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Review Article

Assessment of heavy metal contamination in the groundwater of Gujarat, India using the Heavy Metal Pollution Index

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ABSTRACT

Groundwater serves as a vital water source for a significant population in the Gujarat region of India. However, substantial contamination from heavy metals, pose a serious threat to human health through various pathways, including drinking water. The rapid industrial and agricultural growth in recent years has exacerbated heavy metal pollution in the state. This study focuses on assessing the heavy metal contamination in the groundwater of Gujarat using the Heavy Metal Pollution Index (HPI). The research covers the entire state, considering its diverse physical, climatic, topographical, and geographical conditions. The HPI scores obtained from individual studies highlight the extent of pollution caused by heavy metals. The overall findings underscore the severe problem of heavy metal contamination in Gujarat's groundwater and the associated health risks. Various other pollution indicators, including the Heavy Metal Evaluation Index, Degree of Contamination, Metal Index, and Water Pollution Index are discussed as tools to assess contamination levels. These indices compare concentrations of different heavy metals with established limits to determine the pollution level. The goal is to provide valuable insights for investors and policymakers in formulating strategies to manage and reduce heavy metal contamination across the state. Additionally, the paper explores effective, environmentally friendly, and economically viable treatment techniques to remove heavy metals from aquatic systems, safeguarding the environment. By employing pollution indicators and remedial actions, this study aims to guide efforts in mitigating the impact of heavy metal contamination in the groundwater of Gujarat.

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INTRODUCTION

The quality and accessibility of water sources are crucial for the survival of all living organisms, including humans, and the well-being of the environment. However, these invaluable resources are susceptible to contamination by both organic and inorganic pollutants, compromising water purity and its suitability for sustaining life [1, 2]. In India, a significant portion of the population relies on groundwater for daily needs, with approximately one-third of the country's groundwater being unsuitable for human consumption [3]. Groundwater pollution, particularly from heavy metals, stands as a critical environmental challenge due to the highly toxic nature of these contaminants, even at low concentrations. The word "heavy metal" refers to a broad category of metals and metalloids having an atomic density of more than 4,000 kg/m^3, or five times that of water [4]. These elements exist in water in various forms, including colloidal, particulate, and dispersed segments, with their presence being either natural or anthropogenic [5]. Cu, Cd, Zn, Pb, Hg, As, Ag, Cr, Fe and Pt are some examples of heavy metals. The human body can be exposed to these toxic elements through

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multiple pathways, such as direct ingestion, dermal contact, inhalation, and oral ingestion, with drinking water serving as a primary source for the entry of heavy metals into the human body [3, 6]. The introduction of these toxic elements into water sources occurs regularly from both natural and human-induced sources. In numerous locations globally, the levels of Cr, Mn, Fe, Co, Ni, As, and Cd in surface water exceed permissible values for drinking water, raising widespread concerns. Heavy metals do not break down easily, leading to bioaccumulation in organisms over time. Their persistent nature, coupled with biomagnification, can have detrimental effects on various organisms. Many heavy metal ions are known carcinogens and pose risks to organs such as the respiratory system, urinary tract, liver, prostate, stomach, digestive system, skin, as well as contributing to neurodegenerative conditions like Alzheimer and Parkinson [7].

Gujarat exhibits distinctive geographical features and considerable variability in annual rainfall. The rocky terrain and coastal areas render three-fourths of the state unsuitable for groundwater extraction. Additionally, historical instances of droughts have been prevalent due to limited surface water availability. The state encounters unpredictable and uneven rainfall patterns, leading to disparities in water distribution across regions. Despite having only 5% of the nation's population, Gujarat possesses merely 2% of the country's water resources [8]. Notably, both the industrial and agricultural sectors in Gujarat have undergone rapid expansion. However, the surge in heavy metal pollution poses significant risks to public health, with policymakers yet to address this pressing environmental concern. Although there is a lack of comprehensive scientific investigations into heavy metal contamination in the groundwater of Gujarat, several studies have assessed the groundwater quality for heavy metals across multiple regions in the state [9–12].

This study aimed to assess the groundwater quality in Gujarat, focusing on the presence of heavy metal contamination. The research outlines the primary sources of heavy metals in water and discusses their potential impacts on human health. Additionally, the study explores various methods for eliminating heavy metals from water. Consequently, the review provides evidence regarding the prevalence of heavy metals in the groundwater of Gujarat and its implications for safeguarding human health.

MATERIALS AND METHODS

Data Collection

We identified 14 research articles, conference papers, and scientific studies focusing on surface and groundwater bodies in Gujarat, India, spanning from 2007 to 2024. These publications are accessible through Web of Science, Science Direct, Google Scholar, ResearchGate, and PubMed. Our search targeted terms like "heavy metals pollution," "surface water," "groundwater," "pollution index," and "Gujarat," as these platforms primarily utilize English for broader international dissemination. We did not include some local databases or publications that solely report heavy metal concentration levels without additional applications.

Study Area

The Indian state of Gujarat (1,96,024 km^2) is situated between the longitudes of 68° 10' 00" and 74° 28' 00" in the east and the latitudes of 20° 06' 00" to 24° 42' 00" in the north. Gujarat has the longest coastline in the country, spanning approximately 1600 km from Daman in the south to Lakhpat in the north, surpassing all other states in India. The state of Gujarat opens international borders in the northwest with Pakistan as well as shared borders with the states of Rajasthan, Madhya Pradesh, and Maharashtra. The Union territory of Daman & Diu covers 106 km^2 area which is included in Gujarat. Different regions of the state exhibit distinct groundwater conditions because of diverse physiography, climate, topography, and geology. Groundwater presence and movement are influenced by a range of rock formations with varying compositions and structures, spanning from the Archean to Recent eras. Similarly, the landforms vary, encompassing hilly tracts, uplands in Kachchh and Saurashtra, alluvial plains from Banaskantha in the north to Valsad in the south, low-lying coastal areas surrounding the uplands of Kachchh and Saurashtra, and marshy to saline areas like the Rann of Kachchh and Little Rann of Kachchh. The climate across the state also exhibits diversity, transitioning from a humid climate in the south to sub-humid in the centre and further to semi-arid and arid conditions in the north and west. Due to insufficient and unpredictable rainfall, droughts are a frequent occurrence in the northern Gujarat, Saurashtra, and Kachchh regions [13, 14]. Figure 1 shows the regions studied up till now for heavy metal ion pollution in the state of Gujarat.

Hydro-Geological Setup of Study Area

According to geological formation, Gujarat offers a diverse range of rock types with varying ages, ranging from unconsolidated alluvial and sandy gravel that is only a few thousand years old in the central and western parts of the state to 2500 million years old in the north-eastern region. The state contains metamorphic rocks, igneous rocks, and sedimentary rocks of every type. Gujarat's geology is made up of younger rocks from the Mesozoic (Jurassic and Cretaceous), Tertiary, and Quaternary deposited over a Precambrian basement. However, there are no rocks from the Palaeozoic era. Deccan basalt covers the majority of Saurashtra, a small portion of Kachchh, and the majority of South Gujarat, with numerous locations having stepping in Cretaceous and Tertiary rocks [13]. Different groundwater conditions have emerged in the state because of the state's varied topography. Gneisses, schists, phyllites, intrusive, medium- to coarse-grained sandstones, basalts, and recent alluvium are among the rock formations with ages ranging from the Archaean to the recent. There is not much groundwater potential in the high relief area in the eastern and north-eastern part occupied by the Archaean and Deccan Trap due to the steep gradient that allows for high runoff. The yield of wells in these formations ranges from 5 to 10 m^3/h, while that of wells tapping quaternary alluvium in the Cambay basin ranges from 75 to 150 m^3/h and that of sandstones from 50 to 170 m^3/h. Due to excessive withdrawal, the top aquifer among the five main ones in alluvial sediments has begun to dry up. Almost the

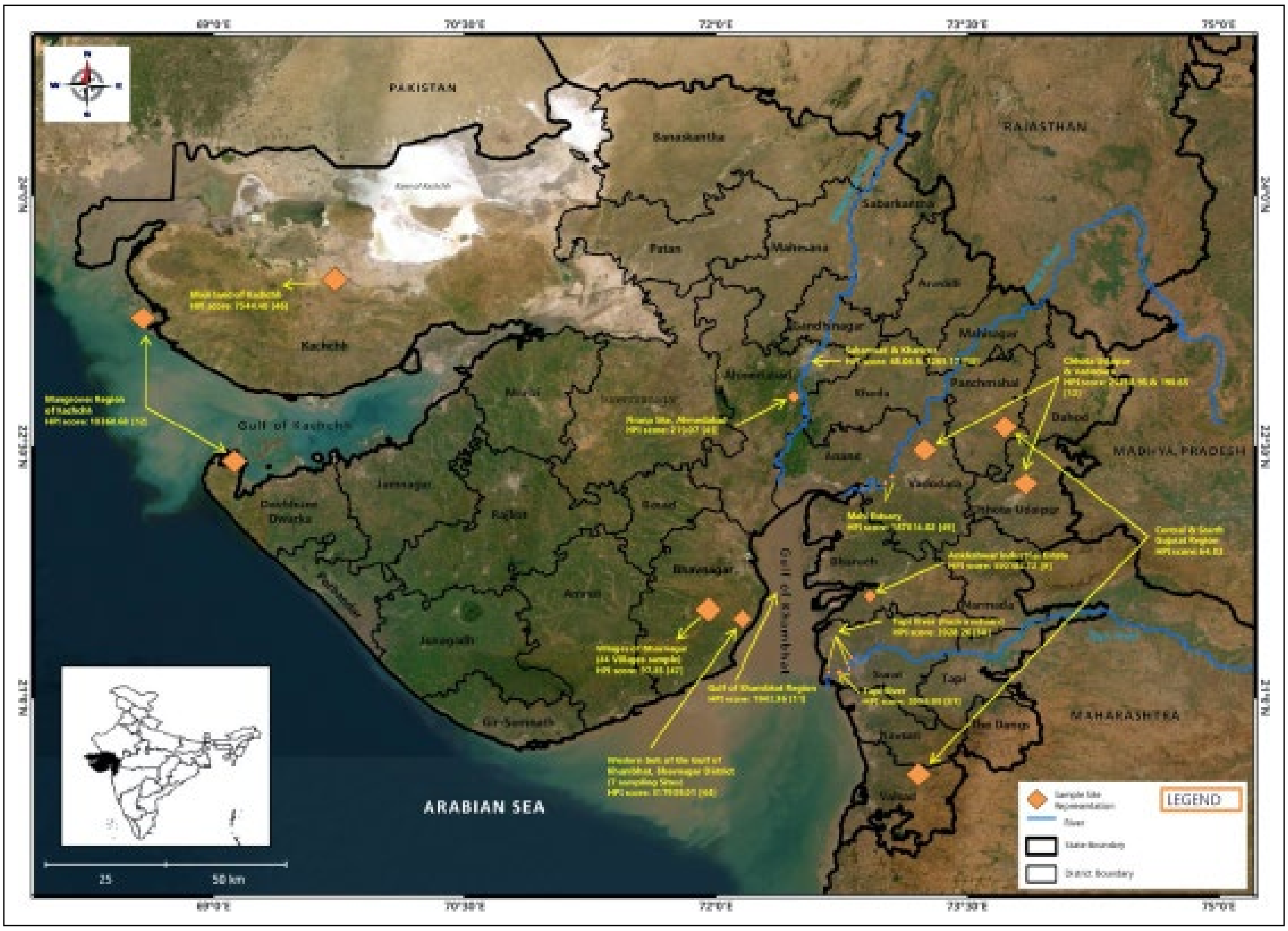

Figure 1. Map showing the regions studied for heavy metal ion pollution in the state of Gujarat.

entire Saurashtra and Kachchh areas are covered in a variety of hard and fissured formations that include basalt and consolidated sedimentary formations in addition to semi consolidated sediments, improving the low-lying coastal zones. Both the irregular aquifers created by the compact and fissured rocks and the aquifer created by the friable semi-consolidated sandstone have a moderate yield potential [14].

Sources of Heavy Metals in Groundwater

Contamination with heavy metals in water sources is now recognised as a major worldwide threat to the environment, endangering aquatic ecosystems as well as human wellness. Due to industrialization, climate change, and urbanisation, pollution from heavy metals in water bodies is on the rise. Mining waste, landfill leachates, municipal and industrial wastewater, urban runoff, and natural occurrences such as eruptions of volcanoes, weathering, and rock abrasion are all pollution sources [15]. Heavy metals can be identified in organic matrices in different forms, including hydroxides, oxides, sulphides, sulphates, phosphates, silicates, and carbonates. They come from both anthropogenic and natural sources [16].

Natural Sources

The concentration of ions in groundwater and its quality are influenced by natural factors such as local geology, weathering rates, rock-water interactions during recharge, and groundwater flow characteristics [17, 18]. Volcanic eruptions, a natural occurrence, release particles and ash into the atmosphere, often containing heavy metals. These metals can be washed into the environment during rain and transported over distances. Volcanic ash, a byproduct of eruptions, contains impurities like Pb, Zn, Cu, Cd, Cr, Fe, and Al [16]. While geogenic sources typically have lower heavy metal concentrations within the acceptable ranges set by local or international protecting environment agencies, the collision of volcanic rocks with water is a geogenic source of metals like As, B, Fe, Pb, Zn, and Cu [18]. Heavy metals can manifest in various forms like sulphates, hydroxides, oxides, sulphides, phosphates, and silicates [19].

Dissolved ions in groundwater and surface water primarily come from the weathering and dissolution of silicate, carbonate, sulphide minerals, and evaporates [18, 20]. The speed of mineral weathering is influenced by factors such as climate and chemical composition, with silicates and carbonates generally reacting more slowly than sulphides [18, 21]. Soils with significant heavy metal content may have natural sources from the weathering of the bedrock beneath them. Heavy metals can be obtained from rocks as minerals, appearing as ores in different chemical states, including sulphides and oxides [6]. Mining and ore processing contribute to heavy metal presence in surface water through water-intensive ore processing and potential contamination from mine effluent discharges and waste rock reservoirs [22].

The connection between surface water and groundwater poses a risk of groundwater pollution, as chemicals from sewage and ores can travel through soil fragments via gravitational processes and end up in groundwater [23].

Anthropogenic Sources

Numerous human activities contribute to the introduction of heavy metals into the environment. The main anthropogenic activities include the production and transportation of energy sources, manufacturing of microelectronic devices, waste disposal, and metallurgical processes such as mining, smelting, and metal finishing. Additionally, heavy metals from fertilizers, livestock waste, and pesticides are commonly utilized in agricultural practices. The details of these anthropogenic sources are elaborated below.

Mining and Mineral Exploration

Mining stands out as one of the most perilous human endeavours globally, despite its numerous societal benefits. The various stages of mineral extraction, such as grinding, concentrating ores, and disposing of residues, along with mine and mill water runoff, contribute significantly to soil pollution [24]. Ore deposits often contain metals in low concentrations, leading to the generation of substantial amounts of waste rock during extraction. These waste rocks retain heavy metal residues from the ore-bearing rock and are typically deposited in mine tailings or rock spoils. In cases involving pyrite, exposure to oxidizing environmental conditions in the tailings can result in the formation of acid mine drainage, mobilizing heavy metals due to the acidic conditions. The disposal of waste rock in tailings or rock spoils can lead to the leaching of heavy metals, posing environmental and health risks through water consumption, respiration, and the consumption of crops grown in soils influenced by irrigation with contaminated water [25]. Additionally, mineral processing activities, including leaching from ore and tailings stockpiles, as well as extraction methods that involve size reduction, can intensify heavy metal contamination by increasing the contact area for mass conversion [26].

Agricultural Route

Agricultural activities have been identified as a significant contributor to groundwater pollution, primarily due to the use of pesticides and fertilizers that release substantial amounts of chemicals into water bodies. Farmers rely on fertilizers and manures to enhance productivity and meet the growing demand for food caused by the increasing global population [22, 27]. Chemical elements like nitrate, phosphate, and potassium from fertilizers can persist in the Earth's crust for extended periods, posing a risk of water contamination through runoff and soil erosion. This nutrient influx into water bodies not only jeopardizes water quality for drinking but also has ecological consequences, impacting both groundwater and surface water ecosystems [22, 28]. Modern crop varieties heavily depend on agrochemicals, contributing to the frequent use of these substances by farmers. Agrochemicals, including fertilizers and pesticides, often contain various heavy metals and metalloids such as Cu, Co, Cr, Mo, Sr, Ti, V, Mn, Fe, Ni, Zn, Cd, Pb, Hg, Ba, Sc, and As [29]. Despite the significant role pesticides play in global agricultural production, their adverse effects have gained more attention. The use of pesticides has been steadily increasing, with an annual usage of 2.3 million metric tonnes. Some widely used pesticides contain high concentrations of heavy metals, including Cu, Hg, Mn, Pb, and Zn, along with hazardous organophosphate and organochlorine compounds like DDT, lindane, endosulfan, and chlordane [29, 30]. Furthermore, animal manure has been identified as another source of heavy metals (Cu, Zn, and Cd) and metalloids (As) in varying concentrations. These contaminants can accumulate in surface soils over time due to the prolonged use of animal manure, leading to runoff and leaching that contaminate water sources [29].

Industrial Activities

Gujarat boasts one of the fastest-growing economies in India and holds the fourth-highest GDP in the country. However, it has emerged as a source of environmental concern due to the proliferation of industries in recent decades [12]. Several industrial processes, such as petro-coal combustion, waste disposal, effluent streams, and wastewater irrigation, contribute to the release of heavy metals into the environment. This has led to an increase in heavy metal levels in waterways, causing soil and sediment contamination with detrimental effects on the ecosystem and irreversible damage to nature [31]. The combustion of fossil fuels, especially in coal-burning power plants for electricity generation, significantly influences heavy metal emissions in the environment. Only a third of fly ash, a by-product of coal combustion, is recycled, while the rest is used in various industrial applications. The composition of parent coal, combustion conditions, efficiency of emission control devices, by-product storage, handling, and climate all impact heavy metal emissions [25]. Notably, heavy metals like As, Cd, Mo, Se, and Zn exhibit significant mobility due to natural weathering of coal residues. Coal fly ash has garnered attention for its high levels of heavy metals and metalloids, such as Cd, Cr, Cu, Ni, Mo, Pb, Se, Zn, and As, making it a concern for soil and water contamination [29, 32]. Urban, peri-urban, and rural areas contribute to heavy metal emissions through manufacturing processes, domestic septic tanks, vehicle leaks, and exhaust emissions. Specifically, urban areas face heavy metal emissions from moving vehicles, petrol spills, and light industries [33].

Improper wastewater management in sewage treatment plants leads to the release of organic contaminants, thus contaminating groundwater. Sewage sludge, rich in organic pollutants like triclosan and aromatics, poses a threat to groundwater when improperly managed. Industries, such as wood and pharmaceuticals, release chlorophenols into the environment without adequate treatment, adding to pollution concerns. These chlorophenols, characterized by high chlorination levels, join alkylphenols (APs), volatile organic compounds (VOCs), and polycyclic aromatic hydrocarbons (PAHs) in industrial wastewater [34]. Roads and automobiles, among other sectors, contribute significantly to heavy metal pollution. Particulate matter in traffic emissions contains heavy metals like Pb, Cd and As, amplifying the adverse effects on the environment [35].

Circulation and Distribution of Heavy Metals in Groundwater

Contaminants introduced into the groundwater system can spread through various mechanisms, namely advection, dispersion, and retardation, influenced by environmental factors and the characteristics of the contaminants. Advection refers to the movement of contaminants at the average groundwater flow rate, determined by effective flow velocities calculated using aquifer properties and hydraulic gradients [22, 36]. Effective flow velocities are calculated using the bulk characteristics of aquifer structures and the mean hydraulic gradient that induces the flow. This method overlooks pollutant behaviour, such as solubility, impacting the flow rate measured by advection. Dispersion involves the movement and distribution of dissolved pollutants due to groundwater flow, resulting from mechanical mixing and molecular diffusion. Molecular diffusion is the process of components moving from lower to higher solute concentrations, while mechanical mixing occurs when factors like pore geometry or friction alter groundwater velocity. Retardation is the process wherein the velocity of the contaminant decreases compared to advective groundwater velocity due to interaction with porous media. Retardation methods, like adsorption and biodegradation, can significantly slow down contaminant transport, with retardation rates varying up to ten times slower than advective velocity. The slower the transport, the more the contaminant is absorbed in a small area [22, 36].

POLLUTION INDICES FOR EVALUATION OF HEAVY METAL CONTAMINATION

In recent decades, considerable attention has been dedicated to assessing heavy metal pollution in both ground and surface waters [37]. Various pollution indices have been employed to comprehensively analyze the extent of heavy metal contamination in water bodies, utilizing multiple reproducible assessments to streamline the evaluation process. The subsequent sections provide a detailed explanation of these indices.

Table 1. Standard permissible values and ideal values for heavy metals

Sr. No.	Heavy metal	Standard permissible value (S_i) µg/L	Ideal value (I_i) µg/L	Reference
1	Fe	300	0	[55]
2	Cr	50	0	[55]
3	Zn	15000	5000	[55]
4	Mn	300	100	[55]
5	Cd	3	0	[55]
6	Pb	10	0	[55]
7	Ni	20	0	[55]
8	Cu	1500	50	[55]
9	Co	0.05	0	[55]
10	Mo	70	0	[55]
11	As	50	10	[55]
12	Cs	1	0	[58]
13	Sr	4000	0	[56]
14	Al	200	30	[55]
15	Hg	1	0	[55]
16	Tl	2	0.5	[57]
17	Ti	1	0	[12]

Heavy Metal Pollution Index (HPI)

In recent years, there has been significant focus on evaluating heavy metal pollution in surface and groundwater. One notable approach is the development of a Heavy Metal Pollution Index (HPI), which aims to assess the combined impact of various metals on water quality. While traditional assessments often focus on individual metals, the HPI provides a comprehensive measure of overall pollution by considering the collective influence of all monitored heavy metals. HPI is used to evaluate the overall impact of heavy metals in water and determine the extent of water contamination. The HPI involves a two-phase process and employs a weighted numerical quality mean approach. Initially, a rating scale with assigned weights for selected parameters is established. Subsequently, a pollution level parameter is chosen to serve as the foundation for the index. The rating scale is arbitrary, ranging from 0 to 1, and the selection of values depends on the relative importance of each quality factor in comparison to other considerations. Alternatively, values can be determined by their inverse proportionality to the standard applicable to the respective parameter [37, 38]. HPI can be calculated using equations (1), (2) and (3):

$$\mathrm{HPI} = \frac{\sum_{i=0}^{n} Wi\, Qi}{\sum_{i=0}^{n} Wi} \qquad \text{Eq. 1}$$

Where, W_i represents the unit weightage of the i^{th} parameter, Q_i represents its sub-index, and n represents the number of parameters to be considered.

The unit weight (Wi) is calculated through the following equation:

$$\mathrm{Wi} = \frac{K}{Si} \qquad \text{Eq. 2}$$

Here, K is the proportionality constant, and S_i represents the i^{th} parameter's standard permissible limit.

The sub-index (Q_i) for the parameter is calculated from the following expression.

$$Q_i = \sum_{i=0}^{n} \frac{\mathrm{Mi}\,(-)\,\mathrm{Ii}}{\mathrm{Si} - \mathrm{Ii}} \times 100 \qquad \text{Eq. 3}$$

Where, M_i represents the measured heavy metal value of the ith parameter, I_i is the ideal value, and Si is the standard value. A negative sign (−) indicates a numerical difference between two values. The standard and ideal values used for calculating HPI for different heavy metals are given in Table 1. A HPI value below 100 indicates a minimal presence of heavy metal pollution, while a score of 100 signifies a potential risk at the threshold of heavy metal pollution. If the HPI surpasses 100, the water is deemed unsafe for consumption [38].

Heavy Metal Evaluation Index (HEI)

The equation used to calculate the HEI represents the total surface water quality in terms of heavy metal content [39].

$$HEI = \sum_{i=0}^{n} \frac{Hc}{Hmac} \qquad \text{Eq. 4}$$

Where, H_c and H_{mac} represent the measured value and highest permissible concentration of the i^{th} parameter, respectively. A HPI below 100 indicates a minimal presence of heavy metal pollution, while a score of 100 signifies a potential risk at the threshold of heavy metal pollution. If the HPI surpasses 100, the water is deemed unsafe for consumption [40].

Degree of Contamination (C_d)

The degree of contamination (C_d) can be determined through the combination of the effects of various quality of water parameters.

$$C_d = \sum_{i=0}^{n} C_{fi} \qquad \text{Eq. 5}$$

Here, $C_{fi}=[C_{Ai}/C_{Ni}] - 1$

Where, C_{fi} is the contamination factor, C_{Ai} is the measured value of the ith parameter and C_{Ni} is the i^{th} component's maximum allowable concentration (N stands for the "normative" value). Based on C_d values, the levels of heavy metal pollution in a surface water body are categorized as follows: A score of less than one [<1] indicates low pollution, a score between one to three [1–3] signifies moderate pollution, and a score exceeding three [>3] indicates high pollution [40, 41].

Metal Index (MI)

The metal index is a tool used for rapidly assessing the overall water quality, considering the potential combined effects of metal elements on human health. The mathematical expression is used to calculate the metal index [42].

$$MI = \sum_{i=0}^{n} \frac{Ci}{MACi} \qquad \text{Eq. 6}$$

Here, C_i represents the average concentration of each component, and MAC_i is the maximum permissible concentration. Different contamination levels are categorized based on the metal index value: highly pure if MI <0.3, pure if 0.3< MI <1, mildly affected if 1< MI <2, moderately affluent if 2< MI <4, strongly affluent if 4< MI <6, and seriously affluent if MI >6. A metal index value greater than 1 is considered a warning sign, indicating a decline in water quality, with higher metal levels compared to the corresponding maximum permissible concentrations [43].

Water Pollution Index (WPI)

The utilization of water, encompassing the control and supervision of water pollution, is governed by the Water Purity Index (WPI). This index offers a numerical value relative to the minimum allowable threshold for a specific heavy metal as shown below [40].

$$WPI=(M_i–Min_i)/R_i \qquad \text{Eq. 7}$$

Here, Mi represents the monitoring value, Mini is the minimum permissible limit, and Ri denotes the acceptable limit range for a specific heavy metal as extracted from relevant sources.

CURRENT SCENARIO ON THE PRESENCE OF HEAVY METALS IN GUJARAT

Access to clean water is crucial for both humans and the environment, as water is a vital resource for life on Earth. Water quality has been negatively impacted by population growth, accelerating urbanisation, and unsustainable resource use in recent years. Heavy metal ions are one of the most commonly released contaminants, making them a cause for concern [7].

In a study conducted at Bhavnagar, which is located on the western coast of the Gulf of Khambhat in Gujarat. The Gulf of Khambhat is a distinct tropical coastal marine habitat with strong continental effect. The region has diverse habitats and is a susceptible ecological area. The industrial zone releases treated or untreated wastewater into the Gulf of Khambhat. In this study, approximately 63 samples were collected from the Bhavnagar coastal line over three seasons and at seven different locations. Together with the physicochemical parameters, seasonal dissolved heavy metal levels were also examined. The mean amount of dissolved heavy metals in all sites decreased in the following order: Pb > Cr > Ni > Co > Fe > Cd > Mn > Cu > Zn. Compared to the monsoon period, the dry season (pre- and post-monsoon) had higher levels of dissolved heavy metals in coastal waters. During the dry season, anthropogenic activities lead to higher levels of heavy metals in the water. The amount of Pb exceeded the acceptable limit. Except for Pb and Ni, all metals are within permissible limits. The high concentration of Pb in coastal water was ascribed to ship paint and repair activities, as well as the discharge of waste from industries. Ni levels were above the BIS standards. Ni was found in sewage sludge, paint and dyes, old batteries, fertilisers, and industrial wastewater. The study revealed significant spatial and temporal variation in the physical and chemical characteristics of water and dissolved heavy metals, which may pose a threat to marine ecosystems [44].

In a study conducted in Ankleshwar Industrial Estate (AIE), South Gujarat, 38 water samples collected to analyse heavy metal contamination. The sampling wells were selected using a method of random sampling, considering industrial, urbanised and oil field regions, as well as road networks and polluted streams. The hydrogeology of AIE is dominated by quaternary alluvium. The alluvial (shallow alluvial aquifer) sediments have been classified according to their depositional surroundings. The AIE, characterized by urban and industrial areas comprising of chemical, fertiliser, paint, dye, glass, pharmaceutical, and other allied industries, has undergone significant environmental impact. The work aimed to characterize spatial variations in toxic metals, identify potential sources, and assess their impact on surface water using GIS-based methods. Geochemical maps were created to estimate concentrations of ten trace elements, revealing high levels of heavy metals, especially Mo, Zn, Pb, Ni, Co, Fe, and Cd. Groundwater in the oil field area exhibited alarming concentrations, implicating oil field development as a major contributor to subsurface environmental damage, affecting over 20 km^2 area. Heavy metal concentrations were found to be higher in Panoli region compared to Ankleshwar and surrounding areas due to industrial sources located in recharge zones. The study also assessed metal concentrations in the Amla Khadi stream, distinguishing between geological (U) and anthropogenic (P) sources. The "extremely" high P/U ratio for Mo and "high" ratios for Cr indicated significant contaminant growth in the polluted stream area, raising concerns about potential migration into cultivated food crops due to elevated technological elements in groundwater [9].

Singh et al. [45] conducted a study at the Pirana landfill site in Ahmedabad, focusing on assessing the quality and toxicity of waste, particularly in terms of heavy metals, and its impact on groundwater quality. They collected a total of 11 groundwater samples, 5 municipal solid waste (MSW) samples, and 1 leachate sample. The hydrogeology of the study area is characterized by extensive Quaternary alluvial deposits, which are notably thick. These deposits consist of a mixture of sand, silt, clay, and gravel beds, forming the lithology of Ahmedabad. Within these deposits, there is a recurring pattern of alternating layers of sand, silt, clay, and gravel. Typically, multiple layers of sand are found within the first 50 m of the ground. Separating the upper unconfined aquifers from the deeper aquifers, which lie beyond 100 m in depth, is a layer of silt or clay, typically measuring 20 to 25 m thick. The study aimed to monitor levels of heavy metals such as Cd, Cr, Cu, Fe, Ni, Mn, Pb, and Zn to evaluate the landfill's influence on groundwater quality. The chemical analysis of MSW indicated a general trend of metal abundance as Fe>Mn>Zn>Cu>Pb>Cr>Ni>Cd. In leachate and groundwater, the observed trend was Fe>Zn>Mn>Cu>Pb>Cr>Ni>Cd. The results suggested that Fe and tin-based wastes at the landfill site might contribute to high iron values, and the Mn concentration was generally elevated except for some samples from coal and municipal waste burning. Cu levels were within acceptable limits, while Zn concentration was high, potentially due to the presence of Zn-based waste like zinc-plated material, fertilizer, and cement. The majority of Ni and Cr values were within acceptable ranges, and Pb and Cd levels were also found to be within acceptable limits. Factor analysis results indicated that pollution sources were more prevalent than natural processes near the landfill site. Positive loading of heavy metal factors demonstrated the landfill's impact on groundwater quality, particularly in the pattern of groundwater movement. Cluster analysis identified two major groups of samples: those with and without landfill impact, along with contaminated leachates.

Another study was aimed to investigate the seasonal variations in water and sediment quality in the Sabarmati River and its tributary, the Kharicut canal, at Ahmedabad, Gujarat [10]. These locations receive industrial waste from various sectors such as plastics, engineering, machinery, chemicals, paints, pharmaceuticals, foundries, and textiles. The concentrations of heavy metals in sediments were notably higher than those in water samples, with Cr being the most prevalent metal. The hierarchy of heavy metal concentrations observed in water samples was Cr > Zn > Cu > Ni > Pb. The study revealed seasonal variations in heavy metal concentrations, with the highest levels during the pre-monsoon season, followed by the monsoon and post-monsoon seasons. The Pollution Load Index (PLI) indicated that surface sediments were more contaminated with heavy metals than river waters. The contamination degree (Cd) values demonstrated a very high level of contamination in the Kharicut canal and a significant level of contamination at three sites along the Sabarmati River.

Keesari and co-workers [46] conducted a study where they collected and analyzed 25 groundwater samples from the Mainland Kachchh. Their study focused on examining the general geochemistry and levels of trace metals present. The study area encompasses hydrogeological formations dating back to the Mesozoic (up to 250 million years) and Cenozoic (up to 65 million years) eras. The drainage patterns in this region are shaped by lithological characteristics, tectonic activities, and fluctuations in sea levels during the Quaternary period. The results revealed that the levels of all trace elements fell within the permissible drinking water limits set by the World Health Organization (WHO) in 2008, except for manganese (Mn2+) in two samples [10]. This suggests that there is no significant influence from industrial waste or essential geological contributions affecting the groundwater system.

Upadhyaya et al. [11] conducted a study on the presence and distribution of specific heavy metals (As, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) in the Gulf of Khambhat (GoK), Gujarat, during different seasons (post-monsoon, winter, and pre-monsoon). They collected and analyzed groundwater samples from 11 stations. The hydrogeology of the GoK region consists of a typical alluvial landscape characterized by shallow water tables and moderate to high salinity levels. Due to the composition of the alluvium, which is primarily fine clay with a layer of silty sand on top in the unconfined aquifers, groundwater flow is notably sluggish in these regions. Through different seasons, Zn exhibited the highest average concentrations, followed by Cu, Cr, and B in the pre-monsoon, post-monsoon, and winter periods. Post-monsoon seasons had relatively high concentrations of Cd, Co, Ni, and Pb, while pre-monsoon seasons showed elevated levels of As, Cr, and Mn. The decreasing trend in average metal levels was observed as follows: Zn > Cu > Pb > Ni > Cr > Cd > B > Co > Mn > As for pre-monsoon, Zn > Cu > Pb > Ni > Mn > Cd > As > Co for post-monsoon, and Zn > B > Cr > Cu > Mn > As > Ni > Pb > Cd > As > Co for winter seasons. Principal Component Analysis (PCA) was employed to understand the underlying data structure. PC1 revealed that Co, Cu, Cd, and Zn accounted for 31.72% of total variances, originating from sources like municipal sewage, metallurgical industries, and landfill leachate infiltrating aquifers. PC2 contributed 20.6% of total variance, characterized by high Mn, Ni, and B loadings. PC3 with 11.26% total variance had moderate As loading and minor B loading, while PC4, accounting for 9.17%, comprised Cr and Pb. According to the PCA, groundwater chemistry in the study area was primarily influenced by mineral weathering, anthropogenic pollutants, and atmospheric deposition. The detection of toxic metals like Cd and Pb in some samples raises concerns about the health implications for those consuming the water.

An evaluation of the hydrochemical characteristics of groundwater in Bhavnagar District, Gujarat, revealed that heavy metal analysis indicated elevated values in most samples, surpassing permissible limits [47]. Building on this, Patel et al. [48] provided substantial insights into the groundwater quality evolution in the southern and central regions of Gujarat. Most of the studied region is enveloped by Quaternary deposits, with older Proterozoic rocks predominantly found in the north and Deccan basalt covering the southern part of the area. The study specifically investigated heavy metal concentrations, including Cr, Zn, and Pb. Zn emerged as the most prevalent metal in the groundwater samples, followed by Cr and Pb. Importantly, none of the metal concentrations exceeded the limits set by the Bureau of Indian Standards (BIS). The study suggested that the adequate concentrations of these metals during both post-monsoon and pre-monsoon seasons could be attributed to an abundance of HCO_3^- ions in water. This excess of ions may play a regulatory role by precipitating toxic metals, such as Pb, out of solution.

A two-year study spanning from June 2015 to May 2017 was conducted, focusing on the levels of heavy metals such as Cd, Pb, Ni, Cr, Hg, Cu, Zn, Fe, and Mn in water, sediment, and fish tissues within the aquatic region of the River Mahi in Gujarat [49]. Sampling was carried out at two designated stations, E1 (upstream) and E2 (downstream). The water samples from E1 exhibited elevated concentrations of all examined heavy metals compared to those from E2. This disparity was attributed to the discharge of industrial waste into area E1 through a canal connected to the Nandesari industrial zone. Additionally, the industries in and around Vadodara were identified as sources of substantial amounts of hazardous chemicals dumped into the Mahi River, contributing to the heightened heavy metal concentrations at station E1. Analysis revealed that heavy metal concentrations in water peaked during the monsoon period (June to August) and decreased during the summer months (March to May) at both E1 and E2 stations. Notably, both stations displayed positive correlations between the levels of heavy metals in the water. The sequence of heavy metal concentrations in the water at stations E1 and E2 was found to be Fe>Mn>Zn>Pb>Ni>Cu>Cd>Hg>Cr. Except for Zn, the concentrations of other heavy metals exceeded permissible limits in the surrounding environment.

Siddha and Sahu [50] conducted a study utilizing Principal Component Analysis (PCA) to gain insights into the significant hydrogeochemical processes influencing groundwater changes in the Vishwamitri River Basin (VRB) in Gujarat, India. PCA, a statistical technique, was employed to identify and reduce data outliers. The normal distribution of the dataset was assessed using the Shapiro-Wilk statistic. The analysis included the examination of trace heavy metals such as Fe, Zn, Mn, Mo, Li, Sr, As, Se, Tl and V, which were integrated into the PCA framework. The overall PCA results indicated that the groundwater chemistry was influenced by both mineral dissolution and human activities.

Dubey and Ujjania [51] studied the water quality in the estuarine vicinity of the Tapi River in Gujarat, focusing on heavy metal pollution and concentrations. Water samples were collected monthly from the Hazira estuary of the Tapi River between January and September 2014, analysing Cd, Cr (VI), Pb and Co levels. To assess pollution levels, they utilized statistical techniques for metal concentration, specifically the contamination factor (CF) and pollution load index (PLI), which are interrelated. The results revealed a consistent order of increasing metal concentrations as Pb < Co < Cd < Cr(VI), with both CF and PLI indicating a state of extreme pollution, attributed to the direct discharge of industrial wastewater.

A study was performed to assess the hydrochemical processes influencing spatial and seasonal variations in nutrient and heavy metal concentrations in the water of mangroves located in the Gulf of Kutch (GoK), India [12]. GoK is a semi-closed basin surrounded by Kachchh mainland to the north, Saurashtra peninsula to the south, and the Arabian Sea to the west. Kachchh's major lithological features include sandstone, shale, limestone, and basalt. The Saurashtra peninsula is made up of tertiary shale and limestone, as well as late-cretaceous basalt and laterite rocks that form the shoreline. Surface water samples were collected during the pre-monsoon and monsoon seasons, specifically during low tide in May 2018 (pre-monsoon) and December 2018 (post-monsoon). A total of 36 mangrove locations in the northern and southern Gulf of Kachchh were sampled. The analysis focused on heavy metals, including As, Cu, Fe, Li, Mn, Mo, Pb, Si, Sr, Ti, Tl, and Zn. GIS software was employed to create spatial distribution maps, and statistical techniques such as agglomerative hierarchical clustering (AHC), PCA, and correlation analysis were applied to the hydrochemical data to identify spatial patterns, relationships between variables, and the sources of chemical components. During the pre-monsoon period, the mean concentrations of heavy metals were ranked as follows: Sr> Fe> Zn> Cu> Li> Mn> As> Ni> Pb> Ti> Tl> Mo. In the post-monsoon season, the mean concentrations were as follows: Fe> Sr> Zn> Mn> Cu= Li> Ti> As = Pb> Ni> Tl= Mo. Overall, heavy metal concentrations increased during the pre-monsoon season, with Fe, Sr, Zn, and Mn being the most abundant. Elevated levels of Fe and Mn suggested a prevalence of related biological productivity and redox processes at the sediment-water interface. The study identified metal contaminations (Zn, Cu, Li, As, Ni, Pb, Ti, Tl, and Mo) as originating from non-point sources due to human activities in the investigated area.

A two-year study was conducted to investigate the presence of heavy metals, including Hg, Cd, Pb, and Zn in the Tapi river estuary in Surat [52]. The average concentrations of these heavy metals in water over the two sampling years were found to follow the order Pb>Zn>Cd>Hg. Statistical analyses indicated significant differences in the levels of mercury, cadmium, lead, and zinc in water among the three sampling sites. Patel et al. [53] conducted a study to assess the status of groundwater quality in Vadodara and Chhota Udaipur districts. Groundwater in both areas exists in unconfined and confined conditions. Unconfined aquifers consist of saturated zones of unconsolidated shallow alluvium, weathered zones, and shallow depth jointed and fractured rocks. Multilayered aquifers are present beneath impervious clay horizons in alluvium formation and interflow zones of basalts, intertrappean beds, deep-seated fracture zones, and shear zones in basalts, granites, and gneisses, leading to semi-confined to confined conditions. The study included an examination of both physicochemical parameters and the presence of various heavy metals. To identify potential heavy metal pollution in groundwater, they analysed Pb, Cd, Fe, Ni, Cr, Zn and As. The findings indicated that, except for Fe and Pb, the levels of heavy metals fell within permissible limits as per Indian standards, set at 0.3 mg/L for Fe and 0.01 mg/L for Pb. The analysis revealed a maximum Fe concentration of 9.9 mg/L and a maximum Pb concentration of 0.057 mg/L. It was noted that Fe concentrations generally exceeded the recommended range of 0.3 mg/L to 0.8 mg/L. Prolonged exposure to heavy metals beyond the established limits could pose severe health risks, potentially leading to fatal outcomes. The details of the study area, methodology followed, and significant observations are summarized in Table 2.

ASSESSMENT OF CONTAMINATION USING THE HEAVY METAL POLLUTION INDEX

Quality indices play a crucial role in consolidating the impact of all pollution factors to provide a comprehensive evaluation. Numerous methods have been proposed for estimating surface water features using water quality parameters [54]. Monitoring heavy metals in drinking water is especially vital for human health, and assessing heavy metal pollution in the groundwater of Gujarat is imperative. This study aims to demonstrate the extent of heavy metal contamination in the region by applying the HPI to existing work on heavy metals in the groundwater of Gujarat.

The HPI is a tool that gauges the collective influence of individual heavy metals on water quality, offering insights into the overall impact on environmental health. The weighted factors in HPI correspond to the inverse of the suggested standard for each metal. Notably, the sum of these weighted factors does not equal 1. In contrast to other Water Quality Indices (WQI) where higher values indicate better quality, higher HPI values signify deteriorated water quality concerning metals. Unlike other WQIs that calculate sub-indices using only standard values, HPI incorporates both ideal (Ii) and standard (Si) values, making it a more comprehensive metric [37]. In the HPI calculations performed in the present study, the values for Si and Ii were adapted from BIS (2012) [55], representing the standard permissible limit and ideal acceptable limit values of heavy metals in drinking water. If there is no ideal acceptable limit, the Ii value is considered 0. For certain heavy metals such as As, Cd, Co, Cu, Cr, Mn, Ni, Pb, and Zn, recommended values were used [55]. The standard limit for strontium (Sr) is 4 mg/L, according to ATSDR (2004) [56]. Thallium (Tl) values were obtained from USEPA (2009) [57], with Si and Ii values set at 0.5 ppb and 2 ppb, respectively. Cesium (Cs) value of 1 µg/L was adopted from ATSDR (2004) [58].

The HPI was employed to assess groundwater accessibility in pollution studies conducted in Gujarat. The tabulated results display the index, which holds applicability across various water usage scenarios (Table 2). The critical threshold for this pollution index was set at 100. Heavy metal values contributing to the HPI are expressed in µg/L. The calculation of HPI involved utilizing the mean concentrations of heavy metals measured at distinct sampling sites during the conducted studies. In instances where values for different seasons were available, the overall mean value was selected for HPI computation. If the study provided a direct mean value, the calculation was performed accordingly.

Cobalt (Co): With Co making a major contribution of 317882.34, the total composite HPI score at the Bhavnagar Costal line was 317939.01. This result indicates the impact of human-induced disturbances and the proliferation of diverse activities in the area [44]. The AIE recorded a comprehensive HPI score of 550182.72, with Co contributing significantly at 550052.27, indicating substantial groundwater contamination. This contamination is attributed to the dispersal pattern of elevated Co concentrations, primarily observed in industrial areas where coal combustion serves as a major energy source [9]. However, in the mainland of the Kachchh region, there was negligible contributions from industrial wastes and geological factors to the groundwater system [46]. Nevertheless, the HPI calculation revealed that the score of Co exceeded the established threshold in the Gulf of Khambhat. In this region, the HPI score for Co also surpassed the critical limit of 1941.99, indicating a notably high level of Co contamination within the broader context of heavy metal pollution [11].

Lead (Pb): According to a study conducted by Kumar et al. [10] at the Sabarmati River and Kharicut canal in Ahmedabad, the HPI score for Pb at the Sabarmati River was below the permissible limit, indicating that this site was free from heavy metal contamination. However, at the Kharicut canal, the HPI score for Pb was notably high at 632.44, classifying it as a major contaminant, alongside Cr with an HPI score of 565.67. This indicates significant heavy metal pollution at this site, with industries like dyeing, chrome plating,

Table 2. Groundwater studies of different regions of Gujarat for heavy metal ion pollution

Sr. No.	Ref.	Study area	Water type	No of samples analysed; heavy metals studied	Methods/parameters evaluated	Heavy Metal Pollution Index (HPI) score	Remarks
1	[44]	Western belt of the Gulf of Khambhat, Bhavnagar	Surface water	7; Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn	Correlation Coefficient, Principal Component Analysis, Cluster Analysis	317939.01	The HPI score was significantly higher than the threshold limit, with Co (317882.3445) being the major contributor.
2	[9]	Ankleshwar Industrial Estate, Bharuch	Groundwater	38; Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Zn	Clutching geochemical analysis, GIS-based colour composites methods	550182.72	Overall, the HPI score was much higher than the threshold limit; The major contributor for high HPI score was Co (550052.27) and to a lesser extent Cd (106.45).
3	[45]	Pirana Site, Ahmedabad	Groundwater	17#; Cd, Cr, Cu, Fe, Ni, Mn, Pb, Zn	Correlation analysis, Cluster analysis, Factor analysis	219.07	Overall, the HPI score was above the threshold limit; Major contributor for high HPI was Fe (113.13).
4	[10]	Sabarmati River, Ahmedabad	Surface water	15; Cr, Cu, Ni, Pb, Zn	Contamination factor, Contamination degree and Pollution load index	48.06	Overall, the HPI score was much below the threshold limit. Free from heavy metal ion contamination
		Kharicut canal, Ahmedabad	Surface water			1269.17	Overall, the HPI score was above the threshold limit; The major contributor for high HPI score were Cr (565.67) and Pb (632.45).
5	[46]	Mainland of Kachchh, Kachchh	Groundwater	25; Al, As, B, Ba, Cu, Co, Cs, Fe, Mn, Ni, Sr, Pb, Zn	Isotope analysis, Graphical methods	7544.40	Overall, the HPI score was above the threshold limit; The major contributor for high HPI score was Co (7521.47).
6	[11]	Gulf of Khambhat, Khambhat	Groundwater	11; As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn, B	In-situ parameters analysis; Correlation matrix analysis, Principal component analysis	1943.36	Overall, the HPI score was above the threshold limit; The major contributor for high HPI score was Co (1941.99).
7	[47]	Villages of Bhavnagar	Groundwater	174; Fe, Pb	In-situ parameters analysis	97.85	Overall, the HPI score was below the threshold limit. Free from heavy metal ion contamination
8	[48]	Bharuch, Dang, Anand, Tapi, Narmada, Surat, Navsari, Chhota Udaipur, Mahisagar, Dahod, Valsad, Vadodara, Panchmahal	Groundwater	45; Cr, Zn, Pb	Irrigation Indies, Correlation analysis	64.82	Overall, the HPI score was below the threshold limit. Free from heavy metal ion contamination
9	[49]	Mahi Estuary, Vadodara	Surface water	50; Cr, Cd, Cu, Fe, Hg, Mn, Ni, Zn	Correlation analysis	187814.02	Overall, the HPI score was much higher than the threshold limit; The major contributor for high HPI score was Hg (187624.07) and to a lesser extent Cd (132.39).

Table 2 (cont). Groundwater studies of different regions of Gujarat for heavy metal ion pollution

Sr. No.	Ref.	Study area	Water type	No of samples analysed; heavy metals studied	Methods/parameters evaluated	Heavy Metal Pollution Index (HPI) score	Remarks
10	[50]	Vishwamitri River Basin, Vadodara, Panchmahal	Groundwater	60; As, Fe, Li, Mg, Mo, Se, Sr, Th, V, Zn	Principal component analysis	–	–
11	[51]	Tapi River (Hazira estuary), Surat	Surface water	3; Cd, Cr(VI), Pb, Co	Contamination factor, Pollution Load Index	3928.26	Overall, the HPI score was above the threshold limit; The major contributor for high HPI score were Cd (2349.48) and Pb (1570.48).
12	[12]	Mangroves Region of Kachchh	Surface water	36; As, Cu, Fe, Li, Mn, Mo, Pb, Si, Sr, Ti, Tl, Zn	Correlation Analysis, Cluster analysis, Principal component analysis	10360.68	Overall, the HPI score was above the threshold limit; The major contributor for high HPI score were Ti (9456.62) and Tl (778.20).
13	[52]	Tapi River, Surat	Surface water	--; Cd, Hg, Pb, Zn	Statistical analysis	2099.09	Overall, the HPI score was above the threshold limit; The major contributor for high HPI score were Hg (1772.01) and Pb (296.85).
14	[53]	Chhota Udaipur	Groundwater	162; As, Cd, Cr, Fe, Ni, Zn	Water quality index, Correlation, and regression analysis	25238.96	Overall, the HPI score was above the threshold limit; Major contributor for high HPI was Pb (25215.83).
		Vadodara	Groundwater			190.65	Overall, the HPI score was above the threshold limit; Major contributor for high HPI was Pb (155.12).

textiles, tanning, leather, and paints being particularly susceptible to elevated metal levels. In the estuary of the Tapi River, the calculated HPI score was 3928.26 [51]. Pb emerged as the predominant pollutant with a score of 1570.48, attributed to direct discharges of industrial effluents into the river. Cadmium (Cd) also affected the Tapi River, as indicated by its HPI score of 2349.48. Another study on the Tapi River estuary highlighted Pb as a dominant metal pollutant, with an HPI score of 296.84 [52]. In the villages of Vadodara and Chhota Udaipur districts of Gujarat, a study revealed significant dominance of metal pollutants in both the districts [48]. The overall HPI scores were 190.64 and 25238.96, and the Pb scores were 155.11 and 25215.83, respectively. This underscores the substantial impact of Pb pollution in these regions.

Mercury (Hg) is a non-essential metal devoid of recognized physiological functions and exhibits toxicity even at low concentrations. According to a study [49], the Mahi River estuary recorded an overall HPI score of 187814.01, with Hg contributing significantly through an individual HPI score of 187624.07. This indicates a pronounced contamination attributed to human activities. Similarly, in the Tapi River ecosystem [52], an increased level of metal ions was evident due to anthropogenic influences. Specifically, the HPI score for Hg at the Tapi estuary reached 1772.01, underscoring a substantial pollution impact.

Cadmium (Cd): A study conducted by Kumar et al. [9] revealed elevated levels of Cd contamination in AIE, South Gujarat, India. The HPI score for Cd in this region surpassed the critical limit of 106.49, indicating significant pollution in the analyzed water sample. Additionally, Pandey et al. [49] highlighted heavy metal pollution in the Mahi River, with a Cd HPI score of 132.38, rendering the water unsafe for drinking and other purposes. Notably, the Tapi river exhibited the highest Cd contamination, with an HPI score of 2349.48, underscoring Cd as the predominant contaminant at this site [52].

Research conducted at the Pirana site in Ahmedabad focused on assessing the quality and toxicity of waste in relation to heavy metals [45]. The application of the HPI revealed high score for Fe, exceeding the threshold limit, registering at 113.12, indicating the presence of heavy metals. In a separate study conducted by Maurya and Kumari [12], the investigation aimed to analyze the spatial and seasonal variations of nutrients and heavy metals in the water of mangroves located in the Gulf of Kachchh. The primary heavy metals contributing to overall pollution were Ti and Tl, with corresponding HPI scores of 9456.62 and 778.20, respectively.

TECHNOLOGIES FOR REMOVAL OF HEAVY METALS IN GROUNDWATER

The degradation of heavy metals in water poses a challenge due to their complex bioaccumulation characteristics. Excessive exposure to these metals beyond permissible limits can lead to health issues in humans, as heavy metals are highly toxic and often carcinogenic, accumulating in various bodily systems [59]. Given the potential health risks associated with even slight excesses of metal ions, the removal process is as crucial as detection. To ensure the complete elimination of specific metal ions from water systems, it is essential to employ an appropriate removal technique. Care must be taken to choose a method that is not only effective but also safe, environmentally friendly, and cost-effective [60]. Various methods are employed for removing heavy metals from contaminated water, including membrane filtration, ion exchange, coagulation, adsorption, reduction or oxidation, and chemical precipitation [61]. The selection of a suitable method is critical to achieving comprehensive removal while meeting safety and cost considerations.

Chemical Precipitation

Chemical precipitation is a widely used and effective industrial process due to its simplicity and cost-effectiveness. This method involves the reaction of chemicals with heavy metal ions, forming insoluble precipitates. The precipitates can then be separated from water through sedimentation or filtration. After treatment, the water can be released or recycled. Hydroxide precipitation and sulphide precipitation are two common chemical precipitation processes, with hydroxide precipitation being particularly popular due to its simplicity, low cost, and easy pH control [59]. In hydroxide precipitation, chemicals like lime are often used to react with heavy metal ions in the pH range of 8.0 to 11.0, minimizing the solubility of metal hydroxides. Flocculation and sedimentation processes are employed to remove the metal hydroxides. While hydroxide precipitation is cost-effective, the method produces large amounts of low-density sludge, presenting challenges in dewatering and disposal [62]. The addition of coagulants, such as alum and iron salts, can enhance heavy metal removal. Sulphide precipitation is another successful technique for removing toxic metallic ions. Unlike hydroxide precipitation, sulphide precipitates have lower solubilities and are not amphoteric, allowing for high metal removal over a broad pH range. The resulting metal sulphide sludges also have better dewatering and dehydration properties. However, there are risks associated with the sulphide precipitation process, as heavy metal ions and sulphide precipitants in acidic environments can lead to the formation of toxic H2S emissions. Therefore, the process must be conducted in a neutral or basic medium [62]. Alternatively, chelating precipitants like trimercapto triazine, potassium-sodium thiocarbonate, and sodium dimethyl dithiocarbamate can be used as another option for removing heavy metals from aquatic environments [63]. The data highlights the presence of heavy metals such as Pb, Cr, Ni, Cd, and Zn in various water bodies across Gujarat. Chemical precipitation, particularly hydroxide precipitation and sulphide precipitation, can be effective in treating water contaminated with these heavy metals. For instance, hydroxide precipitation using lime can help reduce the solubility of metal hydroxides like Pb and Cd, while sulphide precipitation can target metals like Ni and Zn.

Adsorption Method

Adsorption has been identified as a highly effective method for purifying contaminated water due to its economic and technical viability. The design and functionality of this technique are practical, and the treated water meets high-quality standards. Furthermore, the adsorbents can be reused after regeneration through appropriate desorption procedures [64]. Various adsorbents, such as carbon-based compounds, polymers, resins, clays, minerals, nanoparticles, and nanocomposites, have been utilized for removing heavy metals from wastewater [65]. The process of removing heavy metal ions through adsorption is known for its cost-effectiveness, high removal capacity, ease of implementation, and straightforward treatment [66].

Activated Carbon

The effective removal of metal pollutants from aquatic environments has been demonstrated through the utilization of activated carbon as a potent adsorbent. This method is frequently employed in wastewater treatment owing to the substantial surface area offered by activated carbon. The effectiveness of activated carbon stems from its diverse surface functional groups and well-established pore structure, making it a proficient purifier of contaminated water [60]. Carbon-based nanoporous adsorbents, including activated carbons (ACs), carbon nanotubes (CNTs), and graphene (GN), are widely applied in the removal of heavy metals due to their significant surface areas ranging from 500 to 1500 m^2/g. Common modification methods such as nitrogenation, oxidation, and sulfuration are employed to enhance specific surface area, pore structure, adsorption capacity, thermal stability, and mechanical strength [66].

Biosorption

The utilization of dry biomass to extract harmful metallic elements from industrial effluents, known as biosorption, represents an alternative approach in commercial wastewater treatment. In the process of adsorbing heavy metal ions, both physisorption and chemisorption play crucial roles [59, 66]. The notable advantages of biosorption include its remarkable efficiency in reducing heavy metal ions and the use of cost-effective biosorbents. Biosorption processes are particularly well-suited for treating diluted heavy metal wastewater. These biosorbents can be derived from three main sources: (1) non-living biomass such as bark, lignin, prawns, krill, squid, crab shell, etc., (2) algal biomass and (3) microbial biomass, including bacteria, fungi, and yeast [61, 67]. Biosorbents offer extensive source coverage, cost-effectiveness, and rapid adsorption. However, it is important to note that these investigations are still in the experimental and theoretical stages, and the separation of biosorbents after absorption poses a potential challenge [62].

Mineral Adsorbents

Mineral adsorbents like zeolite, silica, and clay are considered cost-effective options for water purification. Clay possesses favourable characteristics such as high cation exchange capacity (CEC), selectivity for cation exchange, hydrophilic surface, swelling capability, and surface electronegativity. Various enhancement techniques like acid washing, thermal treatment, and the addition of pillars can increase pore size, volume, and specific surface area, significantly improving adsorption efficiency [65, 68, 69]. Clay components inherently contain exchangeable cations like Na^{+}, Ca^{2+}, and K^{+}, enhancing their adsorption capabilities. Most clay minerals carry a negative charge due to the substitution of Si^{4+} and Al^{3+} with other cations, making them effective in removing heavy metal cations from water. The process of heavy metal adsorption by clay and clay composites involves ion exchange, surface complexation, and direct bonding of heavy metal cations to the clay surface. Furthermore, clay materials can become more organophilic and hydrophobic through treatment or modification, expanding their ability to absorb non-ionic organic substances [70].

Carbon Nanotubes

Carbon nanotubes (CNTs) have received a great deal of attention due to their excellent properties and applications. CNTs, as relatively new adsorbents, have demonstrated great potential for removing heavy metal ions such as Pb, Cd, Cr, Cu and Ni from wastewater. They are classified as either single-walled CNTs (SWCNTs) or multi-walled CNTs (MWCNTs). The processes by which metal ions are absorbed onto CNTs are complex but they involve electromagnetic attraction, sorption-precipitation, and chemical interaction among metal ions and CNT surface functional groups [61, 70, 71].

Adsorption techniques using activated carbon, biosorbents, and mineral adsorbents can be applied to remove heavy metals like Pb, Cd, Cr, Cu, Ni, Zn, and Fe from contaminated water. Activated carbon, with its high surface area, can effectively adsorb various heavy metal ions present in water samples from different locations in Gujarat.

Membrane Filtration

Membrane filtration has become increasingly popular for the treatment of inorganic wastewater due to its ability to eliminate suspended solids, organic matter, and heavy metals. Various membrane filtration techniques, including ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), are employed depending on the particle size. Ultrafiltration, with a membrane pore size of 5–20 nm, selectively separates heavy metals, macromolecules, and suspended solids from water, permitting the passage of water and low-molecular-weight solutes while retaining larger macromolecules [72]. RO relies on osmosis, reversing the natural flow by applying pressure to a semipermeable membrane separating solutions of different concentrations. RO membranes, which are essentially nonporous, allow water to pass through while retaining most solutes, achieving ion removal rates of 95–99.9%. This process, characterized by high operational pressures (2,000–10,000 kPa), is commonly used to produce pure water for industrial purposes but may not be optimal for highly concentrated solutions. Nanofiltration membranes, featuring pores of 2 to 5 nm, partially retain ions, allowing small monovalent ions and low-molecular-weight organics to pass through. NF membranes exhibit higher water permeability than RO membranes, operating at lower pressures (700–3,000 kPa) [73]. Microfiltration (MF) employs microporous membranes with a separation limit of 0.02 to 10 m to separate particles, microorganisms, and large molecules through a sieving effect. Inorganic (ceramic) membranes, with lower porosity than polymer membranes, offer thermal stability for use at high temperatures. MF is effective in wastewater and water treatment, removing dissolved materials and colloidal particles that are too large for other separation methods [73]. In Gujarat, UF, NF and RO can be employed to remove suspended solids and heavy metals like Pb, Cd, Ni, and Zn from water. This is particularly relevant in areas where water samples showed elevated concentrations of heavy metals during certain seasons.

Ion Exchange

The ion exchange technique is a reversible chemical process employed to replace harmful metal ions in wastewater with beneficial ones. In this method, a heavy metal ion is extracted from a wastewater solution by binding it to an immobile solid particle, serving as a substitute for the cation of the solid particle. The composition of these solid ion-exchange particles can be either natural, such as inorganic zeolites, or synthetic, like organic resins. Heavy metal ions such as Pb^{2+}, Hg^{2+}, Cd^{2+}, Ni^{2+}, V^{4+}, V^{5+}, Cr^{3+}, Cr^{4+}, Cu^{2+}, and Zn^{2+} can be effectively removed from wastewater through ion exchange [74]. Different types of ion exchange materials, including Diaion CR11 and Amberlite, have been investigated for cation removal. Zeolites, due to the negative charge generated by Si^{4+} at the center of the tetrahedron, with isomorphous replacement by Al^{3+} cations, exhibit a high capacity for ion exchange. The ion exchange mechanism for metal removal is explained by the reaction that occurs when an ion exchange particle, with an ion exchanger of $M{-}EC^{+}$ (where M^{-} is the fixed anion and EC^{+} is the exchange cation, commonly Na^{+} and H^{+}), exchanges its cation (EC^{+}) with the wastewater cation (WC^{+}) [66].

$$\text{M-EC}^{+}+\text{WC}^{+} \leftrightarrow \text{M-WC}^{+}+\text{EC}^{+} \qquad \text{Eq. 8}$$

Ion exchange techniques using materials like zeolites can help in removing heavy metal ions such as Pb, Cd, Ni, and Zn from wastewater. This method can be applied in regions of Gujarat where groundwater quality is affected by industrial activities and urbanization.

Electrodialysis

Electrodialysis (ED) is a versatile technology that can be used to treat acidic effluents which include metallic species. Its perpetual operation capability, scalability, and ease of operation can overcome most of the shortcomings of current technologies, and the direct reuse of concentrated metal streams eliminates the need for chemical addition and precipitation. The application of an electric field causes anions and cations to migrate across anion exchange membranes (AEM) and cation exchange membranes (CEM). The CEM attracts metallic cations because it is negatively charged, whereas the AEM attracts anions as it is positively charged. The electric field acts as a driving force for species migration, promoting or preventing migration, removal, and recovery [75]. Electrodialysis, although less commonly used, can be effective in treating acidic effluents containing metallic species like Cr, Cu, and Zn. This method can be suitable for targeted removal of specific heavy metals based on their ionic properties.

Phytoremediation

Phytoremediation represents a sustainable approach for cleansing polluted soils, sewage, sediments, and water containing various organic and inorganic pollutants. This eco-friendly and cost-effective strategy harnesses the unique capabilities of plant root systems, enabling the absorption and uptake of metals, as well as the translocation, bioaccumulation, and breakdown of contaminants throughout the plant body. Diverse techniques within phytoremediation, such as phytoextraction, phytofiltration, phytostabilization, phytovolatilization, phytodegradation, and rhizodegradation, are employed to address different types of pollution [65]. While phytoremediation is effective for shallow contamination, remediating metal-contaminated groundwater can be achieved through rhizofiltration, where plant biomass adsorbs pollutants. Phytoextraction involves the absorption of metals by crops, grasses, trees, and herbs from the soil. Phytostabilization, on the other hand, entails plants releasing elements to lower soil pH and form metal complexes. It is crucial to isolate these plants from agricultural and wildlife areas, considering factors like climate and metal bioavailability. Proper disposal methods, including drying, incineration, gasification, pyrolysis, acid extractions, anaerobic digestion, oil extraction, and plant chlorophyll fibre extraction, are necessary when plants become contaminated. For phytoremediation to be effective, it is recommended for polishing shallow soils with low contamination levels (2.5–100 mg/kg). Despite its advantages, the main drawback of phytoremediation is its time-intensive nature. Certain plants, such as Thlarpi, Urtica, Chenopodium, Polygonum rachalare, and Alyrrim, known for accumulating cadmium, copper, lead, nickel, and zinc, can serve as indirect agents for treating contaminated soils and aquifers [76]. Phytoremediation techniques, can be explored in Gujarat's main agricultural areas or near water bodies where plants can naturally uptake heavy metals from the soil and water, contributing to environmental sustainability. Especially rhizofiltration and phytoextraction, can be beneficial in areas where heavy metals like Cd, Cu, Pb, Ni, and Zn have contaminated soils and groundwater. Specific plant species known for their metal-accumulating properties can be utilized for remediation purposes.

CONCLUSION

Groundwater serves as a crucial resource for drinking, agriculture, and industrial purposes in Gujarat. However, the escalating heavy metal pollution poses a significant threat to its quality and, consequently, public health. Both human activities such as mining, agriculture, and industry, as well as natural processes like weathering and volcanic eruptions, contribute to this contamination. Assessing heavy metal pollution through indices like HPI, HEI, C_d, MI, and WPI is essential for evaluating water quality. In Gujarat, common heavy metal contaminants include cobalt, lead, mercury, and copper. Research indicates that dry seasons in the Bhavnagar region exhibit higher levels of heavy metals due to human activities. Seasonal variations are observed in the Kachchh mangrove region, with elevated concentrations before the monsoon. The AIE, Mahi River, and Tapi River are heavily contaminated with mercury, rendering the water unsuitable for consumption. Direct industrial effluent discharge contributes to lead pollution, particularly in the Sabarmati River, Kharicut Canal, Tapi River, Vadodara, and Chhota Udaipur districts. The ecosystem of the Tapi River and Mahi River estuary bears evident signs of mercury contamination, indicating severe pollution from human activities. Various methods for reducing heavy metal pollution have been discussed, emphasizing the importance of tailored approaches to specific contaminants and environmental conditions. Implementing environmentally friendly and cost-effective remediation methods is crucial to mitigate health risks and safeguard groundwater quality in Gujarat. Long-term solutions must be prioritized to address this pressing issue effectively.

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DATA AVAILABILITY STATEMENT

The author confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

USE OF AI FOR WRITING ASSISTANCE

Not declared.

ETHICS

There are no ethical issues with the publication of this manuscript.

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