Effect of high nitrate contamination of groundwater on human health and water quality index in semi-arid region, South India

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Abstract

The specific objective of the present is to evaluate the human health issue due to the continuous consumption of nitrate-contaminated groundwater among the various age groups of people. In the study, 40 groundwater samples were collected during the post-monsoon season, and the major ions were analysed in a laboratory. Chadha plot revealed that weathering of parent rocks, ion exchange process and leaching of salts from the rocks are primary sources of groundwater contamination. Nitrate concentration varied from 24 to 78 mg/L with a mean of 46.45 mg/L. Nitrogen pollution index (NPI) value divulged that 40% and 17.5% of sample locations are moderately and significantly polluted due to elevated nitrate concentration in groundwater. The human health risk assessment model revealed that health issues are among the various age groups which are infants > kids > children > aged peoples > adults. The nitrate's identified sources are leaching of salts from the rocks, using synthetic fertilizers, uncovered septic tanks and improper disposal of household waste from the residential area. Therefore, periodic inspection of water supply, health check-up and inspection of underground pipelines are the remedial measures that should be taken to reduce the severe effects of nitrate-contaminated drinking water in the study area.

Keywords Groundwater quality · Nitrate contamination · Nitrogen pollution index · Human health risk assessment

Introduction

Nitrogen in the various forms of nitrate, nitrite, or ammonium in groundwater is a nutrient needed for enhancing the crop yield and plant growth. In general, hundreds of tons of nitrogen spill unnoticeably into the soil, water and air every day from various man-made activities such as farms, smoke stacks and vehicle emission (Adimalla 2020; Kumar and Balamurugan 2018; Abd Al-Khodir and Albayati 2020). The result of the nitrate contamination causes unhealthy air, polluted drinking water, degraded ecosystem and consequences for climate change. In view of degraded ecosystem,

the excess nitrate might be the reason for water contamination, reduced biodiversity and loss of certain plant species (Balamurugan and Kumar 2016; Balamurugan and Balakumaran 2015; Alardhi et al. 2020b). Groundwater is a primary source of water and higher percentage of world population depends on it for their day-to-day needs (Balamurugan et al. 2020a; Kumar and Balamurugan 2019; Alardhi et al. 2020c). In India, most urban and rural peoples depend on groundwater for domestic, agriculture and industrial purpose. However, with the rapid increase in population growth, urbanization, industrialization and modernization of agricultural activities are major threats to the quality of groundwater (Balamurugan et al. 2020b). The effects of the groundwater contamination have become a serious issue in community of public health and livestock. Expressly, the consumption of contaminated water can cause many health effects on human community and it is essential to assess the suitability of groundwater for drinking uses. Among the various contaminations, nitrate (NO_3^-) pollution is the widespread environmental disaster, which has two different sources such as natural and anthropogenic sources. The excessive anthropogenic loading such as agricultural waste that includes fertilizer, pesticides, organic, inorganic waste

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from households, and leakage of sewer pipelines are the primary reasons for nitrate contamination in groundwater. (Alardhi et al. 2020a, 2020d; Balamurugan et al. 2020c). Compared to other contaminants in groundwater, nitrate plays a vital role in groundwater quality aided with human health issues. The excess concentration of nitrate and continuous consumption of nitrate in groundwater causes serious health diseases on infant and different ages of peoples (Alardhi et al. 2020a, 2020b, 2020c, 2020d, Albayati and Doyle 2013; Albayati et al. 2020).

In arid and semi-arid region, low precipitation and high evaporation rates enhance the salinity of water and it leads to increase the toxicity of certain chemical such as nitrate in groundwater. The reason for many researchers involved in identifying the source of nitrate is excessive concentration of nitrate in groundwater which may involve co-contamination with potentially toxic elements (Khader et al. 2021). Nevertheless, in Asian countries like China, India, Pakistan and Bangladesh are facing issue like nitrate-contaminated groundwater which causes higher percentage of health issue than other diseases on such research exists (Albayati et al. 2019; Doyle 2015). The recent studies have recognized an effect of nitrate on human health and correlation between agriculture activities and nitrate contamination in groundwater. Gutierrez et al. (2018) conducted a detailed investigation of nitrate sources and operating processes in arid and semi-arid aquifer systems in China and stated that concentration of nitrate distributed non-uniformly and 40% and 20% of the samples exceed the maximum permissible limit (50 mg/L) in shallow and deep aquifers, respectively. Zhang et al. (2020) found that rapid increase in urbanization, leakages in domestic sewer lines and demolished waste from construction industries are the principal driving forces for nitrate contamination of groundwater in South China.

Soomro et al. (2017) carried out a study in occurrence and delineation of high nitrate contamination of groundwater in Thar Desert, Pakistan, and stated that 88.5% of the sample locations exceed the permissible limit recommended by the WHO for drinking purpose. Agriculture land leachates and livestock manure are the primary source of nitrate in open well in arid and semi-arid region of Pakistan (Ali et al. 2019; Balamurugan et al. 2020d; Soomro et al. 2017). However, in Indian background, approximately 85% of the population live in rural areas and they depend on groundwater for drinking and irrigation uses. Moreover, in southern part of India, it was estimated that 85% for drinking and 60% for irrigated agriculture water supplies are from the groundwater (AQUASTAT). Hence groundwater plays a vital role in human health and agriculture industry. Adimalla et al. (2019); Karunanidhi et al. (2019); Kumar et al. (2014); and Panneerselvam et al. (2020a) carried out the detailed investigation to assess the groundwater

quality and nitrate contamination in South India and commonly exposed that high densified residential region and rapid development in urban areas are highly affected due to elevated concentration of nitrate in groundwater, and listed that the significant sources of nitrate in South India are improper maintenance of sewer lines, uncovered septic tank and high usage of synthetic fertilizers. Panneerselvam et al. (2020a, b) carried out the detailed investigation on groundwater quality associated with human health risk due to high nitrate contamination in the semi-arid region of India and also reported that the major factors such as lithological and anthropogenic activities highly influenced the quality of groundwater in the study region (Kadhum et al. 2021a; Kalasha and Albayatib 2021).

The previous study focused to identify that nitrate contamination, source and health effects on human with three categories of Men, women and children. In the present study, the specific objectives were to (1) identify the contamination zone in the study area, (2) evaluate the source of pollution in the specific region, (3) integrate the nitrogen pollution index and human health risk assessment and (4) assess the human health risk of nitrate contamination in 6 different ages of peoples such as 6 to 12 months, 5 to 10 years, 10 to 15 years, 15 to 20 years, 20 to 60 years and more than 60 years (Albayati et al. 2019; Albayati and Abd Alkadir 2019). The novelty of the research is to integrate the nitrate pollution index and human health risk assessment with different age groups of peoples. The result and findings of the present study are helpful to decision makers to easily identify the different categories of people who were highly exposed to elevated nitrate in the study region (Albayati et al. 2014). The research objective is extended to increase the public and industry awareness in terms of waste disposal and its impact on ecological system.

Study area

Salem is a fast-developing city in north part of Tamil Nadu and it is located between latitude and longitude at an elevation of 278 m above the mean sea level. The study area is surrounded in four directions by hills, Nagarmalai on north, Jarugumalai on south, Kanjamalai on west and Godumalai on east. Physiography characteristics and drainage pattern of the study area are undulating and plain terrain at an elevation of 100 to 150 m from the mean sea level. The Vellar River is a source of surface water and also drain in the eastern part of study area. The climate of the city is generally hot and dry during the pre-monsoon (March to May). The relative humidity ranges between 40 and 80% from morning to evening. The average maximum temperature ranges from 26.7 to 38.56 °C and average minimum temperature ranges from 18.7 to 29.3 °C.

The average rainfall intensity was recorded as 967 mm per annum. The study area is rich in mineral deposit such as magnesite, bauxite, granite, limestone and quartz. The mineral-based active industries are Dalmia, MALCO, India Cements Limited and TATA refractories. It was noted that mining of minerals causes severe water and air pollution. Also, waste from mining industries is dumped into open land which also causes serious environmental issues. The products such as alumina silver ornaments and artefacts are the fast-growing industrial works in the study region.

Geological setting of study area

The entire study area can be classified as hard rock formation and about 90% of the area is underlain by Archaean age group. Figure 1 shows that gneissic type of formation

is the major formation among the various types of hard rocks. Quartz, feldspar, limestone and magnesite stone are major types of rock formation which are resistant to weathering also seen as patches in the surface of the charnockite and gneissic rocks. These rocks are grouped with migmatite complex and grey in colour at many places of the study region. The major geomorphic units were identified in the district through interpretation of satellite imagery, namely structural hill, shallow pediments and alluvial plain. The results of weathering of rocks are red soil, thin layered red soil and black loam. Magnesite and bauxite are the major minerals found in the northeast part of the study area. The reason for studying the geological formation and types of soil is to understand about the weathering of minerals into water and roughness and contact angle of the soil. The roughness of the soil affects the contact angle of a liquid passes through the pores in the earth layer (Kadhum et al. 2021a, b).

Fig. 1 Geological setting of study area

Hydrogeology

Groundwater occurs under phreatic conditions. The weathered, fissured and fractured crystalline rocks are identified as aquifer system in the study area. These aquifers comprise boulders, cobbles, gravels, sands and silt. The average thickness of aquifers is 35 m. The depth of bore well is in the range of 85 to 105 m with yield capacity of 100 to 600 L/min for domestic and irrigation uses. In the study area, groundwater is majorly used for domestic and irrigation purpose and secondary for industrial purpose. The maximum number of home bore well (individual) connections and over exploration of groundwater was noticed during the sample collection and filed surveying.

Sampling and analysis

A total of 40 sample locations were identified in the study area based on the densified residents, industrial area and waste dumping yards. The identified location water samples were regularly used for domestic uses. Before collecting the sample, the bore wells were continuously pumped for 20 min to avoid the influence of stagnant water in the pipe line. The samples were collected in pre-washed polyethylene bottles and sealed at the time of sampling. The analysis procedures are followed by standards recommended by the American Public Health Association (APHA 2005). The groundwater quality parameters such as pH, EC and TDS were measured in the sampling site using potable kit. The major cations, namely Ca^{2+} and Mg^{2+} , were estimated using EDTA followed by titration method; Na^+ and K^+ were calculated using flame photometer (S-931). The major anions, namely chloride, carbonate and bicarbonate, were estimated using silver nitrate and hydrochloric acid solution followed by titration method, respectively. SO_4^{2-} and NO_3^- were calculated using UV visible spectroscopy (LMSP UV1000B). Fluoride concentration was estimated using ion selective electrode at 25 °C. The ion balance error (IBE) methods were used in the present study to attain the accuracy in the analytic results of concentration of water quality parameters. Equation 1 was used to compute the IBE.

$$\text{IBE} = \frac{\sum \text{cations} - \sum \text{anions}}{\sum \text{cations} + \sum \text{anions}} \times 100 \quad (1)$$

Chadha plot

The formation of geological setting and environmental factors such as rainfall, evaporation rate, runoff and movement of water under the surface are the primary factors that govern

the concentration of ions in groundwater (Eyankware et al. 2020). The pictorial representation of hydrogeochemical, proposed by Chadha (1999), identifies the major influencing factor on groundwater quality. The quality parameters are converted into milliequivalent per litre to draw the Chadha plot of groundwater. The plot consists of four quadrants and each represents the influencing factors on groundwater quality and it is expressed as difference between $\text{Ca}^{2+} + \text{Mg}^{2+}$ (alkaline earth) and $\text{Na}^+ + \text{K}^+$ (alkali metals) for cations and the difference between $\text{HCO}_3^- + \text{CO}_3^{2-}$ (weak acidic) and $\text{Cl}^- + \text{SO}_4^{2-}$ (strong acidic) for anions. The four fields are recharging water ($\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$), reverse ion exchange water ($\text{Ca}^{2+}\text{-Mg}^{2+}\text{-Cl}^-$), sea water ($\text{Na}^+\text{-Cl}^-$) and base ion exchange water ($\text{Na}^+\text{-HCO}_3^-$). Recharging water field indicates that surface water enters into the subsurface which carries major ions such as Ca^{2+} , Mg^{2+} and HCO_3^- . Reverse ion exchange indicating that, excess concentration of $\text{Ca}^{2+} + \text{Mg}^{2+}$ mineral release from weathering of host rock. The base ion exchange indicating reactions of $\text{Ca}^{2+} + \text{Mg}^{2+}$ in groundwater and followed by adsorption of Na^+ from the mineral surfaces. Seawater types indicate that the study region is controlled by coastal area and possible way of sea water intrusion (Wagh et al. 2019).

Nitrate pollution index (NPI)

Nitrate is the one of the most commonly man-made pollutants into surface and groundwater sources. It is a serious issue to evaluate the human health impact and significant level of contamination in groundwater (Panneerselvam et al. 2020b). NPI is an effective tool to evaluate the pollution level in the groundwater. The maximum permissible level of threshold value of nitrate in groundwater is 20 mg/L. The concentration that exceeds the threshold value is considered NO_3^- -contaminated groundwater. Equation 2 was used to compute the value of NPI in groundwater;

$$\text{NPI} = \frac{C_s - \text{HAV}}{\text{HAV}} \quad (2)$$

where HAV is the threshold value of nitrate due to anthropogenic activities and it is taken as 20 mg/L, and C_s is the nitrate concentration of groundwater sample.

Human health risk assessment

Human health risk assessment is a significant method to evaluate the risk due to the excess concentration of chemical parameters in groundwater. It also reveals that negative impact on human health in the study region. The consumption of contaminated water can cause serious problem in

human health through diversities of exposures such as oral (direct consumption) and dermal contact (bathing and washing). The United States Environmental Protection Agency (USEPA 2006, 2014) recommended four steps to assess the health risk which are identification of hazards, dose response evaluation, exposure assessment and risk characterization. The main objective of the present study is to evaluate the risk due to nitrate-contaminated groundwater. In the study region, higher percentage of the population can be exposed to nitrate-contaminated water by both oral and dermal contact pathways. The chronic daily intake and dermally absorbed dose were calculated to estimate the doses received through specific pathways (Eqs. 3 and 4).

$$CDI = \frac{CPW \times IR \times ED \times EF}{ABW \times AET} \quad (3)$$

$$DAD = \frac{TC \times K_i \times EV \times ED \times EF \times SSA \times CF}{ABW \times AET} \quad (4)$$

The hazards quotient value for oral and dermal for the nitrate health risk assessment was calculated using the following Eqs. 5 and 6, where CDI is the chronic daily intake (mg/kg per day), DAD is the dermally absorbed dose (mg/kg per day) and RfD is the reference dose of a nitrate contamination which is 1.6 mg/kg per day (Table 1). The summation of hazards quotient for oral and dermal is total hazards index (HI_i). The total hazards value for all sample locations in the study area was computed using Eq. 8 and the value greater than 1 is significant risk, while less than 1 is no significant risk to non-carcinogenic risk on human health (Fig. 2).

$$HQ_{Oral} = \frac{CDI}{RfD} \quad (5)$$

$$HQ_{Dermal} = \frac{DAD}{RfD} \quad (6)$$

$$HI_i = HQ_{Oral} + HQ_{Dermal} \quad (7)$$

$$HI_{total} = \sum_{i=1}^n HI_i \quad (8)$$

Result and discussion

General hydrogeochemistry

The descriptive statistical analysis of groundwater in the study region is presented in Table 2. The concentration of hydrogen ions was expressed in terms of pH and it is significant parameter to evaluate the groundwater quality. In the present study, pH value varies from 6.9 to 8.69 with a mean of 7.93. About 5% of the sample locations exceed the maximum permissible limit of 6.5 to 8.5 recommended by the WHO (2017). EC concentration of groundwater in the study region ranged from 154 to 2475 µS/cm with an average of 855.95 µS/cm. The excess concentration of EC was observed in 6 sample locations and enhancement of salt concentration is medium. The concentration of TDS in groundwater varies from 116 to 1962 mg/L with a mean of 474.6 mg/L and about 32.5% of the sample locations exceed the permissible limit of 500 mg/L (WHO 2017). The statistical analysis result shows that the minimum and maximum concentrations of Ca²⁺, Mg²⁺, Na⁺ and K⁺ were 24 to 156 mg/L, 6.15 to 193.26 mg/L, 10 to 194 mg/L and 1 to 18 mg/L with a mean of 83.50 mg/L, 48.70 mg/L, 59.53 mg/L and 7.55 mg/L, respectively. About 60%, 37.5% and 17.5% of the sample locations exceed the permissible level of concentration of Ca²⁺, Mg²⁺ and K⁺, respectively, recommended by the WHO (2017). The concentrations of Na⁺ in all the sample locations fall under the permissible limit of 200 mg/L. Chloride concentration plays a vital role in groundwater quality and the

Table 1 Human health risk parameter value for different age groups of peoples

Parameters	Unit	6 to 12 months	Values for different age groups				
			5 to 10 years	10 to 15 years	15 to 20 years	20 to 60 years	> 60 years
Ingestion ratio (RI)	mL/day	0.8	1.35	1.9	2.2	2.94	2.6
Exposure duration (ED)	years	0.75	8	13	18	40	64
Frequency of exposure (EF)	days	365	365	365	365	365	365
Body weight (BW)	kg	11	25	35	55	76	65
Average age (AT)	days	274	2920	4745	6570	14,600	23,360
Contact duration (TC)	h/d	0.4	0.4	0.4	0.4	0.4	0.4
Dermal absorption (K _i)	cm/h	0.001	0.001	0.001	0.001	0.001	0.001
Frequency of bathing (EV)	times/day	1	1	1	1	1	1
Skin surface area (SSA)	cm ²	4500	10,500	15,700	19,550	19,800	19,400
Conversion factor (CF)	-	0.001	0.001	0.001	0.001	0.001	0.001

Fig. 2 Methodology for human health risk assessment

Table 2 Descriptive statistical analysis of groundwater in the study area

Parameter	Minimum	Maximum	Avg	WHO (2017)	BIS (2012)
pH	6.90	8.69	7.93	6.5–8.5	6.5–8.5
EC	154.00	2475.00	855.95	1500	-
TDS	116.00	1962.00	474.60	1500	2000
Ca ²⁺	24.00	156.00	83.50	200	200
Mg ²⁺	6.15	193.26	48.70	150	100
Na ⁺	10.00	194.00	59.53	200	-
K ⁺	1.00	18.00	7.55	10	-
Cl ⁻	104.00	565.00	215.46	250	1000
SO ₄ ²⁻	21.00	390.00	140.30	400	400
HCO ₃ ⁻	127.94	636.50	258.86	600	-
F ⁻	0.25	1.70	0.89	1.5	1.5
NO ₃ ⁻	24.00	78.00	46.45	50	45

concentration varies from 104 to 565 mg/L with a mean of 215.46 mg/L. In the study region, 40% of the sample location exceeds the acceptable level of 200 mg/L. Sulphate concentration of groundwater in the study region was within the permissible limit of 400 mg/L in all the sample

locations (Shunmugapriya et al. 2021). The concentration of bicarbonate varies from 172.94 to 636.5 mg/L with a mean of 258.86 mg/L. About 25% of the sample location exceeds the permissible limit of 300 mg/L. In the study region, about 50% of the sample locations exceed the permissible concentration of nitrate in groundwater. Fluoride concentration varies from 0.25 to 1.7 with a mean of 0.89 and only 7.5% of groundwater samples exceed the permissible limit of 1.5 mg/L recommended by the WHO (2017). The results divulged that the porosity and permeability of the soil layers plays a vital role in quality of groundwater. The porosity of the soil and permeability of soil influenced the quantity of water stored in the soil layers. It results the alteration of chemical composition of groundwater in the study area.

Groundwater type

The Chadha plot of groundwater in the study region divulged that 90% of the sample locations fall in the field of reverse ion exchange water which indicates Ca²⁺-Mg²⁺-Cl⁻ type, 5% of the sample locations fall in the field of recharging water which indicates

Fig. 3 Chadha plot of ground-water in study region

Ca^{2+} - Mg^{2+} - HCO_3^- and remaining 5% of sample locations fall in the field of sea water types which indicates Na-Cl type (Fig. 3). The major source of higher concentration of Ca, Mg and Cl in groundwater is weathering of parent rocks, ion exchange process and leaching of salts from the rocks. The problem identified in the study region is permanent hardness and it requires advanced method of treatment process such as reverse osmosis, base ion exchange process and desalination techniques to treat the groundwater before use (Jamshidzadeh 2020).

Concentration of nitrate in groundwater

The main aim of the research work is to evaluate the source, significant level and impact of nitrate on human health in the semi-arid region which includes industrial area. In the present study, concentration of nitrate varies from 24 to 78 mg/L with a mean of 46.45 mg/L. About 50% of the sample locations exceed the permissible limit of 45 mg/L recommended by the WHO (2011 and 2017). A spatial analysis of nitrate concentration revealed that 52.56 sq.km of area is suitable and 91.14 sq.km of area fall under the unsuitable category for drinking purpose in the study area (Fig. 4a). Excessive concentration of nitrate will accelerate the growth of algae and aquatic plants in water bodies. The result of this organism growth is eutrophication which causes harmful algal blooms, fish transience and water column anoxia, all of which have a negative impact on environmental quality human health and increased the water demand for agriculture uses (Panneerselvam et al. 2021a, b).

NPI of groundwater

NPI of groundwater sample were calculated and presented in Table 3. The NPI classification of groundwater revealed that 42.5% of sample location is light pollution, 40% of sample location is moderate pollution and 17.5% of sample locations is significant pollution in the study region. The result of the spatial analysis shows that 21.75 sq.km of area is light, 117.44 sq.km of area is moderate and 4.33 sq.km of area is significant pollution level (Fig. 4b). It indicates that diffuse source of nitrate such as excessive usage of synthetic fertilizers for crop yield and improper management of nitrogen source in the agriculture filed increases the leaching rate and concentration of nitrate into groundwater (Obeidat et al. 2012; Panneerselvam et al. 2021a). The transformations of nitrate into the groundwater are leaching of higher percentage of nitrate from the root zone of plant.

Correlation of nitrate with major ions

Correlation matrix and diagram showing the correlation coefficient between the nitrate with major ions such as calcium, magnesium, sodium, potassium, chloride, fluoride, bicarbonate and sulphate. In the present study, nitrate positively correlates with calcium ($r=0.02$) and magnesium ($r=0.05$) which indicates that rock water interaction and weathering of parental rock contribute to elevate the concentration of nitrate in groundwater (Fig. 5a and b). Nitrate shows positively correlated with sodium ($r=0.04$) and potassium ($r=0.12$); it confirmed that excess utilization of nitrogen-, phosphorus- and

Fig. 4 a Concentration of nitrate in groundwater, b NPI classification of groundwater

potassium-rich fertilizers in agricultural field for increasing the crop yield (Balamurugan et al. 2021) and residential and industrial waste disposal contribute to the enhancement of the concentration of nitrate in groundwater (Fig. 5c and d). Nitrate negatively correlate with major anions such as chloride ($r = -0.17$), bicarbonate ($r = -0.18$) and sulphate ($r = -0.08$) it conveyed that increases in rainfall infiltrate rate, sewage water intrusion, and uncovered septic tank increases nitrate level in groundwater respectively (Fig. 5e, f and h). Nitrate positively correlated with fluoride ($r = 0.13$) confirmed that man-made source of predominant condition of leaching effects increases the concentration of nitrate in groundwater (Fig. 5g).

Source of nitrate in the study area

The source of nitrate contamination of groundwater in the study area was identified through field visit and based on groundwater quality. The source was classified into two types, namely diffused and point source. The diffused source of nitrate contamination was identified in the rural area of the study region. The peoples were highly depending on synthetic fertilizers for crop yield and followed the modern methods of agriculture techniques such as usage of nitrogen-based fertilizers such as urea and feathers which contain approximately 45% and 15% of nitrogen (Kouadri et al. 2021; Pande et al. 2021). The plant roots absorbed the nitrogen and higher percentage of nitrate can be released to the soil. Another source of nitrate found in the study area is

anthropogenic activities such as uncovered septic tanks, livestock waste disposal, improper maintenance of open well, waste disposal from the residents and mining activities.

Human health risk assessment

The USEPA suggested that concentration of nitrate exceeds the limit of 45 mg/L which can cause serious health issue on human bodies. It developed a model to evaluate the impact of nitrate in two different ways of injection, namely oral and thermal. In the present study, the human population has been classified into six categories such as 6–12 months, 5–10 years, 10–15 years, 15–20 years, 20–60 years and greater than 60 years. The summation of oral and thermal hazards value has been calculated for each group of peoples in the study region. The THI values vary from $1.10\text{E}+00$ to $4.00\text{E}+01$ with a mean of $2.12\text{E}+00$, $8.23\text{E}-01$ to $1.00\text{E}+02$

Table 3 NPI classification of groundwater sample in the study area

Range	Class of water	No of samples	Percentage of samples
Less than 0	Clean	0	0
0–1	Light pollution	17	42.5
1–2	Moderate pollution	16	40
2–3	Significant pollution	7	17.5
> 3	Very significant pollution	0	0

Fig. 5 Correlation plot for nitrate with **a** Ca²⁺, **b** Mg²⁺, **c** Na⁺, **d** K⁺, **e** Cl⁻, **f** F⁻, **g** HCO₃⁻, **h** SO₄²⁻

with a mean of 1.58E+00, 8.28E-01 to 9.00E+01 with a mean of 1.59E+00, 6.11E-01 to 5.75E+01 with a mean of 1.17E+00, 5.88E-01 to 5.50E+01 with a mean of 1.13E+00

and 6.09E-01 to 5.75E+01 with a mean of 1.17E+00 for the six different age groups, respectively (Table 4). The result shows that all the groundwater samples can cause health

effects for 6–12 months (infants) and 5–10 years (children), 90% of the samples can cause health effects for 10–15 years, 57.50% of samples can cause health effects for 15–20 years, 55% of samples can cause health effects for 20–60 years and 57.50% of samples can cause health effects for greater than 60 years. The spatial analysis revealed that 144.09 sq.km of area is risk for 6–12 months; 0.80 sq.km of area is safe and

143.30 sq.km of area is risk for 5–10 years; 85.40 sq.km of area is safe and 58.69 sq.km of area is risk for 10–15 years; 13.57 sq.km of area is safe and 130.53 sq.km of area is risk for 15–20 years; 20.72 sq.km of area is safe and 123.39 sq.km of area is risk for 20–60 years; and 13.80 sq.km of area is safe and 130.31 sq.km of area is risk for greater than 60 years of peoples (Fig. 6).

Table 4 Health risk assessment of various age groups of peoples in the study area

Sample ID	6 to 12 months	5 to 10 years	10 to 15 years	15 to 20 years	20 to 60 years	> 60 years
S1	2.64E+00	1.97E+00	1.98E+00	1.46E+00	1.41E+00	1.46E+00
S2	3.56E+00	2.65E+00	2.66E+00	1.96E+00	1.90E+00	1.96E+00
S3	1.19E+00	8.83E-01	8.88E-01	6.55E-01	6.32E-01	6.54E-01
S4	3.14E+00	2.33E+00	2.35E+00	1.73E+00	1.67E+00	1.73E+00
S5	2.18E+00	1.63E+00	1.63E+00	1.20E+00	1.16E+00	1.20E+00
S6	2.87E+00	2.14E+00	2.15E+00	1.58E+00	1.53E+00	1.58E+00
S7	2.06E+00	1.53E+00	1.54E+00	1.14E+00	1.10E+00	1.13E+00
S8	1.14E+00	8.53E-01	8.59E-01	6.33E-01	6.10E-01	6.32E-01
S9	1.10E+00	8.23E-01	8.28E-01	6.11E-01	5.88E-01	6.09E-01
S10	2.10E+00	1.57E+00	1.58E+00	1.16E+00	1.12E+00	1.16E+00
S11	1.91E+00	1.43E+00	1.43E+00	1.06E+00	1.02E+00	1.06E+00
S12	1.96E+00	1.46E+00	1.47E+00	1.08E+00	1.04E+00	1.08E+00
S13	2.91E+00	2.17E+00	2.18E+00	1.61E+00	1.55E+00	1.60E+00
S14	2.10E+00	1.56E+00	1.57E+00	1.16E+00	1.12E+00	1.16E+00
S15	2.42E+00	1.80E+00	1.81E+00	1.33E+00	1.29E+00	1.33E+00
S16	1.46E+00	1.09E+00	1.09E+00	8.07E-01	7.79E-01	8.06E-01
S17	2.82E+00	2.10E+00	2.11E+00	1.56E+00	1.50E+00	1.56E+00
S18	3.10E+00	2.30E+00	2.32E+00	1.71E+00	1.65E+00	1.71E+00
S19	2.46E+00	1.83E+00	1.84E+00	1.36E+00	1.31E+00	1.36E+00
S20	2.32E+00	1.73E+00	1.74E+00	1.28E+00	1.24E+00	1.28E+00
S21	1.69E+00	1.26E+00	1.27E+00	9.35E-01	9.02E-01	9.34E-01
S22	1.83E+00	1.36E+00	1.37E+00	1.01E+00	9.74E-01	1.01E+00
S23	1.19E+00	8.86E-01	8.91E-01	6.57E-01	6.34E-01	6.56E-01
S24	1.74E+00	1.29E+00	1.30E+00	9.59E-01	9.25E-01	9.57E-01
S25	1.78E+00	1.32E+00	1.33E+00	9.82E-01	9.48E-01	9.81E-01
S26	2.55E+00	1.90E+00	1.91E+00	1.41E+00	1.36E+00	1.41E+00
S27	2.09E+00	1.56E+00	1.57E+00	1.15E+00	1.12E+00	1.15E+00
S28	1.69E+00	1.26E+00	1.27E+00	9.37E-01	9.03E-01	9.35E-01
S29	1.73E+00	1.29E+00	1.30E+00	9.57E-01	9.24E-01	9.56E-01
S30	1.60E+00	1.19E+00	1.20E+00	8.82E-01	8.51E-01	8.81E-01
S31	2.19E+00	1.63E+00	1.64E+00	1.21E+00	1.17E+00	1.21E+00
S32	2.69E+00	2.00E+00	2.01E+00	1.48E+00	1.43E+00	1.48E+00
S33	2.96E+00	2.20E+00	2.22E+00	1.63E+00	1.58E+00	1.63E+00
S34	1.74E+00	1.29E+00	1.30E+00	9.59E-01	9.26E-01	9.58E-01
S35	1.78E+00	1.33E+00	1.34E+00	9.84E-01	9.50E-01	9.83E-01
S36	2.37E+00	1.77E+00	1.78E+00	1.31E+00	1.26E+00	1.31E+00
S37	2.69E+00	2.00E+00	2.02E+00	1.49E+00	1.43E+00	1.48E+00
S38	1.64E+00	1.22E+00	1.23E+00	9.06E-01	8.75E-01	9.05E-01
S39	1.69E+00	1.26E+00	1.27E+00	9.37E-01	9.03E-01	9.35E-01
S40	1.65E+00	1.23E+00	1.24E+00	9.12E-01	8.79E-01	9.10E-01

Fig. 6 Human health risk assessment of groundwater in the study area

Health effects among the different age group of peoples

The continuous consumption of elevated concentration of nitrate in groundwater can cause serious effects on human among the different age groups of peoples. The impact on 6–12 months is infant methemoglobinemia which is a life-threatening disease among the infants; on 5–10 years group of people, type 1 childhood diabetes, blood pressure and acute respiratory infection; on 10–20 years group of people, prematurity, blood pressure, acidity, following of vasodilation, antithrombotic and immunoregulatory effects (Zeman et al. 2011; Aschebrook-Kilfoy et al. 2012; Benson et al. 2010; Ward et al. 2010); on 20–60 years group of people, pregnancy-related

issues such as spontaneous abortion, foetal deaths, intrauterine growth retardation, low birth weight, congenital malformation and neonatal deaths; and on greater than 60 age groups of peoples, they can be affected by cardiovascular hypertrophy, heart attack, heart diseases, myocardial infraction and lipid peroxidation in the retina (Garcia Torres et al. 2020; Manassaram et al. 2010; Migeot et al. 2013; Abu Naser et al. 2007).

Recommendation

The study recommended to create an awareness to the farmer to use organic fertilizers (OF). The OF has the more advantage than synthetic fertilizers such as it does

not make an impermeable skin to the surface of the soil layer. It improves the water carrying capacity of soil, retention time and structure of soil. It also recommended the people who are working in the water management system to inspect the water pipe line, sewage lines and create a knowledge about the impacts of waste disposal into open land. The research and study also suggested to treat the nitrate-contaminated groundwater before use for domestic purpose. In recent days, reverse osmosis and biological de-nitrification methods are more effective method to treat the high nitrate groundwater. The cost and method of treatment for excess nitrate in groundwater is the future scope of the present study.

Conclusion

The present study carried out the detailed investigation of impact of nitrate on human health among the various age groups of peoples. In general, nitrate is a most significant issue in southern part of India and it causes serious effects on human health. The study concluded the following:

- Groundwater geochemistry revealed that chloride was exceeding the acceptable level of 200 mg/L in 40% of the sample location and 50% of the sample locations exceed the permissible concentration of nitrate in groundwater.
- Chadha plot represented that the major sources of higher concentration of Ca, Mg and Cl in groundwater are weathering of parent rocks, ion exchange process and leaching of salts from the rocks. The NPI value divulged that 40% of sample location is moderate pollution and 17.5% of sample locations is significant pollution in the study region.
- Human health risk assessment divulged that methemoglobinemia, cardiovascular hypertrophy, heart attack, heart diseases, myocardial infraction and lipid peroxidation in the retina are the major health effects identified in the study region.
- The major sources identified in the study region are diffused source such as usage of nitrogen rich fertilizers, livestock and non-point source such as uncovered septic tank, leakages in sewage pipe lines, improper method of house hold disposal and mining activities.

Data availability Not applicable.

Declarations

Conflict of interest The authors declare no competing interests.

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References

- Abd Al-Khodori YA, Albayati TM (2020) Employing sodium hydroxide in desulfurization of the actual heavy crude oil: theoretical optimization and experimental evaluation. *Process Saf Environ Prot* 136:334–342
- Abu Naser AA, Ghbn N, Khoudary R (2007) Relation of nitrate contamination of groundwater with methaemoglobin level among infants in Gaza. *East Mediterr Health J* 13:994–1004. <https://doi.org/10.26719/2007.13.5.994>
- Adimalla N (2020) Spatial distribution, exposure, and potential health risk assessment from nitrate in drinking water from semi-arid region of South India. *Hum Ecol Risk Assess Int J* 26(2):310–334
- Adimalla N, Li P, Qian H (2019) Evaluation of groundwater contamination for fluoride and nitrate in semi-arid region of Nirmal Province, South India: a special emphasis on human health risk assessment (HHRA). *Hum Ecol Risk Assess Int J* 25(5):1107–1124
- Alardhi SM, Albayati TM, Alrubaye JM (2020a) A hybrid adsorption membrane process for removal of dye from synthetic and actual wastewater. *Chem Eng Process: Process Intensif* 157:108113
- Alardhi SM, Albayati TM, Alrubaye JM (2020b) Adsorption of the methyl green dye pollutant from aqueous solution using mesoporous materials MCM-41 in a fixed-bed column. *Heliyon* 6(1):e03253
- Alardhi SM, Alrubaye JM, Albayati TM (2020c) Adsorption of Methyl Green dye onto MCM-41: equilibrium, kinetics and thermodynamic studies. *Desalination Water Treat* 179:323–331
- Alardhi, S. M., Alrubaye, J. M., & Albayati, T. M. (2020d). Removal of methyl green dye from simulated waste water using hollow fiber ultrafiltration membrane. In *IOP Conference Series: Materials Science and Engineering* (Vol. 928, No. 5, p. 052020). IOP Publishing.
- Albayati TM, Abd Alkadir AJ (2019) Synthesis and characterization of mesoporous materials as a carrier and release of prednisolone in drug delivery system. *J Drug Deliv Sci Technol* 53:101176
- Albayati TM, Doyle AM (2013) Shape-selective adsorption of substituted aniline pollutants from wastewater. *Adsorpt Sci Technol* 31(5):459–468
- Albayati TM, Doyle AM (2015) Encapsulated heterogeneous base catalysts onto SBA-15 nanoporous material as highly active catalysts in the transesterification of sunflower oil to biodiesel. *J Nanopart Res* 17(2):1–10
- Albayati TM, Wilkinson SE, Garforth AA, Doyle AM (2014) Heterogeneous alkane reactions over nanoporous catalysts. *Transp Porous Media* 104(2):315–333
- Albayati TM, Sabri AA, Abed DB (2019) Adsorption of binary and multi heavy metals ions from aqueous solution by amine functionalized SBA-15 mesoporous adsorbent in a batch system. *Water Treat* 151(315):e321

- Albayati TM, Sabri AA, Abed DB (2020) Functionalized SBA-15 by amine group for removal of Ni (II) heavy metal ion in the batch adsorption system. *Desalination Water Treat* 174:301–310
- Ali W, Rasool A, Junaid M, Zhang H (2019) A comprehensive review on current status, mechanism, and possible sources of arsenic contamination in groundwater: a global perspective with prominence of Pakistan scenario. *Environ Geochem Health* 41(2):737–760
- APHA (2005) Standard methods for the examination of water and wastewater, 21st edn. New York
- AQUASTAT, 2010. Water Resources Development and Management Service. Food and Agriculture Organization of the United Nations, Rome, Italy and Available at: <http://www.fao.org/nr/water/aquastat/main/index.stm>, Accessed date: 27 March 2015.
- Aschebrook-Kilfoy B, Heltshe SL, Nuckols JR, Sabra MM, Shuldiner AR, Mitchell BD, Airola M, Holford TR, Zhang Y, Ward MH (2012) Modeled nitrate levels in well water supplies and prevalence of abnormal thyroid conditions among the Old Order Amish in Pennsylvania. *Environ Health* 11:6. <https://doi.org/10.1186/1476-069X-11-6>
- Balamurugan P, Balakumaran S (2015) Soil quality assessment around magnesite mines and Salem township using GIS techniques. *Int J Adv Eng Technol* 8(1):1997
- Balamurugan P, Kumar PS (2016) Quality of ground water assessment in Salem District using GIS Techniques. *Adv Nat Appl Sci* 10(3):22–32
- Balamurugan P, Kumar PS, Shankar K (2020b) Dataset on the suitability of groundwater for drinking and irrigation purposes in the Sarabanga River region, Tamil Nadu India. *Data in Brief* 29:105255. <https://doi.org/10.1016/j.dib.2020.105255>
- Balamurugan P, Kumar PS, Shankar K, Nagavinothini R, Vijayasurya K (2020c) Non-Carcinogenic risk assessment of groundwater in southern part of Salem district in Tamilnadu, India. *J Chil Chem Soc* 65(1):4697–4707. <https://doi.org/10.4067/S0717-97072020000104697>
- Balamurugan P, Kumar P.S, Shankar K, Sajil Kumar PJ (2020), Impact of climate and anthropogenic activities on groundwater quality for domestic and irrigation purposes in Attur region, Tamilnadu, India, *Desalination and Water Treatment*, 208, 172–195.
- Balamurugan P.K. Shunmugapriya and R.Vanitha (2020d), GIS Based Assessment of Ground Water for Domestic and Irrigation Purpose in Vazhapadi Taluk, Salem, Tamil Nadu, India, *Taiwan Water Conservancy*, 68(2), 1–10.
- Balamurugan, P., Pauline, S., Kirubakaran, M., & Thomas, M. (2021). Assessment of inverse fluidized bed reactor on the treatment efficiency of distillery spent wash water. *International Journal of Environmental Science and Technology*, 1–14.
- Benson VS, Vanleeuwen JA, Taylor J, Somers GS, McKinney PA, Van Til L (2010) Type 1 diabetes mellitus and components in drinking water and diet: a population-based, case-control study in Prince Edward Island Canada. *J Am Coll Nutr* 29:612–624. <https://doi.org/10.1080/07315724.2010.10719900>
- BIS (2012) Indian standards specification for drinking water, BIS: 10500: 2012. <http://www.cgwb.gov.in/Documents/WQ-standards.pdf>. Accessed 15 Oct 2021
- Chadha DK (1999) A proposed new diagram for geochemical classification of natural waters and interpretation of chemical data. *Hydrogeol J* 7:431–439. <https://doi.org/10.1007/s100400050216>
- Doyle TMAAM (2015) Erratum to: encapsulated heterogeneous base catalysts onto SBA-15 nanoporous material as highly active catalysts in the transesterification of sunflower oil to biodiesel. *J Nanopart Res* 17:269
- Eyankware, M. O., Aleke, C. G., Selema, A. O. I., & Nnabo, P. N. (2020). Hydrogeochemical studies and suitability assessment of groundwater quality for irrigation at Warri and environs., Niger delta basin, Nigeria. *Groundwater for Sustainable Development*, 10, 100293.
- Garcia Torres, E., Perez Morales, R., Gonzalez Zamora, A., Rios Sanchez, E., Olivas Calderon, E. H., Alba Romero, J. D. J., & Calleros Rincon, E. Y. (2020). Consumption of water contaminated by nitrate and its deleterious effects on the human thyroid gland: a review and update. *International Journal of Environmental Health Research*, 1–18.
- Gutierrez, M., Biagioni, R.N., Alarcón-Herrera, M.T., Rivas-Lucero, B.A., 2018. An overview of nitrate sources and operating processes in arid and semiarid aquifer systems. *Sci. Total Environ.* 624, 1513–1522.
- Jamshidzadeh Z (2020) An integrated approach of hydrogeochemistry, statistical analysis, and drinking water quality index for groundwater assessment. *Environ Process* 7(3):781–804
- Kadhum ST, Alkindi GY, Albayati TM (2021a) Eco friendly adsorbents for removal of phenol from aqueous solution employing nanoparticle zero-valent iron synthesized from modified green tea bio-waste and supported on silty clay. *Chin J Chem Eng* 36:19–28
- Kadhum, S. T., Alkindi, G. Y., & Albayati, T. M. (2021). Remediation of phenolic wastewater implementing nano zerovalent iron as a granular third electrode in an electrochemical reactor. *International Journal of Environmental Science and Technology*, 1–10.
- Kalasha KR, Albayati TM (2021) Remediation of oil refinery wastewater implementing functionalized mesoporous materials MCM-41 in batch and continuous adsorption process. *Desalin Water Treat* 220:130–141
- Karunanidhi D, Aravinthasamy P, Subramani T, Wu J, Srinivasamoorthy K (2019) Potential health risk assessment for fluoride and nitrate contamination in hard rock aquifers of Shanmuganadhi River basin, South India. *Hum Ecol Risk Assess Int J* 25(1–2):250–270
- Khader EH, Mohammed TJ, Albayati TM (2021) Comparative performance between rice husk and granular activated carbon for the removal of azo tartrazine dye from aqueous solution. *Desalin Water Treat* 229:372–383
- Kouadri, S., Pande, C. B., Panneerselvam, B., Moharir, K. N., & Elbeltagi, A. (2021). Prediction of irrigation groundwater quality parameters using ANN, LSTM, and MLR models. *Environmental Science and Pollution Research*, 1–25.
- Kumar PS, Balamurugan P (2018) Evaluation of groundwater quality for irrigation purpose in Attur taluk, Salem, Tamilnadu, India. *Water Energy Int* 61(4):59–64
- Kumar PS, Jegathambal P, James EJ (2014) Chemometric evaluation of nitrate contamination in the groundwater of a hard rock area in Dharapuram, south India. *Appl Water Sci* 4(4):397–405
- Kumar, P. S., & Balamurugan, P. (2019). Suitability of Ground Water for Irrigation Purpose in. Omalur Taluk, Salem, Tamil Nadu, India. *Indian Journal of Ecology*, 46(1), 1–6.
- Manassaram DM, Backer LC, Messing R, Fleming LE, Luke B, Monteilh CP (2010) Nitrates in drinking water and methemoglobin levels in pregnancy: a longitudinal study. *Environ Health* 9:60. <https://doi.org/10.1186/1476-069X-9-60>
- Migeot V, Albouy-Llaty M, Carles C, Limousi F, Strezlec S, Dupuis A, Rabouan S (2013) Drinking-water exposure to a mixture of nitrate and low-dose atrazine metabolites and small-for-gestational age (SGA) babies: a historic cohort study. *Environ Res* 122:58–64. <https://doi.org/10.1016/j.envres.2012.12.007>
- Obeidat, M. M., Awawdeh, M., Al-Rub, F. A., & Al-Ajlouni, A. (2012). An innovative nitrate pollution index and multivariate statistical investigations of groundwater chemical quality of Umm Rijam Aquifer (B4), North Yarmouk River Basin, Jordan. *Vouddouris K, Voutsas D. Water Quality Monitoring and Assessment. Croatia: InTech*, 169–188.
- Pande, C. B., Moharir, K. N., Panneerselvam, B., Singh, S. K., Elbeltagi, A., Pham, Q. B., ... & Rajesh, J. (2021). Delineation

- of groundwater potential zones for sustainable development and planning using analytical hierarchy process (AHP), and MIF techniques. *Applied Water Science*, 11(12), 1–20.
- Panneerselvam B, Paramasivam SK, Karuppannan S, Ravichandran N, Selvaraj P (2020b) A GIS-based evaluation of hydrochemical characterisation of groundwater in hard rock region, South Tamil Nadu, India. *Arab J Geosci* 13(17):1–22. <https://doi.org/10.1007/s12517-020-05813-w>
- Panneerselvam B, Muniraj K, Thomas M, Ravichandran N, Bidorn B (2021) Identifying influencing groundwater parameter on human health associate with irrigation indices using the Automatic Linear Model (ALM) in a semi-arid region in India. *Environ Res* 202:111778
- Panneerselvam, B., Karuppannan, S., & Muniraj, K. (2020b). Evaluation of drinking and irrigation suitability of groundwater with special emphasizing the health risk posed by nitrate contamination using nitrate pollution index (NPI) and human health risk assessment (HHRA). *Human and Ecological Risk Assessment: An International Journal*, 1–25.
- Panneerselvam, B., Muniraj, K., Pande, C., Ravichandran, N., Thomas, M., & Karuppannan, S. (2021). Geochemical evaluation and human health risk assessment of nitrate-contaminated groundwater in an industrial area of South India. *Environmental Science and Pollution Research*, 1–18.
- Shunmugapriya K, Panneerselvam B, Muniraj K, Ravichandran N, Prasath P, Thomas M, Duraisamy K (2021) Integration of multi criteria decision analysis and GIS for evaluating the site suitability for aquaculture in southern coastal region, India. *Mar Pollut Bull* 172:112907
- Soomro F, Rafique T, Michalski G, Ali SA, Naseem S, Khan MU (2017) Occurrence and delineation of high nitrate contamination in the groundwater of Mithi sub-district, Thar Desert, Pakistan. *Environ Earth Sci* 76(10):355
- U.S. EPA. 2006. USEPA Region III Risk-based Concentration Table: technical background information. United States Environmental Protection Agency, Washington, DC
- U.S. EPA. 2014. Human Health Evaluation Manual, Supplemental Guidance: update of standard default exposure factors-OSWER Directive 9200.1-120. PP.6
- Wagh VM, Mukate SV, Panaskar DB, Muley AA, Sahu UL (2019) Study of groundwater hydrochemistry and drinking suitability through Water Quality Index (WQI) modelling in Kadava river basin India. *SN Applied Sciences* 1(10):1251
- Ward MH, Kilfoy BA, Weyer PJ, Anderson KE, Folsom AR, Cerhan JR (2010) Nitrate intake and the risk of thyroid cancer and thyroid disease. *Epidemiology* 21:389–395. <https://doi.org/10.1097/EDE.0b013e3181d6201d>
- WHO (2017) Guidelines for drinking water quality, 4th edition incorporating the first addendum. World Health Organization, Geneva
- Zeman C, Beltz L, Linda M, Maddux J, Depken D, Orr J, Theran P (2011) New questions and insights into nitrate/nitrite and human health effects: a retrospective cohort study of private well users' immunological and wellness status. *J Environ Health* 74:8–18
- Zhang M, Huang G, Liu C, Zhang Y, Chen Z, Wang J (2020) Distributions and origins of nitrate, nitrite, and ammonium in various aquifers in an urbanized coastal area, south China. *J Hydrol* 582:124528