

Hydrochemical signatures of industrial pollution: Impacts on surface and groundwater in the Aluva–Kochi Industrial Belt, Kerala, southern India

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ABSTRACT

Water pollution caused by industrial activities poses a significant threat to surface and groundwater resources, particularly in regions with rapid industrialization. This study examines the impact of industrial pollution on the Periyar River and associated groundwater systems in the Aluva–Kochi Industrial Belt, Kerala, southern India. A comprehensive hydrochemical analysis of 50 water samples was conducted to assess drinking and irrigation suitability, identifying key constituents such as heavy metals, organic pollutants, and high salinity levels. The study employs multivariate statistical techniques, including hierarchical cluster analysis and Pearson correlation, to determine pollution sources and hydrogeochemical processes influencing water quality. Findings indicate elevated concentrations of heavy metals such as Ti, Ga, Ba, Sr, and Ag in the collected samples, with levels exceeding the permissible limits prescribed by WHO and BIS standards. Moreover, hydrogeochemical assessments reveal a transition from Ca–Mg–HCO₃ to Na–Cl and Na–HCO₃ water types, suggesting pollution from industrial discharge influence. The study highlights the urgent need for improved wastewater management and regulatory interventions to mitigate the adverse effects of industrial pollution on regional water resources. This study fills a critical gap by providing a comprehensive assessment of how industrial effluents contribute to hydrochemical alterations and water quality degradation in the Aluva–Kochi Industrial Belt of Kerala.

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1. Introduction

Water pollution is an increasing global issue, particularly groundwater and surface water contamination from industrial activities. Groundwater and surface water are interconnected parts of the hydrological cycle, and their quality directly affects ecosystems, public health, and socioeconomic development

(Gleick, 1996). Industrial pollution threatens the sustainability of these crucial water resources, with contaminants like heavy metals, organic compounds, and toxic chemicals seeping into water bodies through different pathways. As industrialization expands globally, managing and reducing its impact on water resources has become a critical challenge (UNESCO UN-Water, 2020).

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Industries primarily contribute to water pollution by discharging untreated or inadequately treated wastewater into rivers, lakes, and oceans, which can seep into groundwater systems. Heavy metals like lead, mercury, and cadmium, along with organic pollutants such as polycyclic aromatic hydrocarbons (PAHs), are commonly present in industrial effluents (Gagan et al., 2016). These pollutants degrade surface water quality and can infiltrate aquifers, contaminating drinking water sources (Khan et al., 2008). Industries discharge harmful pollutants, including phosphates, sulfides, ammonia, fluorides, heavy metals, and pesticides, into aquatic environments. An alarming pattern has developed in which factories are dumping chemicals, electronic waste (e-waste), and various biological wastes (such as poultry waste) into open wells and ponds (Shaji, 2013). Once pollutants enter groundwater, they can remain for decades due to groundwater's slow movement and limited ability to naturally break down contaminants (Christensen et al., 2000).

The impact of industrial pollution is especially severe in areas where industries are concentrated near water bodies, with minimal regulatory oversight or poor enforcement of environmental laws. Industrial activities like mining, chemical manufacturing, and metal processing generate large volumes of hazardous waste, which, if improperly managed, can widely contaminate both groundwater and surface water (Morrison et al., 2001). For instance, improper disposal of industrial waste in unlined landfills can cause contaminants to leach into groundwater, endangering nearby communities and ecosystems (Ibrahim et al., 2021).

The Periyar River, the longest in Kerala, is crucial to the region's socioeconomic and environmental health. However, rapid industrialization in the Aluva–Kochi Industrial Belt has caused severe pollution, affecting both the river and nearby groundwater. This region, home to many chemical industries, oil refineries, and fertilizer plants, has become a major source of contamination (Fehmida and Bindu, 2018). The main sources of pollution are industrial effluents, agricultural runoff, and domestic waste. Industrial effluents in the Aluva–Kochi belt contain harmful heavy metals like lead, mercury, chromium, and cadmium (Arun et al., 2024; Kumar et al., 2011). Moreover, industrial discharge introduces phenolic compounds and petroleum hydrocarbons, posing serious risks to both aquatic life and human health (Mani et al., 2023).

Agricultural runoff, containing fertilizers and pesticides from nearby farms, contributes to nutrient loading in the river, leading to eutrophication (Pericherla and Vara, 2023). Additionally, untreated domestic sewage further degrades water quality by increasing organic pollution. Groundwater, closely connected to the surface water of the Periyar River, is also at risk. Studies show that industrial leachates and effluents have contaminated groundwater with high levels of nitrates, fluoride, and heavy metals like cadmium and lead, posing health risks to local populations that depend on groundwater for drinking. Several studies have reported alarmingly high levels of heavy metals in both the river and groundwater, often exceeding the permissible limits set by the Central Pollution Control Board (CPCB). Specifically, lead, chromium, cadmium, and arsenic levels are elevated near industrial discharge areas (Paul and Pillai, 1983).

Besides heavy metals, organic pollutants from industrial effluents and domestic sewage have increased levels of biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total suspended solids (TSS) in the river (Hamdhani et al., 2020; Pathak et al., 2022). These organic pollutants, including toxic substances like benzene and toluene, reduce dissolved oxygen in the water, endangering the river's aquatic ecosystems (Kannel et al., 2007). Groundwater quality has also been severely affected by high levels of nitrate, fluoride, and sulfate, likely caused by industrial activities (Krishna et al., 2019). Long-term exposure to these contaminants can cause serious health problems, including methemoglobinemia (blue baby syndrome) from nitrate contamination and skeletal fluorosis from high fluoride levels (Kumar et al., 2024; WHO, 2019).

Overall, pollution in the Periyar River and its connected groundwater resources is a major environmental and public health concern, driven by industrial activities, agricultural practices, and poor waste management. Urgent interventions are required to mitigate these risks and protect the region's water resources. Assessing the quality and suitability of groundwater for various uses is essential today. Thus, hydrochemical analysis is vital in determining if water resources are suitable for their intended applications (Mohamed et al., 2022; Salih and Shaji, 2024). The objective of this study is to evaluate the impact of industrial effluents on the hydrochemical characteristics and water quality of the Periyar River and adjacent

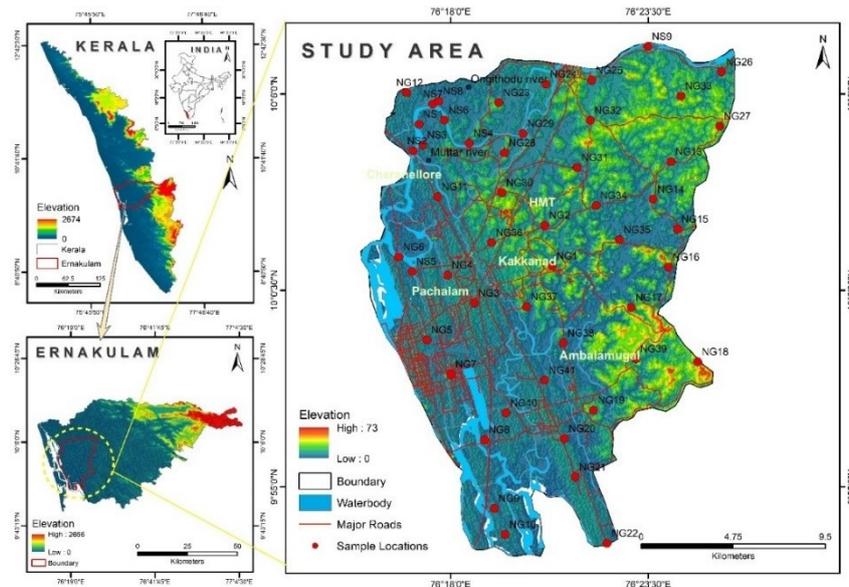


Fig. 1. Study area map with sampling locations.

groundwater systems in the Aluva–Kochi Industrial Belt, Kerala.

2. Study Area

The study area Aluva–Kochi Industrial belt in the Ernakulam District, is located within north latitudes $9^{\circ}55'$ and $10^{\circ}6'$ and east longitudes $76^{\circ}12'30''$ and $76^{\circ}29'$. Fig. 1 represents the study area map with sampling locations. The industrial belt located along the banks of the Periyar River in Kerala has a population of over 40,000. The river originates from the Western Ghats and flows westward for 244 km. Various chemical industries situated on the river's banks discharge approximately 17.35 million liters of highly polluted effluents containing hazardous substances such as pesticides, heavy metals, and other organic compounds directly into the river or store them in ponds and sludge heaps, making the area one of the most toxic hotspots in the world (Ambily and Menon, 2019, Nimisha and Sheeba, 2014). Ernakulam district has a wet monsoon climate. The area receives substantial rainfall during the southwest and northeast monsoon seasons but much less during the other months. The hottest months are March through May, while the coldest are December through February. Annual rainfall in the district ranges from 3,233 to 3,456 mm across different locations. Geomorphologically, the district is divided into three physiographic units: (1) Coastal plains (lowlands), (2) Midlands, and (3) Highlands, and our study area falls within

lowland and midland regions. The general elevation of the coast is less than 8 m amsl, and that of the midlands is between 8 and 76 m amsl. Groundwater generally occurs under phreatic conditions in weathered and fractured crystalline rocks, laterites and unconsolidated coastal sediments. It occurs under semi-confined to confined conditions in the deep-seated fractured aquifer of the crystalline rocks and Tertiary sediments. The weathered zone in the crystallines below acts as good storage for groundwater (Shyam, 2013). The main geological units in the district consist of charnockite and gneisses from the Archean age, laterite from the sub-recent age, and unconsolidated alluvium of recent formation containing sand and clays mainly in the western part of the study area (Sumangala et al., 2013).

3. Materials and Methods

In the study area, 50 water samples were collected during the months of December and January (post-monsoon season). Out of these, 41 samples were from wells, and 9 samples were from surface water sources. The samples were collected in 1-liter High-Density Polyethylene (HDPE) bottles, filled to the brim, and immediately sealed to prevent air exposure. They were systematically labeled. Before filling the bottles, each bottle was rinsed 3–5 times with the same water sample. The collected samples were then analyzed for pH, Electrical Conductivity (EC), Total Dissolved Solids (TDS), and major ions such as calcium

(Ca²⁺), magnesium (Mg²⁺), sodium (Na⁺), potassium (K⁺), carbonate (CO₃⁻), bicarbonate (HCO₃⁻), chlorine (Cl⁻), nitrate (NO₂⁻), nitrite (NO₃⁻), and sulfate (SO₄²⁻), Silicate (SiO₄)⁴⁻, Phosphate (PO₄)³⁻ in the chemical laboratory of the Department of Geology, University of Kerala. Alkalinity, total hardness, calcium, and chlorine concentration were determined using the titration method. Sodium and potassium were analyzed using a flame photometer. UV-visible spectrophotometers were used to determine SiO₄⁴⁻, SO₄²⁻, PO₄³⁻, NO₃⁻, and NO₂⁻. All the analyses were carried out according to the standard procedures given by the American Public Health Association (APHA, 2005). The suitability of water resources for irrigation was based on Sodium Adsorption Ratio (SAR), Sodium Percent (Na%), and Magnesium Ratio (MAR) as calculated by the following equations,

$$\text{SAR} = \frac{\text{Na}}{\sqrt{\frac{\text{Ca} + \text{Mg}}{2}}} \quad (1)$$

$$\text{Na}\% = \frac{(\text{Na} + \text{K})}{(\text{Ca} + \text{Mg} + \text{Na} + \text{K})} * 100 \quad (2)$$

$$\text{MAR} = \frac{\text{Mg}}{(\text{Ca} + \text{Mg})} * 100 \quad (3)$$

The heavy metals Li, B, Ti, Cr, Mn, Co, Ni, Cu, Zn, Ga, Sr, Ag, Cd, In, Ba, Pb, and Bi were analyzed using ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) at the School of Environmental Sciences, MG University, Kottayam, India. 0.1 mg sample was added to a Teflon tube (bomb), followed by the addition of 8 ml of trace metal grade HNO₃ and 2 ml of trace metal grade H₂SO₄. Pressure and temperature were increased using a microwave digestion system to accelerate the thermal breakdown of the sample, thereby enhancing the solubility of the metals. Between 1–8 ml of the sample solution, along with up to 10 ml of the acid mixture, was used for digestion. The digestion process was completed within 2 hours.

The microwave was programmed to reach 160 ± 4°C in 10 minutes and then increase to 165–170°C over the subsequent 10 minutes. After digestion, the vessels were cooled and uncapped in a fume hood. The digested solution was transferred to a 25 ml volumetric flask, diluted, filtered, and stored below room temperature for further analysis.

The ICPMS was standardized using ICP Multi-Element Standard VI by Merck KGaA, which con-

tained various elements including Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Ti, and Zn. The detection limits for Cr, Mn, Ni, Cu, Zn, Cd, Pb, Li, B, Co, Bi, Ba, In, Ti, Sr, and Ga were 12, 0.7, 2.0, 0.8, 2.9, 0.2, 0.2, 1.4, 9.0, 0.2, 0.1, 0.15, 0.0007, 0.0004, 0.06, 0.01 in ppb respectively. The average of three readings for each sample was taken as the final value for each element. The ICP-MS results were subjected to multivariate statistical analysis such as Hierarchical Cluster Analysis (HCA) and Pearson correlation matrix using R-programme and OriginPro software.

4. Results and Discussion

4.1. Drinking Water Quality

The physio-chemical parameters of the water samples are analyzed, and the results were compared with WHO 2012 and BIS 2012 and are given in Table 1. The pH of the water samples from the study area ranges from 4.69 to 7.8, with an average of 6.2 indicating an acidic nature of the samples. pH measures the relative concentrations of hydrogen ions (H⁺) and hydroxyl ions (OH⁻) in water, offering crucial insights for various geochemical processes. It plays an essential role in determining chemical equilibrium and solubility in water, helping to assess the behavior and interactions of minerals and other substances in aquatic environments (Hem, 1985). The acidic nature of water can be attributed to human activities such as the disposal of industrial waste and the use of fertilizers in agricultural areas. While acidic water is unsuitable for drinking, it may still be used for purposes such as irrigation, industrial applications, and domestic tasks. The pH of water is typically influenced by the geology of the region and its buffering capacity (Vijith and Satheesh, 2007; Weber Jr and Stumm, 1963).

EC and TDS in the studied water samples range from 25.32 to 728.5 µS/cm and 12.68 to 364 ppm, respectively, with mean values of 152.99 µS/cm and 76.55 ppm. These values fall within the permissible limits established by the WHO and the BIS (2012). It is important to note that EC and TDS are directly correlated, higher EC values typically indicate increased concentrations of dissolved solids, which contribute to overall conductivity. This relationship underscores the significance of monitoring these parameters, as elevated levels of dissolved solids can directly influence water quality and its suitability for various

Table 1. Drinking water standard specifications given by WHO (2012) and BIS (2012) and statistical information of ion concentrations for 16 physico-chemical parameters.

Parameters	Max	Min	Average	WHO (2012)	BIS (2012)
pH	7.8	4.69	6.2	6.5–8.5	6.5–8.5
EC ($\mu\text{S}/\text{cm}$)	728.5	25.32	152.99	1500	—
TDS (ppm)	364	12.68	76.55	1500	2000
Total Hardness (mg/L)	234	10	62.04	—	600
Total Alkalinity (mg/L)	595.2	48	148.32	—	600
Ca (mg/L)	90.58	2.4	20.28	200	200
Mg (mg/L)	15.45	0.47	2.72	150	100
Na (mg/L)	449.2	0.43	50.23	200	200
K (mg/L)	31.7	0.31	7.97	12	—
Cl (mg/L)	316.35	20.02	64.83	600	1000
HCO ₃ (mg/L)	561.6	48	143.33	500	—
CO ₃ (mg/L)	33.6	0	4.99	—	—
SO ₄ (mg/L)	76.8	0.95	14.89	250	400
PO ₄ (mg/L)	4.46	1.81	2.86	—	—
NO ₃ (mg/L)	4.46	0.38	1.66	45	45
SiO ₂ (mg/L)	48.12	1.81	2.96	—	—

uses (Srinivas et al., 2000). Water with TDS upto 1,000 mg/l is considered to be suitable for drinking as recommended by (Jasrotia and Singh, 2007; Tiwari and Singh, 2010).

The concentrations of Ca²⁺, Mg²⁺, and K⁺ ions in the study area range from 2.4 to 90.58 mg/L (mean value of 20.28 mg/L), 0.47 to 15.45 mg/L (mean value of 2.72 mg/L), and 0.31 to 31.7 mg/L (mean value of 7.97 mg/L), respectively. These values fall within the standard limits prescribed by BIS (2012) and WHO (2012). However, the Na⁺ concentration varies from 0.43 to 449.20 mg/L, with an average of 50.23 mg/L. Elevated Na⁺ concentrations, especially in samples collected from surface waters, exceed the acceptable limits set by both BIS and WHO (2012). Sodium ranks sixth among elements in terms of abundance and is commonly present in most natural waters. In this study, the occurrence of sodium can be attributed to anthropogenic activities such as industrial waste disposal, agricultural runoff, silicate weathering, and mineral dissolution (Khan et al., 2021; Srinivasamoorthy et al., 2013). The cationic abundance follows the order: Na⁺ > Ca²⁺ > Mg²⁺ > K⁺.

Among the anions, HCO₃⁻ is the dominant ion in the water resources. HCO₃⁻ concentration in the study area ranges from 48 to 561.6 mg/L, with a mean value of 143.33 mg/L, exceeding the prescribed limits of WHO and BIS (2012) in one sample. The majority of the samples, however, exhibit relatively high bicarbonate concentrations. The concentrations of Cl⁻, CO₃²⁻, SO₄²⁻, PO₄³⁻, NO₃⁻, and SiO₂⁴⁻ vary from 20.02 to 316.35 mg/L (average of 64.83 mg/L), 0 to 33.6 mg/L (average of 4.99 mg/L), 0.95 to 76.80 mg/L (average of 14.89 mg/L), 1.81 to 4.46 mg/L

(average of 2.96 mg/L), 0.38 to 4.46 mg/L (average of 1.66 mg/L), and 1.81 to 48.12 mg/L (average of 2.86 mg/L), respectively. All these values fall within the permissible limits prescribed by WHO and BIS (2012). The relatively higher concentration of HCO₃⁻ compared to Cl⁻ suggests mineral dissolution as the dominant process, it may be due to effluents released from fertilizer industries (Thivya et al., 2015). The order of anionic abundance is as follows: HCO₃⁻ > Cl⁻ > SO₄²⁻ > CO₃²⁻ > SiO₂⁴⁻ > PO₄³⁻ > NO₃⁻.

The total hardness (TH) and total alkalinity (TA) in the study area range from 10 to 234 mg/L (mean value of 62.04 mg/L) and 48 to 595.8 mg/L (mean value of 148.62 mg/L), respectively. Both parameters fall within the acceptable limits of 600 mg/L as set by WHO (2012) and BIS (2012). Water alkalinity reflects its capacity to neutralize strong acids and is generally due to the presence of bicarbonate, carbonate, and hydroxide compounds of calcium, sodium, and potassium. These compounds are indicative of the water source and the natural processes occurring at any given time (Patil and Patil, 2010; Sharma, 2004). The total hardness is primarily attributed to the presence of Ca²⁺ and Mg²⁺ ions.

A detailed classification of groundwater quality based on TDS and TH is presented in Fig. 2 (Sawyer et al., 1994) and shows that all water samples fall within the “Soft-Freshwater” category, making them suitable for drinking purposes.

4.2. Irrigation Suitability

The suitability of irrigation water depends on several factors, including water quality, soil type, plant characteristics, irrigation method, drainage, climate,

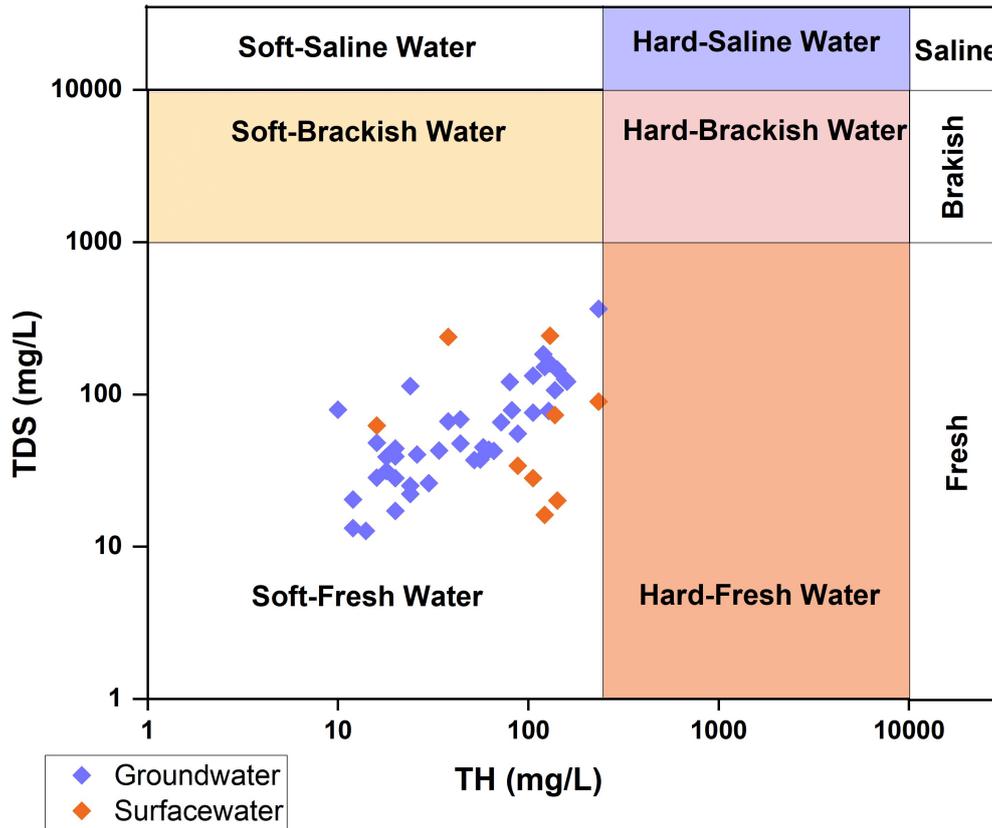


Fig. 2. Water quality in the study area based on TDS and TH shows that almost all samples fall within Soft-Fresh water (Sawyer et al., 1994).

and local conditions. The concentration of certain ions in the water is important. An excess of salts such as calcium, magnesium, sodium, and potassium in the irrigation water can harm plants by reducing their osmotic activities and preventing adequate aeration. High levels of sodium, bicarbonate, and other substances can also reduce the rate at which water enters the soil, leading to inadequate water supply for the crops. Diagrams like Wilcox and USSL are used to assess the suitability of water resources for irrigation, as it depends on the mineral content of the water and its impact on plants and soil (Wilcox and Durum, 1967; Selvakumar et al., 2017; Paliwal, 1986).

4.2.1. Sodium Adsorption Ratio (SAR)

SAR is a measure of alkali/sodium hazard to crops. As sodium in irrigation water increases, it replaces Ca^{2+} and Mg^{2+} in the soil by Base Exchange. This process alkalizes the soil into sticky clays of low permeability, which dry up into hard lumps and are difficult to plough and would support little or no plant growth. This impermeability also impedes

the leaching of salts, and as a result, soil salinity increases. Thus, it can destroy soil structure, and continued use of water with high SAR value leads to a breakdown in the physical structure of the soil. Fine textured soils, those with high clay content, are especially subject to this action. High values of SAR imply soil structure damage (Todd and Mays, 2004). The SAR value in the area is calculated to vary from 0.05 to 18.60. The classification of water samples based on SAR values is shown in Table 2.

Table 2. Classification of groundwater in the study area based on Sodium Adsorption Ratio (SAR) values (Todd, 1980; Richards, 1947).

Water quality	SAR	Percentage of samples
Excellent	<10	92%
Good	10–18	6%
Doubtful	18–26	2%
Unsuitable	>26	—

The relationship between Electrical Conductivity (EC) and Sodium Adsorption Ratio (SAR) is represented in the USSL diagram (Fig. 3). The majority of the water samples are located in the C1–S1 field, indicating low conductivity and low salinity, making

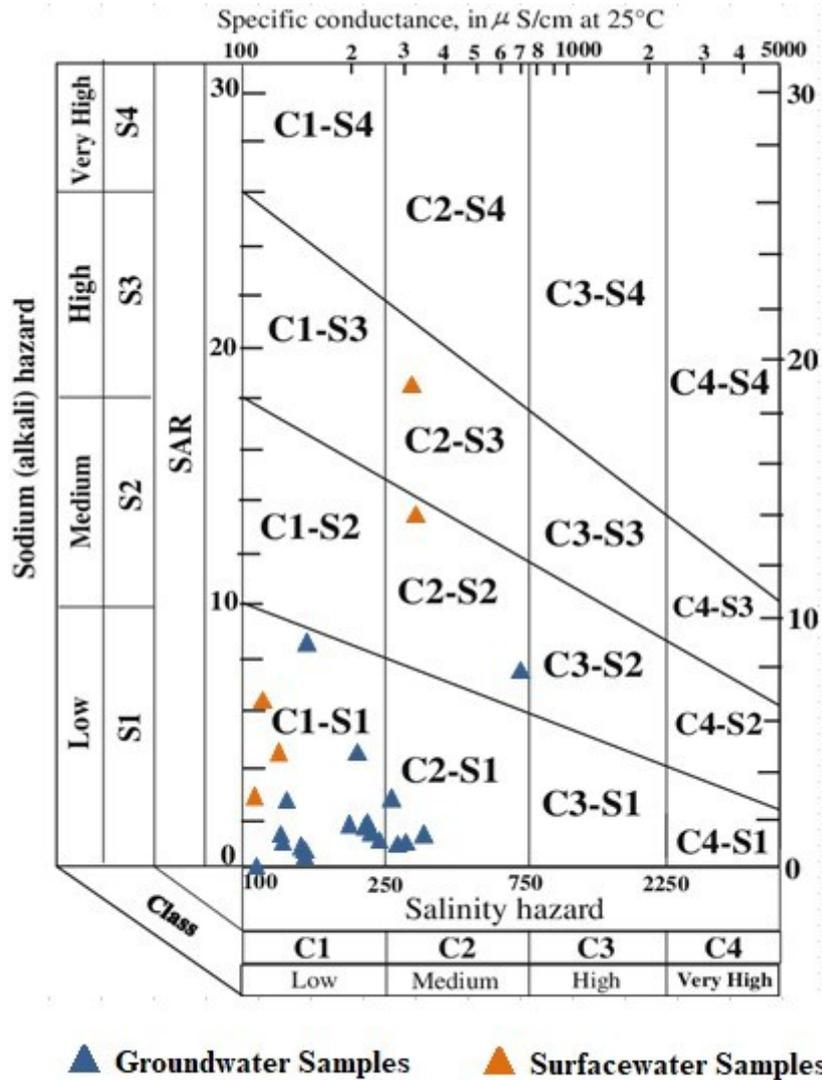


Fig. 3. Water chemistry of the samples plotted in the US Salinity classification for irrigation (USSS, 1954). Most samples fall in the C1–S1 category, making the water excellent for irrigation.

the water excellent for irrigation. Some samples are in the C2–S1 field, representing moderately saline water with low sodium content, suitable for soils with medium permeability for most plants. However, some surface samples are in the C2–S2 and C2–S3 fields, indicating high sodium content, making the water unsuitable for irrigation.

4.2.2. Percent Sodium (Na%)

The concentration of sodium is crucial in determining the suitability of irrigation water. This is because sodium reacts with salt to decrease permeability. Excessive sodium in water can lead to undesirable effects, such as changes in soil properties and reduced soil permeability. Therefore, it is important to assess the sodium concentration when evaluating the suitability of irrigation water. In natural waters,

the Percent Sodium content is used as a parameter to assess its suitability for agricultural purposes (Wilcox and Durum, 1967). Soils that contain a high proportion of sodium with carbonate as the main anion are referred to as Alkali soils, while those with chloride or sulfate as the main anion are known as Saline soils. The Na % of the study area ranges from 9.32 to 95.32. The classification of water samples based on Na% values is shown in Table 3.

Table 3. Classification of groundwater based on Percent Sodium (Na%) (Wilcox and Durum, 1967).

Water quality	Na%	Percentage of samples
Excellent	<20	10%
Good	20–40	22%
Permissible	40–60	24%
Doubtful	60–80	30%
Unsuitable	>80	14%

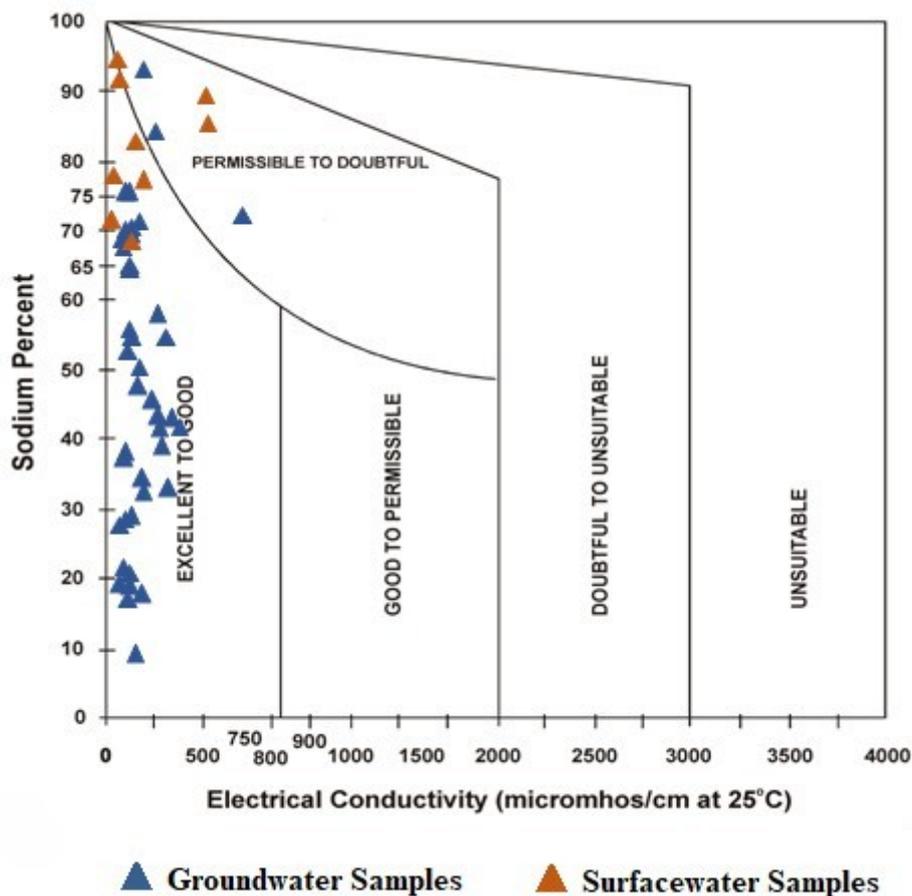


Fig. 4. Water chemistry of the samples plotted in the Wilcox Diagram for irrigation quality (Wilcox and Durum, 1967). Majority of the samples fall within the Excellent to Good category, making the samples excellent for irrigation.

The Wilcox diagram is created by plotting Na% and electrical conductivity. Fig. 4 represents the Wilcox diagram of the study area. 80% of the water samples fall in the excellent to good category, while the remaining 20% fall in the permissible to doubtful category.

4.2.3. Magnesium Adsorption Ratio (MAR)

The magnesium adsorption ratio, also known as the magnesium hazard (MH), is used to assess the impact of high magnesium concentrations on irrigation water (Szabolcs and Darab, 1964; Todd, 1980; Ayers and Westcot, 1985; Raghunath, 1987; Mohammed et al., 2022). The classification of water samples based on MAR values is shown in Table 4. It shows that 90% of the water samples are suitable for irrigation, whereas the remaining 10% are unfit for agricultural purposes.

4.3. Hydrogeochemistry

The hydrogeochemistry of the area is interpreted using diagrams like Schoeller, Hill-Piper, Durov dia-

Table 4. Classification of groundwater based on Magnesium Adsorption Ratio (MAR) (Raghunath, 1987).

Water quality	MAR	Percentage of samples
Suitable	<50	90%
Unsuitable	>50	10%

gram, and Chadha’s plot.

4.3.1. Schoeller Diagram

The Schoeller diagram is a semi-logarithmic graph used to visually represent the relative ionic concentrations of anions and cations in water samples from different sources, typically expressed in milliequivalents per liter. Schoeller diagram is given in Fig. 5. The diagram shows that Na⁺ is the dominant ion, followed by HCO₃⁻ and Cl⁻, indicated by a sharp peak.

High peaks are commonly found in samples collected from surface waters, and elevated sodium levels are often associated with industrial discharges from sectors such as chemical manufacturing, metal processing, and salt-based industries. Sodium can enter groundwater through effluent discharge,

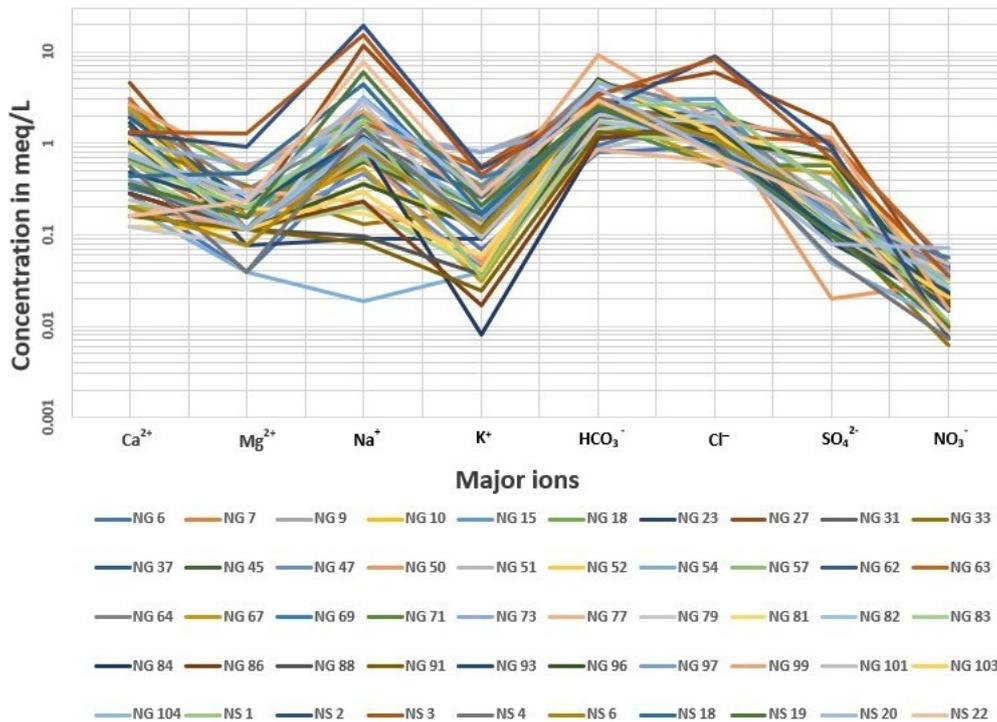


Fig. 5. Schoeller diagram of the water samples from the study area showing Na⁺, HCO₃⁻, and Cl⁻ being the dominant ions.

urban runoff, and improper waste management (Gan-guli et al., 2022). In industrial regions, the cation-exchange process is significant, with sodium replacing calcium and magnesium in clay minerals, leading to higher sodium concentrations and lower calcium and magnesium levels in groundwater. Industrial discharges can intensify this exchange process, altering the chemical equilibrium of the aquifer. The high bicarbonate (HCO₃⁻) concentrations observed in many samples could be attributed to industrial emissions contributing to CO₂ in the atmosphere, leading to increased bicarbonate in water through CO₂ dissolution. Industrial activities such as mineral processing and concrete production can also contribute to bicarbonate levels via carbonation processes. Bicarbonate dominance also suggests silicate weathering and mineral dissolution, which can be accelerated in areas with industrial runoff (Srinivasamoorthy et al., 2011). Elevated chloride concentrations can stem from saltwater intrusion, cooling water discharge, or direct release of industrial effluents containing salts. Chloride can be a tracer for industrial contamination, particularly in metal finishing industries, chemical plants, and fertilizer industries (Sarath Prasanth et al., 2012).

4.3.2. Hill piper Diagram

The Hill-Piper diagram is a widely used graphical method for classifying and visualizing the chemical composition of both groundwater and surface water. This method aids in tracing the chemical evolution of groundwater and identifying water quality issues, including salinity, hardness, and contamination from anthropogenic sources (Piper, 1944). Fig. 6 represents the hill-piper diagram of the study area. The analysis of the sample points indicates that the water samples are categorized into Ca–Mg–HCO₃, mixed, and Na–Cl water types. The study area exhibits a transition from Ca–Mg–HCO₃ to Na–Cl water types, with an intermediate presence of mixed facies. The Ca–Mg–HCO₃ water type suggests mineral dissolution, the interaction between rock and water, and freshwater recharge. The observed shift from Ca–Mg–HCO₃ to mixed, and subsequently to Na–Cl water types, indicates the mixing of high salinity water from surface contamination sources. These sources include liquid and solid waste discharge, domestic wastewater, septic tank effluents, and irrigation return flow, which mix with the existing groundwater. This process is often followed by ion exchange (Jeyaraj et al., 2016; Mondal and Singh, 2012).

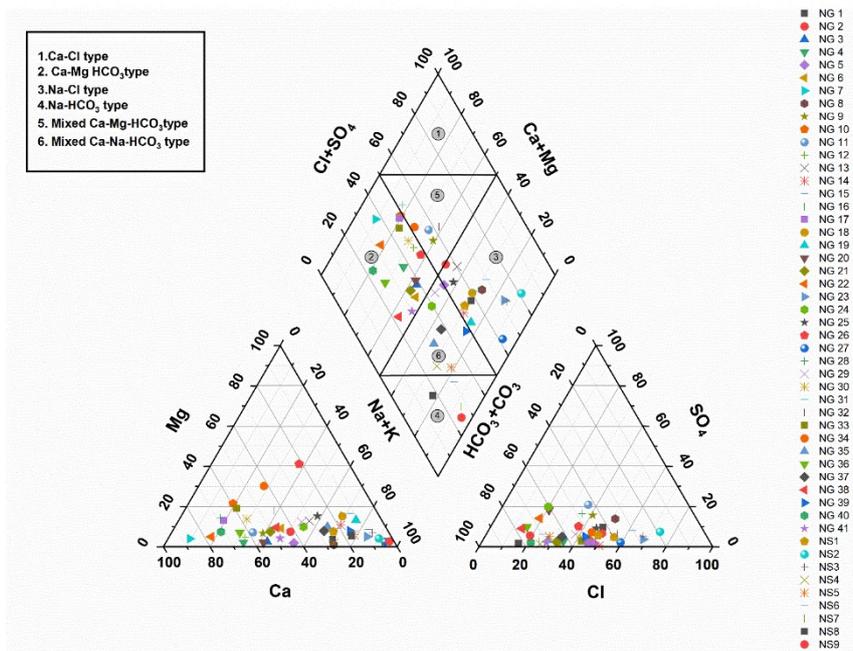


Fig. 6. Hill-piper diagram representing the hydrochemical facies of the study area. A shift in hydrochemical facies from Ca–Mg–HCO₃ to mixed type to Na–Cl and Na–HCO₃ water types is observed.

4.3.3. Durov Diagram

In order to understand the spatial patterns and hydrochemical processes in the aquifer in relation to groundwater flow, chemical data from water samples have been plotted on the Durov diagram (Burdon and Mazloum, 1958; Lloyd, 1965). The Durov diagram is a useful tool for identifying the mixing of surface water and groundwater (Durov, 1948). In the cationic triangle of the Durov diagram (Fig. 7), all samples fall within the Ca and Na–K types, while in the anionic triangle, the samples align along the HCO₃ + CO₃ and Cl types. These findings are consistent with the results obtained using the Piper diagram. The central rectangular plot indicates that the dominant hydrochemical processes in the area are simple dissolution and mixing (Vincy et al., 2015). The data further reveal a shift in water chemistry, with increased concentrations of cations such as Ca²⁺ and Na⁺ and a transition from HCO₃⁻ to Cl⁻, which suggests the influence of industrial effluents from metal processing units (Tao et al., 2013). The extended Durov diagram incorporates a TDS rectangular plot on the right side and a pH plot at the bottom.

4.3.4. Chadha's Plot

Chadha's Plot is a graphical method used to classify various types of water based on the chemical composition of groundwater. This plot emphasizes the relative concentrations of major cations and an-

ions, serving as a tool to better understand water quality and its suitability for different purposes, such as drinking, irrigation, and industrial use. Additionally, it offers insights into the hydrochemical processes that shape water resources in specific regions (Chadha, 1999). The plot (Fig. 8) reveals that the majority of groundwater samples typically fall into the Ca–Mg–HCO₃, Na–Cl, and Na–HCO₃ fields. The Ca–Mg–HCO₃ quadrant indicates groundwater dominated by alkaline earth metals (Ca + Mg) over alkali metals (Na + K), with weak acidic anions (HCO₃ + CO₃) exceeding strong acidic anions (Cl + SO₄). The chemistry in this field often reflects water that has been influenced by the weathering or dissolution of carbonate rocks, which results in temporary hardness due to the presence of bicarbonates (Bhat et al., 2016). Groundwater falling in the Na–Cl quadrant is characterized by a dominance of alkali metals (Na + K) over alkaline earth metals (Ca + Mg), with strong acidic anions (Cl + SO₄) exceeding weak acidic anions. This water type frequently represents brackish or saline water, often influenced by factors such as saltwater intrusion, agricultural runoff, or mineralization. It is also commonly associated with areas affected by industrial pollution, where effluents rich in sodium and chloride are present (Hussain and Rao, 2013). The majority of surface water samples tend to fall within the Na–HCO₃ quadrant. In this quadrant,

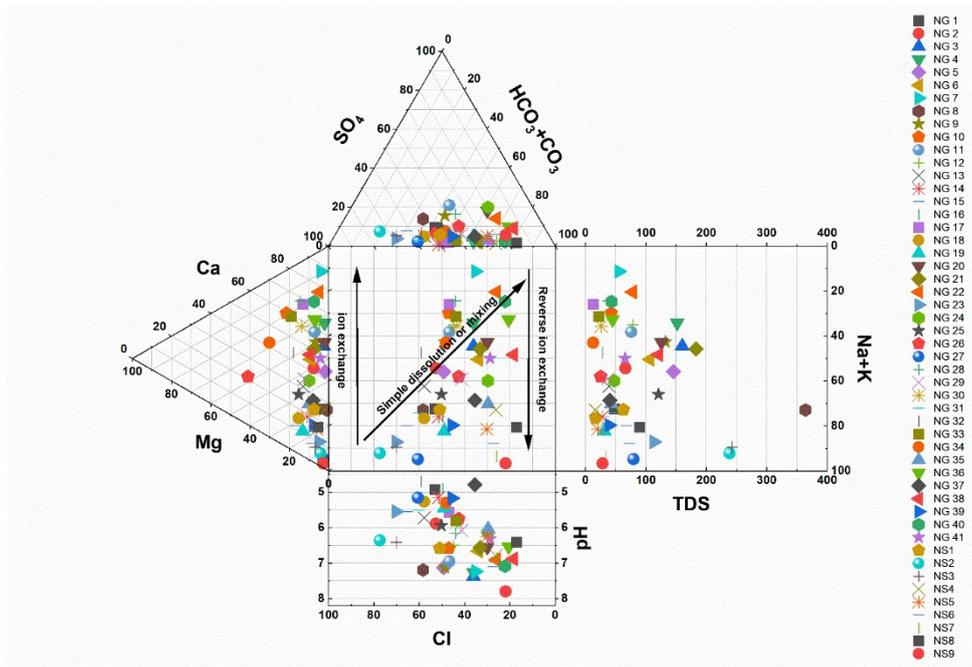


Fig. 7. Durov diagram of the water samples from the study area, indicating mixing and simple dissolution being the dominant hydrochemical processes.

alkali metals (Na + K) dominate over alkaline earth metals, while weak acidic anions (HCO₃ + CO₃) exceed strong acidic anions. This water type typically represents alkaline water, which is commonly found in areas with high evaporation rates or where significant cation exchange occurs. Such conditions are often characteristic of arid regions or areas affected by anthropogenic activities, such as agriculture or industry, which can increase both the salinity and alkalinity of the water which implies surface water is affected by industrial activities (Subramani et al., 2005; Nagaraju et al., 2006; Srinivasamoorthy et al., 2012).

4.4. Multivariate statistical tools

Multivariate statistical analysis is a quantitative technique used to examine the spatial and temporal variations in water quality datasets. It helps interpret sources of pollution resulting from anthropogenic and natural processes, as well as hydrological and geological phenomena without loss of information and considerable economic involvement (Bhuiyan et al., 2011; Singovszka and Balintova, 2012; Brahman et al., 2013; Varol and Davraz, 2015; Edokpayi et al., 2018; Miranda et al., 1996; Sahoo and Patra, 2019). In this study, Hierarchical cluster analysis (HCA) and Pearson correlation coefficient (r) are applied to heavy metal concentrations (Table 5) because of their importance in water resources-related studies.

4.4.1. Hierarchical cluster analysis (HCA)

Hierarchical cluster analysis (HCA) is a quantitative method for interpreting and representing water hydrochemistry data. In this study, HCA was conducted using the Unweighted Pair Group Method with Arithmetic Mean (UPGMA), a commonly applied technique in environmental studies, particularly in assessing heavy metal contamination. UPGMA helps to identify clusters of similar elements or sampling sites based on their concentrations and other attributes. The dendrogram (Fig. 9) revealed four distinct clusters of elements.

The first cluster includes pH, Ti, Ni, Sr, EC, TDS, B, and Li, suggesting these variables may be associated with non-point source pollution. This pollution likely originates from general industrial activities, such as construction, vehicle emissions, or road dust, which often contains Ti and Ni. Nickel (Ni), in particular, generally originates from sources like domestic sewage, port area effluents, and paints used on fishing boats. Electrical conductivity (EC) and total dissolved solids (TDS) are linked with dissolved ions, indicating general water pollution, potentially from mixed industrial runoff. Lithium (Li), boron (B), and strontium (Sr) are typically associated with geological formations, such as silicate minerals and evaporite deposits, which might be influenced by industrial groundwater extraction (Gu et al., 2012;

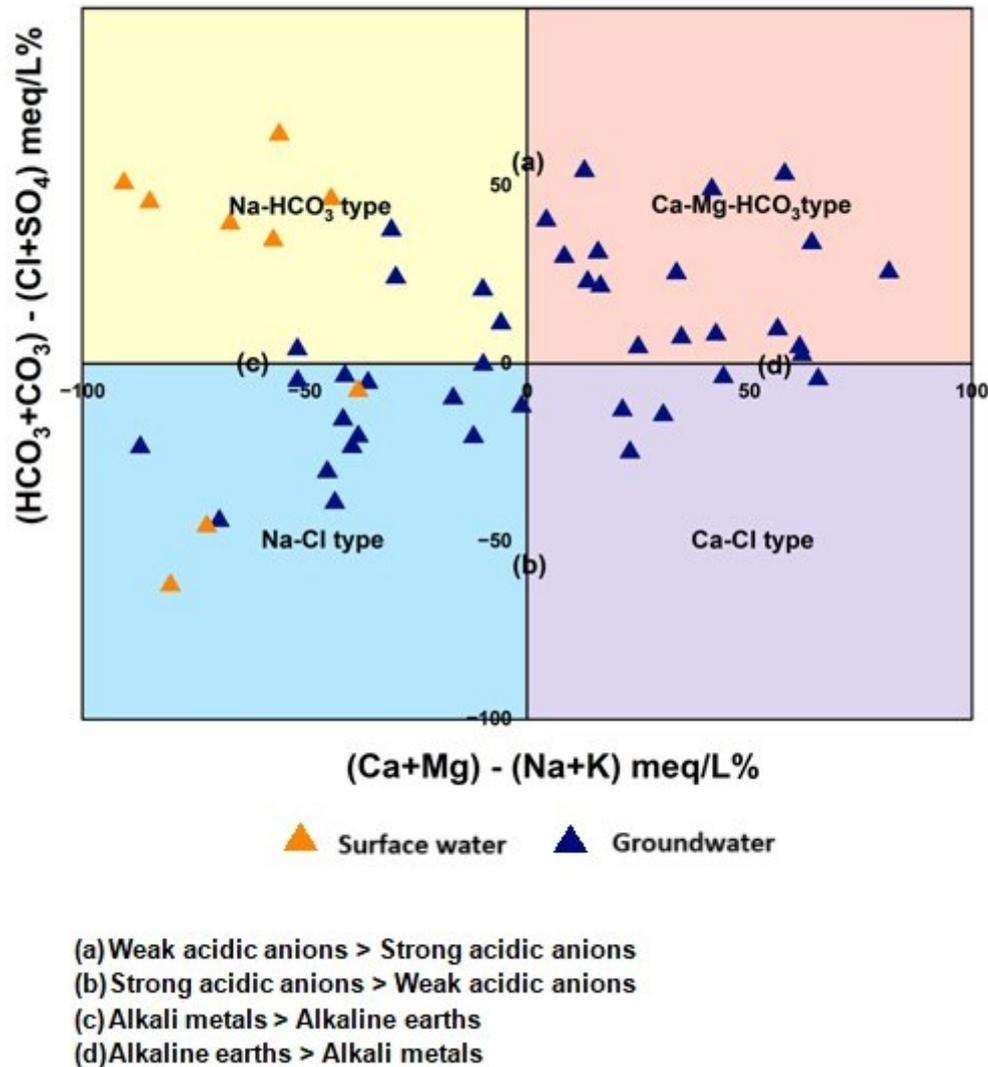


Fig. 8. Chadha's Plot illustrating the distribution of groundwater and surface water samples into distinct hydrochemical facies, revealing dominant geochemical processes and anthropogenic influences on water quality.

Krishna et al., 2009; Sikakwe et al., 2020).

The second cluster consists of chromium (Cr) and bismuth (Bi), both of which can be released into the environment through industrial effluents, especially in areas involved in metal-finishing, tanning, and alloy manufacturing. Chromium, particularly in its hexavalent form (Cr(VI)), is a common pollutant in wastewater from electroplating, leather tanning, and dyeing industries, while bismuth may enter the environment as a trace element in waste from electronics and chemical production (Agrawal et al., 2006; Sebastian et al., 2016; Mishra and Bharagava, 2018).

The third cluster includes heavy metals such as manganese (Mn), cobalt (Co), zinc (Zn), lead (Pb), and cadmium (Cd), which are often associated with direct industrial sources, including metal smelting and refining. Zinc, lead, cadmium, and cobalt

are commonly emitted from metal processing plants, while lead and cadmium are frequently used in battery production. Lead was historically used as an additive in gasoline to increase its octane rating. Indium (In) and bismuth (Bi), also part of this cluster, are used in electronics and specialty pigments. The similarity of these elements within this cluster suggests a common origin or similar transport and deposition mechanisms in the environment. Known for their toxicity and persistence, these metals are heavily regulated in industrial settings (Alloway, 2012).

The fourth cluster includes metals like copper (Cu), indium (In), gallium (Ga), barium (Ba), and silver (Ag), which are associated with metal and ore processing, as well as mining industries. Effluents from these industries are often enriched with these elements. Collectively, these clusters indicate

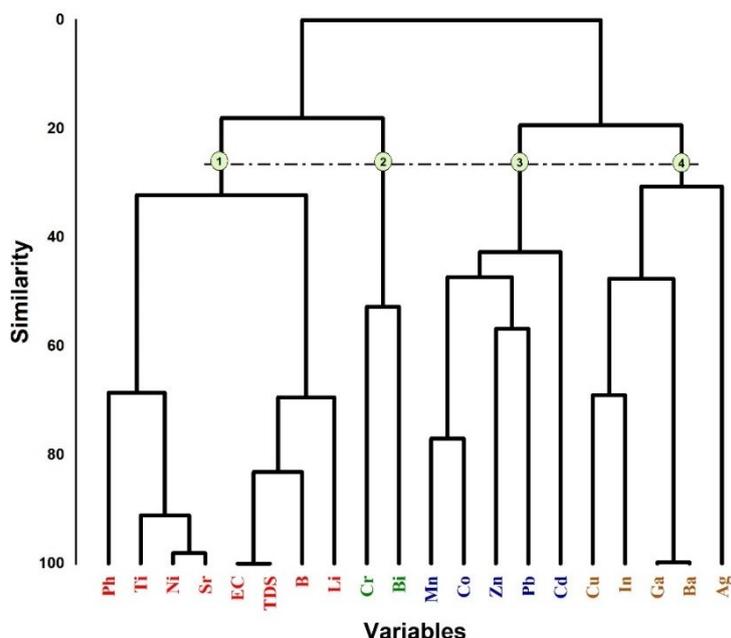


Fig. 9. Dendrogram showing similarity of the heavy metals within the study area.

pollution stemming from various sources, especially anthropogenic activities (WHO, 2012; Shaganimol et al., 2022).

4.4.2. Pearson Correlation Coefficient (r)

Pearson correlation coefficients are widely used to examine the linear relationship between two variables. A coefficient of -1 indicates a perfect negative correlation, while a coefficient of +1 signifies a perfect positive correlation, with a value of zero suggesting no relationship between the variables. Relationships are typically considered significant when $p < 0.05$, with strong correlations observed at $p < 0.01$. A positive correlation implies that as one variable increases, the other tends to increase as well; conversely, a negative correlation means that as one variable rises, the other tends to decrease, indicating co-variation between the two variables (Khan, 2011; Varol and Davraz, 2015).

In this study (Fig. 10), pH shows a positive correlation with Sr ($r = 0.62$), Ni ($r = 0.72$), and Ti ($r = 0.69$). Electrical conductivity (EC) is strongly correlated with TDS ($r = 1$), Li ($r = 0.69$), B ($r = 0.83$), Ti ($r = 0.64$), and Sr ($r = 0.8$). Similarly, TDS shows a significant correlation with Ti ($r = 0.64$), Sr ($r = 0.8$), Li ($r = 0.69$), and B ($r = 0.83$). The positive correlation of pH, EC, and TDS with metals like Ni, Ti, Li, B, and Sr suggests a nonpoint source of contamination, likely from both geogenic and anthropogenic origins, such as runoff from agricultural, municipal, and industrial waste (Maqbool et al., 2012; Han et al.,

2014; Adeyi and Majolagbe, 2014).

Nickel (Ni) also exhibits a strong positive correlation with elements such as Bi ($r = 0.94$), Ba ($r = 0.83$), Ag ($r = 0.79$), Sr ($r = 0.98$), Ga ($r = 0.82$), and Cu ($r = 0.52$). This pattern of correlation suggests pollution from industrial and anthropogenic sources. These elements are commonly associated with direct industrial activities, including metal smelting and refining, ore processing, and electroplating. During these processes, metals often arise as byproducts, and the direct discharge of metal-rich effluents poses a significant threat to the environment and water resources (Li et al., 2013; Martínez Guijarro et al., 2021; Jiang et al., 2022).

5. Conclusions

The findings of this study underscore the critical and far-reaching impact of industrial pollution on both surface and groundwater quality in the Aluva–Kochi Industrial Belt. Elevated levels of heavy metals, organic pollutants, and other contaminants in water resources exceed recommended safety limits, posing significant and multifaceted risks to human health, aquatic ecosystems, and agricultural productivity. Comprehensive hydrochemical analyses reveal a substantial shift in water composition due to the direct influence of industrial effluents, highlighting the dominance of sodium and chloride and bicarbonate ions in contaminated sites. The study also identifies

Table 5. Heavy metal concentrations (in PPB) groundwater (NG) and surface water (NS) samples from the study area. (BDL: below detection limit).

Sl. No	Samples	Li	B	Ti	Cr	Mn	Co	Ni	Cu	Zn	Ga	Sr	Ag	Cd	In	Ba	Pb	Bi
1	NG 1	1.37	50.21	212.26	1.15	39.28	0.95	1.41	23.21	75.57	33.76	31.33	2.21	0.36	0.00	247.41	3.21	0.00
2	NG 2	0.42	11.08	333.45	0.85	7.12	0.11	4.74	16.99	26.66	10.22	39.10	2.21	0.14	0.00	95.44	1.03	BDL
3	NG 3	3.32	25.61	1258.97	3.02	BDL	0.16	BDL	2.92	5.95	17.66	119.90	1.37	0.03	0.00	164.63	0.53	BDL
4	NG 4	1.73	33.91	1038.11	0.89	2.29	0.20	BDL	10.91	4.46	145.96	163.49	3.79	0.08	0.00	1007.05	3.01	0.00
5	NG 5	1.85	19.67	1375.61	1.26	18.37	0.29	BDL	11.97	13.31	36.17	127.83	0.92	0.04	0.00	281.54	0.53	BDL
6	NG 6	1.28	46.49	961.97	1.38	11.51	0.28	BDL	6.73	3.45	29.54	80.66	3.53	0.09	0.00	232.86	1.03	0.00
7	NG 7	0.26	20.06	859.57	0.92	1.09	0.09	BDL	3.24	1.34	23.79	72.60	2.49	0.01	0.00	225.27	0.64	BDL
8	NG 8	4.86	93.63	1017.25	0.36	BDL	0.16	BDL	4.05	1.83	15.04	210.08	1.77	0.02	0.00	161.04	0.45	BDL
9	NG 9	0.51	23.12	870.33	0.60	BDL	0.13	BDL	3.75	2.69	3.28	65.07	0.67	0.03	0.00	30.37	0.22	BDL
10	NG 10	0.36	18.94	707.79	0.18	BDL	0.08	BDL	4.86	0.55	6.60	47.12	2.00	0.01	0.00	61.04	0.04	BDL
11	NG 11	0.58	55.30	854.95	0.49	0.38	0.12	BDL	2.53	6.28	15.15	116.35	1.11	0.02	0.00	146.49	0.23	BDL
12	NG 12	0.83	17.27	619.47	0.73	0.63	0.09	BDL	6.05	6.31	35.51	82.02	3.01	0.03	0.00	282.92	1.01	0.00
13	NG 13	0.82	7.68	119.35	0.53	0.95	0.08	BDL	2.24	13.32	10.35	32.33	0.70	0.10	0.00	98.31	0.25	BDL
14	NG 14	1.25	10.28	127.31	0.95	2.11	0.11	BDL	4.57	8.79	14.72	21.78	1.92	0.10	0.00	140.17	0.46	0.00
15	NG 15	0.64	11.19	185.53	0.08	1.37	0.08	BDL	1.71	5.93	7.18	40.59	0.75	0.02	0.00	70.87	0.08	BDL
16	NG 16	1.50	12.67	57.61	0.08	42.82	0.40	BDL	2.51	3.73	4.59	11.35	5.12	0.01	0.00	43.27	0.32	BDL
17	NG 17	0.30	6.91	83.64	BDL	BDL	0.03	BDL	1.75	6.17	7.22	13.04	1.09	0.02	0.00	67.23	BDL	BDL
18	NG 18	1.33	3.39	110.33	1.30	BDL	0.07	BDL	1.57	5.63	8.58	42.49	1.55	0.10	0.00	83.32	0.15	BDL
19	NG 19	0.41	7.81	89.41	BDL	BDL	0.02	BDL	1.60	1.47	2.90	13.58	0.95	0.01	0.00	26.68	BDL	BDL
20	NG 20	0.14	40.06	752.49	0.07	0.00	0.11	BDL	1.89	0.04	5.91	116.81	0.86	0.02	0.00	58.34	BDL	BDL
21	NG 21	0.12	26.23	976.24	0.49	0.60	0.25	BDL	2.53	2.21	3.37	78.02	0.46	0.01	0.00	33.21	0.26	BDL
22	NG 22	2.03	18.28	994.27	0.14	16.37	0.17	BDL	2.22	1.59	6.76	125.69	0.42	0.02	0.00	67.07	0.62	BDL
23	NG 23	0.47	12.85	294.06	0.72	44.35	0.53	BDL	6.24	40.68	13.13	39.82	0.68	0.14	0.00	136.43	10.82	BDL
24	NG 24	0.52	9.74	360.49	0.47	3.95	0.05	BDL	2.46	0.74	14.96	66.08	1.46	0.01	0.00	146.56	0.40	BDL
25	NG 25	0.47	18.34	622.15	5.09	6.76	0.35	BDL	6.52	14.04	109.92	64.91	0.90	0.15	0.00	823.34	0.58	0.00
26	NG 26	0.67	8.26	155.91	0.31	0.96	0.14	BDL	2.21	2.16	23.39	43.37	2.23	0.01	0.00	228.11	0.34	BDL
27	NG 27	1.35	8.49	82.47	0.25	23.74	0.64	BDL	4.30	7.69	55.96	26.87	1.21	0.02	0.00	447.09	0.65	BDL
28	NG 28	1.43	16.61	510.60	0.61	1.09	0.07	BDL	5.25	11.76	22.82	51.55	5.64	0.08	0.00	226.52	1.23	0.00
29	NG 29	0.52	10.41	363.66	0.83	1.09	0.07	BDL	2.17	5.12	11.34	76.90	0.87	0.02	0.00	113.63	0.22	BDL
30	NG 30	0.64	11.61	274.56	0.20	3.38	0.07	BDL	3.54	5.17	62.30	32.53	4.47	0.02	0.00	476.40	0.60	BDL
31	NG 31	0.59	12.22	142.00	0.19	BDL	0.04	BDL	2.07	5.18	4.65	20.33	0.91	0.01	0.00	45.38	0.27	BDL
32	NG 32	1.21	7.80	150.33	BDL	24.98	0.79	BDL	2.47	11.41	98.34	19.71	4.13	0.04	0.00	690.01	0.72	BDL
33	NG 33	0.96	7.19	189.11	0.08	1.05	0.06	BDL	0.61	35.12	10.77	27.69	BDL	0.02	0.00	106.12	BDL	BDL
34	NG 34	1.52	8.28	75.65	1.56	1.41	0.12	BDL	3.32	13.94	10.77	20.81	1.17	0.10	0.00	106.44	0.39	0.00
35	NG 35	0.84	5.64	261.43	0.31	BDL	0.06	BDL	3.43	5.20	70.36	26.30	5.41	0.05	0.00	529.40	0.75	BDL
36	NG 36	0.22	13.78	620.98	0.87	BDL	0.08	BDL	1.99	1.56	6.04	52.90	2.43	0.01	0.00	56.50	0.11	BDL
37	NG 37	1.14	8.00	68.88	0.87	BDL	0.05	BDL	2.58	8.92	22.30	18.94	7.59	0.02	0.00	219.76	0.56	BDL
38	NG 38	0.33	17.25	1195.72	1.05	4.06	0.20	BDL	3.49	18.78	17.51	133.31	0.96	0.05	0.00	180.21	0.85	BDL
39	NG 39	1.43	9.66	187.81	1.04	29.56	0.40	BDL	4.63	15.43	10.51	25.59	2.11	0.07	0.00	99.94	0.46	0.00
40	NG 40	0.39	11.53	694.59	0.65	1.36	0.12	8.27	28.27	4.41	177.94	57.02	4.13	0.08	0.00	1261.80	1.20	0.00
41	NG 41	0.40	13.71	671.10	0.29	7.69	0.16	BDL	3.24	22.19	8.99	69.56	0.60	0.01	0.00	89.41	0.31	BDL
42	NS 1	0.94	20.03	311.09	1.23	1.75	0.10	BDL	2.28	4.74	6.62	51.74	1.12	0.11	0.00	65.69	0.13	BDL
43	NS 2	3.62	73.12	444.85	0.47	0.40	0.13	BDL	4.43	8.82	2.66	98.27	0.57	0.14	0.00	29.19	BDL	BDL
44	NS 3	3.19	72.78	748.68	1.00	2.71	0.13	BDL	3.99	2.55	6.36	106.86	0.93	0.05	0.00	69.55	0.16	BDL
45	NS 4	0.19	6.72	127.23	BDL	BDL	0.01	BDL	1.32	0.20	3.18	28.15	1.80	0.00	0.00	29.90	0.01	BDL
46	NS 5	0.32	6.36	95.28	0.16	BDL	0.02	BDL	1.82	0.36	15.85	24.38	0.80	0.22	0.00	150.47	0.87	BDL
47	NS 6	0.39	6.40	247.68	0.91	1.11	0.04	BDL	1.60	0.42	3.64	33.05	0.77	0.13	0.00	34.19	0.25	BDL
48	NS 7	0.37	7.46	240.70	0.91	2.42	0.08	3.10	13.51	25.52	11.29	35.33	1.01	0.22	0.00	111.69	3.01	0.00
49	NS 8	1.58	21.76	353.72	0.80	52.51	0.37	BDL	2.51	22.90	5.06	53.58	2.35	0.62	0.00	51.55	0.07	BDL
50	NS 9	0.08	5.59	91.62	0.11	BDL	0.02	BDL	2.20	0.63	7.72	22.97	0.80	0.01	0.00	76.27	0.40	BDL

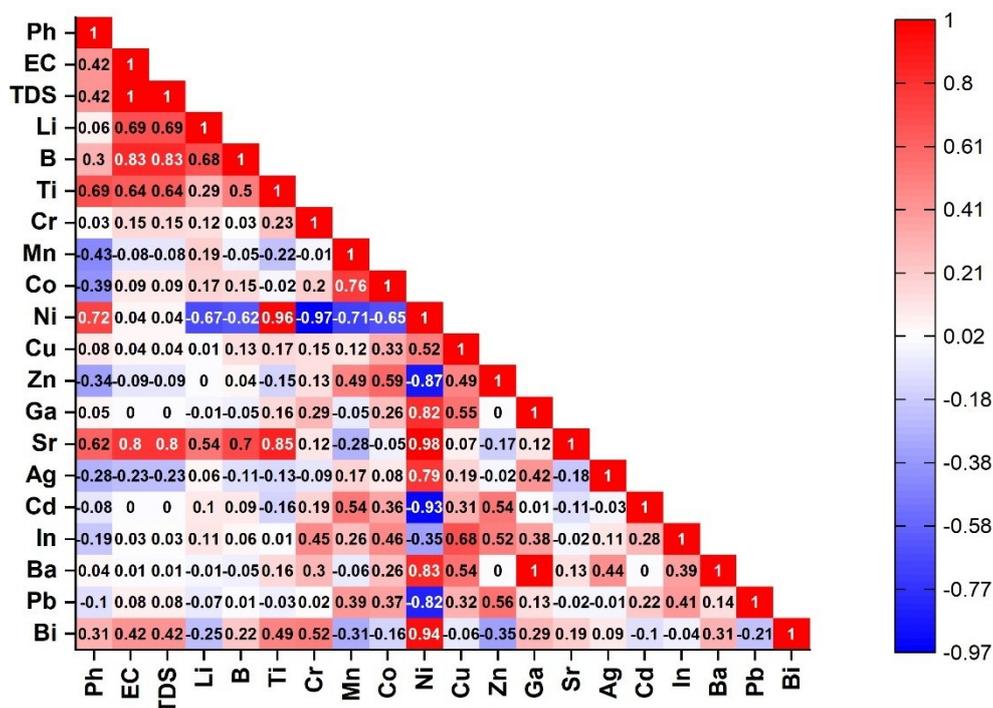


Fig. 10. Correlation coefficient between heavy metal concentrations and physio-chemical parameters. A 2-tailed test of significance is used. Correlation is significant at the 0.05 level.

specific areas where groundwater is unsuitable for irrigation due to excessive sodium hazard, which can lead to soil degradation and reduced crop yields. Multivariate statistical analyses conducted as part of this study firmly confirm that industrial activities are the primary contributors to the pervasive water pollution in the region. Urgent and comprehensive regulatory measures, enhanced wastewater treatment practices, and the development of more sustainable industrial policies are now necessary to protect and restore the quality of these vital water resources. Future research should focus on long-term monitoring and the development of innovative remediation strategies to ensure the sustainable management of these essential resources for the benefit of local communities and ecosystems.

CRedit statement

Nakul T Sabu: Writing - review and editing, Writing - original draft, Software, Methodology, Investigation, funding acquisition, Formal analysis, Conceptualization. **R. Megha:** Writing - review and editing, Writing - original draft, Visualization, Methodology, Investigation. **J.U. Jyothi:** Visualization, Validation, Formal analysis, Data curation. **P.K. Krishnaprasad:** Writing - review and editing,

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Declaration of competing interests

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

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