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Regional Case Study

Identification of Fe and Mn Heavy Metal in Stream Sedimentation at Putri Cempo Landfill

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Abstract

The Putri Cempo landfill serves as the final disposal site for organic and inorganic waste. Waste from the landfill can dissolve and settle in river sediments, potentially accumulating heavy metals like iron (Fe) and manganese (Mn), which bind easily to organic matter. This study aims to determine the content of Iron (Fe) and Manganese (Mn) in rivers around the Putri Cempo landfill. The concentration of Fe and Mn was analyzed using Atomic Absorption Spectrometry (AAS) referring to SNI 6989.84:2019, with sediment sampling conducted in rivers around the Putri Cempo landfill. Sediment sampling was conducted in these rivers, revealing Fe levels of 1519.414245 mg/L and Mn levels of 130.033 mg/L. Analysis indicates that Fe concentrations exceed the established quality threshold, while Mn levels remain below it. Heavy metals like Fe and Mn negatively impact abiotic and biotic environments, including human health and agricultural productivity. Elevated heavy metal levels disrupt ecosystem balance and pose health risks, making their management crucial. Reducing heavy metals in river sediments near the landfill is essential. Remediation efforts using bioremediation and phytoremediation technologies can help mitigate these impacts. Ongoing efforts are necessary to control heavy metal contamination in river sediments, ensuring ecosystem stability and public health.

Keywords: Identification; heavy metal ; iron; manganese; Putri Cempo Landfill

1. Introduction

Putri Cempo is one of the landfills located in Jebres District, Surakarta City, Central Java. This landfill has an important role in managing waste generated by the surrounding communities. Therefore, it is important to understand the role and impact of the Putri Cempo landfill on the environment and surrounding communities. Waste disposed to the Putri Cempo landfill can come from various sources, such as household, industrial, and commercial waste. It can also be organic waste, which is biologically degradable material derived from plants, animals, and food waste, and can be decomposed (Atelge et al., 2020). There is also non-organic waste, which is waste that is difficult to decompose, including paper plastics, metals, and others (Hakiki, 2023).

Waste, especially inorganic waste, has a variety of contents in it, one of which is heavy metals (Krishnan et al, 2021). Waste has metal compounds that decompose and also dissolve along with the formation of liquid waste called leachate (Karamina et al., 2020). Heavy metals themselves are metals that are included in the group of metal elements that have a specific gravity ≥ 5gr / cm^3 (Al-Khuzaie et al., 2020). This metal has a detrimental effect on the environment at certain levels (Groffen et al., 2021). Heavy metals have properties that easily bind and settle to the bottom of the waters which will then collect into sediments (Yanti and Afdal, 2021). Heavy metals are elements that cannot be degraded or destroyed (Rosita, 2023). There are various types of waste collected in the Putri Cempo landfill such as utensils, plastic, glass, and various other waste. Items such as tools, used tires, can produce heavy metals iron or Fe. Waste such as batteries, glass and used fireworks can produce heavy metals manganese (Dey et al., 2023).

Heavy metals Fe and Mn enter the river sediments around the Putri Cempo landfill mainly due to human activities and natural processes. The open dumping process at the landfill allows heavy metals from waste to be leached and carried into the river, especially during rainfall or through surface runoff. Poorly managed waste disposal also causes heavy metal accumulation in river sediments (Fathassabilla and Budianta, 2023). Geological and anthropogenic factors around the landfill contribute to the distribution of heavy metals in soil, which can reach the river and settle in sediments, potentially causing pollution (Darmansyah et al., 2020). In addition, the weathering process of rocks and soils also contributes to the release of heavy metals into streams, adding to the complexity of interactions between the environment and human activities in the context of pollution (Aprilia, 2021).

Since the Putri Cempo landfill uses an open dumping system in its waste management, hazardous substances such as heavy metals contained in waste can easily seep into the soil and groundwater causing several problems such as river and groundwater pollution (Khaira and Afdal, 2022). Water quality monitoring is an important part to determine the level of pollution that occurs. Sediment can be used as an indicator of heavy metal pollution in river water (Fuad and Pane, 2023). This is because heavy metals are toxic and persistent, so they easily accumulate in the water column and sediments (Milasari et al., 2023). Heavy metals can also easily bind to sediments (Kluska and Jabłońska, 2023).

This research was conducted because no research has been found that examines the content of heavy metals iron (Fe) and manganese (Mn) in the sediments of the Putri Cempo landfill river, even though this landfill has the potential to be polluted with heavy metals due to the open dumping system used. In addition, sediments that have been contaminated with heavy metals can spread or move to other ecosystems through water and the food chain, causing widespread pollution (Liu et al., 2024). Based on the background that has been described, the objectives of this study are to identify the content of heavy metals in the form of iron (Fe) and manganese (Mn) in the sedimentation of the Putri Cempo landfill river, analyze the suitability of the content with quality standards, determine the impact of the presence of these heavy metals on environmental components, and formulate strategies to reduce heavy metal levels in river sedimentation around the Putri Cempo landfill.

2. Methods

2.1. Research Time and Location

This research was carried out at the Putri Cempo landfill, Surakarta (Figure 1 and 2). The activities carried out in the form of river sedimentation sampling in the Putri Cempo landfill area with coordinates 7°32'0.91" N and 110°51'29.9" East. This location was chosen because the Putri Cempo landfill is in the vicinity of residential areas, so it is important to know whether or not the environment is contaminated and can endanger the people who live around it. Then, the wet destruction process was at the Laboratory of the Soil Science Study Program, Sebelas Maret University, Surakarta. Fe and Mn heavy metal testing using Atomic Absorption Spectrometry (AAS) method was conducted after obtaining the required mother liquor at the chemistry sub-lab of UPT Laboratorium, Sebelas Maret University, Surakarta.

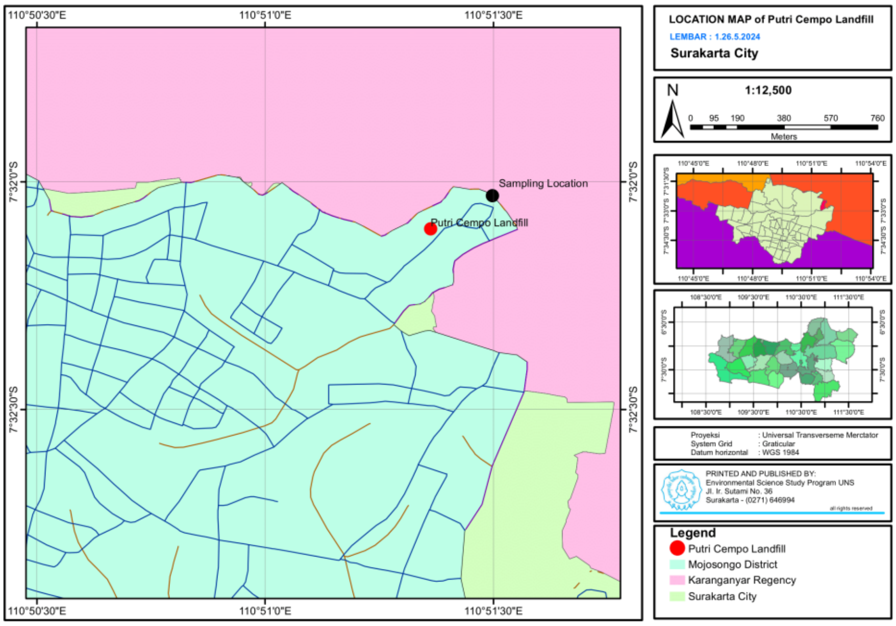

Figure 1. Map of the research location

2.2. Tools and Materials

The equipment used in this research are shovels or spoon, plastic bottle, plastic container, 250 mL beaker glass, 50 mL volumetric flask, 1 mL measuring pipette, Whatman filter paper, destructor, and AAS instrument (Husna, 2022). While the materials used in this study are soil sedimentation from the river around the Putri Cempo landfill, $HClO_4$, aquabides, 1000 ppm Fe mother liquor, and 1000 ppm Mn mother liquor.

2.3. Data Collection

Determination of sampling locations was carried out based on SNI 6989.57:2008 guidelines using a Global Positioning System (GPS) device. The river sediment sampling method in the Putri Cempo landfill area uses the Simple Random Sampling (SRS) principle, where each point in the population has the same opportunity to be selected as a sampling location (Amalia et al., 2020). In this case, the selected river sediment sampling point is the point that is close to the residential area or precisely behind the Putri Cempo landfill. Sediment collection was carried out using a shovel, then the sediment was put into a polyethylene bottle and labeled. After that, the river sedimentation samples were dried in the sun, then the samples were sieved. After becoming a fine sand sample, the sample was immediately taken to the laboratory for testing.

2.4. Sample Analysis

Testing of heavy metals in this study was carried out by the Atomic Absorption Spectrometry (AAS) method referring to SNI 6989.84:2019 using the principle of energy absorption using radiation of a wavelength by atoms, resulting in excited electronic energy (Hidayati et al., 2022). The parameters tested were iron (Fe) solution with a concentration of 0.5 ppm; 1 ppm; 2 ppm; 3 ppm; 5 ppm. Before testing, heavy metal samples were subjected to wet deconstruction first. There is also an manganese (Mn) levels with concentrations of 0.1 ppm; 0.2 ppm; 0.5 ppm; 1 ppm; 2 ppm.

2.5. Data Analysis

Data analysis in this heavy metal test research was carried out by calculating the value of metal content using a linear equation from the Atomic Absorption Spectrometry (AAS) test results in iron (Fe) and manganese (Mn) standard solutions. Then the results of the metal content are then compared with the heavy metal test results with river water quality standards in accordance with Appendix VI of

Government Regulation of the Republic of Indonesia Number 22 of 2021, concerning the Implementation of Environmental Protection and Management. Calculation of heavy metal content is done using the standard curve linear regression formula. The description of the formula (1) is as follows:

$$y = mx + c \quad (1)$$

Description :

y = sample uptake

m = coefficient of x

c = constant

3. Result and Discussion

The final disposal site in Surakarta City is the Putri Cempo TPA. Sources of waste at the Putri Cempo landfill include domestic waste, market waste and general waste (Prasenja et al., 2022). The waste accumulates together at final disposal. In the sediment compartment, heavy metal compounds tend to be higher than in the water compartment, this is like in the Sukawinatan Palembang landfill, where Pb compounds in the sediment are higher than in the water (Warsinah et al., 2015). The environment and the health of living organisms are both affected by heavy metal pollution. Sedimentation will occur over an extended period of time for heavy metals (Karamina et al. 2021; Oktasari et al. 2018).

3.1. Fe Content of Sediment

Table 1. Result of Fe testing on sediments

	y (abs)	m	x	c
Fe kel P 400x	0.162	0.04507	1519.41424	0.0092

In table 1, showing the relationship between absorbance and Fe metal concentration, we see the application of Beer's Law which describes the direct proportionality between the two variables (Delgado, 2022). Research from the Microchemical Journal shows that within a certain concentration range, the relationship between absorbance and Fe concentration is linear, with a correlation coefficient reaching 0.9997, indicating an excellent fit between the experimental data and the linear model (Henríquez et al., 2021). The linear equation y = 0.04507x - 0.0092 given indicates that any increase in Fe concentration will be followed by a proportional increase in absorbance. Since the absorbance depends directly on the concentration of the substance, any increase in Fe concentration causes the absorbance to increase proportionally according to the gradient, so this indicates that Beer's law applies within the measured Fe concentration range. The slope coefficient of this equation indicates the rate of change in absorbance per unit concentration, while a negative y-axis intersection point may indicate measurement error or instrument background. A study in the New Journal of Chemistry also supports these findings, showing that absorbance spectra can be used to calculate the concentration of iron in solution through a similar linear regression approach (Mira et al., 2022). Although the R^2 value is not visible, this parameter is commonly used to assess how well the data fits the proposed regression model. In laboratory practice, these graphs are very useful for determining the concentration of an unknown solute by measuring its absorbance and utilizing the regression equation. This demonstrates the importance of graphs and equations in analytical chemical analysis, providing an efficient and accurate method for measuring concentration based on the optical properties of solutions (RSC Publishing).

Measurements of Fe content in sediments around the Putri Cempo River showed a very high level of 1519.414245 mg/L. This high level could be because that heavy metal content can be carried by rainwater which then dissolves materials from waste, potentially increasing the concentration of heavy metals in the river.. Water quality in the area is thought to be contaminated with heavy metals, which then settle to the bottom of the water as sediment (Triantoro et al., 2018). Liquid waste containing organic matter will settle in the river, with the sedimentation process dominated by Fe metal. Sediment functions as a nutrient trap, which causes Fe metal that was dissolved in water to accumulate in sediment. This phenomenon of heavy metal deposition in sediments occurs because of the higher density of metals compared to water (Astari et al., 2021).

3.2. Mn Content of Sediments

Table 2. Result of Mn testing on sediments

	y (abs)	m	x	c
Mn kel P 100x	0.0905	0.07029	130.033	0.0009

In table 2, showing the relationship between absorbance and Mn metal concentration, we see the application of Beer's Law which illustrates the direct proportionality between the two variables. The linear equation y=0.07029x-0.0009 given indicates that any increase in manganese concentration will be followed by a proportional increase in absorbance. The slope coefficient of this equation indicates the rate of change in absorbance per unit concentration, while a negative y-axis intersection point may indicate measurement error or instrument background (Dali et al., 2023). Although the R^2 value is not visible, this parameter is usually used to assess how well the data fits the proposed regression model.

Analysis of sediment samples from the Putri Cempo River, which is adjacent to the landfill, revealed heavy metal Mn content of 1130.033 mg/L. Manganese was also found but at lesser levels. The presence of these metals could be due to the discharge of leachate from the landfill into nearby waterways. This leachate is rich in organic matter from domestic waste that is not dissolved and tends to settle in sediments (Siprana and Yenita, 2020). Research in the International Journal of Environmental Research and Public Health shows that river sediments often accumulate heavy metals such as Mn, most of which are in an acid-soluble and oxidized state, suggesting the potential for significant ecological risks (Zhang et al., 2022). Heavy metals such as Mn tend to be bound to these organic materials and deposited on the riverbed. This is because oxidation-reduction occurs which makes heavy metals react with organic matter. Then adsorption can affect the ability of heavy metals to bind to organic matter. Organic matter can have a high adsorption ability to heavy metals, causing heavy metals to bind to organic matter and settle to the bottom of the river (haynes and Zhou, 2022). The sediment composition in this area, which consists of wet sand and liquid mud, also plays a role in the elevated Mn content. It is thought that finer sediments have a greater capacity to bind heavy metals, thus increasing the detected Mn concentration. The distribution of heavy metals in sediments is influenced by their texture; muddy sediments with small size particles tend to have higher heavy metal content due to larger surface areas that allow more heavy metals to bind and settle (Rahmah et al., 2019). These findings emphasize the importance of understanding the interactions between sewage, sediment and heavy metals in effective pollution mitigation and environmental management efforts.

3.3. Comparison of Fe and Mn Heavy Metal Results with Threshold Values

According to the results of Fe metal analysis on sediment samples, Fe content was found to be 1,519.4144 mg/L. These results show that Fe metal concentrations have exceeded the threshold set by the Sediment Quality Guidelines for Metals and Associated Levels of Concern to be used in Sediment Quality Assessments (2003) regarding the quality standard of heavy metal Fe in sediment which is 20 mg/L as listed in Table 3. It is known that the sediment at the sampling location has a texture in the form of mud, where the smaller the particle size, the higher the heavy metal content. The high Fe content in the sediment can also be caused by weathering of bedrock in the area (Sudarningsih, 2020). Thus, it can be concluded that the sediments at the research site have been contaminated with Fe metal which has the potential to have a negative impact on aquatic organisms and humans.

Table 3. Quality standards for Fe and Mn metals in sediment

Metal	Threshold
Fe	20[(a)]
Mn	248,77[(b)]

[(a)]Sediment quality guideline for metals and associated levels of concern to be used in assessments of sediment quality (2003)
[(b)]National sediment quality survey US EPA (2004) (USEPA, 2004)

Heavy metal testing in the form of Mn in sediment samples resulted in samples containing 130.033 mg/L of Mn metal. This indicates that the sedimentation at the sampling site is not polluted by Mn because the concentration value obtained is lower than the threshold value of 248.77 mg/L set by the US EPA's National Sediment Quality Survey (USEPA, 2004) as listed in Table 3. Based on the comparison results, it can be concluded that the Mn metal contained in the sediment at the sampling location is still safe for the life of aquatic organisms or humans. As demonstrated Sudarningsih (2020), have recently shown that the content of manganese (Mn) in sediments can come from weathering of rocks in water basins, volcanic activity, or can also come from active materials from used batteries that have been discharged into rivers and coasts. The persistent, non-biodegradable, and mutagenic nature of heavy metals in sediments can pose a serious threat to human health, living organisms, and ecosystems (Ling et al., 2023).

The presence of Fe and Mn metal concentration values in the study sediment is due to the sediment sampling location near the pollutant source, namely the Putri Cempo landfill. This shows that the level of pollutants is directly correlated with the distance from the pollutant source, where the closer it is, the higher the pollutants. It is also known that heavy metal content in river sediments can come from natural geological conditions or erosion, as well as human activities such as agricultural activities, mining that settles, domestic waste disposal in the form of batteries, electronic equipment, textiles, lubricants, and so on (Milasari et al., 2023). In addition, Fe and Mn in sediments can come from two main sources, namely from minerals or biochemical sedimentation processes that occur in the river (He et al., 2023).

When compared to the results of research conducted by Putri and Afdal (2017) on the sediments of the Batang Ombilin River, the concentration values of Fe and Mn metals obtained from river sediments around the Putri Cempo landfill are still lower. Based on the results of Putri and Afdal's research (2017), the sediments of the Batang Ombilin River have an average Fe metal concentration of 96,181 mg/L and Mn metal of 1,897 mg/L. Both values have exceeded the threshold value based on the provisions of the Sediment Quality Guideline for Metals and Associated Levels of Concern to be used in Assessments of Sediment Quality (2003) for Fe metal and the US EPA National Sediment Quality Survey (USEPA, 2004) for Mn metal as listed in Table 3. The high values of Fe and Mn in the sediment are due to the study location which is close to the iron sand mining area and illegal coal mining (Putri and Afdal, 2017). Researchers compared the results of the study with studies using river sediments because no previous studies have been found that discuss the content of Fe and Mn metals in sedimentation around the landfill.

3.4. The Impact of Heavy Metals on Abiotic, Biotic, and Cultural Elements

Heavy metals are hazardous and non-degradable elements. If waste containing heavy metals is disposed of carelessly, it can accumulate in soil and water, making it very dangerous for environmental ecosystems (Widyasari, 2021). Heavy metals are also a type of environmental pollutant that is most commonly found in waters and can have a negative impact on humans who use water and organisms that live in these waters (Kamarati et al., 2018). The location of the Putri Cempo landfill itself, which is close to residential areas, is one of the problems. The types of heavy metals studied in this research are manganese (Mn) and iron (Fe). Manganese is a heavy metal that is toxic and can accumulate in biological stages. Manganese (Mn) can be found in solids in soil. This is because if organisms such as plants, animals, or microbes absorb manganese from contaminated soil or water, the content can increase toxicity in higher-level organisms. While in the environment manganese is usually found in the form of solid compounds, such as oxides, hydroxides, or carbonates of manganese, which are part of the minerals in the soil. particles in water, and dust particles in the surrounding air, high manganese (Mn) content resulting from landfills can produce leachate which causes environmental polluting factors (Afrianti, 2022).

Increased levels of heavy metal manganese (Mn) in the environment can have a significant impact on abiotic, biotic, and cultural elements. Abiotically, high manganese content in soil can cause changes in the physical and chemical properties of an environment, because manganese can clump soil particles that can change the texture of soil aeration (Abuzahrah et al., 2023). Manganese (Mn) can also affect the availability of nutrients for plants and soil microorganisms, because as an essential microelement, manganese is needed in the process of photosynthesis, respiration, and plant metabolism. However, when manganese levels are excessive, it can serve as an inhibitor for the uptake of other nutrients, such as calcium, magnesium and iron, which are important for plant growth. Excess manganese can form complexes with iron, reducing its availability in a form that plants can assimilate. Elevated levels of manganese (Mn) can also impair water quality because manganese dissolved in water can impair the clarity of the water which can ultimately reduce the biological productivity in it (Amoah et al, 2024). Because of this, it can reduce the availability of clean water for living organisms and society. If consumed by humans, it can cause health problems for humans. Plants, animals and microorganisms can also be exposed to manganese through food or water contaminated with heavy metals (Munir et al., 2021). This can lead to impaired growth and reproduction, organ damage, and oxidative stress in plants and animals. Cultural elements can also be affected as elevated levels of manganese in agricultural soils can damage crop productivity, affect food security, and affect the local economy.

Iron is the fourth most abundant metal in the Earth's crust (Gutteridge and Halliwell, 2024). Iron-mediated reactions can support most aerobic organisms in their respiration process (Liu et al., 2024). If not properly protected, it can catalyze reactions that involve the formation of ratios that can damage cells, tissues, and organisms. iron's original form is silver-white, which is strong and tough, but today it is difficult to find pure iron. Most iron found contains carbides, silicides, foricides, and sulfides, while some have been found to contain contaminants. Iron (Fe) is an essential heavy metal whose presence is needed in certain amounts by every living organism, but if it has an excessive amount it can have a toxic effect on the ecosystem and those in it (Supriyanti and Endrawati, 2015). Heavy metals, including iron (Fe), are elements that have high atomic weights and often accumulate in the environment, significantly impacting various aspects of life and ecosystems (Mitra et al., 2022). Excessive levels of iron can have direct and indirect impacts on abiotic, biotic and human cultural elements. degradation of soil and water quality and disruption of the balance of microbiota in soil and water are effects of iron metal contamination on abiotic elements. Decreased health of organisms in the ecosystem and bioaccumulation of heavy elements in species in the ecosystem are the effects on biotic elements. While in the social environment, public health occurs, this can occur without the community itself realizing it. Increased iron levels in water and soil are caused by excessive industrial or agricultural activities. This has the potential to poison aquatic organisms and disrupt the food chain. Some plants may experience poisoning or impaired growth due to high iron (Fe) levels, but there are some other organisms that can utilize it for better growth. In the context of culture, iron (Fe) levels in agriculture and industry have significant economic and environmental implications. Thus, the treatment of iron (Fe) and manganese (Mn) levels in ecosystems and the environment is very important to maintain ecosystem balance, human health and to minimize their negative impacts on abiotic, biotic, and cultural elements.

3.5. Strategies to Reduce Heavy Metal Contamination in Sediments of the Putri Cempo Landfill River Flow

Heavy metals that pollute the environment will be very dangerous for the health of the environment and society (Munir et al., 2021). High concentrations of heavy metals in the environment can cause environmental damage and increase the toxicity of metals. In the Putri Cempo landfill, there is a lot of old waste that is not properly processed. As demonstrated Putra et al. (2016), have recently shown the length of the waste pile in the landfill will greatly affect the amount of heavy metals contained. The increase in heavy metal concentrations in old waste can be caused by the length of time of degradation. Because when waste is not degregated properly, the metals contained in it will not be degredated, then the existing heavy metals can be released and increase the concentration of free heavy metals. In addition, the flow of water, such as during rainfall, can dissolve heavy metals so that the leaching process occurs. Along the sampling river, there was a lot of waste that was washed away and eventually accumulated on the banks of the river. The waste looks like old waste, many of which have been destroyed.

One of the ways that can be done to reduce heavy metal levels in river sediments in the Putri Cempo landfill is by remediation. Remediation itself is a technology used to restore the environment both land, water, and air that has been polluted. With this method, at levels of heavy metals found to be degraded by microorganisms or absorbed by plants, it can work more effectively. The less degraded environment provides better conditions for microbial and plant growth, and the lower cost is also the reason why this method is chosen. More specifically, the reduction of heavy metals in the sediment can use bioremediation. Bioremediation itself is the process of cleaning soil pollution using microorganisms (Supriatna et al., 2021). One of the organisms that can bind Fe and Mn heavy metals is Aspergillus. In addition, phytoremediation can also be done. Phytoremediation itself is the process of converting pollutants that have complex molecular chains into simple ones using plants (Irhamniet et al., 2018). Plants used in the phytoremediation process are plants that have the ability to accumulate high concentrations, which are called hyperaccumulator plants (Christofer et al., 2022). Plants that can be used to reduce Fe and Mn levels are Fimbristylis globulosa Retz. Kunt mendong (Putri and Estuningsih, 2021). This plant is also easy to plant because it does not require special soil types

4. Conclusions

From the research that has been carried out, it is found that in the river sediment around the Putri Cempo River, the Fe level is 1519.414245 mg/L while the heavy metal Mn level is 130.033 mg/L. When viewed from the quality standards based on the US EPA, Fe metal has exceeded the quality standards and Mn has not exceeded the threshold. Increased levels of heavy metals both Fe and Mn can have a significant impact on abiotic, biotic, and cultural elements. If the level of pollution continues to increase, it will be harmful to vegetation and organisms that live around the sediment. Therefore, efforts can be made to reduce heavy metal levels in sediment in the Putri Cempo TPA river flow by remediating, especially bioremediation techniques using Aspergillus organisms and phytoremediation using mendong plants.

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