

*Regional Case Study***Analysis of Heavy Metals Pb and Mn in River Water at Putri Cempo Landfill**

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**Abstract**

Waste is a crucial issue with far-reaching impacts on the environment, public health, and economy. The Putri Cempo landfill receives waste from Surakarta City. Waste can pollute the river near the landfill, given the location of the river that adjoins and is close to residential areas. The purpose of this research was to analyze the river water quality around the Putri Cempo landfill for heavy metals Pb and Mn. The research was conducted by taking samples directly from the river and then analyzing the heavy metal content. The results were compared with river water quality standards according to Indonesian Government Regulation 22/2021. The results showed that the Pb content in river was 0.02392344 mg/L and Mn was 4.206021703 mg/L. From these results, the Pb content in the river did not exceed the quality standard limit, whereas the Mn content exceeded the quality standard limit. It can be concluded that the river water around Putri Cempo landfill has been contaminated with Mn. Heavy metals in high levels can harm living things and the environment, can cause death to aquatic biota and plants, disease in humans, degrade water quality and damage river aesthetics. Further evaluation of stakeholders is required to address heavy metal pollution.

Keywords: Heavy metals; lead (Pb); manganese (Mn); river; Putri Cempo landfill

1. Introduction

Waste is a crucial issue that has a broad impact on the environment, public health and the economy. Along with population growth and urbanization, waste volumes continue to increase, causing enormous pressure on existing waste management systems. In urban areas, improperly managed waste contributes to land, water, and air pollution. In various parts of the world, including Indonesia, the uncontrolled increase in waste volume is a major challenge that requires serious and sustainable handling. The Putri Cempo landfill, which has been operating since 1987, receives waste input from all corners of the city of Surakarta. With a waste landfill area of 8 ha, the Putri Cempo landfill is currently implementing an open dumping system, which means that the waste that enters the landfill will only be piled up (Romala et al., 2020). Landfilling is the most profitable waste disposal technique in many developing countries around the world (Ojekunle et al., 2022). The accumulation of this waste can

negatively impact the lives of people around the landfill. However, the Surakarta city government continues to strive for various ways to reduce the impact of landfills. One example is the creation of a PLTSa 'Pembangkit Listrik Tenaga Sampah' (Trash Power Plant). It is hoped that with the construction of the PLTSa, the 'mountain' of rubbish at the Putri Cempo landfill can be converted into a source of electricity that can be utilized by the people of Surakarta City.

Rivers are open water ecosystems vulnerable to pollution (Indriyani et al., 2024). River flow pollution is generally caused by human activities and environmental conditions around the river. River water pollution by heavy metals is a serious threat to human health, because heavy metals enter the ecosystem as contaminants that are very stable and cannot be decomposed, thereby polluting water resources (Mokarram et al., 2020). Heavy metals are dangerous pollutants that are toxic to living creatures and the environment if present in large quantities. The heavy metal content that has accumulated in water can be an indicator of pollution in aquatic environments (Azizah & Maslahat, 2021). Activities at the Putri Cempo landfill, including waste transportation, accumulation, and processing, as well as activities from the surrounding community, have the potential to produce waste that acts as a source of heavy metal pollutants. Heavy metals are classified as contaminants if their concentrations exceed a certain threshold (Okechukwu et al., 2024). Inorganic waste buried in landfills contains heavy metal compounds which dissolve and decompose simultaneously with the formation of leachate (Karamina et al., 2021). Various activities at the Putri Cempo landfill have the potential to contribute solid or liquid waste to the river flow, considering the river is quite close to the landfill area. This can trigger various problems that arise in river flows, both in terms of quality and aesthetics. Poor river water quality has a negative impact on the abiotic, biotic, and cultural components around the Putri Cempo landfill river flow.

This research provides a new contribution in understanding the impact of heavy metal pollution, especially Pb (lead) and Mn (manganese), on river water quality around Putri Cempo landfill which has not been widely studied. The results of this research provide the latest data on the level of heavy metal pollution in the area which is important as a basis for recommendations for safer waste management and environmental protection around the landfill. In addition, this research discusses the relationship between activities at the landfill and increasing levels of heavy metals which can be an important reference for further research related to mitigating the impact of solid waste on aquatic ecosystems. The goals of this research is to analyze the quality of river water around the Putri Cempo landfill for the content of heavy metals lead (Pb) and manganese (Mn), as well as determine the impact of heavy metal pollution and alternative handling solutions. The benefit of this research is that the public can determine the distribution of lead (Pb) and Manganese (Mn) in the Putri Cempo landfill, thereby becoming more aware of heavy metal pollution in the river flow around the Putri Cempo landfill.

2. Methods

2.1. Time and Location of Research

This research was carried out from March to May 2024. Research samples were obtained by collecting directly in the river around the Putri Cempo landfill as at the research location (Figure 1). Sampling is located at coordinates 7°31.998'S and 110°51.563'E. Water sampling was conducted based on Indonesian National Standard (SNI) 6989.57:2008 Water and wastewater-Part 57 on surface water sampling methods. Sample preparation was carried out at the Soil Chemistry Laboratory, Faculty of Agriculture, Sebelas Maret University. Analysis of the heavy metals Lead (Pb) and Manganese (Mn) in the samples was carried out at the Sebelas Maret University Integrated Services Unit, Integrated Laboratory Chemistry sub-laboratory.

2.2. Tools and Materials

The tools used in this research were a dropper pipette, 1 mL measuring pipette, 50 mL measuring flask, 100 mL Erlenmeyer, pump, 500 mL Erlenmeyer, 1000 mL Erlenmeyer, 50 mL measuring cup, 150 mL

beaker, 5 mL measuring flask, and Atomic Absorption Spectroscopy (AAS). The materials used in this research were river water around the Putri Cempo landfill, aquabidest, concentrated nitric acid (HNO₃, 1,000 ppm Pb standard solution, Pb standard solution (0.05; 0.1; 0.25; 0.5; and 1 ppm), Mn standard solution 1,000 ppm, Mn standard solution (0.1; 0.2; 0.5; 1; and 2 ppm), and Whatman filter paper.

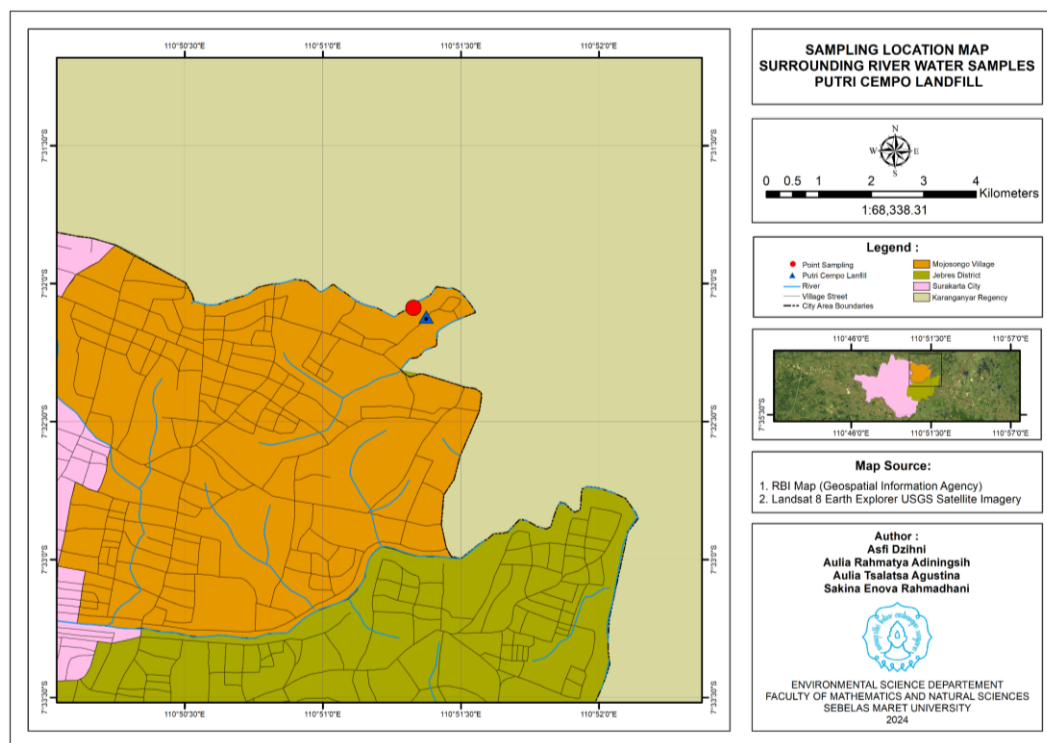


Figure 1. Water sampling location

2.3. Heavy Metal Testing

The research conducted refers to SNI 6989.8: 2009 on How to Test Lead (Pb) Atomic Absorption Spectrophotometry (AAS) and SNI 6989.5: 2009 on How to Test Manganese (Mn) Atomic Absorption Spectrophotometry (AAS) to determine the concentration values of heavy metals Pb and Mn in river water samples around the Putri Cempo landfill. River water samples around the Putri Cempo landfill and standard solutions were prepared first, then tested using AAS (Atomic Absorption Spectrophotometry).

2.4. Data Analysis

The data analysis used is by comparing the results of heavy metal tests with river water quality standards according to Appendix VI of the Government Regulation of the Republic of Indonesia Number 22 of 2021 concerning the Implementation of Environmental Protection and Management. The amount of Mn concentration allowed in class 1 is 0.1 mg/L and the concentration of Pb in classes 1, 2, and 3 is 0.03 mg/L, and class 4 is 0.5 mg/L. Calculation of heavy metal content was carried out using the standard curve linear regression using equation (1):

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

Description: y = sample uptake; m = coefficient of x ; c = constant

3. Result and Discussion

3.1. Environmental Hue

Putri Cempo landfill is located on the border between Mojosoongo Village (Surakarta) and Plesungan Village (Karanganyar Regency) (Ramadhanti et al., 2021). This landfill has been the pulse of waste management in Surakarta City for more than 37 years. According to data from the Surakarta City

Environment Agency in 2019, Putri Cempo Landfill has a total area of 17 hectares, with 8 hectares or 80,000 m² used for landfilling. This landfill accommodates waste from various regions in Surakarta, with an average of 300 tons of waste per day. The average height of the waste pile is about 10 meters, so the total volume of waste is estimated to reach around 800,000 m³. Assuming an average density of 1.0875 tons/m³, the total waste in the Putri Cempo landfill is estimated to be around 870,000 tons. In its operation, the Putri Cempo landfill uses the open dumping method, which means that waste is dumped directly without special treatment.

In addition to landfilling activities, there are also other activities in the landfill area and its surroundings such as transportation, sorting, recycling, and leachate treatment. Untreated leachate can enter the river causing pollution of the river water. In addition, leachate spillage that seeps into the ground can also contaminate groundwater below the surface. The river used for sampling had an unpleasant odor and brownish color.



Figure 2. Overview of river water conditions

3.2. Concentration of Heavy Metals Pb and Mn in River Water

In the context of this study, the analysis of heavy metal concentrations of Pb and Mn in the waters around the Putri Cempo Landfill was conducted as a preventive measure to protect environmental quality. Based on Pb testing that has been done, it is known that the concentration of 0.05 ppm has an uptake of 0.0012, at a concentration of 0.1 ppm has an uptake of 0.0034, at a concentration of 0.25 ppm has an uptake of 0.009, at a concentration of 0.5 ppm has an uptake of 0.0171, and at a concentration of 1 ppm has an uptake of 0.0331. The highest absorption value is located at a concentration of 1 ppm. There are differences in uptake values at each concentration tested. This absorption value will depend on the levels or substances contained in a solution. The more levels of a substance in a sample, the greater the absorption value. This happens because there are more molecules that absorb light. Meanwhile, the Pb metal content in river water around the Putri Cempo landfill is -0.02392344 mg/L.

In the Mn test that has been carried out, it is known that the concentration of 0.1 ppm has an absorption of 0.0041, at a concentration of 0.2 ppm has an absorption of 0.011, at a concentration of 0.5 ppm has an absorption of 0.0313, at a concentration of 1 ppm has an absorption of 0.0643, and at a concentration of 2 ppm has an uptake of 0.1293. The highest absorption value is located at a concentration of 1 ppm. There are differences in uptake values at each concentration tested. This absorption value will depend on the levels or substances contained in a solution. The Mn metal content in river water around the Putri Cempo landfill is 4.206021703 mg/L.

Table 1. Calculation results of lead and manganese levels

Parameters	Y (Abs)	m	X (mg/L)	C
Lead (Pb)	0.0008	0.03344	-0.02392344	0.0000
Manganese (Mn)	0.2737	0.06543	4.206021703	0.0015

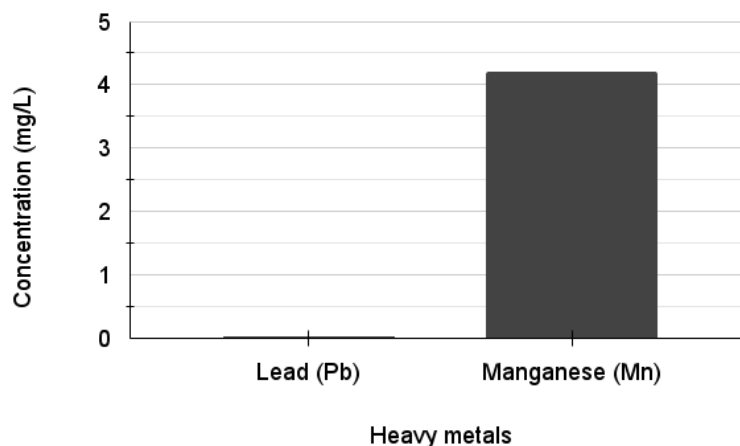


Figure 2. Concentration of heavy metals Pb and Mn at the research location

In the table 1, it is shown that the Pb level in river water samples around the Putri Cempo landfill is -0.02392344 mg/L. This figure is considered not to exceed the quality standard limit in appendix VI of Government Regulation of the Republic of Indonesia Number 22 of 2021 concerning the Implementation of Environmental Protection and Management. From the table it is also known that the Mn level in river water samples is 4.206021703 mg/L. This figure has exceeded the quality standard in appendix VI of Government Regulation of the Republic of Indonesia Number 22 of 2021 concerning the Implementation of Environmental Protection and Management. The Mn concentration is considered higher than the Mn concentration found in water bodies around the Mogla Bazar landfill, Sylhet, Bangladesh, which is 0.01-0.99 mg/l (Alam et al., 2020) . From the tests conducted, it is known that the river water samples around the Putri Cempo landfill tested are contaminated with heavy metal Mn.

3.3. Causes of Heavy Metals in Waters

The appearance of heavy metals in the environment occurs through various processes, both natural and anthropogenic in origin (Zhou et al., 2020). Natural sources have little impact on the ecological environment, while intense human activities generally bring additional heavy metal substances and environmental pollution (Zhang et al., 2021). Heavy metals are present in the Earth's crust along with other minerals and will be deposited into aquatic systems from dry and wet fallout from atmospheric aerosols formed from windblown dust, volcanic emissions, forest fires, and vegetation (Tony et al., 2021). The main sources of heavy metal pollution can come from anthropogenic activities such as waste disposal, pesticides and agricultural activities, domestic emissions, combustion, waste incineration, vehicle exhaust, and mining (Karimian et al., 2021). The location of the river, which is adjacent to the Putri Cempo landfill and close to residential areas, is certainly the cause of this problem. Based on research that has been conducted, a lot of plastic waste was found in the river. In addition, the birth of industrialization and also rapid urbanization can reduce the carrying capacity of water. The high mountains of waste in the landfill also threaten the small streams below. The avalanche from the mountain will carry various organic and inorganic waste containing heavy metals and will further pollute the river. This is due to the close proximity between the mountain of waste and the river. In fact, it can be said that the edge of the mountain of garbage is directly in contact with the river flow below without being limited by anything. Leachate or liquid from waste also contributes to the contamination of river flow by heavy metal compounds. Higher levels of heavy metals were found in streams close to the landfill where pollution is

thought to come from landfill activities and leachate disposal (Sulistyowati et al., 2023). Leachate can contain heavy metals as a result of the decomposition process of waste that accumulates with various toxic chemicals, bacteria, organic compounds, and inorganic compounds. Small rivers along the landfill become the initial channels and estuaries where leachate from the main landfill collects. During the rainy season, the leachate will move from the waste accumulation site to the river. This creates a sour smell and changes the natural color of the river.

3.4. Impact of Heavy Metals on Environmental Aspects

Low levels of Mn are necessary for enzyme activity. However, when in high concentrations, it will then accumulate in the muscles, liver, and affect the brain and central nervous system. Similarly, heavy metal Pb can be used as an indicator of water pollution. Pb with concentrations above normal quality standards can pollute the aquatic environment and endanger living things in it. Both heavy metal compounds can settle and accumulate in river sediments, then when the temperature increases the sediments will spread and dissolve carried by the flow of the river. The sediment acts as a sink from the heavy metal source, then the sediment will release the absorbed heavy metals into wider waters, thus contributing to river and ground water pollution (Ali et al., 2021).

In addition to adversely affecting abiotic components, heavy metal pollutants also affect the lives of biotic organisms along the river. At high concentrations, heavy metals become toxic and will cause death to various types of organisms living in the waters. The results of research also showed the immunotoxicity of Pb in aquatic organisms (Paul et al., 2014). Heavy metal Pb causes a certain level of immunotoxicity in aquatic organisms by disrupting the normal function of organs and the immune system of aquatic organisms. Heavy metals can be absorbed into the fish body in three ways, namely through the gills, skin surface cells, and the hypodermis layer, the heavy metals will accumulate into various organs or body tissues through the blood and digestive tract (Hong et al., 2020). Heavy metals accumulated in the body of aquatic biota will then undergo a process of bioaccumulation, bioconcentration, and biomagnification (Lukmanulhakim et al., 2023). Heavy metals not only have a major impact on aquatic organisms, but also seriously threaten human health. Heavy metals can enter the human body through fish that have been contaminated with heavy metal pollutants. If the fish is cooked and eaten by humans, heavy metals will simultaneously enter and accumulate in the human body, which can cause organ damage. As a result, various disease disorders will arise because these organs cannot function as they should (Syafriiliansah et al., 2022). Lead that accumulates in the human body can be toxic and an enzyme inhibitor, but it can also cause damage to nerves, blood, brain and hematology. High levels of Mn can cause disorders of the brain and central nervous system (Tony et al., 2021). The toxic effects of heavy metals cause loss of brain and nervous system function, as well as serious damage to the blood, liver, spleen, kidneys, internal organs and other organs. This damage results in physical weakness, hypomnesia, allergic skin reactions, hypertension and other symptoms (Krystofova et al., 2009). Leachate from waste disposal sites contains heavy metals such as lead and manganese in high concentrations. This leachate then enters the river adjacent to the waste disposal site, especially in the lower reaches of the river. This increases the problem of river water pollution compared to the upstream part of the river which is located far from the waste disposal location. The Enugu landfill also showed that water contaminated with heavy metals is acidic (Ozoko et al., 2022). Water that is too acidic can cause a decrease in biodiversity in waters because only organisms that are tolerant of acidic conditions can survive. In the abiotic aspect, this can change the availability of nutrients and minerals in river water. Apart from that, it causes health problems in the people who use it. One of the biodiversity in question is aquatic plants. The toxic effects of heavy metals on aquatic plants include damage to cell membrane structures; inhibition of respiration, photosynthesis, growth and development; and toxicity to genetic material (Hong et al., 2020). Heavy metals entering plants can change the activity of antioxidant enzymes, induce ROS production, and cause oxidative damage effects. At the same time, heavy metals can disrupt normal physiological and biochemical reactions.

River water contaminated with heavy metals due to runoff from the Putri Cempo landfill cannot be used by residents for daily needs such as bathing, washing or cooking. Surface water pollution has an important role in triggering stress, because humans depend on the presence of water (Mekonnen et al., 2020). Residents are forced to look for other sources of clean water. Polluted rivers can also reduce the welfare of residents who depend on rivers. If polluted rivers are used as a source of food, such as fish or aquatic plants, the availability and safety of consumption of these foods will be disrupted. Essential heavy metals such as Mn (in sufficient levels) maintain good metabolic activity in living organisms while other non-essential heavy metals such as Pb cause poisoning in the human body (Dey et al., 2021).

3.5. Efforts and Recommendations

Heavy metal pollution originating from landfills at the Putri Cempo landfill needs to be processed to reduce the concentration of substances and the quantity of pollutants. One step that can be taken to overcome the metal contamination problem is to further optimize the waste-powered power plant (PLTSa) in the city of Surakarta. The existing waste will be converted into raw materials for PLTSa (Aprilianto & Manar, 2024). Then, these raw materials will be used to produce electrical energy. This will result in the previous pile of rubbish being used up, and the rubbish going to the Putri Cempo landfill will be directly processed into electrical energy.

The location chosen must be far from settlements and river flows so as not to affect the sanitation system as seen from the aspect of cleanliness and health of the population around the landfill. The landfill also needs to be equipped with a leachate collection system, so that leachate cannot seep and be absorbed into water sources and the soil. Based on the calculation of the geo-accumulation index (Igeo), soils affected by waste/leachate in non-sanitary landfills experience moderate to severe pollution, especially in As, Cd, and Pb levels (Hussein et al., 2021). The accumulation of Igeo As and Cd in non-sanitary landfills shows heavier pollution than sanitary landfill samples. The level of toxicity of heavy metals, especially in open dumping landfills and waste dumps that are not well managed, can pose a major risk to water flows around waste dumps, plants and ecosystems, as well as public health (Vaverková et al., 2018).

Apart from that, bioremediation can also be carried out in river flows that have been contaminated with heavy metals using the help of microbes. Bioremediation uses certain microorganisms to grow on a pollutant with the aim of breaking down and reducing the levels of the pollutant. When the bioremediation process takes place, microorganisms will produce enzymes that can change the structure of pollutants into non-complex ones and convert them into non-toxic and dangerous metabolites (Widiatmono et al., 2020). Bioremediation using microalgae is one step to reduce heavy metal levels in waters, microalgae can accumulate heavy metal pollutants in their bodies so that they can be used as biosorbents to deal with the problem of heavy metal pollution in waters (Zakir et al., 2022). Microalgae are considered as promising biosorbents for the removal of toxic heavy metal ions from wastewater (Makhanya, et al., 2021). Compared with traditional wastewater treatment methods, microalgae can efficiently remove nutrients, organic pollutants, heavy metals and pathogens in wastewater and tolerate certain toxic substances (Yan et al., 2022) Microalgae cells can absorb heavy metals through different physiological and biological methods and use them as a nutrient source to regulate metabolic processes for biomass production (Goswami et al., 2022) To date, bioremediation using microalgae is considered economically efficient and environmentally friendly (Singh et al., 2022)

4. Conclusions

The river water around the Putri Cempo landfill has been contaminated by the heavy metal Mn because it has exceeded the quality standard limit. The Mn metal content in river water around the Putri Cempo landfill is 4.206021703 mg/L. Meanwhile, the Pb metal content in river water around the Putri Cempo landfill is -0.02392344 mg/L, which means it is still below the quality standard limit. Heavy metal pollution has a negative impact on abiotic, biotic and cultural components. This pollution can contaminate the aquatic environment and harm various aquatic organisms. Apart from that, this pollution

also threatens the welfare of residents who depend on the river for their daily needs. Bioremediation using microalgae, increasing the efficiency of PLTSA, and collecting leachate by paying attention to location can be steps to reduce heavy metal levels in polluted waters.

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