it are major study topics. Fluoride-contaminated groundwater has affected nearly 300 million people, both directly and indirectly [29-32]. Groundwater contains the most electronegative and sensitive element because of geogenic practices involving the dissolution of F-containing minerals [33, 34]. Long-term fluoride exposure of more than 1.5 mg/l is harmful to the development of children [35]. Excessive fertilizer use in industry and agricultural pollution are the main anthropogenic reasons for F [36-38].

It is determined by the hazard quotient considering fluoride in drinking water in the human health assessment [39, 40]. The fluoride exposure was assessed using EPA standards [41]. However, there have been no comprehensive studies on the health effects of high fluoride concentrations in south Indian hard rock terrains. The current study region is characterized by rapid population increase, industrialization, and agricultural activity. The groundwater in this area is over-extracted to fulfil everyday demands, resulting in significant water quality issues. The unregulated use of pesticides and fertilizers has also harmed groundwater quality. F concentrations in the groundwater in this location are high. Fluoride and nitrate contamination in groundwater is now being studied for possible health risks. The current study's goals are to describe groundwater using the GWQI and examine the health risks of high fluoride in drinking water. Eventually, a proposal to improve the current situation was proposed.

2. Study Area

2.1. The geographical position of the study area

The District of Namakkal in the Indian state of Tamilnadu has been chosen as the research region. It is bordered by Salem, the south side of Karur, Perambalur, and Erode to the west and east. Study area latitude and longitude: 11° 00' and 11° 30' in the north, and 77° 45' and 78° 15' in the east. Statewide, it is among the largest districts in the state. The study region occupies an area of 3406.37 km^2 (Figure 1). Groundwater is utilized for drinking, irrigation, and industrial purposes. Total irrigation is 78.12% groundwater (81,110 open wells and 5144 public boreholes). Groundwater pumping has increased due to local water shortages, scarcity, and rapid urbanization. Replenishment of groundwater is needed from rainfall.

2.2. Drainage

The District's western and southern borders are bordered by the Cauvery River, which is perennial. The Tirumanimuttar river, the District's major tributary of the Cauvery, rises in the Manjavadi region and winds its way across the District until joining the Cauvery near Nanjai Edayar hamlet in the Paramathi taluk. There are two major rivers in Northeast District; Nadi and Sweta Nadi. The Cauvery river rises from them perennially in the District's western and southern boundaries. At Nanjai Edayar in Paramathi taluk, the Tirumanimuttar river, once regarded as Salem's most significant hill, joins the Cauvery. Vasista southern bounds of the District mostly drain a small region in the northeastern section. The Tirumanimuttar river, the districts most major tributary of the Cauvery, rises in the Manjavadi part of Salem district Shevroy hills and winds its way across the District until joining the Cauvery near Nanjai Edayar hamlet in Paramathi taluk. Rivers, tributaries of the Vellar River, drain a tiny region in the city's northeastern section.

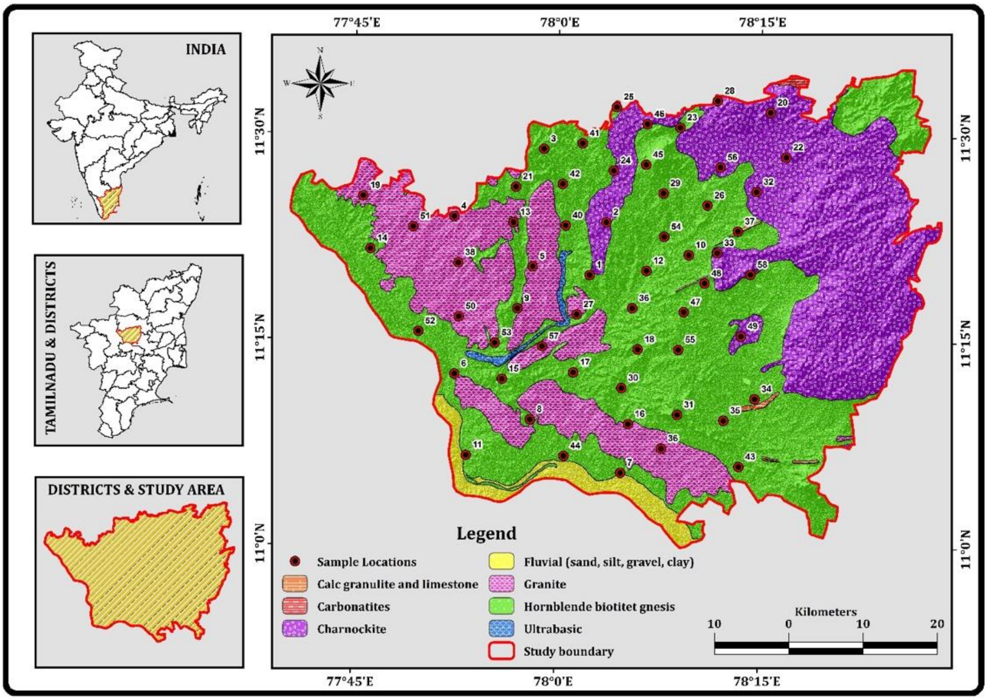

Figure 1. Location, Geology and groundwater sampling points of the study area.

2.3. Climate Condition and Rainfall Data

In April and May, temperatures reach their peak. From mid-June, the weather gradually cools. December is the coldest month at Salem and Mettur Dam, with mean daily maximum temperatures of 31.3°C and 18.3°C, respectively. Winter evenings are more substantial than summer nights. The daily temperature variation is significant, especially in the dry and hot seasons. From February to March, winter temperatures peak around 15.3°C, while winter temperatures hover at about 11°C from October to November. A total of six rain gauge station data were used from 1901 to 2010. The data shows that the District receives between 642 and 891 mm of rain per year. Around Paramathi (641.53 mm) in the southwest of the District, it is the least. A high of 882.51 mm is recorded in Rasipuram (northern area). The Nammakal District has a tropical climate. November through January has good weather. Mornings are often more humid than afternoons, with an average humidity of 77%. Summer midday humidity averages 65% from June to November.

2.4. Geology of the study area

The geology of the studied area is mainly based on the Archaean crystalline and metamorphic complex. The pre-Cambrian epoch's frequent tectonic and magmatic activity complicated the region's geology. This region has the well-known Sithampoondi complex, known for its complex geology. Gneisses are the oldest rocks in the area, and they are found all across the plains. The gneisses rock formations have a lot of wear on them. The Charnockites are coarse-grained and blue to dark grey. Quartz is the second most frequent form of rock in the region, behind sandstone. They are typically larger and less weathered than gneisses. In some areas, iron ore deposits are related to felspathic quartz gneisses and garnetiferous quartz gneisses. These rocks have many folds and joints and are weathered. Along with Cauvery and Thirumanimuthar, a thin veneer of alluvium may be discovered. Around the confluence of the rivers Thirumanimuthar, however, there is an alluvium of a few meters in thickness (Figure 1). There are many faults and shears, especially along with the northeast-southwest trend. They are predicted to impact the district's groundwater circulation, storage, and development potential.

2.5. Hydrogeology

Namakkal's dominant geological formation is the Archaean Crystalline Formation, surrounded by recent riverine alluvial deposits and colluvial deposits near the foothills. The district's major aquifer systems are composed of crystalline rocks that are weathered and fractured and of colluvial deposits. Alluvium and colluvium are examples of porous formations in the cross-section. Only the main river channels have alluvial deposits. The phreatic properties of groundwater Depending on the topography, these aquifers may reach 5 m saturation thickness. The colluvial material generated from adjacent hill ranges comprises sands and gravels. Depending on geographic factors, these aquifers may get a saturation thickness of 20 m. The phreatic properties of groundwater. Rocks of the Archaean age that are crystalline are composed of worn and fractured granite gneiss, granite, and charnockite rocks. In the district, the weathered mantle is thicker than 30m, so groundwater develops due to phreatic conditions. Within a 20-meter depth, most of the research area lies, while the north-north-east western and northernmost parts are deeper. A drilled well reached a depth ranging from 7 to 45 meters below ground level (BGL). Open wells can produce up to 400 m3/day.

3. Material and Methodology

3.1 Sampling and data analysis

Groundwater samples were obtained from 58 bore well sites across the study area during the North-East Monsoon (NEM) of 2015 (Figure 1). The specific coordinates of such sampling stations were obtained using a GARMIN GPS device. Acid-washed transparent polythene bottles were used for the sampling process. Before testing, existing waters in boreholes were cleared by temporarily pumping the wells. While filling the vials with samples, extra care was taken to avoid air bubbles. The samples were then sealed and delivered to the laboratory. Precautions were made by keeping the samples at 4°C and filtering them using 0.45-m paper for further analysis. The measurement of various cations and anions is done following APHA, 2005 [42]. One of the aspects investigated is the behavior of hydrogen ion concentrations. The pH and TDS meter were used to detect the temperature, EC, TDS, and pH on the spot that used the portable instrument. The trimetric technique helps detect

Calcium(Ca^{2+}) by combining it with a standard acid such as Ethylene Diamine Tetra Acetic (EDTA). The content of bicarbonate (HCO_3^-), magnesium (Mg^{2+}), and potassium (K^+) were all determined using the conventional Silver Nitrate ($AgNO_3$) titration method. A flame photometer was used to determine the concentration of sodium (Na^{2+}) (Elico SL 198). A spectrophotometer also measured levels of Nitrate (NO_3^-), Sulphate (SO_4^{2-}), and phosphate (PO_4^-) (Elico SL 207 Mini). Calibration standards were applied to equipment and instruments, and the results were compared to the specifications of the standard water. The USSL and Gibbs diagrams were generated using the WATCLAST programme in C [43]. The total components equivalents per million concentrations are derived by multiplying the ppm concentrations by the weight common. The concentrations of major ions were converted to meq/L, and the analytical accuracy for major ion measurement ranges from 5 to 10%. Anion balancing [44]. The geological and water sample location maps were prepared in ArcGIS version 10.2.1.

3.2 The calculation of the Groundwater Quality Index (GWQI)

The most significant factor in determining drinking water quality is groundwater chemistry [45-49]. The GWQI is useful for calculating groundwater quality for drinking and irrigation. Physical and chemical parameters (pH, EC, TDS, Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, Cl^-, SO_4^{2-}, and F) were weighed (wi) to determine the concentration. Table 1 shows the assigned weight (wi) and relative weights (Wi) for all chemical characteristics according to WHO (2017) [22].

Weights vary from 1 to 5. Due to its importance in assessing groundwater quality, TDS, NO_3^-, Cl^-, and SO_4^{2-} have been given a maximum weight of 5 [49, 50]. Bicarbonate and phosphate were assigned a weightage of 1 since they are minor water quality components. We assigned weights to several criteria such as calcium, magnesium, and other elements to evaluate the water quality [51]. When calculating relative weight, use Equation 1 in the following section:

$$W_i = \frac{w_i}{\sum_{i=1}^{n} w_i} \qquad \text{(Eg.1)}$$

This equation has 'n' parameters, and 'Wi' is the relative weightage. Each parameter's quality rating scale is constructed using Eq. 2 [22]

$$qi = \frac{C_i}{S_i} \times 100 \qquad \text{(Eq.2)}$$

According to this equation, qi indicates the quality score, Ci represents each chemical parameter's absorption (mg/l), and Si represents the anticipated value, according to the World Health Organization (2017) [22]. Using Eq. 3 to calculate GWQI, SI is first calculated for each chemical parameter. This information is then used by Eq. 4 to calculate GWQI according to the SI.

$$SI_i = W_i \times q_i \qquad \text{(Eq.3)}$$

$$WQI = \sum SI_i \quad \text{(Eq.4)}$$

The value is equivalent to a sub-index of the parameter, where 'SI' is the sub-index. When dealing with many factors, 'qi' provides an overall rating based on how concentrated each parameter is in the surrounding environment. The estimated GWQI map is divided into five stages: excellent categories (less than 50), decent categories (50-100), bad categories (100-200), very poor categories (200-300), and unfit for drinking (more than 300).

Table 1. The relative weight of physicochemical parameters and WHO standards

Parameters	Units	Range	Average	WHO (2011)		Weight *(wi)*	Relative Weight *(wi)*
				Most desirable	Not permissible		
pH	-	8 - 8.80	8.48	6.5 – 8.5	6.5 – 8.5	4	0.103
EC	µs/cm	570 - 7650	2002	< 1500	> 1500	4	0.026
TDS	mg/l	313 - 13504	1148.47	< 500	> 1500	5	0.064
Ca^{2+}	mg/l	6 - 152	42.59	< 75	> 200	3	0.026
Mg^{2+}	mg/l	28 -306	85.22	< 50	> 150	3	0.026
Na^{+}	mg/l	14 - 667	209.79	< 200	> 200	3	0.077
K^{+}	mg/l	3 - 47	24.67	< 10	> 10	2	0.026
HCO_3^-	mg/l	671 - 128	337.14	< 300	> 300	3	0.077
Cl^-	mg/l	39 - 2127	349.31	< 200	> 600	2	0.077
SO_4^-	mg/l	15 - 768	160.05	< 400	> 400	4	0.051
F	mg/l	0.27 - 2.24	1.12	< 1.5	> 1.5	5	0.128
						$\sum wi = 0.38$	$\sum wi = 0.68$

3.3 Health Risk Assessment

This study assessed the non-carcinogenic health risk of heavy metals in the drinking water of children and adults in the Namakkal district by oral ingestion. The following formulae were used to use the traditional USEPA (2014) approach [52]. This study's principal exposure route seems to be drinking water rather than the other two previously described. So F was chosen as a contaminant to measure health [53-54]. Calculate the oral exposure using Eq. 5.

$$\mathrm{CDC} = \frac{\mathrm{CPW} \times \mathrm{EF} \times \mathrm{ED} \times \mathrm{IR}}{\mathrm{AET} \times \mathrm{ABW}} \quad \text{(Eq. 5)}$$

Where,

CDC – Chronic Daily Consumption (mg/kg/day); CPW - F concentration in the groundwater (mg/l); FE - Frequency of exposure (days/year), which is 365 days/year for children, women, and men; ED - Exposure duration (years), 12 years for children, 64 years for women, and 67 years for men; IR - Ingestion rate per unit time (L/day), 0.78 L/day for children and 2.5 L/day for women and men; ABW - adults weigh an average of 65 kg, children weigh an average of 20 kg, and babies weigh an average of 10 kg; AET - In adults, the average exposure time was 23360 days; in children, it was 4380 days; and in newborns, it was 365 days (AET = ED X 365).

The hazard quotient increases when the pollutant exposure dosage exceeds the permissible level (Eq. 11) when the pollutant exposure dosage exceeds the permissible level (Eq. 6).

$$\mathrm{HQ} = \frac{\mathrm{CDC}}{\mathrm{RfD}} \quad \text{(Eq. 6)}$$

Where, HQ - hazard quotient; RfD - F (0.6 mg/kg/d) was collected from the IRIS data source [52].

The total chronic hazard index (TCHI) was created to assess the danger of non-carcinogenic effects on the body. In certain cases, the TCHI limit of 1.0 may be exceeded [55]. It is assumed that the TCHI is less than 1.0, so there is no cancer risk. A TCHI score of 1.0 or greater indicates a potentially hazardous situation.

4. Results and Discussion

4.1 Hydrochemistry

Table 2 shows subsurface samples' physical and chemical properties obtained in the Namakkal district through NEM seasons. The groundwater quality parameters were evaluated using descriptive statistics such as minimum, maximum, mean, and standard deviation [22]. It is essential that water used for consumption be physiologically soft, lower ion soluble substances, and contaminant-free [56]. In a process in equilibrium, the pH represents the condition in which water precipitates [57]. When measured during the NEM seasons, the pH value varies from 8 (Sowdapuram) to 8.80 (Ayilpatti). On average, pH ranges from 8.48, indicating that monsoon effects change the groundwater's pH from acidic to basic. The high pH readings indicate the presence of carbonate due to temperature fluctuations and water movement from the Charnokite highlands to the gneissic rock formation. It is alkalinity that is produced by the bicarbonate and carbonate ions. When the pH is high, hydrogen oxide, iron, and silicate may affect alkalinity. Groundwater pH concentrations in suitable drinking water regions during the seasons assist in limiting the availability of groundwater for drinking purposes in such areas. The pH of groundwater decreased little from the seasons, indicating the rock-water interaction [45, 58].

The electrical conductivity (EC) concentrations ranged from 570 (Solaiyudaiyampatti) to 7650 µS/cm (Malayalapatti), respectively, with an average electrical conductivity of 2002 µS/cm for the groundwater samples (Table 2). As per the WHO (2017) standard, the EC of groundwater samples falls between the desired limit categories of 45% of the desirable limit category [22]. 55 % of the samples were considered unsuitable for drinking during NEM. The high concentrations of Na+ and Cl^- in these samples are mainly due to the high EC values. In humans, it has been shown that high EC in groundwater may cause gastrointestinal awkwardness after long exposure [56]. Total dissolved solids (TDS) of the Namakkal district vary from 313 (Solaiyudaiyampatti) to 3504 (Unjanai), averaging 1148.47 mg/l. TDS are an important factor in determining water suitability for various purposes. Only 10% of samples are freshwater, while the rest, 90 %, are unfit for human consumption. These changes indicate that rainfall has a significant impact on reducing TDS in groundwater. TDS has also been added to rainfall due to its interactions with minerals and rocks.

The groundwater sample in the study area shows cation domination in ascending order of Na^+>Ca^{2+}>Mg^{2+}> K^+ due to the dissolution of aquifer minerals in rainfall in the study area. In the NEM seasons, rock dominance and anthropogenic contributions to higher Na^+> Mg^{2+}> Ca^{2+} > K^+ values. The Ca^{2+} content varies from 6 (Erayamangalam) to152 (Muthugapatti) with an average of 42.59 mg/l for NEM seasons, respectively. World Health Organization (WHO) classification of 2017 states that more than 75 mg/l of calcium is desired for good drinking water quality. Most groundwater samples (88 %) fell within the most desirable concentration range. The rest of the 12% samples occur within the not permissible limit during the NEM season, respectively (Table 2). The increasing Ca^{2+} content in groundwater is a result of might be due to silicate weathering minerals.

Magnesium is an alkaline earth metal with a 2+ oxidation state, Mg^{2+}, and Ca^{2+}. It has similar effects on water chemistry, as their contribution leads to the permanent hardness of the water. The geochemical behaviour of magnesium is relatively different from that of calcium. It is lower than sodium ions and can fit in the middle of six octahedral coordination oxygen atoms. Therefore, the hydration effects are stronger than those of calcium and sodium [59]. A concentration range of 28 mg/l to 306.00 mg/l was observed in groundwater, with an average content of 85.22 mg/l observed in the water sample. A higher concentration of 306 mg/l is noted during NEM, which might have been derived from rock water interaction of magnesium-bearing silicate minerals.

Table 2. Physicochemical parameters for different groundwater samples in Nammakal District, Tamilnadu, India

Parameters	Min	Max	Median	SD	Average	WHO (2017)		% of Samples in Most desirable	% of Samples in Not permissible
						Most desirable	Not permissible		
pH	8	8.80	8.50	0.19	8.48	6.5 – 8.5	> 8.5	60	40
EC(μs/cm)	570	7650	1530	1352.43	2002	< 1500	> 1500	45	55
TDS (mg/l)	313	13504	898	751.15	1148.47	< 500	> 1500	10	90
Ca^{2+} (mg/l)	6	152	33	29.41	42.59	< 75	> 200	88	12
Mg^{2+} (mg/l)	28	306	63	57.32	85.22	< 50	> 150	29	71
Na^{+} (mg/l)	14	667	157	145.68	209.79	< 200	> 200	60	40
K^{+} (mg/l)	3	47	24.5	10.65	24.67	< 10	> 10	16	84
HCO_3^- (mg/l)	128	671	308	131.86	337.14	< 300	> 300	45	55
Cl^-(mg/l)	39	2127	220	362.81	349.31	< 200	> 600	48	52
SO_4^-(mg/l)	15	768	106	154.52	160.05	< 400	> 400	91	9
F^-(mg/l)	0.27	2.24	1.07	0.53	1.12	< 1.5	> 1.5	76	24

Besides, the lower range of 28.00 mg/l noted during the season is mainly due to the ionic exchange process by Ca. During the NEM season, 71% of samples surpass the standard. The remaining 29% of groundwater samples are suitable for drinking.

Sodium is the element with the greatest abundance in the alkaline earth group of metals. The element sodium is somewhat more plentiful than the element potassium in igneous rocks. Igneous rock in Earth's crust contains feldspar minerals, according to Clarke (1996) [60]. The feldspars are tectosilicates with aluminum replacing silica to compensate for the lack of positive charge. The plagioclase series ranges from albite to anorthite in orthoclase and microcline. Orthoclase and microcline include sodium, which replaces potassium. Sodium concentrations vary from 14.0 to 667 mg/l with an average of 209.79. Higher concentration was noted during the seasons (667 mg/l). The majority of the samples had greater Na levels, suggesting that the chemical weathering of Na feldspars and the dissolving of Kankar have played a factor [61-63]. Groundwater sodium concentrations may be greatly influenced by human activities [57]. Salt from wells used to deice roadways in the winter has had direct regional consequences. Water reused for irrigation often has a substantially greater salt content than the initial water. The minimum concentration of 14.0 mg/l noted during the NEM season signifies adding fresh recharge water into the aquifer and eliminating pre-existing mineral components in the water.

Neither plants nor animals can survive without potassium. Feldspars (Orthoclase and Microcline), micas, Feldspathoid, and Leucite, are potassium minerals in silicate rocks. Minerals such as Potassium Feldspars are resistant to chemical weathering. On the other hand, it is considered that they go through the same transition as the other feldspars but at a slower pace. Naturally, occurring water has extremely little sodium because of the extraordinary stability of potassium-containing aluminosilicate minerals [64]. In groundwater samples from the study area, potassium ranges from 3.0 to 47 mg/l. During the NEM season, the average was 24.67 mg/l, about 24.67 mg/l. During the NEM, a higher concentration of K (47.0 mg/l) was observed, which might be related to soil leaching through runoff. 84 % of samples surpass the legal level and are thus unfit for human consumption in the research region. The remaining 16% of groundwater tests are potable.

The alkalinity of water is defined as the total amount of substances present in water that can neutralize the acidity of the water. In other words, the ability of a solution to react with acid, buffer pH, and prevent pH from changing—the greater the alkalinity, the greater the buffering capacity against pH changes. Alkalinity can be calculated mathematically using the following equation. (Eq.7 & 8).

$$CaCO_3 + H_2CO_3 \longrightarrow Ca^{2+} + 2HCO_3^- \quad \text{(Eq.7)}$$

$$CaMg(CO_3)_2 + H_2CO_3 \longrightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^- \quad \text{(Eq.8)}$$

According to Drever and Stillings (1996), HCO_3^- can be produced by the dissolution of silicate and calcic minerals and the carbonic acid produced by organic materials. HCO_3^- can also be produced by the atmosphere [61, 65]. HCO_3^{2-} concentrations in the NEM range from 128 to 671 mg/l, with an average value of 337.14 mg/l. The concentration of HCO_3^{2-} in water is directly proportional to the alkalinity of the water, and larger HCO_3^{2-} concentrations in groundwater indicate that the groundwater is alkaline. The weathering of anorthite, sodium, and potassium feldspar raises the HCO_3^{2-} concentration of groundwater samples in the study area. The direct mixing of municipal sewage and industrial water with streams from the northeastern portion of the research area has resulted in a comparably high HCO_3^{2-} concentration in the water.

A lithophile element, chloride has five oxidation states (-1, +1, 3, 5, and 7). The -1 state is often found in groundwater [66]. Sources for chloride in groundwater are mainly anthropogenic, like halide usages, industrial sewages, and road salts. The natural chloride-bearing rock minerals are sodalite, phosphate, and apatite but have lower concentrations. Underground water chloride behavior is considered conservative, suggesting that it circulates through to the hydrological cycle under the direction of mechanical instead of chemical reactions. During the research period, concentrations of Cl^- ranged from 39 to 2127 mg/l, with an average of 349.31 mg/l. The chloride (Cl-) concentration of water is employed as a metric of pollution and is recognized as the primary source of groundwater pollution [67]. These geological sources of chloride, including appetite, sodalite, connate water, and hot springs, are important [68]. The research area's southwestern part had a high Cl- level due to the effect of urban sewage waste and environmental runoffs land. 52 % of groundwater samples collected in the research region during the NEM season surpass the limit considered not allowed. The remaining 48 % of groundwater samples are appropriate for drinking purposes.

Sulfate hydrogen ions presumably formed in aquatic settings due to sulfate and gypsum deposition [69]. Sedimentation of sulfuric acid into groundwater [70]. The groundwater's highest sulfate (SO_4^{2-}) limit is less than 200 mg/l. A concentration of 200 to 400 mg/l is the highest allowable limit [22]. It is estimated that the SO_4^{2-} concentration varies from 15 mg/l to 768 mg/l throughout NEM seasons, with an average of 160.05 mg/l. Nine percent of the groundwater samples collected in the research region during the NEM season are classified as unfit for human consumption; nevertheless, the remaining 91 percent of groundwater samples are appropriate for human consumption. The contribution of dissolved sulfate ions varies in minerals like gypsum and marcasite [71]. The other sources of this ion may also be due to bacterial fixation, the impact of fertilizer, tannery, and anthropogenic sources [72].

Fluoride (F) ions play an important role in affecting groundwater quality. However, fluoride causes severe health risks to humans [48, 73-76]. The high F content groundwater source is the parent rocks with F-bearing minerals [77]. Human teeth and bones are affected by water with F^- over 1.5 mg/l. Geological and environmental factors determine the concentration of F-ions in groundwater. The subsurface ion-exchange allows fluoride ions from host rocks to leak into groundwater. Fluoride leaching raises groundwater silica. It occurs naturally when hornblende discharges in Na^{+} and HCO^{3-} rich in the freshwater environment. Aridity and evaporation make the research area's alkaline water more suited to fluorite mineral disintegration [78-79].

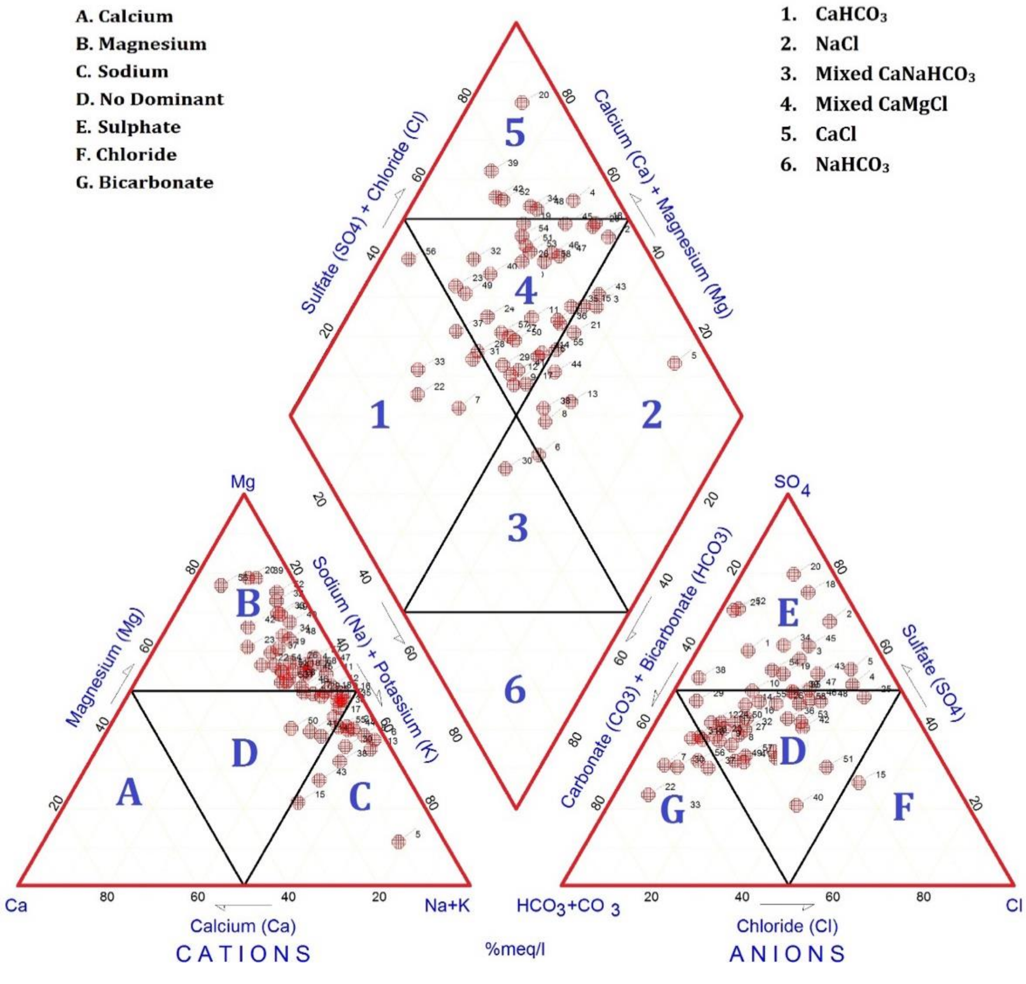

Figure 2. Hill piper plot for groundwater samples.

In addition, fluoride-rich minerals such as fluorite and muscovite prevalent in the host rocks of the region may leach fluoride into the groundwater as a result of their presence [80]. With an average of 1.12 mg/l, the F- concentration in the study area ranged from 0.27 to 2.24 milligrams per liter. During the NEM season, 24 % of tests are deemed unacceptably contaminated. According to the results, 76 % of groundwater samples are appropriate for drinking. In excess or deficit levels, fluoride ions found in groundwater are considered dangerous to human health when they are present in excessive or deficient amounts. Fluoride intake exceeding 1.50 mg/l may affect bones and surrounding tissues such as erythrocytes, the skeletal system, digestive tissues, and joints [81]. Dental fluorosis is the term used to describe the action of fluoride on teeth, which results in a mottled look in the teeth. The impact of fluoride in bone is called skeletal fluorosis, where the rigidity of bone increases, and the curvature of the bone and severe pain. Paralysis of the lower part of the body with legs and quadriplegia is paralysis of all limbs. A lower fluoride concentration in groundwater increases the risk of tooth decay.

The spatial distribution map of Fluoride concentration differentiates into three groups such as < 0.5 indicates low risk, 0.5 to 1.5 indicates moderate risk, > 1.5 means high risk. More than 2 fluoride implies very high risk, whereas fluoride in the range of 1.5 to 2.24 suggests a very high risk [39]. The spatial distribution map represents 460.56 km^2 area covers high risk categories (Sample.no.1, 3, 17,18, 24, 25, 27, 31, 34, 40, 42, 44, 47, 55, 57). Medium-risk categories occupied 2919.62 km^2 area, and the remaining 26.18 km^2 area covers low-risk categories (Figure 2). 14 % of the samples are classified as high risk of infection in this research location. 86 % and 1 % of the samples are classified as medium and low risk.

4.2 Hydro-geochemical facies

The hydrochemical technique understands groundwater movement and provides access to a paleoenvironmental data database [82-84]. A Hill Piper plot is adopted to determine the geochemical assessment of groundwater. Triangular-shaped fields and a diamond-shaped center field make up the diagram. The % epm values of main cations (Ca, Mg) alkali earth, (Na + K) alkali, (HCO_3 + CO_3) weak acid, and (SO_4+Cl) strong acid are displayed individually in the two triangle fields before being projected onto the center field to indicate overall water properties. Applications of the diagram pointed out by Piper include testing groups of water analyses to determine whether particular water may be a simple mixture of others for which analyses are available or whether it is affected by the solution or precipitation of a single salt. It can be shown easily that the analysis of any mixture of waters.

The Piper plot shows large sample classifications and interactions. The sample points indicated in the database are also highlighted in many other open graphical presentations. Several authors have applied this plot to understand the hydrogeochemical facies [32]. This AQUACHEM-based major-ion trilinear diagram (Figure 3) indicates that the groundwaters have different chemical compositions. $CaHCO_3$, NaCl, Mixed $CaNaHCO_3$, CaMgCl, and CaCl are the most common elements found in groundwater samples collected during the NEM, with only modest concentrations of CaCl and $NaHCO_3$ observed.

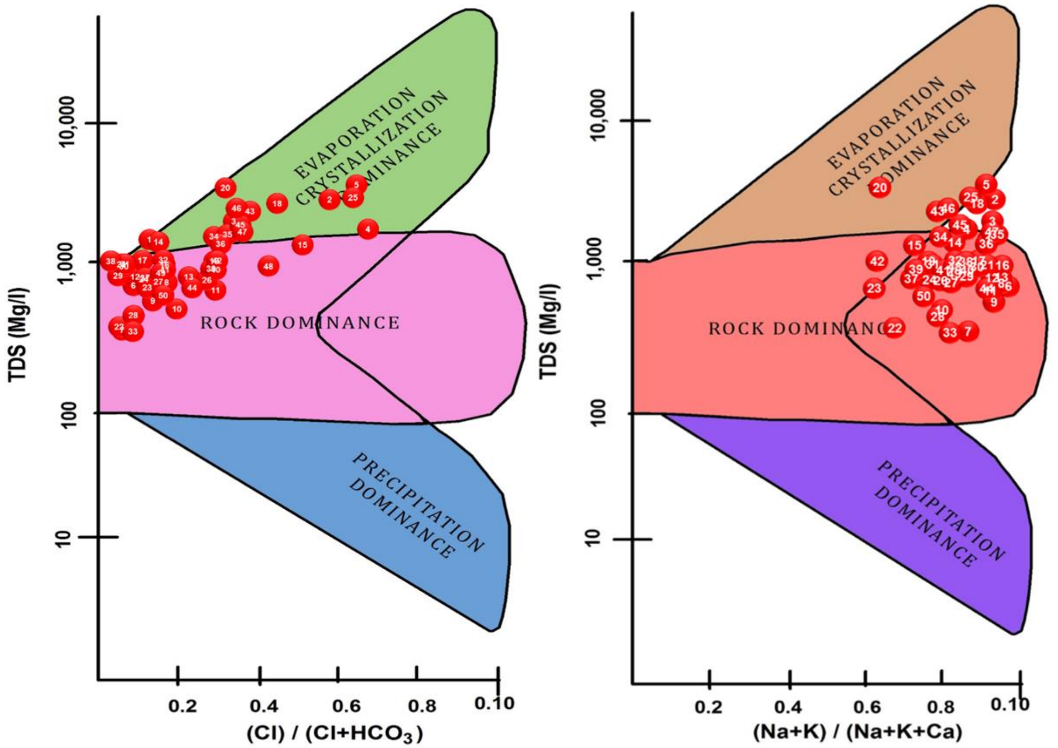

Figure 3. Gibbs plot for groundwater samples.

During NEM, groundwater samples cluster into $CaHCO_3$, NaCl, Mixed $CaNaHCO_3$, CaMgCl, and CaCl types. In NEM, Na decreases with Ca and Mg increases, signifying ion-exchange weathering. Calcareous minerals solubilization primarily produces water containing calcium hydroxide ($CaHCO_3$), and its source is due mainly to precipitation events recharge. Surface water saturated with environmental and biological CO_2 penetrates the subsurface, resulting in mixed Ca-Mg-Cl water. Reverse cation exchange produces CaCl2 waters when it removes Na from a solution in exchange for bound Ca. $CaCl_2$ water can be created by mixing younger, fresh, healthy water with older, saltier water [85]. The recharge of rains that delivered saline water mixing is more likely to produce calcium-sodium bicarbonate water. The figure shows that an alkali (Na + K) is more powerful than alkaline earth (Ca + Mg), and strong acids ($Cl + SO_4$) are more powerful than weak acids (HCO_3^-). The water chemistry in the research region is mostly controlled by silicate weathering, secondary leaching, ion exchange, and human activities.

4.3 Gibb's Diagram

Gibbs (1970) proposed the Boomerang envelope model to represent groundwater sources geochemical influences and divided them into the following types: rock control, evaporation/crystallization, and precipitation. Precipitation events water has the highest concentration of Na^{+}, whereas weather-dominated water has a high concentration of Ca^{2+}, Cl^{-}, and HCO_3^{-}, and evaporation/crystallization-dominated water has a high concentration of Na^{+} [86]. By creating a curve with two arms graphing total dissolved salt concentrations against relative proportions of the principal anions for various surface water drinks worldwide. As the lower arm moves to the right, the salt percentage of the water decreases, and the water takes on a rainwater-like composition (indicated by a high Cl to HCO_3 ratio) (Figure 4).

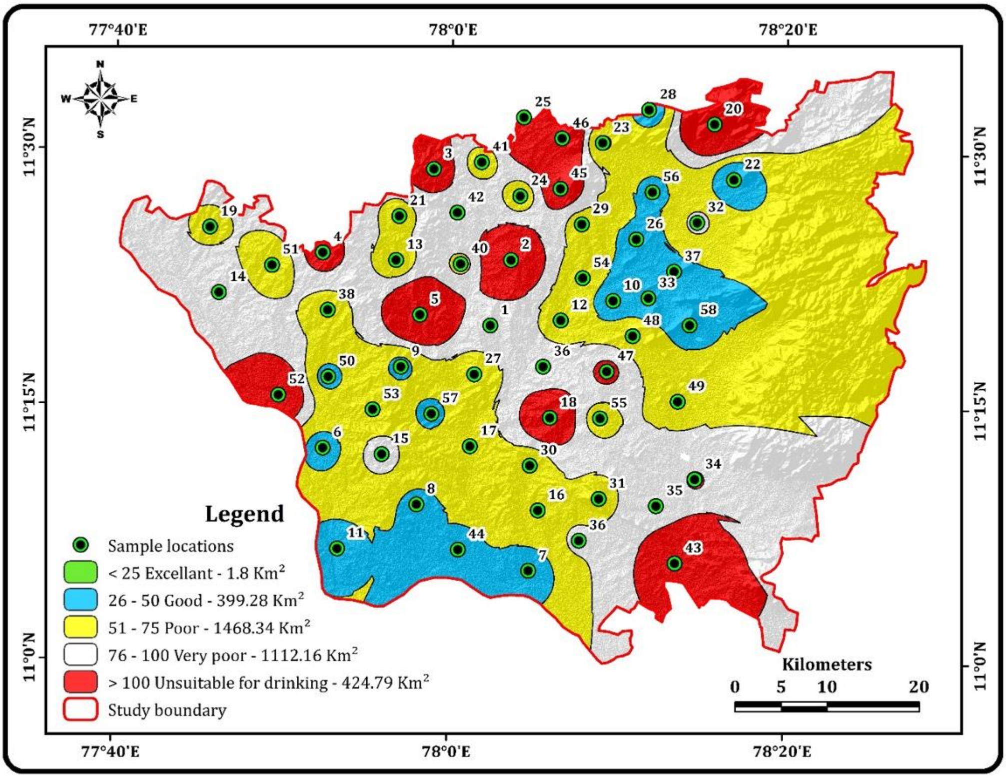

Figure 4. Spatial distribution map of Water Quality Index in the study area.

The figure shows the ratios of Na: (Na+K) and Cl: ($Cl+HCO_3$) as a function of total dissolved solids (TDS), which are commonly used to analyze the availability of dissolved chemical elements from various sources (such as precipitation, rock, and evapotranspiration dominance). Some processes and mechanisms regulate the water's chemistry in the study region. Furthermore, most of the rocks in the studied region are made of silicates. It is unavoidable that it will influence water chemistry. During NEM, the plot for most samples of cations and anions falls within the rock dominance zone with minor indications in the evaporation zone (Figure 4). However, Major representations are also noted in the rock dominance zone, indicating effective interaction between rock and groundwater. The NEM sample is moved towards evaporation, increasing salinity (Na) and increasing the TDS.

4.4 Spatial distribution of Groundwater Quality Index (GWQI)

Geology may be used to verify the quality of water that is safe for human consumption [87]. For 58 samples, the Groundwater Quality Index (WQI) was calculated using the values of total dissolved solids (TDS), calcium and magnesium ions (Ca^{2+} and Mg^{2+}), chlorine, hydrogen peroxide (Cl^{-}), Sulfate (SO_4^{2-}), fluoride (F), dissolved oxygen (EC), and pH. During the NEM seasons, the GWQI ranges from 22.08 to 211.64, with a mean of 78.90 during the NEM season. According to the WQI, 3 excellent samples and 15 locations fell under good water type. In the poor and very poor groups, 19 and 8 samples, respectively. The acceptable category for drinking water consists of 18 groundwater sampling locations. As a consequence, if very poor (14 % of samples), poor (33 % of samples), or not suitable (22 % of samples) water is used for drinking, health hazards may occur. Furthermore, the GWQI findings revealed that 31% of samples fell into the "good" category, meaning they may be taken without causing harm to one's health (Figure 5). It might be due to the gypsum-bearing and rock salt deposits being effectively leached and dissolved. High absorption of EC, chloride, and sodium, followed by calcium, are the main drivers of water quality degradation in the research region, suggesting that the rock-water interaction mechanism is at work. The results listed the appropriate and insufficient water quality for drinking purposes (Table 3 & 4).

Table 3. Water quality classification and type of WQI value

Range (mg/l)	Type of water	No. of Samples	No. of Sample (%)
< 25	Excellent water	3	5
26 – 50	Good water	15	26
51 – 75	Poor water	19	33
76 – 100	Very poor water	8	14
> 100	Unsuitable for drinking purposes	13	22

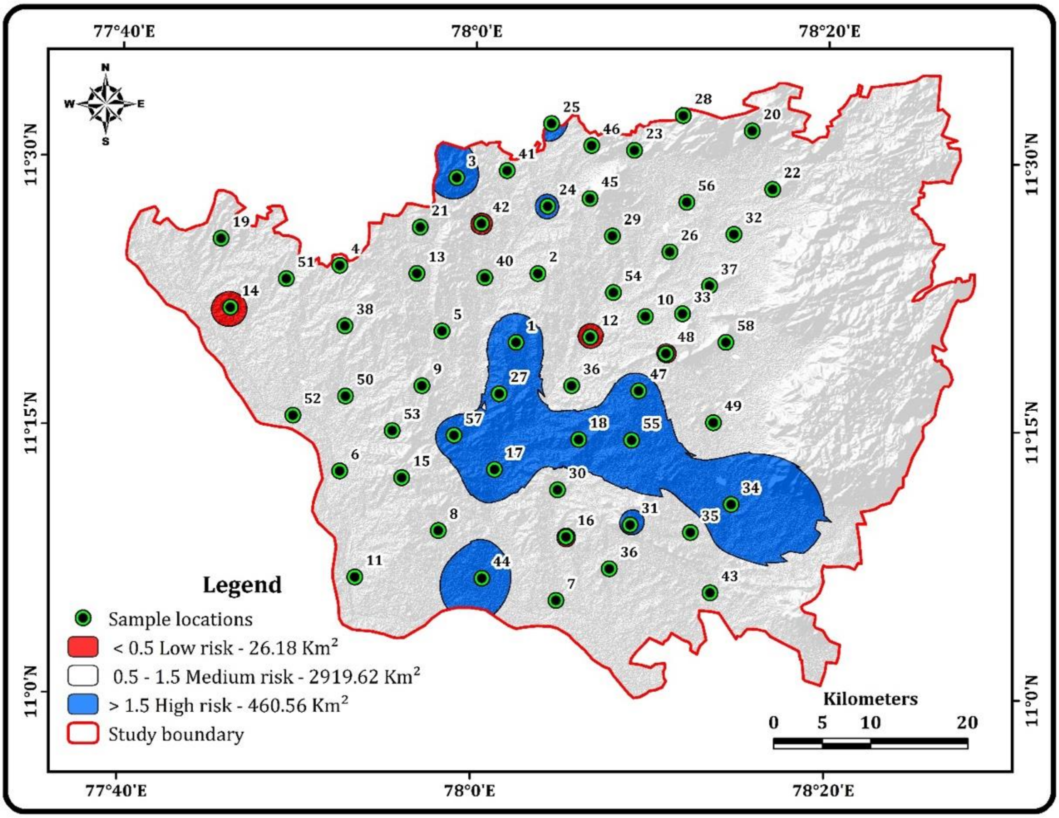

Figure 5. Spatial distribution map of health risk based on fluoride concentration in groundwater of the Namakkal district

Table 4. Calculated hazard quotient (HQ) and water quality index (WQI) results.

Sample no.	HQ for Men	HQ for women	HQ for children	WQI value	Water type
1	1.34	1.27	1.81	84.57	Very poor water
2	0.90	0.85	1.21	192.98	Unsuitable for drinking purposes
3	1.43	1.35	1.93	126.08	Unsuitable for drinking purposes
4	0.72	0.68	0.97	119.80	Unsuitable for drinking purposes
5	0.50	0.47	0.68	211.64	Unsuitable for drinking purposes
6	0.65	0.61	0.88	37.0	Good water
7	0.44	0.42	0.60	25.5	Good water
8	0.88	0.84	1.20	45.83	Good water
9	0.38	0.36	0.51	42.02	Good water
10	0.44	0.41	0.59	28.8	Good water
11	0.62	0.58	0.83	42.64	Good water
12	0.17	0.16	0.23	58.16	Poor water

13	0.33	0.32	0.45	53.28	Poor water
14	0.24	0.22	0.32	91.85	Very poor water
15	0.58	0.55	0.78	91.68	Very poor water
16	0.24	0.23	0.33	72.31	Poor water
17	1.13	1.07	1.53	69.16	Poor water
18	1.09	1.03	1.47	164.96	Unsuitable for drinking purposes
19	0.84	0.79	1.14	72.19	Poor water
20	0.72	0.68	0.97	208.85	Unsuitable for drinking purposes
21	0.54	0.51	0.73	64.53	Poor water
22	0.60	0.56	0.81	22.1	Excellent water
23	0.72	0.68	0.98	44.08	Good water
24	1.08	1.02	1.46	53.07	Poor water
25	1.18	1.12	1.59	181.57	Unsuitable for drinking purposes
26	0.51	0.48	0.68	42.06	Good water
27	0.99	0.93	1.33	48.25	Good water
28	0.50	0.47	0.68	31.4	Good water
29	0.37	0.35	0.50	63.45	Poor water
30	0.00	0.00	0.00	54.37	Poor water
31	1.02	0.96	1.38	64.09	Poor water
32	0.38	0.36	0.51	81.43	Very poor water
33	0.72	0.68	0.98	23.8	Excellent water
34	1.44	1.36	1.94	100.87	Unsuitable for drinking purposes
35	0.87	0.82	1.17	94.33	Very poor water
36	0.89	0.84	1.20	84.47	Very poor water
37	0.58	0.55	0.79	47.09	Good water
38	0.53	0.50	0.71	62.27	Poor water
39	0.29	0.28	0.40	77.62	Very poor water
40	0.97	0.92	1.32	66.88	Poor water
41	0.56	0.53	0.76	56.61	Poor water
42	0.19	0.18	0.25	82.96	Very poor water
43	0.81	0.77	1.10	144.53	Unsuitable for drinking purposes
44	1.33	1.25	1.79	41.75	Good water
45	0.47	0.45	0.64	130.67	Unsuitable for drinking purposes
46	0.34	0.32	0.46	167.41	Unsuitable for drinking purposes
47	1.31	1.24	1.78	111.84	Unsuitable for drinking purposes
48	0.22	0.21	0.29	70.48	Poor water
49	0.78	0.73	1.05	62.28	Poor water
50	0.40	0.38	0.54	40.15	Good water
51	0.53	0.50	0.71	53.56	Poor water
52	0.88	0.83	1.19	165.01	Unsuitable for drinking purposes
53	0.90	0.85	1.22	56.36	Poor water
54	0.50	0.47	0.68	61.83	Poor water

55	1.23	1.16	1.66	61.63	Poor water
56	0.78	0.73	1.05	39.6	Good water
57	1.12	1.05	1.51	41.47	Good water
58	0.59	0.56	0.80	41.08	Good water

4.5 Human health risk assessment of fluoride

Fluoride concentrations in several rural water wells are significant. It also is critical to assess health hazards based on fluoride exposure in the research region. The HQ is a valuable tool for expressing non-carcinogenic risks in the human system. Children and adults in the study area had HQ calculated. Many parameters were used to estimate non-carcinogenic dangers in children, teens, and adults, including ingestion rate, average time, exposure frequency, duration, and body weight (RfD). Increased fluoride intake has been associated with numerous health problems in humans. Fluoride ingestion is linked to a variety of health problems. Table 4 shows the calculated HQ values for the research region. For males, women, and children, they ranged from 0.00E+00 to 1.43E+00, 0.00E+00 to 1.36E+00, and 0.00E+00 to 1.94E+00. The findings show that 48 men, 46 women, and 30 children constitute possible health hazards, accordingly (Figure 6). According to the survey, people are particularly vulnerable to health risks than men and women. Various researchers in various parts of the globe have reached the same conclusion [73-75, 88-91].

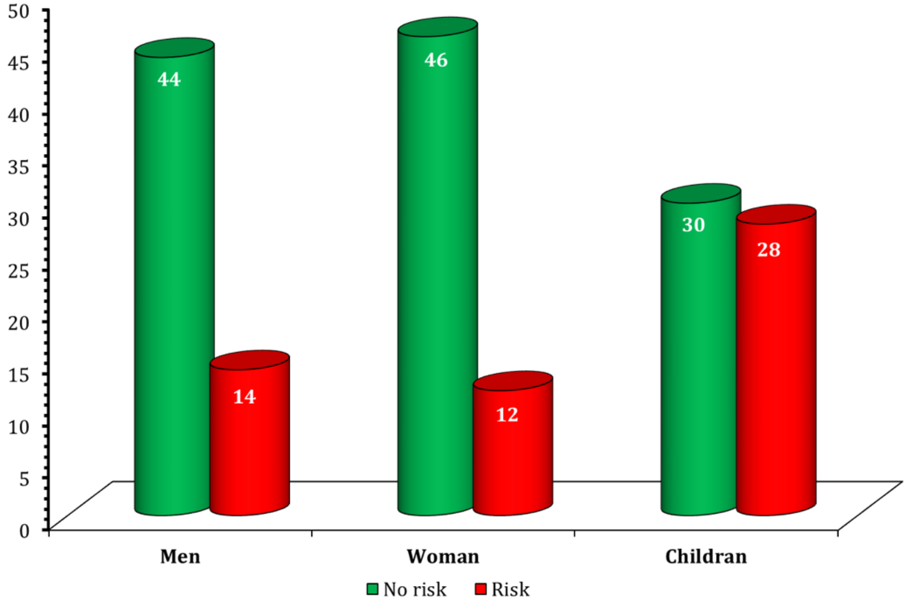

Figure 6. Health risk (Total Hazard Index) in groundwater samples of the Namakkal district. (a) Men (b) Women and (c) Children.

5. Conclusions

This study region's groundwater quality was assessed using the water quality index (WQI) applied to 58 groundwater samples. This research focuses on fluoride and its impact on groundwater. It also assesses the human health risk. The groundwater is slightly alkaline and maintains an average TDS value of 1148.47 mg/l. Cations and anions predominate ions observed in larger amounts during the NEM periods. These ions reflect the activity of erosion, degradation, deterioration, and human impacts on groundwater quality. This water has a fluoride content ranging from 0.27 mg/l to 2.24 mg/l, with an average value of 1.12 mg/l. Approximately 24% of the groundwater samples collected in this location exceed the permissible level based on the World Health Organization (> 1.5 mg/l). The major mechanism for the increase in the groundwater parameter is the weathering of rocks and leaching. The piper trilinear diagram exposes that the groundwater samples fall under the mixed type indicating the impact of weathering of ion exchange. The $CaHCO_3$ water is produced by the breakdown of carbonate minerals and is recharged by rainfall over decades or millennia. The mechanism of groundwater chemistry Gibbs plots reveals that all the samples fall under the rock water interface. The appraisal of non-carcinogenic risk was done to stress the health issues that succeed due to the intake and dermal contact of drinking water in the Namakkal district. The percentage of risk HQ >1 shows that 48 men groundwater samples, followed by 46 groundwater samples women and 30 groundwater samples children, constitute possible health hazards, accordingly. According to the survey, people are particularly vulnerable to health risks than men and women. Overall, health risk estimation results showed that all the groundwater samples have surpassed the permissible limit of HQ <1 for children. As a result, the current study determines that distinct sensitive zones at a single site have varying spatial intensities, allowing for effective management strategies to protect groundwater resources from contamination and, as a result, to improve human health.

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Acknowledgements: We would also like to express our gratitude to the editors and anonymous reviewers for their important comments on the work.

Credit authorship contribution statement: K. Sankar: Writing – original drift, methodology, investigation. D. Shanthi: Data analysis and Review & editing. K. Kalaivanan: Software conceptualization and writing review & editing.

Declaration of competing interest: There are no known conflicting financial interests or personal ties amongst the authors that may have seemed to affect the work presented in this study, the authors state.

Supplementary data: All data are provided as tables and figures.