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ASSESSMENT OF CONTAMINATION LEVEL AND SOURCE APPORTIONMENT OF HEAVY METALS IN SERAYU RIVER WATER, INDONESIA

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Abstract

Diverse community activities along the river can alter water quality, particularly heavy metal pollution, which can negatively affect public health. This study examines the contamination and distribution of heavy metal sources in the Serayu River, one of the longest and largest rivers in Central Java Province in Indonesia. Along the Serayu River, water samples were obtained from 18 distinct sampling points. Heavy metals content in water samples was measured for lead, cadmium, chromium, nickel, arsenic, cobalt, iron and manganese. Pb, Cr and Ni Concentrations have surpassed government rule No. 22 of 2021 regarding quality criteria in several locations. The contamination factor (CF) determines the level of heavy metal pollution in the Serayu River. The average value of CF, from highest to lowest, is as follows: Pb (2.03); Ni (0.24); Cr (0.24); Fe (0.21); Mn (0.10); Co (0.04); Cd (0.04); As (0.02). The modified degree of contamination (MCD) suggests that the bulk of river water falls into moderate contamination. Agricultural practices in the upper reaches of the Serayu River are regarded as the primary source of surpassing the quality level. Multivariate statistical analyses, namely principal component analysis (PCA), pearson correlation matrix and cluster analysis (CA), revealed that most heavy metals originated from various human activities. Pb, Cr and Ni were primarily derived from agricultural activities, whereas Cd, Co and Mn were primarily derived from industrial, agricultural, settlements and tourism. As and Fe are primarily derived from mining. The alternative recommendation for contamination recovery is the application of biochar which is economically affordable material to be applied in the river.

***Keywords**: Heavy metal; River; Water contamination; Indonesia*

Introduction

Water is a precious natural resource since it can regulate an ecosystem, preserve environmental quality, and support life [1]. Water that humans can consume is fresh water in tiny amounts. Fresh water that is accessible to humans generally comes from a primary source such as rivers, lakes, and aquifers. Still, these freshwater sources are only about 0.26% of global ones. Other sources are challenging to reach by humans because they are locked in glaciers, ice sheets, or deep groundwater [2].

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One of the sources of freshwater that the community may acquire and use is river water. Hence, river water pollution has become a global issue [3], especially river water pollution due to heavy metal concentrations [4]. Both non-essential and essential metals are found in heavy metals; however, non-essential metals are harmful and have no positive effects on human health. In contrast, essential metals benefit living things to a certain extent [5, 6].

This contamination enters the human body and causes various diseases such as cardiovascular disease [7], obesity [8], lung cancer [9], gastric [10], breast [11], kidney [12], thyroid [13] and other serious diseases. Several activities in the river's vicinity are responsible for the presence of heavy metals in the water, including the existence of various industrial activities around the river [14], agricultural activities in the vicinity that use agrochemicals intensively [15] and mining activities around the river [16], livestock activities [17] and domestic waste discharged into rivers [18].

Currently, many rivers in Indonesia are contaminated with heavy metals and it is expected in the Serayu River. Several rivers that have been indicated to be contaminated with heavy metals include the Lowatag River in Southeast Minahasa Regency, North Sulawesi [19], the Citarum River in West Java Province [20], Singingi River in Kuantan Singingi Regency, Riau [21] and the Brantas River in East Java Province [22].

Serayu River is an important river for people in Central Java Province. Alongside of Serayu watershed covered of Wonosobo, Banjarnegara, Purbalingga, Banyumas and Cilacap districs, the Serayu River is utilized to meet the needs of the population. The status water quality of the Serayu River has decreased due to the existence of heavy metals [23]. This is strongly influenced by various activities of the community around the river that dump their waste into the river. Community activities that are allegedly able to pollute the water of the Serayu River include mining activities [24], agriculture, industry and population density [25].

Water contamination causes economic loss for its damage to humans and nature. Therefore, there is a need to give solutions, especially affordable ones to solve the water contamination. Aside of change the agricultural practices in the contamination’s source area, there is an approach to solve this problem that is technically simple, available in the local environment, and affordable in price. However, it shall economically effective and efficient. The availability of local materials will reduce the import cost of wastewater treatment materials. In addition, the dependence on naturally available materials makes technology and materials more easily available to users, thereby boosting the country's economy while saving time and money. For cost-effective and similar technologies to be introduced and adopted in a country or region, the application cost must be analyzed.

The existence of various community activities around the river can affect the quality of river water, especially heavy metal pollution which will impact public health that uses the water source from the river. This research intends to evaluate pollution levels, heavy metal distribution sources in the Serayu River and provides an alternative recommendation.

Study sites and methods

Research sites

This study was conducted in Serayu Watershed or Serayu River which is located in Central Java Province. This river is positioned at coordinates 07°01′52 - 07°31′54″ South Latitude and 108°50′16 - 110°04′20″ East Longitude. The Serayu River flows through a number of Central Java Province’s districs, including Wonosobo, Banjarnegara, Purbalingga, Banyumas and Cilacap. The upper Serayu River is located in the Wonosobo Regency, in the Dieng mountain area. The lower part of the Serayu River empties into the Indian Ocean, which is situated in Cilacap Regency. The length of the Serayu River is 138,310 kilometers, with an upstream discharge of 656 m^3/second and a downstream discharge of 2,866m^3/s.

The population living along the Serayu River is about 4.2 million people consisting of 50.49% male and 49.51% female. This river is spreading out into 55 sub-rivers across the five regencies in Central Java Province.

Sampling location

The number of locations for water sampling (WS) was 18 points. The sampling sites were determined based on river water sources, including natural, polluted and used water sources. The water sampling location points can be seen in figure 1. The technique of taking water samples at each location point was very dependent on the water discharge, so the sampling technique was adjusted following the standard rules of SNI 6989.57:2008 Section 57 regarding the method of taking surface water samples. River water samples were taken using a simple water sampling device with ballast.

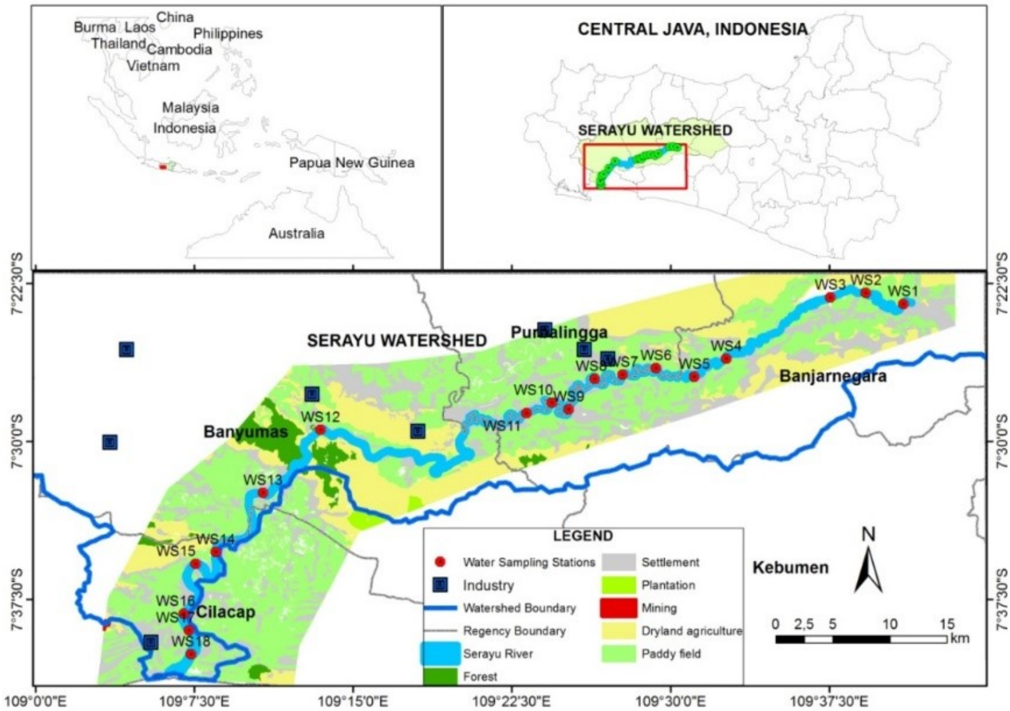

Fig. 1. Map of water sampling location in the Serayu River

Analysis of heavy metals

Water samples were prepared by filtering using filter paper. The filtrate of clear water extract was directly measured by AAS (Atomic Absorption Spectrophotometer). The heavy metal analysis includes Pb, Cd, Cr, Ni, As, Co, Fe and Mn. Heavy metal analysis was carried out at the Laboratory of the Indonesian Agricultural Environment Research Institute, The Indonesian Agency for Agricultural Research and Development.

Contamination factor (CF)

The CF can provide an overview of the heavy metal contamination level in river water, making it an efficient approach for monitoring river water pollution on occasion. The CF is the ratio of the metal content in river water to the metal concentration criterion for river water quality established [26] in Government Regulation (GR) no. 22 of 2021. The formula calculates the value of the contamination factor in equation 1:

$$CF = \frac{C_{si}}{C_{bi}} \quad (1)$$

C_{si} is is the metal concentration measured in the soil, while Cbi is the metal concentration standard for river water quality. The CF value is classified into four parts, namely i) low contaminated soil with a CF value of <1, ii) moderately contaminated soil with a value of 1 CF 3, iii) highly contaminated soil with a value of 3 CF < 6 and highly contaminated soil with CF values > 6 [27].

Modified degree of contamination (MCD)

MCD is a comprehensive method for determining the level of heavy metal contamination [28]. This method modifies by adding all metal contamination factors in the observed sample [29] and dividing by the total observed heavy metal. This index describes the current condition of heavy metal pollution in general. The purpose of MCD is to provide a measure of the overall contamination of the surface layer, including surface water (river water) at the observed sampling location. The formula calculates the value of the degree of contamination in equation 2:

$$\text{MCD} = \frac{1}{n}\sum_{i=1}^{n=8} \text{CF}_{\text{i}} \quad (2)$$

Where: n is the amount of heavy metal observed. MCD values were classified into seven categories as follows: (i) uncontaminated with MCD value 1.5, (ii) moderately contaminated with 1.5 MCD < 2, (iii) moderately contaminated with 2 CD < 4 and (iv) moderately to heavily contaminated with a value of 4 MCD < 8, (v) heavily contaminated with a value of 8 MCD < 16, (vi) severely contaminated with a value of 16 MCD < 32 and very heavily contaminated with an MCD value of 32.

Spatial and statistics analysis

Spatial analysis is used to visualize the heavy metal concentrations at each water sampling location along the Serayu River spatially with maps made with GIS software. The Pearson correlation matrix is used to determine the relationship between variables. The correlation coefficient matrix measuring the variance of each variable can be explained by the relationship with each other [30]. This study used IBM SPSS software (version 20) to perform an experimental statistical analysis of river water data.

Principal component analysis (PCA) reduces the dimensions of a significant variable set to a small variable set by a linear combination of the original data. The linear combination produces new variables that are orthogonal and uncorrelated with each other and still contain most of the information in the large set. It can be seen in the eigenvalues and eigenvectors of the original variable covariance matrix [31]. This analysis was used to extract the principal component (PC) from the sampling point and to evaluate the possible sources and variations of heavy metals in surface water samples.

Cluster analysis or hierarchical cluster analysis (HCA) was used to determine the similarities and differences in the characteristics of the concentration values of all observed heavy metals between river water sampling locations. Hierarchical clustering is the most common approach, in which clusters are formed sequentially by starting with the most similar object pairs and gradually forming higher groups [32].

Partial cost analysis

The research used partial cost analysis to estimate the need for biochar as simple technology for river recovery from water contamination. The partial cost analysis is the current cost of applying technology. The initial cost for preparing a new technology is one- time cost which is mostly for material application. The partial cost analysis is calculated based on an assumption and scope for the need of the recovery.

Results and discussion

Mn was detected in all water sampling locations, while Pb, Cd, Cr, Ni, As, Co and Fe were not detected at all sites. Cd metal was detected only at one sampling location, namely at location WS6, Cr metal was detected at 7 locations, Ni metal was detected at nine sites, As the metal was detected at four locations, Co metal was detected at 12 locations, Pb metal was detected at 17 locations and Fe metal was detected at 16 sites.

The maximum values of heavy metals Pb, Cd, Cr, Ni, As, Co, Fe and Mn found in the Serayu River water samples ($mg\cdot L^{-1}$) were 0.1248, 0.0063, 0.0738, 0.0738, 0.0136, 0.0242, 0.2895 and 0.0415. Based on the maximum value, the metal concentration values from the highest to the lowest were Fe > Pb > Cr > Ni > Mn > Co > As > Cd. Table 1 displays the amounts of heavy metals in river water at each sampling site.

Table 1. Heavy metals concentration in river water at several water sampling locations

Sites location	Pb	Cd	Cr	Ni	As	Co	Fe	Mn
	$mg\cdot L^{-1}$							
WS1	0.1120	0.0000	0.0738	0.0738	0.0000	0.0000	0.0102	0.0396
WS2	0.1248	0.0000	0.0470	0.0470	0.0000	0.0000	0.0000	0.0415
WS3	0.1223	0.0000	0.0524	0.0524	0.0000	0.0040	0.0289	0.0396
WS4	0.1095	0.0000	0.0000	0.0000	0.0000	0.0000	0.0543	0.0415
WS5	0.0864	0.0000	0.0000	0.0000	0.0000	0.0000	0.0422	0.0383
WS6	0.0711	0.0063	0.0000	0.0000	0.0000	0.0242	0.0503	0.0415
WS7	0.1043	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0408
WS8	0.1018	0.0000	0.0000	0.0000	0.0000	0.0141	0.0249	0.0371
WS9	0.0506	0.0000	0.0000	0.0000	0.0029	0.0208	0.2895	0.0390
WS10	0.0353	0.0000	0.0000	0.0000	0.0025	0.0175	0.0503	0.0396
WS11	0.0506	0.0000	0.0000	0.0021	0.0000	0.0130	0.1412	0.0371
WS12	0.0276	0.0000	0.0000	0.0000	0.0014	0.0051	0.0503	0.0377
WS13	0.0379	0.0000	0.0000	0.0000	0.0000	0.0175	0.1612	0.0396
WS14	0.0199	0.0000	0.0000	0.0021	0.0000	0.0186	0.0000	0.0408
WS15	0.0327	0.0000	0.0085	0.0085	0.0136	0.0063	0.0623	0.0359
WS16	0.0000	0.0000	0.0096	0.0096	0.0000	0.0096	0.0289	0.0396
WS17	0.0000	0.0000	0.0042	0.0042	0.0000	0.0000	0.0275	0.0346
WS18	0.0097	0.0000	0.0203	0.0203	0.0000	0.0051	0.0850	0.0371
River water quality standards (GR No. 22 of 2021)	0.0300	0.0100	0.0500	0.0500	0.0500	0.2000	0.3000	0.4000

Based on GR No. 22 of 2021 [33] regarding river water quality standards, it is indicated that several locations have exceeded the quality standard for heavy metal concentrations. The concentration of Pb showed there were as many as 13 locations or 72.22%, which had exceeded the quality standard. The concentration of Cr and Ni indicated that there were as many as 2 locations, or 11.11%, which had exceeded the quality standard, namely at locations S16 and S18. In contrast, for the concentration of Cd, As, Co, Fe and Mn, no location exceeded the quality standard.

The heavy metal content of the Serayu River compared globally with the rivers of the world is presented in table 2. The Serayu River has a higher metal content than the Voghji (Armenia), Liuyang (China), Bogacayi (Turkey) and Saigon (Vietnam) rivers; and lower than the Halda (Bangladesh) and Yamuna (India) rivers. The heavy metal concentration of Pb, Cd, Cr and As in the Serayu river exceeds the water quality standard according to WHO requirements.

The spatial distribution shows that the water sampling locations WS1, WS2, and WS3 upstream have a relatively high concentration of heavy metals and above the quality standards for some metals such as Pb, Cr and Ni, while for metals Cd, As, Co, F and Mn concentration values are still below the quality standard. Some are not detected. In the middle, namely at points S4-S11, which is on the border between Banjarnegara and Purbalingga regencies, the concentration of Pb is above the quality standard ($0.0300 mg \cdot L^{-1}$) for all locations, while for other metals, it is still below the quality standard and some are not detected. In the downstream part, namely in Banyumas and Cilacap Regencies, the water sampling points WS12-WS18 have heavy metals Pb, Cd, Cr, Co, Ni, As, Fe and Mn, which are low and below the quality standards for all locations.

Table 2. Concentrations of heavy metals in river water globally

Heavy metals	River, Country							
	Voghji, Armenia	Liuyang, China	Halda, Bangladesh	Saigon, Vietnam	Bogacayi, Turkey	Yamuna, India	Serayu, Indonesia	WHO
Pb	0,039-0,522	0,14-4,00	44-105	0,88-2,08	25,04 ± 0,12	6,8-1.112	nd-124,8	10
Cd	0,009-1,891	0,02-0,19	30-50	0,04-0,1	2,50 ± 0,02	1,7-433	nd-6,3	3
Cr	0,297-1,030	0,24-1,42	10-120	-	10,05 ± 0,05	2,6-1.983	nd-73,8	50
Ni	0,805-2,920	0,24-1,79	30-620	0,87-8,3	50,07 ± 0,34	1,4-2.748	nd-73,8	200
As	0,616-4,590	1,30-4,46	-	-	50,04 ± 0,37	-	nd-13,6	10
Co	0,082-2,570	0,10-0,44	30-70	0,72-3,36	10,03 ± 0,05	-	nd-24,2	400
Fe	0,038-0,376	88,18-751	-	19,9-163	-	878,5-53.940	nd-289,5	300
Mn	0,003-0,181	11,08-68,71	60-280	62,8-172,5	50,04 ± 0,34	-	34,6-41,5	-
Reference	Gabrielyan *et al.* [34]	Liang *et al.* [35]	Bhuyan *et al.* [36]	Nguyen *et al.* [37]	Cengiz *et al.* [38]	Bhardwaj *et al.* [39]	Present study	WHO (2017)

Heavy metal concentrations, especially Pb, Cr, N and Mn, appear to be greater inupstream than downstream, a phenomenon that can be attributed to human activity in the area. The upstream part of the Serayu River in Wonosobo Regency, precisely in the Dieng area, has experienced the conversion of conservation land into agricultural land, resulting in environmental damage and causing erosion that transports nutrients to the soil [40]. Potato farmers carry out increased soil fertility with an intensive application of fertilizers and pesticides throughout the year [41]. Accumulation of heavy metals from fertilizers and pesticides on the soil is transported by rainwater when erosion occurs and pollutes river water research conducted by *S. Ngabekti et al.* [42] showed that river water in the Dieng area does not meet river water quality standards because of high levels of water in the river. Pesticides and fertilizers generate elevated BOD and COD levels in all potato-growing regions. Figure 2 depicts the spatial distribution of the heavy metals Pb, Cd, Cr, Co, Ni, As, Fe and Mn at each sampling location along the Serayu River.

Contamination factor (CF)

The CF value in Pb metal is the highest compared to other heavy metals. Based on the average metal CF values from the highest to the lowest, respectively, are Pb > Ni > Cr > Fe > Mn > Co > Cd > As. The value of the expected heavy metal pollution factor in river water is likely to be in the low category with a contamination factor value of < 1. The CF value of Pb metal at each water sampling location varies, but the dominant value is more than one; 14 sites have a value of more than one that ranges from 1,090-4,160. Cr and Ni metals have CF values > 1 but only in 1 spot, while for Cd, Co, As, Fe and Mn metals, there are no locations that have CF values > 1.

In category 3, the highest CF values of Pb are located at locations WS2, WS3 and WS1, with CF values of 4,160, 4,077 and 3,733, respectively. Location WS1, besides having a high CF value of Pb metal, also has a CF value of >1 for Ni and Cr metals with a CF value of 1,476. These areas are in the upper portions of the Serayu River, specifically in Wonosobo Regency; this is due to the exceedingly high concentrations of heavy metals Pb, Cr and Ni in the upstream river water. Figure 3 depicts the value of the CF at each water sampling point.

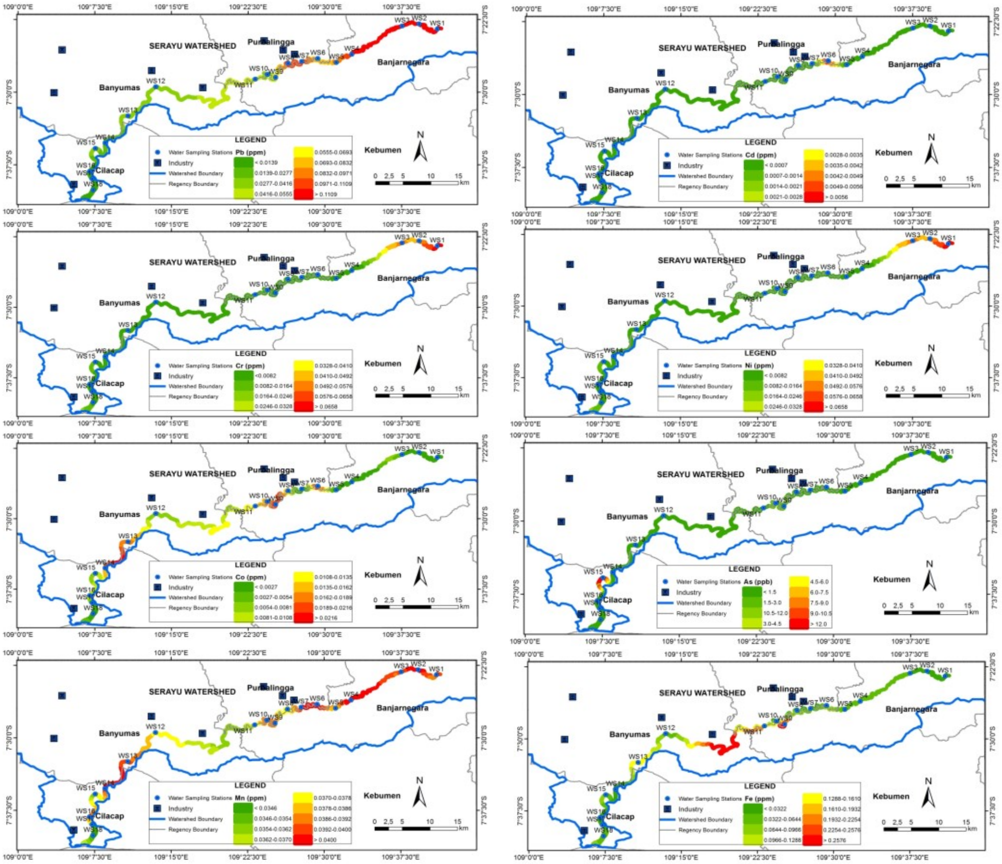

Fig. 2. Distribution map of heavy metals Pb, Cd, Cr, Ni, As, Co, Fe and Mn in the Serayu River

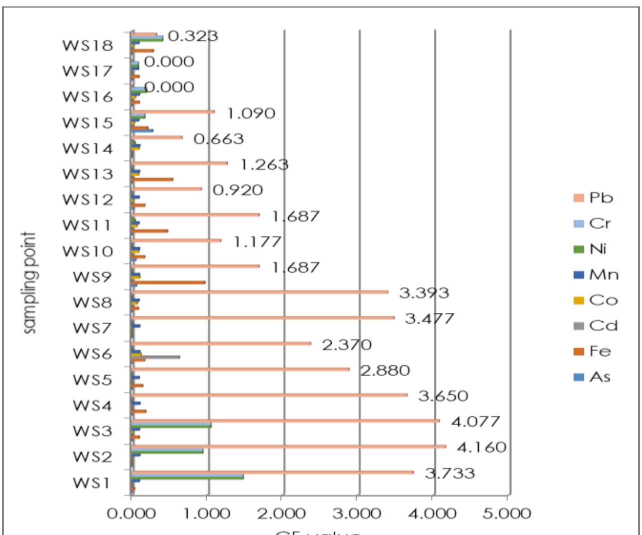

Fig. 3. Contaminant factor (CF) values at each water sampling location

The percentage value of the contamination factor in each category is described in table 3 below.

Table 3. Percentage of contamination factor values in each category

Heavy metal	Low degree	Moderate degree	Considerable degree	Very high degree
As	100	0	0	0
Fe	100	0	0	0
Cd	100	0	0	0
Co	100	0	0	0
Mn	100	0	0	0
Ni	88.89	11.11	0	0
Cr	88.89	11.11	0	0
Pb	27.78	38.89	33.33	0

Based on table 1, heavy metals whose values are As, Fe, Cd, Co and Mn metals are all included in the low sort. Ni and Cr metals have the same percentage of contamination factor values, namely 88.89% in the low category and 11.11% in the medium category. Pb metal is in 3 categories, namely low (27.78%), medium (38.89%) and large (33.33%); this indicates that Pb is the primary metal polluting the water of the Serayu River.

Modified degree of contamination (MCD)

MCD is also used to determine the overall level of heavy metal contamination in river water. Prevalent heavy metals from the contamination factor (CF) value were observed to measure the MCD value. The highest MCD value is at location WS1 and the lowest MCD value is at location W17. The MCD value on WS1 is 6.82 and the MCD value on WS17 is 0.35. The location of WS1 is on the upstream Serayu River and the site of WS17 is on the downstream side. In general, the MCD value from upstream to downstream has decreased; the highest MCD values are in the upstream part of the Serayu River. The MCD value at each water sampling location can be seen in figure 4.

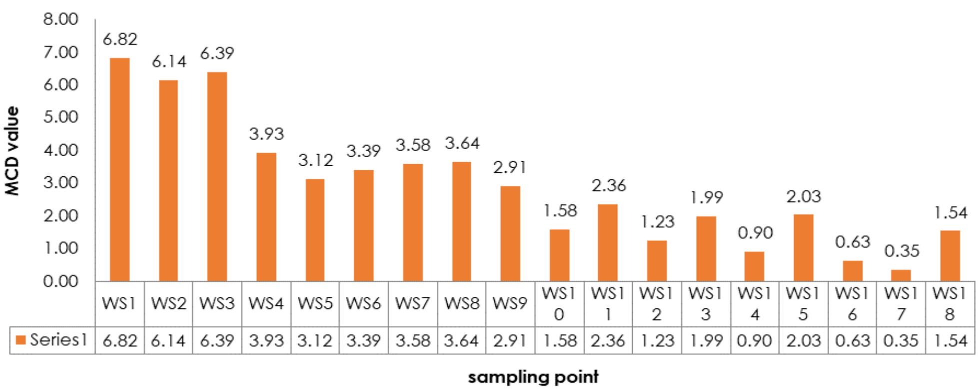

Fig. 4. MCD value at each water sampling location

The percentage of MCD values in each category can be seen in figure 5. The MCD value included in the moderately contaminated category was 44.44%, the slightly soiled class was 22.22%, while the lowest value in the uncontaminated and moderate to heavily contaminated category was 16.67%. It shows that the medium contamination category has the highest percentage, so most of the Serayu River water sampling locations have been polluted with heavy metals even though they are in moderate status.

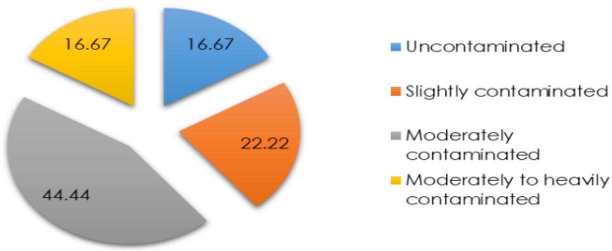

Fig. 5. Percentage of MCD values in each category

Pearson Correlation Matrix (PCM) analysis

The PCM for heavy metals is shown in table 4. The p-value indicates the level of significance of the correlation matrix, but it also shows the strength of the correlation between metals. The p-value, which has a meaning below 0.01 or 0.05, indicates a strong correlation and the significance of each relationship. The Pearson correlation matrix shows several significant relationships, including a robust correlation between Ni and Cr metals (r 1,000) with a 99% confidence level, a strong correlation shown by Pb metal to Cr, Ni and Mn metals with a correlation value (r) of respectively 0.479, 0.475 and 0.497, strong correlations were also shown between Fe and Co metals (r 0.489) at the 95% confidence level. A strong positive correlation may indicate a common source of origin for heavy metals in several water samples. [43]. The correlation between Pb, Cr, Ni and Mn metals, as well as the correlation between Fe and Co metals, indicate that there may be similarities at the source. To better understand the relationship between these metals, multivariate analysis with Principal component analysis (PCA) was used to further investigate the relationship.

Table 4. Correlation matrix between heavy metals in water

Element	Pb	Cd	Cr	Ni	As	Co	Fe	Mn
Pb	1							
Cd	0.058	1						
Cr	**0.479***	-0.135	1					
Ni	**0.475***	-0.138	**1.000****	1				
As	-0.219	-0.087	-0.105	-0.109	1			
Co	-0.337	0.463	-0.444	-0.437	0.044	1		
Fe	-0.246	-0.039	-0.307	-0.307	0.156	**0.489***	1	
Mn	**0.492***	0.317	0.169	0.170	-0.371	0.158	-0.158	1

Note: *. Significant correlation at the 0.05 level (2-tailed).
**. Significant correlation at the 0.01 level (2-tailed).

Multivariate analysis

Principal component analysis (PCA) was used to identify the main components associated with heavy metal sources in Serayu River water at different water sampling locations. The scree plot of the eigenvectors as a function of factor numbers is shown in figure 6. The scree plot is used to identify the sum of the principal components. The number of principal components is determined based on elements with eigenvalues greater than 1. Three eigenvalues meet the requirements to form the main features, namely 3,023, 1,795 and 1,006.

This analysis also uses varimax rotation to explain better the possible factors that influence heavy metals (Table 3). The component plot in the rotating space of the principal component analysis is shown in figure 5. There are three factors according to this criterion which can represent 72.80% of the total variance so that it can display information on most of the heavy metals in river water. The three main components (PC) proportions were 37.796%, 22.44% and 12.58%, respectively. The relationship between the main element and the type of heavy metal shows factors related to the composition of the heavy metal source [44].

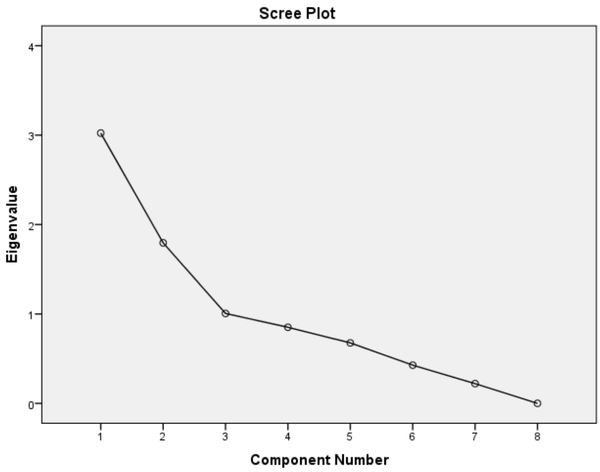

Fig. 6. Scree plot of the characteristic roots of principal component analysis

The first significant component (PC1) is the component with the highest cumulative variance value of 37.79%. In this component, metals with high positive values are Pb (0.636), Cr (0.961) and Ni (0.965). The components with high positive values are associated with the same anthropogenic sources [45]. The source of the Pb, Cr and Ni metals is allegedly derived from agricultural activities carried out by the people living in the upper reaches of the Serayu River. Several water samples were observed to have exceeded the quality standards for Pb, Cr and Ni metals from water sampling locations in the upstream area, precisely in Wonosobo Regency.

The intensive use of fertilizers and pesticides in potato cultivation has resulted in the accumulation of heavy metals in agricultural land [46]. Some fertilizers which are suspected of containing heavy metals include fertilizers from livestock manure [47] such as chicken manure [48], pig manure [49], goat manure and cow manure [50] in addition there are urea and phosphate fertilizers [51]. Pesticides are also indicated to contain heavy metals such as herbicides [52] and functionals [53]. Heavy metals in agricultural land will be transported by rainwater so that heavy metal transformation occurs [54] and can further pollute rivers [55].

Pb metal that has exceeded the quality standard was also found in the water sampling location in the middle of the Serayu River, namely on the border of Banjarnegara Regency and Purbalingga Regency. Agricultural activities are also intensive at this location, namely lowland rice cultivation. Sources of Pb apart from farm activities can also be sourced from motor vehicle emission activities [56], industrial activities [57] and dense settlements [58] in the area.

Table 5. Principal component analysis (PCA) with varimax rotation for all heavy metals found in the studied water sample

Element	Component		
	PC1	PC2	PC3
Pb	,636	,223	-,395
Cd	-,077	,760	-,036
Cr	,961	-,125	-,067
Ni	,959	-,124	-,067
As	-,006	-,275	,686
Co	-,387	,704	,441
Fe	-,206	,253	,720
Mn	,280	,685	-,435
Eigenvalues	3.023	1.795	1.006
% of variance	37.789	22.441	12.575
cumulative %	37.789	60.23	72.805

In the second principal component (PC2), high positive values for heavy metals Cd (0.760), Co (0.704) and Mn (0.685). Cd metal is found in the middle of the river; Co metal is located in the center to downstream and Mn metal along the Serayu River. Sources of Cd, Co and Mn come from anthropogenic activities carried out by the community around the Serayu River, especially in the middle and downstream parts. Community activities in the middle and lower reaches of the Serayu River, which are suspected to be a source of Cd, Co and Mn metals, include agricultural activities in paddy fields [51], industrial activities [59], dense settlements [14] and the number of hotels or other tourist facilities [60].

In the third principal component - PC3 (Fig. &)), high positive values for heavy metals As (0.686) and Fe (0.720). Arsenic was found at the water sampling location in the downstream Serayu River, while Fe metal was mainly found in the middle of the river. The source of heavy metals As and Fe is allegedly from mining activities carried out around the river. Mining activities around the Serayu River are iron sand mining [61] in Banyumas Regency and Cilacap Regency and gold mining [62] in Banyumas Regency. Gold mining is allegedly the primary source of Fe [63] and As [64] metals that pollute the environment around mining areas. Sand mining in rivers is a source of Fe metal in water rivers [65].

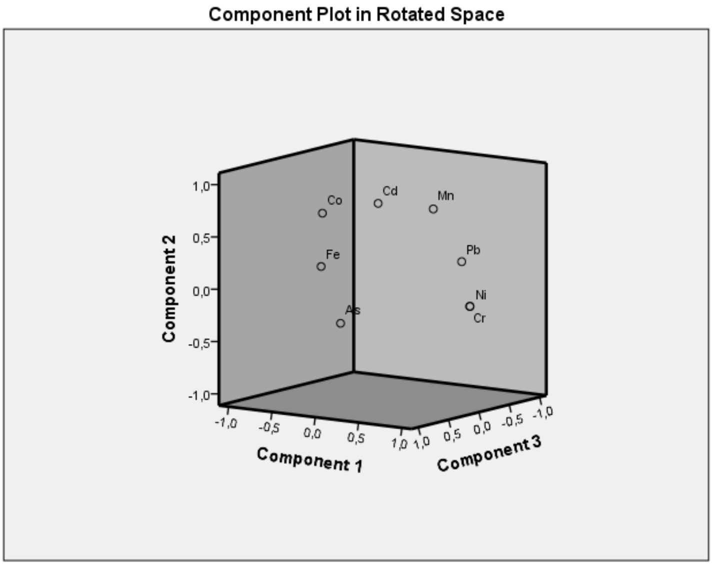

Fig. 7. Component plot in rotated space of principal component analysis

Cluster analysis (CA)

The similarities and differences in the characteristics of the concentration values of all heavy metals observed between water sampling locations can be seen in hierarchical cluster analysis (HCA) figure 6. The dendrogram shows the process/stages in forming clusters, starting from the initial stage at the leftmost level. The highest number of groups is as many as 6 clusters up to the rightmost level, which eventually becomes 2 clusters. In the early stages of cluster formation, there have been similarities in character at various points in different water sampling locations. The cluster formed at the initial step is the first cluster includes three sites (WS14, WS16, WS17), the second cluster consists of 4 locations (WS10, WS12, WS15, WS18), the third cluster includes five areas (WS4, WS5, WS6, WS7, WS8), the fourth cluster consists of 3 locations (WS1, WS2, WS3), the fifth cluster includes two sites (WS11, WS13) and the sixth cluster has 1 area (WS9). The formation of groups in the early stages is by the Pearson correlation analysis and PCA analysis [66]; it is based on the sampling locations of WS1, WS2 and WS2, which are in one cluster. Locations WS1, WS2 and WS3 are locations with high heavy metal contamination of Pb, Cr and Ni.

In the final stage, 2 clusters were formed with the most members in the first cluster, namely 17 locations and the second cluster only consisted of 1 location, namely the WS9 location. It shows that the character values of heavy metals Pb, Cd, Cr, Ni, As, Co, Mn and Fe at 17 water sampling locations are almost uniform. In contrast, the WS9 location has the most different characters compared to other places (Fig. 8).

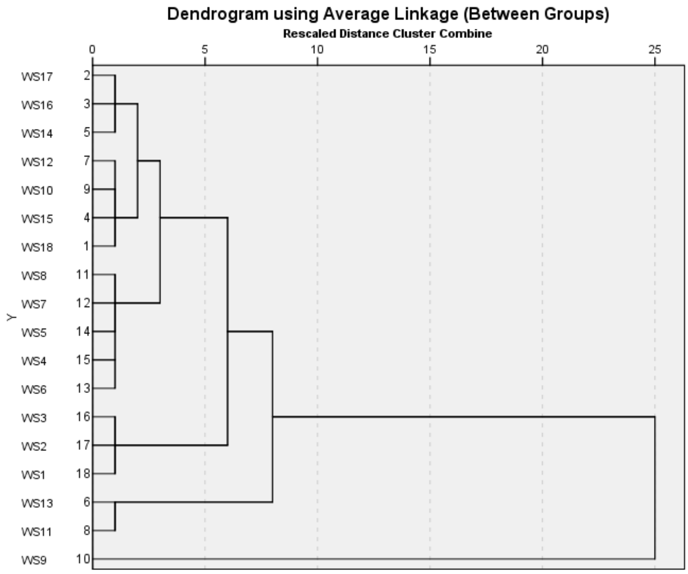

Fig. 8. Dendrogram shows the clustering of heavy metals

Estimated cost for the treatment process

Referring to GR 22 of 2021, the content of Pb, Cr and Ni metals must be reduced to meet water quality standards for irrigation. The amount of Pb, Cr and Ni that must be removed from the water is at least 94.8 g/L (94.8 mg/m^3), 23.8 g/L (23.8 mg/m^3) and 23.8 g/L (23.8 mg/m^3). Indonesia is promoting a green economy, so selecting materials to remove heavy metals is directed at using environmentally friendly materials. Biochar derived from agricultural waste is abundant, easy to obtain and environmentally friendly. Biochar is a bio adsorbent used to remove Pb, Cr and Ni from water.

The adsorption capacity of biochar to bind Pb, Cr and Ni (mg/g) is 2.58, 116.97 and 11, respectively [67, 68]. The following table 6 represents the need for biochar to remediate river water from heavy metals.

Table 6. Biochar requirement for Remediation

Metals	Metals Removal (mg/m^3)	Biochar (gr)	Cost (IDR)
Pb	94.8	36.74	146.98
Cr	23.8	0.20	0.81
Ni	23.8	2.16	8.65
Total	142.4	49.10	156.45

Based on the analysis in Table 6, the minimum need for biochar to reduce the heavy metal content of Pb, Cr and Ni to comply with the required quality standard is 49.10g. Therefore, one-kilogram biochar which cost IDR 4,000, can be used to remediate water in the Serayu River to a maximum of 25.57m^3. Furthermore, the remediation of heavy metals in Serayu River using biochar is an easy, inexpensive and environmentally friendly option.

Conclusions

Overall, the results of this study indicate that the concentration of heavy metals consisting of Pb, Cr and Ni in Serayu River water has exceeded the quality standard (Government Regulation No. 22 of 2021) at some water sampling locations. The MCD value indicates that most river water is moderately contaminated. Agricultural activities in the upper reaches of the Serayu River are considered the main source of heavy metals, which have been identified as having exceeded the quality standard. Spatial analysis shows high values of heavy metals, especially metals Pb, Cr and Ni, in the upstream area and their values will be lower in the downstream area. Multivariate statistical analyses such as PCA, PCM, and CA showed that most heavy metals came from different anthropogenic sources. The analysis indicates that Pb, Cr and Ni are mainly derived from agricultural activities, Cd, Co and Mn are from industrial, agricultural, residential and tourism activities and As and Fe metals are coming from mining activities. This study suggests that an alternative recommendation for the contamination recovery is the application of biochar which is affordable material can be applied to reduce metals contamination from the river.

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