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Identification of Heavy Metal Concentrations in Seawater as an Index of Pollution in Central Java Ports

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ABSTRACT

This research aims to measure the heavy metal pollution index (Cu, Pb, Cd) in sea waters around ports in Central Java, namely KSOP Semarang, Rembang, Semarang, Kendal, Batang, Cilacap and Kebumen Ports. Sampling was conducted in December 2023, coinciding with the rainy season. Seawater samples were measured using the atomic absorption spectrophotometry (AAS) method to determine the concentration of heavy metals. The analysis results show that the Cu concentration in all locations is below the safe limit set by the Minister of Environment No. 51 Decree of 2004. The Pb concentration exceeds the safe limit in the Batang Sea (0.109 mg/L), while it is below the threshold in other locations limit Cd concentrations exceed safe limits in the Semarang Sea (0.022 mg/L), while in other locations, they are still within safe limits. Based on these results, the pollution index for Pb in the Batang Sea and Cd in the Semarang Sea are in the "lightly polluted" category.

Factors influencing heavy metal content include industrial waste, port activities, and surface runoff during the rainy season. Recommendations for environmental management include regular monitoring, strict waste management, environmental rehabilitation, increasing awareness, use of environmentally friendly technology, multi-stakeholder collaboration, and the preparation of stricter environmental policies. Implementation of these recommendations is expected to maintain water quality and reduce the risk of heavy metal pollution around Central Java ports.

1. Introduction.

A port is a multifunctional facility, not only a means of transportation but also a means of trade and business, industry, recreation, cultural heritage, and settlement. Apart from implementing occupational safety and health programs in business activities, environmental quality such as water quality, cleanliness of port workplaces, air quality, and noise (Pelindo et al. III, 2022).

The increasing demand for port services causes increased port activities, which need to be balanced with an appropriate environmental management system within the port. (Anisyah and Joko, 2016). Apart from that, shipping activities are increasing, especially in the transportation of goods and goods that have the potential to cause pollution, which causes damage to the marine environment due to oil, dangerous and toxic liquid materials in bulk form, or large quantities in packaged form, and potential pollution from ship operations. These are difficult to avoid, such as dirty oil and exhaust gas from ship machinery, the use or release of heavy metals into the aquatic environment, sewage and rubbish waste, and ship accidents (Malisan, 2011).

Marine pollution is the entry of dirt or waste from the activities of living creatures into sea waters. Besides the causes already mentioned, marine pollution comes from leftover war ammunition, ship waste, industrial waste, oil drilling, rubbish carried from land via rivers, maritime transport emissions, and pesticide waste from agriculture. However, the leading cause of marine pollution is oil spills from ship activities, offshore drilling, or ship accidents. Oil pollution in the sea is a primary concern for society because residents around the coast quickly feel its impact, and it is very damaging to life in coastal areas.

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Activities that cause environmental pollution produce waste that pollutes seawater, hurting marine life. The presence of heavy metals in seawater can occur naturally or as a result of human activities. Examples of natural sources of heavy metal pollution are volcanic processes, erosion, rock chemistry, soil weathering, and cliffs. Sources of heavy metal pollution from human activities include mining, traffic, household, agricultural, and industrial waste (Hutagalung and Rozak, 1997). There are several types of heavy metals, namely Lead (Pb), Cadmium (Cd), and Copper (Cu).

Heavy metals in waters will settle to the bottom and cannot be destroyed, so they accumulate to form sediment. As a result, organisms that feed on the bottom of waters are at high risk of exposure to heavy metals. Some marine biota, such as blood cockles, can absorb heavy metals in much higher quantities than those in the water. People's consumption of contaminated marine biota can cause health problems. Lead poisoning, for example, can cause various problems, such as shortening the life of red blood cells, reducing learning ability, and causing hyperactivity in children. This poisoning can also affect the nervous, kidneys, reproduction, endocrine, and heart (Palar, 2008). Therefore, research is needed to monitor the concentration of heavy metals in seawater.

(Anisyah and Joko, 2016) researched lead (Pb) metal pollution in the ballast water of cargo and passenger ships at Tanjung Emas Port, Semarang, showing that ship ballast water samples contained the heavy metal lead (Pb) exceeding the quality standards set by the Minister of Environment Regulation—number 5 of 2015, namely more than 0.01 mg/l. The average lead content in ship ballast water is 2.59 mg/l, 259 times higher than the quality standard, ranging between 1.12 mg/l to 4.12 mg/l. However, the results of research conducted by (Suryono and Djunaedi, 2017) showed that the seawater in Semarang's Tanjung Mas Harbor pool contained the heavy metals Pb, Cr, and Cd, although in relatively low concentrations.

Based on the pollution problem in marine waters and water quality, the government issued the Republic of Indonesia Government Regulation Number 21 of 2010 concerning Maritime Environmental Protection. Maritime environmental protection is an effort to prevent and overcome water environmental pollution from shipping-related activities. One way to prevent and overcome this is by analyzing seawater quality around Central Java ports.

In addition, the Minister of the Environment has issued Minister of Environment Regulation Number 03 of 2010 concerning Waste Water Quality Standards for Industrial Areas and Government Regulation 82 of 2001 concerning Management of Water Quality and Water Pollution. Water quality is determined based on the standard conditions of the water, and any deviation from these normal conditions is referred to as water pollution. Analyzing and determining water quality is very important for water users because it provides information about the presence of chemical compounds in water (Agustira and Lubis, 2013).

This research will be carried out under "Identification of Heavy Metal Concentrations in Sea Water as a Pollution Index in Central Java Ports." Three types of heavy metals, namely Lead (Pb), Cadmium (Cd), and Copper (Cu), were analyzed through physicochemical parameter analysis. So, the research results are expected to determine whether or not the heavy metal levels in the research area have exceeded the predetermined threshold.

2. Material and Methods.

2.1. *Types and Research Approaches.*

The type of research used is quantitative research, which aims to find out whether the seawater around the Central Java Ports, namely Semarang, Kendal, Rembang, Batang, Cilacap, Kebumen, and KSOP Semarang, meets the criteria for polluted water or is still suitable for use (quality). The research approach used in this research is a quantitative approach with pure experimental methods.

2.2. *Research Sample.*

The samples in this research were seawater from the ports of Central Java, namely Semarang, Kendal, Rembang, Batang, Cilacap, Kebumen, and KSOP Semarang. The research concentration was divided into 7 points with three samples of ± 600 ml each at different times for three consecutive days.

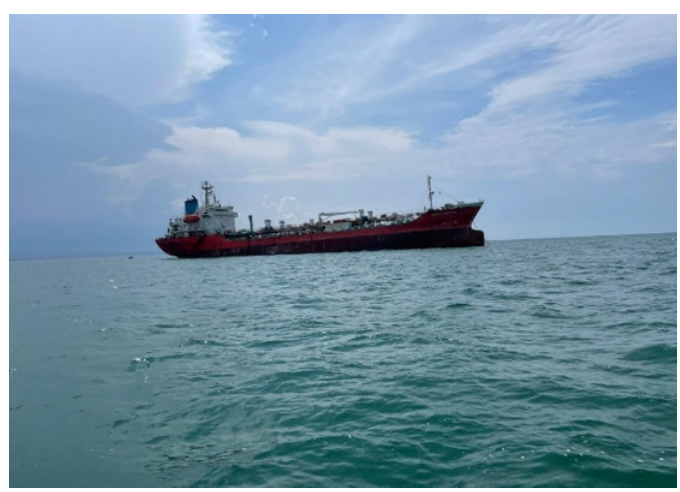
2.3. *Time and Place of Research.*

1. Research Time: January – September 2024
2. Research Place:

Seawater samples were taken around the ports of Semarang, Kendal, Rembang, Batang, Cilacap, Kebumen, and KSOP Semarang.

Testing for heavy metal content (Cu, Pb, Cd) contained in sea water was conducted at the Environmental Engineering Laboratory, Diponegoro University, Semarang.

Figure 1: Sampling in the Semarang Sea.



Source: Authors.

2.4. *Research Instrument.*

2.4.1. *Tools.*

a. 600 mL seawater sample bottle.
b. Atomic Absorption Spectroscopy (AAS) Buck Scientific type 210 VCP to measure heavy metal content.
c. OHAUS pH Meter type Aquasearcher to measure pH.

2.4.2. Material.

a. Seawater.
b. HNO_3 solution.
c. Aquades.

2.5. Research Methods.

The following steps are used to measure metal content in seawater samples using atomic absorption spectroscopy (AAS).

1. A 25 ml sample was taken using a dropper pipette, and then the sample was put into a 50 ml beaker, and 2.5 ml of HNO_3 solution was added to the sample. Before adding the HNO_3 solution, the pH of the sample was measured first.
2. After that, the sample mixed with the HNO_3 solution is placed on the hotplate until the sample volume becomes 10-15 ml, then the sample is transferred to a 25 ml measuring flask.
3. Next, the beaker glass is rinsed using distilled water three times, then the water from rinsing the beaker glass is put into a measuring flask, and distilled water is added to the measuring flask until it reaches the 25 ml mark.
4. In The final step, the sample is transferred to a plastic bottle (tightly closed) before being put into Atomic Absorption Spectroscopy (AAS). After these steps, the computer will read the heavy metal content and display the results on the computer screen.

3. Results and Discussion.

3.1. Heavy Metal Concentration Measurement Results.

In this research, levels of the heavy metals Copper (Cu), Lead (Pb), and Cadmium (Cd) were measured in the waters around the Port of Central Java. The research samples were taken from several locations, namely Semarang, Kendal, Rembang, Batang, Cilacap, Kebumen, and KSOP Semarang. Apart from measuring the heavy metals Cu, Pb, and Cd, the pH of seawater samples was also measured (Table 1). The research showed that seawater samples found the heavy metals Cu, Pb, and Cd in relatively low concentrations. The results obtained at the seven points can be seen in Table 2.

From the pH measurement results in Table 1, it can be seen that pH is the degree of acidity of a solution. pH is an important indicator for determining water quality. A pH that is within the normal range indicates that seawater has not experienced significant chemical changes that could harm marine life. The degree of acidity changes in value over a certain period, the pH will change erratically depending on the factors that influence it. These factors include 1) temperature, 2) the decomposition process of organic material, 3) photosynthesis, or 4) the presence of other elements submerged in the water (Sudewa & Hadiatna, 2018). The pH obtained in this measurement varies, some are less than 7 so it is acidic, and there are also pH measurement results that are more than 7 so it is alkaline.

Table 1: Results of pH Measurement of Seawater Samples.

No.	Sample	pH
1	KSOP Semarang	6.92
2	Rembang Sea	6.62
3	Semarang Sea	7.27
4	Kendal Sea	7.17
5	Batang Sea	7.29
6	Cilacap Sea	7.41
7	Kebumen Sea	7.06
Seawater Quality Standards (Source: Kementerian Lingkungan Hidup Republik Indonesia (KLH), 2024)		**6.5 – 8.5**

Source: Authors.

The solubility of the heavy metals Cu, Pb, and Cd in water is controlled by the pH of the water. At low pH (acid), the solubility of heavy metals such as Cu, Pb, and Cd increases. Higher levels of hydrogen ions (H+) in solution can interact with heavy metals, increasing their solubility in water. At higher (alkaline) pH, the solubility of heavy metals decreases. Heavy metal ions can react with hydroxide ions (OH-) to form insoluble hydroxide compounds, which then precipitate as sludge.

Based on the Decree of the Minister of Environment No. 51 of 2004, concerning Sea Water Quality Standards for Port Areas, it is stated that the quality standard for pH is between 6.5 – 8.5. If you pay attention to the overall pH measurement values obtained at the seven sampling points, all measurement results do not exceed the predetermined threshold, this shows that the seawater around the Central Java Harbor is still suitable for use, in other words, it does not enter the in the polluted water category.

Sampling was carried out in December 2023 during the rainy season. Rainfall greatly influences the heavy metal content in water. High rainfall in December can cause the dissolution and dilution of heavy metals in water. Rainwater entering the waters will reduce the concentration of heavy metals by diluting the contaminants so that the heavy metal content tends to be smaller during the rainy season. After all, the increased water volume can dilute the existing heavy metal concentration.

In contrast, in the dry season, the heavy metal content tends to be high because the metal becomes concentrated (Hanifah, Rudiyanti and Ain, 2019). Apart from dissolving and diluting the concentration of heavy metals, the heavy metal deposition process can also influence the analysis results, where heavy metals can precipitate in the form of solid particles at the bottom of the water. This can reduce the measured concentrations of heavy metals in the water column.

Table 2: Seawater Sample Test Results using AAS.

No.	Sample	Cu (mg/L)	Pb (mg/L)	Cd (mg/L)
1	KSOP Semarang	<0,01	<0,01	<0,01
2	Rembang Sea	<0,01	<0,01	<0,01
3	Semarang Sea	<0,01	<0,01	**0,022**
4	Kendal Sea	<0,01	<0,01	<0,01
5	Batang Sea	<0,01	**0,109**	<0,01
6	Cilacap Sea	<0,01	<0,01	<0,01
7	Kebumen Sea	<0,01	<0,01	<0,01
Seawater Quality Standards (Source: Kementerian Lingkungan Hidup Republik Indonesia (KLH), 2024)		**0,05**	**0,05**	**0,01**

Source: Authors.

Based on the Decree of the Minister of Environment No. 51 of 2004 concerning Sea Water Quality Standards for Port Areas, it is stated that the quality standard for Cu metal is 0.05 mg/L. From the results of Cu metal concentration measurements taken in Table 2, all measurement results are still below the threshold determined by the government. This shows that the Cu metal contained in the waters of Central Java Harbor is still small and is still classified as good/unpolluted water.

The quality standard for Pb metal is 0.05 mg/L. From the results of measurements of Pb metal concentrations taken in Table 2, all sampling points, except Batang Port, show that Pb metal concentrations are still below the threshold of 0.05 mg/L set by the government. This means that the quality of seawater around these ports is still in the safe category for Pb metal parameters, except in the Batang Sea at 0.109 mg/L.

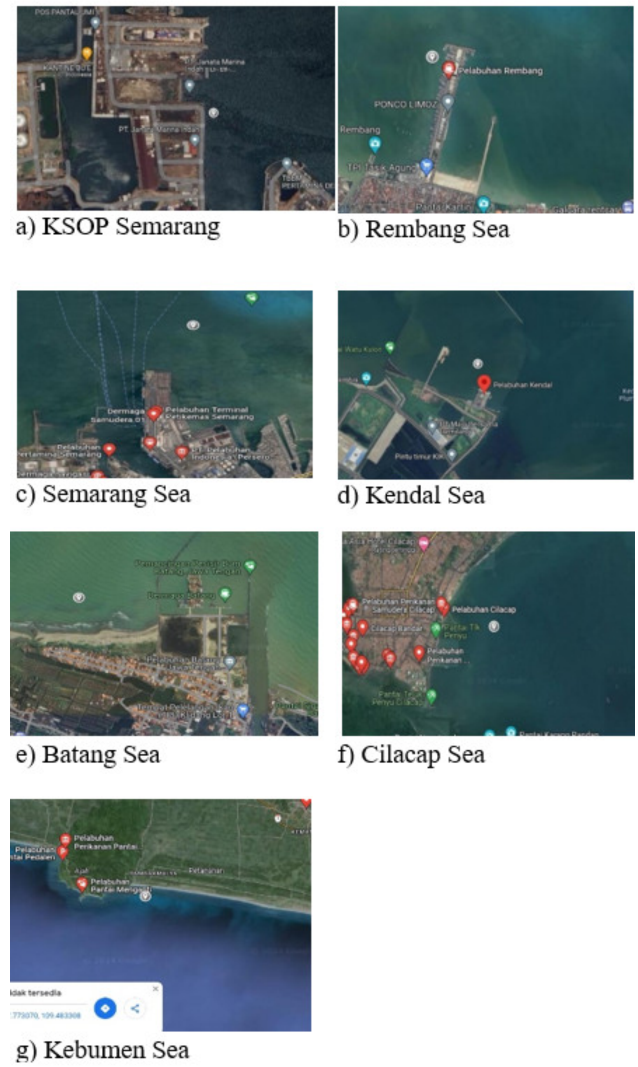
Seawater Quality Standards for Port Areas state that the quality standard for Cd metal is 0.01 mg/L. From the results of measurements of the Cd metal concentration taken in Table 2, all sampling points, except the Semarang sea, show that the Cd metal concentration is still below the threshold of 0.01 mg/L set by the government. This means that the seawater quality in these ports is still in the safe category for the Cd metal parameter, except for the Semarang sea, which is 0.022 mg/L.

In this research, the rainy season plays an important role in reducing the concentration of heavy metals in waters through the processes of dissolution, dilution, deposition, and transportation of heavy metals to the open sea. However, the measurement results show heavy metal concentrations that exceed the threshold at several points, indicating the existence of significant local pollution sources.

3.2. Identify Pollution Sources.

Based on the results of data analysis in Table 2, it is known that water pollution is a change that occurs in the water system caused by humans or nature, which results in the quality of the water being reduced. The presence of heavy metals in seawater actually exists naturally or is input from outside the environment, but the largest input comes from human activities (Nriago J., 1996). Human activities are the biggest contributor to dangerous heavy metals in water; besides that, these heavy metals can be distributed into the atmosphere and enter the aquatic environment and, ultimately, into the sea (Badr, N.B.E. et al., 2009).

Figure 2: Location Map of Research Area.



Source: Authors.

Figure 2 shows a map of seawater sampling carried out at various locations (white marks). Analysis was carried out at the Laboratory of the Faculty of Engineering, Diponegoro University, to determine the concentration of heavy metals. The condition of sea waters in the Semarang, Kendal, Rembang, Batang, Cilacap, Kebumen, and KSOP Semarang Sea areas is greatly influenced by various factors, including industrial activities and waste disposal from factories around the port.

The measurement results show that the concentration of Cd metal in the seawater around Tanjung Emas Harbor, Semarang, is 0.022 mg/L. This figure exceeds the threshold set by the Decree of the Minister of Environment No. 51 of 2004, namely 0.01 mg/L. Semarang's Tanjung Emas Port is one of the largest ports in Central Java which functions as a center for shipping and marketing goods. The condition of the seawater around this port is affected by industrial activities around the area, such as textile, chemical, and electronic factories operating around Tanjung Emas Port. These industries often produce waste containing heavy metals such as Cd. Disposal of waste that is not properly treated can cause Cd metal pollution in the waters around the port. In addition, intensive ship loading and unloading activities at ports can contribute to Cd metal pollution. For example, the use of anti-rust paint and other chemicals containing Cd metal can pollute sea water through weathering and ship cleaning processes (Nasution and Siska, 2011).

Furthermore, (Zhang et al., 2017) stated that the high rate of urbanization and reclamation in coastal areas will seriously increase pollution, especially in the marine environment. The process of industrialization, reclamation, and urbanization has occurred in the Semarang coastal environment. Hence, the consequences of high levels of pollutants such as heavy metals are inevitable. Industrial and residential areas surround the location of Semarang's Tanjung Mas port, and reclamation is still being carried out to expand the land (Suryono and Djunaedi, 2017).

The measurement results show that the concentration of Pb metal in the seawater around Batang Harbor is 0.109 mg/L. This figure exceeds the threshold set by the Decree of the Minister of Environment No. 51 of 2004, namely 0.05 mg/L. The condition of the sea waters around Batang Port and the high content of the heavy metal Pb is influenced by a number of factors, such as industrial activities around the port, shipping activities, and ship docking. There is an increase in the concentration of metals in the water, especially related to shipping and ship docking activities that use fuel oil, lubricants, and residue from ship docking work that is scattered and directly enters the water, thus providing an opportunity for an increase in the concentration of heavy metals in water bodies. The high concentration of Pb metal in the aquatic environment can be caused by various factors, namely human activities such as workshop activities, disposal of household waste containing Pb, erosion of mineral rocks, and high use of Pb-based gasoline (Astuti, Karina and Dewiyanti, 2016). This is in accordance with previous research conducted by (Nurhidayati, Didik and Zohdi, 2021), where a large number of boat activities using fuel and passing through this area caused the Pb metal content in the area around Selamat Harbor also to increase.

3.3. *Heavy Metal Pollution Index.*

Table 1 shows the measurement model results of the surveybased analysis conducted among UMT University Maritime students to assess the impact of self-e-learning, classroom teaching, and simulation training on COLREG knowledge. The table provides information on the constructs and items' reliability, internal consistency, convergent validity, full collinearity VIFs, outer loadings, composite reliability, and AVE. The table shows that all constructs had good reliability and internal consistency, with Cronbach's alpha values ranging from 0.682 to 0.992. All constructs had good convergent validity, with all items having outer loadings greater than 0.5, and AVE values greater than 0.5. All constructs had VIF values less than 3.3, indicating no multicollinearity issues.

Table 2 presents the HTMT results of the survey-based analyses. The table shows the constructs' heterotrait-monotrait ratio of correlations (HTMT). The HTMT values were all less than 0.9, indicating good discriminant validity between the constructs. Table 3 presents the structural model results of the survey-based analyses. This table provides information on the beta coefficients, 95% confidence intervals, t-values, p-values, decisions, R-squared, F-squared, effect size, and VIF of the relationships between the constructs. The results show that classroom teaching and self-e-learning positively impact the learning of COLREGs among UMT Universiti Maritime students, whereas simulation training does not significantly impact them. The effect size of classroom teaching on the learning of COLREGs was moderate, whereas the effect size of self-e-learning on the learning of COLREGs was small. The VIF values were all less than two, indicating no multicollinearity issues. The beta coefficients of classroom teaching and self-e-learning were 0.455 and 0.224, respectively, indicating that classroom teaching had a stronger impact on learning COLREGs than selfelearning. The beta coefficient of simulation training was 0.142, which is insignificant, indicating that simulation training does not significantly impact the learning of COLREGs.

Heavy metals are a contaminant often found in marine waters, especially around industrial areas and ports. High concentrations of heavy metals can harm marine ecosystems and human health. Therefore, monitoring and analysis of heavy metals such as copper (Cu), lead (Pb), and cadmium (Cd) in marine waters is very important. Based on the Minister of Environment No. 51 Decree of 2004, the quality standards for heavy metals in marine waters are Cu: 0.05 mg/L, Pb: 0.05 mg/L, and Cd: 0.01 mg/L.

The pollution status is determined by using the following equation: pollution index, according to Nemerow and Sumitomo (1970).

$$IP = \sqrt{\frac{(C_i/B_i)_m^2 + (C_i/B_i)_R^2}{2}} \quad (1)$$

where *Ci* is the measured concentration, and *Bi* is the quality standard.

Pollution Index categories are determined as follows.

$0<IP<1$: Meets quality standards.

$1 \leq IP < 5$: Lightly polluted category.

$5 \leq IP < 10$: Moderately polluted category.

$IP \geq 10$: Heavily polluted category.

Based on the measurements and pollution index calculations, KSOP Semarang, Rembang Sea, Kendal Sea, Cilacap Sea, and Kebumen Sea show low heavy metal pollution index values, being in the lightly polluted category. This indicates that the concentration of heavy metals in this area is still within safe limits and does not indicate significant pollution. Meanwhile, the Semarang Sea shows a higher pollution index for Cd metal (2.2) but is still in the lightly polluted category. This indicates that the concentration is still manageable despite the heavy metal Cd above the threshold. Furthermore, the Batang Sea shows a higher pollution index for Pb metal (2.18) but is still in the lightly polluted category. This may be caused by industrial activities or waste containing Pb around the area.

Table 3: Pollution Index Results.

No.	Sample	Cu (*IP*)	Pb (*IP*)	Cd (*IP*)	*IP*	Category
1	KSOP Semarang	0,2	0,2	1	1	Lightly polluted
2	Rembang Sea	0,2	0,2	1	1	Lightly polluted
3	Semarang Sea	0,2	0,2	2,2	2,2	Lightly polluted
4	Kendal Sea	0,2	0,2	1	1	Lightly polluted
5	Batang Sea	0,2	2,18	1	2,18	Lightly polluted
6	Cilacap Sea	0,2	0,2	1	1	Lightly polluted
7	Kebumen Sea	0,2	0,2	1	1	Lightly polluted

Source: Authors.

3.4. Environmental Implications.

Monitoring the quality of marine waters and hefty metal content is essential in maintaining ecosystem health and human safety. This study measured the concentrations of heavy metals Cu, Pb, and Cd in several locations in port waters in Central Java. It evaluated the level of pollution using the Pollution Index (IP). Based on the results of measurements and calculations of the Pollution Index, the following is a discussion of the environmental implications of heavy metal content at each location.

3.4.1. Rembang Sea, Batang, Cilacap, Kebumen, and KSOP Semarang.

All results measuring heavy metal concentrations (Cu, Cd, and Pb) were below the specified threshold. Furthermore, the Pollution Index calculation results for all metals are in the ”Lightly Polluted” category. However, even though it is in the ”Lightly Polluted” category, this condition shows that the waters are still relatively safe for marine ecosystems and human activities. However, continuous monitoring is still needed to ensure that heavy metal concentrations do not increase.

3.4.2. Semarang Sea.

The results of measuring the concentration of Cd metal (0.022 mg/L) exceeded the specified threshold (0.01 mg/L), while Cu and Pb metals were below the threshold. The Cd Pollution Index calculation results are at a value of 2.2, which categorizes this area as ”Lightly Polluted.” Cd content that exceeds the threshold indicates pollution in the Semarang Sea. This could harm the health of marine life and potentially harm humans who consume seafood from this area. Cd pollution can come from industrial waste or port activities.

3.4.3. Batang Sea.

The measurements in the Batang Sea show that the metal Pb content exceeds the threshold (0.109 mg/L). Furthermore, the Pb metal pollution index calculation results reached 2.18; this location was categorized as ”Lightly Polluted.” The high Pb content in the Batang Sea is hazardous for marine organisms and can cause health problems for humans. It is necessary to identify sources of pollution and mitigation efforts to reduce Pb concentrations.

Conclusions.

The concentration of heavy metals around Central Java Harbor in seawater is below the established safe limits, except for the Semarang Sea (Cd metal) and the Batang Sea (Pb metal).

Sources of heavy metal pollution can be caused by industry, especially from waste that is not processed correctly, port activities such as loading and unloading activities, ship repairs and sea transportation, and surface flows during the rainy and dry seasons, which affect the concentration of heavy metals in the seawater.

Based on the Pollution Index calculation, all locations have an index under the ”lightly polluted” category, except for Cd metal in the Semarang Sea (IP = 2.2) and Pb metal in the Batang Sea (IP = 2.18), which are included in the category ”lightly polluted.”. However, most of the seawater samples were in the ”unpolluted” or ”lightly polluted” category.

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