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Heavy Metal Identification in Water Resources and the Surrounding Environment of the Cirasea Riparian Zone, Indonesia

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Abstract: *The Cirasea River can provide water for both the Bandung basin and agricultural irrigation. Intensive agriculture, industry, and land use changes could have an impact on water quality. The purpose of this study is to look at the origins of heavy metals in riparian water resources. Heavy metal analysis was performed on 13 groundwater and river water samples. Heavy metals in water sources were compared with sediment and soil. The samples were analyzed for heavy metals using an AAS instrument. The research method employs statistical, geographical, and heavy metal pollution index (HPI). The HPI for river water was 131, whereas groundwater was 93. River water with an HPI value of more than 100 is highly polluted, indicating that it is unsafe for human consumption and has negative health consequences. Data verification with heavy metals in sediments reveals the presence of heavy metals coming from geogenic circumstances in various locations in the upstream area. Heavy metals in downstream areas result from geological factors and anthropogenic activities in the surrounding area. The long-term effects of heavy metal pollution along the riparian zone will become apparent. More research is needed on communities that depend on groundwater supplies along the Cirasea watershed.*

Keywords: *heavy metals; geogenic; anthropogenic; river water; groundwater*

■ INTRODUCTION

The riparian zone refers to the transitional area between land and river. The existence of similarities between terrestrial and aquatic environments is significant in enhancing biodiversity among biota [1]. These areas play a crucial role in preventing or managing stream bank erosion, offering habitat for wildlife, and mitigating water pollution throughout the entire ecosystem. The presence of water and fertilizers has a crucial role in sustaining substantial plant populations within riparian ecosystems. They typically form clusters and have a higher density, characterized by fast growth and increased levels or strata. The riparian system exhibits a widespread distribution of heavy metals in its water body, soils, and sediments [2]. The increase of heavy metals in the environment can be ascribed to the rapid growth of agricultural and urban areas [3].

Groundwater is considered the largest source of drinking and irrigation purposes water for most of the lower-middle-income and developing countries [4]. The issue of contamination in aquatic systems has emerged as a significant global concern in recent years. Triggered by the economic growth of the past decades and the continuing population growth and urbanization, the pressures on the aquatic water systems in Indonesia are increasing in the highly urbanized areas, affecting both the freshwater systems and the groundwater systems [5]. Heavy metals, as a result of agricultural practices, are a major cause of deterioration in water quality [6]. Wastewater pollution loads were determined from domestic municipal, industrial, and agricultural sources [7].

Water has key responsibilities in acting as a transporter and medium for the dispersion and modification of heavy metals. The possible influence of heavy metals on the aquatic environment and pollution levels can be inferred by examining the distribution features of these metals in different environmental media [8]. The distribution of heavy metals in aquatic ecosystems can be influenced by various factors, such as rock weathering, changes in water flow patterns, disturbance of sediments on the seafloor, soil erosion, runoff from terrestrial areas, sewage discharge, leaching of agricultural chemicals, and the release of industrial wastewater [9-10]. Increased heavy metal levels in water sources, including surface and groundwater, reduce the overall quality of water used for agriculture and drinking. This river has become contaminated over the past decade due to extensive human activities in its watershed region [11-13].

The Cirasea riparian zone, as one of the Citarum Rivers upstream, serves as a crucial water source for the residents of West Java. This river is the primary water source for a variety of activities, including irrigation, and it meets the natural water requirements for domestic and industrial purposes [14]. Cirasea River can support agricultural needs, primarily agricultural land in Ciparay, Ibun, Kertasari, Majalaya, Pacet, and Paseh Districts [15]. Multiple research studies conducted in the upper area of the Citarum watershed are polluted by heavy metals such as Pb, Hg, As, Cr, Cu, Cd, Zn, Ni, Fe, and Mn [16-24]. Geogenic sources may influence the presence of heavy metals in the upper Citarum watershed, in addition to anthropogenic sources (e.g., agriculture, domestic, and industrial activities). In addition, it should be noted that the upper region of the Citarum River receives an above-average amount of precipitation [10,25-26], which has the potential to facilitate the dissolution of various chemical substances, including heavy metals, into the water resources. This study aims to investigate the origins of heavy metals in the groundwater of the riparian zone. This study serves as a supplementary investigation to prior studies, specifically examining the river water and groundwater inside the Cirasea riparian area at more precise geographical points. The findings derived from the study on the accumulation of heavy metal concentrations in the riparian hold significant value in informing future conservation strategies.

■ EXPERIMENTAL SECTION

Study Area

This study was conducted in the Cirasea riparian zone, part of the Citarum watershed in West Java, Indonesia (Fig. 1). Geographically, the study area was located at 107°38'30" to 107°45'30" E and 7°02'30" to 7°12'30" S with a total area of 3.95 km^2. The altitudes ranged between 674 to 1,562 m above sea level. The majority of the Bandung Regency is characterized by its mountainous terrain and tropical climate, which experienced an annual precipitation of 1,679 mm in 2022. Land use in this area consisted of secondary forest (12%),

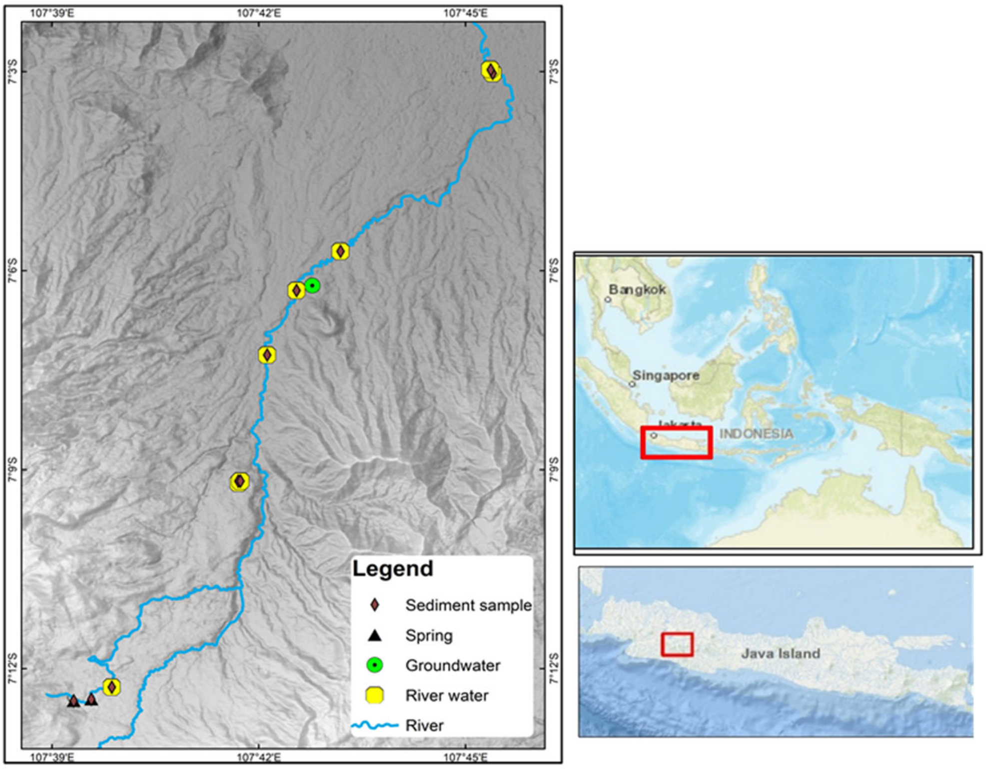


Fig 1. Research location in the Cirasea riparian zone

upland agriculture (84%), and paddy fields (4%) [27]. The Cirasea River is classified as a sub-catchment of the Citarum River system, specifically located in the Bandung Regency. The geographical feature in the northern region is Mount Tangkuban Perahu. The eastern region comprises Mount Munggang and Mandalawangi. The southern region comprises several prominent mountains, namely Mount Malabar, Puncak Besar, Puntang, Haruman, Mount Tilu, Mount Wayang, and Mount Windu. The western section exhibits irregular mountain ridges [28]. The Cirasea watershed encompasses six districts, namely Ciparay, Ibun, Kertasari, Majalaya, Pacet, and Paseh Districts [29].

The geological conditions within the study region encompass The Beser Formation (Tmb) is the earliest geological stratum during the late Miocene epoch, characterized by the presence of tuffaceous breccias, lava, andesite, and basalt. The Quaternary volcanic rocks are found to overlie the Tertiary volcanic rocks. The Pleistocene-aged Qopu volcanic deposits are characterized by the presence of fine-coarse crystalline tuff, dacite, tuff breccia containing aged pumice, and andesite lava layers that have undergone unraveling over time. The most recently formed rock unit is comprised of lake deposits (Qd) that can be attributed to the Holocene epoch [30]. The geological description can be observed in Fig. 2.

Materials

The method employed in this work involves the administration of a survey, the selection of a representative sample, the quantification of water quality parameters, and the interpretation of the collected data through the utilization of descriptive and correlation statistics. For heavy metal analysis, samples were taken from thirteen different water sources, including three springs, two dug wells and eight river waters. Following that, the results of heavy metals in the water sources were compared with the values of heavy metals in the sediment and soil. Sampling from dug wells and springs attempts to acquire fundamental information on human activities in addition to geological elements. The purpose of river water sampling is to acquire information about anthropogenic influences on water sources, which include a variety of pollutant inputs.

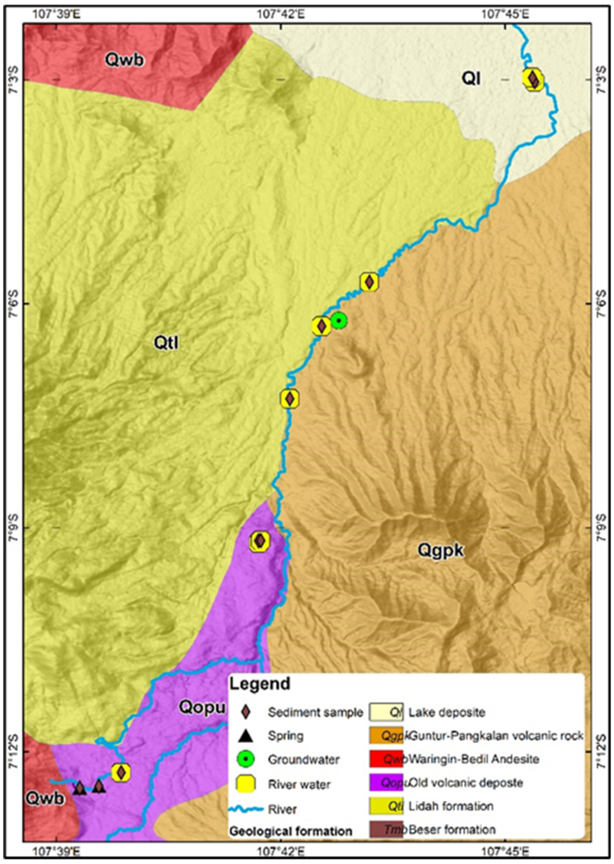


Fig 2. Geological condition in the Cirasea riparian zone (modification from Bachri et al. [30])

Instrumentation

The water sampling procedure involved the utilization of the Yieryi water checker pen test and a digital pH meter tester. The instruments are employed for the assessment of in-situ parameters, including temperature, pH, electrical conductivity (EC), total dissolved solids (TDS), and oxidation-reduction potential (ORP). The heavy metal characteristics (Pb, Cd, Cu, Fe, Mn) were analyzed in the laboratory of the National Research and Innovation Agency (BRIN) using an atomic absorption spectrophotometric (AAS) instrument, namely the Shimadzu AA 7000.

Procedure

The collection of data relevant to groundwater samples and the evaluation of the physicochemical parameters of groundwater in the designated area included the taking of pH, EC, and temperature readings, respectively. The Yieryi water checker pen test and a digital pH meter tester were utilized to carry out these measurements. The water samples were placed into a 500 mL plastic bottle that had been rinsed with water from the well, collected, and stored. Prior to analysis by AAS, the water samples underwent filtration utilizing Whatman filter paper number 41. Regarding solid materials, namely sediments, the process of sample preparation was conducted in accordance with the procedures outlined in SNI 8910-2021, employing the acid digestion method [31].

Data verification

Sediment and soil sampling were performed as a step to verify the results from the analysis of groundwater and river water samples. Sediment sampling was conducted via a grab sampler. The sediment samples were placed inside plastic ziplock bags. The samples were promptly placed in a refrigerated container at 4 °C. The sediment samples were extracted by combining 10 g of desiccated sediment samples with 30 mL of aqua regia in a beaker, which was then covered with a watch glass. The sample was subjected to heat over a water bath for approximately 8 h until it was removed [32]. The strained sample was transferred into a volumetric flask and combined with a 10% HNO_3 solution until the total volume reached 50 mL. The obtained extraction results were transferred into vials and subsequently subjected to analysis using AAS.

Statistical analysis

A multivariate statistical analysis was used in the study to evaluate the variables that influence the geographical characteristics of critical components. The Pearson method was extensively used to establish correlations between several geochemical indicators. A coefficient (r) larger than 0.7 indicates a substantial association, according to [33]. Coefficients between 0.5 and 0.7 are thought to indicate a moderate correlation, whereas coefficients less than 0.3 indicate a weak link. The principal component analysis (PCA) was used in the study conducted by Rakotondrabe et al. [34] to streamline huge geochemical data sets, permitting the identification of previously unnoticed differences through the extraction of numerous components. Several approaches were used to evaluate seasonal quality to clarify the underlying causes contributing to changes in mineral concentration within groundwater. The SPSS Version 26 program was used for statistical analysis.

The heavy metal pollution index for water

The heavy metal pollution index (HPI) is a quantitative evaluation instrument utilized to measure the collective influence of distinct heavy metals on the overall quality of [35-38]. The equations below represent the expression of the HPI, as denoted by Eq. (1–5).

$$\mathrm{HPI} = \frac{\sum_{i=1}^{n} W_i \times Q_i}{\sum_{i=1}^{n} W_i} \qquad (1)$$

$$Q_i = \sum_{i=1}^{n} 100 \times \left(\frac{M_i - I_i}{S_i - I_i} \right) \qquad (2)$$

$$W_i = \frac{K}{S_i} \qquad (3)$$

$$K = \frac{1}{\sum_{i=1}^{n} \frac{1}{S_i}} \qquad (4)$$

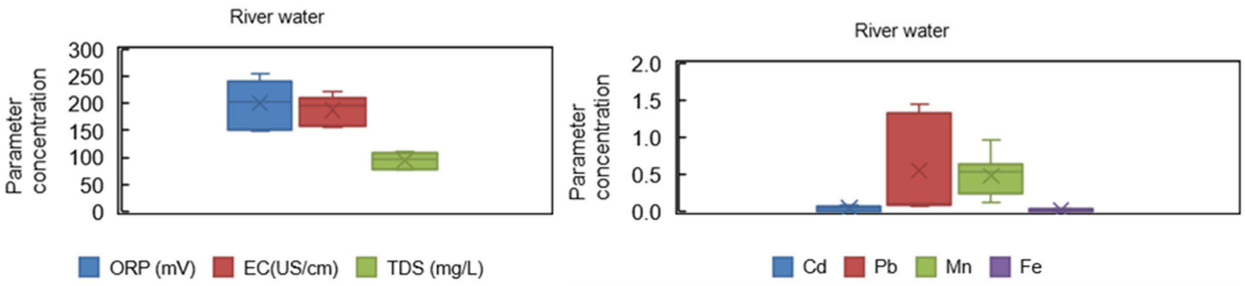
$$\sum_{i=1}^{n} \frac{1}{S_i} = \frac{1}{S_1} + \frac{1}{S_2} + \frac{1}{S_3} \cdots + \frac{1}{S_i} \qquad (5)$$

The weightage of a single heavy metal, denoted as W_i, is interesting in this context. Weights are allocated to individual heavy metals within the range of 0 to 1 based on the relative significance of these elements in relation to the established allowable limit for heavy metals in water. The sub-index Q_i represents a specific parameter of heavy metals. The proportionality constant K is utilized in the calculation of Q_i. S_i denotes the allowed limit for heavy metals in water, whereas S_1, S_2, S_3, and so on indicate the standards for various heavy metals in water, including Cd, Pb, Mn, Fe, Cu, Cr, and Hg. The symbol "I_i" denotes the theoretical or ideal value of specific heavy metals found in water. The optimal values (I_i) for the elements Cd, Pb, Mn, Fe, Cu, Cr, and Hg are reported as 0, 0, 0, 0, 0.05, 0, and 0, respectively, according to previous studies [39-41]. The HPI value can be categorized into three distinct groups based on pollution levels: low heavy metal pollution (< 100) and high heavy metal pollution (> 100) [42]. The value obtained is in accordance with the standard limit for the contamination of heavy metals in water as specified in the regulation of the Minister of Health of the Republic of Indonesia No 2/2023 [43].

■ RESULTS AND DISCUSSION

Natural materials that have been leached into the soil or rocks, residue from agrochemicals, controlled release from sewage, and industrial runoff are the primary anthropogenic sources of heavy metals in groundwater [4]. An alarming scenario has developed about the poisoning of the groundwater in the Cirasea River by an excessive amount of heavy metal. In the Cirasea riparian zone, measurements were taken of the characteristics and objects of both the groundwater and the surface water to determine the heavy metals present and to identify the sources. Fig. 3 displays box and whisker charts of various hydrogeological objects.

The physical and heavy metal parameters of the study region were compared to the guideline values indicated for drinking water and human consumption in Indonesia by the regulation of the Minister of Health of the Republic of Indonesia No 2/2023 [43]. Descriptive statistics are presented in Table 1. The mean values of the physical parameters EC and TDS in groundwater (213 µS/cm and 107 mg/L) are greater than the mean values of the physical parameters in river water (187 µS/cm and 94 mg/L). This condition is affected by



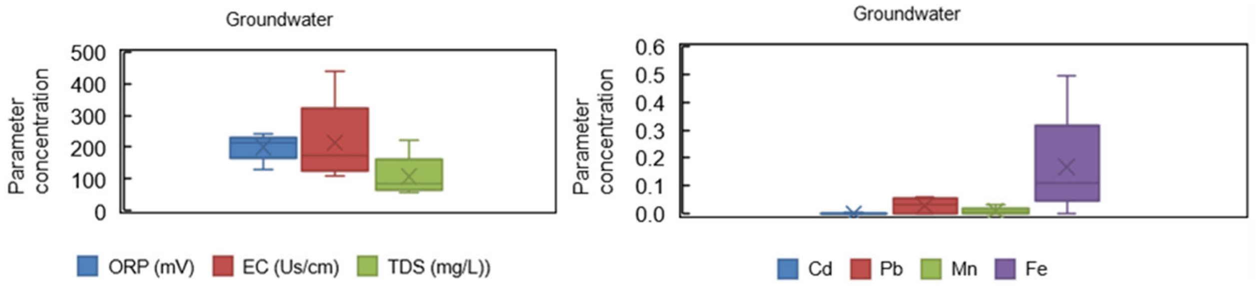


Fig 3. Box and whisker plots of the physical parameters from groundwater and river water (*TDS is mg/L; EC is μS/cm; ORP is mV; Cd, Pb, Mn, Fe, and Cu are mg/L)

Table 1. Summary statistics of analytical data of water resources in the Cirasea River

	Min		Max		Mean		Std. Deviation		Water Standard*
	GW	RW	GW	RW	GW	RW	GW	RW	
pH	6.380	7.070	7.800	7.910	7.070	7.550	0.540	6.380	6.000-9.000
T (°C)	20.500	23.500	28.100	28.000	23.520	25.150	2.750	20.500	
ORP (mV)	130.000	149.000	241.000	254.000	200.600	203.600	37.700	130.000	
EC (μS/cm)	111.000	156.000	441.000	221.000	213.000	187.000	118.000	111.000	
TDS (mg/L)	58.000	78.000	222.000	110.000	107.000	94.000	59.000	58.000	1000.000
Cd (mg/L)	0.000	0.000	0.004	0.003	0.001	0.001	0.002	0.001	0.010
Pb (mg/L)	0.000	0.000	0.063	0.073	0.028	0.030	0.025	0.031	0.030
Mn (mg/L)	0.000	0.069	0.031	1.447	0.009	0.557	0.011	0.537	0.100
Fe (mg/L)	0.000	0.110	0.496	0.953	0.168	0.429	0.170	0.282	0.300
Cu (mg/L)	0.000	0.000	0.021	0.026	0.012	0.012	0.009	0.012	0.020

Source: The result of in-situ measurement, 2023
GW: Groundwater, RW: River Water
*Water quality standard for drinking water in Indonesia (Ministry of Health of the Republic Indonesia Regulation No 2/2023)

the dilution factor in river water, which is higher than in groundwater. The dilution factor in groundwater is primarily linked to water infiltration into the well through rock pores; however, dilution in river water is impacted by seasonal variations and the river's flow rate. The parameter values for heavy metals in groundwater are lower than the values for heavy metals in river water. Heavy metal values in water fluctuate due to the presence of nearby pollution sources in the water source area.

Table 1 shows the concentration of heavy metals present in water resources (groundwater and river water) collected from different stations in sampling sites. The concentration of Mn was the highest in all water samples, with almost all the samples exceeding the maximum allowable limit and one of the samples having the highest concentration (1.447 mg/L). The concentration of Cr metal is still below the quality standard threshold in river water and groundwater. The highest concentration of metals in groundwater is Fe > Mn > Pb > Cu > Cr. Fe and Mn are important minerals for the body in appropriate amounts. Excess Fe and Mn can cause some side effects, such as digestive disorders, but are generally not as dangerous compared to toxic heavy metals such as Pb, Cu, Cr. Although Fe and Mn concentrations in groundwater are higher, they do not significantly affect health when compared to Pb, Cu, and Cr. Differences in concentrations in groundwater and river water are largely influenced by anthropogenic and geogenic processes in the surrounding environment (Table 1).

The Pearson Correlations Matrix

The Pearson correlations matrix for analyzing groundwater heavy metal parameters is presented in Table 2. Pearson correlation matrix analysis divides based on the type of water source, namely groundwater or river water.

Table 2. The Pearson correlations matrix in Cirasea riparian zone

The Pearson correlations of groundwater										
	pH	Temp	ORP	EC	TDS	Cd	Pb	Mn	Fe	Cu
pH	1.000									
Temp	−0.587	1.000								
ORP	**−0.748**	0.494	1.000							
EC	−0.643	**0.891***	0.388	1.000						
TDS	−0.632	**0.884***	0.365	**1.000****	1.000					
Cd	0.096	**−0.794**	−0.398	−0.573	−0.564	1.000				
Pb	0.658	**−0.891***	**−0.805**	−0.695	−0.678	**0.790**	1.000			
Mn	−0.575	**0.734**	0.119	**0.938***	**0.945***	−0.311	−0.429	1.000		
Fe	0.595	−0.383	**−0.972****	−0.292	−0.268	0.418	**0.730**	0.002	1.000	
Cu	0.585	**−0.922***	-0.590	−0.664	−0.652	**0.754**	**0.931***	−0.464	0.460	1.000
The Pearson correlations of river water										
	pH	Temp	ORP	EC	TDS	Cd	Pb	Mn	Fe	Cu
pH	1.000									
Temp	0.301	1.000								
ORP	0.092	−0.631	1.000							
EC	**−0.882****	−0.135	0.033	1.000						
TDS	**−0.930****	−0.205	0.030	**0.990****	1.000					
Cd	**−0.714***	−0.553	0.287	**0.782***	**0.777***	1.000				
Pb	**−0.740***	**−0.719***	0.470	0.542	0.622	0.634	1.000			
Mn	0.421	**0.833***	**−0.830***	−0.379	−0.431	−0.563	**−0.857****	1.000		
Fe	−0.417	−0.561	0.519	0.184	0.248	0.331	**0.858****	**−0.721***	1.000	
Cu	−0.591	**−0.721***	0.623	0.480	0.523	**0.704**	**0.932****	**−0.865****	**0.891****	1.000

**. Correlation is significant at the 0.01 level (2-tailed)

*. Correlation is significant at the 0.05 level (2-tailed)

(*Temp is °C, TDS is mg/L; EC is μS/cm; ORP is mV; Cd, Pb, Mn, Fe, and Cu are mg/L)

Pearson correlations highlight relationships between characteristics in groundwater and river water. Temperature has a substantial impact on EC, TDS, Cd, Pb, Mn, and Cu levels. Water temperature influences its suitability for various human and industrial applications, as well as the operation of aquatic ecosystems. The considerable association demonstrates that TDS, Pb, and Fe have a strong correlation. The ORP indicates whether a solution is more likely to undergo oxidative or reduction processes. Previous studies have demonstrated that pH is a critical driving force governing the distribution of heavy metals [44-45]. While it is not employed for the direct assessment of potable water, it plays a crucial role in governing the presence and behavior of many biological organisms and influencing the rate of their activities. Additionally, it exerts a significant impact on most chemical processes occurring within natural water systems and influences the solubility of gases [46]. The EC of water is closely associated with TDS, which is determined by the composition of dissolved cations and anions [47]. This relationship suggests that the presence of rock minerals in the water contributes to the geochemical characteristics of groundwater [48]. The ORP serves as a measure of the comparative inclination of a solution to undergo either an oxidation or reduction reaction. The ORP has the potential to impact the oxidation state of the chemical present in the solution [49].

In general, the correlation matrices of heavy metals in the water indicate a positive association for multiple elements. These findings indicate that the presence of heavy metals could be attributed to additional environmental elements, such as soil and garbage, in the riparian zone. Nevertheless, it is imperative to maintain ongoing monitoring of heavy metal levels in the water within the Cirasea riparian zone due to its utilization for active agriculture, domestic activities, and cattle farming. Furthermore, anticipated alterations in land utilization could result in a rise in the concentration of heavy metals within the river water.

PCA Results

The PCA loadings can be characterized as strong, moderate, or weak [49]. Table 3 presents the PC loadings and explains the variance for three components of groundwater and river water, illustrating the significance of each variable for each component. The PCA results for groundwater (Table 3) are grouped into a two-component model, which accounted for about 65.814% of all the data variation. In the rotated component matrix, the first principal component (PC1, variance of 65.814%) included EC, TDS, and Mn, while the second principal component (PC2, variance of 19.260%) is made up of ORP and iron. The PC2 could be considered a natural component because the variability of heavy metal concentration appeared to be products of the study area's lithology. The component matrix, Fe, and Mn are observed to have rotated component matrices of 0.924 and 0.987, respectively, which is more than TDS and EC. These parameters suggest that the distribution of Mn has a lithogenic origin, and therefore, these two heavy metals are included in PC1. The second factor (F2) suggests the distribution of ORP and Fe, which are indicative of geological origins or agrochemicals.

The PC loadings for the river water (Table 3), which accounted for 62.076% of all the data variation, heavy metals are grouped into the two-component model. In the rotated component matrix, the PC1 (variance of 62.076%) includes temperature, ORP, Pb, Mn, Fe, and Cu; the PC2 (variance of 23.815%) is made up of pH, EC, TDS, and Cd. The component matrix has been determined to be of natural lithogenic origin as well as anthropogenic origin from the surrounding riparian environment.

Compared to the groundwater, heavy metals are in close proximity to each other in river water. The plausible reason which can be assigned to this observation is the prevailing environmental conditions in the aquatic environment. A decrease in groundwater level and reduction in weathering and dissolution of minerals and ores present in the earth's crust can be assigned as contributing factors for such observations. In river water, dilution of heavy metals concentration, which accumulated from geogenic and anthropogenic.

Table 3. The PCA of groundwater and river water in the Cirasea riparian zone

Rotated component matrix			Rotated component matrix		
Groundwater	1	2	River water	1	2
pH	−0.628	0.747	pH	−0.181	−0.948
Temperature	0.662	−0.261	Temperature	−0.850	−0.136
ORP	0.104	−0.956	ORP	0.855	−0.148
EC	0.889	−0.192	EC	0.065	0.967
TDS	0.897	−0.169	TDS	0.118	0.977
Cd	−0.170	0.119	Cd	0.399	0.773
Pb	−0.360	0.617	Pb	0.777	0.559
Mn	0.987	0.026	Mn	−0.922	−0.286
Fe	0.037	0.924	Fe	0.820	0.198
Cu	−0.409	0.399	Cu	0.855	0.458
Total eigenvalues	6.581	1.926	Total eigenvalues	6.208	2.382
% of variance	65.814	19.260	% of variance	62.076	23.815
Cumulative %	65.814	85.074	Cumulative %	62.076	85.891
Extraction method: PCA Rotation method: Varimax with Kaiser normalization			Extraction method: PCA Rotation method: Varimax with Kaiser normalization		

These variables are indicative of geogenic and anthropogenic origins stemming from agricultural or household activities.

Validation Investigation of Heavy Metals in Sediment and Soil Surrounding Riparian Zone

Heavy metals in soil and sediment were analyzed to compare them and enhance the case for tracing the source of heavy metal pollution. A comparison of heavy metals in sediment was conducted to improve the basis for determining the source of heavy metal pollution in the Cirasea watershed's riparian area. To ensure the heavy metal in groundwater and river water analysis, validation of the interpretation results includes ten soil samples from the riparian Cirasea watershed. The ground-check points were selected through a purposive sampling method, considering the distribution and accessibility of locations (Fig. 4).

Cu concentrations in sediment and soil range from 27.000 to 53.000 mg/kg, with an average of 41.000 mg/kg, which is higher than the sediment threshold of 16.000 mg/kg. Geogenic conditions drive high Cu levels in sediment and soil in upstream areas, whereas geogenic and anthropogenic activities may influence high Cu values downstream. The heavy metal Pb concentration in sediment and soil ranges from 0.000 to 29.000 mg/kg, with an average value of 9.000 mg/L, which is lower than the sediment threshold value of 31.000 mg/kg. The Fe concentration in sediment and soil ranges from 3.128–60.104 mg/kg, with an average of 41.192 mg/kg, which exceeds the sediment threshold value of 20.000 mg/kg. Geogenic factors impact high Fe values in sediment and soil in upstream areas, whereas geogenic and anthropogenic activities can influence high Fe values downstream. The Mn concentration in sediment and soil ranges from 225.000 to 1.646 mg/kg,

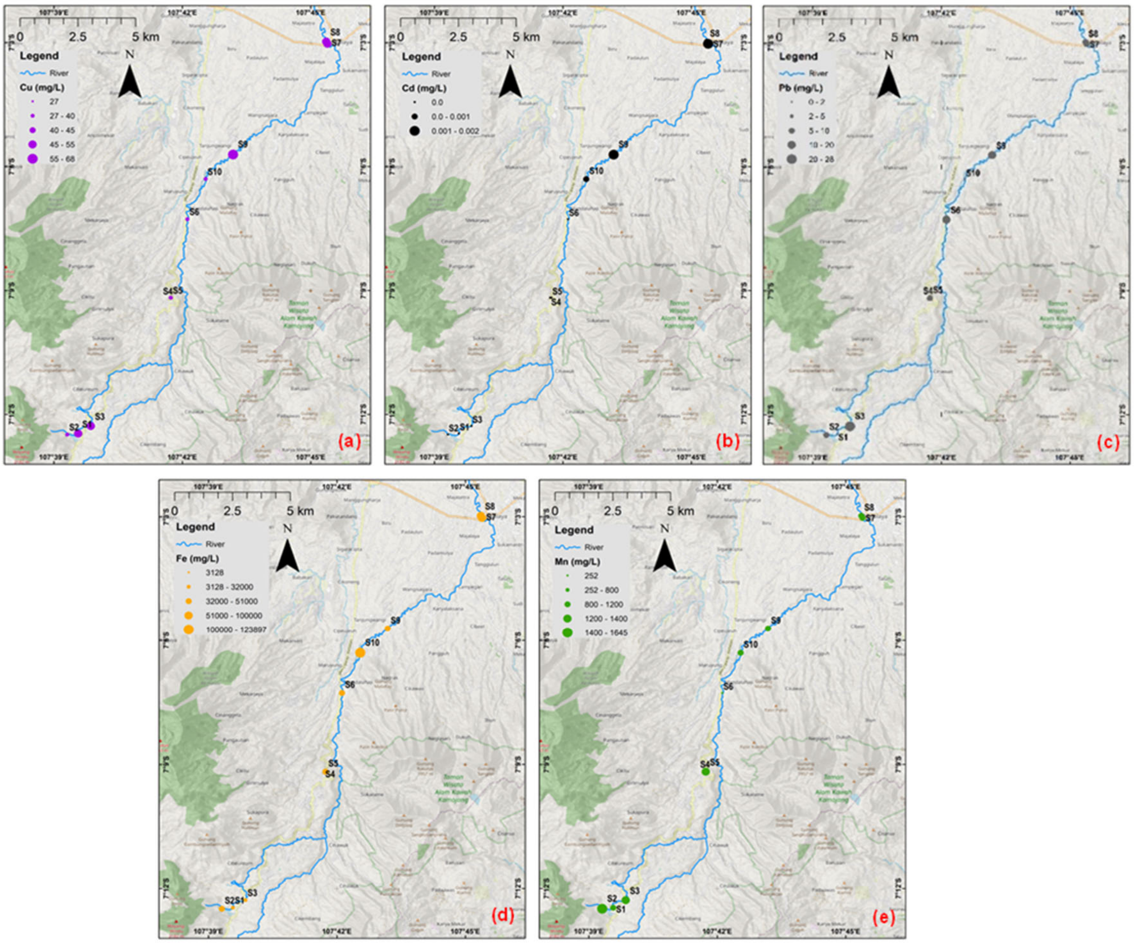


Fig 4. The spatial distribution of (a) Cu, (b) Cd, (c) Pb, (d) Fe, and (e) Mn from soil and sediment

with an average of 960.000 mg/kg, which is higher than the sediment threshold value of 460.000 mg/kg (Fig. 4).

According to the sediment and soil investigation results, some heavy metals have significant concentrations in the upstream area. Geogenic variables could have an impact on high heavy metal levels in sediment and soil in upstream environments. At the same time, geogenic and anthropogenic factors can also influence the high values of heavy metals downstream. This condition explains the way geogenic circumstances affect both groundwater and river water. The volcanic activity has already deposited heavy metals in the rocks in the upstream area.

Spatial Distribution of Heavy Metal in Groundwater and River Water

Spatial distribution is a geospatial technique used to turn attribute database values associated with a collection of points into a surface map [50]. Spatial distribution methods are a valuable tool in the development of maps, as they offer crucial information that is relevant for decision-makers [51]. This map visually represents the spatial variation of heavy metal in the Cirasea riparian zone. Concentrations of heavy metals varied in the groundwater and river water in the study area. They were generally higher than the maximum allowable by the national standards for Mn, Fe, and Pb (Fig. 5).

The findings of this research show that Cu concentrations fluctuate both upstream and downstream. Groundwater (G1 and G2) tends to be higher upstream due to geogenic circumstances of volcanic rock mineralization. In contrast, rivers have a lower Cu value than groundwater due to a dissolving process that has produced a ratio of G1 and G2 > R1 (Fig. 4(a)). The average Cu concentration in all collected

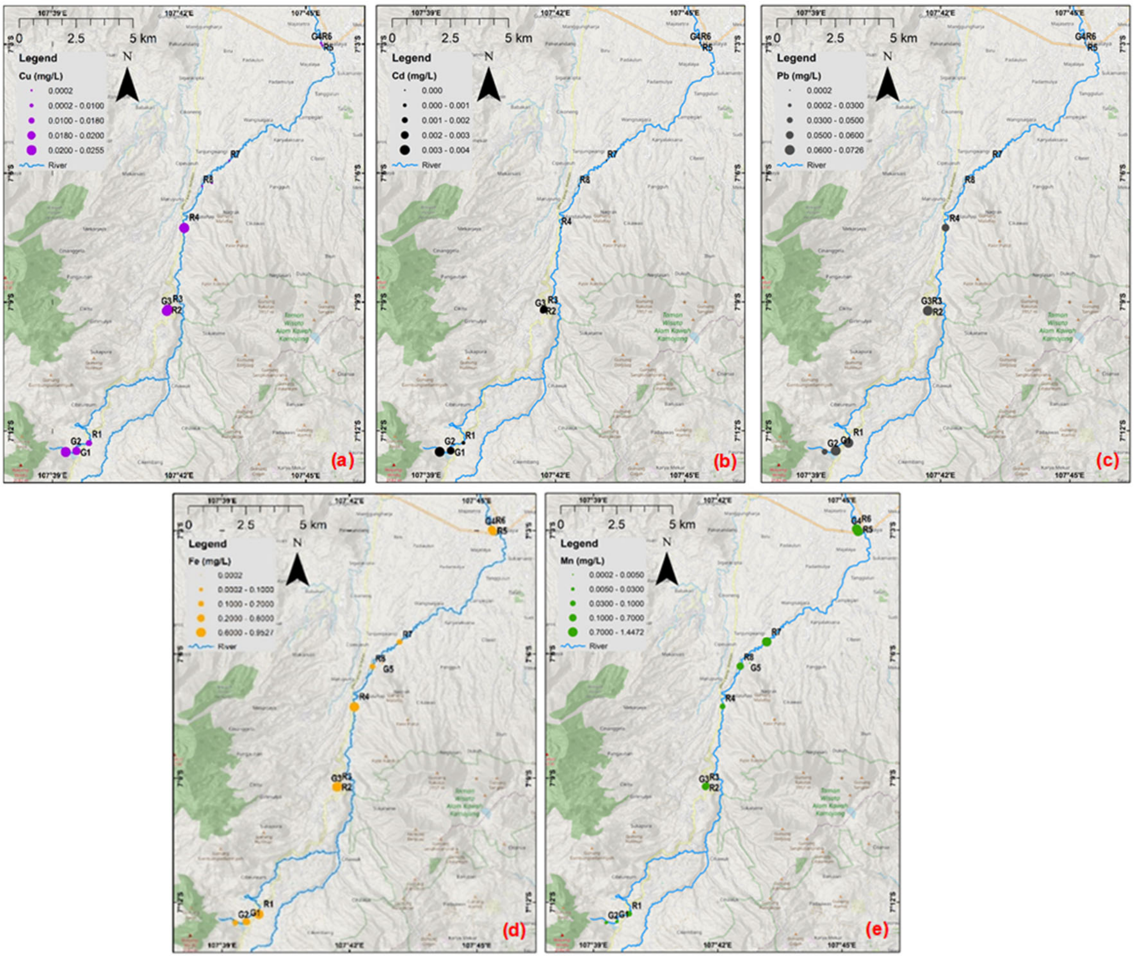


Fig 5. The spatial distribution of (a) Cu, (b) Cd, (c) Pb, (d) Fe, and (e) Mn from groundwater and river water

samples was below the guideline limits set by the WHO standard of 0.05 mg/L [52]. However, it exceeded the water quality standard (0.02 mg/L) standard [53]. The anthropogenic sources of Cu in agricultural soils are Cu-based agrochemicals and phosphate fertilizers [54]. Cu can originate from the discharge of agricultural activities and the waste produced by cattle [55]. Nevertheless, it appears that residential activities, traffic, and mechanical workshops are responsible for elevated levels of Cu emissions [56]. The presence of Cu is a significant risk as it can lead to irritation of the mucosal lining, aggravation of the central nervous system, and damage to the liver and kidneys.

The Cd value in groundwater ranges between 0–0.004 mg/L, while the Cd value in river water ranges between 0–0.003 mg/L (Fig. 5(b)), under the maximum allowable value (0.01 mg/L) of regulation of the Minister of Health of the Republic of Indonesia No 2/2023 [43]. The coordinates of G4, R5, and R7 correspond to rural and suburban areas, which serve as the initial sites for the textile industry, agriculture, and farming. The textile sector is widely regarded as the primary contributor of Cd. The main sources of Cd in the natural processes are atmosphere degradation and the earth's crust [57]. Cd in groundwater is typically caused by industrial wastes as well as pesticides or fertilizers. Cd is a highly mobile heavy metal that can be rapidly transferred from soil to water and other environments [58-60]. Cd was correlated with Fe, Mn, and Cu, implying that Cd in groundwater is derived not only from natural surrounding rock minerals but also from anthropogenic sources such as the use of agricultural fertilizer, particularly phosphate fertilizer.

Pb assessments in river water range from 0.00 to 0.07 mg/L, whereas those in groundwater range from 0.00 to 0.06 mg/L (Fig. 5(c)). The Pb value exceeds the maximum permitted amount (0.03 mg/L) under the regulation of the Minister of Health of the Republic of Indonesia No 2/2023 [43]. The investigation's findings suggest that the Pb contents upstream reflect the differing conditions of groundwater and river water. Pb in the groundwater (G1 < G2) tends to be more abundant upstream because of the geogenic conditions that lead to the mineralization of volcanic rock. In contrast, Pb in the rivers has a high value in R1, and this condition is impacted by the process of dissolving minerals from sediment or soil that contain high Pb elements (Fig. 4(a)). Validation of Pb sources with results in sediment or soil indicates that it derives from geogenic activity.

Furthermore, the observed positive correlation between Pb, Cu, and Fe depicted in Table 2 suggests that the entry of Pb into groundwater may be attributed to the geogenic reaction, as discussed by Soltani-Gerdefaramarzi et al. [61]. The increase in Pb concentration in groundwater is primarily attributed to anthropogenic activities, as evidenced by studies conducted by previous studies [8,62]. However, the occurrence of Pb was seen to escalate in agricultural regions characterized by elevated amounts of Pb. Hence, it may be inferred that agricultural practices are a probable source of elevated levels of Pb, as indicated in Table 3.

The findings of this study revealed that the Fe concentration in river water downstream was observed to be greater than that of groundwater (see Fig. 5(d)). Moreover, it was observed that the Mn concentration exceeded the maximum permissible value of 0.3 mg/L, as stipulated by regulation of the Minister of Health of the Republic of Indonesia No 2/2023 [43]. The elevation of Fe in groundwater mostly arises from both natural geological processes (geogenic) and human-induced activities (anthropogenic), as evidenced by the findings of studies conducted by Okereafor et al [53].

Sediments from Bandung Lake and volcanic activity are the sources of the high Fe value. The weathering of volcanic rock causes an oxidation-reduction reaction that increases the soil's Fe value. One of the reasons for high Fe concentrations in groundwater and river water is the dissolution of rock minerals. Fe was more responsive to the decreasing environment than Mn in groundwater. However, when the groundwater environment was sufficiently reductive, the concentration of organic matter and the residence duration in groundwater may have played an essential role in the release of Fe in sediment [60].

According to the findings of this study, the Mn concentration in downstream river water was higher than in groundwater (Fig. 4(e)), exceeding the maximum allowable value (0.1 mg/L) specified in the regulation of the Minister of Health of the Republic of Indonesia No 2/2023 [43]. According to research conducted by Okereafor et al [53], the rise in Mn concentration in groundwater is mostly caused by geogenic and anthropogenic activities. Furthermore, the moderate association shown in Table 2 between temperature, ORP, Cd, and Cu implies that geogenic and anthropogenic processes may generate Pb influx into groundwater. Fe and Mn were sensitive to redox potential; in a reducing environment, organic matter concentration and water residence time also influence the release of Fe from Fe-bearing minerals. One of the most prevalent metals in the crust of the earth is Mn, which typically occurs in combination with Fe. For humans and other animals, Mn is a necessary element that can be found naturally in various food sources. The most significant source of Mn for drinking water is found naturally in various surface and groundwater sources, especially under anaerobic or low-oxygen circumstances [51].

Relationship of Heavy Metal Concentrations in River Water, Groundwater, and Sediment

Based on the concentration of heavy metals, there was a positive and negative relationship between every heavy metal (Fig. 6). There is a positive correlation between the metals Fe and Pb and a negative correlation between Mn, Cu, and Cd. A positive correlation indicates that while the concentration of heavy metals in the water increases, it also raises the concentration of heavy metals in the sediment. A negative correlation means that while the metal content in the water increases, the metal concentration in the sediment decreases, and vice versa.

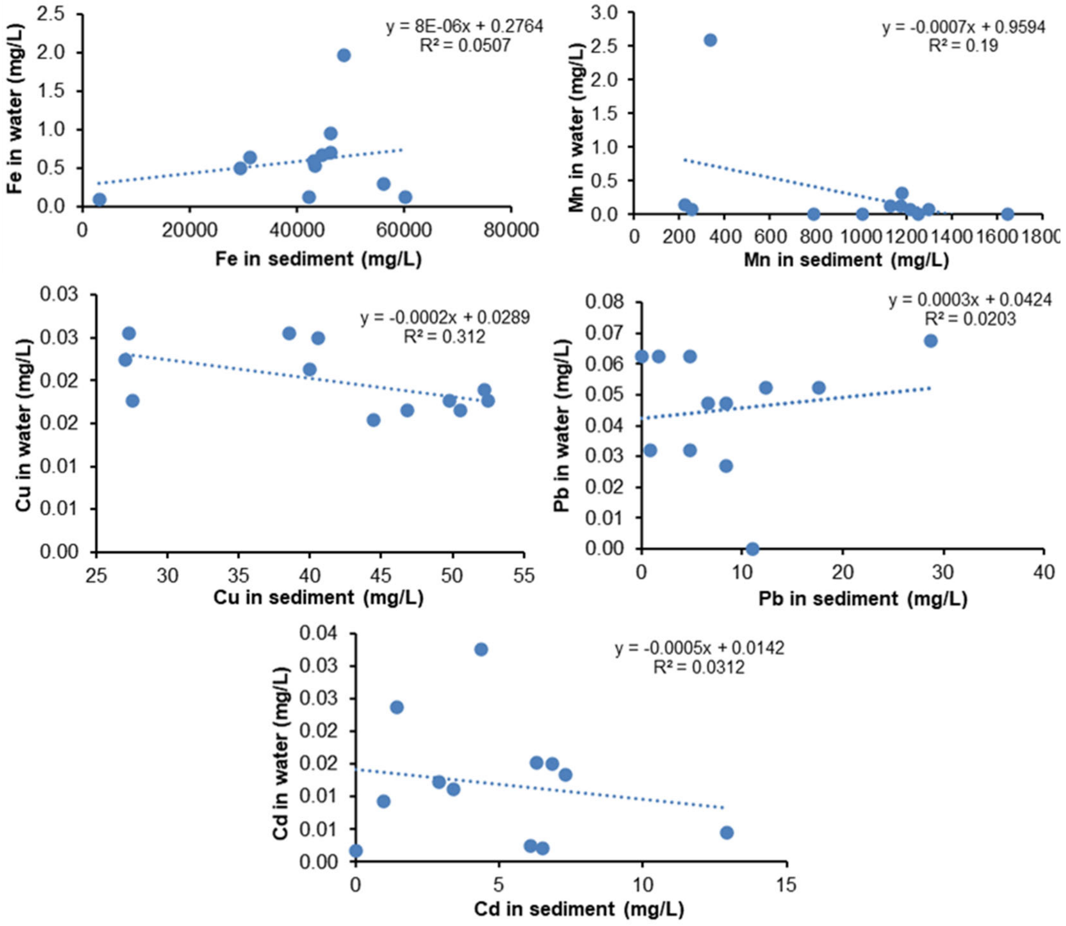


Fig 6. Relationship of heavy metal concentrations in river water, groundwater, and sediment

Geogenic activity in mountainous areas upstream of the Cirasea watershed will eliminate fresh mineral surfaces and substantial quantities of either soil or rock traces, accelerating weathering processes. Fe, Mn, Cu, Cd, and Pb are examples of related metals that can be released into the environment as a result of changes in physicochemical conditions in the secondary mineral phase. Generally, heavy metal levels in surface sediments are higher than in river water due to processing, dilution, and precipitation, resulting in accumulation. Heavy metals bind organic matter, settle at the bottom of rivers and streams, and mix with sediment, resulting in higher levels of heavy metals in sediment than in water. Heavy metals that settle in riparian and surrounding areas will accumulate in sediment in greater proportions than those found in rivers and groundwater. Heavy metals that infiltrate water bodies will deposit, dilute, and diffuse in the riparian ecosystem. Understanding these processes is critical to regulating and mitigating the effects of heavy metal contamination in riparian areas.

Source Identification in Groundwater of the Cirasea Riparian Zone

The findings of the Pearson correlation matrix, PCA, in conjunction with the validation of heavy metals in sediment and soil, determine conditions that are linked to the source of pollution in the riparian zone; this includes both geogenic and anthropogenic. The component matrix has been identified to be both natural lithogenic and anthropogenic in origin, derived from the adjacent riparian environment. Heavy metals are more concentrated in river water than in groundwater. The most plausible explanation for this discovery is the current environmental conditions in the aquatic habitat. Such observations can be attributed to a decrease in groundwater level and a reduction in the weathering and dissolving of minerals and ores found in the earth's crust. Heavy metal concentrations in river water are diluted due to geological and anthropogenic accumulation. These characteristics are indicative of geogenic and human causes resulting from agricultural or domestic processes.

The HPI for Water

Table 4 presents the values of the HPI for samples of river water and groundwater. According to Matta et al. [63], if the HPI value is above 100, it signifies that the water is not safe for ingestion due to its propensity to have negative effects on human health. The findings are displayed in Table 4. The results indicate that the Cirasea River exhibits significant contamination by heavy metals, with potentially detrimental effects on both human populations and other organisms. The HPI value of the river water at sample sites R5 – R8 surpasses the crucial threshold of 100. The findings suggest that the water from the river at that particular site is not suitable for human consumption. Approximately 50% of the test locations exhibited low contamination levels of heavy metal. The calculated average HPI score suggests a high level of pollution in the river water. According to the data presented in Table 4, it can be observed that all of the groundwater samples (40%) exhibited high pollution, as indicated by the HPI value over 100. The HPI for groundwater demonstrated a wide spectrum,

Table 4. Heavy metals pollution index of the river and groundwater in the Cirasea riparian zone

Sampling site code	HPI value	Description
Groundwater		
G1	77	Low polluted
G2	72	Low polluted
G3	48	Low polluted
G4	137	Highly polluted
G5	132	Highly polluted
Mean overall	93	Low polluted
River water		
R1	76	Low polluted
R2	82	Low polluted
R3	67	Low polluted
R4	61	Low polluted
R5	232	Highly polluted
R6	180	Highly polluted
R7	201	Highly polluted
R8	145	Highly polluted
Mean overall	131	Highly polluted

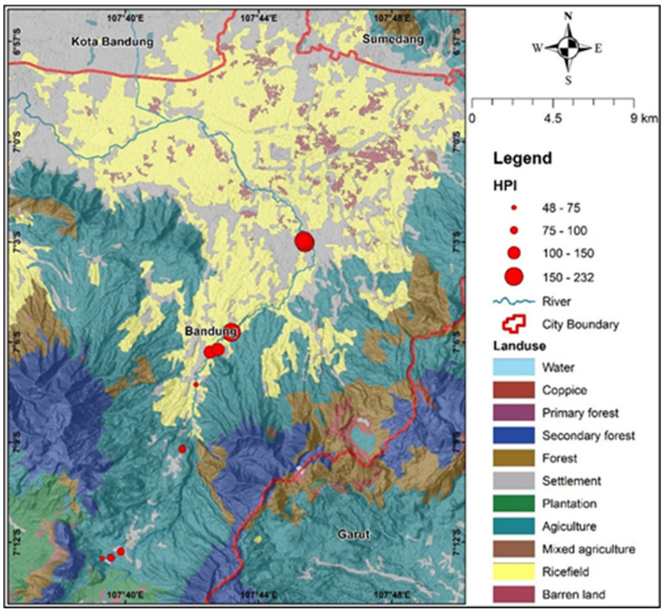


Fig 7. The HPI in Cirasea watershed

ranging from 48 to 137, with a mean value of 93. The results indicated that the groundwater was deemed suitable for human consumption. The site with the greatest HPI value was identified as R5. The presence of Mn, Fe, Pb, Cu, and Cd significantly contributes to the highest possible HPI value seen in groundwater. According to the assessment, the downstream region has the greatest HPI values. The pollution load in the Cirasea River basin is increased as a result of the influence of agricultural inputs obtained from both industrial and residential sources. The HPI, as well as a description of the land uses, can be seen in Fig. 7. The presence of domestic and industrial effluents originating from the upper stream region has an impact on the concentration of heavy metal at the sampling site G4. Heavy metals are present almost everywhere.

■ CONCLUSION

The findings of the analysis detailed the origin of contamination in the riparian zone, arising from both geogenic and anthropogenic sources. The EC, ORP, and Mn are associated with the parent material or geogenic sources, such as natural sources like earth crust material. The Cd, Pb, Cu, and Fe are possibly from anthropogenic sources such as households, active agriculture, cattle farms, and industry. Cu metal derived from anthropogenic sources primarily originates from households and pesticides employed in agricultural practices. The introduction of Cd has been seen to mostly stem from the use of fertilizers and the application of cattle farms. Fe and Mn concentrations were often greater in sediment, showing that geologic conditions had a significant impact on Fe and Mn concentrations in groundwater. The upstream section of the Cirasea River exhibits a significantly greater concentration of heavy metals in its sediment compared to the downstream region. The reason for this phenomenon can be attributed to the high level of agricultural activity in the upstream region, which leads to the transportation of heavy metals from agricultural areas to riparian areas. The long-term persistence of heavy metals in sediment can be observed even in the absence of the contamination source. HPI value for river water indicated that the Cirasea river water was low to highly polluted with heavy metals. According to HPI, river water is unsafe for human consumption; however, groundwater is suitable for human consumption. The long-term effects of heavy metal pollution on the ecology in the riparian zone will become apparent. Additional investigation is required to assess the ecological consequences of high levels of heavy metal contamination on communities residing in the riparian region of the Cirasea watershed, who rely on groundwater supplies.

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■ CONFLICT OF INTEREST

All other authors declare they have no conflicts of interest related to this work to disclose.

■ AUTHOR CONTRIBUTIONS

Rizka Maria, Eki Naidania Dida, Adie Taufiqurrahman, Muhammad Rio Ferdiano, and Detizca Melia Nugraha experimented. Rizka Maria and

Ratna Dwi Puji Astuti conducted the calculations, Heri Nurohman conducted the spatial distribution. Rizka Maria, Anna Fadliah Rusydi, Dyah Marganingrum, Asep Mulyono, Retno Damayanti, Riostantieka Mayandhari Shoedarto, and Yudi Rahayudin made the concept, wrote, and revised the manuscript. All authors agreed to the final version of this manuscript.

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