Approach of Total Water Quality And Total Human Health Hazard Indices For Health Risk Evaluation With Oral Intake Pathway of Groundwater Nitrate And Fluoride From a Rural Region of South India

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Approach of total water quality and total human health hazard indices for health risk evaluation with oral intake pathway of groundwater nitrate and fluoride from a rural region of South India

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Abstract

Evaluation of the chemical quality of groundwater and associated health hazards is a prerequisite for taking remedial measures elsewhere. The rural region of South India was, thus, chosen for the present study to assess the total quality of groundwater and also to decipher the human health risk zones with respect to adults and children due to groundwater pollution with nitrate (NO3−) and fluoride (F−) ions. Groundwater samples collected from the study region were determined for various chemical parameters. According to the total water
quality index, groundwater quality is suitable for drinking purposes. However, the NO$_3^-$ (0.4 to 585.20 mg/L) and F$^-$ (0.22 to 5.41 mg/L) ions exceed the drinking water quality limits of 45 mg/L and 1.5 mg/L in 34% and 25% of the groundwater samples, respectively. Nitrate fertilizers appeared as the chief source of NO$_3^-$, and fluoride minerals as the main source of F$^-$ in the groundwater body, which is further supported by principal component analysis. The total human health hazard index (TTHHI) was observed to be higher than its tolerable limit of 1.0 in 63% and 73% of the groundwater samples in respect of NO$_3^-$ and F$^-$ of adults and children, respectively. The intensity of human health risk zones of TTHHI (>1.0) was 1.37 times higher in children (5.69) than in children (4.15), which cover an area of 71.75% and 66.73%, respectively. Thus, effective strategic measures were recommended for the protection of groundwater resources from pollution and also for improving human health conditions.

**Keywords:** Groundwater, Total water quality index, Total Human health hazard index, Human health risk zones, Rural region, India

**Introduction**

Because of the rapid climatic changes, groundwater is an essential source globally, especially for both drinking and irrigation purposes (Reddy and Sakram 2014). More than 85% of the rural population depends upon groundwater resources for their daily needs (Kulkarni et al. 2015). Though about 60 to 85% of groundwater is utilized for drinking and agriculture purposes, respectively, in India (Sishidia et al. 2016; Sakram and Narsimha 2018), most of it has been contaminated by natural processes and artificial activities (Alaya et al. 2014; Subba Rao et al. 2017). Natural contamination is due to the influence of toxic components existing in the soil and rocks (example: fluoride minerals), while artificial agents such as poor
drainage conditions, spillage of septic tanks, irrigation-return-flows, immense usage of agrochemicals, etc. cause inferior quality of groundwater and consequently, health problems (Sakram et al. 2018; Subba Rao and Chaudhary 2019; Wu et al. 2019a).

Recently, researchers have mainly focused their work on the chemical quality of groundwater and associated health problems with respect to nitrate (NO$_3^-$) and fluoride (F$^-$) ions, as they are the most common toxicities in the groundwater (Qasemi et al. 2018; Subba Rao et al. 2020a, b). Nitrate is the most common ion occurring in the groundwater due to agricultural activities (especially due to nitrogen fertilizers), irrigation-return-flows, flowing of untreated household wastes, sewage and septic tank leakage onto the ground, nitrogen-rich soils, and animal waste (Marghade et al. 2015; Li et al. 2017; Shukla and Saxena 2018; Zhang et al. 2018; He and Wu 2019; He et al. 2019; Karunanidhi et al. 2019; Subba Rao et al. 2021a, b, c). About 118 million people drink water with a NO$_3^-$ level ranging from 45 to 100 mg/L and more than 108 million people consume water with more than 100 mg/L of NO$_3^-$ in India (Karunanidhi et al. 2020). Approximately 200 million people suffer from high F$^-$ content (> 1.5 mg/L) in groundwater globally, especially in countries, such as Africa, China, Iran, Nigeria, Pakistan, South America, and Sri Lanka (Wu et al. 2015; Craig et al. 2015; Chen et al. 2017). The fluoride minerals (fluorite, apatite, biotite, and hornblende) occurring in basement rock such as hornblende-biotite, gneiss, and granite are the chief sources of F$^-$ contamination of groundwater, while agrochemicals like phosphate fertilizers lead to rising concentrations of F$^-$ as a secondary source in the groundwater (Subba Rao 2017a; Karunanidhi et al. 2019; 2020).

It is a well-known fact that the consumption of contaminated groundwater by NO$_3^-$ more than 45 mg/L would cause methemoglobinemia (blue baby syndrome), where red blood
cells reduce their ability to carry oxygen, which leads to shortness of breath, heart attack, and even death, especially in children. Sometimes, it leads to cancer also (WHO 2012). Whereas F\(^-\) higher than 1.5 mg/L causes severe fluorosis (BIS 2012). It was observed that children are more vulnerable in comparison with adults in respect of NO\(_3^-\) and F\(^-\) ions (Zhai et al. 2017; Rezael et al. 2018; Karunanidhi et al. 2020). In India, the potential risk of groundwater is a consequence of contamination of NO\(_3^-\) and F\(^-\) ions, where children are at a greater health risk than adults, leading to non-carcinogenic problems in children (Ding et al. 2020; Kaur et al. 2020; Subba Rao et al. 2021a).

The present study region is a part of Telangana State, India, which is a rural area (Fig. 1). It has intensive and long-term practice. So, the influences of unlimited usage of chemical compost (nitrate, phosphate, and potassium verities), irrigation-return-flows, and animal wastes are the most common phenomena on the groundwater system. Basic sanitary facilities like disposal of household wastes, flow of leakage of septic tanks, etc are in poor condition in the study region, which is known as the most contaminated sources of groundwater. However, there is no scientific study so far on the human health risk, especially due to the drinking of NO\(_3^-\) and F\(^-\) polluted groundwater. People depend upon groundwater resources for their drinking purposes due to the lack of surface water supply. Therefore, the main focus of the present study is on the assessment of health risks caused by NO\(_3^-\) and F\(^-\) contamination in the groundwater. The study facilitates the decision-making authorities for the protection of the groundwater quality from pollutants, and thereby improves the health conditions of the local community.

Figure 1 should be placed here
Study region

The present rural region is located in the southwestern part of Telangana, India. It lies between north latitude 17°23'-17°25' and east longitudes 77°45'-78°50', falling in Survey of India toposheet numbers 56G/15 and 56G/16 and covering a geographical area of 632.45 sq kms (Fig. 1). The region comes under a semi-arid climate with an annual average temperature varying from 14°C to 41°C and an annual average rainfall (5 years) of 937 mm. The surface runoff has resulted from the development of sub-dendritic drainage pattern in the study region.

The prominent rock exposures in the study region are basalt and granite (Fig. 1). Laterite patches also occur. The basalts are fine-grained and dark-colored volcanic rocks, which are composed of calcic plagioclase feldspars and clinopyroxene with olivine, quartz, hornblende, nepheline, orthopyroxene, etc. The granites are generally medium- to coarse-grained. They contain quartz, plagioclase and potassium feldspars, biotite, apatite, hornblende, etc. Basically, they are hard rocks. However, the occurrence of vesicular structures, cracks, and joints become aquifers in the basalts, while the presence of weathered and fractured rocks are the water-bearing formations in the granites. The laterites are porous, but they are slightly permeable with a limited areal extent. Groundwater occurs under the water table and also under semi-confined conditions. The depth of the groundwater table varies from 18 m to 28 m below ground level. The quality of groundwater generally appeared to be potable in the fieldwork.

Materials and methods

A hundred bore wells were observed in the study region during May 2015 (Fig. 1). The groundwater samples were collected from them in one-liter capacity polythene bottles, which
were cleaned with 1:1 dilute hydrochloric acid and washed away with distilled water three
times before collecting the water samples, following the standard procedure (APHA 2012).

The pH and electrical conductivity (EC) were measured in the field, using meters
(Table 1). TDS was calculated by multiplying EC by a 0.64 factor. The other chemical
parameters (Ca$^{2+}$, Mg$^{2+}$, Na$^+$, K$^+$, HCO$_3^-$, Cl$^-$, SO$_4^{2-}$, NO$_3^-$ and F$^-$) were estimated, using
conventional procedures such as titration (Ca$^{2+}$, HCO$_3^-$, and Cl$^-$), calculation (Mg$^{2+}$), flame
photometer (Na$^+$ and K$^+$), UV spectrophotometer (SO$_4^{2-}$ and NO$_3^-$), and ion-selective
electrode (F$^-$), and following the standard water quality methods (APHA 2012). For the
computation of analytical error, the total cations (Ca$^{2+}$+Mg$^{2+}$+Na$^+$+K$^+$) and the total anions
(HCO$_3^-$ + Cl$^-$ + SO$_4^{2-}$ + NO$_3^-$ + F$^-$) were used, which was observed to be 5% (Subba Rao
2017a), reflecting the reliability of the chemical data.

**Comprehensive tool for utilization of groundwater quality for drinking**

The total water quality index (TWQI) is a comprehensive technique to express the overall
drinking water quality in a single term (Subba Rao et al. 2020; Wu et al. 2020a). The first
step in this index is the calculation of relative weight ($W_i$), after assigning the unit weight
($w_i$), for each chemical parameter on the basis of its relative significance to human health (Eq.
1). The second step is the computation of the rating of water quality ($q_i$), which is divided by
the concentration of chemical parameters ($C_i$) and national drinking water quality standard
($S_i$) for each chemical parameter (Eq. 2). The third step is the assessment of $SI_i$ by
multiplication of $q_i$ with $W_i$ for each chemical parameter (Eq. 3). The last step is the
computation of TWQI by adding all $SI_i$ in each sample (Eq. 4).

$$W_i = \frac{w_i}{\sum_{n=1}^{n} w_i} \quad \ldots \ldots \quad (1)$$
When the TWQI is less than 50, it indicates an excellent quality of water; when it is from 50 to 100, it shows a good quality of water; when it is between 100 and 200, it specifies a poor quality of water; when it is from 200 and 300, it represents a very poor quality of water; when it is more than 300, it suggests an unsuitable quality of water for drinking purposes.

### Human Health risk assessment

The NO$_3^-$ and F$^-$ ions were chosen for the human health risk assessment. The oral intake procedure was selected for the computation of the total human health hazard index (THHHI) with respect to adults and children (Li et al. 2019a, b; Wu et al. 2020). The THHHI was calculated as shown in Eqs. 4 to 6 (USEPA 1991, 2006).

\[
MDD = CGW \times IR \times ED \times EF/MBW \times MET \quad \ldots \quad (4)
\]

\[
HHHQ = MDD/RFD \quad \ldots \quad (5)
\]

\[
THHHI = \sum_{i=1}^{n} HQ_i \quad \ldots \quad (6)
\]

where MDD is the mean daily dose of NO$_3^-$ and F$^-$ (mg/kg/day), CGW is the concentration of NO$_3^-$ and F$^-$ in the groundwater (mg/L), IR represents the ingestion rate (3 L/day for adults and 1.5 L/day for children), ED is the exposure duration (66.4 years for adults and 12 years for children), EF is the exposure frequency (365 days for both adults and children), MBW is the mean body weight (65 kg for adults and 18.7 kg for children), MET is the mean exposure
time (24,236 days for adults and 4,380 for children), HHHQ is the hazard quotient, RfD is the reference dose for chronic oral exposure (1.60 mg/kg/d for NO$_3^-$ and 0.06 mg/kg/d for F$^-$ (ICMR 2009; UNDESA 2013; USEPA 2014; Brindha et al. 2016), and TTHHII is the total human health hazard index (non-carcinogenic hazard).

The tolerable limit of TTHHII is 1.0 (USEPA 2014). If it is above 1.0, the non-carcinogenic risk of the pollutant is greater than the tolerable level. If it is below 1.0, the non-carcinogenic risk is at an acceptable limit.

**Results and discussion**

**Groundwater characteristics**

The pH in the groundwater ranged from 6.30 to 8.90 with a mean of 7.14 (Table 1), which indicates that it is slightly acidic to highly alkaline in nature. Three groundwater samples are exceeded the safe limit of pH (6.5 to 8.5) in drinking water, which causes damage to the mucous membranes (BIS 2012). The TDS was from 56 to 1024 mg/L with a mean of 291 mg/L. About 15% of the groundwater samples are higher than the recommended limit of 500 mg/L for drinking purposes, causing gastrointestinal irritation (BIS 2012).

**Table 1 should be placed here**

**Cations**

The Ca$^{2+}$ content was from 8.02 to 152.30 mg/L being a mean of 49.60 mg/L (Table 1). Fourteen percent of the groundwater sample showed a non-acceptable limit (75 mg/L) of Ca$^{2+}$ (BIS 2012). Weathering and dissolution of plagioclase feldspars are the chief sources of Ca$^{2+}$ in the groundwater (Subba Rao et al. 2017). The Mg$^{2+}$ was between 2.43 and 92.42 mg/L with a mean of 23.53 mg/L, which is more than the tolerable limit of 50 mg/L in 6% of the groundwater samples. The Mg$^{2+}$ is mainly attributed to the dissolution of ferromagnesian
minerals (olivine, pyroxene, biotite, etc.) occurring in the host rocks, in addition to human-induced activities (Subba Rao 2021). The Na$^+$ was from 3 to 416 mg/L, with a mean of 54.13 mg/L. Only one groundwater sample shows Na$^+$ more than the threshold limit of Na$^+$ 200 mg/L (BIS 2012). The plagioclase feldspars in the basement rocks are the prime source and the anthropogenic origin (household wastes, irrigation-return-flows, etc) is another source of Na$^+$ in the groundwater (Subba Rao 2021). The K$^+$ ranged from 1 to 118 mg/L and its mean is 6.20. This exceeds the desirable limit of 12 mg/L in 10% of the groundwater samples. The orthoclase feldspars are the prime source and the potassium composts are the secondary source of K$^+$ in the groundwater.

**Anions**

The HCO$_3^-$ was from 146.40 to 2,538 mg/L, with a mean of 1,014.31 mg/L (Table 1), which is caused by soil CO$_2$. This is released from the decay of organic decomposition (Subba Rao et al. 2017). The HCO$_3^-$ is greater than its allowable limit of 300 mg/L for drinking purposes in 99% of the groundwater samples (BIS 2012). The concentration of Cl$^-$ was between 17.73 and 425.40 mg/L with a mean of 127.52 mg/l. According to the drinking water quality standards, the Cl$^-$ is more than 250 mg/L in 10% of the groundwater samples, causing a salty taste and laxative effect. Non-lithological sources (domestic waste water, irrigation-return-flows, etc.) are the prime contributors of Cl$^-$ to the groundwater (Sarath Prasanth et al. 2012; Laxman et al. 2019). The value of SO$_4^{2-}$ was from 30 to 166 mg/L and its mean was 97.90 mg/L. It is not more than its acceptable limit of 200 mg/L in all groundwater samples. Since there are no traces of sulphide minerals in the country rocks, utilization of gypsum for alternation of conditions is the only source of SO$_4^{2-}$ in the groundwater body (Subba Rao et al. 2017).
The NO$_3^-$ ranged from 0.4 to 585.20 mg/L with a mean of 56.27 mg/L. In 34% of the groundwater samples, it is above the desirable limit of 45 mg/L, causing a blue baby disease (BIS 2012). The NO$_3^-$ is a result of the influence of sewage waste, septic tank leakage, agricultural fertilizer and animal waste on the aquifer system (Marghade et al., 2015; Zhang et al. 2018; He et al. 2019). In the present study region, the F$^-$ was from 0.22 to 5.41 mg/L, with a mean of 1.13 mg/L. It exceeds 1.5 mg/L in 25% of the groundwater samples, causing fluorosis. The occurrence of fluoride containing minerals like fluorite, biotite, hornblende, etc. in the host rocks and the usage of phosphate compost in the agricultural areas are the main sources of F$^-$ in the groundwater body (Subba Rao et al. 2016, 2020a).

### Total groundwater quality assessment for drinking purposes

The total water quality index (TWQI) is a scale to measure the overall drinking water quality (Subba Rao et al. 2020a). The computed values of TWQI were from 30 to 91 with a mean of 52.72 (Table 2). According to the classification of TWQI, 51% and 49% of the groundwater samples come under the excellent (TWQI: < 50) and good (TWQI: 50 to 100) water quality types for drinking purposes, respectively. It suggests that the quality of groundwater is fit very well for drinking purposes without any water treatment.

| Table 2 should be placed here |

However, when we observed the individual chemical parameters from Table 1, it is apparent that all chemical parameters such as Ca$^{2+}$, Mg$^{2+}$, Na$^+$, K$^+$, HCO$_3^-$, Cl$^-$ and SO$_4^{2-}$, (except NO$_3^-$ and F$^-$ ions) are more than the highest desirable limits of 75, 30, 200, 12, 300, 250, and 200 mg/L, respectively, in less than 15% of the groundwater samples. But in the case of NO$_3^-$ and F$^-$ ions, they are above the safe limits of 45 mg/L and 1.5 mg/L in 34% and
25% of the total groundwater samples, respectively (BIS 2012; WHO 2012). Further, these two ions are the most common toxicities than the rest of the chemical parameters in drinking water because of their potential to cause non-carcinogenic risk (USEPA 2014).

Since agriculture is one of the main practices in the present study region, a considerable portion of applied agrochemicals (nitrogen fertilizers) are expected to penetrate the soils/rocks, in addition to the influence of household waste water, septic tank leakage, and animal excretion, and reach the aquifer body through the recharge water. This is likely to increase the NO$_3^-$ levels in the groundwater. However, NO$_3^-$ levels less than 45 mg/L were observed in 54.69% of the total study region (Fig. 2a). They were mainly confined to the northern part, and, however, were also found in very limited isolated pockets in the southern part, where the agricultural activities are comparatively less. Next, higher NO$_3^-$ levels (45 to 100 mg/L and > 100 mg/L) were mainly observed in the southern part (46.31%) of the total study region, where agricultural activities are more. Therefore, the influences of the utilization of nitrogen fertilizers, irrigation-return-flows, and animal wastes are expected on the aquifer system. This hypothesis is further substantially supported by the increase in NO$_3^-$ (9.38 to 186.12 mg/L) along with TDS (212.33 to 480 mg/L), Na$^+$ (39.82 to 89.18 mg/L) and Cl$^-$ (112.70 to 178.54 mg/L), and also by the higher loading of NO$_3^-$ (0.813) along with TDS (0.851), Na$^+$ (0.660) and Cl$^-$ (0.768; Tables 3 and 4). These variables are the most common indicators of human-induced pollution (Subba Rao et al. 2017).

Figure 2 should be placed here

Tables 3 and 4 should be placed here

The higher alkalinity (pH and HCO$_3^-$) with Na$^+$ activates the leaching of fluoride minerals occurring in the basement rocks and thus increases the higher F$^-$ content in the
groundwater system (Subba Rao et al. 2016, 2020a). Apart from this, the usage of phosphate fertilizers may also lead to an increase in the concentration of F⁻ in the groundwater (Subba Rao et al. 2021a). The spatial distribution of concentration of F⁻ ion in the groundwater of the present study region showed that the F⁻ level of less than 0.6 mg/L was observed mainly in the northern part and also in very limited isolated patches in the southern part, which covers an area of 20.36% of the total study region (Fig. 2b). A safe limit of F⁻ (0.6 to 1.5 mg/L) was found in the study region (58.47%). The next higher F⁻ content (> 1.5 mg/L was found as isolated pockets (21.17%) from the entire study region irrespective of the agricultural activities. As demonstrated in Tables 3 and 4, the concentration of F⁻ (0.40 to 2.42 mg/L) shows an increase with an increase in pH (7.02 to 7.30), Na⁺ (22.24 to 83.83 mg/L), and HCO₃⁻ (863.98 to 1099.78 mg/L), and the higher loading of F⁻ (0.732) also shows the higher loadings of pH (0.519), Na⁺ (0.552) and HCO₃⁻ (0.555), which obviously indicates the spatial distribution of F⁻ content. This could be due to the influence of weathering and dissolution of fluoride minerals occurring in the host rocks rather than that of phosphate fertilizers on the groundwater system.

According to WHO (2011), excessive NO₃⁻ levels in drinking water affect the health of children and adults, whereas high F⁻ levels provide a health risk to people of all ages. For computation of THHHI, the mean body weight is 65 kg for adults and 18.7 kg for children, and the mean exposure time is 24,236 days for adults and 4,380 days for children are taken into consideration (ICMR 2009; USEPA 2014). From this point of view, we have decided to evaluate the health risks of adults and children with respect to NO₃⁻ and F⁻ pollutants in the present study.
Human health risk with respect to nitrate and fluoride

The values of the human health hazard quotient of nitrate (HHHQ$_{\text{NO}_3}$) varied from 0.01 to 19.08 for adults and from 0.01 to 29.34 for children, with a mean of 1.83 and 2.82, respectively (Table 2). Out of 100 groundwater samples, 39% and 47% of the samples showed HHHQ$_{\text{NO}_3}$ more than 1.0 with respect to adults (4.26) and children (5.68), respectively, causing a health risk. The human health hazard quotient of fluoride (HHHQ$_{\text{F}^-}$) was between 0.19 and 4.70 for adults and between 0.29 and 7.23 for children, with a mean of 0.99 and 1.52, in which 36% and 58% of the groundwater samples had HHHQ$_{\text{F}^-}$ more than 1.0 with respect to adults (1.78) and children (2.14), respectively, causing a health hazard. It is also significantly observed from Table 2 that children are more threatening to health risks due to NO$_3^-$ rather than F$^-$ compared to adults. According to WHO (2011) and Subba Rao et al. (2017, 2019b), the groundwater could have been more contaminated with NO$_3^-$ due to the influence of anthropogenic sources (household wastes, septic tanks leakage, irrigation-return-flows, nitrogen fertilizers, animal wastes, etc) compared to the source of F$^-$. 

Total human health implications

In order to evaluate the total implications of NO$_3^-$ and F$^-$ ions on human health, the total human health hazard index (THHHI) was computed, following Eqs. 4 to 6. The values of THHHI varied from 0.27 to 20.4 for adults and 0.26 to 19.6 for children (Table 2). According to the USEPA (2014), the recommended safe limit of THHHI for the non-cancer-causing hazard is 1.0 in drinking water. In the present study region, the THHHI was more than 1.0 in 63% and 73% of the total groundwater samples with respect to adults and children, respectively. It is also further observed that the mean THHHI is 2.82 for adults and 4.34 for children. It obviously suggests that the danger is a threat to children rather than to adults. This
appears to be caused not only by the consumption of more contaminated groundwater with a higher concentration of NO$_3^-$ than that of F$^-$, but also by the smaller weight of the body and the lesser exposure time of children compared to adults (USEPA 2014).

For the identification of the intensity of human health risk zones, the spatial distribution of THHHI for adults and children was demonstrated in Fig. 3. The zones with less than 1.0 and more than 1.0 of THHHI were covered by 33.27% and 66.73% for adults and 28.25% and 71.75% for children of the total study region, respectively. The first zone was at safe limit (average THHHI: 0.54 for adults and 0.66 for children) with respect to non-cancer health risk, while the other one was at the unsafe limit (average THHHI: 4.15 for adults and 5.69 for children) for non-cancer health problems (Table 3). Thus, the intensity of the human health risk zone appears to be 1.37 times higher in children than in adults. These two zones have obviously divided the region into the northern safe health zone and the southern unsafe health zone, respectively, depending upon the intensity of agricultural activities.

The human health risk zone of the southern part appears to be caused by the influence of the unlimited application of nitrogen fertilizers compared to that of fluoride minerals and phosphate compost. This fact is established by observing the spatial distribution of NO$_3^-$ and F$^-$ contents (Fig. 2), where the F$^-$ ion shows mostly the safe health zone compared to the NO$_3^-$ associated with non-cancer risk. Li et al. (2019a) from China and Subba Rao et al. (2021a) from India stated that the main NO$_3^-$ content is a result of the influence of agricultural fertilizers on human-induced sources in the groundwater. Furthermore, because of the intensive agricultural practices in the southern part, it is also
important to consider the influences of return-irrigation-flows and animal wastes as a source
of higher NO$_3^-$ in the groundwater (Marghade et al., 2015). Therefore, the study helps to
decipher the specific sites of the human health risk zones (THHHI > 1.0) in the case of
children (71.75%) and adults (66.73%; Fig. 3) for taking remedial measures for sustainable
health conditions.

**Remedial measures**

The intensity of susceptible zones for the purpose of protecting and managing groundwater
resources from pollution is essential for making a healthy society for long-term growth. The
present study area suggests some useful and easily applicable remedial measures, such as (a)
supply of safe drinking water to maintain normal health, (b) arrangements of denitrification
and defluoridation tools to reduce NO$_3^-$ and F$^-$ content, (c) implementation of rainwater
harvesting techniques to dilute the concentrations of NO$_3^-$ and F$^-$ ions, (d) providing
hygienic-sanitary facilities for clean surrounding residential locations, and (e) utilization of
limited chemical fertilizers, according to soil conditions, to arrest contamination activities.

**Conclusions**

The following conclusions were summarized, after observing the chemical quality of
groundwater and associated health problems in respect of NO$_3^-$ and F$^-$ ions in age groups of
adults and children, using the total water quality index (TWQI) and total human health hazard
index (THHHI), from a rural region of Telangana State of India:

- The TWQI suggested that the chemical quality of groundwater is suitable for drinking
  purposes. However, the NO$_3^-$ varied from 0.4 to 585.20 mg/L and F$^-$ from 0.22 to 5.41
  mg/L and exceeded the consumption water quality limits of 45 mg/L and 1.5 mg/L in
34% and 25% of the total groundwater samples, respectively. Nitrate fertilizers are the main source of NO$_3^-$ content and the fluoride minerals as the prime source of F$^-$ content in the groundwater. They are further supported by principal component analysis.

- According to the THHHI, 63% and 73% of the total groundwater samples associated with adults and children were more than the safe limit of 1.0 with respect to NO$_3^-$ and F$^-$, respectively. The intensity of human health risk zones of THHHI was 1.37 times more in children (5.69) than in children (4.15), covering an area of 71.75% and 66.73%, respectively.

- The present study recommended effective management measures not only for the protection of groundwater resources from pollution activities but also for improving the health conditions of the locals.

Declarations:

Ethical Approval: Not applicable to this manuscript

Consent to Participate: Not applicable

Consent for Publication: Not applicable

Authors’ contribution:

Sakram Gugulothu: Supervision, Methodology, and original draft preparation.
Nandipati Subbarao: Writing, Reviewing
Rashmirekha Das: Literature collection, Editing
Laxman Kumar Duvva: Literature collection, draft preparation
Ratnakar Dhakate: Statistical analysis, Literature collection

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Captions to Figures

Fig. 1. Map showing the location of the rural region of the present study
Fig. 2. Map showing the spatial distribution of (a) NO$_3^-$ and (b) F$^-$ ions.
Fig. 3. Map showing the spatial distribution of total human health hazard index (THHHI) with respect to (a) adults and (b) children.
Table 1: Statistical summary of chemical composition of groundwater

| Chemical parameters | Minimum | Maximum | Mean | BIS (2012) | Samples exceeding the drinking water quality limits | Analytical methods | Reference |
|---------------------|---------|---------|------|------------|----------------------------------------------------|-------------------|----------|
| pH                  | 6.30    | 8.90    | 7.14 | 6.5 - 8.5  | 3 17, 26, and 79                                   | pH/EC/TDS meter   | APHA (2012) |
| TDS (mg/L)          | 56      | 1024    | 291.0| 500        | 15 1 to 5, 14, 16, 19, 20, 22, 29, 41, 43, 54, and 55. | EC x 0.645        | Hem 1991  |
| Ca²⁺ (mg/L)         | 8.02    | 152.30  | 49.60| 75         | 14 41, 43, 49, 51, 53 to 55, 63, 64, 66, 68, 70, 90, and 98. | EDTA Titrimetric | APHA (2012) |
| Mg²⁺ (mg/L)         | 2.43    | 92.42   | 23.53| 50         | 6 3, 55, 91, 94, 97, and 99.                        | Calculation (TH-Ca²⁺) | APHA (2012) |
| Na⁺ (mg/L)          | 3       | 416     | 54.13| 200        | 1 43                                                | Flame photometric | APHA (2012) |
| K⁺ (mg/L)           | 1       | 118     | 6.20 | 12         | 10 1, 16, 20, 29, 35, 45, 53, 88, 89, and 96       | Flame photometric | APHA (2012) |
| HCO₃⁻ (mg/L)        | 146.40  | 2538    | 1014.31| 300       | 99 1 to 29, and 31 to 100                          | Titrimetric       | APHA (2012) |
| Cl⁻ (mg/L)          | 17.73   | 425.40  | 127.52| 250        | 10 16, 41, 43, 54, 55, 63, 66, 70, 91, and 99.     | AgNO₃ titrimetric | APHA (2012) |
| SO₄²⁻ (mg/L)        | 30      | 166     | 97.90| 200        | -                                                  | UV Visible spectrophotometer | APHA (2012) |
| NO₃⁻ (mg/L)         | 0.04    | 585.20  | 56.27| 45         | 34 2 to 6, 8, 9 to 11, 13, 14, 16, 18, 20, 22, 24, 25, 30, 33, 41 to 44, 46, 47, 49, 51 to 55, 63, 66, and 67. | UV Visible spectrophotometer | APHA (2012) |
| F⁻ (mg/L)           | 0.22    | 5.41    | 1.13 | 1.5        | 25 3, 7, 19 to 25, 28, 34, 36, 38, 39, 40, 42, 43, 50, 56, 59, 61, 64, and 72 to 74. | Ion selective electrode | APHA (2012) |
### Table 2: Computed values of total water quality index (TWQI), human health hazard quotient (HHHQ) and total human health hazard index (THHHI) (Bold letters denote exceeding the recommended limit)

| Sample No. | TWQI | HHHQ<sub>NO</sub> | HHHHQ<sub>F</sub> | THHHI<sub>NO</sub>|<sub>F</sub> |
|------------|------|-------------------|-------------------|-------------------|----------------|
| Value | Classification | Adult | Children | Adult | Children | Adult | Children |
| 1 | 62 | Good | 0.81 | 1.25 | 0.87 | 1.34 | 1.68 | 2.59 |
| 2 | 53 | Good | 8.39 | 12.90 | 0.78 | 1.20 | 9.18 | 14.11 |
| 3 | 89 | Good | 4.92 | 7.57 | 1.39 | 2.14 | 6.31 | 9.71 |
| 4 | 66 | Good | 4.61 | 7.08 | 0.26 | 0.40 | 4.87 | 7.48 |
| 5 | 60 | Good | 5.85 | 9.00 | 0.35 | 0.53 | 6.20 | 9.53 |
| 6 | 41 | Excellent | 5.35 | 8.23 | 0.61 | 0.94 | 5.96 | 9.16 |
| 7 | 58 | Good | 0.06 | 0.10 | 3.04 | 4.68 | 3.11 | 4.78 |
| 8 | 39 | Excellent | 2.35 | 3.62 | 0.43 | 0.67 | 2.79 | 4.29 |
| 9 | 33 | Excellent | 3.87 | 5.96 | 0.26 | 0.40 | 4.13 | 6.36 |
| 10 | 37 | Excellent | 3.39 | 5.21 | 0.26 | 0.40 | 3.65 | 5.61 |
| 11 | 47 | Excellent | 1.65 | 2.54 | 0.43 | 0.67 | 2.08 | 3.21 |
| 12 | 34 | Excellent | 1.33 | 2.05 | 0.35 | 0.53 | 1.68 | 2.59 |
| 13 | 48 | Excellent | 4.68 | 7.19 | 0.35 | 0.53 | 5.03 | 7.73 |
| 14 | 50 | Excellent | 2.70 | 4.15 | 0.70 | 1.07 | 3.39 | 5.22 |
| 15 | 42 | Excellent | 0.66 | 1.02 | 0.78 | 1.20 | 1.45 | 2.22 |
| 16 | 67 | Good | 19.08 | 29.34 | 1.04 | 1.60 | 20.13 | 30.94 |
| 17 | 62 | Good | 0.12 | 0.18 | 1.04 | 1.60 | 1.16 | 1.78 |
| 18 | 63 | Good | 7.40 | 11.38 | 1.13 | 1.74 | 8.53 | 13.12 |
| 19 | 73 | Good | 0.20 | 0.30 | 1.39 | 2.14 | 1.59 | 2.44 |
| 20 | 70 | Good | 2.88 | 4.43 | 2.00 | 3.07 | 4.88 | 7.51 |
| 21 | 63 | Good | 0.55 | 0.85 | 1.30 | 2.01 | 1.86 | 2.86 |
| 22 | 69 | Good | 3.44 | 5.29 | 2.35 | 3.61 | 5.79 | 8.90 |
| 23 | 80 | Good | 0.95 | 1.46 | 3.57 | 5.48 | 4.51 | 6.94 |
| 24 | 62 | Good | 1.94 | 2.98 | 2.26 | 3.48 | 4.20 | 6.45 |
| 25 | 55 | Good | 2.91 | 4.48 | 2.26 | 3.48 | 5.17 | 7.95 |
| 26 | 50 | Excellent | 0.14 | 0.21 | 0.70 | 1.07 | 0.83 | 1.28 |
| 27 | 40 | Excellent | 0.04 | 0.06 | 0.78 | 1.20 | 0.82 | 1.26 |
| 28 | 63 | Good | 0.07 | 0.11 | 1.65 | 2.54 | 1.73 | 2.65 |
| 29 | 55 | Good | 0.12 | 0.18 | 0.78 | 1.20 | 0.90 | 1.39 |
| 30 | 33 | Excellent | 3.33 | 5.12 | 0.58 | 0.90 | 3.91 | 6.01 |
| 31 | 47 | Excellent | 0.89 | 1.37 | 0.72 | 1.10 | 1.61 | 2.47 |
| 32 | 55 | Good | 0.18 | 0.27 | 1.26 | 1.94 | 1.44 | 2.21 |
| 33 | 58 | Good | 4.16 | 6.40 | 1.07 | 1.64 | 5.23 | 8.04 |
| 34 | 53 | Good | 1.08 | 1.66 | 1.48 | 2.27 | 2.56 | 3.93 |
| 35 | 42 | Excellent | 0.15 | 0.23 | 0.83 | 1.27 | 0.98 | 1.50 |
| 36 | 50 | Excellent | 0.86 | 1.32 | 1.43 | 2.21 | 2.29 | 3.53 |
| 37 | 42 | Excellent | 0.32 | 0.49 | 0.28 | 0.43 | 0.59 | 0.91 |
| 38 | 58 | Good | 1.14 | 1.76 | 1.37 | 2.11 | 2.52 | 3.87 |
| 39 | 59 | Good | 0.76 | 1.18 | 1.63 | 2.51 | 2.40 | 3.69 |
| 40 | 70 | Good | 0.24 | 0.37 | 1.63 | 2.50 | 1.87 | 2.87 |
| 41 | 74 | Good | 6.76 | 10.39 | 0.97 | 1.48 | 7.72 | 11.87 |
|   |   | Good | 1.81 | 2.78 | 1.90 | 2.91 | 3.70 | 5.69 |
|---|---|------|------|------|------|------|------|------|
| 42| 73| Good | 6.18 | 9.51 | 1.89 | 2.90 | 8.07 | 12.41|
| 43| 91| Good | 4.25 | 6.53 | 0.66 | 1.02 | 4.91 | 7.55 |
| 44| 54| Good | 0.28 | 0.43 | 0.71 | 1.10 | 0.99 | 1.53 |
| 45| 60| Good | 1.88 | 2.89 | 0.79 | 1.22 | 2.67 | 4.11 |
| 46| 66| Good | 2.96 | 4.54 | 0.81 | 1.24 | 3.76 | 5.79 |
| 47| 60| Good | 0.85 | 1.31 | 0.95 | 1.46 | 1.80 | 2.76 |
| 48| 60| Good | 3.20 | 4.92 | 1.27 | 1.95 | 4.47 | 6.87 |
| 49| 72| Good | 0.36 | 0.55 | 1.41 | 2.17 | 1.76 | 2.71 |
| 50| 70| Good | 2.27 | 3.49 | 1.03 | 1.59 | 3.30 | 5.08 |
| 51| 54| Good | 3.23 | 4.96 | 0.75 | 1.15 | 3.98 | 6.11 |
| 52| 51| Good | 4.86 | 7.48 | 0.57 | 0.88 | 5.44 | 8.36 |
| 53| 67| Good | 7.36 | 11.32| 0.50 | 0.76 | 7.86 | 12.08|
| 54| 78| Good | 11.79| 18.13| 0.93 | 1.43 | 12.72| 19.56|
| 55| 85| Good | 1.07 | 1.65 | 1.99 | 3.06 | 3.06 | 4.71 |
| 56| 67| Good | 0.98 | 1.50 | 0.80 | 1.23 | 1.78 | 2.73 |
| 57| 44| Excellent | 0.62 | 0.95 | 1.05 | 1.62 | 1.67 | 2.57 |
| 58| 42| Excellent | 1.30 | 1.99 | 2.73 | 4.20 | 4.03 | 6.19 |
| 59| 61| Good | 0.42 | 0.65 | 0.57 | 0.88 | 1.00 | 1.54 |
| 60| 61| Good | 0.27 | 0.42 | 2.41 | 3.70 | 2.68 | 4.12 |
| 61| 67| Good | 0.13 | 0.20 | 1.23 | 1.90 | 1.37 | 2.10 |
| 62| 70| Good | 3.57 | 5.49 | 1.13 | 1.74 | 4.70 | 7.23 |
| 63| 63| Good | 0.36 | 0.55 | 1.55 | 2.38 | 1.91 | 2.93 |
| 64| 57| Good | 1.46 | 2.25 | 1.10 | 1.68 | 2.56 | 3.93 |
| 65| 63| Good | 6.34 | 9.75 | 0.85 | 1.31 | 7.19 | 11.06|
| 66| 52| Good | 3.92 | 6.02 | 0.89 | 1.36 | 4.80 | 7.39 |
| 67| 36| Excellent | 0.15 | 0.23 | 0.51 | 0.79 | 0.66 | 1.02 |
| 68| 45| Excellent | 0.06 | 0.10 | 0.58 | 0.90 | 0.65 | 1.00 |
| 69| 43| Excellent | 0.19 | 0.30 | 0.33 | 0.51 | 0.52 | 0.81 |
| 70| 46| Excellent | 0.01 | 0.01 | 0.81 | 1.24 | 0.82 | 1.26 |
| 71| 56| Good | 0.02 | 0.03 | 1.33 | 2.05 | 1.35 | 2.07 |
| 72| 72| Good | 0.01 | 0.01 | 3.13 | 4.81 | 3.14 | 4.82 |
| 73| 77| Good | 0.01 | 0.01 | 4.70 | 7.23 | 4.71 | 7.24 |
| 74| 36| Excellent | 0.01 | 0.02 | 0.57 | 0.88 | 0.58 | 0.90 |
| 75| 32| Excellent | 0.05 | 0.07 | 0.34 | 0.52 | 0.38 | 0.59 |
| 76| 40| Excellent | 0.02 | 0.04 | 0.35 | 0.53 | 0.37 | 0.57 |
| 77| 42| Excellent | 0.02 | 0.04 | 0.28 | 0.43 | 0.30 | 0.47 |
| 78| 41| Excellent | 0.01 | 0.01 | 0.19 | 0.29 | 0.20 | 0.30 |
| 79| 38| Excellent | 0.01 | 0.01 | 0.33 | 0.51 | 0.34 | 0.52 |
| 80| 47| Excellent | 0.05 | 0.07 | 0.50 | 0.78 | 0.55 | 0.85 |
| 81| 37| Excellent | 0.05 | 0.08 | 0.46 | 0.71 | 0.51 | 0.79 |
| 82| 45| Excellent | 0.05 | 0.07 | 0.75 | 1.15 | 0.79 | 1.22 |
| 83| 30| Excellent | 0.05 | 0.08 | 0.22 | 0.33 | 0.27 | 0.41 |
| 84| 32| Excellent | 0.02 | 0.02 | 0.33 | 0.51 | 0.35 | 0.53 |
| 85| 42| Excellent | 0.01 | 0.01 | 0.39 | 0.60 | 0.40 | 0.61 |
| 86| 38| Excellent | 0.04 | 0.06 | 0.38 | 0.59 | 0.42 | 0.65 |
| 87| 36| Excellent | 0.02 | 0.03 | 0.49 | 0.75 | 0.51 | 0.78 |
| 88| 38| Excellent | 0.00 | 0.00 | 0.59 | 0.91 | 0.59 | 0.91 |
| 89| 33| Excellent | 0.02 | 0.03 | 0.22 | 0.33 | 0.24 | 0.36 |
|    |    |     |    |    |    |    |
|----|----|-----|----|----|----|----|
| 91 | 47 | Excellent | 0.05 | 0.08 | 0.29 | 0.44 | 0.34 | 0.52 |
| 92 | 34 | Excellent | 0.04 | 0.06 | 0.30 | 0.47 | 0.34 | 0.52 |
| 93 | 32 | Excellent | 0.01 | 0.02 | 0.33 | 0.51 | 0.34 | 0.53 |
| 94 | 38 | Excellent | 0.03 | 0.05 | 0.45 | 0.70 | 0.48 | 0.74 |
| 95 | 39 | Excellent | 0.01 | 0.01 | 0.70 | 1.07 | 0.71 | 1.08 |
| 96 | 38 | Excellent | 0.05 | 0.08 | 0.58 | 0.90 | 0.63 | 0.97 |
| 97 | 32 | Excellent | 0.09 | 0.14 | 0.34 | 0.52 | 0.43 | 0.66 |
| 98 | 43 | Excellent | 0.02 | 0.03 | 0.33 | 0.51 | 0.35 | 0.54 |
| 99 | 43 | Excellent | 0.14 | 0.21 | 0.32 | 0.49 | 0.46 | 0.71 |
| 100| 40 | Excellent | 0.12 | 0.19 | 0.38 | 0.59 | 0.50 | 0.78 |
| Mean | | | | | | | | |
| 52.72 | | | | | | | | |
| <1.0 | | | | | | | | |
| >1.0 | | | | | | | | |
Table 3. Mean values of pH, TDS, Na⁺, HCO₃⁻, and Cl⁻ based on the classification of NO₃⁻ and F⁻

| NO₃⁻ (mg/L) | TDS (mg/L) | Na⁺ (mg/L) | Cl⁻ (mg/L) | Percent of samples |
|-------------|------------|------------|------------|-------------------|
| Range       | Mean       |            |            |                   |
| <45         | 9.38       | 212.13     | 39.82      | 112.70            | 66                     |
| 45 to 100   | 74.56      | 378.67     | 68.58      | 115.51            | 12                     |
| >100        | 186.12     | 480.00     | 89.18      | 178.54            | 22                     |

| F⁻ (mg/L) | pH  | Na⁺ (mg/L) | HCO₃⁻ (mg/L) | Percent of samples |
|-----------|-----|------------|--------------|-------------------|
| Range     | Mean|            |              |                   |
| <0.6      | 0.40| 7.02       | 22.24        | 863.98            | 33                     |
| 0.6 to 1.5| 0.98| 7.11       | 62.02        | 1030.62           | 43                     |
| >1.5      | 2.42| 7.30       | 83.83        | 1099.78           | 24                     |
Table 4. Principal component analysis

| Chemical parameters | Principal Component Analysis |   |   |   |
|---------------------|------------------------------|---|---|---|
|                     | 1   | 2   | 3   | 4   |
| pH                  | 0.302 | **0.519** | 0.316 | 0.201 |
| TDS                 | **0.851** | 0.055 | 0.317 | 0.094 |
| Ca$^{2+}$           | 0.439 | -0.125 | -0.585 | -0.026 |
| Mg$^{2+}$           | 0.364 | -0.560 | 0.043 | **0.543** |
| Na$^+$              | **0.660** | **0.552** | -0.010 | 0.130 |
| K$^+$               | 0.469 | 0.030 | 0.404 | -0.634 |
| HCO$_3^-$           | 0.224 | **0.555** | -0.449 | 0.339 |
| Cl$^-$              | **0.768** | -0.267 | -0.023 | -0.113 |
| SO$_4^{2-}$         | -0.195 | -0.150 | **0.654** | 0.430 |
| NO$_3^-$            | **0.813** | 0.043 | 0.166 | -0.113 |
| F$^-$               | -0.033 | **0.732** | 0.176 | 0.107 |
| Eigenvalue          | 3.14 | 1.75 | 1.40 | 1.11 |
| % Total variance    | 28.50 | 15.94 | 12.69 | 10.07 |
| Cumulative %        | 28.50 | 44.44 | 57.13 | 67.20 |