Anthropogenic Nitrate Pollution in Groundwater and Its Health Risks in The View of Background Concentration in a Semi-Arid Area of Rajasthan

Abdur Rahman (✉ alrahman777@gmail.com)

National Geophysical Research Institute

N.C. Mondal

National Geophysical Research Institute

K.K. Tiwari

National Institute of Technology (NIT), Garhwal, Uttarakhand, India

Research Article

Keywords: Hydrochemistry, nitrate pollution, natural background, anthropogenic impacts, health risk assessment, semi-arid area, Rajasthan

Posted Date: January 20th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-147468/v1>

License: This work is licensed under a Creative Commons Attribution 4.0 International License.
[Read Full License](#)

Version of Record: A version of this preprint was published at Scientific Reports on April 29th, 2021. See the published version at <https://doi.org/10.1038/s41598-021-88600-1>.

Anthropogenic nitrate pollution in groundwater and its health risks in the view of background concentration in a semi-arid area of Rajasthan

Abdur Rahman^{a,b*}, N.C. Mondal^{a,b} and K.K. Tiwari^c

^aEarth Process Modeling Group, CSIR-National Geophysical Research Institute, Hyderabad, India

^bAcademy of Scientific & Innovative Research (AcSIR), Ghaziabad - 201 002, India

^cNational Institute of Technology (NIT), Garhwal, Uttarakhand, India

*Corresponding author: alrahman@ngri.res.in

Abstract

An increased nitrate (NO_3^-) concentration in groundwater has been a rising issue on a global scale in recent years. Through different consumption mechanisms, it clearly illustrates the adverse effects on human health. The goal of this present study is to assess the natural and anthropogenic NO_3^- concentration in groundwater and its related risks to human health in the different groups of ages such as children, males, and females. Groundwater samples ($n=101$) were obtained and analysed for their physicochemical components, along with the nitrate concentration in a semi-arid area of Rajasthan. The results show that most of the samples were influenced by anthropogenic activities. The background and anthropogenic levels had been estimated and marked as 7.2 mg/L and 13.3 mg/L for the background and anthropogenic concentrations, respectively. About 83% of nitrate samples were exceeded the background limit, while 28% of the samples were beyond the permissible limit of 45 mg/L as stated by the Bureau of Indian Standards (BIS). Nitrate health risks were also measured by oral intake and dermal contact sources for the residents in this area. The oral exposure of nitrate was very high as compare to dermal contact. With regards to the non-carcinogenic health risk, the total Heath Index (HI_{Total}) values of groundwater nitrate in the study area varied from 0.045 to 3.153 with an average of 0.964 for males, 0.053 to 3.726 with an average of 1.139 for

females, and 0.061 to 4.278 with an average of 1.308 for children. The nitrate health risk assessment shows that about 38%, 46%, and 49% of groundwater samples constitute the non-carcinogenic health risk to males, females, and children, respectively.

Key words: Hydrochemistry, nitrate pollution, natural background, anthropogenic impacts, health risk assessment, semi-arid area, Rajasthan.

Introduction

Groundwater, especially in arid and semi-arid regions, is typically the most valuable water resource, and so the conservation of groundwater supplies is important worldwide¹. However, over the past few decades, groundwater quality in most aquifers worldwide has declined due to increased human effects. The continued growth of the global population is inextricably related to an increase in the generation of waste^{2,3}. Such waste, including domestic waste, waste from building and construction, chemical and toxic waste, sludge, and ash⁴. In this modern era, however, rapid development, population explosion, urbanisation, industrialization, tremendous use of fertilisers in irrigation fields, improper sewage systems, human and animal waste contribute to groundwater pollution⁵. Groundwater pollution is closely correlated with diffuse (non-point) sources for agricultural operations. Several types of inorganic and organic fertilisers are used^{6,7,8}. The risk of groundwater pollution is raised by the improper use of chemicals and fertilisers. Once the groundwater is polluted, remediation is difficult. Thus, the prevention of pollution is also the key water quality control policy⁹. The primary source of inorganic nitrogen within the soil is nitrate, which is necessary for healthy crops to grow and develop¹⁰.

Nitrate (NO_3^-) is an enormously powerful environmental pollutant that not only arises naturally, but also released by a number of anthropogenic exercises. These anthropogenic activities include the manufacture and use of nitrate fertilizers, fossil fuel combustion (occur

as atmospheric deposition, hereinafter AD) and releases of both domestic and industrial sewage systems and modification in nitrogen-fixing crops in natural vegetation¹¹⁻¹³. In most natural waters, nitrate forms a critical portion of the ionic charge. Because of the harmful effects on humans at high doses, NO_3^- ions are used in international regulations and guidelines¹⁴. However, the long-term intake of elevated nitrate concentrations can cause serious health hazards in children, such as methemoglobinemia, which is also known as a blue baby syndrome, and stomach cancer in adults as well^{15,16}. In view of this, the World Health Organisation (WHO) has defined a maximum nitrate level of a contaminant in drinking water as 50 mg/L. As per the Indian situation, 45 mg/L is recommended by the Bureau of Indian Standards (BIS) as the permissible level of NO_3^- in drinking water. As a result of the prolonged ingestion of groundwater nitrate, serious health issues are encountered in the different parts of the world. Thus, nitrate exposure-related health risk assessment research is extensively studied in different countries such as China¹⁷⁻²⁰, Pakistan²¹, Iran^{22,23}, Mexico²⁴ and India^{5,25-27} have based on the non-carcinogenic risk between adults and children.

Usually, background levels are estimated either temporally (concentrations before anthropogenic activity) or spatially (concentrations in the areas not influenced by anthropogenic activity)²⁸. It may be difficult to establish background concentrations for certain pollutants, mainly those that have several and non-point sources or are environmentally reactive. Nitrate (NO_3^-) is an example of an ion for which it is difficult to establish a threshold concentration due to its different geogenic and anthropogenic origins and its reaction^{28,29}. The issues with establishing a nitrate (NO_3^-) threshold value, is that natural or geogenic processes will differ greatly in time and space that influences $\text{NO}_3\text{-N}$ concentrations. It is generally found that $\text{NO}_3\text{-N}$ concentrations in aquifers decrease with down gradation or with depth^{28,30}. If the groundwater reaches at redoxcline depth (redox

boundary), where nitrate and oxygen suddenly vanish due to denitrification, this will occur within a relatively slight difference in depth^{31,32}. These redox boundaries can shift with time, and there may be a limit to how much NO_3^- can be reduced in some aquifers, mainly those with low concentration organic carbon and ferric iron³³. Thus an important aspect influencing the determination of background concentrations is the well depth from which groundwater samples are taken. The $\text{NO}_3\text{-N}$ concentrations can also be influenced by the water mixing of different ages and/or from different origin. Mixing can takes place naturally (e.g., due to quick recharge) or anthropogenically (e.g., due to construction of the well, wells are frequently uncased over greater depth). Other significant variables include lithology, soil composition, the thickness of unsaturated zone, and bioactivities²⁸.

The investigated area falls under the arid and semi-arid climate state Rajasthan where the only source of fresh water is groundwater. According to the CGWB report³⁴, most of the areas of the state have been categorised as over-exploitation zones. Along with the over-exploitation of groundwater, the quality of this precious resource is also highly degraded. Thus, the key objectives of this research are: to (1) analyse groundwater chemistry, (2) evaluate regional natural background concentration of nitrate, (3) investigate nitrate toxicity for understanding the potential source and contamination mechanism of nitrate, and (4) quantify the potential non-carcinogenic health risk induced by groundwater exposure to nitrate using recommended model of the US Environmental Protection Agency^{35,36}. To our knowledge, this is the first study of health risk assessment considering the natural background level of NO_3^- in groundwater. The findings of this analysis will provide an important scientific and logical understanding of the human health risk of NO_3^- in groundwater and they will also lead to improve the levels of water quality.

Material and Methods

Study area. The area falls between 26° 22' 13.32" to 27° 14' 33.58" north latitudes and 76° 08' 32.62" to 77° 05' 00.41" east longitudes, covering an area of about 3420 km² (Fig.1a). Three significant river basins are present in the study area; Banganga basin (covering about 63% of the study area in the northern part), Morel basin (covering about 34% of area in the southern part), and a small part by Ghambhir basin (around 3% of the area in the south of Mahwa)³⁷. Agriculture production is scattered over both kharif, and rabi cultivation in the area; kharif cultivation is based on precipitation (rainfed) and rabi cultivation is especially based on groundwater source.

Figure 1. Showing the maps of (a) Topography in meters above mean sea level and the sampling location of Dausa district, Rajasthan, India, (b) regional geology, and (c) hydrogeology with the potential aquifers

Because of significant daily temperature variations and low, moderate rainfall, the climate of the area can be categorized as semi-arid. It is markedly seasonal and is characterised by a dry

and steadily increasing hot season between March and May, a dry and cold winter between October and February, but from June to September a monsoon season. In the study region, the minimum and maximum temperatures reported are below 10 °C in January, and 48 °C in June. The gross annual evapotranspiration potential is 1744.7 mm³⁴.

Geology and Hydrogeology. In the study area, the Alwar group of rocks consists of quartzite and schist, alluvium and wind-blown sand occupied the north-eastern and south-western parts (Fig.1b). The 3/4th portion of the study area is covered by quaternary alluvium (Younger alluvium: ~21.6%, and older alluvium: ~58.4%) consisting of Aeolian and fluvial slits, sand, gravel, and occasional pebbles³⁷. In hard rock settings, the weathered, fractured, and jointed hard rocks form aquifers. Quartzite contributes to approximately 9% of the aquifer, gneisses and phyllite aquifers occupy 5.3% of the remaining Quaternary alluvium is the primary water-bearing a formation covering about 84.65% of the area³⁴. Talus and scree deposits and hard rocks of Bhilwara and Delhi Super Group rest in a small portion forming about 15.35 % of the minor aquifers. Alluvium sediments including sand, and kankar (calcareous detrital materials), clay, and gravel forms the potential aquifer in the study area (Fig.1c). The occurrence of groundwater is marked under unconfined to confined aquifer conditions with the primary porosity of alluvium³⁸.

The data used for this study. For assessing nitrate contamination and background criteria, analytical hydrochemical data collected by the State Groundwater Department Jaipur, Rajasthan. The samples were collected in 1.0 L polyethylene bottles and used for the analysis of major ions. Before collecting groundwater samples, the wells were drained for a sufficient time so that the accumulated water, if any, was absolutely removed from storage within the assembly of the well. As defined by the American Public Health Association³⁹, the ions were analysed by the standard methods. The portable kits such as electrical conductivity (EC) and pH meters were used to measure the EC and pH at the time of sampling. Major ions (Na⁺, K⁺,

Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻, HCO₃⁻ and NO₃⁻) and total hardness (TH) at Regional Chemical Laboratory, Ground Water Department, Jaipur, Rajasthan. After verifying the reliability of data, about 97 samples, out of 101 collected data were used for background analysis and hydrochemical characterization. Furthermore, 37 samples were picked based on 11×11 Km equal grid distribution and used for non-carcinogenic human health risk assessment.

Charge balance error. In order to verify the validity and reliability of the analysed hydrochemical dataset, the cation-anion balance procedure was carried out. The basic law of electro-neutrality allows the number of cations to be equal to or almost equal to the number of anions. The error was measured using the methods implemented⁴⁰ to validate and remove low-quality samples. The ion concentration unit was first changed from milligram per litre (mg/L) to milliequivalent per litre (meq/L). To calculate the ionic balance error of each sample, the following given formula was used^{41,42}.

$$\text{Charge balance error} = \left\{ \frac{(\sum \text{Cations} - \sum \text{Anions})}{(\sum \text{Cations} + \sum \text{Anions})} \right\} \times 100 \quad (1)$$

The calculation of groundwater quality results may good if the charge balance error is < ± 5%, and if the charge balance error is <± 5%, it will be considered as poor⁴³. However, the charge balance error of up to ±10% is acceptable for groundwater⁴⁴. The value would not pass the validation test if it is greater than ±10. Among the 101 collected samples, four presented an error of more than ±10 %, and three of them presented an error of more than 5 %. About 97 samples, out of 101, fell within the 10% charge balance errors, which were considered reliable in this research work.

Natural background. Anthropogenic additions above background concentration from the numerous sources of nitrate are now a global issue. Additionally, it can be difficult to determine the background concentration of a specific chemical component. The criteria for identification of anthropogenic contamination had been adopted by using the probability

distribution of random datasets. As a brief way of picking separate population as events in hydrogeochemical databases of a given chemical species, the cumulative probability (CP) approach has been introduced⁴⁵. This method is quick and convenient for identifying the different population with the help of inflection point^{28,46-49} without any type of pre-selection of data. In the lack of long-term temporal databases, this method gives more reliable outcomes⁴⁹.

Shapiro-Wilk test was used to test the normality assumption of the different populations of the datasets. The SPSS statistics package programme was utilised to do all the statistical analysis (SPSS software, IBM SPSS product version 20 at $P < 0.05$). A value of $P < 0.05$ had been measured as statistically significant in all data analyses.

Health risk assessment. In general, the intake of polluted groundwater can cause a severe threat to humans, primarily by two exposure routes, first one is the ingestion of drinking water or oral route, and the second one is the dermal interaction route^{25,50}. The US Environmental Protection Agency originally proposed this rigorous model for the assessment of human health risk^{35,36}. In this study, the risk assessment was carried out in three groups of the exposed population, including children, females, and males.

The non-carcinogenic health risk from oral intake was calculated as follows^{5,17,18,51}:

$$CDI = \frac{C \times EF \times ED \times IR}{ABW \times AET} \quad (2)$$

$$HQ_{Oral} = \frac{CDI}{RfD} \quad (3)$$

where, in equation (2), CDI is referred as chronic daily intake (in mg/kg/day); “C” is the concentration of groundwater nitrate (in mg/L); IR is denoted for daily ingestion rate of groundwater (in L/day) for both males and females ingestion rate is 2.5 L/day and for children, ingestion rate is 1 L/day³⁵; EF is denoted for the exposure frequency (in days/year),

and the exposure frequency is considered as 365 days/year for males, females, and children³⁵; ED is denoted for exposure duration (in a year), for children 12 years, for females 67 years, and for males, 64 years have considered for this study^{25,27}; ABW is the average body weight as 65 kg, 55 kg, and 15 kg for males, females, and children, respectively. The mean exposure time (days) for AET is 23360 days, 24455 days, and 4380 days for males, females, and children, respectively. In equation (3), the hazard quotient is presented as HQ. RfD indicates reference dose of nitrate contaminant (in mg/kg/day) which is 1.6 mg/kg/day^{35,36}.

The non-carcinogenic health risk from dermal contact is calculated by the following formulas^{5,17,18,51}:

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

$$HQ_{Dermal} = \frac{DAD}{RfD} \quad (5)$$

$$HI_{Total} = \sum_{i=1}^n (HQ_{Oral} + HQ_{Dermal}) \quad (6)$$

where, in equation (4) DAD indicates the dermal absorbed dose (in mg/kg × day); TC is the contact time (in h/day) taken as 0.4 in h/day; K_i represents the dermal adsorption parameters (in cm/h) taken as 0.001 cm/h; and CF is denoted for conversion factor taken as 0.001^{36,52}. EV represents bathing frequency (in times/day), and the bathing frequency is considered as one time in a day, and SSA indicates the skin surface area (in cm²) and values for SSA are taken as 16,600 sq. centimetres for both males and females, and 12,000 sq. centimetres for children^{36,52}. In equation (6), HI is the hazard index, and non-carcinogenic human health risk is denoted by the value of HI. The HI value greater than one shows the potential human health risk from nitrate contamination, and HI value less than one expresses an acceptable level of health risk on human^{36,52}.

Data treatment. Descriptive statistics were carried out using SPSS 25.0, and the sample concentration results were compared with the Indian Standard of drinking water quality⁵³. We performed principal component analysis (PCA), a commonly used statistical tool for extracting critical knowledge from multivariate data, based on the correlation coefficients^{54,55}. ArcGIS 10.3 software (ESRI, Redlands, California, USA) and Surfer 13 were used to make distribution maps and interpolate the experimental dataset.

Results and discussion

Hydrochemical examination. The detailed statistics of hydrochemical parameters and their drinking limits suggested by the Bureau of Indian Standards⁵³ for groundwater quality are presented in Table 1. The electrical conductivity (EC) values of groundwater varied between 290 and 3800 $\mu\text{S}/\text{cm}$, with the mean value of 1430.5 $\mu\text{S}/\text{cm}$. The pH value ranged from 8.1 to 9.3, with a mean value of 8.8, indicating the groundwater is alkaline in nature. An important characteristic factor, parenting dissolved chemical concentrations, was the total dissolved solids (TDS) values. The TDS value varied between 158.4 mg/l and 2182.5, with the mean value of 820.9 mg/L. The hydrochemical analysis indicates that about 70% of the samples had been exceeded the drinking limits of the BIS guidelines⁵³ in the context of the TDS values. Among cations, Na^+ was observed predominant, followed by $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{K}^+$ based on average cation concentrations. Among anions, HCO_3^- was observed as the predominant anion, followed by $\text{Cl}^- > \text{SO}_4^{2-} > \text{CO}_3^{2-} > \text{NO}_3^- > \text{F}^-$. Bicarbonate was the key component of all largely dissolved groundwater ions in the study area. High concentrations of HCO_3^- were found and ranged from 61.0 to 817.7 mg/L, with the mean value of 336.8 mg/L. The elevated concentration of Cl^- was observed, and it ranges 21.3 to 1049.3 mg/L, with an average of 186.1 mg/L. The spatial distribution of hydrochemical

parameters has shown in Fig. S1. The elevated level of Cl^- was noticed in the northern central, and southern parts of the study area (Fig. S1). The northern portion and the western side of the study area were the zones where EC was high in the groundwater (Fig.S1). The result indicates around 28% of groundwater samples of NO_3^- were beyond the BIS limit, however, spatial distribution had shown (Fig. 5d) that the elevated concentrations of NO_3^- were located especially in the northern, central and southern. The heterogeneous distribution of the hydrochemical variables in groundwater also indicates the discrepancy in the coefficient of variance (CV%) values. The CV of several hydrochemical parameters (K^+ , SO_4^{2-} , NO_3^- , Cl^- , and F^-) in groundwater is more than 100 percent in terms of variance coefficient (CV), as shown in Table1. Very High CV of K^+ (532.64%), SO_4^{2-} (222.55%), NO_3^- (170.37%) and Cl^- (139.58%) demonstrate the potential pollution by anthropogenic activities in the study area.

Table 1. Statistics of groundwater quality parameters and the exceeding percentage of each parameter based on the BIS guidelines (2012)

Parameters	Min.	Max.	Mean	SD	Median	CV %	BIS Standard, 2012	Sample exceeding BIS guidelines (%)
pH	8.1	9.3	8.8	0.26	8.8	3.02	6.5-8.5	86
EC (mS/cm)	290.0	3800.0	1430.5	844.12	1200.0	70.34	1500	46
TDS (mg/L)	158.4	2182.5	820.9	505.95	687.0	73.64	500	70
Na^+ (mg/L)	15.2	733.4	244.7	177.85	223.0	79.75	200	57
K^+ (mg/L)	0.8	129.0	8.3	20.83	3.9	532.64	--	--
Ca^{2+} (mg/L)	4.0	36.1	12.6	6.69	12.0	55.68	75	--
Mg^{2+} (mg/L)	12.2	144.7	39.7	25.56	32.8	77.84	30	86
Cl^- (mg/L)	21.3	1049.3	186.1	188.03	134.7	139.58	250	27
SO_4^{2-} (mg/L)	19.2	422.7	87.3	90.86	40.8	222.55	200	5
CO_3^{2-} (mg/L)	24.0	144.2	64.4	32.64	60.1	54.32	--	--
HCO_3^- (mg/L)	61.0	817.7	336.8	182.23	244.1	74.66	200	73
NO_3^- (mg/L)	1.2	151.3	34.3	36.97	21.7	170.37	45	28
F^- (mg/L)	0.2	4.8	1.2	0.99	1.0	102.84	1	37
TH (mg/L)	80.0	650.0	194.7	107.21	170.0	63.07	200	32

EC is Electrical Conductivity, TDS is Total Dissolved Solids, SD is standard deviation, CV is coefficient of variance, TH is Total Hardness, mS/cm = micro Siemens per centimetre

254 **Background Level of Nitrate.** The majority of published NO_3^- concentrations have been
255 described as suggesting anthropogenic groundwater contamination, which was estimated by
256 different techniques. The background concentration of nitrate in groundwater had been
257 estimated using a statistical approach. In which the cumulative probability method was used
258 to separate different population events of nitrate in groundwater. The background
259 concentrations and anthropogenic concentrations of nitrate had been marked with a sharp
260 inflection point at 9.3 mg/L (Fig. 2a). Then the natural background level (NBL) and
261 anthropogenic level (APL) were calculated as 90th percentile (7.2 mg/L) and 10th percentile
262 (13.3 mg/L) of the events separated by inflection point, respectively. Probability density
263 curves with respect to the nitrate concentration of distinct populations (NBL, APL, and
264 original) have been shown in Fig.2b.

265 The Shapiro-Wilk test was used (in Table S1) to test the normality of different populations
266 (NBL and APL). If the Shapiro-Wilk test significance value is greater than 0.05, the data is
267 normal. If it is smaller than 0.05, the data will deviate greatly from the normal distribution. In
268 this test, the significance value of NBL was obtained as 0.072, which indicated the normality
269 of NBL, while the significance value of APL and original concentrations of nitrate indicated
270 abnormality. Thus this test strengthens and supports the background value of nitrate in the
271 groundwater of the study area. The background concentration of nitrate was high compared to
272 other works related to the nitrate background²⁸. This high level of background concentration
273 may have affected by anthropogenic factors⁴⁸. However, the spatial distribution of NBL along
274 total concentration of nitrate is shown in Fig. 5d. This figure illustrates that the variation
275 between NBL and the experimental concentration of NO_3^- was high in the northern, central,
276 and southern parts of the study area. The same areas were marked as potential health risk
277 threats for adults and children.

Figure 2. Showing (a) Cumulative probability plots of the NO_3^- concentration in groundwater on which two normal subpopulations events (estimated NBL; natural background level, and APL; anthropogenic level). In each plot, a single inflection point is observed on log-scale, and (b) Probability density curve of a distinct population of NO_3^- concentration in groundwaters

Nitrate distribution and mechanism of contamination. Groundwater nitrate vulnerability can be described as the sensitivity of an aquifer's susceptibility to nitrate contamination, based on the redox environment in both the aquifer material and the overlying geological strata^{56,57}. In groundwater, the presence of nitrate is due to various sources and origins. Nitrate pollution happens in several environments for different causes, viz. septic tank leakage, fertilisers used in farm fields, landfill leachate, leakage of sewerage pipes, drainage of poultry waste, and household / cultivation of animal dung^{51,58-60}. There are many approaches that can apply to the overall nitrate concentration of ordinary groundwater, such as geological characteristics, environments, anthropogenic activities, nitrogen-bearing soil, and atmospheric nitrogen fixation⁶¹. The disparity in NO_3^- content in various inspection areas may be due to cyclical precipitation, the energy rate of subsurface water, mechanism of evapotranspiration, and so on⁶²⁻⁶⁴. Nitrate is usually quickly dissolved in surface water and readily enters the groundwater as well. In addition, an oxidising state in the landfill site may

also cause a nitrification reaction that normally converts ammonia (NH₃) to nitrate (NO₃⁻), and hence also raises nitrate concentration in the groundwater^{5,24,65,66}. The following equation can be understood as the whole nitrification mechanism⁶⁷.

The box plots in Fig. 3, demonstrates the chronological change (in time series) in nitrate concentrations in Dausa's groundwater over the past 8 years (2011 to 2018). The study area does not display any distinct temporal shift in nitrate concentrations except in 2018, where the highest groundwater sample exceeded the BIS drinking limit was about 28%. Usually, bivariate plots, NO₃⁻ versus K⁺, and NO₃⁻ versus Cl⁻ are commonly used to classify the possible causes of nitrate contamination^{5,68-70}. The positive correlation between NO₃⁻ and K⁺ (Fig. 4a) indicated that elevated nitrate might derive from the non-point sources (including fertilizers, manure, and sewage), which cause anthropogenic pollution above the background concentration. A good correlation between NO₃⁻ and Cl⁻ was noted in the study area (Fig. 4b). It also indicated that groundwater nitrate was may be due to the sources of animal and human waste from these ions. A researcher⁷¹ claimed that an increase in chloride concentration with an increase in nitrate was mainly due to the septic tank.

In general, principal component analysis (PCA) is widely utilized to describe the relationship between parameters of water quality and their probable source determination. In this analysis, three principal components (PCs) were generated by transformation of hydrochemical parameters including pH, TDS, K⁺, Na⁺, Mg²⁺, Ca²⁺, Cl⁻, SO₄²⁻, HCO₃⁻ and NO₃⁻) adopting Varimax orthogonal rotation and Kaiser normalisation. These PCs were examined with eigenvalues greater than one (Fig. S2) and their total variance at 48.288%, 19.943%, and 11.539%, respectively, with the cumulative variance of 79.77% (Table 2). The high and moderate positive loadings of EC (0.942), TDS (0.933), Na⁺ (0.859), Cl⁻ (0.927) and SO₄²⁻

(0.862) were observed with PC1. This suggests that high NO_3^- in the groundwater may derive from several anthropogenic sources, including fertilisers, septic tanks, domestic sewage, animal waste, and wastewater⁶⁶. The PC3 show high positive loadings of K^+ (0.838) and NO_3^- (0.867), signifying that the source of nitrate in the groundwater was not the same as other ions. This indicates the source of elevated nitrate may come from anthropogenic activities but not from river waters⁶⁶. The study area is dominated by agricultural land, followed by build-up areas. This scenario of the study area itself justifies that the possible source of groundwater nitrate was agricultural inputs or domestic sewage.

Figure 3. Showing the temporal changes of nitrate concentrations during 8 years (2011-2018) in groundwater of the study area. The red lines above the Box and Whisker plots illustrate the percentage of samples beyond the Indian drinking water standards (45 mg/L) and 'n' denoted as the number of groundwater samples

337

338
339 Figure 4. Scatter plots showing the relationship between (a) nitrate and potassium, and (b)
340 nitrate and chloride

341

342
343 Table 2. Significant principal components (PCs) loading for hydrochemical parameters in the
344 study area

Component	Initial Eigenvalues			Component			
	Total	% of Variance	Cumulative %	Parameters	PC1	PC2	PC3
1	5.312	48.288	48.288	pH	-0.062	0.800	-0.045
2	2.194	19.943	68.231	EC	0.942	0.264	0.189
3	1.269	11.539	79.771	TDS	0.933	0.270	0.226
4	0.898	8.164	87.934	Na ⁺	0.859	0.490	0.070
5	0.574	5.221	93.155	K ⁺	0.165	-0.145	0.838
6	0.397	3.606	96.760	Ca ²⁺	-0.114	-0.427	0.031
7	0.213	1.936	98.696	Mg ²⁺	0.641	-0.571	0.296
8	0.135	1.229	99.925	Cl ⁻	0.927	-0.254	0.048
9	0.007	0.064	99.989	SO ₄ ²⁻	0.862	0.128	0.189
10	0.001	0.008	99.997	HCO ₃ ⁻	0.369	0.834	0.200
11	0.000	0.003	100.000	NO ₃ ⁻	0.162	0.123	0.867

345 Bold numbers indicate highly positive PC loadings of one parameter

Figure 5. Showing spatial distribution of non-carcinogenic health risks for (a) Hazard Index (HI) of males, (b) Hazard Index (HI) of females, (c) Hazard Index (HI) of children in the study area, and (d) spatial distribution of nitrate concentration and its background concentrations with the contour lines

Table 3. Summary of the estimated non-carcinogenic risks of Nitrate ingestion of drinking water and dermal exposure

Sample	HQ _{Oral}			HQ _{Dermal}			HI _{Total}		
	Males	Females	Children	Males	Females	Children	Males	Females	Children
W-1	0.581	0.687	0.786	0.002	0.002	0.005	0.583	0.689	0.791
W-2	0.358	0.423	0.484	0.001	0.001	0.003	0.359	0.424	0.487
W-3	0.909	1.074	1.229	0.002	0.003	0.008	0.912	1.077	1.237
W-4	2.638	3.118	3.567	0.007	0.008	0.022	2.645	3.126	3.588
W-5	2.206	2.607	2.982	0.006	0.007	0.018	2.212	2.614	3.001
W-6	0.388	0.458	0.524	0.001	0.001	0.003	0.389	0.459	0.527
W-7	0.388	0.458	0.524	0.001	0.001	0.003	0.389	0.459	0.527
W-8	1.103	1.303	1.491	0.003	0.003	0.009	1.106	1.307	1.500
W-9	1.058	1.251	1.431	0.003	0.003	0.009	1.061	1.254	1.439
W-10	1.803	2.131	2.438	0.005	0.006	0.015	1.808	2.137	2.453
W-11	0.581	0.687	0.786	0.002	0.002	0.005	0.583	0.689	0.791
W-12	0.238	0.282	0.322	0.001	0.001	0.002	0.239	0.283	0.324
W-13	0.522	0.616	0.705	0.001	0.002	0.004	0.523	0.618	0.710
W-14	0.164	0.194	0.222	0.000	0.001	0.001	0.164	0.194	0.223
W-15	1.520	1.797	2.055	0.004	0.005	0.013	1.524	1.801	2.068
W-16	1.103	1.303	1.491	0.003	0.003	0.009	1.106	1.307	1.500
W-17	2.042	2.413	2.761	0.005	0.006	0.017	2.047	2.419	2.778
W-18	0.775	0.916	1.048	0.002	0.002	0.006	0.777	0.918	1.054
W-19	0.477	0.564	0.645	0.001	0.001	0.004	0.478	0.565	0.649
W-20	0.522	0.616	0.705	0.001	0.002	0.004	0.523	0.618	0.710
W-21	0.626	0.740	0.846	0.002	0.002	0.005	0.628	0.742	0.852
W-22	1.893	2.237	2.559	0.005	0.006	0.016	1.898	2.243	2.575
W-23	3.145	3.716	4.252	0.008	0.010	0.026	3.153	3.726	4.278
W-24	0.268	0.317	0.363	0.001	0.001	0.002	0.269	0.318	0.365
W-25	0.238	0.282	0.322	0.001	0.001	0.002	0.239	0.283	0.324
W-26	1.103	1.303	1.491	0.003	0.003	0.009	1.106	1.307	1.500
W-27	0.581	0.687	0.786	0.002	0.002	0.005	0.583	0.689	0.791
W-28	0.045	0.053	0.060	0.000	0.000	0.000	0.045	0.053	0.061
W-29	0.238	0.282	0.322	0.001	0.001	0.002	0.239	0.283	0.324
W-30	0.522	0.616	0.705	0.001	0.002	0.004	0.523	0.618	0.710
W-31	0.671	0.793	0.907	0.002	0.002	0.006	0.672	0.795	0.912
W-32	0.551	0.652	0.746	0.001	0.002	0.005	0.553	0.653	0.750
W-33	0.939	1.110	1.269	0.002	0.003	0.008	0.941	1.113	1.277
W-34	0.984	1.163	1.330	0.003	0.003	0.008	0.986	1.166	1.338
W-35	1.222	1.444	1.652	0.003	0.004	0.010	1.225	1.448	1.662
W-36	1.461	1.726	1.975	0.004	0.005	0.012	1.464	1.731	1.987
W-37	1.714	2.026	2.317	0.005	0.005	0.014	1.718	2.031	2.332
Min.	0.045	0.053	0.060	0.000	0.000	0.000	0.045	0.053	0.061
Max.	3.145	3.716	4.252	0.008	0.010	0.026	3.153	3.726	4.278
Mean	0.961	1.136	1.300	0.003	0.003	0.008	0.964	1.139	1.308

Health risk assessment (Non-carcinogenic). Health risk assessment including males, females, and children had been done based on the guidelines of the United State Environmental Protection Agency^{35,52}, and the calculated results are shown in Table 3. Health risk (Hazard Index-HI) spatial distribution maps for males, females and children were also produced and are shown in Fig. 5. For three different age classes, the findings of HQ_{Dermal} were slightly lower than zero, while HQ_{Oral} ranged from 0.045 to 3.145 with an average of 0.961 for males, 0.053 to 3.716 with an average of 1.136 for females, and 0.060 to 4.252 with an average of 1.300 for children (Table 3). The results show that the exposure of nitrate directly due to drinking water ingestion was higher than the exposure due to dermal interactions in the study area. The reasonable limit for non-carcinogenic health risk is ≤ 1 ($HI \leq 1$), based on the USEPA health risk standards. If the hazard index (HI) value is > 1 , then the possibility of an adverse risk to human health is very high⁵². HI_{Total} values in the study area are varied from 0.045 to 3.153 (average: 0.964) for males, 0.053 to 3.726 (average: 1.139) for females and 0.061 to 4.278 (average: 1.308) for children (Table 3). Out of 37 groundwater samples, 14 samples for males, 17 samples for females, and 18 samples for infants, the nitrate exposure levels in drinking water were found to expose these age groups to serious nitrate problems. More importantly, the findings appear to suggest that children are more vulnerable to non-carcinogenic effects in the study region owing to the intake of higher nitrate concentrations in drinking water. Many other scholars have found that due to lower body weight and personality characteristics, children are more vulnerable to chronic non-carcinogenic threats than adults^{5,72-76}.

The non-carcinogenic hazard index (HI) map (as shown in Fig. 5) clearly indicates that the northern, central, and southern parts of the study area have higher health risk zones for males, females, and children. Especially it can be noticed that the area of health risk due to groundwater nitrate is high for children as compared to the adults (Fig. 5c). As is visible from

388 Fig.5a,b,c, there is no detrimental impact of a non-carcinogenic risk on the visible green
389 colour in the spatial distribution of hazard index in the study area, although the yellow and
390 red regions show that population in these areas pose potential health threats in the study area.
391 It indicates that the areas of yellow and red zones were in danger due to higher HI values;
392 these areas were not recommended for direct intake of drinking water. The spatial distribution
393 of the background values of nitrate (Fig.5d) showed that the health hazard was high at the
394 place where the significant difference between NBL and total concentrations of groundwater
395 nitrate was noticed. Excessive nitrate intake through groundwater can result in adverse
396 biological problems, such as methemoglobinemia, which is also known as blue baby
397 syndrome, causes infant mortality, hypertension, thyroid disorders, goiter, hives, severe
398 cyanosis, cytogenetic defects, congenital malformations, and headaches^{50,66,77-81}. However, in
399 many parts of the globe where a significant populace depends entirely on groundwater
400 resources for drinking without pre-examination of safety problems, the non-carcinogenic
401 health risk of NO_3^- in drinking water becomes a serious issue^{20,66,77,78,80,81}. In northern India, a
402 detailed study done⁷³ and assessed the human health risk of nitrate. Their research found
403 about 36% of samples demonstrated greater non-carcinogenic health issues on children due to
404 higher content of nitrate in groundwater, signifying a tremendous risk to human health of
405 nitrate. Similarly, in southern India, a researcher⁵ had analysed the issues due to groundwater
406 nitrate. Their findings reveal that about 60%, 57%, and 50% of groundwater samples were in
407 the range of potential health risk for children, females, and males, respectively. Likewise,
408 another study related to nitrate health implications was carried⁸² in the northern Shandong
409 Peninsula of China, and found that about 87.6 % of water samples were unfit for nitrate
410 concentration-based consumption. The findings of their analysis also indicate that health
411 hazards are more dangerous to infants and children due to nitrate ingestion via oral and

dermal exposure pathways. Thus, owing to the drinking of contaminated groundwater, the intensity of health risk steadily increases.

Recommendation for drinking water resource management. Both natural and anthropogenic mechanisms regulated the consistency of groundwater during the experimental period. In certain regions, because of abnormal natural environments and long-term anthropogenic factors, as we noticed in Dausa district, Rajasthan, India, the concentration of contaminants, especially nitrate, could be increased from other regions. In general, groundwater contamination has only been measured by taking into account the drinking water requirements for the entire region or the whole country. The consideration of NBL in health risk assessment will be a crucial parameter for a better understanding of geogenic and anthropogenic contamination of any chemical parameter in the groundwater environment. However, as a result of the current study, it is indeed recommended that the local government urgently takes the requisite steps to reduce groundwater nitrate pollution and also ensures the availability of clean drinking water in the affected areas of the study area.

Conclusions

Hydrochemical data were analysed to assess the background concentration of nitrate and possible health risks due to the elevated concentration in the drinking water of Dausa district, Rajasthan, India. The natural background concentration (NBL) of groundwater nitrate is estimated using a statistical approach. In which firstly cumulative probability approach is used to separate the distinct population. Then normality of the individual population is checked by the Shapiro-Wilk test. The estimated NBL of nitrate is 7.2 mg/L in the study area; above this background concentration, anthropogenically added nitrate is responsible for the high concentration in groundwater. The main sources of nitrate in groundwater environments with concentrations above background concentrations are agricultural fertiliser, and human

and animal wastes. In this analysis, principal components (PCs) are generated by the processing hydrochemical parameters using Varimax orthogonal rotation and Kaiser Normalisation. The high and moderate positive loadings of EC, TDS, Na⁺, Cl⁻ and SO₄²⁻ are observed with the PC1. This suggests that high NO₃⁻ in the groundwater may derive from several anthropogenic sources.

The health risk assessment, including males, females, and children has been done based on the guidelines of the United State Environmental Protection Agency, and also calculated. For the non-carcinogenic risk, the values of the total hazard index (HI_{Total}) in the study area are varied from 0.045 to 3.153 (average: 0.964) for males, 0.053 to 3.726 (average: 1.139) for females, and 0.061 to 4.278 (average: 1.308) for children. The result has clearly indicated that Children in the study area are more vulnerable to health hazards than women and men. The spatial distribution of nitrate background values has also revealed that the health hazard is high at the places where the significant difference between NBL and total nitrate concentrations in groundwater has been noticed. Thus the consideration of NBL in health risk assessment will be a crucial parameter for a better understanding of geogenic and anthropogenic contaminations of any chemical parameter in the groundwater environment.

CRedit authorship contribution statement

Abdur Rahman: Conceptualized, processed, analysed and interpreted the data, and drafted the original manuscript. **N.C. Mondal:** Conceptualized, designed the research works, revised critically and significantly to improve the article. **K.K. Tiwari:** Acquired the analytical data.

Acknowledgments

Director of CSIR-NGRI, Hyderabad, Dr. V.M. Tiwari has permitted to publish this article (Ref. No.: NGRI/Lib/2021/pub-09). State Ground Water Department, Rajasthan has helped to

access the hydrochemical data. The first author has contributed this research work under his Senior Research Fellowship funded by CSIR, New Delhi [Ref. No.: 31/023(0240)/2018-ERR-I, dated: 13-07-2018]. The authors are highly thankful to them.

References

1. Jia, X. et al. Groundwater depletion and contamination: Spatial distribution of groundwater resources sustainability in China. *Sci. Total Environ.* **672**, 551–562 (2019).
2. USEPA. Municipal solid waste generation, recycling and disposal in United States. *United States Environmental Protection Agency, Washington, DC*, pp. 01–14 20460 (EPA-530-F-14-001) (2012).
3. NEA. Nature and Environment - Waste Accounts. The Norwegian Environment Agency (<http://www.environment.no/Topics/Waste/> or <http://www.ssb.no/en/natur-og-miljo/statistikker/avfregno> 12/08/2016, 19:23 PM) (2016).
4. Abiriga, D., Vestgarden, L. S., & Klempe, H. Groundwater contamination from a municipal landfill: Effect of age, landfill closure, and season on groundwater chemistry. *Sci. Total Environ.* **737**, 140307 (2020).
5. Adimalla, N., Qian, H. Groundwater chemistry, distribution and potential health risk appraisal of nitrate enriched groundwater: A case study from the semi-urban region of South India. *Ecotoxicol Environ Saf.* **207**, 111277 (2021).
6. Scanlon, B.R., Jolly, I., Sophocleous, M., Zhang, L. Global impacts of conversions from natural to agricultural ecosystems on water resources: quantity versus quality. *Water Resour. Res.* **43**, W03437 (2007).
7. Sebilo, M., Mayer, B., Nicolardot, B., Pinay, G., Mariotti, A. Long-term fate of nitrate fertilizer in agricultural soils. *Proc. Natl. Acad. Sci. U. S. A.* **110**, 18185–18189 (2013).
8. Kim, K. H., Yun, S. T., Kim, H. K., & Kim, J. W. Determination of natural backgrounds and thresholds of nitrate in South Korean groundwater using model-based statistical approaches. *J. Geochem. Explor.* **148**, 196–205 (2015).
9. Cepelch, Z.L., Waskom, R.M., Bauder, T.A., Sharkoff, J.L., Khosla, R. Vulnerability assessments of Colorado ground water to nitrate contamination. *Water Air Soil Pollut.* **159**, 373–394 (2004).
10. Pisciotta, A., Cusimano, G., Favara, R. Groundwater nitrate risk assessment using intrinsic vulnerability methods: A comparative study of environmental impact by intensive farming in the Mediterranean region of Sicily, Italy. *J. Geochem. Explor.* **156**, 89–100 (2015).

- 493 11. Gutiérrez, M., Biagioni, R.N., Alarcón-Herrera, M.T., Rivas-Lucero, B.A. An overview of nitrate
494 sources and operating processes in arid and semiarid aquifer systems. *Sci. Total Environ.* **624**,
495 1513–1522 (2018).
- 496 12. Ward, M. et al. Drinking water nitrate and human health: an updated review. *Int. J. Environ. Res.*
497 *Public Health* **15**, 1557 (2018).
- 498 13. Torres-Martínez, J.A. et al. Estimation of nitrate pollution sources and transformations in
499 groundwater of an intensive livestock-agricultural area (Comarca Lagunera), combining
500 major ions, stable isotopes and MixSIAR model, *Environ. Pollut.* **269**, 115445 (2020).
- 501 14. Torres-Martínez, J. A., Mora, A., Knappett, P., Ornelas-Soto, N., & Mahlknecht, J. Tracking
502 nitrate and sulfate sources in groundwater of an urbanized valley using a multi-tracer
503 approach combined with a Bayesian isotope mixing model. *Water Res.* **182**, 115962 (2020).
- 504 15. Datta, P.S., Deb, D.L., Tyagi, S.K. Assessment of groundwater contamination from fertilizers in
505 the Delhi area based on ^{18}O , NO_3^- and K^+ composition. *J. Contam. Hydrol.* **27** (3), 249–262
506 (1997).
- 507 16. WHO. Guidelines for drinking water quality: fourth edition incorporating the first addendum.
508 *World Health Organization, Geneva* (2017).
- 509 17. Chen, J., Qian, H., Wu, H. Nitrogen contamination in groundwater in an agricultural region along
510 the New Silk Road, northwest China: distribution and factors controlling its fate. *Environ. Sci.*
511 *Pollut. Res.* **24** (15), 13154–13167 (2017).
- 512 18. Chen, J., Wu, H., Qian, H., Gao, Y. Assessing nitrate and fluoride contaminants in drinking water
513 and their health risk of rural residents living in a semiarid region of northwest China. *Exposure*
514 *Health* **9** (3), 183–195 (2017).
- 515 19. Su, H., Kang, W., Xu, Y., Wang, J. Assessing groundwater quality and health risks of nitrogen
516 pollution in the Shenfu mining area of Shaanxi province, northwest China. *Exposure Health* **10**
517 (2), 77–97 (2018).
- 518 20. Gao, S., et al. Health risk assessment of groundwater nitrate contamination: a case study of a
519 typical karst hydrogeological unit in East China. *Environ. Sci. Pollut. Res.* **27** (9), 9274–9287
520 (2020).
- 521 21. Rehman, J.U., Ahmad, N., Ullah, N., Alam, I., Ullah, H. Health risks in different age group of
522 nitrate in spring water used for drinking in Harnai, Balochistan, Pakistan. *Ecol. Food Nutr.* 1–
523 10 (2020).
- 524 22. Qasemi, M. et al. Health risk assessments due to nitrate levels in drinking water in villages of
525 Azadshahr, northeastern Iran. *Environ. Earth Sci.* **77** (23), 782 (2018).
- 526 23. Yousefi, M., Ghoochani, M., Hossein Mahvi, A. Health risk assessment to fluoride in drinking
527 water of rural residents living in the Poldasht city, Northwest of Iran. *Ecotoxicol. Environ. Saf.*
528 **148**, 426–430 (2018).
- 529 24. Pérez Villarreal, J., Avila ´ Olivera, J.A., Israde Alcantara, ´ I., Buenrostro Delgado, O. Nitrate as
530 a parameter for differentiating groundwater flow systems in urban and agricultural areas: the
531 case of Morelia-Capula area, Mexico. *Hydrogeol. J.* **27**, 1767–1778 (2019).

25. Adimalla, N. Controlling factors and mechanism of groundwater quality variation in semiarid region of South India: an approach of water quality index (WQI) and health risk assessment (HRA). *Environ. Geochem. Health* **42** (6), 1725–1752 (2020).
26. Adimalla, N., Li, P., Qian, H. 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.* **25** (5), 1107–1124 (2019).
27. Karunanidhi, D. et al. Evaluation of non-carcinogenic risks due to fluoride and nitrate contaminations in a groundwater of an urban part (Coimbatore region) of south India. *Environ. Monit. Assess.* **192** (2), 102 (2020).
28. Panno, S.V., Kelly, W.R., Martinsek, A.T., Hackley, K.C. Estimating background and threshold nitrate concentrations using probability graphs. *Groundwater* **44** (5), 697-709 (2006).
29. Panno, S.V., W.R. Kelly, C.P. Weibel, I.G. Krapac, and S.L. Sargent. Water quality and agrichemical loading in two groundwater basins of Illinois' sinkhole plain. *Environmental Geology Series* **156**. Champaign, Illinois: Illinois State Geological Survey (2003).
30. Tomer, M.D., and M.R. Burkart. Long-term effects of nitrogen fertilizer use on ground water nitrate in two small watersheds. *J. Environ. Qual.* **32**, 2158–2171 (2003).
31. Appelo, C.A.J., and D. Postma. Geochemistry, groundwater and pollution. Rotterdam, The Netherlands: A.A. Balkema (1994).
32. Kelly, W.R. Heterogeneities in ground-water geochemistry in a sand aquifer beneath an irrigated field. *J Hydrol* **198**, 154–176 (1997).
33. Smedley, P.L., and W.M. Edmunds. Redox patterns and trace-element behaviour in the East Midlands Triassic sandstone aquifer, U.K. *Ground Water* **40**, 44–58 (2002).
34. Central Groundwater Board CGWB. *Groundwater Brochure Dausa District, Rajasthan*. CGWB-WR, Jaipur, p. 21 (2008).
35. USEPA. Risk assessment guidance for superfund, vol I., *Human health evaluation manual (Part A) office of emergency and remedial response* (1989).
37. Tiwari, K.K. et al. Evaluation of fluoride contamination in groundwater in a semi-arid region, Dausa District, Rajasthan, India. *Groundw.* **11**, 100465 (2020).
36. USEPA. Exposure factors handbook, volume 1: *General Factors*. U. S, *Environmental Protection Agency, office of research and development*, Washington (1997).
38. Mondal, N., Tiwari, K., Sharma, K., & Ahmed, S.,. A diagnosis of groundwater quality from a semiarid region in Rajasthan, India. *Arab. J. Geosci.* **9**, 1-22 (2016)
39. American Public Health Association (APHA). *standard methods for the examination of water and waste*, sixteenth ed. Am Public Health Association, Washington DC, p. 100 (1985).
40. Feitosa, F.A.C., Manoel Filho, J., Feitosa, E.C., Demetrio, J.G.A. Hidrogeologia: conceitos e aplicaçoes (Hydrogeology: Concepts and Applications). *CPRM*, ~ p. 812 (2008).
41. Freeze, R.A., Cherry, J.A. *Groundwater*. Prentice-Hall Inc., Englewood Cliffs, NJ, p. 97 (1979).
42. Hem, J.D. Study and interpretation of the chemical characteristics of natural water. *United States Geological Survey Water-Supply Paper* 2254, p. 165 (1985).

43. Hounslow, Arthur W. Water quality data: analysis and interpretation. *Lewis Publisher*, CRC Press LLC, USA, pp. 49-73 (1995).
44. Katz Brian, G., Collins Jerilyn, J. Evaluation of chemical data from selected sites in the Surface-Water Ambient Monitoring Program (SWAMP) in Florida. *Open-File Report 98-559*. USGS, p. 4 (1998).
45. Runnells, D D, Dupon, D P, Jones, R L, Cline, D J. Determination of background chemistry of water at mining and milling sites, Salt Lake Valley, Utah, USA. 997–1000 in Proceedings of the Water Rock Interaction. *Proceedings of the 9th International Symposium on Water-Rock Interaction, Taupo, New Zealand*, (Rotterdam: A A Balkema) (1998).
46. Mondal, N.C. Reconnoitering hydrochemical background using log-probability distribution in a Channel Island, Andhra Pradesh. In: *5th National Conference Proceeding on Water, Environment & Society*, 271-277 (2018).
47. Mondal, N.C. Exploring hydrochemical backgrounds using cumulative probability approach for finding groundwater suitability in an industrial area from Peninsular India. *J. Appl. Geochem.* (in press) (2020).
48. Rahman, A., Tiwari. K.K., Mondal, N.C. Assessment of hydrochemical backgrounds and threshold values of groundwater in a part of desert area, Rajasthan, India. *Environ. Pollut.* **266** (3),115150 (2020)
49. Rahman, A., Mondal, N. C., & Fauzia, F. Arsenic enrichment and its natural background in groundwater at the proximity of active floodplains of Ganga River, northern India. *Chemosphere*, **265**, 129096 (2021).
50. Adimalla, N., Qian, H. Groundwater quality evaluation using water quality index (WQI) for drinking purposes and human health risk (HHR) assessment in an agricultural region of Nanganur, south India. *Ecotoxicol. Environ. Saf.* **176**, 153–161 (2019).
51. Karunanidhi, D., Aravinthasamy, P., Subramani, T., Wu, J., Srinivasamoorthy, K. Potential health risk assessment for fluoride and nitrate contamination in hard rock aquifers of Shanmuganadhi River basin, South India, *Hum. Ecol. Risk Assess.* 250-270 (2019).
52. USEPA. Supplemental guidance for developing soil screening levels for superfund sites. *U. S. Environmental Protection Agency, office of emergency and remedial response*, Washington (2002).
53. Bureau of Indian Standard (BIS). *Indian Standards Specification for Drinking Water*. IS: 10500: 2012, 2nd Rev. BIS, New Delhi (2012).
54. Zhang, X., Wei, S., Sun, Q., Wadood, S. A., Guo, B. Source identification and spatial distribution of arsenic and heavy metals in agricultural soil around Hunan industrial estate by positive matrix factorization model, principle components analysis and geo statistical analysis. *Ecotoxicol. Environ. Saf.* **159**, 354–362 (2018).
55. Gu, C. et al. spatial distribution and health risk assessment of dissolved trace elements in groundwater in southern China. *Sci Rep.* **10**, 7886 (2020).
56. Hansen, B. et al. Nitrate vulnerability assessment of aquifers. *Environ Earth Sci* **75**, 999 (2016).

57. Voutchkova, D.D., Schullehner, J., Rasmussen, P., Hansen, B. A high-resolution nitrate vulnerability assessment of sandy aquifers (DRASTIC-N). *J. Environ. Manage.* **277**, 111330 (2021).
58. Mondal, N.C., Saxena, V.K., Singh, V.S. Occurrence of elevated nitrate in groundwaters of Krishna delta, India. *Afr. J. Environ. Sci. Technol.* **2** (9), 265-271 (2008).
59. Suthar, S. et al. Nitrate contamination in groundwater of some rural areas of Rajasthan, India. *J Hazard Mater* **171**, 189–199 (2009).
60. Abdesselam, S. et al. Anthropogenic contamination of groundwater with nitrate in arid region: case study of southern Hodna (Algeria). *Environ Earth Sci.* **70**, 2129–41 (2013).
61. Khandare, H.W. Scenario of nitrate contamination in groundwater: its causes and prevention. *Int J ChemTech Res* **5**, 1921–6 CODEN (USA): IJCRGG ISSN: 0974-4290 (2013).
62. Shalev, N., Burg, A., Gavrieli, I., and Lazar, B. Nitrate contamination sources in aquifers underlying cultivated fields in an arid region— the Arava Valley, Israel. *Appl Geochem* **63**, 322–32 (2015).
63. Nakagawa, K. et al. On the use of coprostanol to identify source of nitrate pollution in groundwater. *J Hydrol* **550**, 663–8 (2017).
64. Buvaneshwari, S. et al. Groundwater resource vulnerability and spatial variability of nitrate contamination: insights from high density tubewell monitoring in a hard rock aquifer. *Sci Total Environ* **579**, 838–47 (2017).
65. Stuart, M.E., Gooddy, D.C., Bloomfield, J.P., Williams, A.T. A review of the impact of climate change on future nitrate concentrations in groundwater of the UK. *Sci. Total Environ.* **409** (15), 2859–2873 (2011).
66. Zhang, M. et al. Distributions and origins of nitrate, nitrite, and ammonium in various aquifers in an urbanized coastal area, south China. *J Hydrol* **582**, 124528 (2020).
67. Ahamad, A., Raju, N.J., Madhav, S., Gossel, W., Wycisk, P. Impact of nonengineered Bhalswa landfill on groundwater from Quaternary alluvium in Yamuna flood plain and potential human health risk, New Delhi, India. *Quat. Int.* **507**, 352–369 (2019).
68. Sajil Kumar, P.J., Jegathambal, P. & James, E.J. Chemometric evaluation of nitrate contamination in the groundwater of a hard rock area in Dharapuram, south India. *Appl Water Sci* **4**, 397–405 (2014).
69. Zhang, Q., Sun, J., Liu, J., Huang, G., Lu, C., Zhang, Y. Driving mechanism and sources of groundwater nitrate contamination in the rapidly urbanized region of south China. *J. Contam. Hydrol.* **182**, 221–230 (2015).
71. McQuillan D. Ground-water quality impacts from on-site septic systems. *Proceedings, National Onsite Wastewater Recycling Association, 13th annual conference, Albuquerque, NM*, 7–10, **13** (2004).
72. Li, Y. et al. Long term spatial-temporal dynamics of fluoride in sources of drinking water and associated health risks in a semiarid region of Northern China. *Ecotoxicol. Environ. Saf.* **171**, 274–280 (2019).

73. Ravindra, K., Thind, P.S., Mor, S., Singh, T., Mor, S. Evaluation of groundwater contamination in Chandigarh: source identification and health risk assessment. *Environ. Pollut.* **255**, 113062 (2019).
74. Adimalla, N. Spatial distribution, exposure, and potential health risk assessment from nitrate in drinking water from semi-arid region of South India. *Hum. Ecol. Risk Assess.* **26** (2), 310–334 (2020).
75. Singh, G., Rishi, M.S., Herojeet, R., Kaur, L., Sharma, K. Evaluation of groundwater quality and human health risks from fluoride and nitrate in semi-arid region of northern India. *Environ. Geochem. Health* **42**, 1833–1862 (2020).
76. Adimalla, N. Groundwater quality for drinking and irrigation purposes and potential health risks assessment: a case study from semi-arid region of South India. *Exposure Health* **11** (2), 109–123 (2019).
77. Wick, K., Heumesser, C., Schmid, E. Groundwater nitrate contamination: factors and indicators. *J. Environ. Manag.* **111**, 178–186 (2012).
78. Adimalla, N., Li, P. Occurrence, health risks, and geochemical mechanisms of fluoride and nitrate in groundwater of the rock-dominant semi-arid region, Telangana State, India. *Hum. Ecol. Risk Assess.* **25** (1–2), 81–103 (2019).
79. Narsimha, A., Rajitha, S. Spatial distribution and seasonal variation in fluoride enrichment in groundwater and its associated human health risk assessment in Telangana State, South India. *Hum. Ecol. Risk Assess.* **24** (8), 2119–2132 (2018).
80. Karyab, H., Hajimirmohammad-Ali, R., Bahojb, A. A lumped-parameter model for investigation of nitrate concentration in drinking water in arid and semi-arid climates and health risk assessment. *J. Environ. Health Sci. Eng.* **17**, 457–465 (2019).
81. Cui, M., Zeng, L., Qin, W., Feng, J. Measures for reducing nitrate leaching in orchards: A review. *Environ. Pollut.* **263**, 114553 (2020).
82. Wu, J., Lu, J., Wen, X., Zhang, Z., Lin, Y. Severe nitrate pollution and health risks of coastal aquifer simultaneously influenced by saltwater intrusion and intensive anthropogenic activities. *Arch. Environ. Contam. Toxicol.* **77** (1), 79–87 (2019).

Table Captions:

Table 1. Statistics of groundwater quality parameters and the exceeding percentage of each parameter based on the BIS guidelines (2012)

Table 2. Significant principal components (PCs) loading for hydrochemical parameters in the study area

Table 3. Summary of the estimated non-carcinogenic risks of Nitrate ingestion of drinking water and dermal exposure

Figure Captions:

Figure 1. Showing the maps of (a) Topography in meters above mean sea level and the sampling location of Dausa district, Rajasthan, India, (b) regional geology, and (c) hydrogeology with the potential aquifers

Figure 2. Showing (a) Cumulative probability plots of the NO_3^- concentration in groundwater on which two normal subpopulations events (estimated NBL; natural background level, and APL; anthropogenic level). In each plot, a single inflection point is observed on log-scale, and (b) Probability density curve of a distinct population of NO_3^- concentration in groundwaters

Figure 3. Showing the temporal changes of nitrate concentrations during 8 years (2011-2018) in groundwater of the study area. The red lines above the Box and Whisker plots illustrate the percentage of samples beyond the Indian drinking water standards (45 mg/L) and 'n' denoted as the number of groundwater samples

Figure 4. Scatter plots showing the relationship between (a) nitrate and potassium, and (b) nitrate and chloride

Figure 5. Showing spatial distribution of non-carcinogenic health risks for (a) Hazard Index (HI) of males, (b) Hazard Index (HI) of females, (c) Hazard Index (HI) of children in the

713 study area, and (d) spatial distribution of nitrate concentration and its background
714 concentrations with the contour lines

715

716 **Suppl. Table Captions:**

717 **Table S1.** Normality test of distinguished population

718

719 **Suppl. Figure Captions:**

720 **Figure S1.** Spatial distribution of hydrochemical parameters in a semi-arid area, Rajasthan,
721 India

722 **Figure S2.** Scree plot for principal component analysis showing 3 components with >1
723 Eigenvalues value

724

Figures

Figure 1

Showing the maps of (a) Topography in meters above mean sea level and the sampling location of Dausa district, Rajasthan, India, (b) regional geology, and (c) hydrogeology with the potential aquifers

Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

Figure 2

Showing (a) Cumulative probability plots of the NO₃- concentration in groundwater on which two normal subpopulations events (estimated NBL; natural background level, and APL; anthropogenic level). In each plot, a single inflection point is observed on log-scale, and (b) Probability density curve of a distinct population of NO₃- concentration in groundwaters

Figure 3

Showing the temporal changes of nitrate concentrations during 8 years (2011-2018) in groundwater of the study area. The red lines above the Box and Whisker plots illustrate the percentage of samples beyond the Indian drinking water standards (45 mg/L) and 'n' denoted as the number of groundwater samples

Figure 4

Scatter plots showing the relationship between (a) nitrate and potassium, and (b) nitrate and chloride

Figure 5

Showing spatial distribution of non-carcinogenic health risks for (a) Hazard Index (HI) of males, (b) Hazard Index (HI) of females, (c) Hazard Index (HI) of children in the study area, and (d) spatial distribution of nitrate concentration and its background concentrations with the contour lines Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Supplementarymaterial.docx](#)