Fisheries Journal, 15 (1), 387-397 (2025)
http://doi.org/10.29303/jp.v15i1.1408

ANALYSIS OF Fe, Mn, AND Zn CONCENTRATIONS IN MANGROVE SEDIMENTS ALONG THE SOMBER RIVER IN BALIKPAPAN CITY

Analisis Konsentrasi Fe, Mn, Dan Zn Pada Sedimen Mangrove di Sepanjang Sungai Somber Kota Balikpapan

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(Received February 3rd 2025; Accepted February 28th 2025)

ABSTRACT

Somber River is one of the rivers with mangrove ecosystem in Balikpapan city. The high human activity in Somber River area may produce waste and heavy metal pollution in mangrove ecosystem, especially in sediment. The purpose of this study is to determine the concentration of Fe, Mn and Zn in mangrove sediments. In addition, the values of pollution indices such as contamination level (TK), pollution load index (IBP) and geoaccumulation index (I-Geo) in sediments are also determined along Somber river, Balikpapan city. The research method used in this study is purposive sampling. Sediment samples were taken from 9 sampling points along Somber river. Sediment samples were deconstructed using acid and analyzed using the Atomic Absorption Spectrophotometer (AAS) Aurora AI 1200 to determine the concentration of Fe, Mn, and Zn based on dry weight in µg/g. Based on the analysis, it was found that the Fe concentration in the sediment ranged from 5403 to 12268 µg/g with an average of 9462 ± 2294 µg/g. In Mn, the concentration value was between 2,25 and 23,2 µg/g with an average of 11,4 ± 7,43 µg/g. Then, the Zn concentration was between 16,6 and 61,3 µg/g, with an average of 43,4 ± 17,4 µg/g. The varying concentrations of Fe, Mn and Zn might be related to several human activities, such as industrial activities, boat docks, settlements, fisheries, ports and metal distribution from the Somber river. The concentrations of Mn and Fe at all research stations were lower than the sediment quality standards, except for Fe. The level of Fe, Mn and Zn contamination in sediments was low (TK<1) and not polluted (IBP<1) and the geoaccumulation index (I-geo) was not polluted to polluted (0<I-geo<1).

Keywords: Balikpapan, Ecosystem, Metal, Mangrove, Sediment

ABSTRAK

Sungai Somber merupakan salah satu sungai yang memiliki ekosistem mangrove di kota Balikpapan. Tingginya aktivitas manusia di kawasan sungai Somber dapat menghasilkan limbah dan pencemaran logam berat di ekosistem mangrove, terutama di sedimen. Tujuan dari penelitian ini adalah untuk menentukan konsentrasi Fe, Mn dan Zn pada sedimen mangrove. Selain itu, nilai indeks pencemaran seperti tingkat kontaminasi (TK), indeks beban pencemaran (IBP) dan indeks geoakumulasi (I-Geo) pada sedimen juga ditentukan di sepanjang sungai Somber, kota Balikpapan. Metode penelitian yang dilakukan di penelitian ini adalah purposive sampling. Sampel sedimen diambil dari 9 titik sampling di sepanjang sungai Somber. Sampel sedimen didestruksi menggunakan zat asam dan dianalisis menggunakan Atomic Absorption Spectrophotometer (AAS) Aurora AI 1200 untuk menentukan konsentrasi Fe, Mn, dan Zn berdasarkan berat kering (dry weight) dalam µg/g. Berdasarkan hasil analisis, ditemukan bahwa konsentrasi Fe pada sedimen mulai dari 5403 sampai 12268 µg/g dengan rerata 9462 ± 2294 µg/g. Pada Mn, nilai konsentrasinya antara 2,25 - 23,2 µg/g dengan rerata 11,4 ± 7,43 µg/g. Kemudian, konsentrasi Zn antara 16,6 - 61,3 µg/g, dengan rerata 43,4 ± 17,4 µg/g. Bervariasinya konsentrasi Fe, Mn dan Zn mungkin ada kaitannya dengan beberapa aktifitas manusia seperti kegiatan industri, dok kapal, pemukiman penduduk, perikanan, pelabuhan serta distribusi logam dari sungai Somber. Konsentrasi Mn dan Fe di semua stasiun penelitian lebih rendah dari standar baku mutu sedimen, kecuali Fe. Tingkat kontaminasi Fe, Mn dan Zn pada sedimen masih rendah (TK<1) dan tidak tercemar (IBP<1) dan indeks geoakumulasi (I-geo) termasuk tidak tercemar hingga tercemar (0<I-geo<1).

Kata kunci: Balikpapan, Ekosistem, Logam, Mangrove, Sedimen

INTRODUCTION

Balikpapan City is one of the cities in East Kalimantan province that has coastal resources, one of which is the mangrove ecosystem. In addition, Balikpapan City is also one of the buffer zones for the Indonesian Capital City (IKN) which has an important role in terms of transportation mobility through bays and ports (Daniswari *et al.,* 2023). Therefore, the Balikpapan area has experienced many improvements, both in terms of population, economy and industry. According to Tarigan *et al.* (2017), increasing population and industrial activities in an area can produce waste and have the potential to pollute the coastal areas of Balikpapan.

One of the areas that can be affected by many human activities (anthropogenic) in the Balikpapan city area is the Somber River. This can happen because this river functions as one of the shipping routes or traffic for various ships carrying trade commodities, shipping industry, and is adjacent to the industrial area of the Kariangau Industrial Area (KIK). In addition, around the Somber River there are anthropogenic activities such as industry, ports, transportation, fisheries, residential areas, mangrove tourism that is open to the public (Wulandari *et al.,* 2020; Yani & Moersidik, 2003). These activities may cause pollutant waste in aquatic ecology, one of which is heavy metals (Sitorus *et al.,* 2020; Syafira *et al.,* 2023).

Basically, heavy metals with amounts below the quality standards do not harm living organisms. However, these metals can act as nutrients needed by plants and aquatic biota. According to Marschner (2011), heavy metals such as iron (Fe), manganese (Mn), and zinc (Zn) can play a role in chlorophyll synthesis, photosynthesis processes, and plant metabolism. However, if Fe, Mn and Zn have exceeded the threshold, it can have a negative impact on mangrove growth and regeneration. These metals can accumulate in sediments and mangrove leaves, which can cause chronic contamination, antiradicals in mangrove leaves (D'Addazio et al., 2023; Defew et al., 2005). In addition, according to Burger & Gochfeld (2005) that metals can also accumulate in plant tissues, organisms, and potentially spread through the food chain in the ecosystem. For example, Fe, Mn and Zn found in waters can fall and settle at the bottom of the waters, and accumulate in sediments. This can cause biota that feed in the water column and bottom such as fish, shrimp and shellfish to have a high potential for exposure to Fe, Mn and Zn metals (Ray & Vashishth, 2024). If these biota are consumed excessively by humans, it can cause consumer health risks such as metabolic problems, lack of energy, anti-oxidation defense and low immune response (Rozenberg *et al.,* 2022). One effort to find out whether the mangrove sediments along the Somber River have been exposed to Fe, Mn and Zn metals is to conduct a pollution index investigation.

Basically, the pollution index is based on a comparison of the concentration of metals in sediment samples with previous metal concentrations (Maria *et al.,* 2023; Ndhlovu *et al.,* 2023). The most commonly used indices include the level of contamination (TK), the pollution load index (IBP) and the geoaccumulation index (I-geo) (Ndhlovu *et al.,* 2023). The pollution index not only identifies and classifies metal pollution in terms of its toxicity. However, the pollution index can also provide information about the possibility of biological effects on plants, biota associated with sediments that have been exposed to metals (D'Addazio *et al.,* 2023; Ray & Vashishth, 2024).

Basically, research on heavy metals in sediments has been carried out by several researchers around Balikpapan Bay. For example, Sitorus *et al.,* (2020) studied Pb, Cd, Cu, and As in water, sediment and shellfish on the coast of Balikpapan. Then, research on Pb in the Mangrove Center Area (Syafira *et al.,* 2023) and also research on Cr, Ni, Cu, and Zn in sediments in the Balikpapan area. However, information on other types of metals in the form of Fe, Mn and Zn found in mangrove sediments is still very limited. Therefore, the purpose of this study was to detect the concentration of Fe, Mn and Zn in mangrove sediments along the Somber River. In addition, analysis of pollution indices in the form of contamination levels, pollutant load indexes and geoaccumulation of Fe, Mn and Zn in mangrove sediments was also carried out in this study.

RESEARCH METHODS

Time and Place

Sediment sampling was conducted in August 2024 along the Somber River, Balikpapan City with different sampling stations (Figure 1).

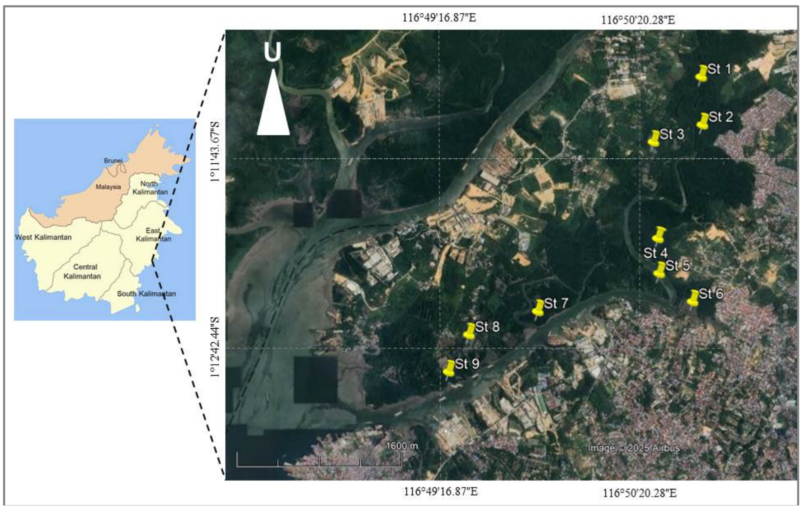


Figure 1. Map of Sediment Sampling Locations (Yellow Push Pins)

Tools and Materials

Some of the tools used in this study consisted of Atomic Absorption Spectrophotometry (AAS) AURORA AI 1200 brand, crucible cup, mortar and pestle, sieve (Whatman No. 41), plastic clip, analytical balance (± 0.001 g), camera, brush, marker, oven (Thermo Scientific brand), vortex mixer, and aluminum foil. While the materials used include mangrove sediment samples, 60% $HClO_4$ and 65% HNO_3 (Merck, Germany) and distilled water.

Research Procedure

Mangrove sediment samples were taken from 9 sampling points along the Somber River, Balikpapan (Figure 1). The sediment sampling method in this study used purposive sampling by considering the location and activities at the sampling location. Each sediment sample was taken one by one on the surface (±30 cm) using a plastic shovel. Each sample was put into a ziplock plastic that had been given a sample code beforehand. After that, each sample was put into a cool box, taken to the laboratory and stored in a freezer (-20ºC) for further analysis.

A few days later, the sediment samples in the freezer were removed and left on the table to melt at room temperature (25ºC). Then, the sediment samples were put into aluminum cups (±100 g), dried using an oven (±100°C) for ±72 hours). The sediment samples were homogenized and ground using a mortar and pestle made of stainless steel. The mashed samples were then filtered and weighed with an analytical balance of 10 grams for each sample. Then, the sediment samples were put into a zip-lock plastic that had been coded beforehand. Afterwards, all sediment samples were stored in a desiccator before further analysis.

The sediment sample destruction process was carried out in the soil laboratory, Faculty of Agriculture, Mulawarman University. Sediment samples of ±2 grams were weighed and put into a crucible (60 ml) and mixed with 2 ml of $HClO_4$ and 3 ml of HNO_3. Then, the samples were left for ±24 hours. Then, each sample was heated using a hotplate at a temperature of 100-130ºC for ±2 hours with multi-stage heating. Then, the temperature was raised again to 150-200ºC until the yellow vapor ran out until white vapor was formed. Furthermore, all samples were cooled, and distilled water was added up to 20 ml. Each sample was homogenized using a vortex. Finally, each sample solution was analyzed using Atomic Absorption Spectrophotometer (AAS) Aurora AI 1200 to determine the concentration of Fe, Mn, and Zn. In this study, the dry weight of the sample was used to determine the concentration of Fe, Mn and Zn (µg/g) in the sediment.

Pollution Index Analysis

Basically, pollution indices can act as potential factors in a comprehensive assessment of environmental pollution levels, one of which is sediment (Ndhlovu *et al.,* 2023). In this study, there were several metal pollution indices studied in sediment, such as contamination level (CL), pollution load index (PLI) and geoaccumulation index (I-Geo).

1. Contamination Level (CL) of Fe, Mn and Zn in Sediment

The contamination level of Fe, Mn and Zn in sediment in this study was calculated based on their concentration values (Hakanson, 1980). The TK value was calculated using the following equation:

$$CL = \frac{C_1}{C_2}$$

Where $C1$ is the concentration of metals (Fe, Mn and Zn) from the analysis. The value of $C2$ is the average concentration of metals in the previous environment, namely Fe of 47200 mg/kg (Turekian & Wedepohl, 1961), while the concentration of Mn (850 mg/kg) and Zn (70 ng/g) is based on Harikumar *et al.,* (2010). Then, the grouping of metal contamination levels in mangrove sediments can be seen in Table 1.

Table 1. Interpretation of Sediment Contamination Levels (CL) (Hakanson, 1980).

CL value	Category
TK < 1	Low
1 < TK < 3	Medium
3 < TK < 6	Fair
TK > 6	Very High

2. Pollution Load Index (PLI)

The PLI value is one of the calculations to estimate the impact of metal pollution at the research location. The formula used to determine the IBP value refers to Ndhlovu *et al.,* (2023):

$$PLI = (TK1 \; x \; TK2 \; x \; TK3 \; x \dots \dots .. TKN)^{1/n}$$

Where n is the amount of metal, CL is the contamination factor and if the IBP value <1 indicates no contamination (Gopal *et al.,* 2017).

3. Geoaccumulation Index (I-Geo)

The I-geo index value in this study follows the Muller equation (1969). This equation is used to determine the level of heavy metal pollution in sediment.

$$Igeo = log_2 \left[\frac{C1}{1,5 \; C2}\right]$$

Where Log_2 is 0.301. C1 is the concentration of Fe, Mn and Zn in sediment (µg/g) and C2 is the average concentration of Fe, Mn and Zn in the previous environment. Then, the constant value used in this study is 1.5.

Interpretation of I-geo values (Muller, 1969) in this study is categorized based on the level of pollution (Table 2).

Table 2. Interpretation of Geoaccumulation Index Values (I-Geo).

I-geo Value	Category
(I-geo<0)	Unpolluted
(0<I-geo<1)	Unpolluted to moderately polluted
(1<I-geo<2)	Moderately polluted
(2<I-geo<3)	Moderately to heavily polluted
(3<I-geo<4)	Heavily polluted
(4<I-geo<5)	Heavily to very heavily polluted
(I-geo≥5)	Very heavily polluted

Statistical Analysis

All data from the analysis of Fe, Mn and Zn concentrations in sediments were conducted using Microsoft Windows Excel. Descriptive analysis was used to explain the findings in the tables and figures in this study. Each concentration of Fe, Mn and Zn in the sediments in this study was compared with the sediment quality standards based on Persaud *et al.,* (1993).

RESULT

Concentration of Fe, Mn and Zn in Sediment

The analysis results found that the concentration of Fe in the sediment was between 5403 - 12268 µg/g with an average of 9462 ± 2294 µg/g. Then in Mn ranging from 2.25 to 23.2 µg/g 2.25 with an average of 11.4 ± 7.43 µg/g. While the concentration of Zn was between

16.6 - 61.3 µg/g) with an average of 43.4 ± 17.4 µg/g. In general, the order of metal accumulation found in the sediment in this study was Fe> Zn> Mn. When compared to the sediment quality standards, the concentrations of Mn and Fe at all research stations were still below the sediment quality standards, except for Fe (Table 3).

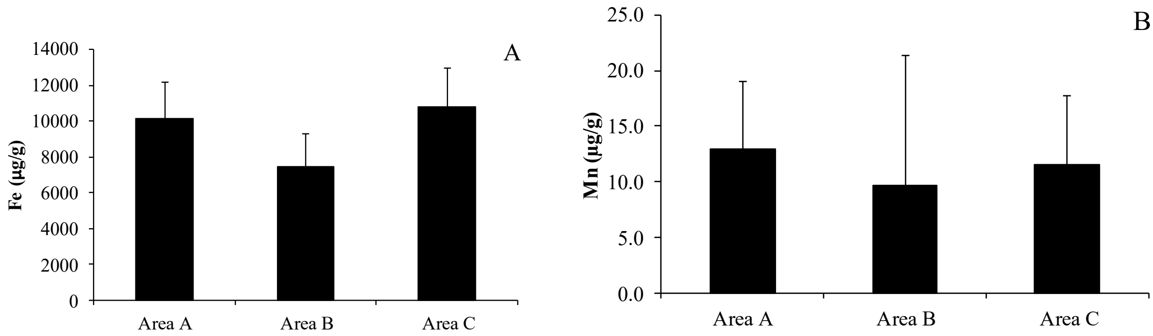
Table 3 Concentrations of Fe, Mn and Zn (µg/g) in Mangrove Sediment

Station	Metal Concentration (µg/g)		
	Fe	Mn	Zn
1	8015	6.56	38,4
2	10445	13,7	44,3
3	11965	18,6	60,9
4	5403	2,25	17,5
5	8347	3,68	61,1
6	8637	23,2	40,0
7	8327	4,99	16,6
8	11747	12,1	61,3
9	12268	17,5	50,4
Minimum	5403	2,25	16,6
Maximum	12268	23,2	61,3
Average	9462	11,4	43,4
STD*	2294	7,43	17,4
Baku mutu**	2	460	120

*STD = Standard Deviation
** Persaud *et al.,* (1993).

Metal Distribution in Sediment

Based on the source of pollutants, the distribution of Fe, Mn and Zn metals in sediments in the study was classified into 3 areas. Area A, consisting of stations 1, 2 and 3. These stations are located quite far from the port and ship dock. Area B (stations 4, 5 and 6) is an area close to residential activities, ports and ship docks. Then, area C (stations 7, 8 and 9) is an area close to the Somber River estuary, ports and ship docks (Figure 1). The concentration of Fe in area C (10781 ± 2140 µg/g) was found to be relatively higher than areas A (10142 ± 1992 µg/g) and B (7462 ± 1789 µg/g). Meanwhile, the concentration of Mn in area A (13.0 ± 6.07 µg/g) was higher than areas C (11.5 ± 6.26 µg/g) and B (9.70 ± 11.7 µg/g). Then, the concentration of Zn in area A (47.9 ± 11.7 µg/g) was relatively higher when compared to areas C (42.8 ± 23.3 µg/g) and B (39.6 ± 21.8 µg/g) (Figure 2).



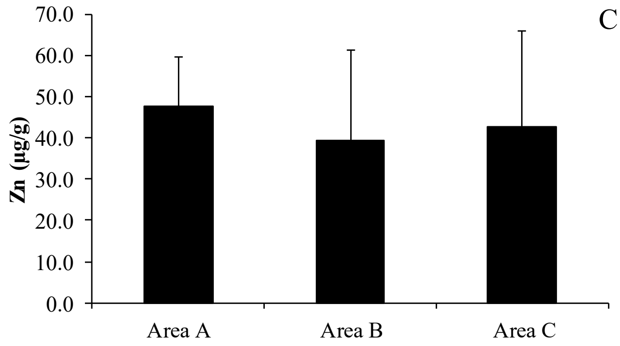


Figure 2. Concentration of Fe (A), Mn (B), Zn (C) Based on Pollution Sources

Contamination Level (CL) and Pollution Load Index (PLI)

The contamination level (CL) of Fe in sediments ranges from 0.11 - 0.26 with an average of 0.20 ± 0.05. While for Mn it ranges from 0.00 to 0.03 with an average of 0.01 ± 0.01. Then, for Zn it ranges from 0.24 - 0.88 with an average of 0.62 ± 0.25. In general, the average TK value for all metals in this study was still below 1 (CL <1). This finding indicates that all concentrations of Fe, Mn and Zn found at stations 1 to 9 have low contamination levels (Table 2).

The PLI value for all metals (Fe, Mn and Zn) ranges from 0.04 to 0.17 with an average of 0.11 ± 0.04. The lowest and highest IBP values were found at stations 4 and 3. In general, the contamination level and pollutant load index in the sediment were still low and unpolluted (PLI <1) based on Fe, Mn and Zn metals at all research stations (Table 4).

Table 4 Contamination Level (CL) and Pollution Load Index (PLI) in Sediment.

Station	CL			CL	PLI	Category
	Fe	Mn	Zn			
1	0,17	0,01	0,55	Low	0,09	Unpolluted
2	0,22	0,02	0,63	Low	0,13	Unpolluted
3	0,25	0,02	0,87	Low	0,17	Unpolluted
4	0,11	0,00	0,25	Low	0,04	Unpolluted
5	0,18	0,00	0,87	Low	0,09	Unpolluted
6	0,18	0,03	0,57	Low	0,14	Unpolluted
7	0,18	0,01	0,24	Low	0,06	Unpolluted
8	0,25	0,01	0,88	Low	0,15	Unpolluted
9	0,26	0,02	0,72	Low	0,16	Unpolluted
Average	0,20	0,01	0,62	Low	0,11	Unpolluted
STD*	0,05	0,01	0,25		0,04	

*STD = Standard Deviation

The I-geo value for Fe is between 0.02 – 0.05 with an average of 0.04 ± 0.01. As for Mn, the I-geo value was found to range from 0.001 to 0.005 with an average of 0.003 ± 0.002. Then, the I-geo value for Zn is between 0.05 – 0.18 with an average of 0.12 ± 0.05. In general, the I-geo value for Fe, Mn and Zn in the sediment in this study is still included in the category of unpolluted to moderately polluted (0<I-geo<1) (Table 5).

Table 5. Geoaccumulation Index (I-geo) Values of Fe, Mn and Zn Metals in Mangrove Sediments

Station	I-Geo			Contamination Level
	Fe	Mn	Zn	
1	0,03	0,002	0,11	Unpolluted to moderately polluted
2	0,04	0,003	0,13	Unpolluted to moderately polluted
3	0,05	0,004	0,17	Unpolluted to moderately polluted
4	0,02	0,001	0,05	Unpolluted to moderately polluted
5	0,04	0,001	0,18	Unpolluted to moderately polluted
6	0,04	0,005	0,11	Unpolluted to moderately polluted
7	0,04	0,001	0,05	Unpolluted to moderately polluted
8	0,05	0,003	0,18	Unpolluted to moderately polluted
9	0,05	0,004	0,14	Unpolluted to moderately polluted
Average	0,04	0,003	0,12	Unpolluted to moderately polluted
STD*	0,01	0,002	0,05	

*STD = Standard Deviation

DISCUSSION

In Table 3, the minimum, maximum, mean and standard deviation values of Fe, Mn and Zn metals in the studied sediments are listed. Among all the metals studied, Fe showed the highest average concentration in the sediments, followed by Mn and Zn. The high concentration of Fe in this study may be related to natural sources and several anthropogenic activities that occurred around the sampling location such as the shipping industry (docks and ship repair shops), transportation, erosion due to the conversion of mangroves into ponds and the disposal of industrial and residential waste. The differences in the concentrations of several metals in this study may also be associated with increased dynamics of metal absorption, sedimentation, and flocculation that occur in the ecosystem (Bao et al., 2024; Jia *et al.,* 2021). In addition, variations in metals in sediments are also related to pH values, total organic carbon (TOC), dissolved oxygen and also the type and size of sediment (Jia *et al.,* 2021; Ndhlovu *et al.,* 2023). Although the total Fe concentration in mangrove sediments was relatively high in this study, the bioavailable Fe concentration may not be sufficient for mangrove plant growth due to geochemical constraints (Alongi, 2010). High Fe in sediments has the potential to increase mangrove growth (Avicennia marina) and increase its tolerance to Cd at physiological and metabolic levels (Li *et al.,* 2023).

Based on the source of the pollutant, in general, the Fe concentration in this study had a pattern of C>A>B. While the concentrations of Mn and Zn had the same pattern, namely A>C>B. These findings indicate that the concentrations of Mn and Zn were higher in areas that were relatively far from the port and ship dock. While lower concentrations were found in areas adjacent to residential activities, ports and ship docks. On the other hand, the highest Fe concentration was found in areas that were relatively far from the Somber River estuary, ports and ship docks (Area C). The high concentration of Fe in sediments in areas C and A in this study may be due to the distribution process of metals from other areas (Kariangau and Balikpapan Bay), river flow (runoff) during the high and low tide of waters from the estuary to the upstream of the Somber River. When the tide occurs, organic matter containing Fe, Mn and Zn can settle to the bottom of the waters and accumulate in the sediment. In addition, the distribution and accumulation of metals in sediments can also be influenced by the size and texture of the sediment, mineral composition and physical and chemical processes (Han *et al.,* 2017; Jia *et al.,* 2021).

In general, the contamination level (CL) for Fe, Mn and Zn in sediments at all research locations is still in the low category. This finding indicates that the concentration of several metals is still good and supports the life of biota and mangroves in the Mangrove Center area. This finding is relatively the same as the results found by Pratikino *et al.,* (2022) on the coast of Ranokomea, Southeast Sulawesi, which found that the CL value in the area was low and the Pollution Load Index (PLI) was still safe or not polluted.

The results of the I-Geo index analysis found that all sampling stations were still safe, because the level of contamination found was not polluted to moderately polluted (0<I-geo<1). These results indicate that the mangrove sediments along the Somber River are still suitable and support the life of their biota. These results are relatively the same as several investigations conducted by other researchers in Indonesia, such as in Sungai Liat, Bangka (Nugraha *et al.,* 2022), Poleang Timur, Southeast Sulawesi (Sakthyar *et al.,* 2023), Pesisir Tanjung Gunung Bangka Tengah (Susanti *et al.,* 2023). However, the investigation conducted by Maria *et al.,* (2023), the I-geo values for Fe and Mn have been extremely polluted (I-geo ≥ 6) at several sampling points in Balikpapan city. Several factors that can cause differences in the levels of contamination (CL) and geoaccumulation of Fe, Mn and Zn metals in this study may be related to the factor of exposure to metals entering the waters due to anthropogenic factors that occur along the Somber River. This assumption is in accordance with the findings made by Syafira *et al.* (2023), in the Mangrove Center Graha Indah area, Balikpapan, where the CL Pb value in sediments in the area can be influenced by differences in sampling locations, pollution sources, and the flow of the Somber River which has the potential to carry metals from other areas such as Balikpapan Bay and the Kariangau River, Balikpapan.

CONCLUSION

The concentration of Mn (2.25 to 23.2 µg/g) and Zn (16.6 - 61.3 µg/g µg/g) in sediments along the Somber River in Balikpapan are below the sediment quality standard, except for Fe (5403 - 12268 µg/g). The contamination level (CL) for Fe is between 0.11 - 0.26 (low contamination). The pollution load index (PLI) value for all metals (Fe, Mn and Zn) is between 0.04 - 0.17 (unpolluted). Differences in sampling locations and several human activities (anthropogenic) around the sampling location play an important role in increasing the TK, IBP and I-geo values in mangrove sediments along the Somber River, Balikpapan City.

ACKNOWLEDGEMENTS

We would like to thank the management of the Soil Science and Oceanography Laboratory (Integrated Laboratory) of Mulawarman University and all parties who have supported the implementation of this research.

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