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ORIGINAL PAPER

Spatial distribution of quality of groundwater and probabilistic non-carcinogenic risk from a rural dry climatic region of South India

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Abstract Having safe drinking water is a fundamental human right, which affects directly the human health. In view of this, an effort has been made for understanding the spatial distribution of quality of groundwater in a rural dry climatic region of Andhra Pradesh, South India, and associated health risks with respect to pollutants of NO_3^- and F^-, which cause the potential production of non-carcinogenic risk, using entropy-weighted water quality index (EWWQI) and total chronic hazard index (TCHI), where the population rely on the groundwater resource for drinking purpose. Groundwater quality observed from the present study region has an alkaline character with brackish type. The concentrations of K^+, HCO_3^-, TDS, Na^+, NO_3^-, F^-, Mg^{2+} and Cl^- come under the non-permissible limits in 100%, 100%, 96.67%, 90%, 73.33%, 46.67%, 13.33% and 6.67% of the groundwater samples, which deteriorate the groundwater quality, causing the health disorders. The overall groundwater quality computed, using EWWQI, ranges from 53.64 to 216.59 (122.22), which classifies the region spatially into 55%, 10% and 35% due to influences of the geogenic and anthropogenic pollutants, which are the respective medium, poor and very poor groundwater quality types prescribed for potable water. According to the TCHI evaluated with respect to pollutants of NO_3^- and F^-, the values of TCHI for men (1.194 to 4030), women (1.411 to 4.763) and children (1.614 to 5.449) are more than its acceptable limit of one. So, the health risk of non-carcinogenic is spatially in the decreasing order of children > women > men, depending upon their sensitiveness to pollutants and also their body weights. Further, the spatial distributions of both TCH1 and EWWQI are more or less similar, following the pollution activities, which help for establishment of the fact to recognize the intensity of various vulnerable zones. Therefore, the present study suggests the suitable environmental safety measures to control the NO_3^-- and F^--contaminated drinking water and subsequently to increase the health conditions.

Keywords Groundwater quality · Entropy-weighted water quality index · Total chronic health index · Rural region · Andhra Pradesh · South India

Introduction

Groundwater is a significant natural resource in dry climatic regions of the world for the survival of life (Li et al. 2018a; Wang et al. 2019). The inferior quality of potable water affects the human health and sustainable development of the society (Li and Wu 2019a, b). Globally, about two billion people depend upon the

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groundwater resource as a primary source for drinking purpose and approximately half of the water utilized for irrigation comes from the subsurface (WEF 2019). India is the highest consumption of groundwater (25%), which is followed by USA (11%) and China (11%; IPS, 2020). In India, about 85% and 60% of the water supply for drinking and agriculture purposes rely on the subsurface water resources, respectively (Sishodia et al. 2016). On the other hand, the underground water can be contaminated naturally due to interactions of water with toxic elements present in the soil cover and rocks as well as artificially due to poor drainage conditions, irrigation return flows and application of huge agrochemicals (Alaya et al. 2014; Abd El-Aziz 2017; Singh and Kumar 2017; Subba Rao et al. 2013a, b; Subba Rao, 2017a; b, 2019a; Abboud 2018; Babanezhad et al. 2018; Ghahremanzadeh et al. 2018; Deepali et al. 2019; Subba Rao and Chaudhary 2019; Wu et al. 2019a, b). Both of these sources deteriorate the groundwater quality, causing the threat to human health.

Recently, extensive work has been emphasized on evaluation of chemical quality of groundwater and associated health problems with respect to NO_3^- and F^-, which are considered the most common pollutants as well as the most toxicities (Li et al. 2014; Tahernezhad et al. 2016; Qasemi et al. 2018; Subba Rao et al. 2020a). For instance, Wu et al. (2015) stated that about 200 million people in 28 countries suffer from the drinking water with the higher concentration of F^-. Craig et al. (2015) reported that the contaminated groundwater with F^- is observed in the parts of China, South America, Nigeria, Africa, Pakistan, Iran, Kenya and Sri Lanka. Li et al. (2016) studied the quality of groundwater and its health risks caused mainly by the pollutants of NO_3^- and F^- ions in the groundwater in a dry climatic zone of Northwest China and found that the pollutants originate from the agricultural and industrial sectors as well as from the lithological (geogenic) origin. They also observed that the males are not as suffered as children and females from the health hazards. Chen et al. (2017) evaluated the contamination of NO_3^- and F^- in the drinking water and health risk conditions from the rural population of a semiarid zone of Northwest China caused by influences of human activities and fluorite in the underground water and found that the children are the most affected groups compared with the adult groups (men and women). Li et al. (2017) reported that the NO_3^-, which is the most common pollutant in the subsurface water, deteriorates the groundwater quality in the agricultural regions. Rezael et al. (2018) estimated the health hazards caused by F^- and NO_3^- in the drinking groundwater in Sanandaj, Kurdistan County, Iran, and found that the higher F^- and NO_3^- contents are observed from the village groundwater than from the urban underground water. Further, they reported that the health risk is more in children compared with men and women. He and Wu (2019) and He et al. (2019) stated that the household wastewaters and septic tank leakages as well as the soils containing the nitrogen and animal wastes are the sources of NO_3^- in the groundwater. Karunanidhi et al. (2019) assessed the impact of groundwater contamination caused by F^--containing minerals present in the country rocks of hornblende–biotite gneiss and granites as well as by leaching of waste disposals and uncontrolled usage of agrochemicals from the river basin of Shanmuganadhi, Tamil Nadu, India, on human risks with respect to pollutants of NO_3^- and F^- ions and found that the threat of non-carcinogenic risk is higher in children than in Men and Women Subba Rao et al. (2019b, 2020b) observed the decline of quality of groundwater due to weathering, dissolution, evaporation and ion exchange processes through the interaction of groundwater with the granites and gneissic granites with pegmatite veins under dry climate and also influences of poor drainage conditions, irrigation return flows and agrochemicals from a part of Telangana, South India, and found that the children are more affected by health hazards compared to men and women with respect to NO_3^- and F^-, because of their small body weights. Ding et al. (2020) evaluated the potential risk of subsurface water caused by NO_3^- and F^- in Ordos basin, China, and observed that the children suffer more from the health risk than adults. Kaur et al. (2020) assessed the influence of human interferences on the groundwater system associated with the pollutants of NO_3^- and F^- in Panipat, Haryana, India, and subsequently its effect on health of exposed population and found that the children suffer from the non-carcinogenic risk than the men and women. Shukla and Saxena (2020) studied the chemical quality of underground water and health hazards in parts of Raebareli District, Uttar Pradesh, North India, and found that the elevated concentration of NO_3^- is due to influence of the application of heavy chemical fertilizers used for agricultural purpose, while the water and rock interactions associated with the F^--bearing minerals are the main contributor for the higher concentration of F^- in the underground water. They also further observed that the non-carcinogenic health hazards are more in children compared with adults.

Geochemical parameters of groundwater, such as high alkalinity (pH and HCO_3^-), low Ca^{2+} and high Na^+, support the enrichment of F^- in the underground water (Subba Rao 2003, 2011, 2017a; Subba Rao et al. 2016, 2020a; Li et al. 2019a). Naturally, NO_3^- exists in soils caused by microbial conversion of organic matter into NO_3^-. Wastewater, landfill leachate, animal excreta and agrochemicals are also the sources of NO_3^- in soils, which subsequently pollute the subsurface water by the recharge water (Chen et al. 2017; Subba Rao et al. 2017a; Zhang et al. 2018).

From the literature, it can be said briefly about the sources of NO_3^-- and F^--contaminated groundwater and their human health risk. Agricultural practices and subsequent application of fertilizers along with other anthropogenic activities like household wastewaters, septic tank leakages, drainage channels, etc., are the main sources behind the elevated levels of NO_3^- in the groundwater. The F^--containing minerals present in the rocks of granites and gneissic granites, etc., are the prime source for the higher concentration of F^- in the subsurface water, apart from the influence of agrochemicals used for agricultural purpose. They deteriorate the quality of groundwater, causing more health hazards on children than on adults (men and women).

The present study region located in a part of Prakasam District, Andhra Pradesh, South India, belongs to rural villages (Fig. 1). The economy of the villages depends upon the agricultural practice. Further, the region is underlain by fluoride accessory minerals in the country rocks so that the present investigation can be significant to the scientific community and also useful in making an efficient strategic water quality management measures. The residents living in the region rely on the underground water for various purposes including drinking, domestic and agricultural needs. However, the previous research has mainly been focused on general groundwater quality and geochemistry of fluoride-bearing groundwater (Subba Rao 2017a, 2018), but not on comprehensive understanding of the chemical quality of groundwater and associated impact on human health in detail. Hence, the present work has been undertaken. The main focus of this study is, thus, on evaluation of (a) the spatial distribution of the overall groundwater quality suitability for drinking use, using entropy-weighted water quality index (EWWQI), and (b) the probabilistic non-carcinogenic health risk assessment, using total chronic hazard index (TCHI), for the public, who are consuming the highly polluted groundwater as drinking water. The outcome of this study helps for establishment of the fact to recognize the intensity of various vulnerable zones at a specific site for implementing the efficient strategies to improve the groundwater quality as well as to increase the human health.

Study area

Location and climate

The present study region is a part of Prakasam district, Andhra Pradesh, South India (Fig. 1), covering an area about 325 km^2. The region comes under the semiarid climatic zone with an annual average temperature of 28 °C in winter to 39 °C in summer. The annual rainfall is 910 mm. Maximum rainfall (69%) receives from the southwest monsoon. The northeast monsoon contributes 29% of the total rainfall. The remaining seasons (winter and summer) receive the rest of the rainfall (12%). The river *Gundlakamma* drains the region, showing a sub-dendritic pattern.

Geology

The present study region shows slope toward the Bay of Bengal. Important soil type is silty clay soils. The soil cover contains the calcium carbonate concretions formed due to dry climate that occurs in the soil cover. Geologically, the present study region is occupied by Precambrian formations, Lower Cretaceous formations and Quaternary Formations (Fig. 2). The Precambrian formations contain the Charnockite Super-group and Unclassified Metamorphic Super-group. The first Super-group contains pyroxene granulites, while the second Super-group comprises the migmatized–quartzo-feldspathic–gneiss/schist and amphibolites. They are also associated with intrusive bodies comprising gabbros/norites. The rocks have the mineral assemblage of quartz, feldspars (plagioclase and orthoclase), amphibolite (hornblende), pyroxene

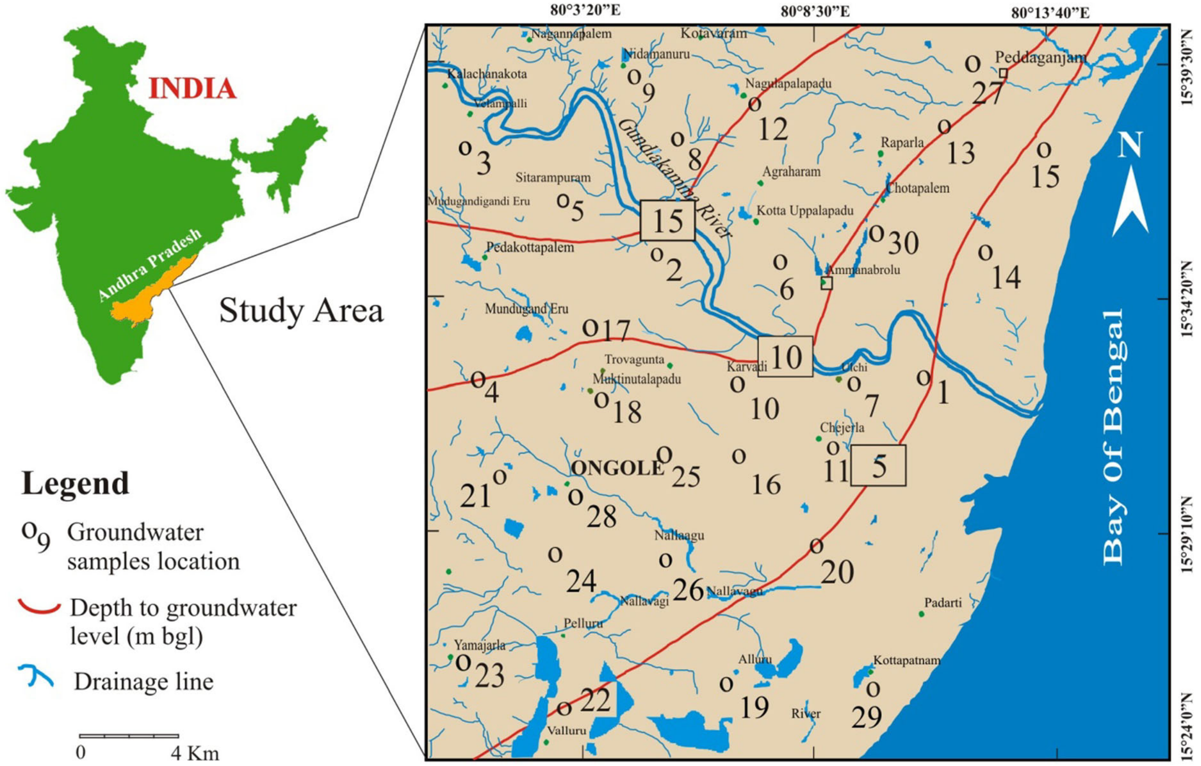

Fig. 1 Location of the study region in Prakasam District, Andhra Pradesh, South India

(hypersthene), sillimanite, garnet, apatite and biotite. The country rocks have a strike direction of NE–SW to NW–SE with moderate to steep dip. The Upper Gondwanas of Lower Cretaceous age contains the sandstones, while the Quaternary deposits have the laterite, black silty clay, brown silty sand, brown silty clay, brown sand and white to gray sand, which occur over the country rocks.

Hydrogeology

The important rocks of Precambrian and Gondwana formations lack primary porosity and hydraulic conductivity to store and to transmit the groundwater from one place to another due to their consolidated nature. But, they become aquifers (water-bearing formations) through the development of weathering process on the surface and tectonic activity in the subsurface. However, the occurrence of clay products formed due to a result of intensive weathering in the surface part of the country rocks, which reduces the hydraulic conductivity to some extent. The weathered rock zone extends up to a depth of 3–6 m, while the fractured rock zone extends up to a depth of 5 to 35 m from the ground surface, depending upon the topographical conditions and geological formations. The Quaternary formations are the best water-bearing formations due to their unconsolidated nature.

Rainwater and irrigation return flows are the recharge source of the groundwater. Shallow open wells and deep bore/tube wells are used to draw the groundwater. The shallow wells extend up to a depth of weathered portion (3 to 6 m) under the unconfined conditions and the deep wells up to a depth of the fractured portion (5 to 35 m) under the semi-confined conditions. The groundwater level is from 3 to 16 m below ground surface, which is higher (> 15 m) at upstream area (northwestern side) and lower (< 5 m) at downstream area (southeastern side), following the topographical features (Fig. 1). The irrigation wells yield about 4 L per second (Reddy et al. 2015). The mean well yield is about 50 cubic meters per day (m^3/day) in the weathered zone, 110 m^3/day in the fractured zone, 250 m^3/day in the coastal formation and 425 m^3/day in the river alluvium (CGWB 2013).

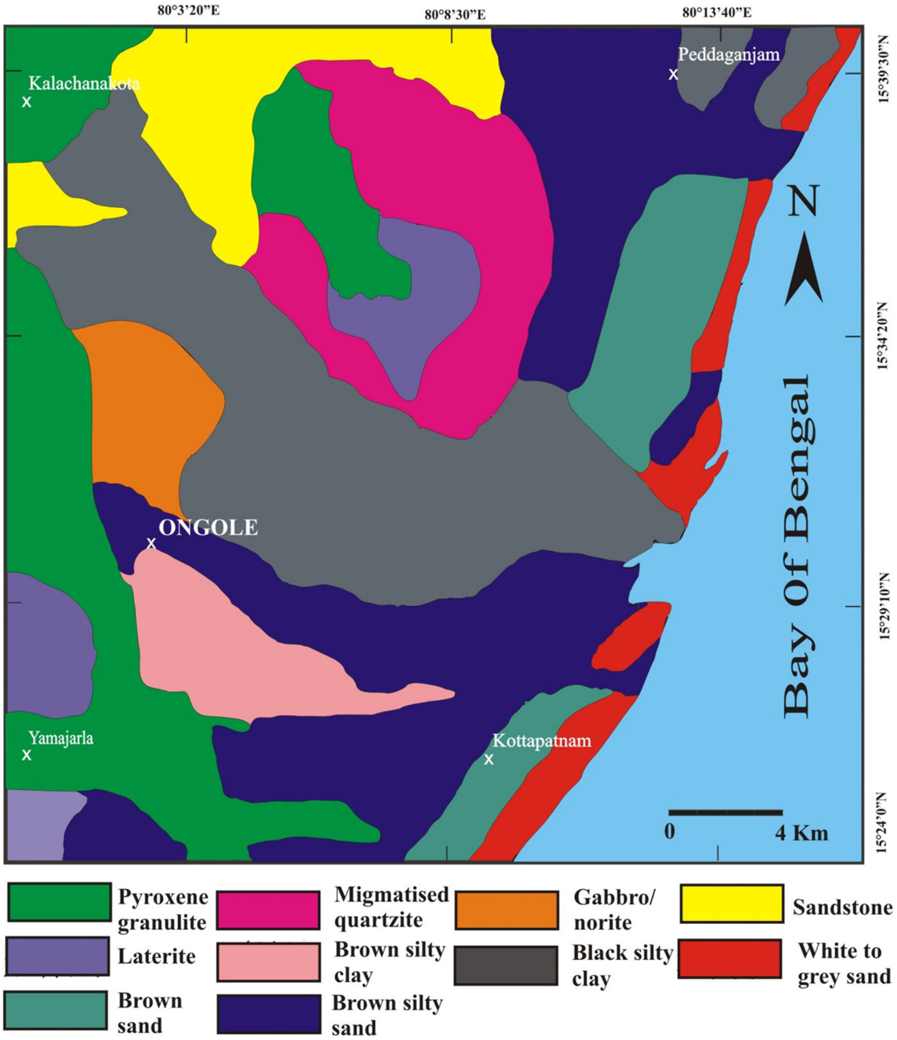

Fig. 2 Geological formations of the study region

In summer season, the people face severe groundwater scarcity for their drinking purpose due to insufficient supply of surface water. Majority of the groundwater samples shows brackish taste during the field work. Health problems like gastrointestinal irritation, fluorosis, etc., were also observed. Disposal facilities of household wastewaters, structural defects of septic tanks and leakage of drainage channels are the most common phenomenon.

Rural people depend on agriculture. Irrigation is intensive and long-term. Unlimited usage of agrochemicals, such as nitrogen (N), phosphate (P) and potassium (K) verities, is common. Main income of the people comes from the agricultural activities.

Materials and methods

Underground water samples from 30 locations were collected in 500-mL plastic containers in pre-monsoon 2012 (Fig. 1). The containers were put in 1:1 HCl for 24 h. They were cleaned with distilled and deionized waters. Then, they were closed tightly capped without any air gaps. Finally, the samples were shifted to chemical laboratory for water quality analysis.

The collected groundwater samples from the field were determined for pH (hydrogen ion concentration), EC (electrical conductivity), TDS (total dissolved solids), TH (total hardness as $CaCO_3$), Ca^{2+} (calcium), Mg^{2+}(magnesium), Na^+ (sodium), K^+ (potassium), HCO_3^-(bicarbonate), Cl^-(chloride), SO_4^{2-}

(sulfate), NO_3^- (nitrate) and F^-(fluoride), following the international standard water quality methods suggested by American Public Health Association (APHA 2012).

The values of pH and EC were determined on the field, using portable water quality kit. The TDS was estimated, using EC values, following the procedure of Hem (1991). The TH and Ca^{2+} were analyzed volumetric procedure, using EDTA. The value of Mg^{2+} was calculated, considering the values between TH and Ca^{2+} into account. The ions, Na^+ and K^+, were estimated, using flame photometer. The HCO_3^- and Cl^- were analyzed titrimetrically, using standard HCl and $AgNO_3$, respectively. The SO_4^{2-} was estimated by turbidimetric method, NO_3^- by colorimetric procedure and F^- by selective ion analyzer method. All chemical parameters are expressed in milligrams per liter (mg/L) and also in milliequivalent per liter (meq/L), excepting pH (no units) and EC (µS/cm at 25° C).

Analytical precision was examined for every groundwater sample collected from the study region, using percentage of ionic error balance (IEB%) among the total cations of Ca^{2+}, Mg^{2+}, Na^+ and K^+ ($\sum$cations) and the total anions of HCO_3^-, Cl^-, SO_4^{2-}, NO_3^- and F^- ($\sum$anions), expressing the ions in meq/L (Eq. 1). The computed value of IEB% is ± 5%, which is within its acceptable limit (Subba Rao 2017b). It confirms the results, which are at reasonable way to interpret the data, according to the objectives of the present study.

$$\text{IEB\%} = \frac{\sum \text{cations} - \sum \text{anions}}{\sum \text{cations} + \sum \text{anions}} \times 100 \tag{1}$$

Entropy-weighted water quality index (EWWQI)

Entropy-weighted water quality index (EWWQI) is a mathematical device for quantitative assessment of its quality, which needs for drinking purpose (Zhou et al. 2016; Alizadeh et al. 2018; Su et al. 2018; Subba Rao et al. 2020b). The computation procedure of EWWQI had five steps (Wu et al. 2017; Li et al. 2018b), as shown below:

In the first step, the eigenvalue matrix (*X*) was used (Eq. 1), which was associated with subsurface water quality data for "*m*" water samples and "*n*" chemical parameters.

$$\text{X} = \begin{vmatrix} x_{11} & x_{12} & ..x_{1n} \\ x_{21} & x_{22} & ..x_{2n} \\ x_{m1} & x_{m2} & ..x_{mn} \end{vmatrix} \tag{2}$$

In the second step, the eigenvalue matrix (*X*) was transformed into a standard-grade matrix (*Y*), using Eqs. 3 and 4.

$$y_{ij} = \frac{x_{ij} - \left(x_{ij}\right)\text{min}}{\left(x_{ij}\right)_{\text{max}} - \left(x_{ij}\right)_{\text{min}}} \tag{3}$$

$$\text{Y} = \begin{vmatrix} y_{11} & y_{12} & ..y_{1n} \\ y_{21} & y_{22} & ..y_{2n} \\ y_{m1} & y_{m2} & ..y_{mn} \end{vmatrix} \tag{4}$$

In the third step, the information entropy (e_j) was computed, using Eqs. 5 and 6:

$$e_j = -\frac{1}{Inm}\sum_{i=1}^{m} P_{ij} In P_{ij} \tag{5}$$

$$P_{ij} = \frac{\left(1 + y_{ij}\right)}{\sum_{i=1}^{m}\left(1 + y_{ij}\right)} \tag{6}$$

In the fourth step, the weight of entropy (*wj*) and scale of quality rating (*qi*) were calculated, using Eqs. 7 and 8:

$$w_j = \frac{\left(1 - e_j\right)}{\sum_{i=1}^{m}\left(1 - e_j\right)} \tag{7}$$

$$q_j = \frac{C_j}{S_j} \times 100 \tag{8}$$

where *Cj* is the chemical parameter (*j*) content (mg/L) and *Sj* is the standard desirable limit of chemical parameter (*j*) expressed in mg/L, following the WHO (2011) and BIS (2012).

In the final step, the EWWQI was computed, using Eq. 9:

$$\text{EWWQI} = \sum_{j=1}^{m} w_j q_j \tag{9}$$

The criteria for assessment of groundwater quality used for drinking can be categorized into five types on the basis of EWWQI. They are Type I (excellent water quality), if the EWWQI is less than 25; Type II (good water quality), if the EWWQI is from 25 to 50; Type III (medium water quality), if the EWWQI is in between 50 and 100; Type IV (poor water quality), if the EWWQI varies from 100 to 150; and Type V (very poor water quality), if the EWWQI is more than 150 (Subba Rao et al. 2020b).

Evaluation of health risk

Assessment of non-carcinogenic risk is an important comprehensive method, which is used to evaluate the possible health hazards on men, women and children, depending upon the intake, dermal contact and inhalation (Wu et al. 2019a, 2020). However, the consumption of drinking water is the oral intake, which appears as the prime exposure pathway rather than other two (dermal contact and inhalation) in the present study region. Thus, the NO_3^- and F^- were chosen as the contaminants for assessment of health problems. According to the United States Environmental Protection Agency (USEPA 1991), both the NO_3^- and F^- are considered as the most common pollutants for assessment of non-carcinogenic risk. In assessment of oral exposure, the mean value of daily dose of NO_3^- and F^- ingested from the drinking water was calculated, using Eq. 10 (USEPA 1991, 2006).

$$DD = \frac{CP \times IR \times ED \times FE}{BW \times ET} \tag{10}$$

where DD is the daily mean dosage of pollutant (mg/kg/day), CP is the pollutant concentrations of NO_3^- and F^- in the groundwater (mg/L), IR is the ingestion rate per unit time (L/day), which is 0.78 L/day for children and 2.5 L/day for women and men; ED is the exposure duration (years), which is 12 years for children, 64 years for women and 67 years for men; FE is the frequency of exposure (days/year), which is 365 days/year for children, women and men; BW is the known mean body weight of a person (kg), which is 15 kg for children and 65 kg for women and men; and ET is the mean exposure time of age (years), which is 4380 years for children, 24,455 years for women and 23,360 years for men.

Generally, the effect of toxicity occurs, where the exposure dose of the pollutant is more than its acceptable dose, which is called as hazard quotient (Eq. 11).

$$HQ = \frac{DD}{PD} \tag{11}$$

where HQ is the hazard quotient and PD is the permissible dose for chronic oral exposure, which is 1.60 mg/kg/day for NO_3^- and 0.60 mg/kg/day for F^-(USEP 2014; Li et al. 2019a, b).

The total chronic hazard index (TCHI) with respect to non-carcinogenic risk was calculated (Eq. 12). The acceptable limit of TCHI is 1.0 (USEPA 2014). When the TCHI is less than 1.0, it specifies that the health hazard associated with the non-carcinogenic risk is within the standard limit. When the TCHI is more than 1.0, it reveals the health risk.

$$TCHI = \sum_{i=1}^{n} HQ_i \tag{12}$$

Results and discussion

Chemical quality of groundwater

Before discussing the overall chemical quality of groundwater suitability for drinking, using EWWQI, it is also essential to explain the influence of individual chemical parameters on human health. This information helps into two ways: (a) to know the causes and sources of geogenic and anthropogenic pollutants, which deteriorate the chemical quality of subsurface water, and (b) to implement the environmental safety measures, which improve the quality of underground water and human health. The results of the analyzed groundwater samples of the present study region are shown in Table 1 to evaluate the quality of groundwater, following the International and national drinking water quality standards laid down by WHO (2011) and BIS (2012).

Hydrogen ion concentration (pH) and total dissolved solids (TDS)

The pH is from 7.2 to 8.3 (mean 7.81), indicating the water in an alkaline condition (Table 1), which is controlled by CO_2–CO_3^{2-}–HCO_3^- equilibrium. The HCO_3^- is formed in the groundwater, as the recharge water (H_2O) infiltrates through the soil CO_2, which releases from the organic matter and root respiration (Eqs. 13 and 14). This shows the variation in the pH. If the pH exceeds its highest desirable limit (6.5 to 8.5) in the potable water, it harms the mucous membrane present in eyes, nose, mouth, abdomen, anus, etc. (Ramesh and Soorya 2012; Ibrahim et al. 2015). In the present study region, the measured values of pH are within the safe limit of 6.5 to 8.5 recommended for potable water (Fig. 3).

$$CO_2 + H_2O \rightarrow H_2CO_3 \quad (13)$$

$$H_2CO_3 \rightarrow H^+ + HCO_3^- \quad (14)$$

The TDS ranges from 995 to 3290 gm/L with a mean of 1983.83 mg/L (Table 1), which comes under the brackish water quality category (TDS: 1000—10,000 mg/L) except in one sample 7 (TDS: < 1000 mg/L). This reflects a lot of variation in the water salinity in terms of various ions dissolved in the water. The dissolved ions are released into the groundwater body due to chemical process of silicate weathering with H_2CO_3 (carbonic acid). A generalized chemical process of the silicate rock weathering is shown in Eq. 15. According to the ionic contributions (%), the control of TDS is in the decreasing order of ions, i.e., Na^+ (65.20%) > Cl^-(51.70%) > HCO_3^-(40.15%) > Mg^{2+}(21.29%) > Ca^{2+} (11.05%) > SO_4^{2-} (4.92%) > NO_3^-(3%) > K^+ (2.46%) > F^-(0.23%). As per the classification of degree of water salinity (TDS) for drinking purpose, the TDS can be classified into three categories. They are desirable limit, when the TDS is less than 500 mg/L; permissible limit, when the TDS ranges from 500 to 1500 mg/L; and non-permissible limit, when the TDS is more than 1500 mg/L. In the present study region, 3.33% of the groundwater samples fall in the permissible limit of 500 to 1500 mg/L, while 96.67% of the groundwater samples belong to the non-permissible limit of 1500 mg/L (Fig. 3). The higher TDS decreases the water taste and increases the stomach troubles. It has also laxative effect while travelling time. According to Garg et al (2009) and Ali and Ali (2018), the prolonged intake of higher TDS water can form kidney stones and develop heart problems.

$$\text{Silicate rocks} + H_2CO_3 \rightarrow H_4SiO_4 + HCO_3^- + Na^+ + K^+ + Ca^{2+} + Mg^{2+} + \text{clay products} \quad (15)$$

Calcium (Ca^{2+}) and Magnesium (Mg^{2+})

The Ca^{2+} is an essential inorganic element for proper growth of bones, which is released into the groundwater due to weathering and dissolution of plagioclase feldspars occurring in the parent rocks (Subba Rao et al. 2013b, 2017a). Low concentration of Ca^{2+} in the potable water leads to not only osteoporosis but also kidney stones, hypertension, stroke and colorectal cancer (Garg et al. 2009; Sengupta 2013). The values of Ca^{2+} vary from 50 to 90 mg/L (mean 65.67 mg/L) in the present study region (Table 1). As per the concentration limit of Ca^{2+} allowing for drinking purpose, it may be classified as desirable limit, when the Ca^{2+} is less than 75 mg/L; permissible limit, when

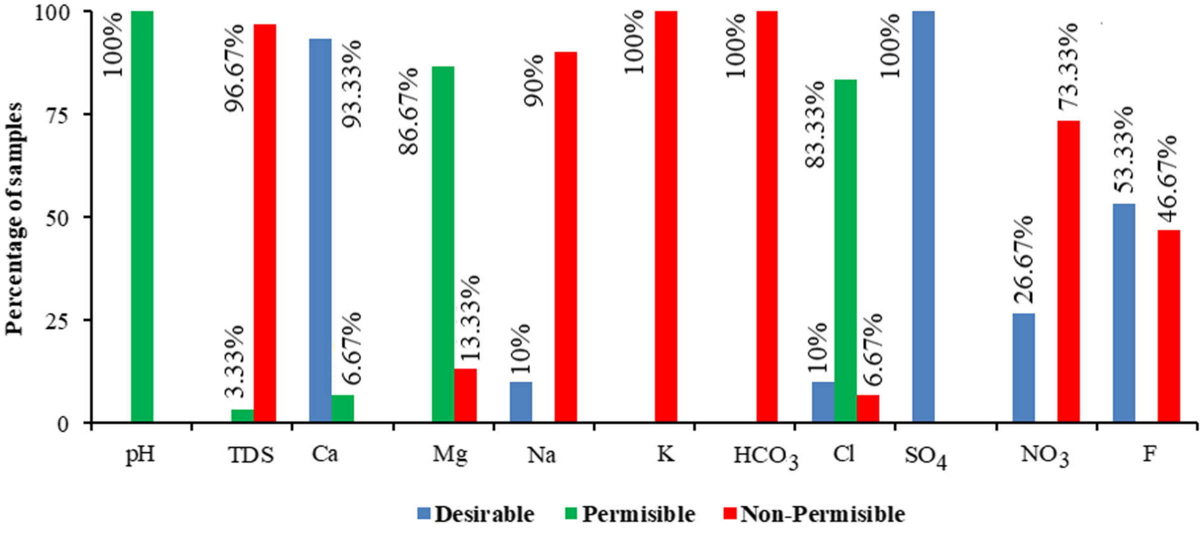

Fig. 3 Suitability of percentage of the groundwater samples for drinking purpose

Table 1 Chemical composition of groundwater in a part of Prakasam District, Andhra Pradesh, India

S. No.	pH (No units)	TDS mg/L	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^{-}	Cl^{-}	SO_4^{2-}	NO_3^{-}	F^{-}
P1	8.2	1260	65	67	208	49	580	300	46	46	0.9
P2	7.4	1095	70	57	197	12	490	255	36	39	0.7
P3	7.3	1115	70	62	185	16	530	245	45	36	0.7
P4	7.4	1675	60	72	346	56	875	350	57	39	1.6
P5	7.9	1230	75	53	224	41	570	270	50	51	0.9
P6	7.2	1680	70	67	365	30	615	500	42	49	0.9
P7	7.3	995	60	42	189	22	510	215	22	31	0.7
P8	7.5	2170	90	95	460	36	980	545	60	53	1.9
P9	8.0	2030	60	90	455	26	880	530	64	49	1.6
P10	7.6	1190	60	62	208	52	560	250	48	48	0.9
P11	7.9	1780	65	75	383	46	890	375	66	52	1.6
P12	7.4	2590	60	63	695	49	900	815	65	45	1.8
P13	8.1	2250	60	97	500	56	630	760	90	46	1.0
P14	7.3	1590	60	82	313	45	570	460	63	46	0.9
P15	7.5	1385	65	83	254	21	480	395	56	44	0.9
P16	8.0	1290	65	52	248	54	580	295	53	54	1.1
P17	7.9	1270	65	62	229	45	550	300	56	52	1.0
P18	7.6	1235	60	57	228	53	580	260	61	54	0.9
P19	7.4	1180	65	63	205	42	490	275	62	44	0.8
P20	7.6	1225	60	57	240	30	560	265	61	50	0.9
P21	8.3	3225	75	105	765	121	990	1035	125	97	1.9
P22	8.3	2850	60	83	725	92	920	890	112	85	1.7
P23	8.2	2880	90	86	714	52	940	940	78	49	2.2
P24	8.3	2990	70	97	736	96	960	920	122	96	1.8
P25	8.3	2990	70	92	735	94	925	970	114	84	2.1
P26	8.3	2990	60	105	701	89	920	940	104	73	1.6
P27	8.3	2980	50	105	735	94	980	920	113	87	1.9
P28	8.3	3290	75	100	823	110	1025	1060	112	93	2.8
P29	7.4	2400	60	70	625	45	860	520	65	42	0.9
P30	8.2	2685	55	105	651	59	940	810	96	52	1.8
AM	7.81	1983.83	65.67	76.87	444.73	54.43	742.67	555.50	71.47	56.20	1.35
SD	0.40	781.93	8.80	18.87	228.72	28.49	198.21	296.22	28.12	18.91	0.56
CV	5.12	39.42	13.40	24.55	51.43	52.34	26.69	53.32	39.35	33.65	1.48
IC	–	–	11.05	21.29	65.20	2.46	40.15	51.70	4.92	3.00	0.23

AM arithmetic mean, *SD* standard deviation, *CV* coefficient of variation (%), *IC* ionic contribution (%)

the Ca^{2+} varies from 75 to 200 mg/L; and non-permissible limit, when the Ca^{2+} is more than 200 mg/L. The Ca^{2+} content is within the desirable limit of 75 mg/L in 93.33% of the total groundwater samples of the present study region, while the rest of the groundwater samples (6.67%) fall in the permissible limit.

The Mg^{2+} content ranges from 42 to 105, being a mean of 76.87 mg/L (Table 1). The occurrence of ferromagnesium minerals (hornblende, hypersthene, sillimanite, garnet and biotite) in the basement rocks are the sources of Mg^{2+} in the subsurface water, apart from the sources of domestic wastewaters, septic tank leakages, etc. (Subba Rao et al. 2013b, 2017a). The

Mg^{2+} plays a significant role in functioning of cells to activate enzymes. However, the deficiency of Mg^{2+} causes structural and functional changes in the human beings. However, the higher content of Mg^{2+} acts as a laxative agent (Garg et al. 2009; Agarwal et al. 2014). The desirable, permissible and non-permissible limits of Mg^{2+} are less than 30, 30 to 100 and more than 100 mg/L prescribed for potable water, respectively. The Mg^{2+} content is observed to be within its permissible limit of 30 mg/L in 86.67% of the groundwater samples, while it falls in the non-permissible limit of 100 mg/L in 13.33% of the groundwater samples (Fig. 3). The contribution of Mg^{2+} (21.29%) is greater than the contribution of Ca^{2+} (11.05%) due to a result of dissolution of ferromagnesium minerals, ion exchange between sodium and calcium, and precipitation of carbonate precipitation, as reported in semiarid regions by Subba Rao et al. (2012, 2020b).

Sodium (Na^+) and Potassium (K^+)

The estimated Na^+ from the groundwater of the present study region ranges from 185 to 823 mg/L with a mean of 444.73 mg/L (Table 1). The weathering of the plagioclase feldspars, which are present in the basement rocks, is the main source of Na^+ in the underground water (Subba Rao et al. 2013b, 2017a). However, the higher Na^+ content reflects the secondary source, which is a result of influence of anthropogenic activities (household wastewaters, leakage of septic tanks, irrigation practice, etc.) on the groundwater (Subba Rao et al. 2017a, 2019a). The Na^+ contributes 65.20% to the total cations, which is the highest contributor among the cations due to virtue of its higher solubility character (Subba Rao et al. 2012). Sodium is the most essential nutrient element. The safe standard limit of Na^+ for drinking water is 200 mg/L. If it exceeds 200 mg/L, it comes under the non-permissible limit. Accordingly, 10% of the groundwater samples come under the desirable limit and 90% come under the non-permissible limit (Fig. 3). The higher the Na^+ content, the greater is the risk due to renal, cardiac and circulatory diseases (Haritash et al. 2008; Nerbass et al., 2018). Therefore, the Na^+ restricted food is recommended to the people, suffering from the cardiovascular (heart) and excretory (kidney) problems.

The groundwater samples collected from the study region show the K^+ content from 12 to 121 mg/L (mean 54.33 mg/L; Table 1). The occurrence of orthoclase feldspars in the basement rocks is the main contributor of K^+, while the uncontrolled application of K^+ fertilizers is the secondary source in the aquifer system (Subba Rao et al. 2013b, 2017a). However, it shows the lowest contribution (2.46%) among the cations. The orthoclase feldspar is the higher resistant to chemical weathering to release the K^+ into the groundwater and also the clays absorb the K^+ (Subba Rao 2017b). The K^+ is the necessary element to keep the fluids in the balance stage in the human body. The desirable limit of K^+ for drinking purpose is 10 mg/L. If it is more than 10 mg/L, it can be treated to be non-permissible limit. Accordingly, all groundwater samples fall in the non-permissible limit (Fig. 3). Thus, the higher K^+ content in the drinking water causes nervous and digestive disorders (Ramesh and Soorya 2012).

Bicarbonate (HCO_3^-), Chloride (Cl^-) and Sulfate (SO_4^{2-})

The concentration of HCO_3^- ranges from 480 to 1025 mg/L, being a mean of 742.67 mg/L (Table 1). The contribution of HCO_3^- to the total anions is 40.15%. It reaches the groundwater body due to recharge water, which infiltrates through the soil cover (containing CO_2) and the weathering zone (Eqs. 13–15). In fact, the HCO_3^- has not shown any adverse effects on human beings. However, it plays a major role in the human body for digestion of food. It also helps not only to generate a buffer lactic acid in exercise, but also to reduce the acidity of dietary components. It acts as a prevention effect on dental cavities (Subba Rao et al. 2012, 2019a). In view of this, less than 300 mg/L of HCO_3^- is considered as desirable limit and more than this limit is treated to be non-permissible limit recommended for drinking purpose. Accordingly, all groundwater samples in the present study area fall in the non-permissible limit (Fig. 3).

The values of Cl^- observed from the groundwater samples of the study region vary from 215 to 1060 mg/L and its mean is 555.50 mg/L, which contributes 51.70% to the total anions (Table 1). Like Na^+, the Cl^- is the dominant ion among the anions due to virtue of its higher solubility nature (Subba Rao et al. 2012).

The Cl^- plays a significant role in balancing level of electrolytes in blood plasma. However, its higher concentration in the drinking water causes risk of stroke, left ventricular hypertrophy, hypertension, osteoporosis, rental stones, asthma, etc. (McCarthy 2004). If the Cl^- is less than 250 mg/L, it is called the desirable limit; if the Cl^- varies from 250 to 1000 mg/L, it is termed to be the permissible limit; and if the Cl^- is more than 1000 mg/L, it is named the non-permissible limit prescribed for potable purpose. Accordingly, 10% of the groundwater samples fall in the desirable limit, 83.33% in the permissible limit and 6.67% in the non-permissible limit (Fig. 3). The higher Cl^- causes the salty taste to the water and shows a laxative effect. The Cl^- releases from a non-lithological source into the groundwater, which is considered to be an index of man-made pollution caused by artificial sources such as household wastewaters, septic tank leakages and irrigation practice (MPCA 2019; Subba Rao et al. 2019a, b).

Generally, the SO_4^{2-} is an important element, which deteriorates the chemical quality of subsurface water at larger extent. It shows the bitter taste and may have laxative effect to human beings. According to Garg et al. (2009), some health disorders, which are dehydration, catharsis, diarrhea and stomach irritation, are associated with the ingestion of SO_4^{2-}-contaminated water. The values of SO_4^{2-} content observed from the groundwater are from 22 to 125 mg/L, being a mean of 71.47 mg/L (Table 1). The desirable, permissible and non-permissible limits of SO_4^{2-} content are less than 200, 200 to 400 and more than 400 mg/L, respectively, prescribed for potable water. The SO_4^{2-} content in the present study region is within its desirable limit in all groundwater samples (Fig. 3). The SO_4^{2-} contributes 4.92% to the total cations. The gypsum ($CaSO_4 \cdot H_2O$), which is used as an amendment in the agricultural field, alters the soil permeability. This appears as the main source of SO_4^{2-} in the underground water, since there are no sulfide-bearing minerals in the present study region.

Nitrate (NO_3^-) and Fluoride (F^-)

Nitrate is a non-lithological source of the contaminant in the groundwater elsewhere in the world due to influence of soil cover with NO_3^- fertilizers, animal wastes, household effluents and septic tank leakages (Li et al. 2019a; Zhang et al. 2018; Subba Rao et al. 2019a). In natural conditions, the NO_3^- should be less than 10 mg/L in the water (Subba Rao et al. 2012). Thus, the higher concentration of NO_3^-, which is higher than 10 mg/L, is an indication of surface water pollution caused by the influence of anthropogenic activities (domestic wastewaters, leakages of septic tanks and unlimited usage of nitrogenous fertilizers) on the aquifer system (Wu and Sun 2016; Subba Rao et al. 2017a, b). In the present study region, the concentration of NO_3^- in the groundwater varies from 31 to 97 mg/L and its mean is 56.20 mg/L. This contributes 3% to the total anions (Table 1). The highest recommended limit of NO_3^- is 45 mg/L in the potable water. Therefore, if it is more than 45 mg/L, it comes under the non-permissible limit. Accordingly, 26.67% of the groundwater samples fall in the desirable limit and 73.33% in the non-permissible limit (Fig. 3). The higher NO_3^- content in the potable water is the source of the blue baby syndrome called *methemoglobinemia* (BIS 2012). According to Bao et al. (2017), the higher NO_3^- in the drinking water also causes goiter, gastric cancer, hypertension and birth malformations. Grant et al. (1996) stated that the spontaneous abortions can occur in women due to consumption of contamination of water with NO_3^-.

The values of F^- in the groundwater are in between 0.70 and 2.80 mg/L, and its mean is 1.35 mg/L (Table 1). The contribution of F^- to the total anions is 0.23%. The occurrence of F^--containing minerals containing the hornblende, biotite and apatite, in the basement rocks, is the primary source of F^- content in the underground water (Eqs. 16–18) which deteriorates the quality of groundwater through the longer contact of water with the aquifer material under the alkaline environment (Subba Rao 2003, 2009, 2011; Rao et al. 2014; Subba Rao et al. 2016). The F^- is also entered into the groundwater body through the unlimited usage of phosphate fertilizers (Subba Rao et al. 2013a, 2017b). Further, the occurrence of calcium carbonate concretions formed by evaporation process in the soil cover indicates the decline of Ca^{2+} content in the subsurface water. This favors to dissolve CaF_2 from the source material for compensation of the requirement of Ca^{2+} in the chemical balance (Subba Rao 2017a; Subba Rao et al. 2020a). Normally, F^- accumulates in the calcified tissues like teeth, bones, etc., of the human body. In the drinking water, the desirable limit is less than 0.6 mg/L, permissible limit varies from 0.6 to 1.5 mg/L and non-permissible is higher than 1.5 mg/L. The F^- comes under the permissible limit in 53.33% of the total groundwater samples and 46.67% in the non-permissible limit in the present study region (Fig. 3). Non-permissible limit of F^- in the drinking water damages the teeth and bones of the human body, which leads to dental fluorosis and skeletal fluorosis (WHO 2011; BIS 2012; He et al. 2020a, 2020b; Subba Rao et al. 2020a). According to Raja Reddy (1979), the consumption of higher F^- content through the drinking water changes the metabolic activities of nervous (brain), genital (reproductive), endocrine (thyroid), digestive (liver) and excretory (kidney) systems. Chlubek et al. (1998) stated that the occurrence of higher F^- in the marginal part of placenta in women shows its high content in plasma.

$$\underset{\text{Hornblende}}{Ca_5Mg_5(Si_6Al_2O_{22})F_2} + 2OH^- \rightarrow Ca_5Mg_5(Si_6Al_2O_{22})(OH)_2 + 2F^- \quad (16)$$

$$\underset{\text{Biotite}}{K(Mg,Fe)_3(AlSiO_3O_{10})F_2} + 2OH^- \rightarrow K(Mg,Fe)_3[AlSiO_3O_{10}](OH)_2 + 2F^- \quad (17)$$

$$\underset{\text{Apatite}}{Ca_5F(PO_4)_3 2OH} \rightarrow Ca_5\,(PO_4)_3(OH)_2 + 2F^- \quad (18)$$

Spatial distribution of overall quality of groundwater for drinking purpose

Since the said groundwater quality specifications depend upon the individual chemical parameters, the justification of their combined effect on human health is essential for taking the environmental safety measures at a specific site. In the present study region, the entropy-weighted water quality index (EWWQI) is adopted, which has been employed as a comprehensive device to evaluate the overall suitability of chemical quality of groundwater for potable purpose (Zhou et al. 2016; Alizadeh et al. 2018; Su et al. 2018; Subba Rao et al. 2020b).

The computed values of EWWQI are presented in Table 2. They range from 53.64 to 216.59 with a mean of 122.22. According to the classification of EWWQI, the excellent groundwater quality comes under the Type I (EWWQI: < 25), good groundwater quality under the Type II (EWWQI: 25–50), medium groundwater quality under the Type III (EWWQI: 50–100), poor groundwater quality under the Type IV (EWWQI: 100–150) and very poor groundwater quality under the Type V (EWWQI: > 150; Subba Rao et al. 2020b). The areas, which fall in the excellent groundwater quality type and good groundwater quality type, are suitable for drinking purpose, while the areas, which fall in the poor groundwater quality type and very poor groundwater quality type, are not fit for drinking use. On the other hand, the area belonging to the medium groundwater quality type is not as good as the first two types and is not as bad as the last two types.

As illustrated in Fig. 4, 50% of the total groundwater samples fall in the medium groundwater quality, 20% in the poor groundwater quality and 30% in the very poor groundwater quality types for drinking purpose. It is also noted from Fig. 4 that the excellent groundwater quality type and good groundwater quality type are not observed from the present study region, which are fit for drinking purpose, while the poor groundwater quality type and very poor groundwater quality type are not suitable for drinking purpose. On the other hand, the medium groundwater quality type, which is in between the above water quality types, can be considered to be intermediate or transition or mixed groundwater quality type, because its quality is not as good as the quality of the first two types (I and II), but somewhat better than the quality of the last two types (IV and V) for drinking purpose. Therefore, this observation obviously suggests that the deterioration of groundwater quality is started from the medium groundwater quality type. As a result, the groundwater quality in Types III, IV and V is not suitable for drinking purpose, as whole (Table 1). However, the medium groundwater quality type may be used for domestic and irrigation purposes, after taking the preliminary treatment, while the poor groundwater quality type and very poor groundwater type may also be used for irrigation purpose, after taking the special treatment methods.

Spatial distribution of EWWQI is illustrated in Fig. 5. This provides information on the occurrence of inferior groundwater quality zones to protect the groundwater resource by taking the management strategies for sustainable development of the society. About 55% of the study region falls in the medium

Table 2 Classification of groundwater quality for drinking purpose based on entropy-weighted water quality index (EWWQI)

S. No.	EWWQI	Classification of groundwater quality				
		Groundwater quality	Type	Suitability for drinking purpose	Alternative suitability for	
					Domestic purpose	Irrigation purpose
P1	85.61	Medium	III	Unfit	Fit	Fit
P2	62.03	Medium	III	Unfit	Fit	Fit
P3	58.96	Medium	III	Unfit	Fit	Fit
P4	89.19	Medium	III	Unfir	Fit	Fit
P5	79.87	Medium	III	Unfit	Fit	Fit
P6	93.63	Medium	III	Unfit	Fit	Fit
P7	53.64	Medium	III	Unfit	Fit	Fit
P8	120.26	Poor	IV	Unfit	Unfit	Fit
P9	124.80	Poor	IV	Unfit	Unfit	Fit
P10	70.78	Medium	III	Unfit	Fit	Fit
P11	106.91	Poor	IV	Unfit	Unfit	Fit
P12	151.80	Very poor	V	Unfit	Unfit	Fit
P13	143.88	Poor	IV	Unfit	Unfit	Fit
P14	89.29	Medium	III	Unfit	Fit	Fit
P15	82.24	Medium	III	Unfit	Fit	Fit
P16	87.04	Medium	III	Unfit	Fit	Fit
P17	83.35	Medium	III	Unfit	Fit	Fit
P18	75.01	Medium	III	Unfit	Fit	Fit
P19	67.52	Medium	III	Unfit	Fit	Fit
P20	75.04	Medium	III	Unfit	Fit	Fit
P21	208.65	Very poor	V	Unfit	Unfit	Fit
P22	188.73	Very poor	V	Unfit	Unfit	Fit
P23	182.57	Very poor	V	Unfit	Unfit	Fit
P24	196.23	Very poor	V	Unfit	Unfit	Fit
P25	197.42	Very poor	V	Unfit	Unfit	Fit
P26	189.01	Very poor	V	Unfit	Unfit	Fit
P27	194.17	Very poor	V	Unfit	Unfit	Fit
P28	216.59	Very poor	V	Unfit	Unfit	Fit
P29	123.89	Poor	IV	Unfit	Unfit	Fit
P30	168.49	Poor	IV	Unfit	Unfit	Fit
Mean	122.22					

groundwater quality type, which is observed from the central part. Poor groundwater quality type is located toward the northeastern and southwestern parts, covering an area of about 10%, which follows the medium groundwater quality type. The area (35%) covered by very poor groundwater quality type is spread from the northeastern and southwestern parts, following the poor groundwater quality type. Therefore, the gradual increase in groundwater quality from the medium to very poor types appears to be caused by interference of pollutants on the aquifer system.

To know the sources of pH, TDS, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, Cl^{-}, SO_4^{2-}, NO_3^{-} and F^{-} on the aquifer system and also their chemical variation from the medium groundwater quality type to very poor groundwater quality type, the mean chemical analysis of groundwater quality types of EWWQI is shown in Table 3. According to this, the mean values of Ca^{2+}

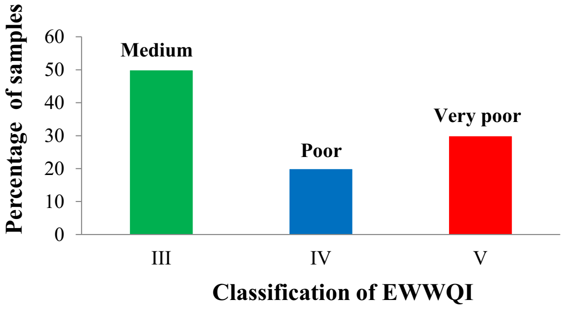

Fig. 4 Suitability of percentage of the groundwater samples for drinking purpose based on the classification of entropy-weighted water quality index (EWWQI) types

(64.67 to 67.78 mg/L), Mg^{2+} (62.53 to 97.89 mg/L), Na^{+} (242.60 to 736.56 mg/L), K^{+} (37.87 to 88.56 mg/L), HCO_3^{-}(569.33 to 951.11 mg/L), Cl^{-}(309 to 943.33 mg/L), SO_4^{2-} (50.53 to 105 mg/L), NO_3^{-}(45.53 to 78.78 mg/L) and F^{-}(0.92 to 1.98 mg/L) increase gradually from the medium groundwater quality type to very poor groundwater quality type. Among these chemical parameters, the ions Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, NO_3^{-} and F^{-} are well known as the common pollutants (Subba Rao et al. 2017a, 2019a, 2020b). They are increasing 1.57, 3.04, 2.34, 3.05, 2.08, 1.73 and 2.15 times, respectively, from the medium groundwater quality type to very poor groundwater quality type. Consequently, the degree of salinity (TDS) is also gradually increased 2.3 times from the medium groundwater quality type (mean TDS 1294.33 mg/L) to very poor groundwater quality type (mean TDS 2976.11 mg/L). It is a known fact that any excess substance than the required one is harmful or poisonous to human health, which is called the contamination (WHO 2011). Therefore, this observation has now confirmed the earlier hypothesis that the chemical quality of groundwater is gradually

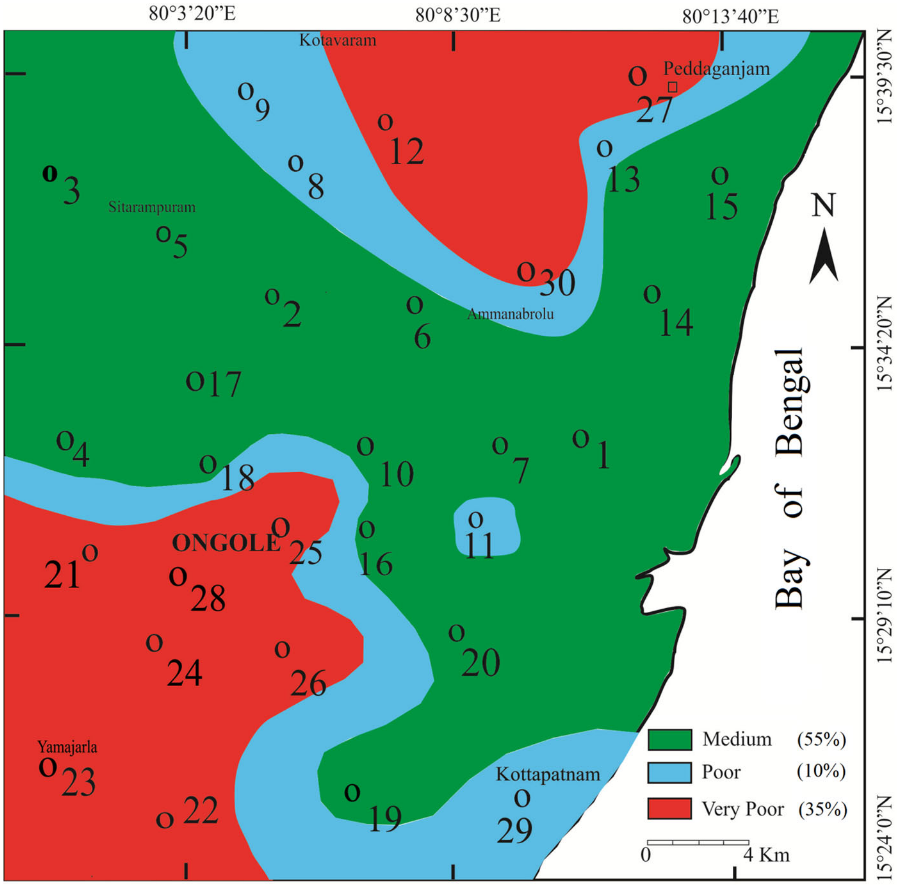

Fig. 5 Spatial distribution of entropy-weighted water quality index (EWWQI) types. The brackets denote the per cent of the coverage area of various groundwater quality types

Table 3 Classification of mean chemical composition of groundwater based on entropy-weighted water quality index (EWWQI)

Groundwater quality type	pH (No units)	TDS mg/L	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^{-}	Cl^{-}	SO_4^{2-}	NO_3^{-}	F^{-}
Medium	7.57	1294.33	64.67	62.53	242.60	37.87	569.33	309.00	50.53	45.53	0.92
Poor	7.85	2214.17	65.00	88.67	512.33	44.67	863.33	590.00	73.50	48.83	1.60
Very poor	8.19	2976.11	67.78	97.89	736.56	88.56	951.11	943.33	105.00	78.78	1.98

deteriorating due to increase in lithological and non-lithological pollutants from the medium groundwater quality type to very poor groundwater quality type (Wu et al. 2019b). As a result, the concentrations of K^+, HCO_3^-, TDS, Na^+, NO_3^-, F^-, Mg^{2+} and Cl^- come under the non-permissible limits in 100%, 100%, 96.67%, 90%, 73.33%, 46.67%, 13.33% and 6.67% of the groundwater samples prescribed for drinking purpose (Fig. 3). They cause the adverse health effects on human beings due to prolonged exposure through the drinking water (Sharma and Bhattacharya 2017; Subba Rao 2017b). Among them, the NO_3^- and F^- are considered as the most common pollutants and also as the higher toxicities, causing the potential production of non-carcinogenic risk (USEPA 2014). This is discussed below in detail:

Spatial distribution of non-carcinogenic risks

According to the classification of EWWQI, the occurrence of groundwater in all observed samples is not generally suitable for drinking purpose. As discussed earlier, the concentrations of NO_3^- and F^- in 73.33% and 46.67% of the groundwater samples fall in the non-permissible limits (Fig. 3), which are the most harmful to human health compared to other chemical parameters due to their potential production of non-carcinogenic risk (USEPA 2014).

Generally, the higher concentration of NO_3^- in the potable water shows the adverse health problems on infants of less than three months of age, while the F^- content shows its health threat irrespective of human age (WHO 2011). However, the estimation of health risk is also necessary for understanding the effect of vulnerability of both NO_3^- and F^- in the case of men and women in the present study region, since the local residents here mainly reply on the groundwater resource for drinking purpose. Thus, the non-carcinogenic risk on human beings through the intake of NO_3^- and F^- contaminated groundwater has been evaluated as per the procedures of USEPA (2014).

The individual health hazards associated with the non-carcinogenic risk on men, women and children caused by the influences of NO_3^- and F^- are evaluated, considering the oral exposure of groundwater into account. Table 4 shows the values of HQ, which were computed for individuals by taking in NO_3^- and F^- for men, women, and children, in the observed groundwater locations of the present study region. The values of $HQ_{NO_3^-}$ vary from 0.745 to 2.332 (mean 1.351) for men, 0.881 to 2.756 (mean 1.597) for women and 1.008 to 3.153 (mean 1.827) for children in 86.67%, 96.67% and 100% of the total groundwater samples, respectively (Fig. 6), while those of HQ_{F^-} are from 0.449 to 1.795 (mean 0.863) for men, 0.530 to 2.121 (mean 1.020) for women and 0.607 to 2.427 (mean 1.167) for children in 43.33%, 46.67% and 46.67% of the groundwater samples, respectively.

It is important to note from Fig. 6 that the influence of percentage of groundwater samples is observed to be higher in the case of NO_3^- compared to that of F^-. In similar way, the effect of health risk on individuals is also noticed to be higher due to NO_3^- rather than due to F^- in the present study region. This difference is due to influence of anthropogenic source, which could be an additional source to the existing geogenic source on the aquifer system, as the non-lithological activities are the only source of NO_3^-, while the lithological origin is the prime source of F^- in the drinking water (WHO 2011; Subba Rao et al. 2017a, 2019b). However, the values of HQ of both the ingestion of NO_3^- and F^- through the potable water imply the adverse health risks in the decreasing order of children > women > men. Therefore, the NO_3^- and F^- are considered as the most common potential pollutants to deteriorate the quality of groundwater and consequently to damage the health of human also.

Table 4 Health risk of non- non-carcinogenic with respect to men, women and children

S. No.	Hazard quotient NO_3^- ($HQ_{NO_3^-}$)			HQ_{F^-}			Total chronic hazard index (TCHI)		
	Men	Women	Children	Men	Women	Children	Men	Women	Children
P1	1.106	1.307	1.495	0.577	0.682	0.780	1.687	1.989	2.275
P2	0.938	1.108	1.268	0.449	0.530	0.607	1.386	1.638	1.874
P3	0.865	1.023	1.170	0.449	0.530	0.607	1.314	1.553	1.777
P4	0.938	1.108	1.268	1.026	1.212	1.387	1.963	2.320	2.654
P5	1.226	1.449	1.658	0.577	0.682	0.780	1.803	2.131	2.438
P6	1.178	1.392	1.593	0.577	0.682	0.780	1.755	2.074	2.373
P7	0.745	0.881	1.008	0.449	0.530	0.607	1.194	1.411	1.614
P8	1.274	1.506	1.723	1.218	1.439	1.647	2.492	2.945	3.369
P9	1.178	1.392	1.593	1.026	1.212	1.387	2.204	2.604	2.979
P10	1.154	1.364	1.560	0.577	0.682	0.780	1.731	2.045	2.340
P11	1.250	1.477	1.690	1.026	1.212	1.387	2.276	2.689	3.077
P12	1.082	1.278	1.463	1.154	1.364	1.560	2.236	2.642	3.023
P13	1.106	1.307	1.495	0.641	0.758	0.867	1.747	2.064	2.362
P14	1.106	1.307	1.495	0.577	0.682	0.780	1.683	1.989	2.275
P15	1.058	1.250	1.430	0.577	0.682	0.780	1.635	1.932	2.210
P16	1.298	1.534	1.755	0.705	0.833	0.953	2.003	2.367	2.708
P17	1.250	1.477	1.690	0.641	0.758	0.867	1.891	2.235	2.557
P18	1.298	1.534	1.755	0.577	0.682	0.780	1.875	2.216	2.535
P19	1.058	1.250	1.430	0.513	0.606	0.693	1.571	1.856	2.123
P20	1.202	1.420	1.625	0.577	0.682	0.780	1.779	2.102	2.405
P21	2.332	2.756	3.153	1.218	1.439	1.647	3.550	4.195	4.799
P22	2.043	2.415	2.763	1.090	1.288	1.473	3.133	3.703	4.236
P23	1.178	1.392	1.593	1.410	1.667	1.907	2.588	3.059	3.499
P24	2.308	2.727	3.120	1.154	1.364	1.560	3.462	4.091	4.680
P25	2.019	2.386	2.730	1.346	1.591	1.820	3.365	3.977	4.550
P26	1.755	2.074	2.373	1.026	1.212	1.387	2.780	3.286	3.759
P27	2.091	2.472	2.828	1.218	1.439	1.647	3.309	3.911	4.474
P28	2.236	2.642	3.023	1.795	2.121	2.427	4.030	4.763	5.449
P29	1.010	1.193	1.365	0.577	0.682	0.780	1.587	1.875	2.145
P30	1.250	1.477	1.690	1.154	1.364	1.560	2.404	2.841	3.250
Mean	1.351	1.597	1.827	0.863	1.020	1.167	2.214	2.620	2.994

The combined influence of non-carcinogenic risk of NO_3^- and F^- through the consumption of potable water is expressed in terms of total chronic hazard index (TCHI), which was calculated, using Eq. 11. The value of TCHI is from 1.194 to 4.030 for men, 1.411 to 4.763 for women and 1.614 to 5.449 for children (Table 4). According to the UPEA (2014), the limit of TCHI for non-carcinogenic risk is one. If the TCHI is less than one, it shows no any health effect due to non-carcinogenic risk. If the TCHI exceeds one, it shows the adverse effect of non-carcinogenic on human beings.

Since the quality of groundwater in all samples occurring in the present study region is not in acceptable limit for drinking purpose (Fig. 7), it causes non-carcinogenic risk on human beings. However, comparatively, the mean value of TCHI is high in children (mean 2.994), which is followed by women (mean 2.620) and men (mean 2.214; Fig. 6). From Fig. 6, it is also observed that the mean values of TCHI

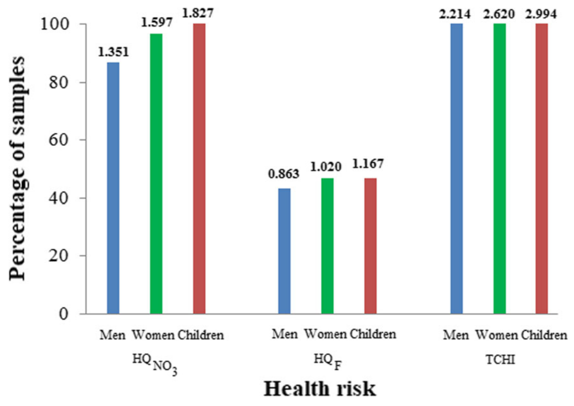

Fig. 6 Percentage of samples with respect to health risk and mean values of health risk shown on upper side of histograms

are more than that of HQ. It specifies obviously that the combined influence of NO_3^- and F^- ions is higher than that of the influence of individual ions on men, women and children. Therefore, the consumption of contaminated water with NO_3^- and F^- ions appears to be the potential source for health risk, which is in the decreasing order of children > women > men. These differences may be due to sensitiveness to pollutants and smaller body weights of children, followed by women and men in the present study region. Li et al. (2016), Ahada and Suthar (2017), Yang et al. (2018), Karunanidhi et al. (2020) and Subba Rao et al. (2020a, b) also reported the similar observations that the children suffer more from the health risk due to their lesser body weight than adults (women and men).

Spatial distribution of potential health risk on the basis of TCHI for men, women and children is illustrated in Fig. 8, which provides information, where the vulnerable zones can occur for implementing the environmental safety measures for improving the quality of groundwater and subsequently the human health. In Fig. 8a, about 63% of the present study region demonstrates the non-carcinogenic risk value of TCHI varying from 1.0 to 2.0 in the entire study region; 26% of the region has the health risk from 2.0 to 3.0 in the north, northeastern and southwestern side; 9% of the region shows the risk between 3.0 and 4.0 in the northeastern and southwestern side; and further higher risk, that is more than 4.0, is observed as isolated patch (2%) from the southwestern side, where men face the adverse health risks. In Fig. 8b, about 22% of the present study region has the non-carcinogenic risk value from 1 to 2, which is observed from the east and northwestern side; 64% of the region shows the health risk from 2 to 3, which is spread in the entire study region; 10% of the region has the adverse risk from 3 to 4, which is in the northeastern and southwestern side; and next higher health risk more than 4 is observed from the southwestern side as isolated patch (4%), where women appear to face the severe health risk. In Fig. 8c, the non-carcinogenic value of TCHI from 1.0 to 2.0 is observed as isolated patches (3%) from the central and northwestern side, where children face the health problems. In 78% of the total study region, the value of TCHI varying from 2.0 to 3.0 spreads the entire study

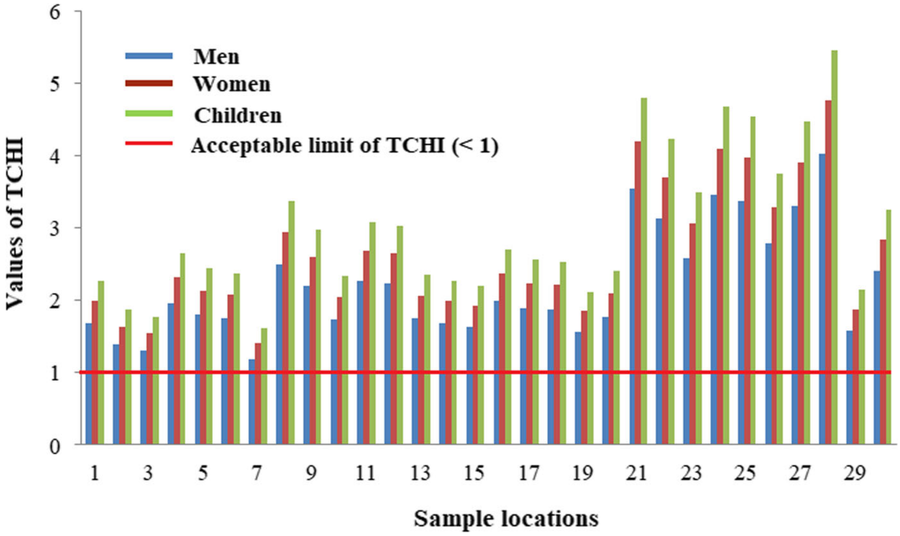

Fig. 7 Sample-wise distribution of total chronic hazard index (TCHI) with respect to men, women and children

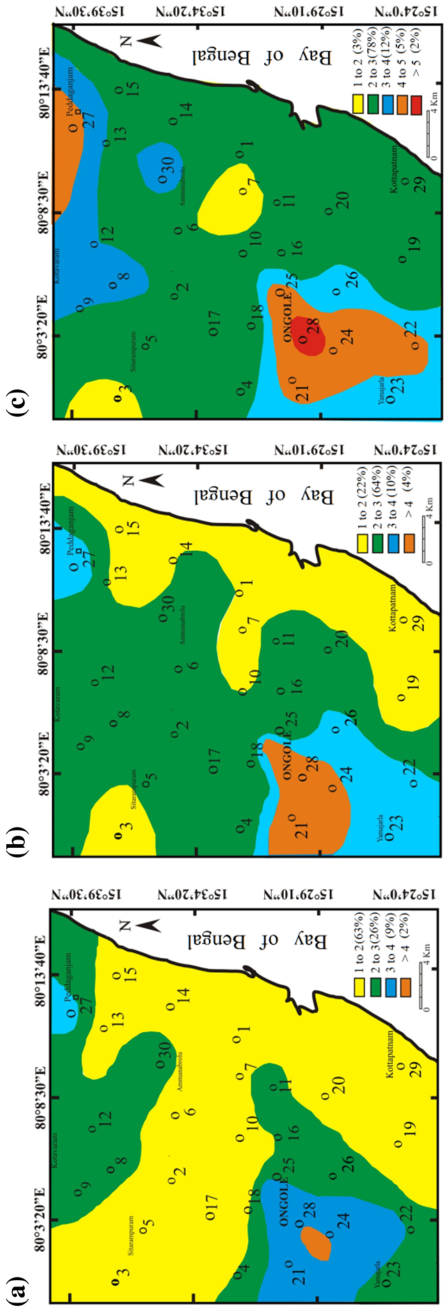

Fig. 8 Spatial distribution of total chronic hazard index (TCHI) with respect to (a) men, (b) women and (c) children. The brackets denote the percentage of the coverage area of various intensities of vulnerable zones

region. The value of TCHI from 3.0 to 4.0 is shown in the north, northeastern and southwestern side, covering 12% of the total study region. The next value of health risk (4.0 to 5.0) is observed from the northeastern and southwestern side as isolated patches (5%). Further, the higher health risk value more than 5.0 is found as isolated patch (2%) in the southwestern side.

The gradual increase in TCHI from the low non-carcinogenic risk area (TCHI: 1.0 to 2.0) to the high non-carcinogenic risk area (TCHI: $>$ 5.0), as shown in Fig. 8, appears to be caused by differences in the influences of the local topographical features and the availability of pollution sources relating to the weathering, dissolution, ion exchange and evaporation processes of fluoride-bearing minerals present in the country rocks as the primary factors, and the domestic wastewaters, septic tank leakages, unlimited usage of nitrogenous and phosphate fertilizers as the secondary factors, which control the quality of groundwater (Subba Rao 2017a, 2018). Accordingly, the health risk conditions are also showing the differences in their spreading intensity.

From Fig. 8, it is important to note that the vulnerable zones of the non-carcinogenic risk increase from men to children due to the intake of NO_3^-- and F^--contaminated drinking water of the present study region. Generally, the children are not only more sensitive to NO_3^- and F^- poisoning, but also have less body weights than men and women so that they face the health risk of non-carcinogenic easily everywhere (Chen et al. 2016, 2017; Li et al. 2019a, 2019b; Karunanidhi et al., 2020; Subba Rao et al. 2019b; Shukla and Saxena 2020).

Further, it is also significant to note that the spatial distribution of TCH1 is more or less similar to the spatial distribution of EWWQI (Figs. 5 and 8). Therefore, such type of comprehensive study helps for establishment of the fact everywhere to recognize the spatial distribution of intensity of various vulnerable zones for protection and management of groundwater from the contamination and consequently to improve the human health conditions for sustainable development of the society.

Environmental safety measures

The present study is useful to the public and decision makers for implementing the environmental safety measures like (a) implementation of rainwater harvesting techniques to reduce the salinity in the groundwater quality, (b) improvement in sanitation facilities and controlling the usage of agrochemicals to arrest the pollution activities on the aquifer system, and (c) immediate supply of safe potable water, calcium-rich food and defluoridation filters to recover the human health. These are the important protection and management measures to take up easily by all, according to the intensity of various vulnerable zones. Thus, they aid in reducing the NO_3^- and F^- levels in the subsurface water body and the corresponding public health risk.

Conclusions

Since the contaminated NO_3^- and F^- groundwater leads to several public health issues everywhere in the world, the present study has been undertaken from a rural part of Prakasam District, Andhra Pradesh, South India, to evaluate the spatial distribution of suitability of chemical quality of groundwater zones for drinking purpose, using entropy-weighted water quality index (EWWQI), and also non-carcinogenic risks caused by exposure of NO_3^- and F^- through intake for children, women and men, using total chronic hazard index (TCHI), for taking the environmental safety measures. The summarized conclusions of this study were as follows:

(a) Groundwater quality shows alkaline condition with brackish type. The concentrations of K^+, HCO_3^-, TDS, Na^+, NO_3^-, F^-, Mg^{2+} and Cl^- fall in the non-permissible limits in 100%, 100%, 96.67%, 90%, 73.33%, 46.67%, 13.33% and 6.67% of the groundwater samples, respectively, which deteriorate the groundwater quality, causing the health disorders. As per the classification of EWWQI, the spatially 55%, 10% and 35% of the total study region fall in the medium groundwater quality, poor groundwater quality and very poor groundwater quality types prescribed for potable water. These differences are observed to be caused by variations in the sources of pollutants related to geogenic and anthropogenic origins.

(b) The values of $HQ_{NO_3^-}$ are from 0.745 to 2.332 (mean 1.351) for men, 0.881 to 2.756 (mean 1.597) for women and 1.008 to 3.153 (mean 1.827) for children, which exceeds its allowable limit of one in 86.67%, 96.67% and 100% of the total groundwater samples, respectively, while those of HQ_{F^-} are from 0.449 to 1.795 (mean 0.863) for men, 0.530 to 2.121 (mean 1.020) for women and 0.607 to 2.427 (mean 1.167) for children, which are more than its acceptable limit of one in 43.33%, 46,67% and 46.67% of the groundwater samples, respectively. The TCHI caused by consumption of NO_3^-- and F^--contaminated groundwater for men (1.194 to 4.030 with a mean of 2.214), women (1.411 to 4.763 with a mean of 2.620) and children (1.614 to 5.449 with a mean of 2.994) implies the adverse health risks decreasing spatially in the decreasing order of children > women > men, which are the potential health risks associated with non-carcinogenic concern. The differences in the health risk among men, women and children are caused by differences not only in their sensitiveness to pollutants, but also in their body weights.

(c) The spatial distribution of TCH1 is more or less similar to the spatial distribution of EWWQI. Hence, the present study helps for establishment of the fact to demarcate the spatial intensity of various vulnerable zones at a specific site for taking the efficient management measures for protection of groundwater resources from the contamination and consequently for improving the human health.

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Compliance with ethical standards

Conflict of interests The authors declare they have no conflict of interests.

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