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Source apportionment and health risk assessment of nitrate in foothill aquifers of Western Ghats, South India

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ABSTRACT

The present research reports the level of nitrate (NO_3^-), associated health risks and possible sources of contamination in groundwater from south India. Many samples (32%) are above or approaching the recommended level of NO_3^- for safe drinking water. The correlation analysis indicates different sources of NO_3^- contamination in different regions rather than a common origin. The isotopic measurements provide information about potential nitrogen sources contributing NO_3^- to the groundwater. Based on isotope analysis, the sources of NO_3^- in the groundwater of this region are likely to be from (a) septic sewage (b) organic nitrogen (animal and livestock excreta) (c) sewage (domestic & chemical fertilizers). Among the sample analyzed sewage, manure and septic sewage contribute 46%, 23% and 31% NO_3^- to groundwater. The HQ > 1 indicates non-carcinogenic health risk due to consumption of high NO_3^- in drinking water. Among the studied age groups, infants are exposed to higher risk than children and adults. Results indicate that groundwater of this region is polluted with NO_3^- due to anthropogenic activities. Continuous consumption of such water may pose serious health risk to the residents.

1. Introduction

Excess application of nitrogen as fertilizer and animal waste to soil and improperly designed septic tank system leads to leaching of nitrate (NO_3^-) through the unsaturated zone to the water table. Contamination of groundwater with NO_3^- leads to a significant environmental problems and health hazards when water is used for drinking (WHO, 2007). NO_3^- is considered as both non-point and point source pollutant of groundwater worldwide. Major non-point sources of NO_3^- in natural water are commonly found to be fertilizer or human and animal wastes, etc. The predominant point sources include, domestic sewage discharges, cess pools and dairy lagoons. Many studies have reported high NO_3^- concentrations in areas with cess-pools (Daniel, 2018; Adimalla and Qian, 2021). The extent of contamination in groundwater, consequences to NO_3^- pollution is well-documented (Huno et al., 2018; Adimalla and Qian, 2021).

Studies have reported the spatial distribution of health risk due to excess NO_3^- in drinking water and identified several hot spots worldwide (Anornu et al., 2017; Ahmed et al., 2019) and also there are several reports on health risk assessment of groundwater by considering the hydrochemical parameters, trace metals etc. (He et al., 2020; Elumalai et al., 2020). The development of methemoglobinemia in children as well as adults is the major concern due to high consumption of nitrate present in drinking water. Thus, many researchers have carried out the health risk assessment by calculating health quotient (HQ) in groundwater (Rahman et al., 2021). Researchers have focused on identification of nitrogen sources leading to NO_3^- contamination in groundwater through various processes including hydro chemical, statistics, and stable isotopic approach (Clague et al., 2015; Xu et al., 2015; Elumalai et al., 2020). The literature reveals the utility of measuring nitrogen isotopes in saturated and unsaturated zones helps in identifying the major sources of nitrate in groundwater (Kendall and Aravena, 2000; Jung et al., 2020). Recent studies have addressed the occurrence of NO_3^- derived from agricultural sources based on mixing models, considering

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the isotopes of oxygen and nitrogen in NO_3^- and stable isotopes of water (Jung et al., 2020) Much of this scientific work have focused on investigating the parameter's fate in the soil root zone and potential for leaching as related to agricultural crops and improved management practices.

The present study area investigates nitrate contamination in a region of the Tirunelveli district of South India with a local population of around 70,000 (District Census Handbook, 2011). During the non-monsoon period, the groundwater serves as the only source for entire habitants to cater to their domestic and drinking purpose. The study area is also a region of tourist attraction and there is fluctuating population around ~ 0.9 million estimated per year, thus the area tourist industry depends on groundwater for drinking and domestic needs (District Census book, 2011). Several previous studies (Jeyaseelan et al., 2013; Sidhardhan et al., 2015) have assessed the potential yield and sustainability of the aquifer in selected patches of Tirunelveli District. A pre-monsoon (PRM) data of the region was utilized to identify the process of recharge in the mountain front (MF) and riparian zone (RZ) in the northwestern (NW) part of the Tirunelveli District (Panda et al., 2017). Later northeast monsoon (NEM) water levels were measured in conjunction with analysis of rainfall and water isotopes by Panda et al. (2018) to understand the aquifer response to seasonal rainfall, variation of geochemistry and water level. Geophysical investigations have delineated potential zones for construction of new borehole wells (Panda et al., 2017). Later, both PRM and post monsoon (POM) hydrochemical data was compared along with stable isotopes of selected samples in groundwater, amount of rainfall and water level fluctuation to obtain a holistic view of the processes governing hydrochemical variations (Panda et al., 2019). An outcome of these studies is that elevated NO_3^- concentrations occur in several locations of the study area suggesting contamination from surface sources. Determination of pollutant sources like NO_3^- will help to better manage water quality and potential health effect. Thus, the main objectives of the study are:

- To determine the interrelationship of NO_3^- concentration with other ions in groundwater.
- To evaluate the potential sources of NO_3^- in groundwater using integrated techniques.
- To perform a health risk assessment in different age group due to consumption of local groundwater.

2. Study area

The study is conducted along the NW part of Tirunelveli District, in

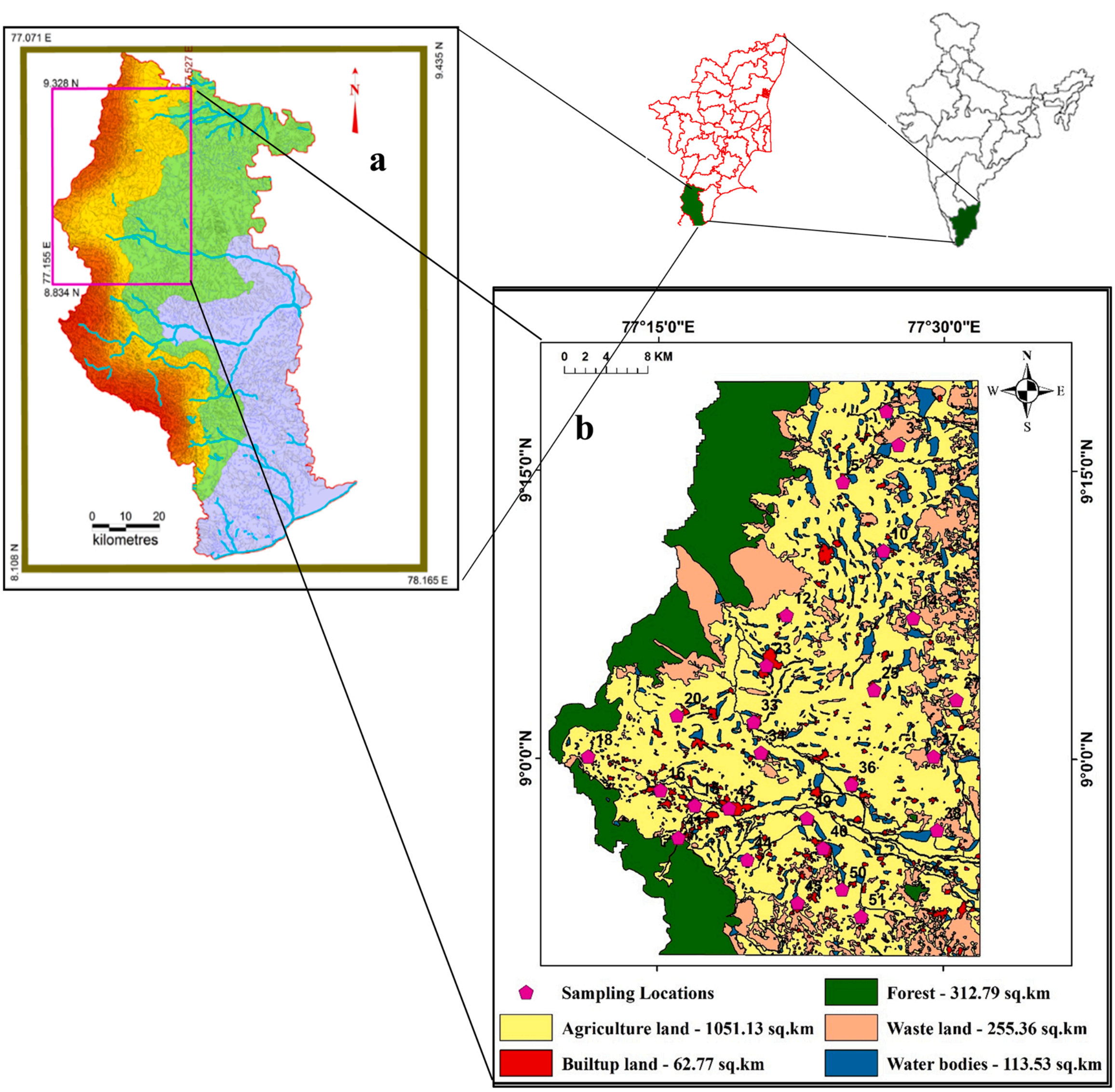

Fig. 1. : Location map representing (a) Elevation (b) Land use patterns with groundwater sampling locations.

the foothills of Courtallam, Tamil Nadu, South India (Fig. 1). The study area is an elevated region with an altitude variation of from 150 m to 1700 m above mean sea level (amsl), endowed with steep slopes and narrow valleys (Panda et al., 2017). The amount of rainfall in 8 stations in the study area have been recorded and the average was 918 mm/year (CGWB, 2009). The NEM comprised 70% of total rainfall and rest 30% attributed by southwest monsoon (SWM), POM and PRM (CGWB, 2009). The PRM water table depth varied between 2.1 and 16 m below ground level (mbgl) and in POM between 0.91 and 16 mbgl (Panda et al., 2017). Groundwater in the study area is mainly drawn from fractured and highly weathered igneous and metamorphic rocks like Charnockites, Fissile Hornblende Biotite Gneisses (FHBG) and actinolite-tremolite schist with a heterogeneous areal extent for each litho-unit. Lineaments are the weak structural planes and formed by a structural disturbance along fracture, partings and joints, thus, considered favorable for groundwater flow and are predominant along the study area's SW-SE direction. The predominant lineaments are also noticed in FHBG litho-units. Thus, charnockites are considered as less weathered, jointed or fractured than the FHBG (Subramani, 2005). Aquifer characteristics like yield of wells, transmissivity, hydraulic conductivity, specific yield and storativity are higher in porous formation followed by fractured and weathered formations are reported separately (Panda et al., 2017). The area comprised of pediplain, piedmont zone, structural hill and denudational hill as the major geomorphological units (Panda et al., 2017). The Chittar River is considered as the major drainage system in the area, which is a non-perennial river, originating from the Courtallam Hills of Western Ghats. The structural trends along SW-SE and considered as the water flow direction of the study area (Panda et al., 2017).

Land use and land cover patterns are categorized into agricultural land, water bodies; waste land, forest and build-up land. Agricultural land covered a total area of 1047.2 Sq. Km (58.53%) followed by forest 311.5 Sq. Km (17%), wasteland 14.27 Sq. Km (14%), water bodies 113.53 Sq. Km (6.31%) and build-up land 62.77 Sq. Km (3.5%). Paddy occupies the largest area of cultivation, followed by pulses. Other than that, the area also grows banana, vegetables and sugar canes (CGWB, 2009). Settlements include nucleated and linear type and are in the riparian regions away from the foothills. The presence of numerous hills and water falls in this region attracts tourist and increases water demand during the non-monsoon seasons. The foothill areas are intensively used for agricultural purposes and covered with thick forest (Fig. 1).

3. Materials and methods

A total of 25 groundwater samples were collected from hand pumps during POM season of 2018 and the samples were filtered immediately with 0.45 μm membrane filter after collection. Physical parameters like electrical conductivity (EC), total dissolved solid (TDS), pH was measured in the field using a portable Thermo Orion five-star meter. Subsequently, all these water samples were stored in precleaned 500 ml plastic bottles without any air bubbles, in temperatures below 4 °C until the analyses. Samples for N-isotope analysis were collected in 1-liter plastic bottles, placed on ice immediately after collection, frozen within 48 h.

Major ion concentrations, including nitrate, phosphate, silicate and sulfate (Cl, PO_4, H_4SiO_4 and SO_4^{-2}) were measured using double beam spectrophotometer (DR 6000) following the standard procedures (APHA, 1995). The levels of NO_3^- was determined by UV Spectrophotometric Screening Method (Armstrong, 1963). The instrument used was UV–VIS SPECTROPHOTOMETER, MODEL DR6000 (HACH, UK). Stock nitrate solution is prepared by dissolving 0.7218 g dry potassium nitrate (KNO_3) in water and dilute to 1000 ml. From the stock, intermediate standards are prepared by appropriate dilutions with water. 1 ml HCl solution was added and mixed thoroughly. NO_3^- reading was obtained at a wavelength of 220 nm.

Titration method was adopted to measure major ions like Ca^{2+}, Mg^{2+}, Cl^-, HCO_3 and the ions Na^+ and K^+ were measured by using flame photometer (CL 378). Each sample was analyzed thrice, and the mean concentration was taken into consideration to achieve accuracy in the analysis. The analytical accuracy for the measurements of major ions was determined by calculating the ionic balance error (IBE) by using Eq. 1, with the values falling within the limit, i.e., 5–10%.

$$[(Tz^- - Tz^+) / (Tz^- + Tz^+) * 100)] \quad (1)$$

Water samples with NO_3^- concentration > 5 mgL^{-1} were selected for ^{15}N isotope determination based upon its spatial distribution. The samples were frozen within 14 h of the sampling and later send to Water Sciences Laboratory (WSL), UNL, USA for analysis. The samples were analyzed for determination of $\delta^{15}N$ and $\delta^{18}O$-$NO_3$by a two-step chemical conversion. The nitrate was converted to nitrous oxide for stable isotope analysis by following cadmium (Cd) reduction of nitrate to nitrite & azide reduction to nitrous oxide (Mcilvin and Altabet, 2005). Samples with previously measured NO_3^- are diluted to mgL^{-1}, and NO_3^- was converted to NO_2 by reaction with spongy cadmium. Nitrite was further reduced to nitrous oxide (N_2O) using sodium azide in an acetic acid buffer. Resulting N_2O was then cryogenically separated and analyzed on a Trace Gas Isoprime IRMS instrument for ^{15}N and ^{18}O with a precision of 0.08% and 0.19% respectively. Isotope calibration was performed through reference standards (USGS 32, USGS 34, USGS 35 and IAEA N3). Working standards were also prepared to check for quantitative conversion and recovery. Results for the stable isotope measurements are expressed as a delta value using the Eq. 2.

$$d(‰) = \frac{R_{sample} - R_{standard}}{R_{standard}} x1000 \quad (2)$$

To determine the non-carcinogenic risk of NO_3^- in groundwater samples of the study area, chronic daily intake (CDI, $mgkg^{-1}day^{-1}$) for three age groups like adult, children and infants were calculated separately by using the formula of Eq. 3 (USEPA, 1993):

$$\text{Chronic Daily Intake(CDI)} = \frac{C * DI * F * ED}{BW * AT} \quad (3)$$

C= NO_3^- concentration in groundwater (mgL^{-1}).
DI=Daily water Intake ($Lday^{-1}$).
F= Exposure Frequency (days $Year^{-1}$).
ED=Exposure Duration (Year).
BW=Body Weight (kg).
AT= Average time for non-carcinogens (days).

The details of all these parameters mentioned above to calculate CDI, are provided in SI Table 1 individually for adults, children and infants.

The reference dose (RfD) provided by USEPA (2015) as 1.6 mg/kg/day was considered along with the CDI to determine the hazard quotients (HQ) to understand the non-carcinogenic risk of NO_3^- in the groundwater samples for drinking purpose. The formula used to calculate HQ as given in Eq. 4 (USEPA, 1999):

$$HQ = \frac{CDI}{RfD} \quad (4)$$

The elevation data were extracted from the ASTER DEM (resolution: 1 ARC – SECOND/ 30 m, Version: 2.0, ASTGDMV2_ 0N08E077, 2011) and 3D model was prepared from the elevation data in SURFER (Version 10) platform. Contours of high NO_3^-concentration (>25 mgL^{-1}) produced by Inverse Distance Weighted (IDW) interpolation were overlaid on elevation, land-uses and groundwater flow direction by using SURFER (Version 10). The advantage of IDW is that it is intuitive and efficient. The IDW method uses average values of sample data points in the neighborhood of each processing cell unlike KRIGING. The method of KRIGING assigns more influence to the nearest data points in the interpolation of values for unknown locations. Hence IDW method has adopted in this study.

4. Results and discussion

4.1. Source determination

4.1.1. Physical parameters

The maximum, minimum and mean concentration of the physico-chemical parameters are plotted in box plot (Fig. 2). Measured pH value in the groundwater samples ranged between 6.40 and 7.93. Temperatures varied from 28 °C to 36 °C with a mean value of 31 °C. The samples analyzed show a highest value 1560 mgL^{-1} for TDS and 8 samples exceed the recommended limit (WHO, 2011). The samples show a highest EC of 5730 μS/cm with 19 samples exceeding the recommended limit for drinking water (WHO, 2011).

4.1.2. Chemical parameters

The average concentration of chemical parameters showed an order of dominance as follows $Cl^- > HCO_3^- > Na^+ > Ca^{2+} > Mg^{2+} > K^+ > NO_3^- > H_4SiO_4 > SO_4^{2-} > PO_4^{3-}$. Out of analyzed samples 4 samples each exceed the permissible limit for Na^+ and Ca^{2+} (WHO, 2011). However only one sample exceed the permissible limit for Mg^{2+} and 5 samples exceed the permissible limit for HCO_3^- (WHO, 2011). Samples show a higher concentration of K^+ and Cl^- for all the samples analyzed, with 16 samples each exceeding the permissible limit (WHO, 2011). NO_3^- shows a highest concentration of 89 mgL^{-1} and two samples exceed the permissible limit of NO_3^- in drinking water (WHO, 2011).

SI Figure1 shows the distribution of measured NO_3^- concentration compared to the recommended limit for NO_3^- in drinking water set by WHO (2011).

The samples below the line were further sub-divided into two Zones A and B. The samples in the zone A (S No.1, 5, 23, 49, 50 and 51), NO_3^- concentration is > 25 mgL^{-1} and Zone B samples with NO_3^- concentration < 25 mgL^{-1}. Two samples (S No.10 and 18) fall above the permissible limit line. The sample (S No. 18) is located along the SW part (along the foothill) of the study area (Fig. 1) and have highest NO_3^- of 89 mgL^{-1} followed another sample (S No. 10) in the northern part of the study area predominantly represented by urban settlement (Fig. 1) with a NO_3^- value of 54 mgL^{-1}.

Agriculture is a major land-use along the foothills (Panda et al., 2020). Thus, it could be inferred that, the NO_3^- concentration of sample No.18 might be influenced by the agricultural activities. It is also very interesting to note, the locations 49, 50 and 51 have a relatively higher concentration of NO_3^- and are in the SE part of the study area (Fig. 1) along the flood plain of Chittar River and predominant groundwater flow direction. The inflow of water from the foothill aquifers to the riparian aquifers was inferred by earlier study (Panda et al., 2019) and these locations are thus influenced by the agricultural activity in the MF region especially by S No.18. Similarly, the NO_3^- concentration of Sample No. 10 could be affected by sewage from the urbanized area. It is also observed that S No's. 1 and. 5 located near to S No. 10 along the groundwater flow direction and waste land (Fig. 1), have relatively higher NO_3^- concentration. Thus, it might be stated that these locations are affected by the NO_3^- of S No. 10.

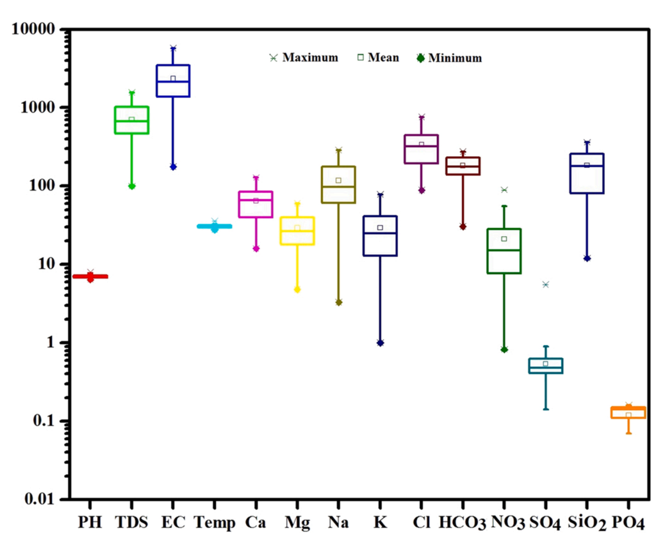

Fig. 2. Box plot showing maximum, minimum and mean values of physico-chemical parameters in groundwater samples of the study area (All parameters are in mgL^{-1} except EC in μS/cm, Temp. in °C and pH).

Local groundwater with elevated NO_3^- may be contaminated with several sources originating from current land uses. Elevated NO_3^- values are associated with both agriculture and urban land-use (Fig. 3). The predominant agricultural practices and urbanization along the SW part may influence the water quality through nitrogen loading. Elevated NO_3^- along the SE part might be due to groundwater flow towards SE (Fig. 3). The water level was shallow at the MF region as reported in earlier study (Panda et al., 2019), so the contaminant like NO_3^- may easily enter the shallow water level near the foothills due to agricultural practices and migrates downgradient along the flow direction as observed in S. No. 18, 49, 50 and 51. Surface water flows from SW to SE direction and the lineaments are also predominant in this direction (Panda et al., 2018) which enhanced the accumulation of water towards SE part of the study area. These regions may be more vulnerable to contamination from surface sources.

4.1.3. Correlation with other measurements

Correlation of NO_3^- with other ions were evaluated across 7 different categories based on valency and charge of ions (Fig. 4 A). NO_3^- showed both negative and positive correlations. NO_3^- is poorly correlated to the univalent and divalent cations, while trivalent and divalent anions showed a moderate correlation with NO_3^- concentrations. A strong correlation found between NO_3^- and univalent anions (Fig. 4 A). Interrelationships between NO_3^- and other variables are also considered from previous studies to characterize the sources and processes leading to nitrate contamination (Fig. 4B a, b, c, d, e). Samples are grouped by their correlation between 0.25 and 0.5 and > 0.5 and further evaluated.

Strong to very strong correlation of NO_3^- with Cl^- and SO_4^{2-}, is observed in (Fig. 4B a, c, d & f), and could be explained by septic systems. Animal waste has been considered to be important sources of NO_3^- and Cl^- apart from fertilizer sources associated with NO_3^- and SO_4^{2-} in groundwater (Srivastava and Ramanathan, 2018). A moderate to strong association of NO_3^- with Na^+ and Mg^{2+} has been previously reported (Fig. 4B b and e) where nitrate sources was associated with point sources such as dump sites and septic/wastewater systems. Correlation of NO_3^- with Na^+ and Mg^{2+}, ions in groundwater was associated with these sources (Keesari et al., 2016). However, no such correlation is observed in the present study (Fig. 4B f).

Previously a strong correlation between NO_3^- and K^+, SO_4^{2-} and Ca^{2+} in Nagasaki, Japan (Fig. 4B c) was attributed to the nitrate from manure and chemical fertilizers (Kei et al., 2016). A moderate correlation of NO_3^- with Ca^{2+}, K^+, SO_4^{2-} and PO_4^{3-} (Fig. 4B e) in the present study could be linked to agricultural sources.

4.1.4. Principal component analysis (PCA)

Three independent factors were extracted from the data set, 63.6% (SI Table 2) of the total data variance (TDV) of the original data set. Another factor TDV percentage might be insignificant as it is under the Eigen value 1. Hence there could be other factors in which NO_3^- plays a significant role and not identified as a major factor by PC analysis.

The following factors are identified:

Factor 1: EC, Ca^{2+}, Mg^{2+}, HCO_3^- and H_4SiO_4

Factor 2: Temp·, Na^+, K^+, Cl^- and SO_4^{2-}

Factor 3: NO_3^- and PO_4^{3}

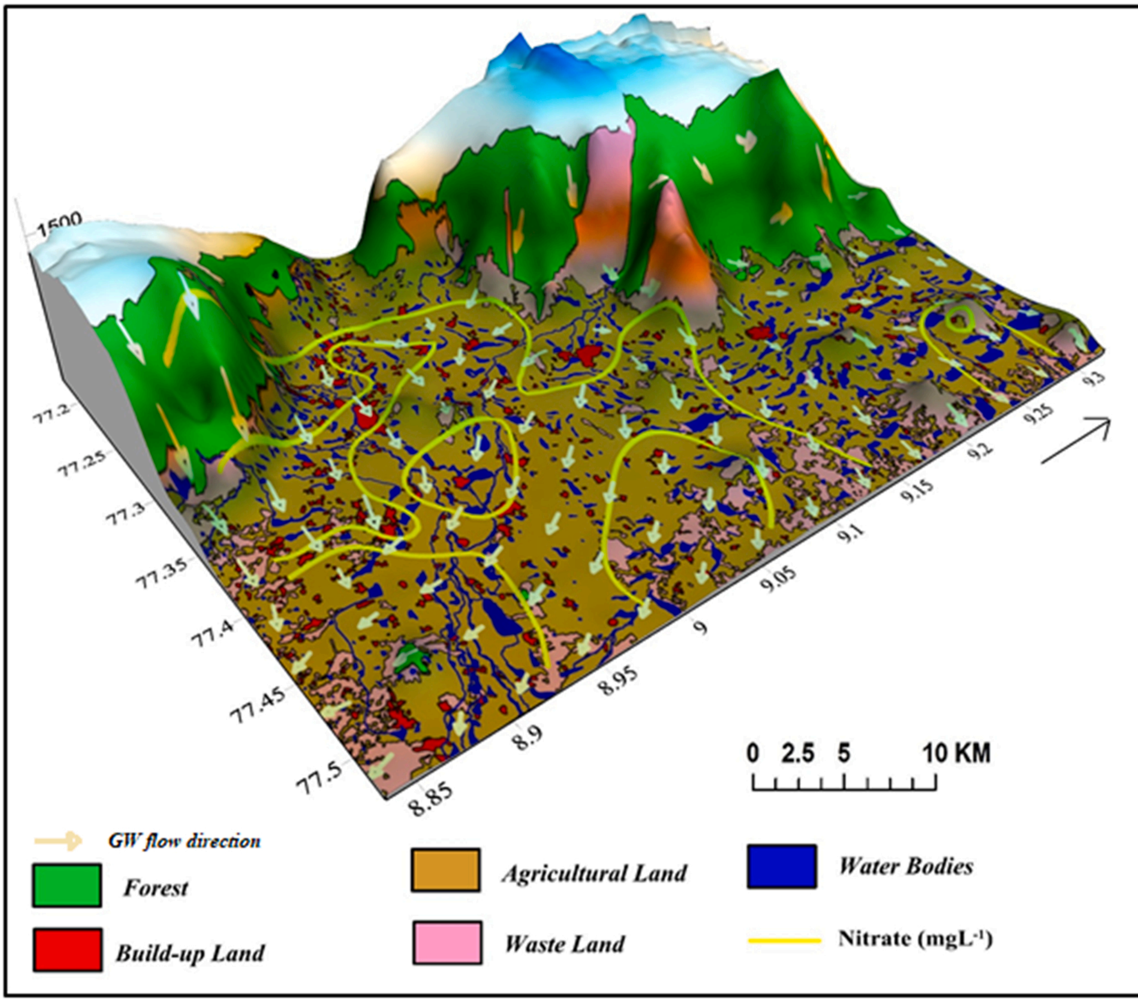

Fig. 3. Surface topography, land use and groundwater flow compared to elevated NO_3^- concentration (>25 mgL^{-1}) in local groundwater.

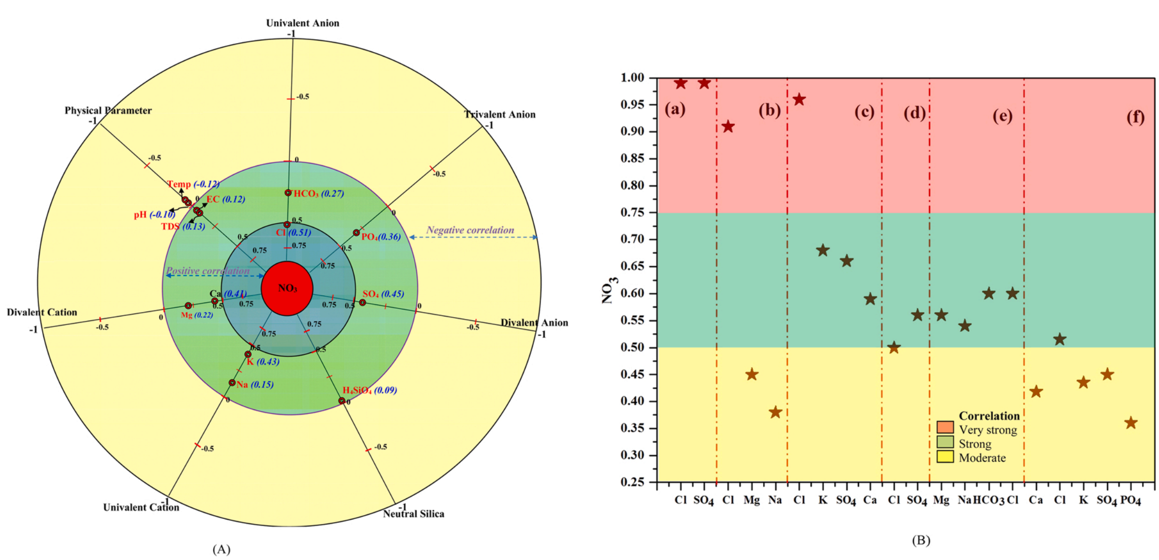

Fig. 4. (A) Correlation of NO_3^- with other variables in the groundwater of the study area. (B) Comparison of inferences drawn from the correlation of NO_3^- with other ions from different studies (a) Human excreta, animal waste and fertilizer (Rajasthan, India; Suthar et. al. 2014) (c) manure, livestock waste and chemical fertilizer (Nagasaki, Japan; Kei et. Al. 2016) (d) anthropogenic inputs and fertilizer (M.P., India; Srivastava & Ramanathan, 2018) (e) leakage of dumping sites and sewer pipelines (Varanasi, India; Ahmed et, al. 2018 (f) Present study.

The positive association of EC, Ca^{2+}, Mg^{2+}, HCO_3^- and H_4SiO_4 in Factor 1 may be linked to rock dissolution by the process of chemical weathering (Love et al., 2004) (SI Table 2). The rock-water interactions are accelerated during crop production and are also responsible for releasing these ions into the groundwater. Bicarbonate (HCO_3^-) is formed by reaction of water with CO_2 in soil through the weathering process. The high CO_2 pressure sub-surface soil zone is associated with the decay of organic matter and root respiration. This CO_2 combines with rainwater (H_2O), to produce HCO_3^-. The entire process is explained through the following Eqs. 5 and 6:

$$CO_2 \text{ (g)} + H_2O => H_2CO_3 \text{ (aq)} \tag{5}$$

$$H_2CO_3 \text{ (aq)} => H^+ \text{(aq)} + HCO_3^- \text{ (aq)} \tag{6}$$

The Factor 2 (F2) is attributed to strong positive loadings of Na^+, K^+, Cl^- and SO_4^{2-} which could be linked to anthropogenic sources and ion-exchange process. House-hold activities like septic waste/cess pool salts, animal and livestock excreta might be responsible for Cl^- in the inland aquifers (Panno et al., 2006). The SO_4^{2-} in the aquifer may be linked to agriculture source (Panno et al., 2006).

The representation of Ca^{2+} and Mg^{2+} is insignificant, however a significant loading of Na^+ and K^+ is noted in F2 (SI Table 2). This could be related to ion-exchange process. The concentration of Ca^{2+} decreases, and Na^+ increases due to ionic substitution of Ca^{2+} by Na^+ as shown in the following Eq. 7:

$$Na^+\text{-}X + ½Ca^+ \; Na^+ + ½Ca^+ + X \tag{7}$$

Where X is the soil exchanger. Na^+ ion replaces with Ca^{2+} ion and become dominant. The $Ca^{2+}$and Mg^{2+}on the surface of clay minerals in the aquifer matrix comes in the form of Na^+ and K^+ in the solution due to ion exchange process leads to the dominance of the Na^+ and K^+ in solution (Keesari et al., 2021).

In third PCA factor (F3), the high positive loading of NO_3^- and PO_4^{3-} could be linked to the soluble fertilizers from agricultural land (SI Table 2). Lambrakis et al. (2004) have described occurrence of PO_4^{3-} and NO_3^- in groundwater likely from excess fertilizers through PCA. The strong association of NO_3^- and PO_4^{3-} in the present study further supports agricultural sources.

Fig. 5 depicts the relationship between NO_3^-, K^+ and PO_4^{3-} in the groundwater samples of the study area. The PO_4^{3-} concentration is not significant and all the samples have an extremely low concentration (below 1 mg/L). Thus, the relationship between NO_3^- and K^+ is considered to delineate the source of these two parameters. There are three significant relationships observed between these parameters from 4 distinct sub-zones like Zone A, B, C and D (Fig. 5).

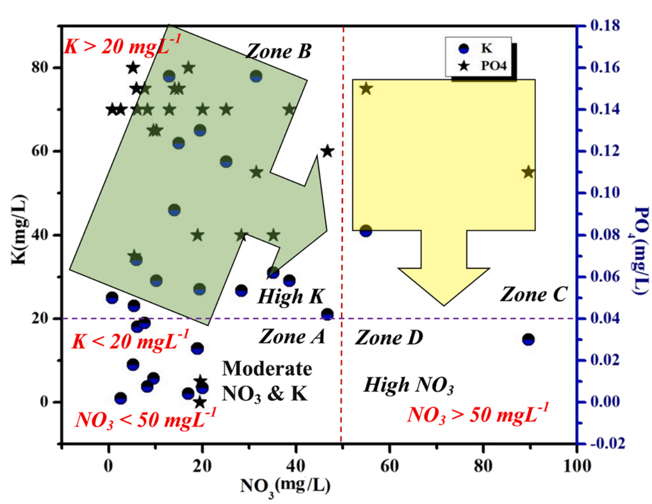

Fig. 5. The relation among NO_3^-, K^+ and PO_4^{3-} concentrations in groundwater of the study area.

All three parameters share a linear relation in zone A with moderate concentration. However, there is a significant correlation noted between K^+ and NO_3^- in zone B samples. The samples of low NO_3^- values show high K^+, which might be associated with weathering of K^+ from the underlying litho-units basically clay minerals or potash feldspar or release of K^+ into the groundwater from the fertilizer used in the agricultural lands. Considering the underlying litho-units, the study area is a hard rock terrain and there is no clay minerals or potash feldspar present in the study site (CGWB, 2009). Since there is no significant association of K^+ with HCO_3^- and H_4SiO_4, it is not released due to the weathering process. Thus, it is evident that the source of high K^+ in groundwater from the fertilizer used in the agricultural lands. Apart from paddy, other crops like sugar cane, banana and vegetables are cultivated in the study area (CGWB, 2009).

Urea is the main nitrogen fertilizer used for growing paddy rice, which constituted 46% of nitrogen and the ratio of NPK fertilizer is 46–0–0. The fertilizers used in growing sugar cane, fruits and vegetables are Muriate Of Potash (MOP), constituting of 50% potassium chloride (KCl) and 50% Nitrate Of Potash (NOP), (District Census Hand Book, 2011). Due to intensive agricultural practices in the study area leads to higher consumption of nitrogenous and potash fertilizers than the other agro-zones in the district (CGWB, 2009). Thus, it could be inferred that intensive agricultural practice and excessive use of inorganic fertilizers are the main factors which influence the groundwater composition of the study area, resulting in high K^+ and moderate NO_3^- in the samples of the zone B. Nitrate in zone C and D samples is associated with low PO_4^{3-} and K^+, suggesting that NO_3- of zone C and D is from other sources.

4.1.5. Stable isotopes of nitrate (NO_3^-)

Nitrate isotopes have been used in many investigations of groundwater contamination for their potential ability to characterize nitrogen sources. The nitrogen isotope composition in most commercial fertilizers is similar to the isotopic composition of atmospheric nitrogen (Kendall et al., 2008), which is fortuitous as atmospheric nitrogen is the reference standard for reporting the isotope composition.

The majority (~80%) of inorganic nitrogen fertilizer sources $\delta^{15}N$ ranges between − 3 and + 3‰ (Michalski et al., 2015) relative to atmospheric nitrogen. In contrast, nitrogen from organic sources such as animal waste, domestic sewage or bio waste is enriched in the heavier $\delta^{15}N$ isotope especially after deposition and converted to the highly volatile ammonia (Kendall et al., 2008), $\delta^{15}N$ generally falls between + 10 and + 25‰ relative to atmospheric nitrogen. NO_3^- fertilizer (KNO_3 or $N_2H_4O_3$) or oxygen atoms in the soil, air, and water during nitrification of ammonia contributes oxygen isotopes in nitrate. Because the oxygen isotope composition of air is relatively constant (+22 to +24‰), and the oxygen isotope composition of water changes in a predictable way (usually −5 to −20‰), it is possible to predict the oxygen isotope composition of soil nitrate formed by nitrification.

Microbial denitrification can change the isotope composition of nitrate from its original source. As the change in composition is predictable, simultaneous measurement of both nitrogen and oxygen isotopes could provide clues about the source(s) of nitrogen, timing of nitrification (nitrate formation), and whether denitrification has occurred (Kendall and Aravena, 2000). Kendall et al. (2008) have used both nitrogen and oxygen isotopes for differentiating sources of nitrate in groundwater and multiple sources (atmospheric, manure, septic systems) along with their related processes. Similar studies were carried out globally in countries like USA, India etc. (Harter et al., 2005; Majumdar and Gupta, 2000). A growing number of studies have used dual isotopic analysis on nitrate to trace the main sources and transformations of nitrate from polluted waters from all over the world. For example, findings show that, mineralization of soil organic N and sewage is the major sources of nitrate with an isotope value ranges from(−5 to 20‰ approx.) in groundwater in the eastern part of China (Zhang et al., 2014); animal manure and domestic sewage contribute nitrate concentration to the groundwater of Po Plain, Italy (Lasagna and De Luca, 2019); manure, fertilizer, and sewage are the major nitrate sources in a lowland agricultural catchment in eastern England and wastewater was an important nitrate source in urbanized streams in the Baltimore metropolitan area (Kaushal et al., 2011). Thus, the bivariate plot of δ^{15}N-NO_3 vs. δ^{18}O-NO_3 was compared to potential sources of NO_3^- in the groundwater of the study region after Kendall 1998 and Kendall et al. (2008). The δ^{15}N-NO_3 and δ^{18}O-NO_3 value ranged from 7.9‰ to 25.3‰ and from − 3.88–12.1‰ respectively (Fig. 6 A). The slope of the regression line (i.e., 1:1 line) is taken as the indicator of microbial denitrification in reference to the other freshwater studies (Kendall, 1998; Aravena and Mayer, 2009). Nitrate isotope composition tends to fall within values for manure and septic sewage, while a few samples show trends consistent with enrichment due to denitrification (Fig. 6 A).

There are three different trends observed in the entire data set, hence the field is again divided into three sub-fields. The zone A samples with depleted δ^{15}N-NO_3 between 5‰ and 10‰, zone B with intermediate δ^{15}N-NO_3 between (12% and 17%) and zone C with enriched δ^{15}N-NO_3 between (20 and 25‰) (Fig. 6 A). According to Cravotta (1995), the δ^{15}N-NO_3 values vary between 4‰ and 6‰ for septic sewage, 0–15‰ for manure combined and 15–30‰ for sewage land use in the waters in the Lower Susquehanna River basin, Pennsylvania. The current study has identified these three sources (septic sewage, manure, and sewage) and classified based on Cravotta (1995) values. It is identified that sewage contributes 46% (N_3 =6/13), manure 23% (N_2 =3/13) and septic sewage 31% (N_1 =4/13) NO_3^- to the total analyzed samples. Subsequently the δ^{15}N-NO_3 of the samples was also correlated with the Cl^- and NO_3^- concentration in local groundwater to corroborate the inference and further sub-divided into three zones A, B & C (Fig. 6B).

Zone A [High Cl^-, variable NO_3^-, low δ^{15}N-NO_3 - Fig. 6 B], might be influenced by large amount of household waste sources potentially discharged through cess pools. Nitrogen enriched wastewater released through septic or cess pool systems percolates and eventually reaches local groundwater. Increasing the Cl^- content in the groundwater is consistent with wastewater sources. However, one sample (S. No. 27) in Zone A has extremely low Cl^- content and noted in the eastern most part of the study area (Fig. 1).

Zone B [High Cl^- and NO_3^-; moderate δ^{15}N-NO_3 - Fig. 6B] can be linked to the application of manure in the agricultural lands for increasing the crop production. Some indirect factors which increase the NO_3^- and Cl^- content in groundwater are animal waste, including livestock and human excreta (Suthar et al., 2009). Cattle farming is an important occupation being adopted by rural communities of this region. Thus, the livestock population is relatively higher in this district around 2.67 million (Statistical handbook of Tamil Nadu, 2019). This livestock population may be expected to produce relatively larger amounts of organic nitrogen. Open dumping of this livestock excreta is a very common practice followed by people and it is also used for cultivation as manure. Excessive amounts of organic nitrogen may leach into the groundwater and contribute higher Cl^- and NO_3^- to the groundwater.

In Zone C [Variable Cl^-, high NO_3^-; enriched δ^{15}N-NO_3 - Fig. 6B]. Nitrate may be linked to the sewage or domestic/municipal wastewater. The sources of sewage include water from both household activities and agricultural source. Due to lack of adequate resources to construct safe sanitation facilities, people in the study region still relay upon pit latrine system. Studies have reported the source of Cl^- and NO_3^- in groundwater from pit latrines (Dzwairo et al., 2006). Wastewater from pit latrines infiltrates and gradually reaches the aquifer. Thus, increasing the Cl^- and NO_3^- content in the groundwater of the study area. Apart from pit latrines, other sources of domestic wastewater include water from kitchen, sinks, shower, wash basin, laundry, etc. which also influence the Cl^- content in groundwater. The study region is well developed in agricultural production and associated with intensive application of fertilizers. Infiltration of agricultural water contributes a high amount of Cl^- and NO_3^- to the groundwater. There are two samples in which Cl^- concentration was relatively lesser than that of NO_3^-. These two samples might be influenced by NO_3^- rich sewage. Thus, it is inferred that the zone C samples are influenced by both domestic and agricultural source. But two samples with less Cl^- is influenced by agricultural water with high NO_3^- and relatively lesser Cl^-, due the process of dilution during recharge.

4.2. Health risk assessment

Groundwater with high NO_3^- concentration can cause human health risks if used for drinking without pretreatment. NO_3^- converts to nitrite (NO_2) in the human body and detoriates human health by, causing Methemoglobinemia, or "Blue Baby Syndrome". Moreover, consumption of drinking water with high NO_3^- has been associated with cancer as well as other health disorders (USEPA 2017). Nitrite can enter the main bloodstream of the human body through the upper gastrointestinal tract. Different organizations and countries have prescribed limits for NO_3^- in portable water, to protect human health from the hazard associated with elevated concentration of NO_3^-. Thus, health risk assessment was carried out by determining the hazard quotient (HQ) for all the three age groups like adults, children and infants to determine the health risk associated with the consumption of local water. The Fig. 7 showed the distribution of HQ for three age groups in the groundwater samples of the study area. For the present study area 3.8% of total samples have a HQ value greater than 1 for adults. However, 30.74% and 34.60% of total samples have HQ value greater than 1 for both children and infants respectively (Fig. 7). Comparison of the HQ values among three age groups reveals that the health risk for infants is higher than in children and adults. Hence the elevated concentration of NO_3^- in groundwater samples of the

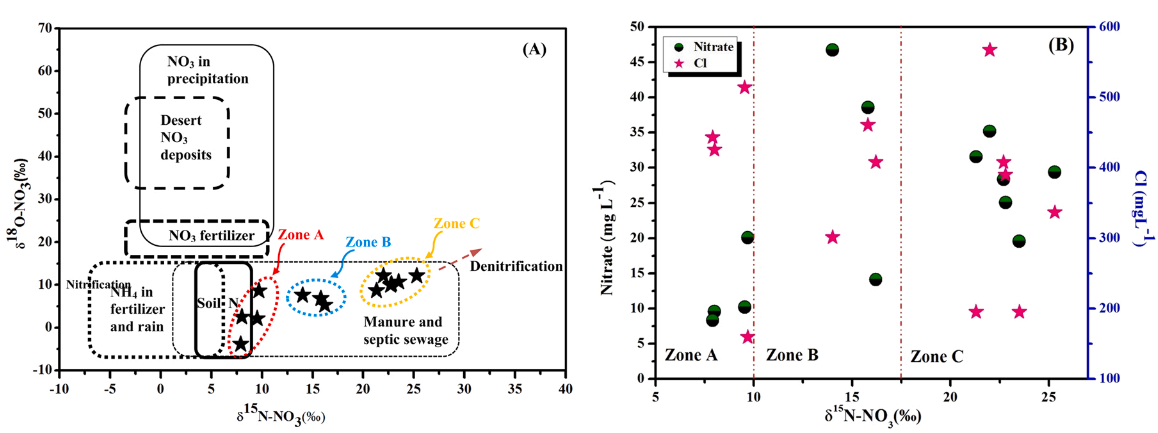

Fig. 6. (A) The relationship between δ^{15}N-NO_3 vs. NO_3^- vs.
(a) $\Delta^{18O\text{-}NO_3}$ of groundwater NO3- compared to different expected source ranges (B) δ15N-NO3 vs. (b) Cl depicting the source of NO3- in local groundwater.

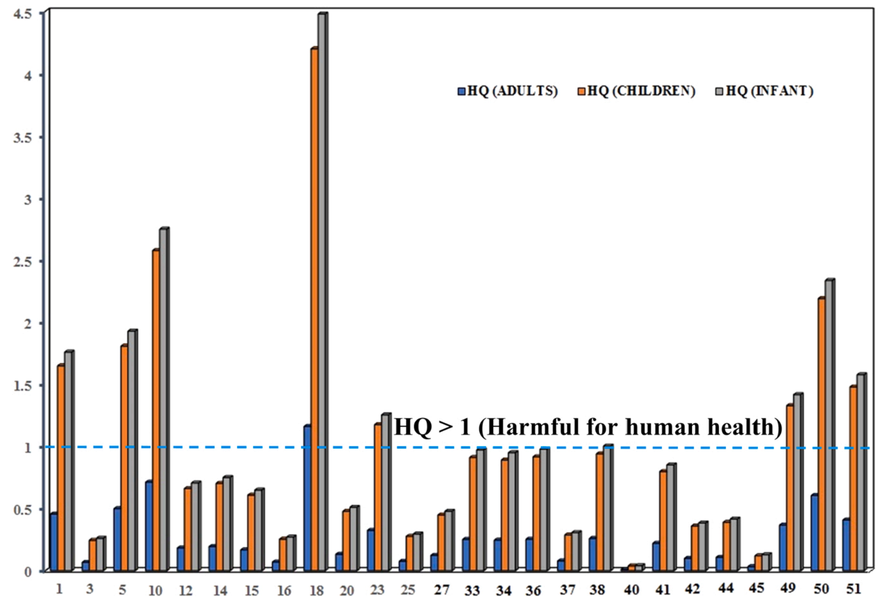

Fig. 7. Hazard Quotient (HQ) of NO_3^- in the groundwater of the study area for adults, children and infants. The value greater than 1 is considered as harmful for human health (Khan et al., 2016).

region has great concern as the water is used for drinking, domestic as well as irrigation purposes. So, the concentration of NO_3^- in the groundwater should be monitored continuously to ensure that the NO_3^-levels are within the desirable limit.

5. Conclusions

The level of NO_3^- varies from 0.11 to 89 mgL^{-1} in the groundwater of the study area with an average level of 21.14mgL^{-1}. Two samples (S No. 10 and 18) exceed the permissible limit which influences the NO_3^- concentration of other samples. The spatial variation of NO_3^- in groundwater indicates the influence of land use patterns and water flow direction. Three major factors like weathering, anthropogenic and agriculture, were identified through PC analysis and found to be responsible for the variation in groundwater chemistry of this region. The isotopic analysis reflects that sewage and manure are the principal source of NO_3^- in groundwater, which was further sub-divided into three different categories based upon $\delta^{15}N$-NO_3. Three different sources like septic sewage, manure (animal and livestock excreta) and sewage (municipal sewage, pit latrines, nitrogenous fertilizers, etc.) are inferred to be the main sources of NO_3^-. Isotopic results revealed that sewage was the predominant contributor of NO_3^- (contributing 46%), followed by septic sewage (31%), manure (23%) to groundwater of the region. The non-carcinogenic risk associated to NO_3^- contamination in groundwater for three distinct age groups like infant, children and adults was determined through HQ. All the three age groups are exposed to non-carcinogenic risk due to the consumption of NO_3^- contaminated water, but infants are at higher risk than children and adults. This is the first inclusive report on NO_3^- contamination in groundwater of this region and its source determination; further detailed study is required to delineate the potential contamination source with more sampling spatially and temporally, as this region may be a threat zone for NO_3-toxicity risks to human health.

The inferences drawn from the study further indicate that groundwater has been approaching an alarming stage of nitrate pollution. Hence, it is urgent to execute a management strategy for sustainable drinking water source and preventive measures be undertaken, relative to these water quality concerns to mitigate their disconcerting effect on human health. Even though the study was focused on a specific area in South India but the inferences are universal. Other parts of South India experiencing similar water quality issues due to over exploitation of water, change in frequency of rainfall owing to climate change, intensive agriculture and other anthropogenic activities should also be studied for the management of groundwater. Consequently, the combined effects of arid climate, existing geogenic risks (aquifer lithology generating the contaminants), and anthropogenic activities may result in several water quality issues, thereby intensifying the human health risk upon consumption of that contaminated water in the southern part of India if timely concern measures are not adopted.

CRediT authorship contribution statement

Panda, Chidambaram, Daniel, Malakar, Ramanathan and Dhiraj formulated the idea, and drafted the manuscript. **Chidambaram, Daniel, Malakar and Ramanathan** reviewed the manuscript and include their comments and suggestions. Everyone did the final review and contributed to the final revision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ecoenv.2021.113075.

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