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ACCUMULATION OF LEAD AND COPPER IN THE SEDIMENTS IN SOUTH KALIH AND PANJANG ISLAND, BANTEN

AKUMULASI TIMBAL DAN TEMBAGA PADA SEDIMEN DI PERAIRAN PULAU KALIH SELATAN DAN PULAU PANJANG, BANTEN

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ABSTRACT

South Kalih and Panjang Islands are located in Banten Bay, small island with environmental conditions adjacent to the center of industrial activities. Industrial activities near the waters can increase the risk of heavy metal pollution, thereby affecting the quality of the aquatic environment. This study aims to evaluate the condition of aquatic environmental quality based on heavy metal content in sediments. Sediment sampling was conducted at ten observation stations using a purposive random sampling method. Heavy metal analysis was performed using the Flame Atomic Absorption Spectrometry (FAAS). The results indicate that South Kalih Island accumulated more Pb heavy metals with an average of 2.7922 mg kg^{-1}, while the highest accumulation of Cu heavy metals was on Panjang Island with an average of 5.7188 mg kg^{-1}. The accumulation of heavy metals Pb and Cu in the sediments in South Kalih and Panjang Island was below the standard threshold, except at PPS5P1 of Panjang Island, where Cu concentrations exceeded the CCME (2002) quality guideline. Areas with dense anthropogenic activities are more likely to increase the accumulation of heavy metals in the waters.

Keywords: Flame Atomic Absorption Spectrometry (FAAS), heavy metals, Panjang Island, sediment, South Kalih Island

ABSTRAK

Pulau Kalih Selatan dan Pulau Panjang terletak di Teluk Banten yang merupakan pulau kecil dengan kondisi lingkungan yang dekat dengan pusat aktivitas industri. Aktivitas industri di sekitar perairan dapat meningkatkan risiko pencemaran logam berat yang dapat memengaruhi kualitas lingkungan perairan. Penelitian ini bertujuan untuk mengevaluasi kondisi kualitas lingkungan perairan berdasarkan kandungan logam berat pada sedimen. Pengambilan sampel dilakukan dengan metode *purposive random sampling* pada sepuluh stasiun pengamatan. Analisis logam berat dilakukan menggunakan metode *Flame Atomic Absorption Spectrometry* (FAAS). Hasil penelitian menunjukkan bahwa Pulau Kalih Selatan terakumulasi logam berat Pb lebih banyak dengan rata-rata 2,7922 mg kg^{-1}, sedangkan akumulasi logam berat Cu terbanyak ada pada Pulau Panjang dengan rata-rata 5,7188 mg kg^{-1}. Akumulasi logam berat Pb dan Cu dalam sedimen di perairan Pulau Kalih Selatan dan Pulau Panjang berada di bawah nilai baku mutu, kecuali pada stasiun PPS5P1 Pulau Panjang, di mana konsentrasi Cu melebihi nilai baku mutu CCME (2002). Wilayah dengan aktivitas antropogenik yang padat lebih berpotensi dalam meningkatkan akumulasi logam berat di perairan.

Kata kunci: *Flame Atomic Absorption Spectrometry* (FAAS), logam berat, Pulau Kalih Selatan, Pulau Panjang, sedimen

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INTRODUCTION

South Kalih and Panjang Islands, situated in Banten Bay, lie adjacent to the metropolitan activity center and industrial areas in Serang Regency and Cilegon City. Various development activities, including marine tourism, industry, settlements, and sea transportation, which is the main route for waste entry from Serang Regency (Lestari *et al.* 2017), have put significant pressure on the bay's waters (Wisha *et al.* 2015; Falah *et al.* 2020). On the other hand, South Kalih and Panjang Islands have diverse fishery resource potential, encompassing natural ecosystems including seagrass, mangroves, and coral reefs (Nurhidayati *et al.* 2023; Satrya *et al.* 2012). The condition of the coral reefs on both islands is estimated to have been damaged (Rustam *et al.* 2018), indicating environmental disturbance due to pollutants.

Sediment is a place where various pollutants originating from the water column accumulate, binding with suspended particles, settling to form layers at the bottom (Moelyo *et al.* 2012). Heavy metals are one of the pollutants commonly found in coastal and marine waters. These heavy metals can accumulate in sediments and then be absorbed by organisms or ecosystems in those waters (Ainun *et al.* 2021). As a result, heavy metals will accumulate in aquatic sediments and cause a decline in water quality (Caroline and Moa 2015).

The heavy metal Pb, as a pollutant, is toxic and has the potential to affect the life cycles of aquatic organisms (Arkianti *et al.* 2019). The presence of Pb in water can threaten the balance of the ecosystem and the survival of surrounding organisms (Putra *et al.* 2022). Meanwhile, high concentrations of the heavy metal Cu in water can inhibit growth, shorten lifespans, and weaken the immune response of aquatic organisms (Garai *et al.* 2021).

Research on the heavy metal content of Pb and Cu in sediments in Banten Bay is still limited and has not specifically evaluated their spatial distribution based on environmental characteristics. Based on research conducted by Juniardi *et al.* (2022) in Banten Bay, Pb concentrations in sediments ranged from <0.002 to 18.447 mg kg^{-1}. Meanwhile, research conducted by Fauziah and Choesin (2014) in Banten Bay found that Pb and Cu concentrations adjacent to industrial areas had high values, namely around 0.172 ppm and 0.731 ppm, respectively. This study aims to evaluate the condition of the aquatic environment quality based on heavy metal content in sediments in the waters of South Kalih Island and Panjang Island.

METHODS

Time and location

Sediment samples were collected in September 2024 from the waters of South Kalih and Panjang Islands, Serang Regency, Banten Province. Samples were taken from several different stations, namely PKS1, PKS2, PKS3, PKS4, and PKS5 on South Kalih Island, and PPS1, PPS2, PPS3, PPS4, and PPS5 on Panjang Island (Figure 1).

The characteristics of the aquatic environment are key factors influence the distribution and accumulation of heavy metals in sediments, meaning they can be a source of pollution or be affected by pollution that is not actually a source of pollution but has been distributed by polluting materials, so it is suspected that the area is affected by pollution. An overview of the environmental conditions at each sediment sampling station in the South Kalih Island area is presented in Table 1, while an overview of environmental conditions at sediment sampling stations on Panjang Island can be seen in Table 2.

Station selection

The station locations were determined based on the areas where pollution activities were taking place and the areas suspected of being polluted. This takes into account various aspects that are indirectly distributed across a wider area. The characteristics of the waters of the two islands are presented in Figures 2 and 3.

Sediment sampling

Sampling was conducted along a transect line from the open sea (offshore) towards the coast (inshore) using a purposive random sampling method, based on environmental conditions and the presence of pollution sources (Hidayati *et al.* 2014). Sediment samples were taken using a grab sampler. Approximately 1 kg of sediment was then placed into a plastic sample bag and given sample code.

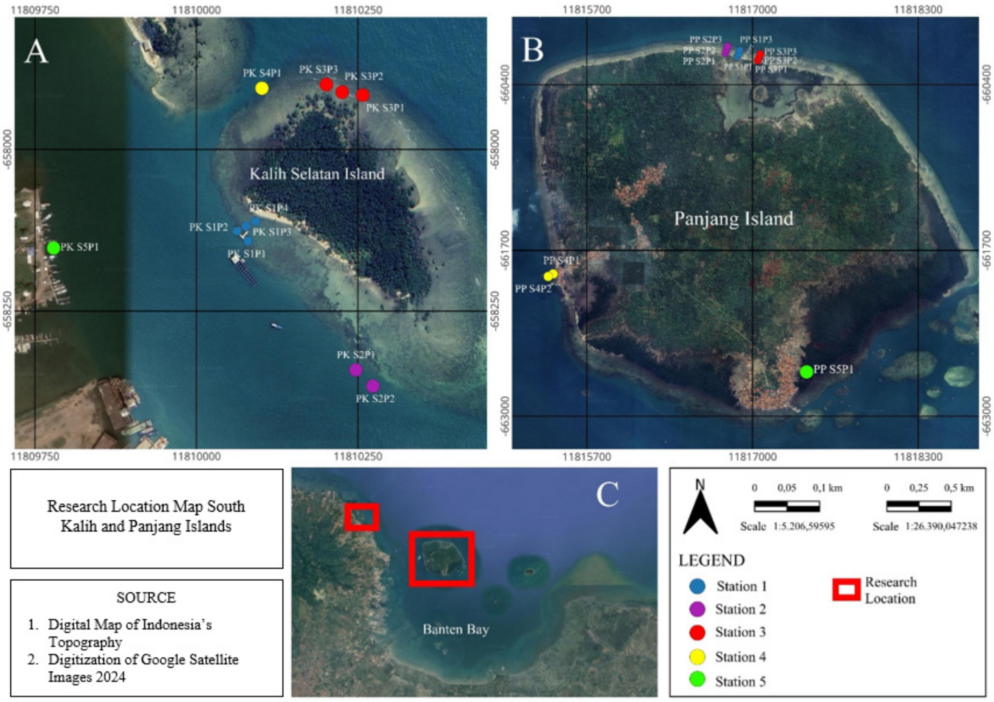

Figure 1. Map of sediment sampling locations in the waters of South Kalih Island and Panjang Island, Serang Regency, Banten Province.

Table 1. Environmental conditions of the South Kalih Island sediment sampling station.

Stations	Environmental Conditions
PKS1	It's located near the floating net cage (KJA) cultivation.
PKS2	It's a coral reef area overlooking the shipping industry.
PKS3	It's an area with abundant mangroves.
PKS4	It's an area with abundant coral reefs.
PKS5	It's a dock area and close to residential areas.

Table 2. Environmental conditions of the Panjang Island sediment sampling station.

Stations	Environmental Conditions
PPS1	An area with abundant coral and seagrass beds, with water conditions influenced by the dynamics of the Java Sea.
PPS2	An area with abundant coral and seagrass beds, with water conditions influenced by the dynamics of the Java Sea.
PPS3	An area with abundant coral, adjacent to mangroves, with water conditions influenced by the dynamics of the Java Sea.
PPS4	A dock area close to residential areas and fixed-net fisheries.
PPS5	A mangrove area and a fishing boat anchorage are adjacent to residential areas and close to Panjang Island Port.

Preparation and analysis of sediment samples

Preparation and analysis of sediment samples were carried out at the Chemical Laboratory of the National Research and Innovation Agency (BRIN), KST Samaun Samadikun, Cisitu, Bandung, following SNI 8910:2021 regarding the method of testing metal content in sediment test samples by the acid digestion method using a Flame Atomic Absorption Spectrometer (FAAS) with two sample repetitions. For heavy metal analysis, sediment samples were oven-dried at 60 °C for 17 hours, then ground and sieved through a 100-mesh stainless-steel sieve. Sediment samples were weighed using an analytical balance, 2 g for Cu analysis heavy metal analysis and 4 g for Pb samples, then placed into a 50 mL Erlenmeyer flask for the wet digestion process in a fume hood. The digestion process was carried out by adding a mixture of HCl and HNO_3 (3:1) as much as 20 mL for Cu samples and 40 mL for Pb samples. The mixture was heated on a hotplate at 250 °C until boiling, until the solvent reduced and slightly thickened. After cooling, the digested solution was filtered into a 50 mL volumetric flask using Whatman No. 41 filter paper, diluted to the mark with distilled water, and homogenized. The determination of the heavy metal series solution was carried out using the standard addition method, with Pb metal concentrations of 0.1, 0.2, 0.3, 0.4, and 0.5 ppm and Cu metal concentrations of 0.15, 0.2, 0.3, 0.4, and 0.45 ppm. The series solution was made using 100 ppm Pb and Cu stock solutions to which 1M HNO_3 solution was added. Analysis of heavy metal content was carried out using the FAAS (Flame Atomic Absorption Spectrometry) AA-7000 method with a Pb wavelength of 283.3 nm and Cu of 324.7 nm.

Data analysis

Data analysis was conducted using a descriptive method, with the results presented in tables and described narratively. The heavy metal content of Pb and Cu was compared with the 2000 Australian and New Zealand Environment and Conservation Council and the Agriculture and Resource Management Council of Australia and New Zealand (ANZECC and ARMCANZ), and the 2002 Canadian Council of Ministers of the Environment (CCME) standards. The standards are presented in Table 3.

Figure 2. Characteristics of the sampling environment on South Kalih Island. Area near floating net cage (KJA) cultivation (ST 1), area facing the industrial area (ST 2), area with many mangrove ecosystems (ST 3), area with many coral reefs (ST 4), and dock area close to residential areas (ST 5).

Figure 3. Characteristics of the sampling environment on Panjang Island. Areas with lots of coral and seagrass (ST 1, 2, 3), dock area close to residential areas and fisheries cultivation (ST 4), residential area facing the mangrove area and where fishermen's boats anchor (ST 5).

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Table 3. Standard quality standards for heavy metals in sediment.

Quality Standards	Min. Max.	Pb (mg kg^{-1})	Cu (mg kg^{-1})
ANZECC/ARMCANZ (2000)	Low	50.0	65.0
	High	220.0	270.0
CCME (2002)	ISQG*	30.2	18.7
	PEL**	112.0	108.0

(*) ISQG = Interim sediment quality guidelines

(**) PEL = Probable effect levels

RESULTS AND DISCUSSION

Heavy metals in sediments of South Kalih Island

The results of the analysis of the heavy metal content of lead (Pb) and copper (Cu) in the sediments that have been analyzed on South Kalih Island showed variations as presented in Table 4.

The concentrations of Pb and Cu at Station 5 (Figure 2) were the highest among all observation sites. This location hosts shipyard activities and serves as a mooring area for fishing boats and speedboats used for maritime transportation. The high Pb concentrations at this location is likely due to shipping activities, particularly the use of fuel that has the potential to produce heavy metal waste, including Pb. This is consistent with research conducted by Rizkiana *et al.* (2017), which states that Pb can be found in ship paint, which functions to accelerate the drying process and prevent corrosion on metal or iron surfaces, where the location is close to ship docking locations and fishing boat moorings. Furthermore, the use of ship fuel can be a major source of lead entry into the waters due to the addition of tetraethyl lead $Pb(C_2H_2)_3$ compounds to the fuel.

The high Cu concentrations at Station 5 are probably related to domestic waste (e.g., discarded plastics and detergents) and shipping activities such as docking and unloading (Idris *et al.* 2007). According to Sires (2017), Cu contamination can arise from various anthropogenic sources, including atmospheric emissions, industrial metal plating, and ship maintenance. The shipyard industry has various activities that can hurt the environment, especially due to its proximity to water, air, and land. One of these impacts is heavy metal contamination (Hidayat 2017). Therefore, the high concentration of heavy metals at this station is likely influenced by shipping activities and its location close to various human activities.

Station 1, the location with the second-highest concentration of Pb and Cu, is located near a coastal area that was previously an abandoned pier and fish farming activities (Figure 2). According to Sudarningsih (2021), fishing activities at sea can trigger the presence of heavy metals in the waters. The presence of heavy metals at this station is suspected to originate from activities around the station, such as fishing activities and shipping routes. One of the main sources of water pollution is the discharge of untreated waste (Sonone *et al.* 2020). Furthermore, the heavy metal content at this station is suspected to be influenced by its location in a coastal area and is an area vulnerable to potential pollution, as it functions as a final accumulation zone for various types of waste released into the marine environment and often contains heavy metals (Hariyanti *et al.* 2021).

Station 4 had the third-highest metal concentration after Stations 5 and 1. However, the values remained relatively low. This is likely because Station 4 is in an area with numerous coral reefs, where coral reef ecosystems have a natural ability to accumulate heavy metals from the aquatic environment, resulting in significantly reduced heavy metal concentrations in the water column (Riska *et al.* 2022). Furthermore, the low concentrations may be attributed to currents and tides, which allow heavy metals to move freely in seawater, leading to natural dilution (Wardani *et al.* 2014).

Station 2 showed the lowest Pb concentration and the second-lowest Cu concentration, with a concentration difference of approximately 1 mg kg^{-1}. Although, this station lies in a coral reef area and directly facing an industrial zone. Industrial activities generally contribute to increased concentrations of heavy metals in the waters. However, the concentration of heavy metals at Station 2 remained low, and the condition of the coral reefs was still good compared to Station 1, which is located farther from the shipping industry. According to Nuraini *et al.* (2017), reported that greater distances from pollutant sources affect metal concentrations in the waters, where the greater the distance from the pollutant source, the lower the accumulation of heavy metals in the sediment. This is related to ocean dynamics, namely physical and chemical factors, especially ocean currents that enable the movement and distribution of heavy metals (Filipus *et al.* 2018). This statement is supported by Ramadhan *et al.* (2024) and Indrawan *et al.* (2018), who stated that the concentration of heavy metals in the waters can be spread due to current movements, causing heavy metals to spread in various directions. Therefore, the low content of heavy metals at Station 2 is thought to be influenced by environmental conditions and physical and chemical factors that support the process of spreading heavy metals in the waters.

Station 3 was the location with the lowest Cu accumulation and the second-lowest Pb concentration. This station is located the coast, adjacent to dense mangrove area, and faces open waters where pollution is distributed by currents heading northwest and northeast. This location significantly influences the dynamics of the surrounding aquatic environment. Its orientation directly facing the open sea allows sediment carried by currents and waves to be more easily dispersed over a wider area. This is due to the high hydrodynamic energy in open waters, where the interaction between tidal currents, waves, and atmospheric conditions, such as wind, contributes to the distribution patterns of sediment material. The absence of significant natural barriers in these waters further accelerates the process of sediment transport and dispersal, which can ultimately impact the ecosystem structure and water quality around the station.

The presence of the mangrove ecosystem is also suspected to be the cause of the low heavy metal content at Station 3. Mangroves act as natural biofilters or hyperaccumulators, trapping sediments, filtering domestic waste, and absorbing heavy metals through their roots, stems, and leaves (Sanadi *et al.* 2018). In addition, mangroves can also filter heavy metals found in sediment (Khairuddin *et al.* 2018). At this station, there are no sources of heavy metal pollution; therefore, the accumulation value is relatively low. South Kalih Island has an average value of Pb heavy metal content of 2.7922 mg kg^{-1} and an average concentration of Cu of 5.0875 mg kg^{-1}. In general, the levels of Pb and Cu heavy metal pollution in the waters of South Kalih Island are relatively low and below the quality standards of ANZECC and ARMCANZ (2000) and CCME (2002).

Heavy metals in Panjang Island sediments

The analysis of Pb and Cu concentrations in sediments on Panjang Island showed variation. Each station represents different environmental characteristics that can influence the level of heavy metal accumulation in the sediment. The results of heavy metal concentration measurements at each station are shown in Table 5.

Table 4. Concentration of heavy metals Pb and Cu in sediments on South Kalih Island.

Stations	Sample Codes	Lead (Pb) (mg kg^{-1})	Copper (Cu) (mg kg^{-1})
1	PKS1P1	1.9072	5.9644
	PKS1P2	2.9536	4.3150
	PKS1P3	5.0506	7.3650
	PKS1P4	4.8928	9.6370
Average		**3.7010**	**6.8204**
2	PKS2P1	1.0612	1.3500
	PKS2P2	0.8611	3.4815
Average		**0.9612**	**2.4157**
3	PKS3P1	1.5586	1.0447
	PKS3P2	1.3182	1.3222
	PKS3P3	2.0233	3.6500
Average		**1.6333**	**2.0057**
4	PKS4P1	2.5895	3.2898
5	PKS5P1	6.5009	14.5425

Table 5. Concentration of heavy metals Pb and Cu in sediments on Panjang Island.

Stations	Sample Codes	Lead (Pb) (mg kg^{-1})	Copper (Cu) (mg kg^{-1})
1	PPS1P1	1.5585	5.1742
	PPS1P2	1.4587	0.8922
	PPS1P3	1.6086	0.4075
Average		**1.5419**	**2.1580**
2	PPS2P1	3.5513	5.7300
	PPS2P2	1.0682	1.7917
	PPS2P3	1.2600	1.1823
Average		**1.9598**	**2.9013**
3	PPS3P1	1.9573	1.0999
	PPS3P2	1.5087	0.1999
	PPS3P3	1.8575	0.4350
Average		**1.7745**	**0.5783**
4	PPS4P1	3.6994	17.3408
	PPS4P2	3.3173	10.8257
Average		**3.5084**	**14.0832**
5	PPS5P1	10.1888	23.5478

Station 5 was the location with the highest levels of Pb and Cu contamination. This is suspected because the sampling location has a significant influence from Station 4 on the distribution of heavy metals in the area. The high Pb concentrations at this station is thought to originate from the dense shipping activity, considering this area is a mooring place for fishermen's boats. The large number of fishing boats at the island's coastal docks has the potential to cause heavy metal pollution (Ramadhan *et al.* 2024). Lead concentrations in the waters can increase due to the use of lead-based paint, welding operations on ships, and fuel from fishing vessels (Rizkiana *et al.* 2017). Another factor suspected of being a source of heavy metal pollution at Station 5 is waste from anthropogenic activities. This is evident from the condition of the waters at the location, which are quite polluted. This can be caused by high water turbidity due to the large amount of household waste, including laundry waste and sometimes even garbage dumped directly into the waters.

Pollution caused by human activities can have significant impacts, particularly from industrial waste such as plastics, which often contain toxic chemicals, including copper (Nurhamiddin and Ibrahim 2018). Plastics are composed not only of polymers or copolymers but also contain various chemicals as residues and contaminants from the production process (Hahladakis *et al.* 2018). Heavy metal content in plastics can originate from the chemicals used in the manufacturing process, including additives containing heavy metals. Generally, these metal additives do not bind permanently to the polymer, so they tend to migrate from the plastic matrix through diffusion and mass transfer processes into the surrounding aqueous phase (Mercea *et al.* 2018; Chen *et al.* 2019; Mao *et al.* 2020). The release of heavy metals from micro- and nano-sized plastics tends to occur more rapidly (Martin and Turner 2019; Smith and Turner 2020). This suggests the possibility of metal release from the surface layer of plastic due to degradation processes. In general, heavy metal mobilization increases as plastics undergo weathering or environmental degradation (Zhang *et al.* 2018). When plastic weather degrades, the copper content in its additives is released and dissolves into the water, eventually accumulating.

The sediment at Station 5 had a more pungent odor and a darker color compared with the other locations. Sediment odor and color are organoleptic parameters used to assess environmental pollution levels. The more pungent the sediment odor, the higher the level of pollution, primarily due to the accumulation of organic compounds (Maharani 2024). Therefore, the sediment at Station 5 can be considered to have undergone significant heavy metal contamination. Furthermore, sediment color can reflect the mineral, organic matter, and nutrient content within it. The presence of organic matter in the sediment plays a role in the binding process of heavy metals during sedimentation, ultimately increasing heavy metal concentrations at this site.

Station 4 was the location with the second-highest concentration of heavy metals, with Cu levels four times higher than Pb. The presence of Pb at this location is thought to be due to its function as a dock serving as a shipping route. Shipping activities have the potential to contribute to heavy metal waste through fuel spills and the use of metal-containing paints, which may have corroded. Furthermore, the station's role as a dock also contributes to the high concentration of Cu. Palar (1994) stated that shipping activities can accelerate the increase in metal solubility in water through this pathway. The main sources of copper pollution generally come from industrial activities, household waste, and the combustion and use of fuel, which likely contribute to the high Cu levels at this location. Therefore, the high heavy metal content at this location is thought to be influenced not only by its function as a dock but also by its proximity to residential areas, which have the potential to contribute waste to the surrounding waters.

Stations 1, 2, and 3 share similar environmental characteristics, with average heavy metal concentrations that are lower or not significantly different from the other stations. Although these locations serve as marine transportation routes, the detected heavy-metal levels remain relatively low. These low concentrations may be influenced by various factors, particularly the characteristics of the ecosystem in the area. The presence of coral reefs and seagrass beds is likely important, as both ecosystems play key roles in reducing heavy-metal accumulation. Coral reefs are known to naturally reduce heavy metal concentrations through complex biological and physical processes (Samawi *et al.* 2014). In addition, the low heavy metal concentrations at these stations are thought to be influenced by the ability of seagrass to absorb water and dissolved substances, including heavy metals, through stomata and cuticles (Ahmad *et al.* 2015). This is in line with the presence of pectin in seagrass leaves, which is located in the cell walls and plays a crucial role in the ion absorption process. Pectin levels tend to increase with the age or growth phase of the seagrass (Santana *et al.* 2018).

Panjang Island has an average Pb heavy metal concentration of 2.7529 mg kg^{-1} and an average Cu concentration of 5.7188 mg kg^{-1}. Overall, Pb contamination in the waters around Panjang Island is low and remains below the ANZECC and ARMCANZ (2000) standards. However, according to the CCME (2002) guideline, Cu levels at one station (PKS5P1) exceeded the recommended threshold.

CONCLUSION

The results of the study indicated that all sediments at the observed stations contained accumulated Pb and Cu, though concentrations below the ANZECC and ARMCANZ (2000) and CCME (2002) quality standards, except for Cu at PPS5P1, which exceeded the CCME (2002) quality standard under the category of probable effect levels with a value of 23.5478 mg kg^{-1}. This finding suggests that the waters in this area have experienced a decline in quality and may pose risks to marine organisms. The high concentration of heavy metals at several stations is thought to be related to anthropogenic activities, such as marine transportation and domestic waste discharge. Conversely, lower concentrations at other stations are associated with the presence of natural ecosystems such as coral reefs and seagrasses, as well as the influence of physical factors in the waters that support the absorption and deposition of heavy metals.

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