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Assessment of Heavy Metals Using the Enrichment Factor and Geoaccumulation Index in Menjer Lake, a Tropical Volcanic Lake

Lintang Nur Fadlillah[1], M. Widyastuti[1*], Alfina Ayu Rachmawati[2], Azura Ulfa[3]

[1]Laboratory of Hydrology and Environmental Climatology, Department of Environmental Geography, Faculty of Geography, Universitas Gadjah Mada, Yogyakarta 55281, Indonesia
[2]Department of Environmental Geography, Faculty of Geography, Universitas Gadjah Mada, Yogyakarta 55281, Indonesia
[3]Research Center for Remote Sensing, National Research and Innovation Agency, Jakarta, Indonesia

*Corresponding author's e-mail: mwiwik@ugm.ac.id

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Abstract: Lakes are recognized as vulnerable to pollution, including Menjer Lake, whose catchment area is dominated by agricultural lands and features floating net cages in the water body. The heightened contamination risk within the lake primarily stems from the accumulation of heavy metals, compounds known for their profound toxicity. The high-level concentration of heavy metal in sediment aligns with the level of water toxicity, underscoring the urgent need for thorough assessment and monitoring. The research focused on assessing heavy metal concentration and distribution through spatial analysis. Toxicity levels were evaluated using the enrichment factor (EF) and Geoaccumulation Index (Igeo). This study collected eight samples each during the rainy season of 2022 and 2023. The heavy metals were tested using an Atomic Absorption Spectrophotometer (AAS), including Pb, Cd, Cr, Fe, Al, and Cu. Comparatively, the mean concentration of heavy metals in 2023 was slightly higher for Fe and Al than in 2022. Moreover, Cd was not detected in either 2022 or 2023. The variety of land use and land cover has consequences on the spatial distribution of toxicity levels, showing an influential correlation between Al, Pb, and Fe metals with locations associated with cropland and floating net cages. Additionally, highly steep slopes significantly affected erosions that induced sediment from agricultural land use, further underscoring the multifaceted nature of environmental risk factors.

Keywords: environmental risk, ecological risk, heavy metals, lake hydrology, water pollution

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1. Introduction

Heavy metals are considered toxic owing to their ability to bind to sediments, accumulate over extended periods, and resist degradation (Yuan *et al.*, 2022). These metals are commonly transported to water bodies through surface runoff and erosion processes and accumulate in the sediment. The natural sources of heavy metals are rock weathering and volcanic sediments. However, anthropogenic factors related to household activities, agriculture, and industrial operations release large quantities of heavy metals into the environment (Looi *et al*., 2019). The previous study found that heavy metals in sediments primarily originated from bedrock and land-based activities. However, lakes in the protected areas may be exposed to heavy metal pollution from forests, agriculture, and other anthropogenic land uses (Sojka *et al*., 2022).

Menjer Lake is a volcanic lake located in Wonosobo City, serving multiple purposes such as tourism, hydropower generation, and fisheries. Moreover, agricultural activities are excessive in its catchment area. Agricultural activities, such as chili, potato, and cabbage farming, in the Menjer Lake catchment area have been identified as potential sources of heavy-metal pollutants. Metals commonly found in fertilizers, including Cr, Fe, Zn, and Cd, contribute to this pollution (Xu *et al*., 2020). The extensive use of fertilizers, driven by intensive agricultural practices, may lead to these heavy metals (Alfarisy *et al*., 2020). Additionally, Menjer Lake is fed by the Serayu River, potentially transporting metals along with dissolved sediments. Heavy metals usually found in lake-surface sediments are Fe, Pb, Cu, Zn, Cd, Hg, and Al (Bentley *et al.,* 2022). However, volcanic lake bedrock commonly contains metals such as Fe, Cu, and Pb.

One method to assess the presence of heavy metals in river sediments is to use the Enrichment Factor (EF) and Geoaccumulation Index (Igeo). The Igeo is used to determine metal contamination in sediments, with its calculation formula developed by Muller in 1969. Meanwhile, the EF assesses metal contamination resulting from anthropogenic activities. Both indices are crucial for identifying anthropogenic contaminants in sediment and surface soil (Barbieri, 2016). This method is essential because the metals accumulated in sediments can dissolve in water and undergo transfer to human bodies and animals (Hasimuna *et al*., 2021). The EF and Igeo serve as metrics for evaluating the presence and extent of anthropogenic contaminants. The EF and Igeo are commonly utilized to assess metal concentrations of environmental concern. These indexes assess soil pollution levels, often based on similar soil fragments, using the numerical formula representing the bio-available fraction (Barbieri, 2016).

Research on assessing toxic metal levels in Indonesian lakes is currently limited. Several studies have been conducted on river sediments, including research by Wardhani *et al.* (2018) on reservoirs, Fadlillah *et al.* (2023) examining toxicity in water and sediments in the Winongo River, and Fadlillah *et al.* (2024) conducting research of ecological risk in nutrient and heavy metals in Menjer Lake using different methods without comparing to temporal changes between years. Conducting such research is crucial to address public concerns about heavy-metal accumulation in sediment. The study aimed to investigate the spatial variation, distribution, and sources of heavy metals (Pb, Cd, Cr, Fe, and Al) in Menjer Lake using the EF and Igeo across different years. Moreover, this research was conducted to create a basis for data on heavy metal concentration in lake sediment in Indonesia.

2. Materials and Methods
2.1 Study Area

Menjer Lake is situated in Maron Village, Garung District, Wonosobo, Central Java (Figure 1).This lake was formed at the base of Mount Pakuwaja due to volcanic eruptions and is positioned at 1300 m above sea level. Hence, it is characterized by extremely steep slopes (>40%). The water sources of Menjer Lake are from various rivers within the Menjer catchment areas, namely the Menjer, Siwedi, and Silumbu Rivers, as well as springs surrounding the lake (Bergen *et al*., 2000). Additionally, this area experiences substantial rainfall, with the Menjer catchment area receiving an annual average rainfall of >3000 mm, classified as very high (Suhendro *et al*., 2022).

2.2. Sampling collection and analysis

This investigation collected 16 surface sediment samples from Menjer Lake during the rainy season. Eight sampling sites (S1-S8) were carefully chosen to encompass different land uses, considering the potential introduction of heavy metals into the lake via runoff from diffuse sources. Field surveys were conducted in March 2022 and January 2023. The initial eight sediment samples were obtained in March 2022, and the remaining eight samples were collected in January 2023. Additionally, three soil samples were taken from the agricultural zone in January 2023 to investigate the correlation between surface sediment. Notably, the sampling sites were consistently maintained in the exact locations throughout the study period in 2022 and 2023 (Figure 1).

The Sediment samples from each site were gathered using a grab sampler for surface sediment, following the method outlined by Ahmed *et al*. (2022). Subsequently, the samples were placed in plastic bags, stored in ice boxes, and transported to the laboratory for analysis. Once there, they were naturally dried at ambient air temperature. Following drying, 0.3 g samples underwent digestion using HNO_3 and were analyzed for heavy metal content using an atomic absorption spectrophotometer (Varol, 2020). The heavy metals tested for Pb, Cd, Cr, Fe, and Al. All sediment analyses adhered to standard operating procedures in accordance with ISO 17025:2017. Calibration Curves were also prepared from a 1000-ppm stock standard solution to ensure quality control and assurance during the analyses.

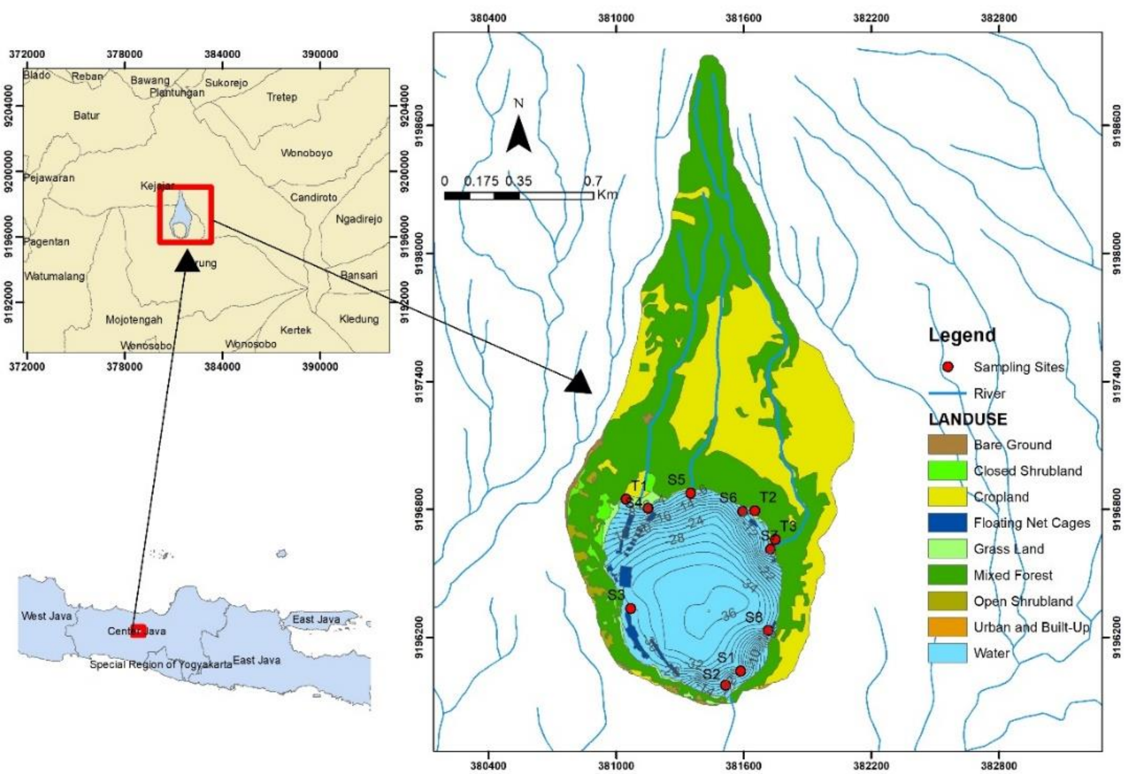

Figure 1. Location of Menjer Lake in Wonosobo, Central Java, Indonesia along with the designated sampling sites.

2.3. Heavy metal risk assessment analysis

2.3.1. *Enrichment Factor (EF)*

The EF is used to evaluate the contamination and pollution of heavy metals from anthropogenic activity (Li *et al.*, 2022). The EF is calculated using Equation 1:

$$EF = \left(\left(\frac{A}{B}\right) \text{sample}\right) / \left(\left(\frac{A}{B}\right) \text{background}\right) \quad \text{....Eq 1.}$$

where A is the element concentration in the observed sample, while B is the reference element concentration in a sample. The value of EF is calculated by the ratio between the observed heavy-metal concentration ((A/B) sample) and the stable concentration of heavy metals with standard samples ((A/B) background). EF can be categorized by the value in sediment: EF < 1 indicates no enrichment; 1 < EF < 3 is low; 3 < EF < 5 is moderate; 5 < EF < 10 is moderately severe; 10 < EF < 25 is severe; 25 < EF < 50 is very severe; and up to 50 is highly severe (Yuan *et al.*, 2022).

2.3.2. *Geo-accumulation Index (Igeo)*

Most studies assess the environmental risk posed by sediment by considering the background concentration of heavy metals. The background concentration of heavy metals in lake sediment varies due to different geological settings and land use types (Birch, 2017; Xu *et al.*, 2020). Therefore, this study utilized Igeo to determine the level of heavy metal contamination in the sediment. The background values were adopted from previous research on rivers in volcanic areas (Fadlillah *et al.*, 2023). The (Igeo) was calculated using Equation 2:

$$\text{Igeo} = \text{Log2}\,\frac{\text{Cn}}{1.5\ \text{Bn}} \quad \text{....Eq 2.}$$

where Cn shows the metal concentration in sediment samples, while Bn is the metal concentration reference. The value of Igeo < 0 is unpolluted; 0 to 1 is lowly polluted; 1 to 2 is moderately polluted; 2 to 3 is moderate to highly polluted; 3 to 4 is highly polluted; 4 to 5 is high to extremely polluted; above 5 is extremely polluted (Xu *et al.*, 2020; Yuan *et al.,* 2022).

3. Results and discussion

3.1. Heavy-metal concentrations

The heavy metal concentrations in Menjer Lake were found to be significantly lower, approximately 40 times less, than those observed in other Indonesian lakes and reservoirs, such as the Saguling Reservoir, where anthropogenic and industrial activities contribute to higher pollution levels (Wardhani *et al.*, 2018). For instance, in the Saguling Reservoir, Pb, Cr, and Cd concentrations were measured at 40.2, 165.25, and 16.68 mg kg^{-1}, respectively. This contrast underscores Menjer Lake's relatively low exposure to pollution. Additionally, comparisons with international lakes reveal that Menjer Lake's concentrations of Pb, Cr, Fe, Al, and Cd are lower than those in lakes like Erhai Lake (Lin *et al.*, 2016) and Lake Taihu (Xu *et al.*, 2020), yet higher than Uchalli Lake in Pakistan (Aftab *et al.*, 2023), with Cd levels being the lowest among all metals in Menjer Lake.

Table 1 illustrates a slight decrease in metal concentrations in 2023, except for Fe and Al levels (Menjer Lake). Cr and Cd concentrations were undetectable due to their minimal amounts. Furthermore, no significant changes in watershed management or land use were observed across the different sampling years.

Table 1. Concentrations of heavy metals in the sediment of Menjer Lake

Name of sample	**Heavy-metal Concentration (mg kg^{-1})**	**Pb**	**Cr**	**Fe**	**Al**	**Cd**
Menjer Lake[a] (n = 8)	Mean	0.129	0.050	9.038	59.858	ND*
	Min	0.067	0.023	0.110	0.110	ND*
	Max	0.207	0.061	25.790	266.940	ND*
Menjer Lake[b] (n = 8)	Mean	0.085	ND*	24.234	35.473	ND*
	Min	0.030	ND*	0.880	5.177	ND*
	Max	0.149	ND*	82.740	105.720	ND*
Soil samples[C] (n = 3)	T1	0.101	ND*	88.100	64.517	ND*
	T2	0.134	ND*	92.500	96.043	ND*
	T3	0.100	ND*	67.040	72.066	ND*
Background value[d]		0.170	0.020	28.820	32.830	ND*

[a]Sediment samples taken in the year 2022. [b]Sediment samples taken in the year 2023. [c]Sediment samples taken from cropland in the catchment area of Menjer Lake. [d]Background value from previous research related to Winongo River (Fadlillah *et al.*, 2023). [e]Heavy metal concentrations in mean value. * Not detected

3.2. Spatial distribution of heavy metals in sediment

Menjer Lake is a deep volcanic lake with a maximum depth of over 36 m (Figure 1). The bathymetry of this lake, shown in Figure 1, displays a remarkably steep slope of lake topography, suggesting that sediments may have accumulated in the deep areas of the lake. The sediment sampling was conducted in the litoral zone up to 17 m depth of the lake due to the limitations of the grab sampler. The spatial distribution shows spatial consistency for each heavy metal related to the sampling sites and the corresponding land use from the samples taken in different years.

Table 2. Pearson correlation matrix for heavy metals in the lake-surface and cropland sediments in the year 2023

Heavy-metal correlations	Pb	Cr	Fe	Al	Cd
Pb	1				
Cr	-	-			
Fe	.86*	-	1		
Al	.88*	-	.72*	1	
Cd	-	-	-	-	-

The spatial distribution of heavy metals is shown in Figures 2 and 3. The highest Pb values in 2022 were recorded at points S3 and S5, while the highest Pb value in 2023 was observed at point S3. Meanwhile, the spatial distribution of Fe metal shows a similar pattern in 2022 and 2023. High Fe values are found at points S3 and S4, while low Fe values are found at points S6, S7, and S8. The highest values for Al metal in 2022 were found at points S4 and S5, whereas the highest values were at points S4 and S6 in 2023.

The results of the correlation analysis (Table 2) and the spatial distribution patterns indicate a strong correlation between locations with Al, Pb, and Fe metals. The high metal concentrations are observed in adjacent locations, specifically at points S3, S4, S5, and S6, which are influenced by floating net cages and agriculture (Wang *et al.*, 2018).

Regarding the distribution of Cr metal, the highest concentrations were found at points S4, S5, and S1 in 2022. Due to the instrument detection limit, the Cd metal results for 2022 and 2023 cannot be presented in spatial form. Similarly, the Cr value for 2023 cannot be presented spatially as well as cannot be calculated for EF and Igeo.

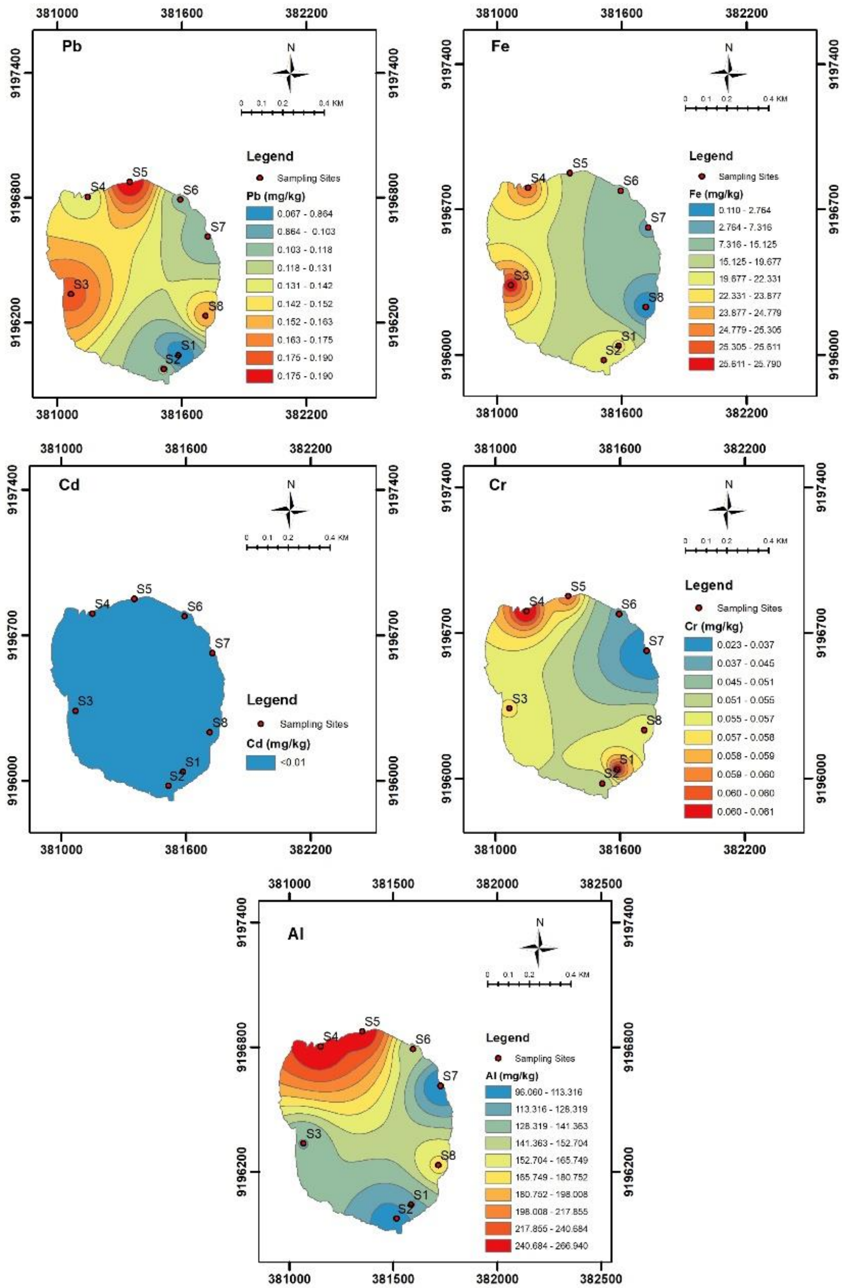

Figure 2. Spatial distribution of heavy metals in 2022

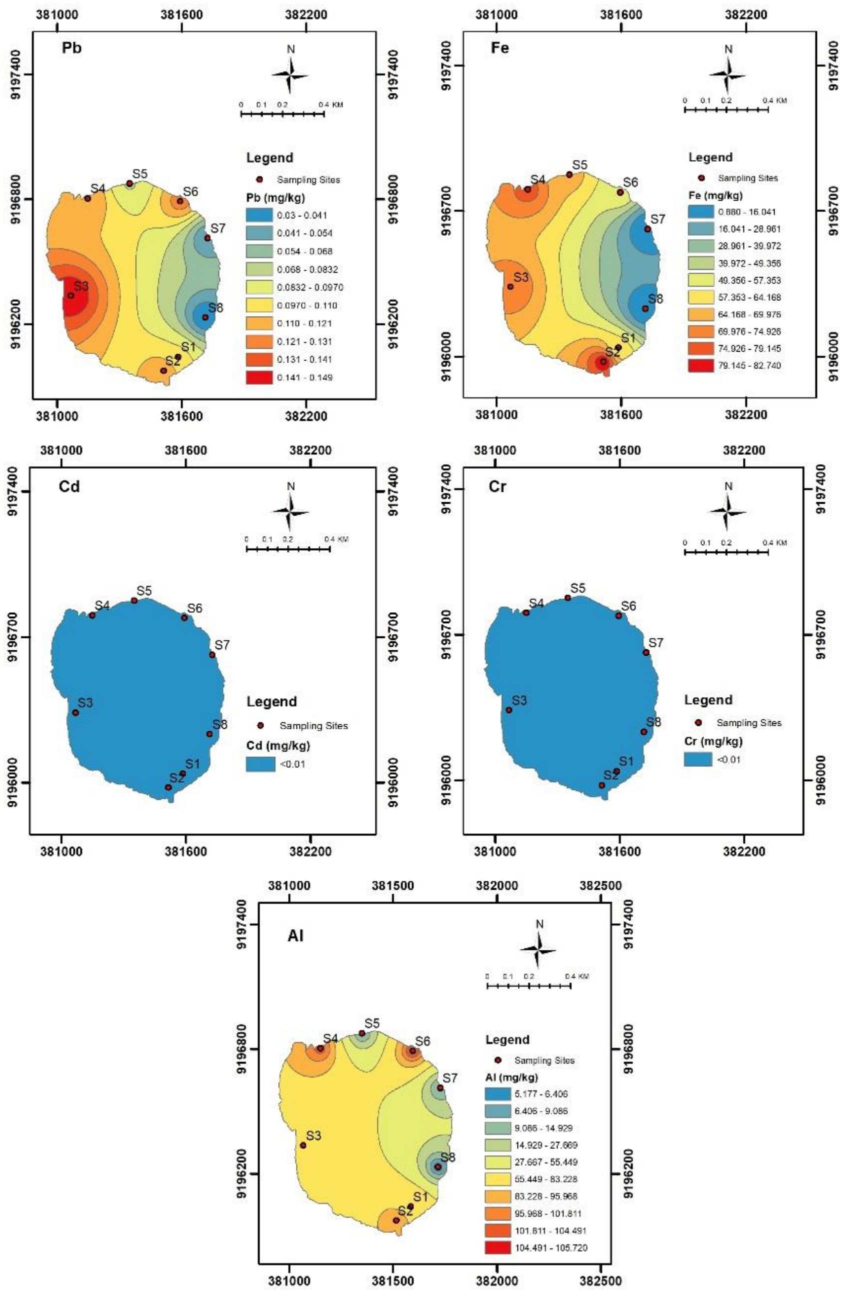

Figure 3. Spatial distribution of heavy metals in 2023

3.2. Assessment of heavy metal pollution in the sediments

The EF and Igeo methods are utilized in this research to characterize geochemical accumulations and compare them with background values from other regions (Tepe *et al*., 2022). In this study, the background value for heavy metals is taken from the Winongo River (Fadlillah *et al.,* 2023), as there is limited research on heavy metals in lakes, especially volcanic lakes. The similar lithological settings between the river and

Menjer Lake suggest that they may receive similar concentrations from runoff originating from parent rocks rather than comparing them to reservoirs. Barbieri (2016) also states that the background values usually came from the natural substance of soil, which has a similar composition to mineralogy. That is why parent material or similar geological sources were more significant in choosing background values.

Table 3 displays the average EF values for 2022 and 2023, with the average heavy metals EF values ranked as follows: Al > Cr > Fe > Pb > Cd. Pollution levels in Menjer Lake are categorized as follows: no enrichment (Pb), low enrichment (Cr and Fe), and moderate enrichment (Al).

Table 3**.** EF and I_{geo} value for five heavy metals from lake-surface sediment

Name of sample	**Heavy-metal Concentration (mg kg^{-1})**	**Pb**	**Cr**	**Fe**	**Al**	**Cd***
EF Value (n = 16)	mean	0.68	2.59	1.19	3.04	ND
	min	0.17	1.15	0.003	0.003	ND
	max	1.21	3.05	2.87	8.13	ND
	Pollution level	No Enrichment	Low Enrichment	Low Enrichment	Moderate Enrichment	ND
Igeo value (n = 16)	mean	−1.28	0.73	−1.54	−0.09	ND
	min	−3.08	−0.38	−8.61	−8.8	ND
	max	−0.3	1.02	0.93	2.43	ND
	Pollution level	Unpolluted	Lowly Polluted	Unpolluted	Unpolluted	ND

*ND Detection Limit: cannot proceed with the calculation.

Additionally, heatmaps were used to analyze the results of each sampling site analysis for each metal parameter. The EF heatmaps are presented in Figures 4 and 5, while the Igeo heatmaps are displayed in Figures 6 and 7. The EF and Igeo heatmaps for 2022 and 2023 exhibit variations, particularly in the Cr EF values. The EF value for Cr in 2023 falls within the low to moderate enrichment range, ranging from 1.15 to 3.05. For the other metal contents, such as Al and Pb, the EF in 2023 ranged from 0.003 to 8.13 and from 0.394 to 1.218 for Al and Pb, respectively, showing a slight decrease from the EF in 2022. The EF value in 2023 ranged from 0.158 to 3.22 and from 0.176 to 0.876 for Al and Pb, respectively. However, the Cr value in 2023 significantly decreased and went undetected. The primary sources of Cr metal in Menjer Lake potentially include soil weathering, as described in the study of Swarnalatha *et al*. (2013).

Furthermore, the Igeo value for Cr in 2022 also demonstrated unpolluted to lowly polluted (−0.4 to 1.0). The negative value indicates that the samples were low polluted or unpolluted (Xu *et al*., 2020; Li *et al*., 2021). The Igeo results for Al and Pb also display a significant decrease for Al and Pb. The values ranged from −8.9 to 2.4 and from −1.9 to −0.3 for Al and Pb in 2022, respectively, while the Igeo values ranged from −3.2 to 1.1 and from −3.1 to −0.8 for Al and Pb in 2023, respectively. Simultaneously, the Fe value 2023 exhibits a noticeable increase in EF and Igeo results. Meanwhile, Cd remains undetected.

The comparison of EF and Igeo values between different years (2022 and 2023) yielded similar results, as reflected in the consistent patterns shown in the heat maps for each heavy metal. Menjer Lake's pollution level is classified as either unpolluted or lowly polluted, with a general trend toward decreasing pollution for Al, Pb, Cd, and Cr. This decrease in concentration could be attributed to changes in the sources of these metals (Zhou *et al.*, 2020). For instance, fertilizer use has been reduced in the areas surrounding the lake. Additionally, several agricultural zones in the lake's vicinity have been transformed into public spaces, contributing to the decrease in pollution levels observed. Conversely, the concentration of Fe is observed to be increasing over time. These fluctuations in heavy-metal concentrations across periods suggest alterations in lake bottom sediment due to resuspension, transport, and deposition processes (Ali *et al.*, 2022), likely influenced by hydrodynamic processes in the deep and steep lake (Broberg, 1994).

The pollution level in Menjer Lake is attributed to nonpoint sources and effluents directly entering the lake bodies (Swarnalatha *et al.*, 2013). However, in protected areas like Menjer Lake, the sources of heavy metal pollution are identified as limited. The surrounding land, primarily covered by forests, croplands, and fishing caged nets for aquaculture, exhibits minimal contamination from heavy metals (Sojka *et al.*, 2022).

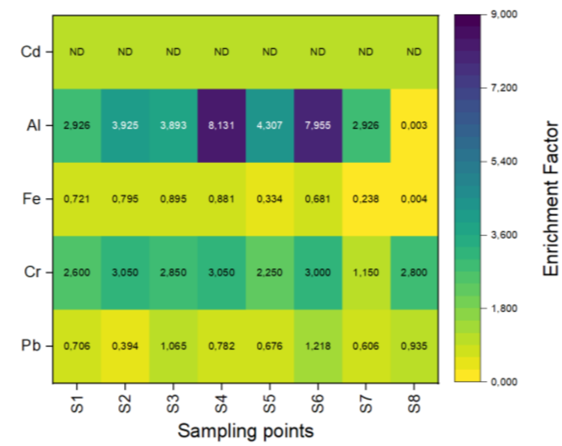

Figure 4. Enrichment factor heatmaps of heavy metals in Menjer Lake year 2022

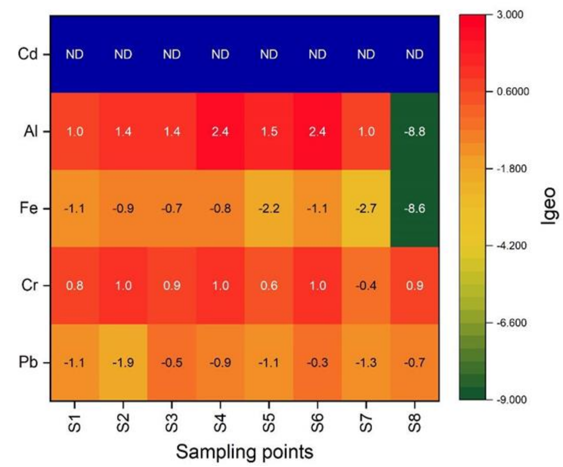

Figure 6. Igeo heatmaps of heavy metals in Menjer Lake year 2022

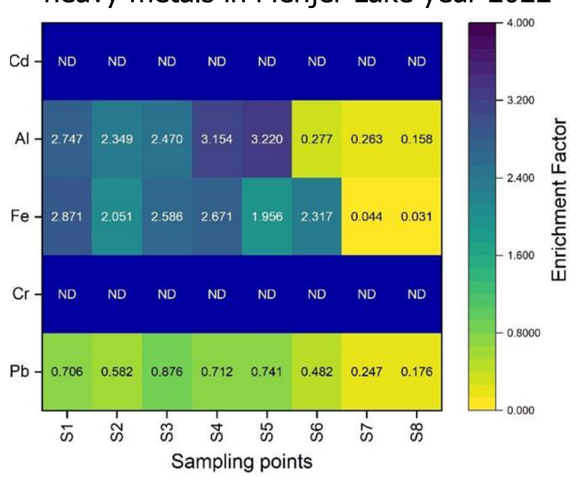

Figure 5. Enrichment factor heatmaps of heavy metals in Menjer Lake year 2023

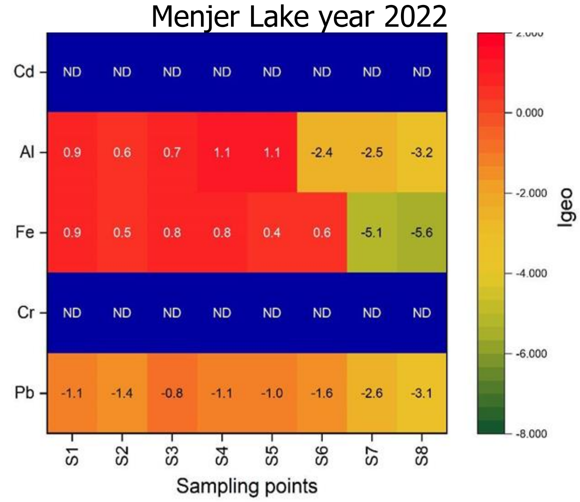

Figure 7. Igeo heatmaps of heavy metals in Menjer Lake year 2023

*)Please note that the scales depicted in the images differ.

4. Conclusion

The study delves into analyzing heavy metal spatial distribution, sources, and associated pollution risks, explicitly focusing on Pb, Cr, Fe, Al, and Cd concentrations in surface sediments within Menjer Lake. This investigation established correlations between sediment and agricultural soil samples, particularly for Pb, Cr, and Fe. The spatial analysis highlighted elevated heavy metal concentrations in areas like S3, S4, S5, and S6, attributed to activities such as floating net cages and agriculture. Furthermore, the lake's steep morphology contributed to the distribution pattern along its shores.

The Igeo analysis for 2022 and 2023 classified pollution levels as "unpolluted" and "lowly polluted," respectively, while EF results indicated varying degrees of enrichment from "no enrichment" to "moderate enrichment." Despite some pollution, Menjer Lake remains relatively unpolluted, mainly due to protective measures in its catchment area. Additionally, projections suggest a decrease in heavy metal pollution levels by 2023, particularly for Al, Cd, Cr, and Pb. Continued research into sediment-related risk assessments in Indonesian lakes is imperative. Sediment is a crucial environmental indicator, offering insights into pollution extents and accumulated contaminants, guiding future environmental management strategies.

Data availability statement

Data will be made available on request.

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Conflict of interests

The authors declare they have no competing interests.

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Author Contributions

LNF provided the conceptual framework, conducted sampling, analyzed the data, and prepared the manuscript. **MW** contributed to sampling and reviewed the manuscript. **AAR** was responsible for mapping and writing the manuscript. **AU** was involved in land use mapping and writing the manuscript.

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