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Statistical Analysis of Urban Non-Point Source Pollution and Nitrate Contamination in the Groundwater at Thuckalay, Kanyakumari District, South India

Bhagavathi Krishnan Ramesh[1*], Sankararajan Vanitha[1]

[1] Department of Civil Engineering, Kalasalingam Academy of Research and Education, Krishnan- Koil, Virudhunagar District, Tamil Nadu, India

* Corresponding author's e-mail: bkramesh1000@gmail.com

ABSTRACT

A statistical analysis of nitrate contamination in the groundwater at the Thuckalay area of Padmanabhapuram town, South India, is conducted using data collected from 2000 to 2019 that includes rainfall, groundwater level, and groundwater quality. The findings indicate that there was a rise in nitrate contamination in the groundwater between 2001 and 2011. This increase can be attributed directly to the 6.69% increase in population and the corresponding increase of 108.79 hectares in residential areas, which accounts for the 17% expansion. The elevated concentrations of EC (1830 µS/cm), Cl (511 mg/L), Na (210 mg/L), NO_3 (150 mg/L), TH (420 mg/L), and precipitation (1,184) in 2011 may have an impact on the non-point source contamination in the subject area, which is caused by flowing water bodies. An investigation was conducted into the sources and regulating factors of elevated nitrate levels through the utilisation of cross plots and fitted line plots of NO_3 in conjunction with other chosen hydrochemical parameters. Nitrate contamination of the groundwater is indicated by a positive Pearson correlation coefficient between NO_3 and Ca, Cl, EC, Na, SAR, SO_4, TH, TA, and WL. Furthermore, a nitrate pollution index greater than three signifies a higher degree of pollution during the years 2005, 2010, 2011, 2013 and 2014. The primary sources of nitrate contamination in the vicinity of the study area were human and animal refuse that was disposed of in open areas. This may be the result of increased fertiliser application on agricultural land. Restoring groundwater quality in the studied area is possible through periodic monitoring, regulation of polluting sources, and implementation of a natural, cost-effective redevelopment technique.

Keywords: statistical analysis, groundwater, agriculture, terms nonpoint source pollution, nitrate contamination, nitrate pollution index.

INTRODUCTION

Water is an essential element for all forms of life and for the growth of many economic and industrial endeavors. Modern population expansion, industrialization, and economic development are the root causes of the ever-increasing water demand. We consider groundwater to be the most important water resource for household use, and the pollution of this resource is becoming worse every year (Saranya et al., 2011). (Guo et al., 2004, Ma et al., 2009, and Sun et al., 2012) all found that nonpoint sources account for over half of the water pollution in the basin. Consequently, nonpoint source pollution from agriculture and human waste management are receiving more global attention. According to Stuart et al. (2012) and Ma et al. (2011), the majority of organic and inorganic pollutants, including nitrogen (N), phosphate (P), fertilisers, organic pesticides, and other contaminants, are the main causes of nonpoint source pollution. Agricultural practices accounted for the vast majority of nitrate contamination and nonpoint source pollution (Wang et al. 2015). The far-reaching, uncertain, and long-lasting effects of agricultural nonpoint source pollution make its regulation significantly more challenging than those of industrial pollution. Consequently, it is of utmost importance to address nonpoint source pollution by doing relevant research (Wang et al., 2015; Taebi and Droste, 2004; Guo et al., 2014). Surface and groundwater nitrate pollution is the most pervasive contaminant. Nitrate contamination in groundwater can be attributed to a multitude of sources, including soil organic matter decomposition, chemical fertiliser leaching, human and animal waste, untreated industrial effluent, improper sewage disposal, and other related issues (Saranya et al. 2011). Methemoglobinemia, that occurs when nitrate attaches to red blood cells and decreases their oxygen-carrying ability, is one of the primary human health issues it mostly causes. Other symptoms include shortness of breath, heart attack, and death. A disease called "blue baby syndrome" may occur in infants who consume water that is high in nitrates and causes their skin to become blue. Nausea, vomiting, an increased risk of heart palpitations, mental illness, and stomach cancer are among side effects of consuming water that is high in nitrates (Subramanian 2011).

Saranya et al., 2011, Subramanian 2011, Sangeetha et al., 2017, and Sajil Kumar et al., 2014 are among the studies that have looked at the level of nitrate contamination in groundwater in Tamil Nadu. Due to its high solubility in water and low retention by soil particles, nitrate is a dominant component of groundwater in town in Tamil Nadu. Nitrate may be produced by biochemical activities of microorganisms or in chemically created forms. There has been a rise in nitrate contamination in the groundwater in the study area of Thuckalay in Padmanabhapuram town due to the poor agricultural practices of growing bananas and rice, as well as the dramatic increase in the residential area (City Corporate cum Business Plan for Padmanabhapuram Final Report, 2013). Thuckalay in the Kanyakumari district was chosen as the research region due to the growing usage of chemical fertilisers and the greater degree of human activities in the agricultural land area.

In a previous article, (Ramesh and Vanitha 2021) detailed an investigation of the suitability of water for both household and irrigational purposes in Padmanabhapuram, Kanyakumari district, according to international standards. (Ramesh et al., 2020) also sought to examine the surface water quality (Ponds) in Padmanabhapuram, Kanyakumari district, to determine its appropriateness. Additionally, we used deep learning, artificial neural networks, and support vector machines to forecast and evaluate mineral pollution in Padmanabhapuram's groundwater (Ramesh and Vanitha 2022). Between 2000 and 2019, researchers used data on groundwater levels, rainfall, and quality from the Central Ground Water Board (CGWB) and the state's water resource department (https://www.cgwb.gov.in/wqreports.html). Specifically, aim of the study is:

1. To compute the nitrate pollution index from the year 2000 to 2019.
2. To study more about NO_3 sources and controlling factors with relation to other hydrochemical parameters based on the statistical analysis.
3. To help the public and administrators by providing scientific and theoretical support for their efforts to control nonpoint source pollution and nitrate contamination using biological de-nitrification and other eco friendly treatment system.

METHODOLOGY

Description of the study area

Located in the Kanyakumari district of Tamil Nadu, India, Padmanabhapuram is a 6.47 km^2 town that served as the capital of the Kingdom of Travancore from 1500 until 1790. It is also the administrative centre of the Kalkulam taluk. In BHUVAN, the national geo informatics site in India created by the Indian Space Research Organization (ISRO), the study area Thuckalay (8°14' N, 77°18'E) was shown, as seen in (Figure 1).

Geography

With an average elevation of 25 meters above mean sea level (MSL), the town may be found in the western section of the Kanyakumari district at 8°14' north latitude and 77°18' east longitude. The town's terrain consists mostly of gentle hills and valleys, with a hard, sandy loom type soil. Data for this town's land usage and land change from 2001 to 2021 (Table 1) were retrieved from the Padmanabhapuram municipality.

Climatology

The highest and lowest temperatures recorded in this area are 32 °C and 22 °C, respectively. Maximum precipitation of 537 mm falls on the town during the southwest monsoons (June–December), and 549 mm during the northeast monsoons (October–November). With a high of 247 mm in October and a low of

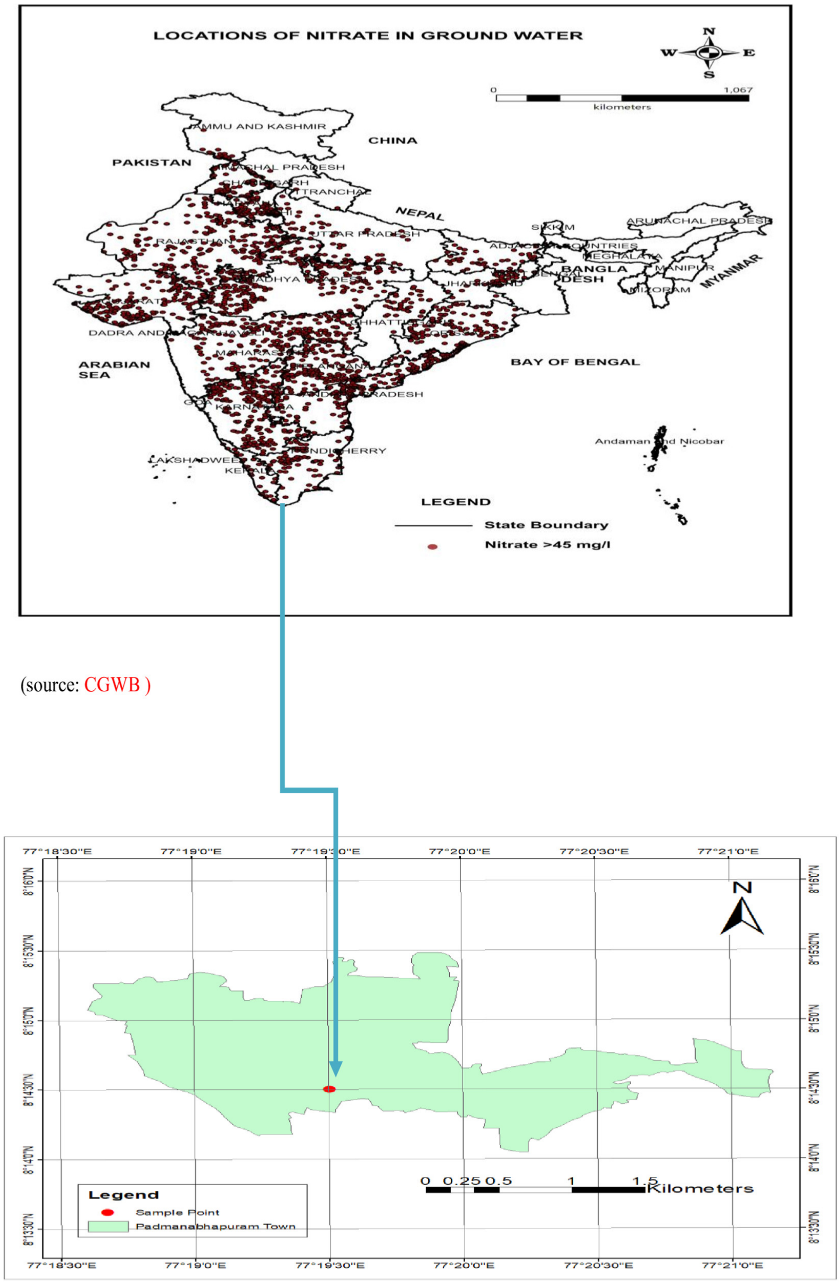

Figure 1. Location map of study area - Thuckalay (Latitude 8°14’N, Longituide 77°18’E), Kanyakumari district in south India

21 mm in February, this area receives an average of 1,465 mm of rainfall every year. The wettest months are October through December. You may find RH values anywhere from 60% to 100%. (https://www.kanyakumaritourism.com/Environment/).

Geo hydrology

Geo hydrology, the district was separated into two domains:

1) An unconsolidated quaternary formation made up of clay, silt, and sand in the south, and;
2) A consolidated Archaean formation made up of crystalline igneous and metamorphic rocks in the north.

Groundwater is found in the quaternary format in peripheral basins with lenticular aquifers. Under phreatic unconfined conditions, groundwater in the hard rock area is restricted to the soil, regolith cover, worn, and fissure zones. Unconfined aquifers that are somewhat thick and discontinuous can be found down to 30 meters below ground level (GSI, 1969).

Table 1. Land use and land change difference in Padmanabhapuram town from the year 2001 to 2021

Specification	2001 (Area/hectare)	2011 (Area/hectare)	2021 (Area/hectare)	Difference 2001–2011 (Area/hectare)	Difference 2011–2021 (Area/hectare)
Residential area	198.16	306.95	330.00	(+)108.79	(+) 23.05
Commercial	8.27	6.83	11.50	(-) 1.38	(+) 4.67
Industries	1.8	1.64	1.80	(-) 0.16	(+) 0.16
Educational	5.65	3.14	6.25	(-) 2.51	(+) 3.11
Public, semi public	71.50	54.56	144.20	(-) 16.94	(+) 89.64
Agriculture	361.62	273.88	153.25	(-) 87.74	(-) 120.63

Note: Data source: Padmanabhapuram municipal master plan.

Population

Padmanabhapuram town has a population of 22,547 people according to the census of 2021. The density of the population is 3485/sq.km and the floating population is 5000 to 10,000/day. The population in the period 1921 to 2021 is mentioned in (Table 2), (Figure 2). The percentage of the population in Padmanabhapuram town was calculated as:

$$(PCDY - PPDY) / PPDY \times 100 \quad (1)$$

where: PCDY – population current decade year, PPDY – population of previous decade year.

Nitrate sources in different ecosystems

Nitrate production is a crucial component of the nitrogen cycle in our surroundings, and it can enter into groundwater via both geological and human causes (Figure 2a).

Geogenic sources

The nitrate generation in soil or water is governed by three natural processes: ammonification, nitrification, and denitrification. Additionally, a number of minerals with nitrogen in its lattice, such as tobelite, nitre, and nitratine, are found in the aquifer strata. These minerals weathering over time, increasing the nitrogen will be released from their lattice. This nitrogen has the potential to transform into nitrate and contaminate the groundwater.

Anthropogenic sources

A multitude of human acitivities, including excessive fertilizer use, inappropriate industrial waste disposal, deforestation, shoddy septic tank and leaching pit construction, are mostly accountable for elevated nitrate levels that seep into the groundwater regime. One of the main ingredients in all inorganic fertilizers is nitrogen, whose application has expanded in an effort to improve agricultural productivity

Nitrate pollution index (NPI)

Illustrate the (Figure 3) is a time series figure showing nitrate levels in the research region from 2000 to 2019. Nitrate concentrations over the human-caused threshold of 20 mg/L were

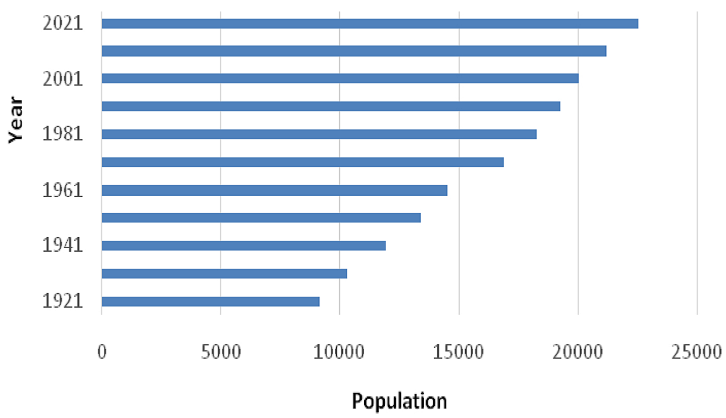

Figure 2. Padmanabhapuram town population from the year 1921–2021

Table 2. Percentage of population growth in Padmanabhapuram town from the year 1921 to 2021

Year	Population	Percentage of growth (%)
1921	9156	–
1931	10313	12.64
1941	11936	15.74
1951	13397	12.24
1961	14491	8.17
1971	16889	16.55
1981	18246	8.03
1991	19269	5.61
2001	20051	4.06
2011	21191	5.69
2021	22547	6.40

Note: Data source: Padmanabhapuram municipal master plan.

denoted as NO_3, and polluted groundwater was determined as NPI (Eqn. 2) (WHO 2012; Spalding and Exner, 1993). This is how the nitrate pollution index came to be:

$$NPI = (Cs - HAV) / HAV \quad (2)$$

Cs is the nitrate concentration from the research area's groundwater sample that was analysed. Twenty milligrammes per liter (mg/L) is the human-caused limit (*HAV*). The five groups of water quality were then determined by looking at the NPI values. According to Obeidat et al. (2012), the NPI ranges from 0 > for no pollution to > 3 for moderate pollution, with 1–2 being moderate, 2–3 being substantial, and > 3 being very significant (Figure 4). The World Health Organisation (2012) sets a limit of 45 mg/L for nitrate as NO_3 in potable water.

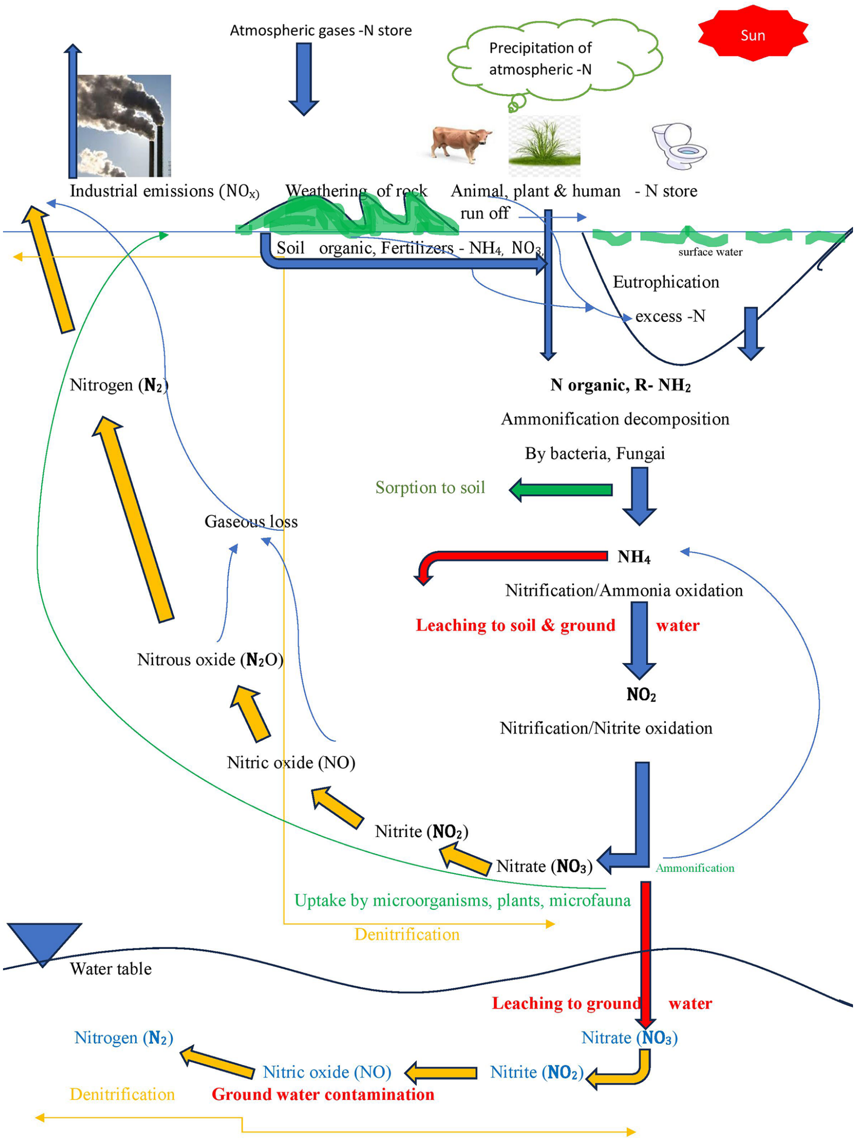

Figure 2a. Nitrate sources in different ecosystems

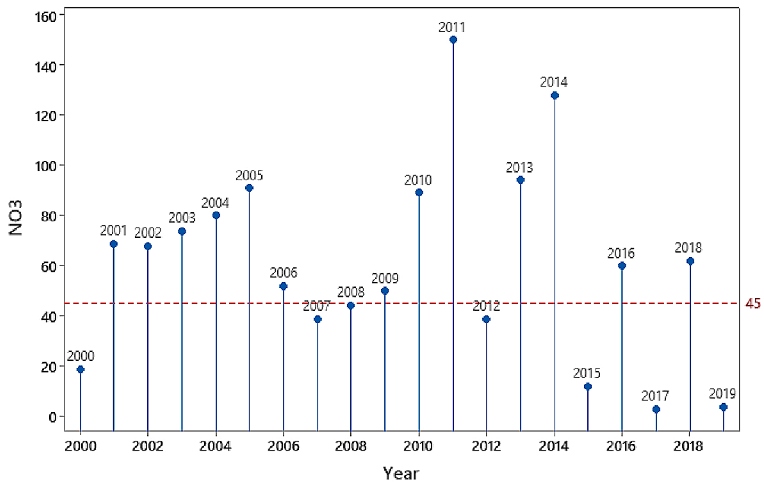

Figure 3. Nitrate levels in the time series plot in the ground water of Thuckalay from the year of 2001 to 2020

Statistical analysis

Groundwater level data were retrieved from the state water resource department and the central groundwater board between 2000 and 2019 (Table 4), and they were compared with the World Health Organization's standard (Table 3). The data was obtained at a single sampling station in Thuckalay for 20 years of groundwater quality and rainfall. The concentration of each ion and total hydroxide were recorded in milligrammes per litre, electrical conductivity was recorded in microohms per centimetre, and pH was not given. Pearson was responsible for statistically interpreting the outcomes of chemical analyses. The following plots have been created using the MINITAB programme: time series, scatter, fitted line, contour, regression, and trend analysis plots. Water quality regression analysis (Eqn. 4) and Karl Pearson's correlation coefficient (Eqn. 3) demonstrated the strong association between the independent and dependent variables of hydrochemical parameters. The high positive and negative correlation is in the range of +0.8 to +1.0 and -0.8 to -1.0. The moderate positive and negative correlation is in the range of +0.5 to +0.8 and -0.50 to -0.8. The weak positive and negative correlation is in the range of +0.0 to +0.50 and -0.0 to -0.50. Karl Pearson's correlation coefficient equation (Ahamad et al., 2015):

$$r = \frac{\sum(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum(x_i - \bar{x})^2 (y_i - \bar{y})^2}} \tag{3}$$

where: r – correlation coefficient; x_i – in a sample, values of the x-variable; $\bar{x}$ – mean values of the x- variable; y_i – in a sample, values of the y-variable; $\bar{y}$ – mean of the values of the y-variable.

Linear regression Equation

$$Y = B^{\circ} + B_1 X \tag{3}$$

$$B_1 = \frac{\sum[(x_i - x)(y_i - y)]}{\sum[(x_i - x)^2]} \tag{4}$$

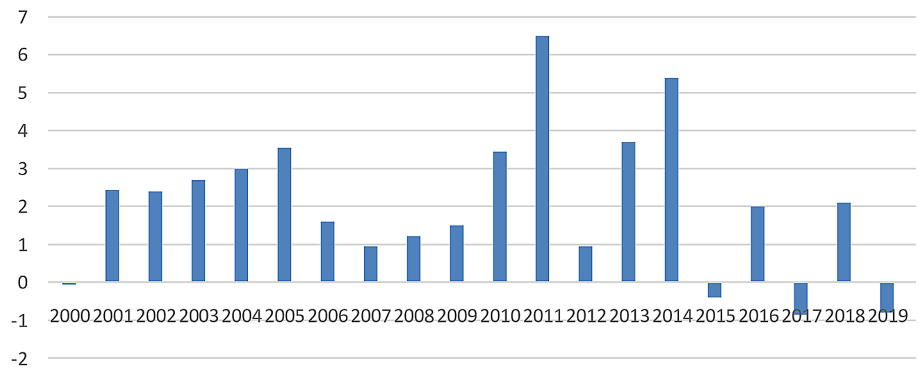

Figure 4. Nitrate pollution index in the ground water of Thuckalay from the year 2000–2019

where: B_0 – constant; B_1 – regression coefficient; X – value of the independent variable, and Y – a value of the dependent variable; r – correlation between x and y; x_i – X value of observation i, y_i – Y value of observation I; x – mean of X, y – mean of Y; s_x – standard deviation of X; s_y – standard deviation of Y" (Ahamad et al., 2015).

PREFORMANCE ANALYSIS

Land-use change and population

Table 1 displays the current state of land use and land change in the town of Padmanabhapuran from 2001 to 2021. The residential land use area was 330 hectares from 2011 to 2021. Between 2001 and 2011, residential land consumption rose by 108.79 hectares, whereas between 2011 and 2021, it climbed by 23.05 hectares (Table 1). Table 2 shows that the town's population rose from 1921 to 2021, with a 6.0% growth from 2011 to 2021.

Hydro-geochemistry of the study area

The hydrochemical properties of the groundwater at Thuckalay are detailed in (Table 4), which covers the years 2000–2019. Nitrate levels were shown in the time series plot (Figure 4), which covered the years 2000–2019. From a low of 3 mg/L in 2017 to a spike of 150 mg/L in 2011, nitrate levels rose steadily from a starting point of 19 mg/L in the year 2000.

The pH range of each water sample is between 6.2 and 8.6. The utmost allowable limit was surpassed by a mere 8.6 components in the 2013 sample. In 2011, the electrical conductivity measured 1,830 µS/cm; in 2017, it was 230 µS/cm. The concentrations of Na varied between 16 and 210 mg/L. The mean Na concentration was 144.4 mg/L, which is significantly lower than the WHO – recommended limit of 200 mg/L (WHO, 2011) (Table 3). In contrast, the K concentrations varied between 1 and 34 mg/L. The minimum and maximum concentrations of Ca and Mg were, respectively, 20 mg/L and 115 mg/L, and 6 and 292 mg/L. The mean concentration of Cl (272.2 mg/L) was found to be greater than the permissible limit of 250 mg/L (Table 5). Nevertheless, a comparatively elevated Cl concentration of 511 mg/L was identified in the study site in 2011, presumably attributable to human activities (WHO 1993). The hydrochemical properties of the groundwater were statistically ranged as shown in (Table 6). The lower fluoride concentrations (1.38) and the acidic pH (2.42) were identified. As previously stated, elevated concentrations were detected in the EC (1600) and rainfall (1777.2). Figure 6 the positive relationship between NO_3 and the hydrochemical properties is evident with respect to TH, TA, Ca, Cl, EC, Na, SAR, SO_4, and WL (Table 8).

Statistical analysis of water quality

The Scatter plot and fitted line plot of hydrochemical properties (WL, HCO_3, and pH) of groundwater versus nitrate in the study area

Table 3. Water quality standard (WHO-2019)

Sl. No	Quality parameters	WHO standards (2019)
1	pH	7.5–8.5
2	Total alkalinity (TA) in mg/L as $CaCO_3$	600
3	Total hardness (TH) in mg/L as $CaCO_3$	200
4	Calcium in mg/L (Ca)	75
5	Magnesium in mg/L (Mg)	50
6	Sodium in mg/L (Na)	200
7	Potassium (K) in mg/L	55
8	Chloride (Cl) in mg/L	250
9	Sulphate (SO_4) in mg/L	500
10	Nitrate (NO_3) in mg/L	45
11	Electrical conductivity (EC) in µmho/cm	250
12	NH_4 in mg/L	3
13	Total dissolved solids (TDS) in mg/L	500
14	Fluoride in mg/L(F)	1.5

are in Figure 5a–f. Nitrate levels peaked at 150 mg/L, following a positive connection (r = 0.12) with increasing WL (Figure 5a). The regression Equation for nitrate with WL is WL = 5.682+0.00874 NO_3, and the analysis of variance (ANOVA) with WL (MS – 2.144; F – 0.35; P – 0.560) is shown in Figure 5b. The results of the analysis of variance (MS – 4747.26; F – 1.94; P – 0.181) (Figure 5d) demonstrated that nitrate and bicarbonate had a negative association (r = -0.31), as seen in Figure 5c. A negative association (r = -0.04) and a regression equation of pH = 7.353 - 0.000656 NO_3 were shown by the scatter plot and fitted line plot (Figure 5e and 5f) in relation to nitrate and pH (see Table 9). Figure 6a shows that when the ionic strength of water increases, there is a rise in NO_3 because EC exhibited a positive connection with nitrate (r = 0.29). Regression analysis using EC and nitrate levels yielded a significant increase, as seen in a fitted line plot (Figure 6b) with an analysis of variance of (MS – 245360; F – 1.64; P – 0.216). The regression equation for EC is 970.2+2.958 NO_3.

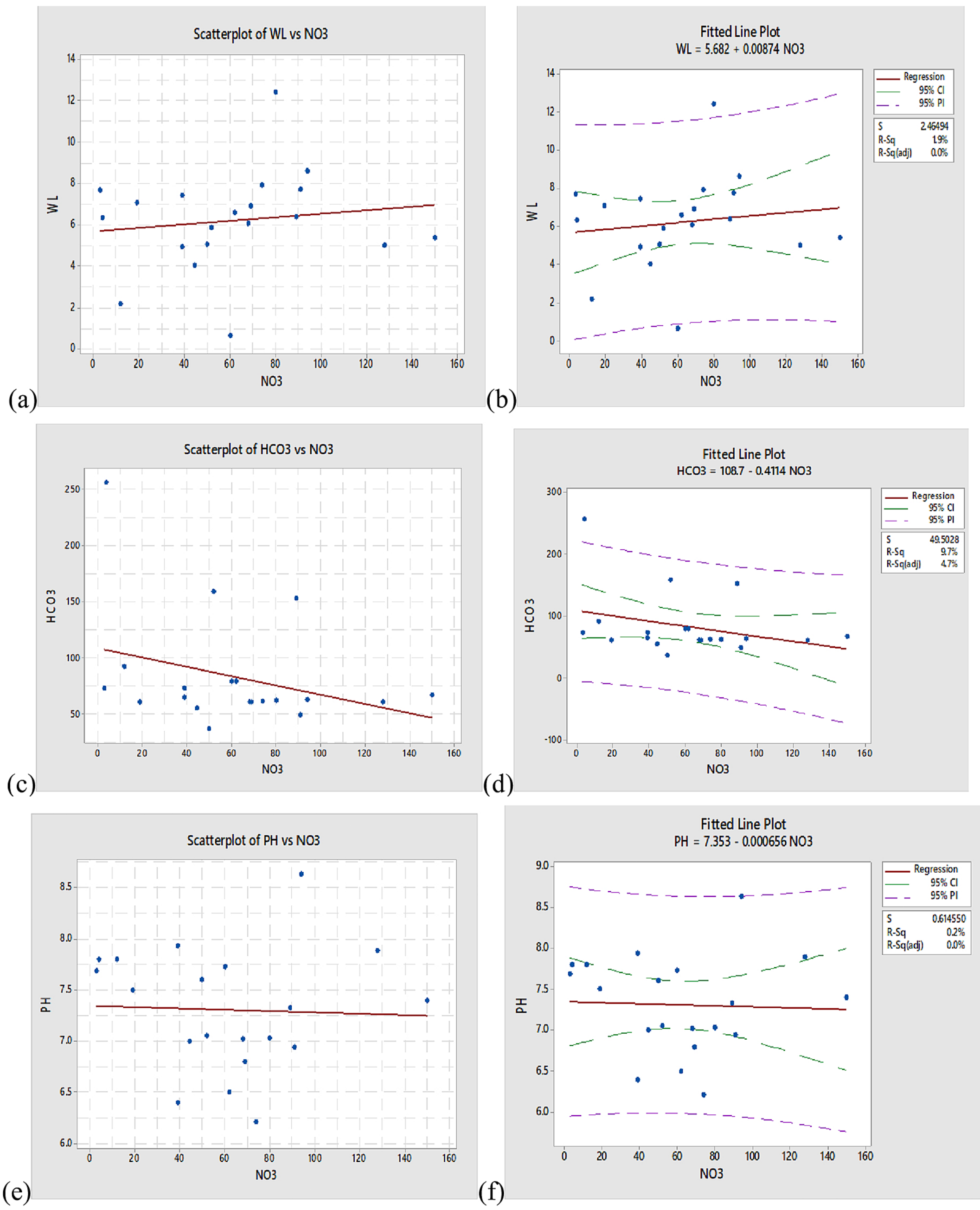

Figure 5. Scatter plot and fitted line plot showing the relationship between hydro chemical properties (WL, HCO3, and pH) vs. nitrate at Thuckalay

An analysis of variance (ANOVA) revealed a negative correlation (r = -0.19) between NO_3 and K (Figure 6c and d) and a significant result (MS – 52.28; F – 0.70; P – 0.412). A positive correlation between NO_3 and SO_4 is shown in Figure 6e (r = 0.40). A similar significant impact was seen in the regression analysis (Figure 6f), which also yielded an analysis of variance (MS-29226.9; F – 3.48; P – 0.079) and a regression equation ($SO_4 = 24.44+1.021NO_3$).

The levels of Cl (MS – 3773.5; F – 0.23; P – 0.636) and Ca (MS – 307.79; F – 0.68; P – 0.422) increased with the rise of NO_3 concentrations, respectively, and there was a positive association between Cl and Ca with NO_3 (Figure 7 a–d). This demonstrates the shared source of NO_3, significant Ca, and Cl ions, as well as their combined impact on the overall ionic strength of groundwater. The regression Equation for Cl is 249.7+0.3668 NO_3, whereas the Equation for Ca is 50.46+0.1048 NO_3 (Table 9). Magnesium (Mg) exhibits a negative correlation (r = -0.15) with nitrate (NO_3) levels, as seen in Figure 8a and 8b. On the other hand, sodium (Na) demonstrates a positive correlation (r = 0.20) with NO_3 levels, as shown in Figure 8c and 8d. Their study of variance yielded comparable findings for Mg (mean square – 1505.99; F – value – 0.41; p – value – 0.528) and Na (mean square – 2665.47; F – value – 0.76; p – value – 0.395).

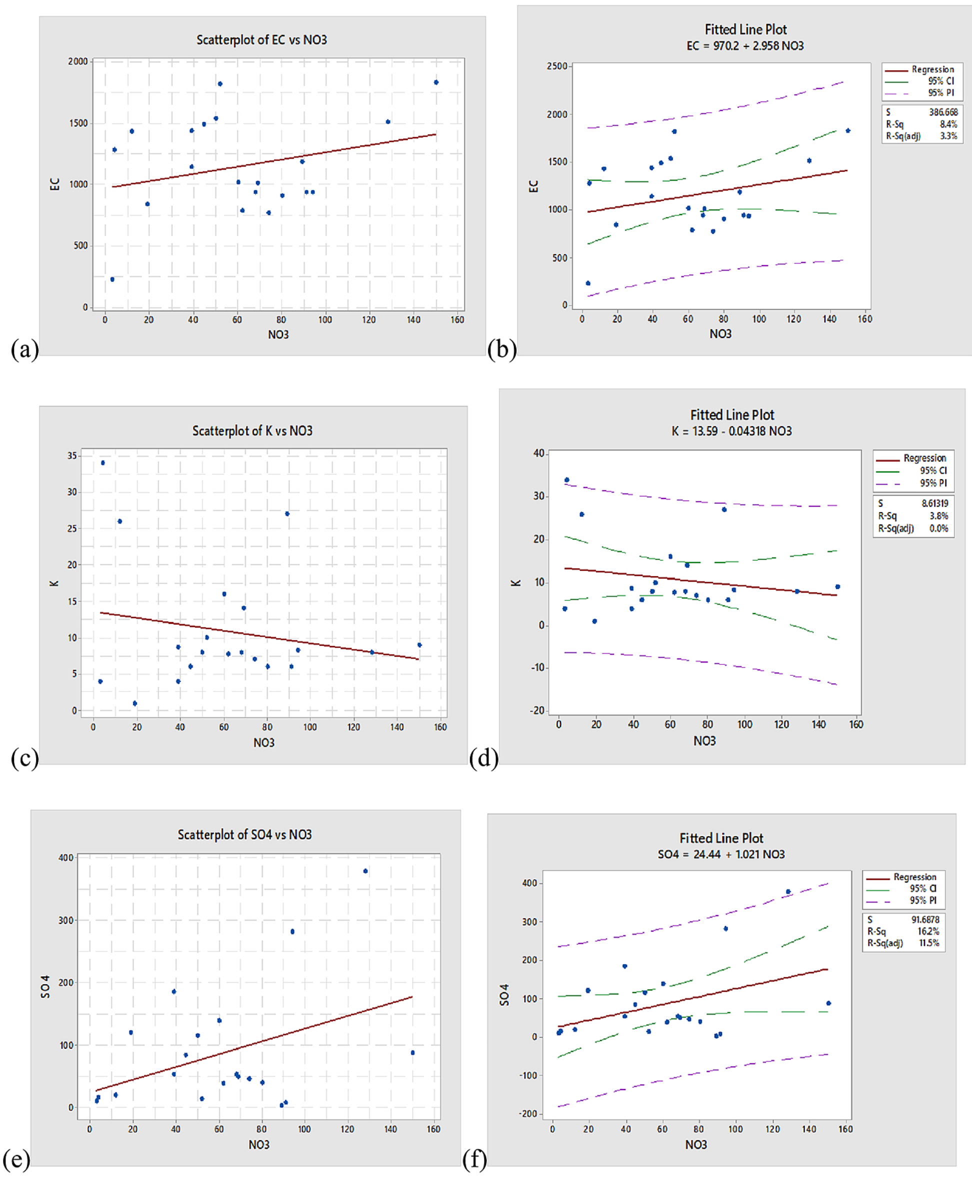

Figure 6. Scatter plot and fitted line plot showing the relationship between hydro chemical properties (EC, K, and SO_4) vs nitrate at Thuckalay

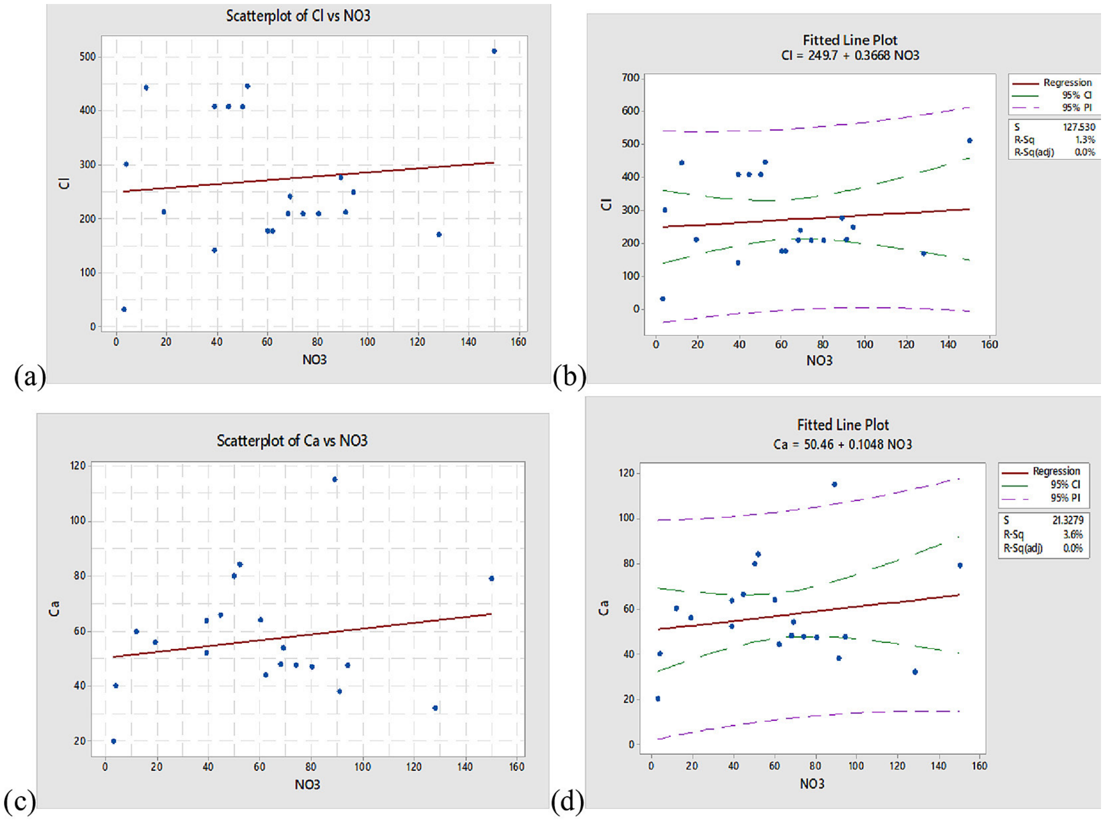

Figure 7. Scatter plot and fitted line plot showing the relationship between hydro chemical properties (Cl and Ca) vs nitrate at Thuckalay

The regression Equation for Mg is Mg = 62.98-0.2317 NO_3, while for Na it is Na = 125.5+ 0.3083 NO_3. Despite the increase in rainfall, there was a negative correlation (r = -0.01) observed between NO_3 levels and rainfall, as shown in Figure 8 e and f. The analysis of variance (ANOVA) results for NO_3 (MS – 155; F – 0.00; P – 0.979) indicate that there is no significant relationship. The regression Equation for the relationship between rainfall and NO_3 is rainfall = 1364-0.074NO_3.

Nitrate pollution index (NPI)

The nitrate pollution index in the designated study area varied between -0.05 and 6.5 mg/L between the years 2000 and 2019 (Table 10). Water quality was categorized into five stages based on NPI values: range 0 > signifies the absence of pollution in 2000, 2015, 2017, and 2019; range 0–1 signifies light pollution in 2007 and 2012; range 1–2 signifies moderate pollution in 2006, 2008 and 2009; range 2–3 signifies significant pollution from 2001 to 2004; range > 3 signifies more significant pollution in 2005, 2010, 2011, 2013 and 2014. (refer to Figure 4)

Contour plot and trend analysis

The contour plot of NO_3 with rainfall, WL, EC, Cl, Na, and SO_4 is shown in (Figure 9a–e). A trend analysis plot for NO_3 was observed using a linear trend model for the year 2000 to 2024 (Figure 10). It represents the maximum nitrate levels in 2011 and 2014; with the lower NO_3 levels observed in 2024 being 46.91 mg/l was beyond the permissible limit.

DISCUSSION

The process by which water travels through the ground or over land and carries pollutants, both natural and artificial, may lead to nonpoint-source pollution. Eventually, these pollutants can wind up in bodies of water such as rivers, marshes, lakes, etc. Rain, untreated wastewater disposal, and irrigation of crops or lawns are all examples of nonpoint-source contamination that can harm aquatic life and humans with nutrients, bacteria, and other harmful chemicals (http://www.waterencyclopedia.com/Po-Re/Pollution-Sources-,

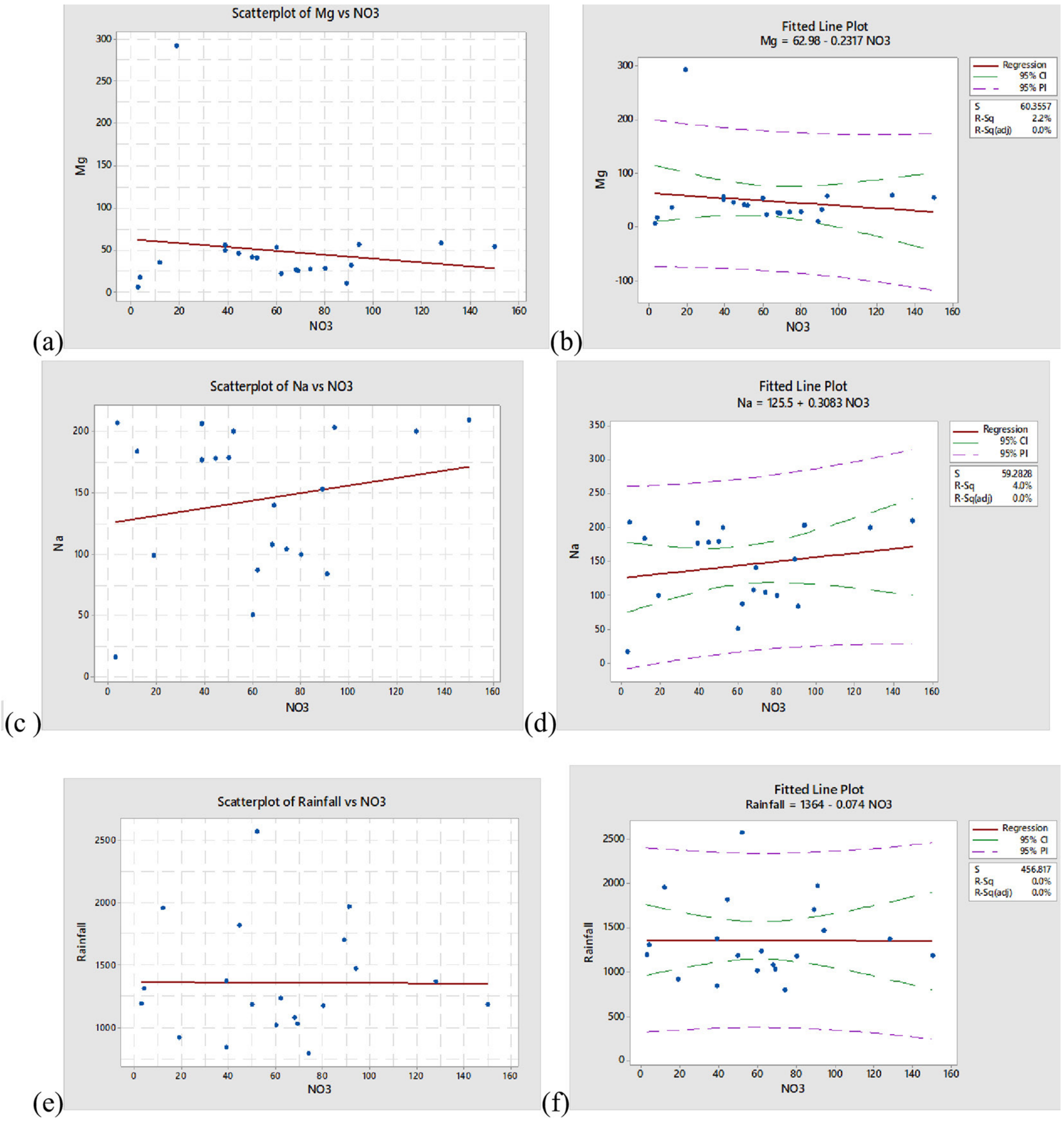

Figure 8. Scatter plot and fitted line plot showing the relationship between hydro chemical properties (Mg, Na and Rain fall) vs. nitrate at Thuckalay; Pl- prediction interval, Cl- confidential interval

Point-and-Nonpoint.html#ixzz7ER6AB5oB-24). Agricultural pesticides, fertiliser, livestock, and aquaculture constituted the bulk of nonpoint source pollution (Wang et al., 2015). In Nigeria, eutrophication may occur when agrochemicals such fertilisers, insecticides, and herbicides seep into surrounding water sources, increasing phosphate and nitrate levels (Ighalo and Adeniyi, 2020). According to the Chinese Research Academy of Environmental Sciences (2006), point source pollutant emissions were calculated using data from both residential and commercial sewage treatment. Water pollution in Nigeria may be attributed to three main sources: industrial effluent (18% of research output), hydrogeology (25% of research output), and roof type (31%). This information was compiled by (Ighalo et al., in 2021.). Furthermore, in order to remove or significantly reduce the presence of possible pollutants, several rules and regulations control the handling, storage, and use of contaminated materials (http://www.epa.gov/OWOW /NPS/facts /index.html). In 2021, the proportion of the population rose 6.0% from 2011 (Table 2). The nitrate contamination in the groundwater, caused by non-point source pollution, grew in tandem with the population growth in Padmanabhapuram town from 1921 to 2021. The largest change from 2001 to 2011 was +108.79 hectares, as shown above, due to the increased residential area as a result of the greater population (Table 1). According to (Lenart-Boroń et al., 2017), water quality in the major rivers of Podhale in Southern Poland is greatly affected by the percentage of built-up areas and agricultural

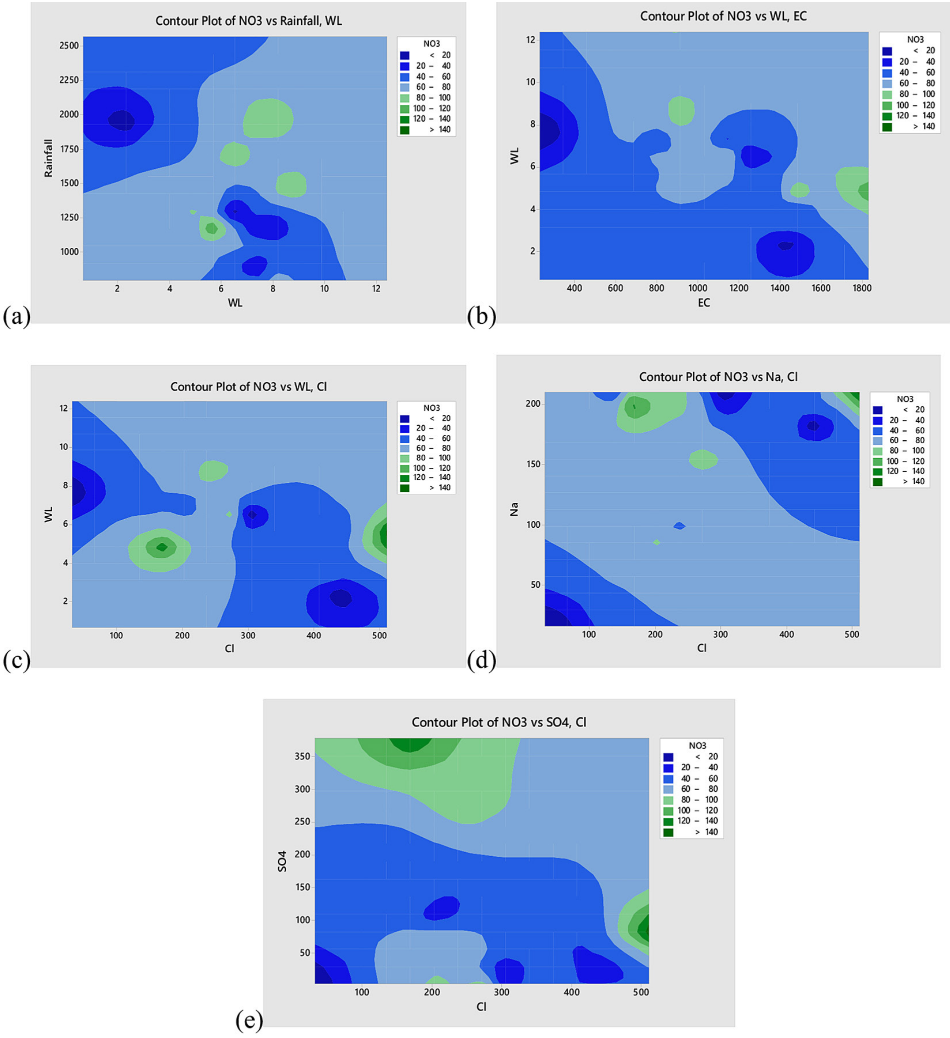

Figure 9. Contour plot showing the relationship between the hydro chemical properties of (EC, Cl, Na, SO_4 and rainfall, WL) with nitrate; a) nitrate (No_3) with rain fall and water levels (WL), b) nitrate (No_3) with water (WL) and EC, c) nitrate (No_3) with water (WL) and chloride (Cl), d) nitrate (No_3) with sodium (Na) and chloride (Cl), e) nitrate (No_3) with sulphate (SO_4) and (chloride (Cl).

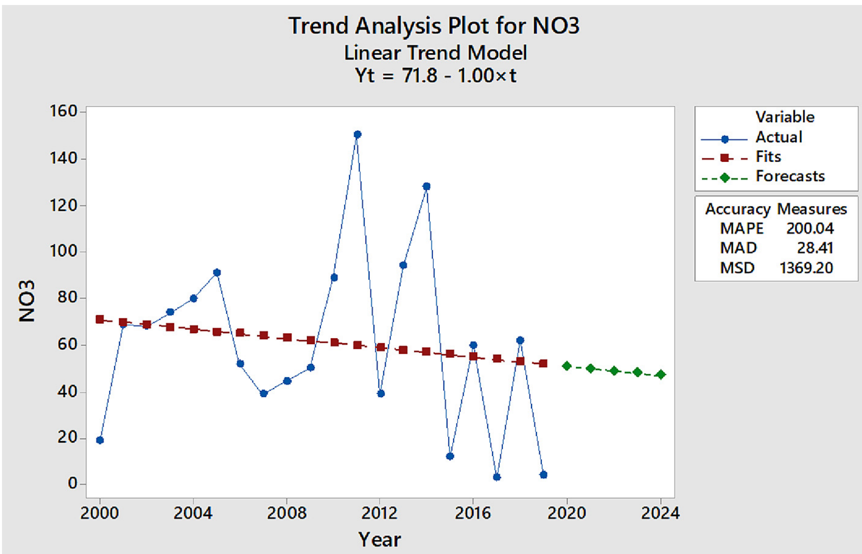

Figure 10. Trend analysis plot (linear trend model) for NO_3 from 2000 to 2024

land, suggesting a strong link between the two. The current investigation evaluated all water quality data with both the Indian and WHO criteria, as shown in Table 3. As you can see from Table 4, we analysed the hydrochemical parameters from 2000 to 2019. With the exception of five samples that fall into the acidic pH range of 6.2–6.9, all of the groundwater samples fall within the pH range of 6.2 to 8.6. In 2013, the maximum allowable value of 8.6 was surpassed in a single sample. According to (Różkowski et al., 2017), the cave waters in the Kraków-Częstochowa Upland in southern Poland were found to be of varying pH levels, from soft to extremely hard, and to be slightly acidic or alkaline. The observed electrical conductivity (EC) ranged from 230 to 1,830 µS/cm. A recent research (Sajilkumar et al., 2014) found that EC values have been on the rise, which might mean that the hydrogeochemistry of the groundwater in the region is being affected by both natural and human-made factors. All the ions as well as TH were measured in mg/L, while EC was measured in µS/cm and pH is unitless. Groundwater quality and main ion chemistry were assessed in a hydrochemical research conducted in the Karur district of the Amaravathi River basin, according to Jafer Ahamed et al. (2015). The concentrations of Cl ranged from 277 to 511 mg/L, which is greater than the 250 mg/L limit. Nevertheless, in 2011, the study region had a notable amount of 511 mg/L, which was likely generated by human activities. It should be noted that the research region contains both agricultural runoff and human waste, the latter of which has a longer time before it enters water bodies (Sajilkumar et al., 2014; Geetha et al., 2008). In addition, the research conducted by (Esakkimuthu et al., 2015) reveals that the primary causes of pollution in Putheri Lake are agricultural runoff and home sewage. As a result, the authors propose organic farming practices and the implementation of centralised sewage treatment facilities as measures to prevent water pollution. According to the World Health Organisation (2011), the values of sodium were from 16 to 210 mg/L, whereas those of potassium were 1 to 34 mg/L. In 2017, there was a decreased content of 20 mg/L of calcium and 6 mg/L of magnesium.

With a concentration of 256 mg/L, bicarbonate reached its peak in 2019. Sulphate levels ranged from 3 to 378 mg/L between 2010 and

Table 4. Hydro chemical properties present in the ground water of Thuckalay from the year 2000 to 2019

Year	HCO_3	Ca	Cl	EC	F^-	K	Mg	Na	NO_3	pH	SAR	SO_4	TH	TA	Rainfall	WL
2000	61	56	213	838	0.8	1	292	99	19	7.5	1.18	120	260	50	918	7.09
2001	61	54	241	1010	0.2	14	25	140	69	6.8	3.95	50	240	50	1029	6.91
2002	61	48	209	939	1.4	8	26	108	68	7.0	3.12	53	225	50	1082	6.09
2003	61	47.5	209	770	0.1	7	27	104	74	6.2	2.98	46	229	50	792	7.92
2004	62	47	209	905	0.1	6	28	100	80	7.0	2.85	40	234	50	1173	12.4
2005	49	38	213	937	0.2	6	31	84	91	6.9	2.43	8	225	40	1967	7.74
2006	159	84	447	1820	0.2	10	40	200	52	7.0	4.49	14	375	130	2569	5.88
2007	73	52	408	1440	0.6	4	49	177	39	6.4	4.2	53	335	59	1375	4.92
2008	55	66	408	1488	0.7	6	45	178	44	7	4.12	84	352	45	1815	4.05
2009	37	80	408	1536	0.8	8	41	179	50	7.6	4.04	115	370	30	1183	5.05
2010	153	115	277	1185	0.3	27	10	153	89	7.3	3.67	3	320	125	1701	6.39
2011	67	79	511	1830	0.6	9	54.1	210	150	7.4	4.45	88	420	54	1184	5.4
2012	65	63.6	142	1143	0.9	8.6	55.5	206	39	7.9	4.59	184	386	53	841	7.45
2013	63	47.6	249	935	0.1	8.3	56.9	203	94	8.6	4.73	281	353	51	1472	8.6
2014	61	32	170	1510	0.1	8	58.3	200	128	7.8	4.87	378	320	50	1370	5
2015	92	60	443	1430	1.5	26	35.3	184	12	7.8	4.66	20	295	75	1953	2.19
2016	79	64	177	1020	0.6	16	53	51	60	7.7	0	139	380	0	1017	0.65
2017	73	20	32	230	0.4	4	6	16	3	7.6	0	10	75	0	1191	7.7
2018	79.3	44	177	788	1.1	7.8	21.8	87.4	62	6.5	0	38.4	200	0	1233	6.6
2019	256	40	301	1280	0.6	34	17.0	207	4	7.8	6.90	16	170	0	1311	6.35

Note: Data source: cgwb.gov.in/wqreports.html. HCO_3-bicarbonate; Ca- calcium; Cl- chlorine; EC-electrical conductivity; F^--fluoride, K-potassium, Mg- magnesium, Na- sodium, NO_3- nitrate, SAR-sodium adsorption ratio, SO_4- sulphate, TH-total hardness, TA-total alkalinity, WL-water level.

2014. According to the World Health Organisation (1993), the maximum permissible fluoride concentration in 2015 was 1.5 mg/L. Examining the water quality using histograms and a Pearson statistic matrix yielded similar results as the current study: 75% of the water was of fair to exceptional quality. It was recommended that residents of Ravolkole village in Hyderabad not drink the water because of the high levels of fluoride in it (Kumar, 2020). In 2011, nitrate concentrations in the research area varied between 3 and 150 mg/L. Nitrate concentrations in groundwater in the coastal parts of Chennai were also found to vary between 9 and 106 mg/L, according to (Saranya et al., 2011). (Sajilkumar et al., 2020) found that agricultural activities did not affect the groundwater quality on Riverine Island, which is located on the west coast of Kerala. The concentrations of nitrate, manganese, and phosphate were far below the acceptable levels. Nevertheless, compared to Chennai, Thuckalay reported lower nitrate levels in 2017 and 2019. At 50 mg/L (BIS 1992) and 45 mg/L (WHO 2011), 35% of the samples were found to meet the nitrate threshold in this investigation. The research by (Madhav et al., 2020) shows that NO_3 pollution in Keonjhar City, Odisha is severe, with 40% of samples showing levels beyond the allowed limit established by WHO (2011). Table 4 shows that nitrate concentrations in water samples were more than 45 mg/L in 2011 (150 mg/L) and in 2014 (128 mg/L). In addition, the findings of (Gupta et al., 2020) indicate that the subsurface Gangetic kankar dominates the southern half of north Bihar when it comes to nitrate-leaching sensitivity. Alluvial deposition in the subsurface was also shown to pose a substantial danger of contamination in the research area's eastern north. Table 5, which shows the highest values of EC and rainfall, also shows the statistical variation of hydrochemical characteristics. It shows that the pH was acidic (0.358) and that the fluorine levels were low (0.1756). Table 6 shows that the EC (1600) and Rainfall (1777.2) had the largest average ranges, as shown before. The non-point source pollution in the research region may be impacted by the flowing water bodies due to higher electrical conductivity (EC) and rainfall.

According to Table 8, NO_3's hydrochemical characteristics were positively correlated with Ca, Cl, EC, Na, SAR, SO_4, TH, TA, and WL. Farmers employ a wide variety of fertilisers to boost agricultural output, and studies have shown that several parameters such as fertiliser application rate, crop rotation, irrigation technique, soil

Table 5. Statistical variance of Hydro chemical properties present in the Ground water of Thuckalay from the year 2000-2019

Variable	N	Mean	SE Mean	Tr Mean	St Dev	Variance
HCO_3	20	83.4	11.3	76.4	50.7	2571.4
Ca	20	56.89	4.73	55.71	21.15	447.14
Cl	20	272.2	27.9	272.3	124.9	15606.5
EC	20	1151.7	87.9	1165.2	393.1	154557.1
F	20	0.5977	0.0937	0.5741	0.4190	0.1756
K	20	10.94	1.91	10.21	8.55	73.03
Mg	20	48.8	13.3	37.6	59.4	3530.3
Na	20	144.4	13.2	147.9	58.9	3469.8
NO_3	20	61.38	8.59	59.69	38.42	1476.08
pH	20	7.313	0.134	7.301	0.599	0.358
SAR	20	3.362	0.412	3.352	1.843	3.398
SO_4	20	87.1	21.8	75.6	97.5	9502.5
TH	20	288.3	19.7	292.8	88.0	7739.4
TA	20	48.38	7.84	46.52	35.08	1230.29
Rainfall	20	1359.3	99.4	1323.6	444.6	197706.9
WL	20	6.219	0.542	6.185	2.423	5.869

Note: HCO_3 – bicarbonate; Ca – calcium; Cl – chlorine; EC – electrical conductivity; F^- – fluoride, K- potassium, Mg – magnesium, Na – sodium, NO_3 - nitrate, SAR - sodium adsorption ratio, SO_4 – sulphate, TH – total hardness, TA – total alkalinity, WL – water level, CumN – cumulative number, CumPct – cumulative percentage; SE Mean – standard error mean; TrMean – treating mean; StDev – standard deviation.

Table 6. Statistical rangesof Hydro chemical properties present in the ground water of Thuckalay from the year 2000–2019

Variable	Coef Var	Sum	Sum of squares	Minimum	Q1	Median	Q3	Maximum	Range
HCO_3	60.80	1668.0	187972.3	37.0	61.0	64.0	79.2	256.2	219.2
Ca	37.17	1137.82	73227.32	20.00	44.75	53.00	65.50	115.00	95.00
Cl	45.89	5444.6	1778734.7	32.0	185.2	227.0	408.0	511.0	479.0
EC	34.14	23034.0	29464842.0	230.0	912.5	1081.5	1476.0	1830.0	1600.0
F	70.10	11.9540	10.4804	0.1200	0.2425	0.6100	0.8225	1.5000	1.3800
K	78.11	218.81	3781.54	1.00	6.00	8.00	13.00	34.00	33.00
Mg	121.87	975.1	114615.0	6.0	25.3	37.8	53.9	292.0	286.0
Na	40.80	2887.6	482837.2	16.0	99.3	165.0	200.1	210.0	194.0
NO_3	62.60	1227.50	103383.25	3.00	39.00	61.00	86.75	150.00	147.00
pH	8.19	146.250	1076.263	6.210	6.955	7.365	7.782	8.630	2.420
SAR	54.83	67.240	290.623	0.000	2.535	3.995	4.565	6.910	6.910
SO_4	111.93	1741.9	332255.7	3.0	17.0	51.5	118.8	378.0	375.0
TH	30.51	5766.0	1809380.5	75.0	226.1	307.5	365.8	420.0	345.0
TA	72.50	967.61	70188.57	0.00	32.79	50.00	54.51	130.33	130.33
Rainfall	32.71	27186.3	40711177.3	792.6	1042.5	1212.6	1644.3	2569.8	1777.2
WL	38.95	124.380	885.030	0.650	5.013	6.370	7.638	12.400	11.750

Note: HCO_3 – bicarbonate; Ca – calcium; Cl – chlorine; EC – electrical conductivity; F^- – fluoride, K – potassium, Mg- magnesium, Na – sodium, NO_3 – nitrate, SAR – sodium adsorption ratio, SO_4 – sulphate, TH – total hardness, TA – total alkalinity, WL – water level. CoefVar-coefficient of variance. Q1 is defined as the middle number between the smallest number and the median of the data set; Q3 is the middle value between the median and the highest value of the data set.

texture, and others impact the variation of nitrate (Suthar et al. 2009). In addition, the poor agricultural yields caused by the continuous use of this groundwater in the Karur area, which has high concentrations of Na+, K+, and Cl-, affects the fertility of the soil and the growth of plants. The Amaravathi River has been overused for groundwater downstream for the last eleven years due to the constant mixing and disposal of urban, agricultural, textile, and dyeing effluents (Jafar Ahamed et al., 2015). According to (Sajilkumar et al., 2014), groundwater nitrate levels are too high because of cattle farm wastes. Along with conducting topographic surveys of water levels and measuring water quality in streams and nearby hand-dug wells in Nepal, (Prajapati et al. 2021) also reported improving the knowledge of the stream-aquifer interactions in the Kathmandu Valley. In this research, WL, EC, SO_4, Cl, Ca, Na, and nitrate are the main variables that might affect the concentration of groundwater (Figure 5–8). The regression equation for WL is WL = 5.682+0.00874 NO_3, and there is a positive connection (r = 0.12) between WL and nitrate levels, which reached a maximum at 150 mg/L in figures 5a and b. The concentration of bicarbonate was found to be decreased (Figure 5c and d). There is a weakly negative connection (r = -0.04) between pH and nitrate, as seen in the scatter plot and fitted line plot (Figure 5e and 5f).

The EC showed a positive correlation (r = 0.29) between nitrate and water ionic strength, suggesting that more NO_3 means stronger water (Figure 7). According to Sathar et al. (2009), groundwater may be contaminated with significant ions such as fertilisers, sewage, and animal wastes via non-point pollution. As shown in Figure 6e–7d, SO_4, Cl, and Ca are excellent fertiliser sources for agricultural use. Few samples had a high concentration of NO_3 and a low concentration of K, owing to the fixing of potassium by the clay minerals. This suggests that fertilisers are only one of many non-point source pollutants, as validated by a 2009 study by Reddy et al. It has been shown that nonpoint source pollution, including agricultural fertilisers, open dumping of animal waste, and inadequate sanitation facilities, are the main causes of nitrate in groundwater (Sajilkumar et al., 2014). Figure 6e and 6f show a positive correlation between NO_3 and SO_4 (r =

Table 7. Statistical ranges of hydrochemical properties present in the ground water of Thuckalay from the year 2000–2019

Variable	IQR	Mode	N for Mode	Skewness	Kurtosis	MSSD
HCO_3	18.2	61	5	2.55	6.91	1938.6
Ca	20.75	*	0	0.98	1.87	269.45
Cl	222.8	209, 408	3	0.34	-0.57	12797.6
EC	563.5	*	0	-0.16	0.26	98638.0
F	0.5800	0.60, 0.64	2	0.82	-0.01	0.2141
K	7.00	6, 8	3	1.66	2.13	58.43
Mg	28.6	*	0	3.95	16.80	2046.8
Na	100.8	200	2	-0.61	-0.71	1566.1
NO_3	47.75	39	2	0.48	0.32	1369.54
pH	0.827	7.8	3	0.05	-0.07	0.199
SAR	2.030	0	3	-0.62	0.11	2.190
SO_4	101.8	53	2	1.90	3.58	5725.6
TH	139.7	225	2	-0.61	0.07	4176.1
TA	21.72	0, 50	4,6	0.77	1.37	894.68
Rainfall	601.8	*	0	1.21	1.48	146711.0
WL	2.625	*	0	0.04	2.27	3.539

Note: HCO_3 – bicarbonate; Ca – calcium; Cl – chlorine; EC – electrical conductivity; F^- – fluoride, K – potassium, Mg – magnesium, Na – sodium, NO_3 – nitrate, SAR – sodium adsorption ratio, SO_4 – sulphate, TH – total hardness, TA – total alkalinity, WL – water level, IQR – interquartile range; MSSD – mean of the squared successive differences.

0.40). According to Table 7, SO_4 has a skewness of 1.90 and a kurtosis of 3.58. The findings from Andhra Pradesh, Tamil Nadu (Dharmapuri), and Rajasthan were comparable to those from previous research (Sajilkumar et al., 2014; Suthar et al., 2009; Reddy 2013), which might indicate that these ions are gradually becoming more abundant, probably due to pollution from sources other than point sources. Since these ions originate in human and animal waste, there was a positive correlation between NO_3 and Cl and Ca in (Figure 7a–d). Agricultural fields are the source of the pollution, according to previous study (Stigter et al., 1998), which demonstrated a positive correlation between Cl and NO_3 (r = 0.11). A research found that exposed septic tank systems increase chloride level with increasing nitrate (McQuillan 2004). Na exhibited a positive correlation (r = 0.20) with NO_3, in contrast to Mg's negative association (Figure 8a–d). There was no statistically significant change in NO_3 when rainfall increased (Figure 8e–f). The presence of nitrate is common in both surface and groundwater sources that have been contaminated by humans. Groundwater pollution is a major problem, and there is a lack of data on the effects on human health (Panneerselvam et al., 2020). In a similar vein to our research, Lake Urmia, formerly thought to be among the biggest hypersaline lakes on Earth, has seen significant environmental deterioration in the last two decades (Schmidt et al., 2021). According to (Ramalingam et al., 2022), NPI is a reliable method for assessing the extent to which groundwater is contaminated with nitrates. Water quality was categorised into five stages based on NPI values: 0 > = no pollution in 2000, 2015, 2017, and 2019; 0–1 = light pollution in 2007 and 2012; 1–2 = moderate pollution in 2006, 2008, and 2009; 2–3 = significant pollution in 2001–2004, 2016–2018; and > 3 = very significant pollution in 2005–2010, 2011–2013, and 2014 (Table 10) as a result of the Swatch Bharat Abhiyan's mandate that all homes install closed septic tanks, or The government of India launched the Clean India Mission in 2014 as a nationwide initiative to enhance solid and liquid waste management and eradicate open defecation (http://www.swachhbharat.mygov.in). In Figure 9 a–e, we can see the contour map that includes rainfall, WL, EC, Cl, Na, and SO_4. Analysing trends Figure 10 shows the NO_3 plot from 2000–2024, produced by a Linear trend model. It shows the highest nitrate levels recorded in 2011 and 2014, with the lowest NO_3 levels recorded in 2024 at 46.91 mg/l, which is more than what is allowed.

Table 8. Pearson correlation table for the hydro chemical parameters of NO_3, HCO_3, Ca, Cl, EC, F, K, Mg, Na, PH, SAR, SO_4TH, TA, Rainfall and WL

	NO_3	HCO_3	Ca	Cl	EC	F	K	Mg	Na	pH	SAR	SO_4	TH	TA	Rainfall	WL
HCO_3	-0.31															
Ca	0.19	0.19														
Cl	0.11	0.17	0.56													
EC	0.29	0.21	0.55	0.85				/								
F	-0.41	-0.04	0.06	0.17	0.07											
K	-0.19	0.77	0.30	0.21	0.22	0.15										
Mg	-0.15	-0.20	0.01	-0.02	-0.03	0.10	-0.34									
Na	0.20	0.28	0.38	0.65	0.80	0.02	0.29	-0.03								
pH	-0.04	0.13	-0.01	-0.10	0.06	0.03	0.27	0.15	0.30							
SAR	0.12	0.40	0.22	0.55	0.66	-0.07	0.43	-0.19	0.90	0.24						
SO_4	0.40	-0.33	-0.17	-0.19	0.15	-0.20	-0.25	0.26	0.34	0.56	0.18					
TH	0.41	-0.16	0.66	0.58	0.75	0.01	-0.03	0.14	0.62	0.23	0.35	0.42				
TA	0.24	0.14	0.66	0.45	0.48	-0.16	0.11	0.03	0.44	-0.09	0.39	-0.09	0.44			
Rainfall	-0.01	0.32	0.28	0.49	0.46	-0.09	0.21	-0.22	0.303	0.01	0.28	-0.23	0.19	0.557		
WL	0.12	-0.07	-0.27	-0.37	-0.43	-0.44	-0.32	-0.00	-0.14	-0.13	-0.01	-0.08	-0.41	0.048	-0.19	

Note: HCO_3 – bicarbonate; Ca – calcium; Cl – chlorine; EC – electrical conductivity; F^-– fluoride, K – potassium, Mg – magnesium, Na – sodium, NO_3 – nitrate, SAR – sodium adsorption ratio, SO_4 – sulphate, TH – total hardness, TA – total alkalinity, WL – water level.

Table 9. Regression analysis of the water quality parameters

Slno	Parameter	Regression equation	R-sq (%)	R-sq (adj) (%)	SS	MS	F	P
1	HCO_3- NO_3	HCO_3 = 108.7-0.4114 NO_3	9.72	4.70	4747.3	4747.26	1.94	0.181
2	pH - NO_3	pH = 7.353-0.000656 NO_3	0.18	0.00	0.01208	0.012077	0.03	0.860
3	EC - NO_3	EC = 970.2+2.958 NO_3	8.36	3.26	245360.0	245360	1.64	0.216
4	K - NO_3	K = 13.59-0.04318 NO_3	3.77	0.00	52.28	52.2791	0.70	0.412
5	SO_4 - NO_3	SO_4 = 24.44+1.021NO_3	16.19	11.53	29227.0	29226.9	3.48	0.079
6	Cl - NO_3	Cl = 249.7+0.3668 NO_3	1.27	0.00	3773.0	3773.5	0.23	0.636
7	Ca - NO_3	Ca = 50.46+0.1048 NO_3	3.62	0.00	307.80	307.797	0.68	0.422
8	Mg - NO_3	Mg =62.98-0.2317 NO_3	2.25	0.00	1506.0	1505.99	0.41	0.528
9	Na - NO_3	Na =125.5+0.3083 NO_3	4.04	0.00	2665.5	2665.47	0.76	0.395
10	Rainfall -NO_3	Rainfall = 1364-0.074NO_3	0.00	0.00	155.0	155.0	0.00	0.979
11	WL - NO_3	WL = 5.682+0.00874 NO_3	1.92	0.00	2.144	2.14417	0.35	0.560

Pollution prevention and best management techniques may be put into place at the federal, state, and local levels to lessen the impact of nonpoint source pollution (Zoller and Uri 1994). Results from a study conducted in northern Missouri can help improve decision-making strategies to improve water quality for the entire river basin. The study aimed to better understand the various land use, geologic, and topographic factors that affect water quality in Midwestern watersheds (Jabber and Grote 2019). The two most popular AI models for water quality monitoring and assessment over the last decade have been Artificial Neural Networks (ANN) and Adaptive Neuro-Fuzzy Inference systems (ANFIS), according to research (Ighalo et al. 2020). Most of the research that has produced neural network monitoring and evaluation systems for surface water quality has been conducted in Southeast Asia and Iran. In terms of surface water quality prediction accuracy, ANFIS, Wavelet-ANN (W-ANN), and Wavelet-ANFIS (W-ANFIS) were the top models. In addition, (Quarto and Zinzani 2021) analyse the Water Framework Directive (WFD), a landmark

Table 10. Nitrate pollution index from the year 2000–2019

Sl no	Year	NO_3	NPI	Range	Classification of water quality
1	2000	19	-0.05	0 >	No Pollution
2	2001	69	2.45	2 to 3	Significant pollution
3	2002	68	2.4	2 to 3	Significant pollution
4	2003	74	2.7	2 to 3	Significant pollution
5	2004	80	3	2 to 3	Significant pollution
6	2005	91	3.55	> 3	More significant pollution
7	2006	52	1.6	1 to 2	Moderate pollution
8	2007	39	0.95	0 to 1	Light pollution
9	2008	44.5	1.225	1 to 2	Moderate pollution
10	2009	50	1.5	1 to 2	Moderate pollution
11	2010	89	3.45	> 3	More significant pollution
12	2011	150	6.5	> 3	More significant pollution
13	2012	39	0.95	0 to 1	Light pollution
14	2013	94	3.7	> 3	More significant pollution
15	2014	128	5.4	> 3	More significant pollution
16	2015	12	-0.4	0 >	No Pollution
17	2016	60	2	2 to 3	Significant pollution
18	2017	3	-0.85	0 >	No Pollution
19	2018	62	2.1	2 to 3	Significant pollution
20	2019	4	-0.8	0 >	No Pollution

law that sought to reshape water administration in Europe via the promotion of participatory and sustainable practices. Women had much higher pro-environmental views than males, according to research by (Okumah et al., 2021). Forest zones were used to assess the environmental and economical sustainability of slum expansion, census data, and normalised difference vegetation index (NDVI) changes (Liu et al., 2021)".

Recommendations for sustainable management of NO_3 contaminated groundwater

In the future, enhancing the organic forming, and optimum utilization of conventional forming, to control the nitrate contamination in the groundwater. To avoid the harmful impacts of nitrate on groundwater quality, precautionary steps such as the construction of wetlands, Miyawaki forests, and sustainable land usage must be taken in water management plans. Cost-effective gentrification techniques such as biological treatment methods, and artificial groundwater recharge structures must be implemented for sustainable management of NO_3-contaminated in groundwater (Sajilkumar et al., 2014).

CONCLUSION

In this study, the geochemistry of groundwater was investigated using statistical analysis to determine the nitrate concentration in groundwater. NO_3 concentrations ranged from 3 to 150 mg/L, and 65% of the water samples were beyond the allowable limit for drinking according to Indian and WHO standards. A positive correlation between NO_3 and WL, EC, Cl, Ca, SO_4, Na, TH, TA, and SAR suggests that nonpoint source pollutant has an impact on groundwater. As per NPI values, water quality was classified into five stages, range 0 > indicates no pollution in the years 2000, 2015, 2017, 2019, range 0–1 indicates light pollution in the years 2007, 2012, range 1–2 indicates moderate pollution in the years 2006, 2008, 2009, range 2–3 indicates significant pollution in the year 2001 to 2004, 2016, 2018, range > 3 indicates very significant pollution in the year 2005, 2010, 2011, 2013, 2014. Due to the increase of the population, and the continuous application of fertilizers in the agricultural lands, the human and animal waste dumped without any treatment is the major cause of the contamination of groundwater with Nitrate in the study area. More detailed studies using modern tools such as modeling and application of isotopes will be useful for a better solution to this problem.

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