Natural Resources for Human Health
eISSN: 2583-1194

Original Research

Received 08 July 2026
Revised 21 Aug 2026
Accepted 08 Sep 2026

Natural Resources for Human Health 2026, Vol. 6 (20s): 751–770

KEYWORDS:
Heavy metals; seasonal variability; monsoon recharge; lead; chromium

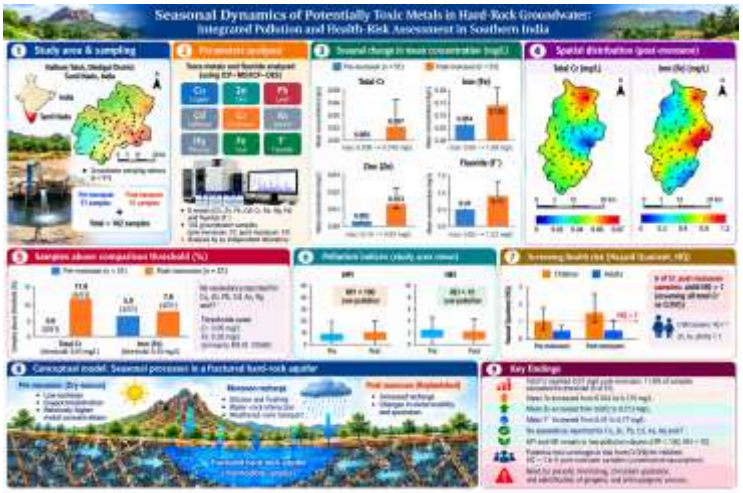
Monsoon-Driven Seasonal Variability of Potentially Toxic Metals in Hard-Rock Groundwater of Natham Taluk, South India: Pollution Indices and Human Health Risk Assessment

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ABSTRACT: The recharge process triggered by the monsoons can influence the mobility and dispersion of potential metal contaminants in hard rock aquifers, thus making the groundwater seasonally variable in terms of its quality. The current study focuses on the assessment of the seasonal variability of eight metals (Cu, Zn, Pb, Cd, Cr, As, Hg and Fe) and fluoride (F^-)in 102 groundwater samples in the premonsoon (n=51) and postmonsoon (n=51) periods in Natham Taluk, Dindigul district, Tamil Nadu state, India. Metal content and threshold exceedances were analyzed in conjunction with the heavy metal pollution index (HPI), heavy metal evaluation index (HEI), Spearman rank correlation, principal component analysis (PCA) and screening level human health risk assessment. The findings show the seasonal difference with postmonsoon maximum metal concentrations of 0.07 mg/L for total Cr. The respective proportion of excess relative to the study threshold levels was 11.8%. The mean Fe concentration changed from 0.054 to 0.135 mg/L, while the respective zinc (Zn) concentration changed from 0.002 to 0.013 mg/L. However, the mean HPI and HEI values stayed within their low pollution classes. Chromium speciation sensitivity revealed possible risks based on the presumption that all the detected chromium was in the form of Cr(VI), where the hazard

quotient values for children were greater than one for six samples after the monsoon period. This reveals the need for periodic groundwater quality assessment with respect to the season and checking of metal concentration, species of chromium, and contamination sources.



1. INTRODUCTION

Groundwater is an essential resource for domestic and agricultural water supply in many parts of peninsular India, where hard-rock aquifers form the major water-bearing and conducting media (Awasthi et al., 2026; Tripathi et al., 2026; Yadav, 2026). Here, groundwater composition results from interactions between recharge by precipitation, weathering of minerals, residence times, presence of fractures, surface soil, and land use practices (Balasubramaniyan, Murugesan, et al., 2026; Kannan, Balasubramaniyan, Karuppannan, et al., 2026; Pragadeeshwaran et al., 2026). Thus, trace metal concentrations should be interpreted in the context of the hydrogeologic system, not merely as concentration levels.

Seasonality is extremely important in regions dominated by monsoons. Dry seasons would result in low recharge and evapoconcentration, leading to increases in dissolved components. In contrast, monsoon infiltration could lead to dilution of groundwater, along with the transport of dissolved or particulate components in the vadose zone and weathered, fractured rocks (Kannan, Balasubramaniyan, Mani, et al., 2026). Thus, seasonal trends of trace metal behavior are very much metal-specific (Balasubramaniyan, G, et al., 2026).

Both lead and chromium need particular emphasis with regard to water quality. WHO categorizes lead as one of the major health hazards and suggests keeping its concentrations in water as low as is reasonably possible. The WHO recommendations also consider chromium as a hazardous chemical that should be monitored properly when there is an indication of a problem. The most recent update of the WHO Guidelines for Drinking-water Quality was done in June 2026.

There is considerable literature on the quality of groundwater in India; however, most of these studies are based either on a single sampling study or on seasonal statistical description without consideration of whether or not recharges affect the presence of metals. A comparative study in pre- and postmonsoon seasons can help find metals that come up, increase or become heterogeneous as a result of recharging.

The purpose of this research is to estimate and understand the changes that occur due to seasonal effects on Cu, Zn, Pb, Cd, Cr, As, Hg and Fe levels in groundwater through the dataset.

Some recent Indian studies add valuable insight to the current seasonal assessment. According to a study of hard-rock aquifers in South India conducted in 2025, monsoon-induced recharge can significantly affect the geochemistry of groundwater because of dilution and changes in hydrogeochemical processes. A 2024 study from Vellore, Tamil Nadu, analyzed potentially hazardous metals in groundwater during different seasons and indicated the importance of evaluating concentrations along with groundwater quality and risk indices (Sridhar & Parimalarenganayaki, 2024). Also, recently, (Thangaraj et al., 2025) noted heavy-metal enrichment in groundwater and rivers of the Amaravati Basin in south India and explained the distribution of metals based on

natural weathering and rock-water interactions as well as anthropogenic factors.

There have been previous studies done in Natham Taluk, which provide an excellent hydrogeological background for the current study. Panneerselvam et al. (2020) conducted an assessment of 37 groundwater samples from Natham and emphasized the role of GIS-based spatial assessment in hard rock formations. Another district-wide study conducted in 2020 had reported elevated TDS levels in several bore wells in Natham (Raja, 2020). Other studies conducted in Dindigul had studied the relationship between the groundwater chemistry and the factors such as evaporation, silicate weathering, and irrigation return flow, while one conducted in 2026 in Natham had focused on the drinking and irrigation potential using WQI and geospatial studies (Subramaniyan et al., 2024; Balasubramaniyan et al., 2026). These studies confirm that the groundwater quality in the area is spatially heterogeneous and hydrogeologically controlled. The present study adds to this local body of knowledge by studying the seasonality of toxic metals in water, specifically Pb and Cr, in the postmonsoon period.

Natham Taluk of Dindigul district is considered a crucial hard rock groundwater scenario of Tamil Nadu, where water is commonly used both for household and agricultural activities. Spatial variations in the groundwater chemistry of Natham Taluk have been previously reported, including the significance of the hydrochemical and GIS-based approach (Panneerselvam et al., 2020). Further research works have additionally analyzed groundwater potential and suitability in the case of Natham and proved the importance of this region for groundwater resource assessment (Gurugnanam et al., 2025). Nevertheless, all previous investigations mainly focused on groundwater potential, major ion hydrochemistry, drinking/irrigation suitability and spatial quality. This manuscript investigates another issue, namely, the response of potentially toxic trace metal concentrations in pre- and postmonsoon periods in the hard rock groundwater of Natham.

2. Study Area

Natham Taluk is situated in the eastern part of Dindigul District, Tamil Nadu, India, between 10°16'30" and 10°26'30" N latitudes and 78°07'0" and 78°24'0" E longitudes (Fig. 1). The taluk covers an area of 574.49 km² and had a population of approximately 158,687 (2011 Census). It lies about 37 km east of Dindigul town and is bordered by Karur and Tiruchirappalli districts to the north and Madurai district to the south. The Karanthamalai and Alagar Malai hill ranges form natural physiographic barriers. The area is a part of the Eastern Ghats, which are distinguished by their rich biodiversity, dense forests, and rough, undulating terrain with many hillocks. The drainage system, influenced to a great extent by the underlying geological structures, has a subparallel pattern in the hilly tracts and a dendritic pattern in the plains. The elevation varies from 192 to 919 meters above the mean sea level. The area's water supply is sourced by wells, boreholes, and hand pumps. Agriculture serves as the predominant occupation in the region, with essential crops such as rice, beans, peanuts, sesame, cotton, sugarcane, and millets. With an annual rainfall of 700-1600mm and an average temperature of 20-37 °C in April-June and November-January, the weather is relatively pleasant.

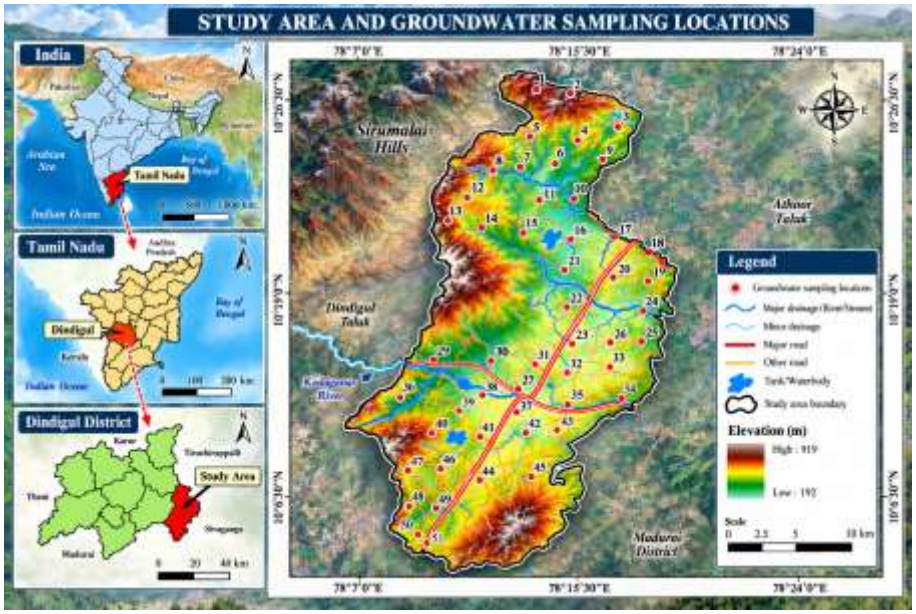


Fig. 1 Study Area Map

Natural Resources for Human Health
eISSN: 2583-1194

3. MATERIALS AND METHODS

3.1 Sampling

A total of 102 seasonal samples were obtained by sampling groundwater at 51 sampling stations in both premonsoon and postmonsoon seasons. Sampling sites were chosen based on the geographical location of the groundwater sources. Groundwater samples were collected from those sites where the source of water is being utilized by the inhabitants, and these collected samples were sent to an outside lab for the analysis of specific heavy metals such as Cu, Zn, Pb, Cd, Cr, As, Hg, and Fe. Laboratory analyses were conducted to establish the concentration of heavy metals in the collected samples of groundwater. The analytical data were recorded for each of the two seasons, premonsoon and postmonsoon, to conduct the seasonal variation study of metal concentration. The analytical concentrations were then compared with the recommended threshold levels of drinking water to find those samples exceeding the threshold values. Analytical data were also considered as a base to study heavy-metal pollution indices, statistical relationships among heavy metals, and the related health hazards posed by the groundwater samples.

Analyses for Cu, Zn, Pb, Cd, Cr, As, Hg, and Fe in the groundwaters were conducted in an independent laboratory. Information on the analytical methods, instrumentation, detection limits, sample storage, and quality control practices used should be provided only if it is recorded in the laboratory records. This information is required to determine the reliability of the results obtained.

3.2 Spearman Rank Correlation

Spearman correlation was selected because of skewness, zero inflation and non-normality.

$$\varrho_s = 1 - [6\Sigma d_i^2 / n(n^2 - 1)] \quad (1)$$

Table. 1 Spearman Rank correlation classification

$\lvert \varrho_s \rvert$	Descriptive strength
0.00–0.19	Very weak/negligible
0.20–0.39	Weak
0.40–0.69	Moderate
0.70–1.00	Strong

3.3 Principal Component Analysis (PCA)

Variables with no variance cannot contribute to PCA. Variable concentrations were standardized before PCA.

$$Z_{ij} = (X_{ij} - \bar{X}_j) / SD_j \quad (2)$$

$$PC_k = a_{k1}Z_1 + a_{k2}Z_2 + \ldots + a_{kp}Z_p \quad (3)$$

$$R = V\Lambda V^T \quad (4)$$

Table. 2 PCA classification

Loading magnitude	Descriptive interpretation
<0.30	Low contribution
0.30–0.49	Moderate contribution
≥0.50	Strong contribution

3.4 Heavy Metal Pollution Index (HPI)

HPI converts individual metal concentrations into a weighted composite index.

$$Q_i = (C_i / S_i) \times 100 \quad (5)$$

$$W_i = 1 / S_i \quad (6)$$

$$HPI = \Sigma(W_i Q_i) / \Sigma W_i \quad (7)$$

Table. 3 HPI classification

HPI	Common classification used in HPI studies
<100	Low pollution
100–200	Moderate pollution
>200	High pollution

3.5 Heavy Metal Evaluation Index (HEI)

$$HEI = \Sigma(C_i / S_i) \quad (8)$$

Table. 4 HEI Classification

HEI	Common classification
<10	Low
10–20	Medium
>20	High

3.6 Boxplot Method

$$IQR = Q_3 - Q_1 \quad (9)$$

$$Lower\ fence = Q_1 - 1.5(IQR) \quad (10)$$

$$Upper\ fence = Q_3 + 1.5(IQR) \quad (11)$$

Table 5 Boxplot method classification

Feature	Interpretation
Median	Central tendency of ranked data
Box (Q1–Q3)	Middle 50% of observations
Whiskers	Non-outlier range under the 1.5×IQR rule
Points beyond fences	Potential statistical outliers; investigate rather than automatically delete

3.7 Human-Health Risk Assessment

The assessment is a screening-level chronic drinking-water exposure assessment. It is not a clinical health diagnosis.

$$CDI = (C \times IR) / BW \quad (12)$$

$$HQ = CDI / RfD \quad (13)$$

$$HI = \Sigma HQ_i \quad (14)$$

Table. 6 and 7 Human-Health Risk Assessment Classification

Natural Resources for Human Health
eISSN: 2583-1194

Exposure parameter	Adult	Child
Ingestion rate, IR	2.0 L/day	1.0 L/day
Body weight, BW	70 kg	15 kg

HQ/HI	Screening interpretation
<1	Exposure estimate below the reference-dose benchmark
=1	At the reference-dose benchmark
>1	Exposure exceeds the screening benchmark; warrants further evaluation

The CDI was estimated based on groundwater concentration, daily ingestion rate, and body weight, while HQ was computed by dividing the CDI by oral RfD. An adult scenario employed an ingestion rate of 2.0 liters per day with a body weight of 70 kg, while a child scenario used an ingestion rate of 1.0 liters per day with a body weight of 15 kg. The RfD for each contaminant selected should be cited together with their credible sources and verified against those utilized in computation.

3.8 Chromium Speciation Sensitivity

$$Cr(total) = Cr\ (III) + Cr\ (VI) \qquad (15)$$

Only total chromium is available. Therefore, actual Cr (III) and Cr (VI) concentrations cannot be solved. Two bounding scenarios were calculated: 100% of total Cr as Cr (III), and 100% as Cr (VI).

Table 8 Chromium Speciation Sensitivity Classification

Scenario	Meaning
100% Cr (III)	Lower-toxicity-speciation screening scenario; not measured speciation
100% Cr (VI)	Conservative upper-bound toxicity scenario; there is no evidence that Cr(VI) is present

3.9 Analytical approach

The overall methodology chart is shown in Fig. 2

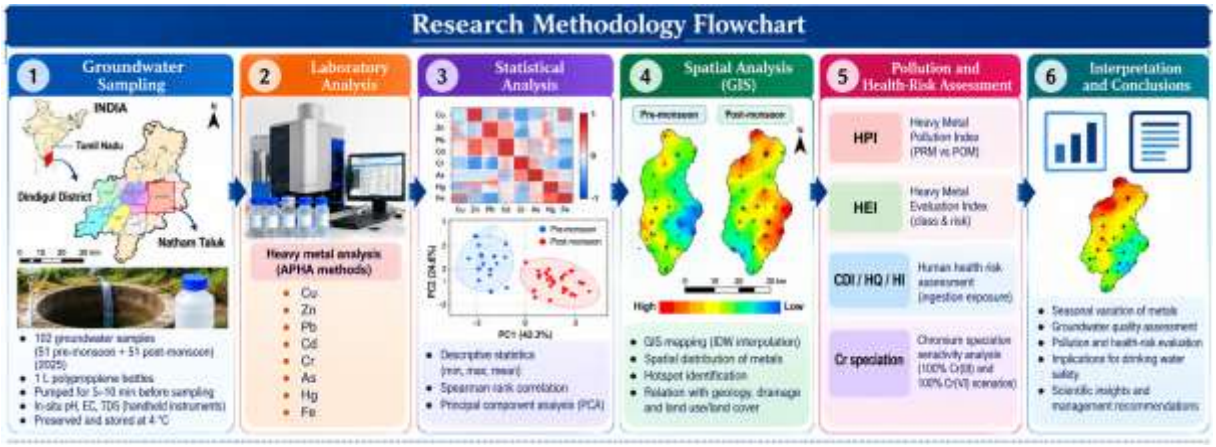


Figure 2. Aligned workflow for the seasonal heavy-metal assessment.

Seasonal interpretation is based on minimum, maximum and mean concentration, as well as the percentage of samples exceeding the comparison threshold. Instrument model, calibration range, reagent grade, detection/ quantification limit, procedural blank,

duplicates, certified reference material/ recovery test, and uncertainty of measurement are required. All these elements of Quality Assurance / Quality Control (QA/QC) are necessary for any reasonable interpretation of trace metals, and they should be taken directly from the laboratory record, not reconstructed.

However, none of these could be found in the sources consulted for this paper. Such information is to be presented based on the laboratory documents. Since there have been no consultations of such documents yet, it is not possible to independently assess the analytical technique and QA/QC performance and the lack of information on that must not be considered the absence of the corresponding elements.

4. RESULTS

Table 9. Seasonal summary of heavy-metal concentrations in groundwater during premonsoon and postmonsoon periods

Parameter	Limit (mg/L)	PRM Min (mg/L)	PRM Max (mg/L)	PRM exceedance (%)	POM Min (mg/L)	POM Max (mg/L)	POM exceedance (%)
Copper (Cu)	2.000	0.00	0.00	0.0	0.00	0.00	0.0
Zinc (Zn)	0.100	0.00	0.09	0.0	0.00	0.09	0.0
Lead (Pb)	0.010	0.00	0.00	0.0	0.00	0.070	9.8
Cadmium (Cd)	0.003	0.00	0.00	0.0	0.00	0.00	0.0
Total Chromium (Cr)	0.050	0.00	0.00	0.0	0.00	0.07	11.8
Arsenic (As)	0.010	0.00	0.00	0.0	0.00	0.00	0.0
Mercury (Hg)	0.001	0.00	0.00	0.0	0.00	0.00	0.0
Iron (Fe)	0.300	0.00	0.60	5.9	0.00	1.08	7.8
Fluoride (F^-)	1.500	0.07	0.82	0.0	0.12	1.22	0.0

Note: PRM = premonsoon; POM = postmonsoon. Concentrations are expressed in mg/L. Comparison thresholds are based primarily on the WHO. WHO guideline values are cited separately where relevant. Exceedance percentages were calculated using the stated threshold for each parameter.

The seasonal analysis identified variations in the concentrations of heavy metals in groundwater in the premonsoon and postmonsoon seasons. Total Cr had its highest recorded concentrations at 0.070 mg/L in the postmonsoon season, 11.8%, respectively, of samples surpassing the comparison thresholds in the study (Table.9). Moreover, the average concentrations of Fe increased from 0.054 to 0.135 mg/L, respectively (Table.9). The above information suggests that there was variation in the concentration of the metals due to seasonality. Recharge by monsoon rains, dilution, interaction between the minerals and water, and variations in the transport of contaminants could be responsible for the observed variations.

4.1 Overall seasonal pattern

The key outcome of the study is the presence of detectable/reported levels of Pb and Cr during the postmonsoon period. Lead increased from a premonsoon maximum of 0.00 mg L−1 to 0.006 mg L−1 during the postmonsoon period, with a mean postmonsoon level of 0.005 mg L−1 (Table.9). Cr likewise showed an increase from pre- to postmonsoon, rising to 0.07 mg L−1 with a mean level of 0.007 mg L−1 and 11.8% exceeding the comparison threshold (Table 9).

Iron was detected in both periods, increasing from a mean of 0.054 to 0.135 mg L−1. The maximum level increased from 0.60 to 1.08 mg L−1, and the percentage above the comparison value increased from 5.9% to 7.8% (Table.9). Zinc had a low overall concentration. Still, it means an increase of nearly sevenfold from 0.002 to 0.013 mg L−1.

Zero values were found for copper (Cu), cadmium (Cd), arsenic (As), and mercury (Hg) in all 51 samples, both before and after monsoons. Zero values were obtained for lead (Pb) and total chromium (Cr) in all premonsoon samples, while the maximum values of 0.07 mg/L were obtained in the postmonsoon samples (Table.9). The reported zero levels must be understood carefully since their meanings would depend on the reporting limits of the laboratory. It is difficult to determine the significance of the zeros without the reporting limits of the laboratory since it could mean that the metal was not detected, levels were below the reporting limit, or there were no metals at all.

From Table 9, the postmonsoon values above the threshold values included those of total chromium, lead, and iron. The total chromium was above its threshold value in 6 out of 51 samples (11.8%), lead in 5 out of 51 samples (9.8%), and iron in 4 out of 51 samples (7.8%). In the premonsoon data set, iron was above its threshold value in 3 out of 51 samples (5.9%), but there was no exceedance of lead and total chromium. There were no exceedances in the post and premonsoon seasons for zinc because the values did not surpass the adopted threshold of 0.10 mg/L in both seasons.

Monsoon recharge may have contradictory influences on groundwater quality. For example, on the one hand, it may lead to the dilution of dissolved constituents, but at the same time, it can flush the soil and the weathered zone of solutes, mobilize metals retained before, change pH and redox conditions, and increase the mineral-water contact. Thus, the detected presence of Cr is an indication of a seasonal hydrogeochemical response. Still, it does not prove the existence of a unique source (Abishek et al., 2025) The impact of monsoon recharge on groundwater chemistry has also been recently proved in India; heavy metal pollution of groundwater is connected with the rock-water interaction and anthropogenic factors (Abishek et al., 2025; Thangaraj et al., 2025) In the case of Natham Taluk, this interpretation is especially relevant since the previous hydrogeochemical studies have proven spatial variability of groundwater chemistry and importance of weathering, evaporation and irrigation processes.

4.2 Lead

Lead was found to be zero for all premonsoon water samples. For postmonsoon samples, the concentration of lead varied from 0.00 to 0.070 mg/L, with an average of 0.005 mg/L. Only five out of the total number of 51 postmonsoon water samples (9.8%) were higher than the selected value of 0.010 mg/L (Table 9).

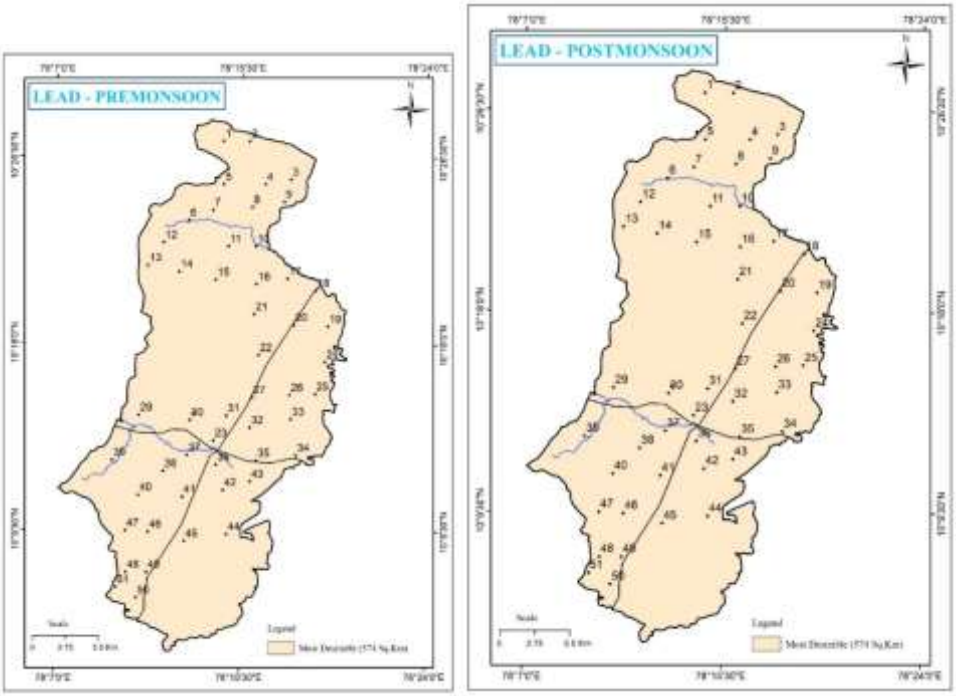


Fig. 3 a and b

4.3 Chromium

Zero concentration of chromium was observed in the premonsoon data set, but the concentration rose to 0.07 mg L−1 during the postmonsoon period, with 11.8% samples exceeding the 0.05 mg L−1 threshold concentration during the postmonsoon

period (Table.9) and (Fig. 4a and b). The guidelines of the WHO on chromium are based on the total amount of chromium since reliable speciation analysis is still not possible; besides, the health implications also depend heavily on the chromium species. As such, the current research should use the measured parameter as total chromium except where Cr(III)/Cr(VI) speciation was performed. The rise in the chromium content during the postmonsoon period indicates a trend that may warrant further investigation, which includes chromium speciation and identifying the anthropogenic sources of chromium.

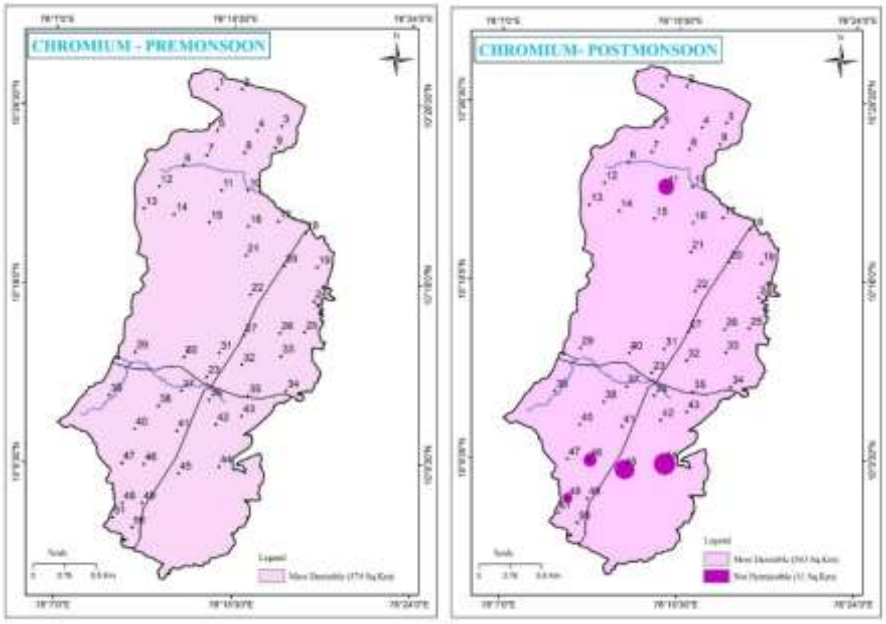
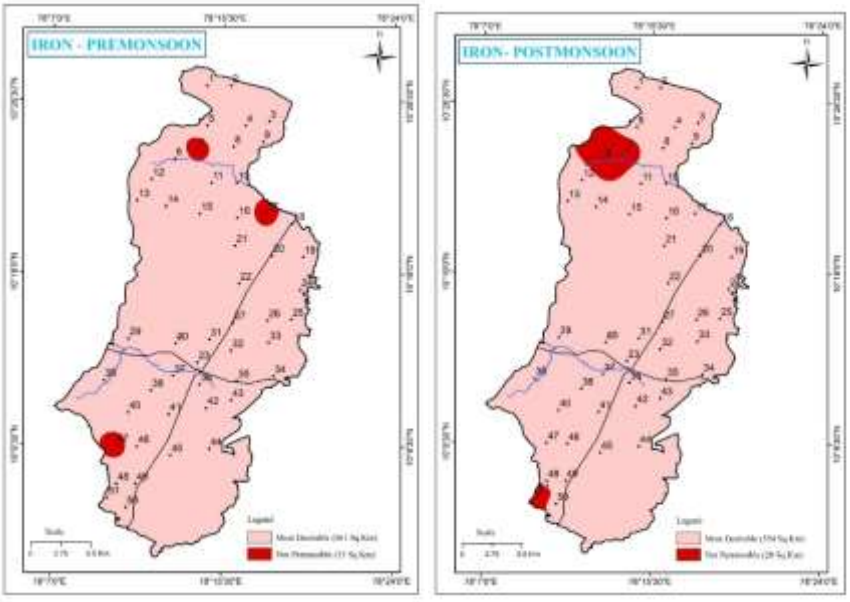


Fig. 4 a and b

4.4 Iron and zinc

There was a significant increase in iron content following the monsoon season, both in terms of mean and peak concentration levels (Table.9) and (Fig 5, 6a and b). Iron in groundwater usually shows strong dependence on processes such as mineral dissolution, redox state, solid suspension and mobility of iron-bearing minerals. WHO states that iron in drinking water is usually more of a cosmetic and operational issue rather than a direct health hazard. Zinc levels were high in premonsoon season at a particular location and did not cross the study threshold value, in postmonsoon season, but still showed an increase in mean level from 0.002 to 0.013 mg L−1.



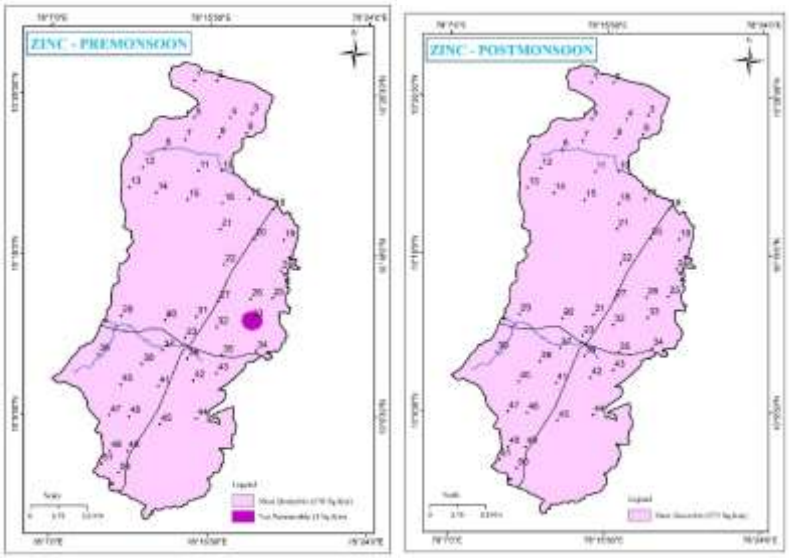


Fig. 5 a and b a, Fig. 6a and 6b

4.5 Copper

Copper levels were between 0.000 mg/L for both seasons, and the maximum permissible limit was taken as 2.000 mg/L (Table.9) and (Fig. 7a and b). The measured results show that the Cu was within the permissible limit, with 0% of the samples being out of the acceptable range. The absence of Cu enrichment implies that copper pollution is not a problem in the study site. Cu in the hard rock environments can result from weathering of accessory minerals containing Cu. However, its limited presence could be because of minimal dissolution of the minerals and/or anthropogenic activities.

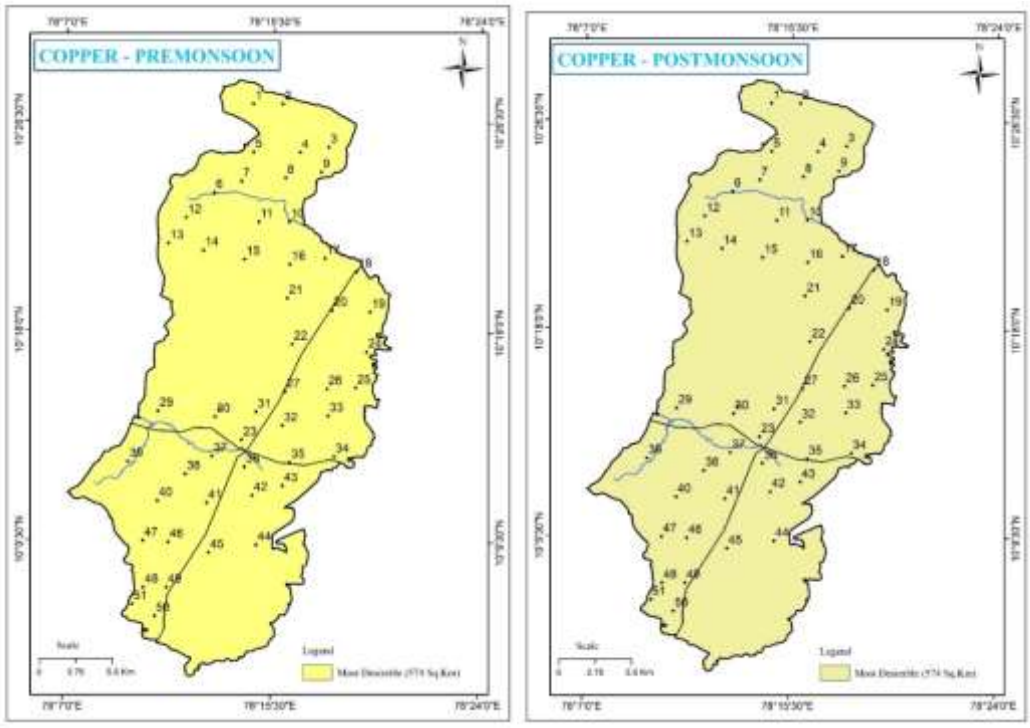


Fig. 7 a and b

4.6 Mercury (Hg)

Concentrations of Hg have been found to lie in the range of 0.000 mg/L for both seasons, without any sample surpassing the

permissible limit and 0% of the samples being inappropriate (Table.9) and (Fig. 8a and b). Very low concentrations of Hg imply that mercury pollution is minimal in the groundwater system. Given that mercury is linked with certain mineralization areas and activities like industrial releases, mining, and improper disposal of materials containing mercury, the non-existence of higher concentrations implies that there is minimal anthropogenic input of mercury in the study area.

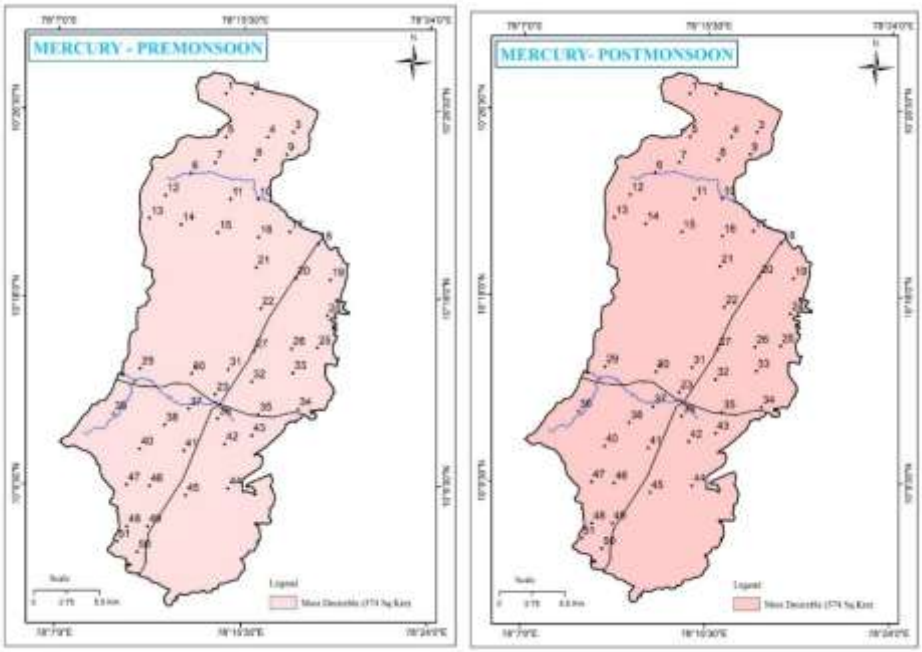


Fig. 8 a and b

4.7 Arsenic (As)

The concentration of arsenic varied between 0.000 mg/L for both seasons, staying within the acceptable limit, thus producing 0% non-acceptable samples (Table.9) and (Fig. 9a and b). It should be noted that low concentrations of As imply that groundwater does not contain any traces of arsenic pollution. Arsenic may be leached out from its bearing minerals by means of weathering and dissolution, and from iron and manganese oxides via desorption provided the appropriate geochemical environment exists. Nevertheless, the fact of no samples exceeding the acceptable limit indicates that this process is not well-developed in the area.

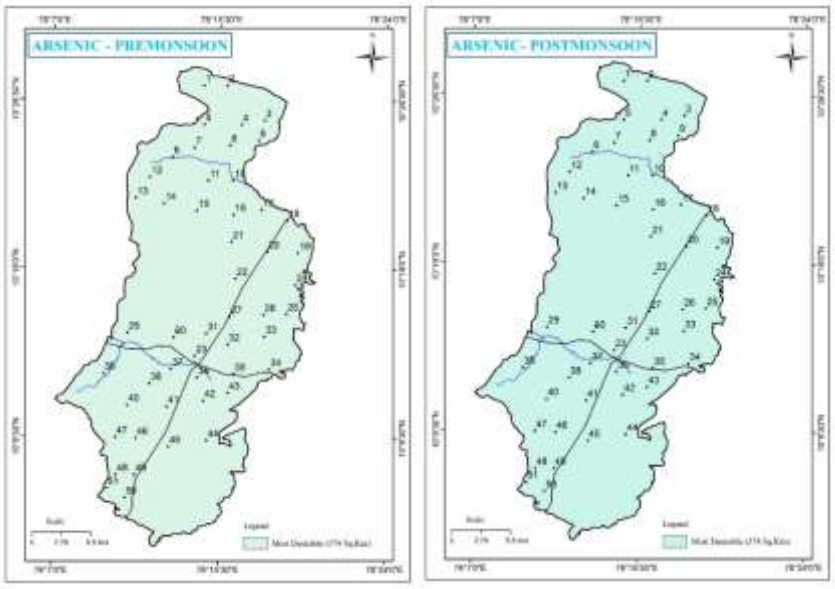


Fig. 9 a and b

Natural Resources for Human Health
eISSN: 2583-1194

5.8 Fluoride (F^-)

Fluoride concentrations ranged from 0.07 to 0.82 mg/L during the premonsoon season, with a mean of 0.410 mg/L (Table 9) and (Fig. 10 a and b). During the postmonsoon season, concentrations ranged from 0.12 to 1.22 mg/L, with a mean of 0.774 mg/L. The higher postmonsoon mean indicates an increase in fluoride concentration during this sampling period, although the observed maximum remained below the 1.5 mg/L reference value used in this study.

Fluoride is a substance that occurs in groundwater due to the dissolution of fluoride-containing minerals and long-term interaction between water and rocks. This implies that the concentration of fluoride is too low, probably because there is insufficient dissolution of fluoride-containing minerals or geochemical conditions for fluoride accumulation.

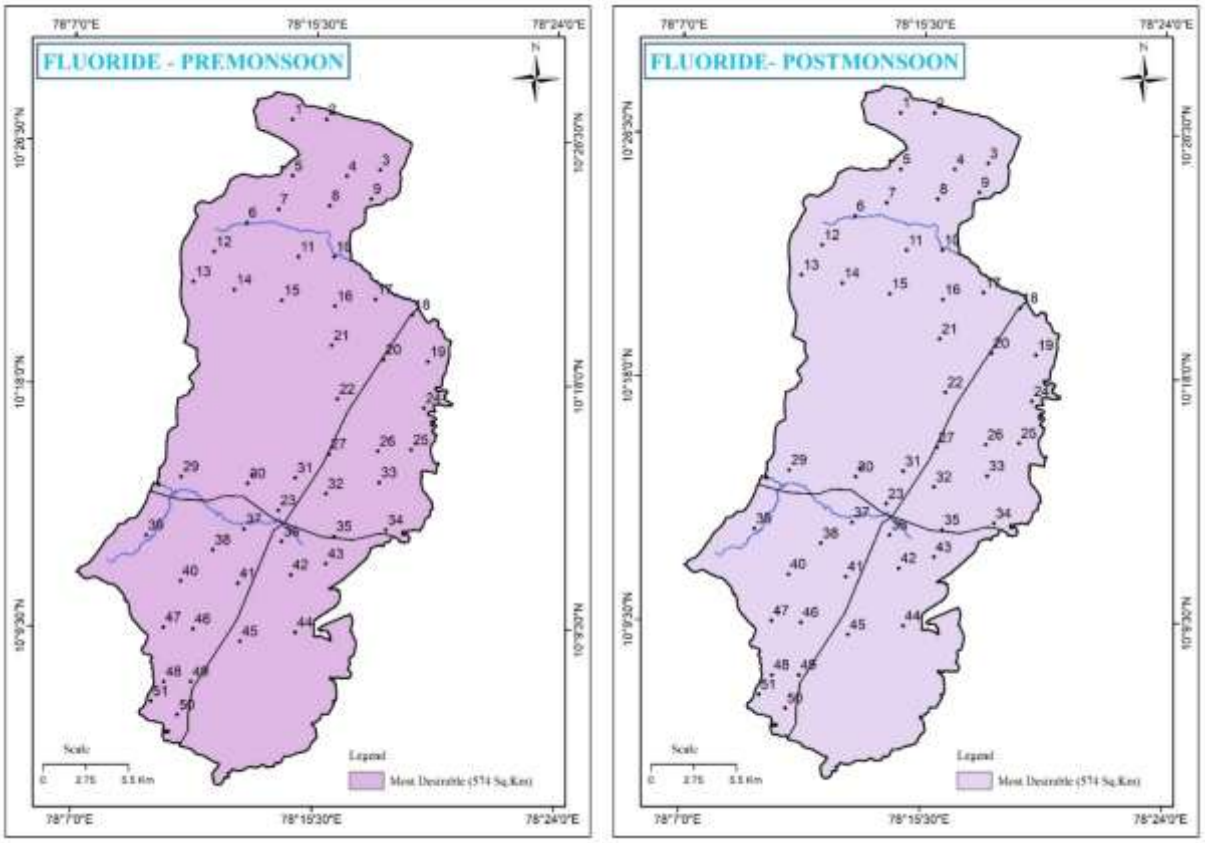


Fig. 10 a and b

5. GEOGENIC VERSUS ANTHROPOGENIC CONTROLS

The hard rock environment offers a plausible geogenic route via weathering and fracture-controlled groundwater movement, while land-use practices, man-made structures, and localized metal contamination might provide an anthropogenic source of metals. Postmonsoon occurrence of Pb and Cr conforms to increased recharge and related transport, but further studies will be needed for source identification. (Thangaraj et al., 2025). Novelty of the current research is geographically and procedurally based: it deals with Natham Taluk, a previously studied groundwater aquifer, but shifts the attention from traditional major ion quality to potential seasonal metal mobilisation. This is critical to highlight, as one can have groundwater with excellent major ion water quality but still have trace metal markers due to local circumstances. Therefore, the current research should be viewed as a trace metal study done seasonally rather than an addition to numerous groundwater indices studies.

6. SPEARMAN CORRELATION MATRIX

Results of the premonsoon Spearman correlation between Zn, Fe, and F^- were mostly weak correlations. The highest absolute value of the correlation coefficient was that between Fe and F^- ($\varrho = -0.167$), then Zn and Fe ($\varrho = -0.082$), followed by Zn and F^- ($\varrho = -0.058$). This is an indication of weak monotonic correlations between the variables investigated. Nonetheless, this does

not signify significance and pollution sources. The correlation between Zn and Fe was very weak and negative ($\varrho = -0.082$), whereas between Zn and F^-, the correlation was near zero but negative ($\varrho = -0.058$). The Fe–F^- couple had the highest absolute value of the correlation coefficient of all investigated couples, though still very weak ($\varrho = -0.167$) (Table 10) and (Fig. 11). Thus, the findings demonstrate weak co-variation of the investigated parameters during the premonsoon period. It can be stated that Zn, Fe and F^- were not influenced by one dominating process of concentration control during this period, because of the lack of significant correlations. However, correlations cannot provide information about common sources and the contribution of geogenic or anthropogenic factors; thus, these findings should be interpreted along with the results of the other analyses.

Table 10 Spearman results

Zn	Fe	F
1.000	-0.082	-0.058
-0.082	1.000	-0.167
-0.058	-0.167	1.000

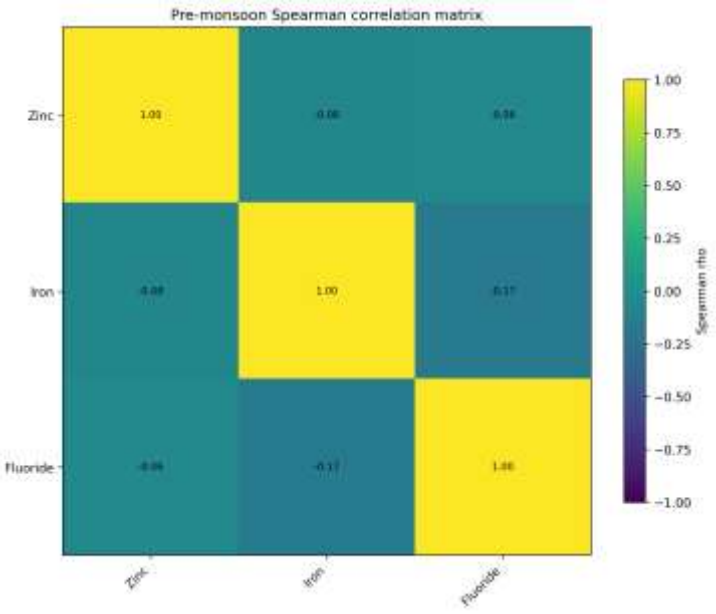


Figure 11. PRM Spearman correlation matrix.

In postmonsoon Spearman correlation, there was a dominance of weak to very weak correlation between Zn, Pb, total Cr, Fe, and F^-. Pairwise Pb-Cr ($\varrho = 0.273$) and Zn-Fe ($\varrho = 0.267$) were found to be weakly positively correlated, whereas Fe-F^- ($\varrho = -0.279$) was found to be weakly negatively correlated (Table. 11) and (Fig. 12). All other pairs of parameters were very weakly correlated with an absolute value of ϱ less than 0.20. Weak correlation between Pb and Cr implies the existence of some sort of simultaneous variability between the two trace metals, while Zn and Fe have some limited co-variability. However, since the correlation coefficient was quite small, no strong monotonic relationship was observed between the investigated parameters.

Table. 11: Correlations

Zn	Pb	Cr	Fe	F
1.000	-0.093	0.042	0.267	-0.161
-0.093	1.000	0.273	-0.069	-0.039
0.042	0.273	1.000	0.063	0.048

0.267	-0.069	0.063	1.000	-0.279
-0.161	-0.039	0.048	-0.279	1.000

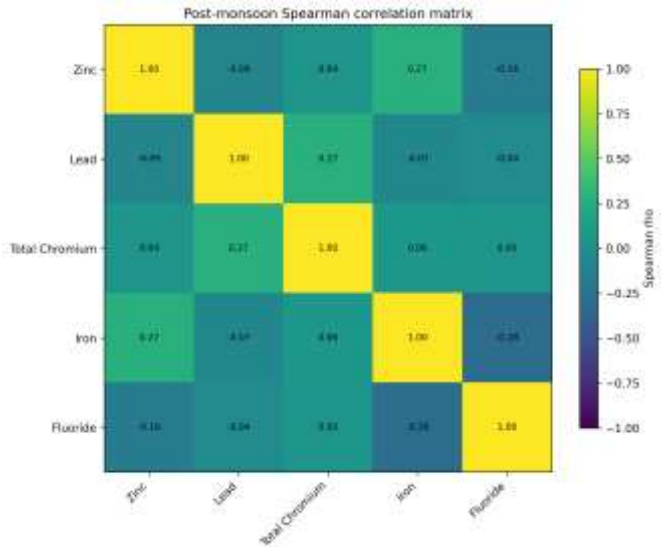


Figure 12. POM Spearman correlation matrix.

Premonsoon groundwater samples showed mostly very weak correlations, in which the only correlation observed was a negligible negative correlation for Zn–Fe ($\varrho = -0.082$), while the postmonsoon groundwater samples showed a comparatively wider set of correlations, which included weak positive correlations for Pb–Cr ($\varrho = 0.273$) and Zn–Fe ($\varrho = 0.267$). There was an increase in the strength of the negative correlation for Fe–F^- from PRM ($\varrho = -0.167$) to POM ($\varrho = -0.279$). Due to the presence of Pb and Cr ions in postmonsoon season samples, a few more correlation patterns were observed. The significance of Spearman's rank correlations was tested with a two-tailed test. The p-values were corrected for multiple comparisons using the Benjamini-Hochberg false discovery rate method. P-values less than 0.05 after correction were considered significant. Overall, the postmonsoon groundwater samples showed more trace-metal co-variations than those for premonsoon season samples.

7. PRINCIPAL COMPONENT ANALYSIS

PCA of premonsoon data set revealed three principal components that explained 39.42%, 34.40% and 26.18% of the total variation, respectively. The first two principal components accounted for 73.82% of the cumulative variation. PC1 had high positive loading for fluoride (0.7158) and high negative loading for Fe (−0.6955), while zinc had negligible influence (−0.0625) (Table 12) and (Fig. 13). PC2 had high dominance of zinc (0.9292), with moderate negative contribution from Fe (−0.3022) and fluoride (−0.2125). In addition, PC3 had high positive loadings of Fe (0.6519) and F^- (0.6652). Therefore, based on PCA results, it was evident that zinc contributed significantly as an independent source of variation during premonsoon, while Fe and fluoride were the major contributors to the rest of the multivariate structure. However, the association of components in PCA is merely a statistical representation of co-variations and should not be taken as a conclusive source of geogenic or anthropogenic origin unless supported by further evidence such as geology and hydrochemistry.

Table. 12 PCA results

Variable	PC1	PC2	PC3
Zn	-0.0625	0.9292	0.3641
Fe	-0.6955	-0.3022	0.6519
F	0.7158	-0.2125	0.6652

PC	Variance %	Cumulative %
PC1	39.4193	39.4193
PC2	34.4049	73.8242
PC3	26.1758	100.0000

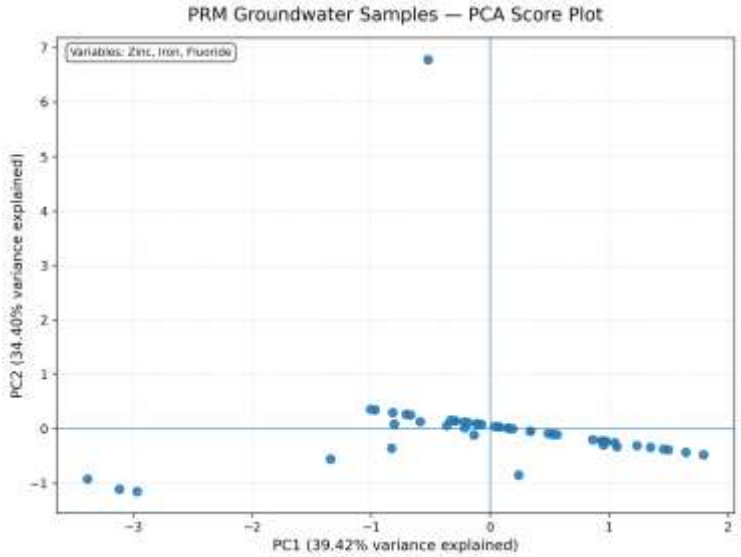


Fig 13. Premonsoon principal component analysis (PCA) score plot based on standardized Zn, Fe and F^- concentrations.

PCA of postmonsoon groundwater revealed that there were five principal components that represented 26.45%, 24.04%, 19.48%, 16.32% and 13.70% of the total variance, respectively. Together, the first two principal components represented 50.49% of the total variance, while the first three principal components accounted for 69.97% of the total variance (Table. 13) and (Fig. 14). PC1 had a prominent representation of Pb (0.6176) and total Cr (0.5127) loadings, along with secondary loading of F^- (0.4069), and a moderate loading of Zn (−0.4348). PC2 was dominated by Fe (0.6060) and Zn (0.5667), along with secondary loading of Cr (0.4586). PC3 was represented strongly by F^- (0.7524) and Fe (0.5403). These findings suggest a distinct pattern of Pb–Cr, Zn–Fe, and F^-–Fe co-variation in the postmonsoon season. Overall, the PCA results are in general agreement with those of Spearman correlation results, especially the weak positive correlations of Pb–Cr and Zn–Fe. However, PCA principal components are statistical patterns of co-variation and not evidence of any geogenic/anthropogenic sources.

Table. 13 POM PCA

Variable	PC1	PC2	PC3	PC4	PC5
Zn	-0.4348	0.5667	-0.0071	-0.4657	0.5224
Pb	0.6176	0.2089	-0.3436	0.3389	0.5849
Cr	0.5127	0.4586	-0.1545	-0.4916	-0.5111
Fe	-0.0331	0.6060	0.5403	0.5529	-0.1846
F	0.4069	-0.2403	0.7524	-0.3476	0.2996
PC		Variance %		Cumulative %	
PC1		26.4536		26.4536	
PC2		24.0361		50.4897	

PC3	19.4838	69.9735
PC4	16.3237	86.2973
PC5	13.7027	100.0000

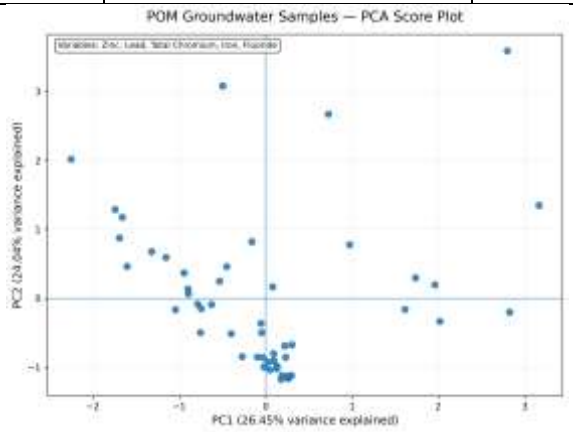


Fig 14. Postmonsoon principal component analysis (PCA) score plot based on standardized Zn, Pb, total Cr, Fe and F^- concentrations.

In the PCA results, a marked difference in the seasonal variation in the multivariate groundwater chemistry has been observed. For the premonsoon season, the first component PC1 (39.42%) was influenced mainly by F^- and Fe, while PC2 (34.40%) was dominated mostly by Zn, which together represented 73.82% of the total variance. On the other hand, in the case of postmonsoon PCA, a distributed model was observed wherein PC1 (26.45%) was dominated by Pb-Cr, and PC2 (24.04%) was dominated mostly by Zn-FE, which together represented 50.49%. It can be observed from the POM results that diversification has been observed with respect to the co-variation of trace metals, especially Pb-Cr, whereas PRM variation was more concentrated.

8. HEAVY METAL POLLUTION INDEX (HPI)

The mean HPI values rose from 0.0383 in the premonsoon season to 3.6816 in the postmonsoon season, the median from 0.0000 to 0.1070, and the maximum value from 0.4280 to 44.9581 (Table. 14) and (Fig. 15). This increase in HPI with the season is expected due to the increased frequency and magnitude of detectable heavy metal concentrations, especially Pb, Cr, Zn, and Fe, during the postmonsoon season. The significant discrepancy between the mean and median value of the POM season shows a right-skewed distribution due to a relatively smaller number of samples with higher composite metal loadings. However, not a single sample had a value greater than 100, signifying that the level of the composite pollution is low under the chosen classification system. Thus, the use of HPI is appropriate as an additional criterion for assessing the heavy metal composite pollution; nevertheless, the concentration of individual metals has to be taken into account since it can conceal the higher concentration of one of the metals despite its relatively lower total pollution index. Moreover, since the HPI depends directly on the selected comparison standards and their respective weights, the analysis was carried out within ±10% of the deviation from these standards.

Table 14 HPI Results

Season	Mean HPI	Median HPI	Maximum HPI	Samples >100
PRM	0.0383	0.0000	0.4280	0
POM	3.6816	0.1070	44.9581	0

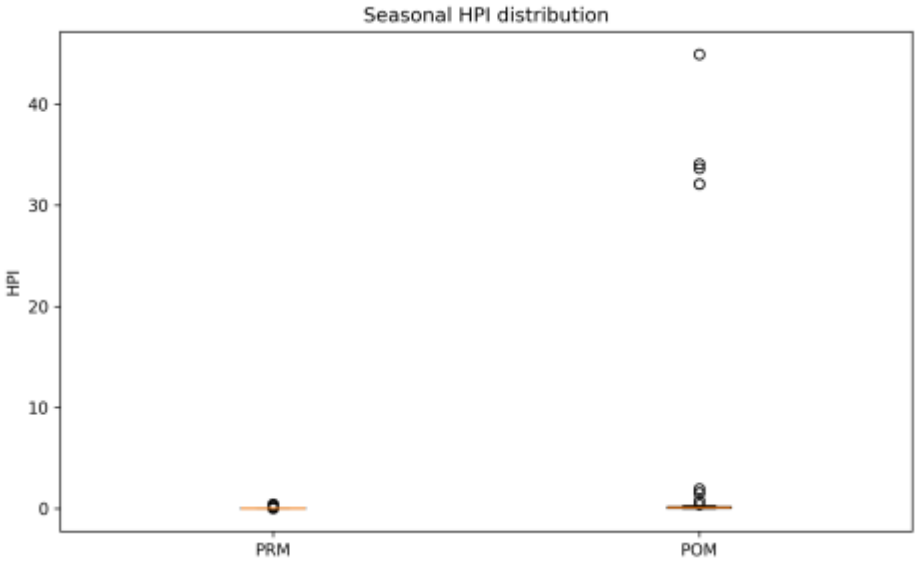


Figure 15. Seasonal HPI distribution.

The average HEI rose from 0.1797 in the premonsoon season to 1.1279 in the postmonsoon season, whereas the maximum value raised from 2.0000 to 8.2733. The elevated HEI in postmonsoon season could be attributed to monsoon recharge and hence enhanced water-rock interaction, which can result in enhanced dissolution and mobilization of natural elements from weathered and fractured crystalline rocks. On the other hand, agricultural return flow, domestic use, inputs from roads/settlements, and other anthropogenic sources can play their roles in the observed variations of metals when such sources are spatially available. The presence of Pb and Cr in the postmonsoon season, along with increased prevalence of Zn and Fe, suggests that monsoon recharge might have caused changes in the mobility of these metals and hence changes in groundwater chemistry. Yet, at present, the obtained HEI, correlation, and PCA analysis could not independently identify whether the observed variations are geogenic or anthropogenic, so that the above processes may be considered as possible contributing factors but not sources. However, the right-skewed POM distribution with few samples having relatively high HEI values may be due to geochemical and anthropogenic effects. In any case, the maximum HEI was less than 10, implying that the metal-loading class is low based on the specified classification. In summary, it can be said that while the total metal load was low, the postmonsoon variability observed can be explained by hydrogeochemical processes and possibly localized anthropogenic contributions.

9. Human Health Risk

All values of the hazard quotient (HQ) computed for Zn and Fe were less than one, where the maximum HQ value was 0.102857, which was computed for postmonsoon child exposure to Fe (Fig. 16). All these suggest that the calculated non-carcinogenic risk of individual exposure to Zn and Fe via drinking water was lower than the RfD for both these elements. The increased CDI and HQ values, especially for Fe, may be attributed to seasonal variations in the recharging of groundwater and water-rock interactions. Monsoons result in the flushing out of weathered material and changes in the chemistry of groundwater due to alterations in water-rock interaction. For the charnockite-gneiss environment in Natham Taluk, the weathering of Fe-containing minerals could thus add Fe in the form of solution; similarly, Zn may also be derived from the weathering of Zn-containing minerals, even though the mineral sources have not yet been determined. Anthropogenic influences are also possible. Return flow from agricultural activities can carry dissolved solids from the soil. In contrast, infiltration of wastewater and activities from the urban or settlement sector may bring in more solutes into the groundwater system. Studies conducted on hard rock aquifers in South India have identified linkages between land use, wastewater recharge, irrigation return flows, and variations in groundwater chemistry (Rajmohan et al., 2025). Nevertheless, it is not possible to confirm that these processes serve as sources of Zn and Fe in this case due to the lack of necessary information about land use, spatial, mineralogical and geochemical aspects in the dataset that is currently available. Lead has not been considered in the HQ calculation since there is no oral reference dose in the model selected for the analysis. Additionally, total chromium levels do not differentiate between Cr(III) and Cr(VI) species that differ in their toxicological properties and reference doses. In such a way, it is important to evaluate the risk of exposure to chromium separately using certain speciation assumptions.



Fig. 16

10. CHROMIUM SPECIATION SENSITIVITY

The HQ values were very low, but the assumption that all Cr was Cr(VI) led to relatively high HQ values, with the highest adult postmonsoon HQ value being 0.6667 and the highest child postmonsoon HQ value being 1.5556; six postmonsoon child HQ values were above 1 (Fig. 17). Higher postmonsoon presence of Cr could possibly be related to monsoon recharge of the aquifer, increased water-rock interactions and mobilization of Cr-bearing minerals/accessory phases from the weathered and fractured hard rock aquifer, but the current data does not allow pinpointing a geological source of Cr. Additionally, local anthropogenic inputs (such as agriculture, domestic waste, waste in general, road material, metal industries, etc.) could contribute to the mobilization of Cr.

It seems that the increase of chromium after the monsoon season can be attributed to a mixture of natural geochemical processes and local anthropogenic impacts; however, the source of these processes cannot be determined based only on the total concentrations of Cr. It should be mentioned that the case study with the all Cr(VI) scenario is a conservative scenario and does not indicate that Cr(VI) exists in the groundwater system. The big difference between Cr(III) and Cr(VI) scenarios shows that chromium valence poses a large uncertainty in the health-risk assessment and necessitates the measurement of Cr (III)/Cr (VI) speciation in future studies. Therefore, this sensitivity analysis gives an objective assessment of the uncertainty in chromium toxicity. The high chromium hazard index after the monsoon period in the case of Cr(VI) could possibly be due to monsoon recharge and increased water-rock interaction in the weathered and fractured charnockite-gneiss aquifer of Natham Taluk. However, the release and oxidation state change of chromium would depend on geochemical conditions in the locality, and this is still unknown without conducting site-specific geochemical analysis.

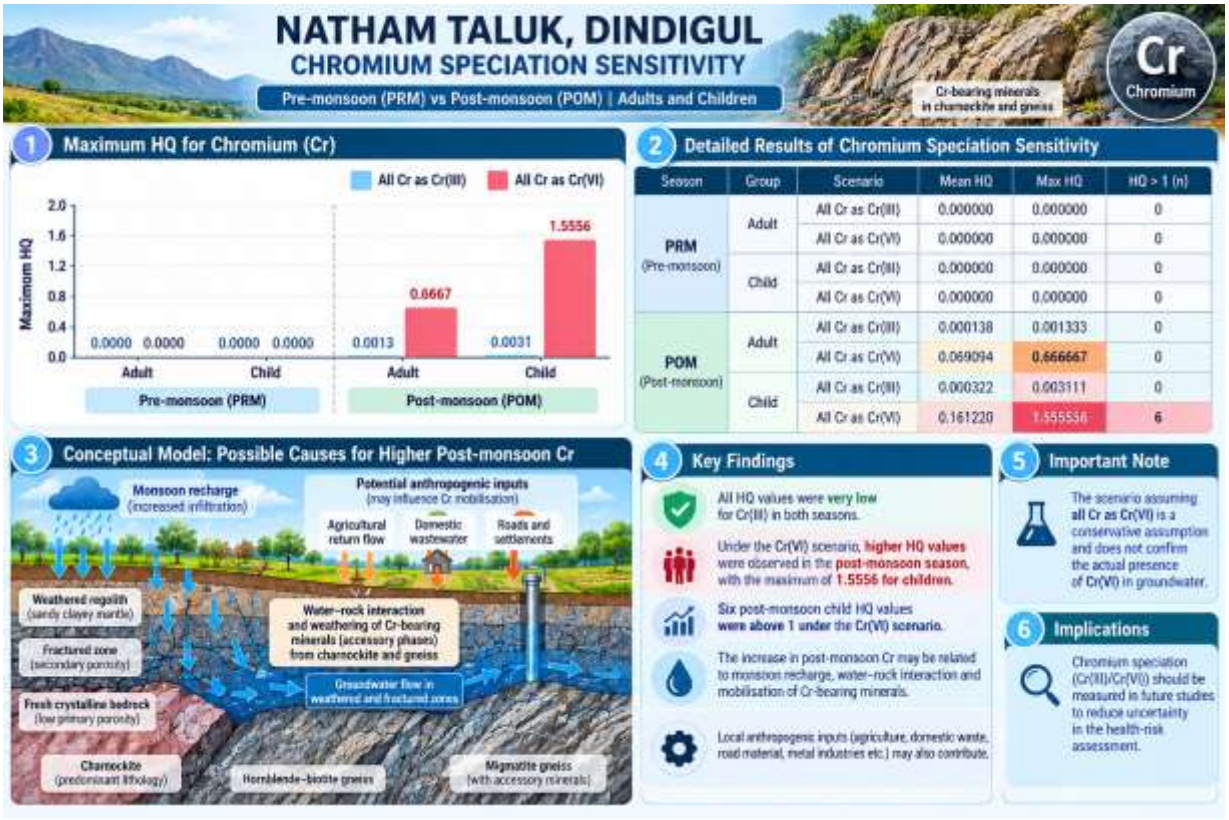


Fig. 17

11. CONCLUSIONS

The present study showed distinct seasonality in the levels of heavy metals in groundwater in Natham Taluk, especially concerning the reported postmonsoon presence of total Cr, showing peak values of 0.07 mg/L. Exceedance rates for these is 11.8%, respectively. Similarly, the mean Fe and Zn concentrations showed an increase during the postmonsoon period. Even though the HPI and HEI belonged to the low pollution category, some exceedances of individual metals demonstrate the shortcomings of using an index-based approach in assessing groundwater quality. The seasonal variations in the Spearman correlation and principal component analysis further indicated the variation in metal inter-correlation. The results of the health-risk assessment showed possible risk on the assumption that all the chromium is present in its hexavalent form, since the hazard quotient values were greater than one in six postmonsoon samples. From these observations, it can be suggested that monsoon recharge affects the metal mobility via mineral-water interaction; however, it cannot be stated whether the geogenic or anthropogenic sources have contributed more towards it. In this context, the validation of laboratory results, the determination of chromium speciation and seasonal monitoring are critical. The risk assessment for human health was done at a screening level to assess the risk from possible chronic exposures from ingestion of the drinking water. In the interpretation of the hazard quotient (HQ) values, those that exceed a value of 1 need more evaluation, and they are not considered as indicators of adverse health impacts because the screening benchmark is set at 1. Since the chromium concentration was reported as total chromium and there was no identification of the oxidation states of the chromium, the chromium-based risk assessments, assuming that all the measured chromium is chromium VI (Cr(VI)) are only conservative sensitivity assessments, and they do not indicate that there was Cr(VI) in the groundwater. Six postmonsoon exposure assessments for children had HQ exceeding 1.

REFERENCES

[1] Abishek, S. R., Pitchaimani, V. S., Sidhu, N., Ravindran, A. A., Sharma, S., & Priya, R. S. (2025). Hydrogeochemical Evolution and Salinity Risk Assessment in Hard Rock Aquifers of Southern India: A Chemometric Perspective. *Cleaner Water*, 100115.

[2] Awasthi, A., Singh, S. K., Sidharthan, B., Pawar, M., Yadav, H. S., Ali, H., & Kannan, P. (2026). Legal and Environmental Challenges in the Conservation of Freshwater Ecosystems Under Climate Change Policies. *International Journal of Special*

Education, *41*(17s), 1492–1500.

[3] Balasubramaniyan, G., G, D. A., Murugesan, B., Swaminathan, B., Mani, S., & Alemayoh, A. T. (2026). Spatial assessment of groundwater potability and irrigation suitability using water quality index and geospatial analysis in Natham Taluk Tamil Nadu India. *Discover Sustainability*.

[4] Balasubramaniyan, G., Murugesan, B., Swaminathan, B., Nandakumar, E., Kannan, P., Karuppannan, S., & Suresh, M. (2026). Fluoride contamination and its health implications in the groundwater using multivariate and geospatial analysis in Mettur Taluk, Tamil Nadu, India. *Discover Environment*, *4*(1), 64. https://doi.org/10.1007/s44274-026-00563-0

[5] Kannan, P., Balasubramaniyan, G., Karuppannan, S., Swaminathan, B., Murugesan, B., & Duraisamy, K. (2026). Groundwater quality assessment and spatio-seasonal variation using GIS and statistical analysis in parts of Dindigul district, Tamil Nadu, India. *Scientific Reports*, *16*(1), 21921. https://doi.org/10.1038/s41598-026-52274-4

[6] Kannan, P., Balasubramaniyan, G., Mani, S., Swaminathan, B., & Murugesan, B. (2026). Hydrogeochemical assessment and suitability evaluation of groundwater in a hard rock region: A case study of Jambuduraikottai, Tamil Nadu. *DYSONA-Applied Science*, *7*(1), 142–151.

[7] Panneerselvam, B., Paramasivam, S. K., Karuppannan, S., Ravichandran, N., & Selvaraj, P. (2020). A GIS-based evaluation of hydrochemical characterisation of groundwater in hard rock region, South Tamil Nadu, India. *Arabian Journal of Geosciences*, *13*, 1–22.

[8] Pragadeeshwaran, K., Gurugnanam, B., Bagyaraj, M., Bairavi, S., Karunanidhi, D., & Berhe, B. A. (2026). Groundwater potential zones demarcation in the hard rock province of South India: insights from remote sensing, GIS and AHP techniques. *Scientific Reports*, *16*(1), 6186. https://doi.org/10.1038/s41598-026-35734-9

[9] Raja, C. E. (2020). Assessment of physicochemical characteristics of groundwater collected from different taluks, Dindigul district, Tamilnadu, India. *Environmental Research and Technology*, *3*(1), 1–7.

[10] Rajmohan, N., Senthilkumar, M., & Alqarawy, A. M. (2025). Hydrogeochemistry and its relationship with land use pattern and monsoon in hard rock aquifer. *Applied Water Science*, *15*(3), 1–18.

[11] Sridhar, D., & Parimalarenganayaki, S. (2024). Evaluation of human and ecological health risks associated with the potentially toxic heavy metals in groundwater of Vellore city, Tamil Nadu, India. *Journal of Hazardous Materials Advances*, *16*, 100497.

[12] Subramaniyan, A., Balaji, A., & Andimuthu, R. (2024). Assessment of groundwater quality for drinking and irrigation in Dindigul district, southern India: Hydrochemical characterization and spatial analysis. *Desalination and Water Treatment*, *320*, 100772. https://doi.org/10.1016/J.DWT.2024.100772

[13] Thangaraj, K., Karthikeyan, S., Rajendran, M., Kulandaisamy, P., Senapathi, V., Velmayil, P., & Krishnamoorthy, R. (2025). Hydro-environmental risk assessment of heavy metal pollution in the groundwater and river water of the Amaravati Basin, Southern India. *Discover Geoscience*, *3*(1), 231.

[14] Tripathi, P. K., Sultana, Q., Sethy, N., Choubey, M. R., Haqqani, M. H., & Kannan, P. (2026). Air Quality and Human Health: A Comparative Analysis Of Urban and Rural Areas. *International Journal of Aquatic Research and Environmental Studies*, *6*(S3), 304–309.

[15] Yadav, D. (2026). Integrated Water Resource Management and Climate Resilience: Sustainable Approaches to Address Water Scarcity in Developing Regions. *International Journal of Special Education*, *41*(20s), 1643–1651.