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# **Study of Heavy Metal Lead (Pb) and Manganese (Mn) Concentrations in Pekalongan City Water Sediments**

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#### ABSTRACT

The issue of waste containing heavy metals in organic materials has drawn attention in the city of Pekalongan due to its association with industrial activities. Heavy metals such as Lead (Pb) and Manganese (Mn) tend to accumulate in waste and have toxic effects on the environment. This study aims to determine the concentration and distribution of heavy metals Lead (Pb) and Manganese (Mn) in sediment in the waters of Pekalongan City and the factors influencing them. Field data collection was conducted in June 2022 at 11 sample station points. Sediment samples were collected using a sediment grab and analyzed using Atomic Absorption Spectrophotometry (AAS) at the Laboratory of the Center for Industrial Pollution Prevention Technology, Semarang. The distribution map of heavy metal concentrations was created using ArcGIS with Sentinel 2 satellite imagery. The concentration of Lead (Pb) ranged from 8.239 mg/kg to 37.56 mg/kg, while Manganese (Mn) ranged from 309.2 mg/kg to 740 mg/kg. The distribution pattern indicates the lowest content near the coastline and the highest in the northwest direction. The distribution of Lead (Pb) and Manganese (Mn) in sediment is influenced by oceanographic physicochemical factors such as tides, currents, sea waves, depth, and organic matter content in sediment.

Keywords: Lead (Pb), Manganese (Mn), Heavy Metal Concentration, Sediment, Pekalongan City

#### 1. Introduction

Pekalongan is a cultural city located on the north coast of Central Java with the most famous culture, namely batik. Batik itself is spread across various regions in Indonesia and not only Pekalongan City is the center for batik, but Pekalongan Regency also has many batik centers so that Pekalongan was named by UNESCO the "Creative City of the World" in 2014 so it has been successful to date (Hazliansyah, 2014). Behind the success of the Pekalongan Batik Center, there is a complicated problem that persists today, namely the problem of water environmental pollution caused by industrial waste and community waste. The industries in Pekalongan City itself are very diverse, such as batik, textile, metal, wood, and many others. The level of public awareness that is lacking in protecting the environment means that pollution cannot be avoided. In fact, in research conducted by Paramnesi & Reza (2020), data was obtained from the 2014 Pekalongan City Environmental Agency that the batik industry waste that was dumped into the river in Pekalongan area. The heavy metal elements in this waste cannot be destroyed or degraded so they are water pollutants in ditches, rivers, and even the sea. The heavy metal content that accumulates in sediment, both bottom sediment and suspended solid material (MPT), will be absorbed by organisms in these waters and cause toxic effects on organisms (Ramlia *et al.*, 2018). Types of heavy metals commonly found in batik industry waste include lead (Pb), chromium (Cr), cadmium (Cd), and many more (Indrayani, 2018).

Lead, which makes up only about 0.0002% of the Earth's crust, is commonly associated with global mining activities and has similar toxic impacts on organisms, as discussed by Sarkar *et al.* (2022). The toxic effects of lead include acute health problems that can harm aquatic organisms and threaten the sustainability of aquatic ecosystems, as found (Pratiwi, 2020). On the other hand, manganese, a metal with chemical properties similar to iron, is also a problem in waters with potential toxicity to humans and the environment, as stated by Misno & Nirmala (2016), and Sari *et al.* (2016). These two metals come from various industrial and agricultural activities, requiring monitoring and management strategies to maintain water quality and the sustainability of aquatic ecosystems, as discovered by Matveeva *et al.* (2022) and Sumarno & Syafiuddin (2023). Likewise, Chan-Pacheco *et al.* (2021) and Nkele *et al.* (2022) studied the potential for manganese hydroxide deposits in the aquatic food chain, showing the importance of monitoring and appropriate treatment of manganese pollution. Organic matter in sediments plays a vital role in maintaining the balance of aquatic ecosystems by providing substrates for microbial life and supporting various biogeochemical processes (LaRowe *et al.*, 2020; Nagar *et al.*, 2021). These microorganisms utilize organic material as an energy source through the decomposition process, which also affects water and sediment quality as well as biogeochemical processes (Nelson *et al.*, 2023; Ravn *et al.*, 2020). Meanwhile, complex organic metal compounds in sediments play an important role in the complex interactions between organic materials and heavy metals (Velusamy *et al.*, 2021). The formation of these complex compounds can change the physicochemical processes for heavy metals, affecting their mobility and distribution in aquatic ecosystems, as well as toxicity for living organisms (Boguta & Sokołowska,

2020; Yunus *et al.*, 2020). This process can produce significant changes in the behavior of heavy metals in sediments, including mobility influenced by the availability of complex compounds and varying toxicity depending on the type of complex compound formed (Miranda *et al.*, 2021; Ukalska-Jaruga *et al.*, 2021).

Based on research by Susanti *et al.* (2014), the condition of the waters of Pekalongan City shows that the Pb content in waste reaches levels of 57.40 ppm, while the Mn value has never been measured. These results show that the waste content in situ is quite high. Observations by Ridarto *et al.* (2023) and Zainuri *et al.* (2022) show that waste spreads and changes in quantity are influenced by factors such as tides, sea level rise due to tidal waves, and seasonal changes. The distribution of heavy metal waste in the waters of Pekalongan City requires continuous observation. Community activities that are less aware of processing their waste cause an increase in pollution levels and heavy metal concentrations. These heavy metals are toxic to the surrounding environment. The distribution of pollution needs to be understood to determine its direction and impact. Based on the distribution map, pollution prevention points can be determined so that it does not spread to other areas (Mardizal and Rizal, 2024).

In previous research conducted by Frances *et al.* (2022), it was found that the concentrations of the heavy metals arsenic (Ar), lead (Pb), zinc (Zn), and chromium (Cr) were still below quality standards and Kriging interpolation method is used to analyze the spatial distribution of these heavy metals. The research also obtained results that the concentration of heavy metals became smaller as you moved away from the river estuary. In another study by Tampubolon *et al.*, (2021), the concentration of the heavy metal Cuprum (Cu) spreads following the direction of current movement according to the time of research data collection. The concentration of the heavy metal Cu is also a pollutant, making the waters lightly polluted and approaching the threshold value for marine biota, making it quite difficult for fishermen to catch fish around the coast of Pekalongan City. The research results of Khotimah *et al.* (2022) show that the heavy metal lead (Pb) content in the Genuk River and estuary is related to metal industrial waste, vehicles, paint, etc. which results in heavy sediment accumulation. The research results of Warni *et al.* (2017) showed the same pollution conditions, namely the presence of heavy metals lead (Pb), manganese (Mn), copper (Cu), and cadmium (Cd), in rivers and estuaries as a result of industrial waste discharge.

This research is important to carry out considering the complexity and escalation of environmental pollution problems that occur in Pekalongan City. With a deeper understanding, it is hoped that appropriate and sustainable solutions can be found to deal with the negative impacts. The implications of these findings extend to various sectors, not only affecting the health of aquatic ecosystems and the living organisms around them but also potentially affecting community welfare and the cultural and economic sustainability of the city. Environmental problems that occur are not solely the responsibility of the government or related institutions but are also the collective responsibility of the entire community. Therefore, the hope from the results of this research is that the findings obtained can be a trigger to mobilize collaboration and concrete action from various parties, including the government, non-governmental organizations, industry, and the general public, to preserve the environment of Pekalongan City and leave it with a legacy. good for future generations.

#### 2. Material and Method

#### Materials

The research material used in this research consists of primary data and secondary data. Primary data includes the results of concentrations of heavy metals lead (Pb) and manganese (Mn) as well as organic matter in bottom sediments in Pekalongan City Waters. Meanwhile, secondary data includes sentinel-2 image data, wind data, tidal data, and bathymetry data. Primary data was obtained through direct collection and measurement, while secondary data was obtained from website sources or related literature.

#### **Tools and Materials**

The tools and materials used in this research include a boat with a capacity of 15 people as a means of transportation to the location of the data collection station, a Garmin 78s GPS with an accuracy of 0.01" to determine the position of the station location point, a Sediment Grab with a capacity of 5 kg as a tool for taking sediment samples base, plastic samples as a place to hold sediment samples, cellphones for documenting activities, and Atomic Absorption Spectrophotometry (SSA) to calculate the absorbance values of Pb and Mn metals, analytical scales, porcelain cups, ovens, measuring cups, digestion vessels, electric baths, funnels, watch glass, filter paper, Erlenmeyer, volumetric flask, volumetric flask, centrifuge, and laptop. The research materials used include a 1 kg sediment sample which is the focus of research regarding the concentrated not flast and organic materials, 2L analyte-free distilled water as a compound solvent, concentrated nitric acid (HNO<sub>3</sub>) solution, and concentrated hydrochloric acid (HCl) solution as an oxidizing agent.

#### Method

This research uses quantitative descriptive-analytical methods with a descriptive-analytical method approach to describe conditions or phenomena according to the data that has been collected. The method for determining location points uses a purposive sampling method to select samples that represent the condition of the research area as a whole. Sediment data collection was carried out by opening the sediment grab lever, attaching an iron hook, sinking it into the water, pulling the sediment to the surface, and inserting the sediment into a plastic sample.

Table 1. Sampling Location Points Coordinates

Station Coordinates

	Longitude	Latitude	
1	109° 41' 22,834"	6° 50' 47,149"	
2	109° 41' 39,014"	6° 50' 47,536"	
3	109° 41' 54,294"	6° 50' 48,142"	
4	109° 41' 20,739"	6° 50' 58,850"	
5	109° 41' 37,645"	6° 51' 2,676"	
6	109° 41' 51,516"	6° 51' 5,549"	
7	109° 41' 50,279"	6° 51' 23,836"	
8	109° 41' 36,036"	6° 51' 14,711"	
9	109° 41' 19,595"	6° 51' 15,774"	
10	109° 41' 36,104"	6° 51' 33,333"	
11	109° 41' 19,158"	6° 51' 57,636"	

#### **Data Analysis Method**

In this research, the method used to analyze heavy metal data involves acid digestion using Atomic Absorption Spectrophotometry (SSA) following US-EPA standards, SW 846 Method 3050 of 1996, and SM 3111 B 23rd edition of 2017. Steps The analysis includes weighing the sample, adding an acid solution, heating, cooling, and finally analyzing the absorbance values for Pb and Mn metals. Apart from that, this research also analyzes organic materials, the spatial distribution of heavy metals and organic materials as well as modeling analysis of tidal currents. Measurement of organic matter used the dry ashing technique (Loss of Ignition) as described by Jamaludin *et al.* (2021), carried out by drying the sample at 105°C for 12-24 hours until no water remains. After that, the organic material content in the sediment was measured by reheating at 550°C for 2 hours.

The spatial distribution was processed using ArcGIS 10.8 software by utilizing research location maps from sentinel-2 imagery, sampling point coordinates, and heavy metal concentration results which had previously been processed in Microsoft Excel. The IDW interpolation method was chosen based on research by Susetyo & Syetiawan (2016), which showed superiority in accuracy with the lowest RMSE. Current and tidal modeling involves wind, tidal, bathymetry, and satellite imagery data. Wind and tidal data were processed in Excel and realized in graphs of windrose and tidal patterns during June 2022. Meanwhile, bathymetry data and satellite imagery were processed in ArcGIS 10.8 to obtain the required mesh and water depth data. All this data was then entered into MIKE21 software and adjusted to the relevant time to obtain a model of currents and tides for June 2022.

#### **Results and Discussion**

This research provides an overview of several water conditions in Pekalongan City, by measuring and analyzing wind data, tides, and bathymetry which are visualized sequentially in Figures 1, 2, and 3.



#### Figure 1. Windrose in June 2022

Figure 1 displays data regarding wind direction and speed. From these data, it can be concluded that the dominant wind direction is from southeast to northwest, with a percentage of occurrence of 9.44% and 9.30%, and speeds ranging from 3.60 m/s to 5.70 m/s. Apart from that, there is wind moving from east to west, reaching a percentage of 8.33% with a speed of between 5.70 m/s to 8.00 m/s.



Figure 2. Tides in June 2022

(Source: iPASOET BIG 2022)

The tidal data in Figure 2 shows variations in seawater height during certain periods. The highest tide was recorded on June 20 2022 at 15.00 WIB with a height reaching 2.3 cm. On the other hand, the lowest tide occurred at several points in time, namely June 8 2022 at 23.00 WIB, June 11 2022 at 00.00 WIB, June 19 2022 at 22.00 WIB, and 23.00 WIB with a height reaching 1.41 cm. This shows natural fluctuations in sea level during that period.

#### Figure 3. Depth in Pekalongan Water



(Source: BATNAS BIG 2022)

Figure 3 displays bathymetric data showing variations in water depth in Pekalongan City. From this data, it can be seen that the water depth varies, ranging from 0.56 m to 10.82 m. Points 1-3 show relatively deeper depths, ranging from 7.40 m to 9.11 m. Meanwhile, points 4-6 have depths ranging from 5.69 m to 7.40 m. At points 7-9, the water depth drops from 3.98 m to 5.69 m. At points 10 and 11, the depth reaches between 0.56 m and 2.27 m. From this data, it can be concluded that the water depth conditions in Pekalongan City vary greatly, with some areas having relatively deeper depths than others.

In this study, the results of the concentration of the heavy metal lead (Pb) contained in the samples have been analyzed and presented in Table 2. In addition, a map visualization of the data is presented in Figure 4, which provides a clear and comprehensive picture of the distribution of Pb concentrations in the samples. -the sample studied.

Table 2. Lead (Pb)	Concentration	Analysis	Results
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No	Station	Lead Concentration (mg/kg)	Quality Standards (ANZECC (2000)	Results
			(mg/Kg)	
1	1	37,56		<qs< td=""></qs<>
2	2	8,239		<qs< td=""></qs<>
3	3	8,807		<qs< td=""></qs<>
4	4	13,86		<qs< td=""></qs<>
5	5	11,2	50	<qs< td=""></qs<>
6	6	13,86		<qs< td=""></qs<>
7	7	10,6		<qs< td=""></qs<>
8	8	17,88		<qs< td=""></qs<>
9	9	8,972		<qs< td=""></qs<>

10	10	9,298	<qs< th=""></qs<>
11	11	10,77	<qs< th=""></qs<>

\*QS=Quality Standards



Figure 4. Lead (Pb) Concentration Spatial Distribution Patterns in Bottom Sediment in Pekalongan Water

The research results show that the concentration of lead (Pb) in the bottom sediment of Pekalongan City waters varies between 8.239 mg/kg to 37.56 mg/kg, as shown in Table 2. Figure 4 shows that the lowest concentration was recorded at station 2 with a value of 8.239 mg/kg, while the highest concentration was seen at station 1 with a value of 37.56 mg/kg. The difference in concentration values between station 1 and station 2 is not only influenced by differences in depth but also by several other factors that play a role in sediment dynamics in these waters. First of all, strong currents around these stations are one of the main factors influencing sediment movement. The strong currents that occur at stations 1, 2, and 3 cause sediment to be carried towards station 1, especially because the depth is greater than at station 2. Apart from that, the difference in sediment grain size at the two stations is also a factor that influences the sedimentation process. According to research by Istianah *et al.* (2018), larger sediment particle sizes tend to have higher sedimentation rates. Pawitra *et al.* (2022) added that the percentage of silt content at point 2 is higher (95%) compared to point 3 (75%), which is assumed to have a similar position to stations 1 and 2. The dominant type of sediment is silt, which has a high possibility of experiencing sedimentation. Thus, a deeper understanding of the interaction between currents, depth, and sediment grain size is important in modeling sedimentation processes in these waters. The average lead (Pb) concentration at all stations is around 13.7315 mg/kg. This shows that the lead content in Pekalongan City waters is still below the quality standard threshold value set by the Australian and New Zealand Environment and Conservation Council (ANZECC) of 50 mg/kg.

The source of the heavy metal lead concentration in Pekalongan City mainly comes from the high accumulation of heavy metals in sediment, which originates from various industrial activities including the batik industry. Research by Ragil *et al.* (2023) highlighted that waste from the batik industry which is directly dumped into the waters is the main cause of pollution in the waters of Pekalongan City. This is because the batik production process uses various chemicals that have the potential to pollute water, including heavy metals such as lead. High lead concentrations in estuary sediments (55.77 mg/Kg) and sea waters (157.07 mg/Kg) indicate a significant level of pollution. These findings indicate that batik waste directly contributes to increasing lead concentrations in waters. In the latest research, lead concentrations in river estuary sediments and marine waters decreased to 9,298 mg/Kg and 11.2 mg/Kg, respectively. This decline may be due to pollution control efforts undertaken by the government or industry. Apart from waste from the batik industry, other sources of pollution include waste from coastal community activities, such as motor vehicle ship pollution and the use of lead-based paint in ship painting, as stated by Zammi *et al.* (2018). The presence of heavy metals such as lead demands serious action in industrial management and the implementation of steps to reduce pollution, protect the aquatic environment, and maintain the sustainability of marine resources. Furthermore, the results of the analysis of the concentration of the heavy metal Manganese (Mn), are shown in table 3 and visualized in figure 5.

Table 3. Manganese (Mn) Concentration Analysis Results

No	Station	Manganese (mg/kg)	Concentration	Quality (ANZECC (2000) (mg/Kg)	Standards	Results
1	1	495,4				>QS
2	2	450				>QS
3	3	452,2				>QS
4	4	624,9				>QS
5	5	504,3				>QS
6	6	740		5		>QS
7	7	488,3				>QS
8	8	309,2				>QS
9	9	681,8				>QS
10	10	517				>QS
11	11	607,1				>QS

\*QS=Quality Standards



Figure 5. Manganese (Mn) Concentration Spatial Distribution Patterns in Bottom Sediment in Pekalongan Water

Based on the data listed in Table 3 from research on the concentration of manganese (Mn) in the bottom sediment of Pekalongan City waters, the range of values ranges from 309.2 mg/kg to 740 mg/kg. Analysis in Figure 5 shows that the lowest concentration was recorded at station 8 with a value of 309.2 mg/kg, while the highest concentration was at station 6 with a value of 740 mg/kg. The distribution of manganese as a heavy metal is influenced by hydro-oceanographic factors in the waters of Pekalongan City. The highest manganese concentration was recorded at station 6, influenced by battery waste from the final disposal site (TPA) in Degayu Village. Ocean currents moving west and northwest carry sediment containing manganese from battery waste, which then accumulates at station 6. Station 9, located in front of Pasir Kencana Beach, also shows high manganese concentrations, which likely come from rivers such as Sungai Banger and Pencongan Rivers as well as human activities in coastal areas. Station 8, which is located at the mouth of the river, shows the lowest manganese concentration due to the influence of tidal currents which are not strong enough to deposit sediment containing manganese. Irwan et al. (2021). The average manganese (Mn) concentration from all stations is 533.655 mg/kg. It should be noted that the quality standard threshold value for manganese, as set by the Australian and New Zealand Environment and Conservation Council (ANZECC) in 2000, is 5 mg/kg. This shows that the manganese concentration in this study far exceeded the threshold set to maintain water quality. The results of this study consistently describe high concentrations of the heavy metal manganese in sediments, in line with previous findings by Warni et al. (2017), which shows that the concentration of the heavy metal manganese at Meulaboh port reached 1119.5 mg/kg to 1216.7 mg/kg, far exceeding the established quality standard threshold. Another study by Darmansyah et al. (2020) and Irwan et al. (2021) found similar results, where the manganese concentration in the sediments of Marunda Beach, Jakarta Bay ranged from 746.25 mg/kg to 1873 mg/kg, and in Peunaga Pasie Beach, West Aceh, it ranged from 420.54 mg/kg to 618.82 mg/kg. These findings highlight the lack of attention to heavy metal manganese pollution, both in processing the source of the pollution and in educating the public. Furthermore, this research also shows the total organic matter content in the bottom sediment of Pekalongan City waters which is shown in table 4 and visualized in figure 6 below.

Station	Total Organic Materials (%)	
1	12,98	
2	14,28	
3	13,9	
4	15,44	
5	17,48	
6	15,16	
7	11,22	
8	14,82	
9	14	
10	0,72	
11	15,5	

Table 4.	Organic	Materials	Analysis	Results
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Figure 6. Organic Materials (%) Spatial Distribution in Bottom Sediment in Pekalongan Water

Based on the information listed in Table 4, research on the total organic matter content in the bottom sediment of Pekalongan City waters shows variations between 0.72% to 17.48%. From Figure 6, it can be observed that the lowest concentration was recorded at station 10 with a value of 0.72%, while the highest concentration was seen at station 5 with a value of 17.48%. The average value of total organic matter content from all stations reached 13.22%. From these results, it can be concluded that there is significant variation in total organic matter levels across the area, with certain stations showing much higher levels than others. The binding of heavy metals to sediment is influenced by the role of the organic material in it. A study by Maslukah (2013) confirmed that organic material functions as a binder that controls the attachment of heavy metals to sediment. The total organic matter content in the sediments varied, as recorded between 0.72% and 17.48%. Analysis at various stations shows this variation, for example, the organic material content at station 1 reached 12.98%, while at station 5 it reached the highest point, namely 17.48%. Research also shows a pattern of decreasing and increasing organic material content at certain stations. Organic material in sediment plays a role in binding heavy metal ions through the formation of covalent bonds, as explained (Boguta & Sokołowska, 2020). The complex compounds formed influence the mobility and toxicity of heavy metals in sediments, which is supported by research by Miranda et al. in 2021. Apart from that, the accumulation of organic material is also influenced by the size of the sediment grains. Research by Jamaludin et al. (2021) shows that the finer the grain size of the sediment, the higher the organic matter content. A related study by Pawitra et al. (2022) confirmed that finer grain sizes, such as silt, tend to have lower organic matter content. This means that in this study, the size of the silt grains contributed to the relatively low organic matter content. This phenomenon can ultimately result in the capture of heavy metals by organic material which is then deposited in bottom sediments, causing changes in the physicochemical properties of heavy metals in the sedimentary environment.

#### 4. Summary

Based on research on Pekalongan City water sediments, it was concluded that there were heavy metals lead (Pb) and manganese (Mn). Even though the lead concentration does not exceed the quality standard threshold, indicating the absence of water pollution, the manganese concentration exceeds the quality standard threshold, indicating the presence of pollution. The distribution of heavy metals in sediment is influenced by oceanographic physico-chemical factors, such as tides, currents, ocean waves, depth, and organic matter content. For further research, it is recommended to examine the distribution of other types of heavy metals in Pekalongan City Water sediments. In addition, it is necessary to increase public awareness through outreach and education, as well as more effective waste management to protect the aquatic environment and maintain the sustainability of marine resources.

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