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Spatial distribution of micronutrients in Pekalongan coastal waters: water quality and environmental impact assessment

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ABSTRACT

The coastal areas of Pekalongan, which are densely populated with activities such as ports, industries, and settlements, are highly vulnerable to changes in water quality due to nutrient distribution. This study aims to explore the distribution patterns and abundance of micronutrients in Pekalongan coastal and their implications for water quality and environmental impacts. Samples were taken from Mrican River, Pencongan River, and Wonokerto Beach. The analysis involved spatial distribution, statistical tests with Principal Component Analysis (PCA), and water quality assessment using CCME-WQI. The results showed that the highest concentrations of micronutrients were found in iron in RW 6 of Mrican River, copper in SW 4 of Wonokerto Beach, and zinc in SW 5 of Wonokerto Beach. Based on the CCME-WQI, the quality of Pekalongan coastal waters is classified as poor, potentially posing a great risk to aquatic biota and the health of humans who consume polluted biota. These findings underscore the urgency of taking mitigation measures against micronutrient contamination in coastal areas.

Introduction

Coastal areas are highly vulnerable to environmental change because they function as the meeting point between land and ocean (Noor *et al.*, 2021). Geographically, the north coast of Pekalongan has ± 6.15 km of coastline directly adjacent to the Java Sea. This area is under environmental pressure due to port, aquaculture, agriculture, industry, and settlements that can potentially change the distribution of nutrients in the waters (Gunawan *et al.*, 2022).

Nutrients in aquatic ecosystems are essential in supporting organisms' metabolism and physiological functions (Pratiwi *et al.*, 2019). Both macronutrients and micronutrients are utilized by organisms in the surface layer to depths still reachable by light for photosynthesis (Aprianto *et al.*, 2023). Macronutrients (NO_3, NO_2, PO_4^{3-}, and SiO) are needed in large quantities. In contrast, micronutrients like iron (Fe), copper (Cu), and zinc (Zn), although only needed in small amounts, have a crucial role (Pratiwi *et al.*, 2019).

Iron is an essential metal that regulates phytoplankton growth and nitrogen cycling and is abundantly available in the aquatic environment (Rahman *et al.*, 2022). In addition, organisms require copper to support the metabolism and synthesis of hemocyanin, hemoglobin, and pigments for oxygen transport, generally in the form of $CuCO_3$ and CuOH ions (Pratiwi, 2020). Zinc is a cofactor in enzymes such as carbonic anhydrase and alkaline phosphatase enzymes, which are involved in the hydration/dehydration process (Tian *et al.*, 2023).

These three micronutrients can enter waters naturally through various geochemical processes such as erosional deposition, dilution, dissolution,

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and dispersal (Nugraha *et al*., 2023). In addition, human activities can also increase micronutrient content in waters through river flow and runoff from port areas, agriculture, and industry (Najamuddin *et al*., 2020; Akbar *et al*., 2025a). Limited micronutrient availability can limit primary productivity, while excessive concentrations can lead to water pollution and significant ecological losses (Pan *et al*., 2020; Akbar *et al*., 2025b).

Previous studies have examined the distribution of micronutrients in coastal waters and their relationship with primary productivity and environmental quality. For example, Thirunavukkarasu *et al.* (2020) analyzed the distribution of macronutrients (NO_3^-, NO_2^-, NH_3, PO_4^{3-}, and SiO_2) and micronutrients (Ni, Cu, Zn, Fe, Mg, Co, and Cr) in South Indian waters (Kalpakkam, Nemmeli, Muttukadu, Kasimedu, Ennore, and Kattupalli). The study found that high micronutrient concentrations in industrialized areas can negatively affect aquatic ecosystems, causing DNA fragmentation of aquatic organisms and reducing ecosystem productivity and coastal water quality. However, research on the distribution and bioavailability of micronutrients (Fe, Cu, and Zn) in Pekalongan coastal waters is still scarce. Ismanto *et al.* (2024) focused more on heavy metal contamination (Cr and Cu) in the Loji River, Banger River, and Pasir Kencana Beach area which are located in the eastern part of the study site known for the batik industry. This study did not specifically address the distribution and bioavailability of micronutrients in Pekalongan coastal waters. Therefore, this study offers a new perspective to explore the distribution and bioavailability of iron, copper, and Zinc in Pekalongan coastal waters, especially in the Mrican River, Pencongan River, and Wonokerto Beach for the first time. With high anthropogenic activities in the region, this study provides an overview of micronutrient distribution patterns and their implications for water quality and environmental impacts.

Materials and Methods

Location and time of research

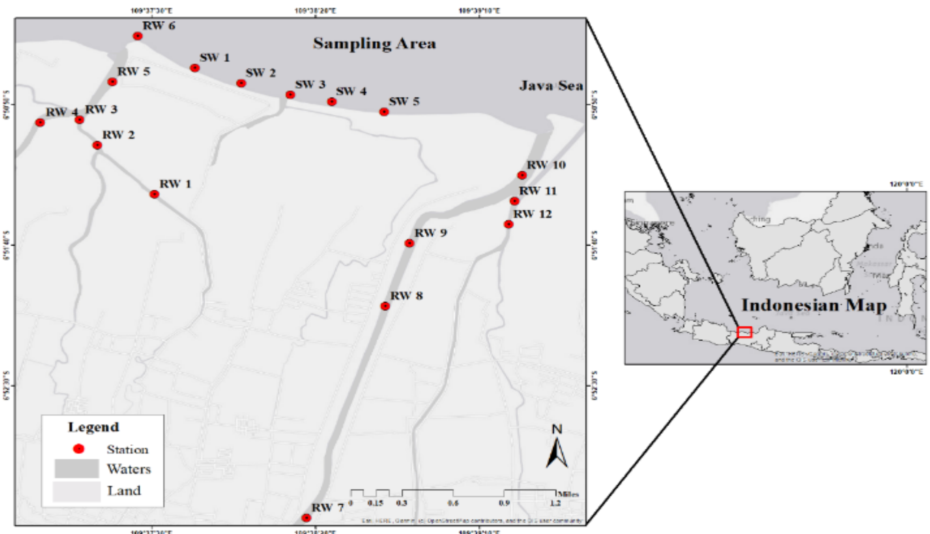

Figure 1. Map of water sampling

Water sampling in January 2023 was conducted in coastal Pekalongan, covering three main areas, Mrican River, Pencongan River, and Wonokerto Beach. These three locations have different characteristics. The Mrican River is located in an area with shipping activities, former agricultural land, mangrove areas, and a relatively strong current. The Pencongan River is influenced by shipping activities, batik production waste, fish auctions, and settlements and it has a slow current. Meanwhile, Wonokerto Beach, the estuary of Mrican River (west), and Pencongan River (east), are tourist areas where the water sample's characteristics can be affected. Furthermore, samples were taken from 17 points, consisting of 12 river water stations (RW) for freshwater and 5 seawater stations (SW) for seawater, each representing a utilization zone in the region. The coordinates of each station are described in Table 1, and a map of the sampling locations is shown in Figure 1.

Table 1. Specification of water sampling location

Location	Station	Coordinates
Mrican River	RW 1	6°51'21.9"S 109°37'30.9"E
	RW 2	6°51'04.4"S 109°37'13.5"E
	RW 3	6°50'55.4"S 109°37'08.1"E
	RW 4	6°50'56.5"S 109°36'56.1"E
	RW 5	6°50'42.7"S 109°37'18.8"E
	RW 6	6°50'25.6"S 109°37'25.8"E
Pencongan River	RW 7	6°53'17.1"S 109°38'17.3"E
	RW 8	6°52'01.7"S 109°38'40.5"E
	RW 9	6°51'39.2"S 109°38'47.9"E
	RW 10	6°51'15.2"S 109°39'23.0"E
	RW 11	6°51'24.3"S 109°39'20.7"E
	RW 12	6°51'32.6"S 109°39'18.9"E
Wonokerto Beach	SW 1	6°50'38.3"S 109°37'42.3"E
	SW 2	6°50'43.4"S 109°37'56.8"E
	SW 3	6°50'47.9"S 109°38'11.5"E
	SW 4	6°50'51.5"S 109°38'23.4"E
	SW 5	6°50'55.3"S 109°38'39.8"E

Sample collection

River water was sampled using a Van Dorn water sampler lowered to a depth of ± 10 meters to obtain representative water quality from the entire water column, thus allowing more accurate analysis of water quality parameters and contaminants (Ahdiaty & Fitriana, 2020). In contrast, seawater samples were taken using plastic buckets at a depth of ±10 cm because the surface layer of the sea is an active interaction zone between the atmosphere and the ocean, where photosynthesis, gas exchange, and the impact of human activities occur (Ly & Benilov, 2003). Water samples were placed in plastic buckets for in-situ observation and in 1 L polyethylene bottles for ex-situ analysis in the laboratory. The polyethylene bottles were previously acid-washed with 1 M HNO_3 solution and rinsed with deionized water several times. Samples were then filtered using a 0.45 µm cellulose acetate membrane. Next, the samples were preserved with 1 M $HNO_3$and stored for further laboratory analysis (APHA, 1999).

Sample analysis

During sampling, in-situ observations, including temperature, pH, Dissolved Oxygen (DO), and salinity, were carried out using water quality meter (Lutron WA-2017SD) (Hariyanti *et al*., 2021). The collected water samples were then analyzed ex-situ. Trace metal working standards were prepared from standard iron, copper, and zinc solutions with initial concentrations of 10 mg/L each that were diluted in a volumetric flask with HNO_3 and homogenized. The final concentrations of the working solution included 0.1, 0.5, 1.0, 1.5, 2.0, and 3.0 mg/L (iron), 0.5, 1.0, 1.5, 2.0, and 2.5 mg/L (copper), and 0.2, 0.4, 0.8, and 1.0 mg/L (zinc). Calibration curves were made, followed by measurement the concentration of trace metals using an atomic absorption spectrophotometer (AAS) (Shimadzu AA-7000) at wavelengths of 248.3 nm (iron), 324.7 nm (copper), and 213.9 nm (zinc) (Maghfiroh & Wibowo, 2021).

Data analysis

The results were then interpreted from geochemical distribution, statistical, and water quality perspectives. Distribution analysis was conducted to visualize the distribution pattern of trace metals. Statistical analysis using Principal Component Analysis (PCA) was done to simplify variable descriptions by finding correlated variables (Hidayah *et al*., 2020). Water quality was also assessed according to the Canadian Council of Ministers of the Environment Water Quality Index (CCME WQI), which evaluates water quality in various water bodies (Hu *et al*., 2022).

Result

The analysis results in Table 2 show the spatial distribution of Fe, Cu, and Zn micronutrients in Pekalongan coastal waters, referring to the quality standards of Government Regulation of the Republic of Indonesia Number 22 of 2021. Fe concentrations ranged from 0.0092-0.6295 mg/L, with the highest value found at sampling point RW 6, located at the mouth of the river. Cu concentrations were 0.0328-0.2820 mg/L, with the highest accumulation in SW 4 in the Wonokerto Beach tourist area. Meanwhile, Zn had concentrations of 0.0207-0.1571 mg/L, with the highest accumulation in SW 5, located not far from the mouth of the Pencongan River.

Environmental parameters also show variations that reflect the condition of Pekalongan coastal waters. DO values ranged from 2.9-7.3 mg/L, with the lowest value found in RW 12 of the water pump area. The pH of the waters was relatively stable within the range of 7.0-7.9, indicating conditions that still support the life of aquatic organisms. Salinity varied between 0.01-2.01%, with the lowest value in the river water. Meanwhile, water temperature ranged between 24.4-32.8°C, with the highest temperature recorded in RW 4.

Table 2. Measurement results of water quality parameters

Station	Iron (mg/L)	Copper (mg/L)	Zinc (mg/L)	DO (mg/L)	pH	Salinity (%)	Temperature (°C)
A. Mrican River							
RW 1	0.1477	0.0985	0.0642	5.3	7.1	0.14	29.2
RW 2	0.0092	0.1183	0.0403	4.5	7.3	0.87	30.3
RW 3	0.1918	0.0328	0.0324	5.7	7.3	0.78	31.0
RW 4	0.2450	0.0466	0.0207	4.4	7.2	0.06	32.8
RW 5	0.1698	0.1370	0.0342	4.4	7.0	0.10	26.7
RW 6	0.6295	0.1665	0.0445	4.4	7.4	0.27	29.0
B. Pencongan River							
RW 7	0.0101	0.1710	0.0226	7.3	7.2	0.01	24.4
RW 8	0.0642	0.1875	0.0256	6.4	7.4	0.01	25.6
RW 9	0.0129	0.2013	0.0498	3.7	7.2	0.08	29.3
RW 10	0.0496	0.2387	0.1222	5.3	7.4	0.01	25.2
RW 11	0.0789	0.2431	0.0585	4.0	7.4	0.18	28.7
RW 12	0.0945	0.2458	0.0565	2.9	7.2	0.27	29.1
C. Wonokerto Beach							
SW 1	0.2964	0.0675	0.0308	4.3	7.8	1.36	29.8
SW 2	0.2937	0.0806	0.0591	3.7	7.9	1.65	31.2
SW 3	0.5157	0.2091	0.0757	4.2	7.9	1.64	30.5
SW 4	0.5937	0.2820	0.0682	4.5	7.9	1.82	31.0
SW 5	0.5387	0.2615	0.1571	4.9	7.8	2.01	30.7

Screen plots of eigenvectors as a function of factor number are used to identify the principal components. The number of primary components is determined based on components with an eigenvalue greater than 1 (Handayani *et al.*, 2023). The eigenvalue interprets how much variation the component can represent (Hidayah *et al.*, 2020). Nath Roy *et al.* (2024) suggested selecting components based on the highest variance or eigenvalue >1. In this study, eigenvalues <1 show a significant decrease in variability, as in PC1 with an eigenvalue of 1.680, which explains 23.997% of the variablity, much higher than PC5 with an eigenvalue of 0.589, which only explains 8.414%. Therefore, only components with eigenvalues >1 are used. Table 3 shows PC1 has an eigenvalue of 3.264 with a variability of 46.634%, and PC2 has an eigenvalue of 1.644 with a variability of 23.492%, which, when combined, results in a cumulative variance of 70.126%, while components with eigenvalues <1 are ignored.

Table 3. Total diversity of major components of water quality

	PC1	PC2	PC3	PC4	PC5	PC6	PC7
Eigenvalue	3.264	1.644	0.998	0.449	0.389	0.176	0.080
Variability (%)	46.634	23.492	14.251	6.416	5.559	2.511	1.137
Cumulative %	46.634	70.126	84.377	90.793	96.352	98.863	100.000

Water quality was further assessed using the CCME-Water Quality Index method listed in Table 4.

Table 4. Result of water quality status analysis

No	Location	CCME	Desc
1	Mrican River	54.779	Less
2	Pencongan River	34.179	Less
3	Wonokerto Beach	28.107	Poor

Discussion

Micronutrient

Iron (Fe), copper (Cu), and zinc (Zn) are essential micronutrients for aquatic organisms (Zaeni *et al.*, 2021). These three metals can enter waters through erosion, fishing boat activities, aquaculture, and agricultural activities (Hasanuddin & Leonard, 2023). Although needed in small amounts, the presence of these metals in waters needs to be monitored because high levels can pollute the ecosystem.

The zinc and copper analysis results in several locations of the Mrican River and Wonokerto Beach exceed the quality standards of the Indonesian Government Regulation Number 22 of 2021. Zinc is limited to 0.05 mg/L in the river and sea, whereas copper is 0.02 mg/L (river) and 0.008 mg/L (sea). Iron is still within the safe limit of 1 mg/L (sea) and does not require quality standards for rivers (Government Regulation, 2021).

Long-term excess levels of zinc can be toxic, disrupting essential biological processes such as protein, nucleic acid, carbohydrate, and lipid metabolism, and inhibiting cell signaling, potentially reducing the fertility of aquatic organisms and inhibiting photosynthesis of aquatic plants (Hogstrand, 2011; Sharma *et al*., 2024). On the other hand, copper in high concentrations can trigger oxidative stress, inhibit enzyme activity and cause immunosuppression. Other impacts will interfere with organisms' development, growth and reproduction, which can threaten the survival and balance of aquatic ecosystems (Cao *et al*., 2022).

The micronutrient distribution map (Figure 2) shows the spatial variation of iron, copper, and zinc in Pekalongan coastal waters, with the highest concentrations marked in red and the lowest in dark green. Iron concentrations are highest in RW 6, located at the mouth of the Mrican River and part of Wonokerto Beach. This accumulation is thought to be influenced by the flow of material from the mainland as well as the sedimentation process in the estuary, where weak north coastal currents cause suspended particles to settle around the estuary without being carried far into open water (Lahopang *et al*., 2023).

Copper has a different distribution pattern from iron distribution with the highest concentration in SW 4 or partly in Wonokerto Beach and Pencongan River. The high distribution of copper in RW 7 to RW 10 indicates the presence of streams carrying pollutants from industrial activities and fishing boat lines along the Pencongan River, which is marked by a change in yellow to red color (Yona *et al*., 2018; Ishak *et al*., 2023). In addition, meteorological factors such as the westerly monsoon in January may play a role in the movement of the longshore current, which transports copper from the west coast area to the east to the estuary area and east coast. Therefore, the accumulation of copper in SW 4 and SW 5 indicates that the current dynamics and the basin-shaped geographical conditions of Wonokerto Beach allow this metal to be trapped in the area (Tampubolon *et al*., 2021).

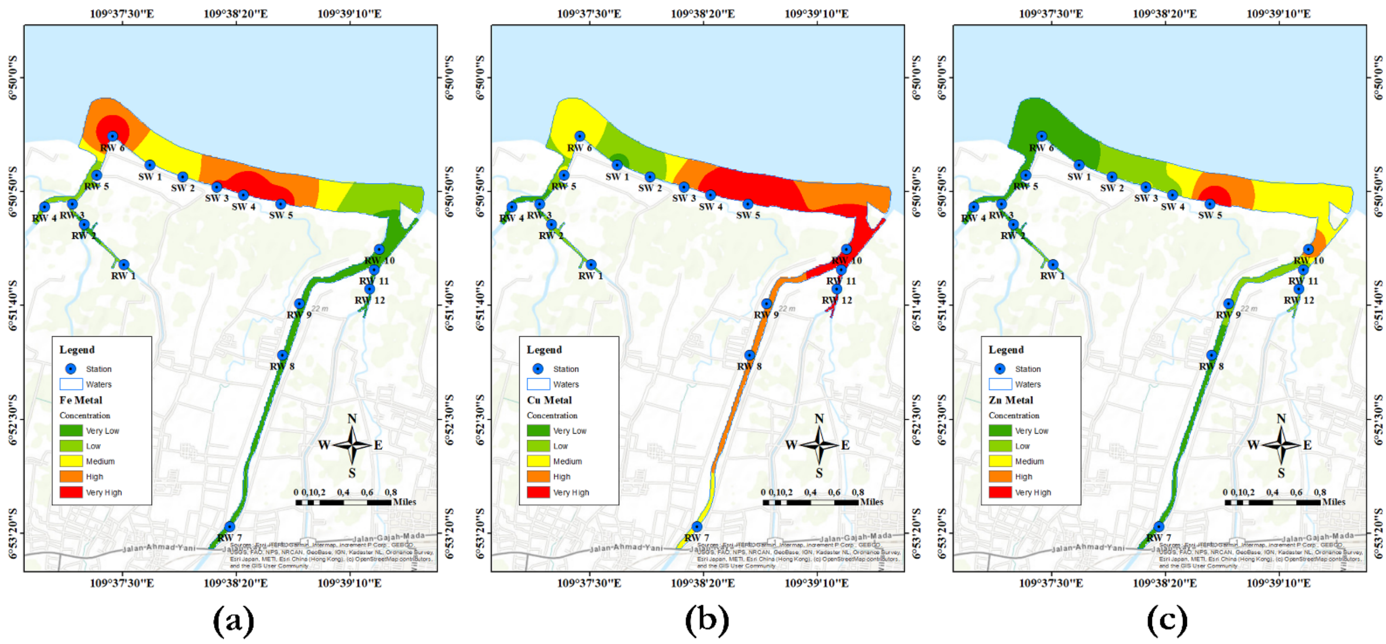

Figure 1. Micronutrient distribution of (a) iron; (b) copper; and (c) zinc in coastal area of Pekalongan

Zinc showed a more even distribution than iron and copper with the highest concentrations in SW 5 (Wonokerto Beach) and RW 10 (Pencongan River). The main factors contributing to the high zinc content in these two locations include the flow from the Pencongan River which carries industrial and domestic effluents, and fishing and shipping activities around the river mouth. Fishing boats may be a significant source of zinc pollution through anti-rust paint coatings, oil seepage, and fuel spillage, settling on the water bottom and increasing Zn levels (Lahopang *et al*., 2023).

Iron, copper, and zinc distribution patterns show that SW 5 has the highest metal accumulation. This location is in the basin area which slows the movement of currents, allowing the metals to be trapped and concentrated. In addition, the river estuary adjacent to this location becomes an accumulation point for river flow that carries various pollutants from the land (Lahopang *et al*., 2023). Coastal and tidal current patterns also play a role in micronutrient transport, causing the transfer of metals (Tampubolon *et al*., 2021).

Environmental Parameters

Government Regulation No. 22 of 2021 sets the quality standard values for supporting parameters of river and marine waters, such as dissolved oxygen (DO) at 2-4 mg/L (river) and >5 mg/L (sea), temperature at deviation 3 (river) and in accordance with the natural conditions of marine waters (sea), and pH at 6-9 (river) and 7-8.5 (sea) (Government Regulation, 2021). Based on the data in Table 2, some river and ocean waters still meet these quality standards. However, some others have deviations, such as DO and ocean salinity levels that are lower than the quality standards and DO in rivers that are higher than the set limits.

These supporting parameters will have different effects on water quality characteristics. For example, dissolved oxygen (DO) is an essential factor for aquatic life that determines water quality (Rosyadi & Ali, 2020). Meanwhile, the pH of water affects the solubility and toxicity of metals. When the pH rises, the solubility of metals will be lower, while when the pH drops, it will increase the toxicity of metals (Wandi *et al*., 2021). Salinity also affects the presence of metals, where low salinity will increase bioaccumulation, while high salinity can increase metal toxicity (Indrawati *et al*., 2022). Temperature plays a role in accelerating the reaction of metal ion formation at high temperatures and vice versa (Hariyanti *et al*., 2021).

Statistical Analysis

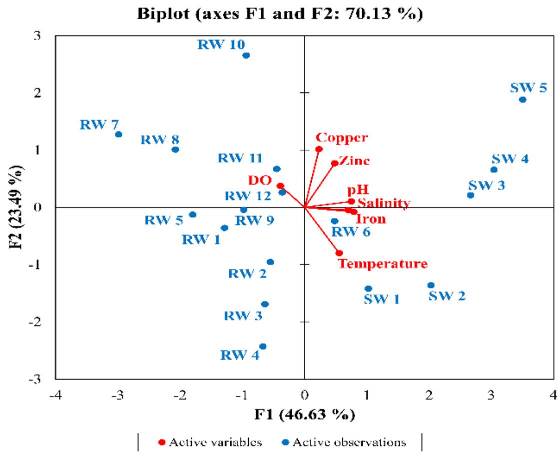

Figure 2. Relationship results between parameters

Correlation matrix analysis of the water quality parameter (Figure 3) shows that the first prominent factor (F1) accounts for 46.63% of the total data variation, while the second factor (F2) accounts for 23.49%. Overall, the contribution of these two main factors amounted to 70.13% of the total data variation. The biplot graph also illustrates the correlation between the water quality parameters at the study site, where the parameter values occupy quadrants I to III. In contrast, quadrant IV does not produce values of the parameters. Positive correlations are seen from parameters close to each other, while negative correlations are seen from opposite parameters (Hidayah *et al*., 2020).

PCA analysis illustrates the distribution of stations based on the characteristics of water quality parameters. Each parameter that moves away from axis zero is then shown as the main characteristic of each station (Wiyoto & Effendi, 2020; Mudloifah & Purnomo, 2023). In quadrant I, stations RW 7, RW 8, RW 10, RW 11, and RW 12 are characterized by high DO values. Quadrant II includes stations SW 3, SW 4, and SW 5 by metals Cu, Zn, and pH. Quadrant III at stations RW 6, SW 1, and SW 2 by parameters Fe, salinity, and temperature. Meanwhile, in quadrant IV, stations RW 1, RW 2, RW 3, RW 4, RW 5, and RW 9 do not have significant supporting parameters because they only have a minimal influence on water quality.

Water Quality

The CCME WQI analysis shows that the micronutrient content of the Pekalongan coastal area is low. Most contaminants come from human activities that produce metals such as copper (Cu) and zinc (Zn). When these metals enter water, they interact with other metal ions and undergo redox reactions, forming complex compounds. Under stable water conditions, these compounds will bind to water particles and eventually settle into sediments (Emersida, 2016).

The consequences of this metal accumulation directly impact aquatic ecosystems, where high metal concentrations can inhibit the growth of aquatic plant cells (Sihotang *et al*., 2021) and even cause the death of aquatic biota (Lukmanulhakim *et al*., 2023). Then, if this polluted biota is used as food, the health risk for humans increases because these harmful metals can enter the food chain and cause adverse health effects (Kusumastuti *et al*., 2020; Akbar and Rahayu, 2023).

Conclusion

This research successfully revealed the distribution pattern and bioavailability of iron (Fe), copper (Cu), and zinc (Zn) in Pekalongan coastal waters, especially in Mrican River, Pencongan River, and Wonokerto Beach. The analysis showed that the highest concentration of iron was found in RW 6 of the Mrican River estuary at 0.6295 mg/L. At the same time, copper and zinc concentrations varied along the coastal area, where the highest concentration of copper was found at 0.2820 mg/L in SW 4 Wonokerto Beach and zinc at 0.1571 mg/L in SW 5 Wonokerto Beach. This distribution pattern is influenced by anthropogenic activities, such as industrial, domestic, and fishing boat waste, as well as natural processes, such as sedimentation in the estuary, seasonality, current dynamics, and the basin-shaped geographical conditions of Wonokerto Beach. The bioavailability of these metals has the potential to degrade water quality and disrupt coastal ecosystems if it exceeds the threshold. Based on the CCME WQI water quality index, the water quality in Mrican River (54.779), Pencongan River (34.179), and Wonokerto Beach (28.107) as a whole can be said to be classified as poor. This condition has the potential to inhibit algae growth, endanger aquatic biota, and increase health risks for humans who consume polluted biota. Based on this research, the surrounding community can improve industrial waste management by implementing a stricter waste treatment system around the Pencongan River to reduce the impact of micronutrient pollution.

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