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Speciation and Bioavailability of Heavy Metals Pb and Cd in Palu Bay Sediments after the Earthquake and Tsunami

Husain Sosidi✉, Khairuddin, Ruslan, Rahma Lolita Abustiana, Aksar Ramli, Erwin Abdul Rahim

Department of Chemistry. Faculty of Mathematics and Natural Sciences. Tadulako University
Jl. Soekarno-Hatta Km. 9. Kampus Bumi Tadulako. Tondo-Palu. Central Sulawesi

Abstract. Major disturbances to seafloor morphology and input of terrestrial material due to the earthquake-tsunami in Palu City in 2018 have the potential to alter the chemical form (speciation), bioavailability, and flux of lead (Pb) and cadmium (Cd) in Palu Bay sediments. This study was conducted to analyze the speciation of Cd^{2+} ions and Pb^{2+} ions and determine the concentration of elusion ions using Diffusive Gradient in Thin Film (DGT). In this study, two methods were carried out, namely the fractionation method and the DGT method. The results showed that the analysis of ion speciation at 3 locations using the fractionation method obtained the highest concentration of Cd^{2+} ions of 1.4492 mg/L at location 1 and the highest concentration of Pb^{2+} ions of 0.0200 mg/L at location 3. The results of ion analysis at 3 locations using the DGT method obtained the highest elution yield concentration of Cd^{2+} ions of 0.0225 mg/L at location 1 and the highest elution yield concentration of Pb^{2+} ions of 0.0155 mg/L at location 3. This study shows that the presence of heavy metals Pb and Cd in Palu Bay sediments after the earthquake-tsunami is still detected with varying concentrations between locations. The fractionation method is able to describe the distribution of metal speciation in sediments, while the DGT method provides information on labile fractions that are more relevant to bioavailability. The combination of these two methods is important for understanding the potential risk of heavy metals to Palu Bay aquatic ecosystems and can be used as a basis for post-disaster environmental monitoring and management efforts.

Keywords: *Fractionation, diffusive gradient in thin films (DGT), cadmium, lead*

Abstrak. Gangguan besar pada morfologi dasar laut dan input material darat akibat gempa-tsunami di Kota Palu pada tahun 2018 berpotensi mengubah bentuk kimia (spesiasi). ketersediaan hayati (bioavailabilitas). serta fluks Pb dan Cd di sedimen Teluk Palu. Penelitian ini dilakukan untuk menganalisis spesiasi ion Cd^{2+} dan ion Pb^{2+} serta menentukan konsentrasi ion hasil elusi menggunakan *Diffusive Gradient in Thin Film* (DGT). Pada penelitian ini dilakukan dua metode yaitu metode fraksinasi dan metode DGT. Hasil penelitian menunjukkan bahwa analisis spesiasi ion pada 3 titik lokasi menggunakan metode fraksinasi diperoleh konsentrasi tertinggi ion Cd^{2+} 1.4492 mg/L pada lokasi 1 dan konsentrasi tertinggi ion Pb^{2+} 0.0200 mg/L pada lokasi 3. Hasil analisis ion pada 3 titik lokasi dengan metode DGT diperoleh konsentrasi hasil elusi tertinggi ion Cd^{2+} 0.0225 mg/L pada lokasi 1 dan konsentrasi hasil elusi tertinggi ion Pb^{2+} 0.0155 mg/L pada lokasi 3. Penelitian ini menunjukkan bahwa keberadaan logam berat Pb dan Cd di sedimen Teluk Palu pasca gempa-tsunami masih terdeteksi dengan konsentrasi yang bervariasi antar lokasi. Metode fraksinasi mampu menggambarkan distribusi spesiasi logam pada sedimen, sementara itu metode DGT memberikan informasi mengenai fraksi labil yang lebih relevan terhadap ketersediaan hayati. Kombinasi kedua metode ini penting untuk memahami potensi risiko logam berat terhadap ekosistem perairan Teluk Palu serta dapat dijadikan dasar dalam upaya pemantauan dan pengelolaan lingkungan pascabencana.

Kata kunci: *Fraksinasi, diffusive gradient in thin film (DGT), kadmium, timbal*

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✉ Corresponding author
E-mail: husainasfah.chem@gmail.com

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INTRODUCTION

On 28 September 2018, the city of Palu and its surrounding areas were shaken by a 7.4 magnitude tectonic with its epicenter on the mainland of Donggala, Central Sulawesi. The earthquake triggered a 4–7-meter tsunami that hit the coast of Palu Bay just minutes after the main shock. In addition to the tsunami, liquefaction and submarine landslides caused severe damage to infrastructure and huge loss of life (Paundanan *et al*., 2025; Alfauzi *et al*., 2025).

This disaster not only had socio-economic impacts, but also caused significant changes to the coastal environment and aquatic ecosystems of Palu Bay. Sediment material from land, debris and heavy metal contaminants were washed into the waters. causing changes in sediment and seawater quality. These conditions have the potential to increase the bioavailability of hazardous heavy metals such as lead (Pb) and cadmium (Cd). which can harm aquatic organisms and human health.

To date, studies of heavy metals in Palu Bay have generally been limited to measuring total metal concentrations, without addressing aspects of speciation or labile bioavailability that are more relevant to ecological risks. This is important given the chemical forms (speciation) of Cd and Pb, and the labile fractions potentially available to biota. Thus, the results of this study provide a more comprehensive understanding of post-disaster impacts on heavy metal dynamics, and can provide a new scientific basis for monitoring and managing coastal environments after natural disasters.

The presence of heavy metals in marine waters also occurs due to pollution that occurs naturally or due to human activities and nature will have an impact both directly on the life of organisms, and indirectly on human health. Heavy metals, in addition to polluting waters. will also settle in sediments and will become contaminants into the bodies of living things through the process of bioaccumulation (Niyogi *et al*., 2024; Chen *et al*., 2023). Cadmium (Cd) is one of the heavy metals that has soft and corrosion-resistant properties so it is widely used in the chemical industry and electronic equipment. While Lead (Pb) has a soft blackish brown color and is easily purified which can be found in pure metal form as well as inorganic and organic compounds (Anggraeni *et al*., 2025; Liu *et al*., 2024).

The presence of various types of heavy metal ions that dissolve in seawater and that form sediments will enter the food chain system and affect the lives of various types of organisms in it, both aquatic plants and fish. Contamination of cadmium and lead in aquatic organisms can have a toxic impact on the survival of these organisms. Pollution in waters due to heavy metals certainly cannot be left unchecked, special monitoring is needed and frequent measurements of heavy metal levels in the aquatic environment.

Speciation is an approach method that can be used to determine the concentration of metals that are in various forms of compounds and species of both organometallic compounds and minerals that can determine the total concentration in a water sample (Anggraeni *et al.,* 2025). Meanwhile, bioavailability is a form or species of a metal that can be absorbed by living things; therefore, it can change physical properties and can then cause toxic effects.

The method used in this study is fractionation, which is a chemical compound speciation defined as the process of classifying and grouping various species and phases contained in a medium.

In addition, post-disaster studies are needed to assess the speciation and bioavailability of heavy metals in Palu Bay sediments using modern methods such as *diffusive gradient in thin films* (DGT). The DGT method in the study was chosen because it has the unique ability to measure labile and bioavailable heavy metal fractions in situ. Unlike conventional analytical methods such as chemical extraction or fractionation that only provide a total picture or distribution of metal speciation, the DGT method is able to simulate the process of metal diffusion from sediments to aquatic organisms. Thus, the data obtained from DGT are more representative for assessing the actual ecotoxicological risk in the aquatic environment (Zhang *et al*., 2024; Akkermans *et al*., 2023; Luo *et al*., 2023).

The DGT method works on the principle of passively binding heavy metal ions in situ. where metals in labile form (free ions or weak inorganic/organic complexes) diffuse through the diffusive gel and bind to the binding resin. Thus, DGT directly measures the labile fraction of ecologically relevant metals, not just total metals.

MATERIALS AND METHODS

Materials

The materials used in this study were cadmium (Cd) metal, lead(II) acetate ($Pb(C_2H_3O_2)_2$) p.a. (Merck), nitric acid (HNO_3) p.a. (Merck), hydrochloric acid (HCl) p.a. (Merck), hydrogen peroxide (H_2O_2) p.a. (Merck), acetic acid (CH_3COOH) p.a. (Merck), ammonium acetate (CH_3COONH_4) p.a. (Merck), Chelex-100 resin, marine sediment, seawater, and distilled water.

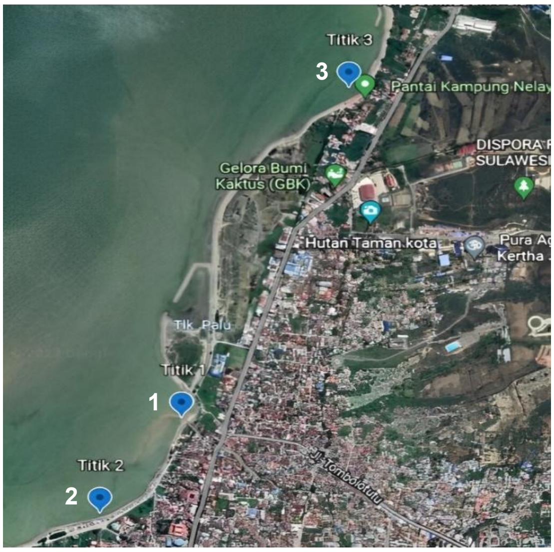
Instrumentation

The tools used in this study included measuring pipettes, pipette fillers, micropipettes, 60-mesh sieve, DGT probes, oven, centrifuge, analytical balance, hotplate, pH meter, and Atomic Absorption Spectrophotometer (AAS) (Shimadzu).

Procedures

Sampling

Sediment sampling was carried out at 3 locations and 3 points each location around the Talise River, Palu Bay. Before the seawater was taken, its acidity was measured first and then stored in polyethylene bottles. At each point. sediment samples were taken at a depth of about 15 to 30 cm from the surface. Sediment of as much as 1000 g was then put in polyethylene plastic and stored in a cool box. Sampling was carried out 2 times and samples that were still mixed with seawater were sedimented separated and then dried.



1. Point 1 of the Pondo River estuary at 0º52'46.213ºS 119º52'15.133ºE
2. Point 2 to the south at 0º53'2. 853ºS 119º 52'5.327ºE
3. Point 3 to the north at 0º51'51.422ºS 119º 52'39.191ºE

Figure 1. Map of sampling locations in the Nelayan village of Talise sub-district

Easily, freely, leachable, and exchangeable (EFLE) fraction analysis

Weighed 5 g of sediment in a 100 mL Erlenmeyer flask, added 25 mL of 0.1 M CH_3COOH, and then shaken for 3 hours. Then centrifuged, the filtrate obtained was filtered and diluted with distilled water in a 50 mL measuring flask. The solution was then analyzed by AAS at a wavelength of 228.8 nm for Cd^{2+} ions and a wavelength of 217.0 nm for Pb^{2+} ions.

Analysis of the oxidizable fraction

The residue in the EFLE fraction was previously washed with 10 mL of distilled water. and then 10 mL of 8.8 M H_2O_2 solution was added. and heated at 85°C in a water bath for several minutes. Then 20 mL of 1 M CH_3COONH_4 was added and the acidity was adjusted to pH 2 by adding HNO_3. The mixture was then shaken for 3 hours and centrifuged. The resulting supernatant was filtered and diluted to 50 mL with distilled water in a volumetric flask. The filtrate was then analyzed by SSA at a wavelength of 228.8 nm for Cd^{2+} ions and a wavelength of 217.0 nm for Pb^{2+} ions.

Resistant fraction analysis

The residue obtained in the previous stage (oxidizable fraction) was washed with 10 mL of distilled water and then 10 mL of aquaregia solution was added and heated using a hotplate at 140°C for 45 minutes. Then centrifuged, the filtrate obtained was filtered and diluted with distilled water in a 50 mL measuring flask. The solution was then analyzed by AAS at a wavelength of 228.8 nm for Cd^{2+} ions and a wavelength of 217.0 nm for Pb^{2+} ions.

DGT application on samples

Weighed 500 g of finely ground sediment and then put it into a 1000 mL beaker. Then 100 ppm Cd^{2+} ion solution as much as 100 mL and diluted with seawater to a volume of 800 mL. The DGT device that has been made is then immersed in the solution in a floating position using a thread for 3 times 24 hours. then lifted and eluted using 10 mL of 1 M HNO_3 for 24 hours. The metal content in the elution solution is then analyzed by AAS at a wavelength of 228.8 nm for Cd^{2+} ions and a wavelength of 217.0 nm for Pb^{2+} ions.

RESULTS AND DISCUSSION

Fraction Analysis on Sediments

The results of sediment analysis at 3 different locations show the distribution of metals in various fractions in the sediment as can be seen in Table 1.

Table 1. Results of EFLE fraction analysis

Location	Ion Concentration (mg/L)	
	Cd^{2+}	Pb^{2+}
1	1.2125	0.002
2	0.5331	0.002
3	0.1829	0.006

Based on the data obtained in Table 1, the determination of speciation and bioavailability of Cd^{2+} ions and Pb^{2+} ions was carried out using the fractionation method. Metal bioavailability is obtained from the metal ion species associated with each fraction phase. In the EFLE fraction, metal ions move in water until they reach equilibrium (bioavailable). The addition of CH_3COOH aims to form a precipitate caused by denaturation; therefore, metal ions can be measured. The highest ion concentration was obtained in Cd^{2+} ions originating from location 1. This is because at location 1 the source of water flow passes through a residential area whose domestic waste is discharged into the river. This domestic wastewater is not treated before being discharged, resulting in pollution.

In the oxidizable fraction, metal ion species are strongly bound to the sediment, requiring a strong oxidant to dissolve them. The results of the oxidizable fractionation analysis can be seen in Table 2 below.

Table 2. Results of oxidizable fraction analysis

Location	Ion Concentration (mg/L)	
	Cd^{2+}	Pb^{2+}
1	0.0725	0.001
2	0.0808	0.002
3	0.1079	0.0065

Based on the data in Table 2, it is known that the extraction results using H_2O_2 which is a strong oxidizer can extract metal ions from sediment by releasing metal bonds in organic compounds and sulfides. Potentially bioavailable metals if there is a change in sediment conditions due to the addition of strong oxidizers to the sediment will become non-bioavailable (Gasparatos *et al.*, 2005). Cd^{2+} ions and also Pb^{2+} ions are associated with the oxidizable fraction with the lowest concentration at location 1.

In the resistant fraction, metal species are not bioavailable because they are strongly bound to the primary minerals present in the sediment. The results of the resistant fractionation analysis can be seen in Table 3.

Table 3. Results of resistant fraction analysis

Location	Ion Concentration (mg/L)	
	Cd^{2+}	Pb^{2+}
1	0.1642	0.0025
2	0.1475	0.0035
3	0.1475	0.0075

Based on the data in Table 3, it is known that the results of the analysis of non-bioavailable fractions were carried out to extract this species by grinding it and then destroying it with aquaregia. Aquaregia will oxidize all metals contained in the sediment (remaining fraction). The metals in this fraction are not the same as other fractions because of their non-bioavailable nature. According to Yap *et al*. (2003), the presence of metals in this fraction is not dangerous because aquatic organisms cannot consume them to change their properties. From the three stages of fractionation. the analysis results obtained were then accumulated to determine the total ions contained in the sediment. The results of the C_{total} ion Cd^{2+} and Pb^{2+} tests are shown in Table 4.

Table 4. Result of C_{total} ion Cd^{2+} dan Pb^{2+}

Location	Ion Concentration (mg/L)	
	Cd^{2+}	Pb^{2+}
1	1.4492	0.0055
2	0.7614	0.0075
3	0.4383	0.0200

In general, the extraction stage based on the distribution pattern of species in the sediments of Palu Bay after the Earthquake and Tsunami using the fractionation method in the analysis of Cd^{2+} ions is F1>F2>F3. The marine sediments of Palu Bay are not classified as polluted by Cd^{2+} ions. Based on the sediment distribution pattern, the metal is bioavailable at location 1, potentially bioavailable at location 2, and not bioavailable at location 3. The source of Cd^{2+} ion contamination accumulated in the sediment comes from natural activities. In the analysis of Pb^{2+} ions, the distribution pattern of species based on the average concentration of Pb^{2+} ions in sediments by zone is F3>F2>F1.

According to Bintal Amin (2002), the type of sediment can affect the concentration of heavy metal ions with the category of heavy metals in mud to sandy mud to sand. This is thought to affect the increasing depth and distance from the coast, and the course of the sediment grains; therefore, the smaller the concentration of Pb^{2+} ions in the sediment.

Results of Analysis of Cd^{2+} ion and Pb^{2+} Ion Concentrations Using the DGT Method

In this DGT method, metal ion species in the sediment will diffuse through the filter membrane and *diffusive* gel and then accumulate in the *binding* gel layer. Therefore, the metal species will not undergo chemical changes, because it will be stored in the *binding gel* and then eluted with an acid to determine its concentration. In the DGT technique, the average solute concentration measured over a certain time can be known, sample contamination can be reduced, and it is possible to preconcentrate without damaging the sample. The concentration of analyte species bound by the binding gel in DGT can be considered equal to the concentration of analyte species diffusing from the water to the fertiliser phase. Therefore, this method can be used to predict the bioavailability of labile metals such as $Pb^{2+}$and Cd^{2+} ions.

The application of the DGT tool to sediment is carried out using the standard addition method. namely the addition of a standard solution with a known concentration to the sample to be analyzed (spike method). This is done to increase the concentration of ions in the solution so that they can enter the calibration curve. The results of the analysis of the concentration of Cd^{2+} ions and Pb^{2+} ions can be shown in Table 5.

Table 5. Results of analysis of Cd^{2+} and Pb^{2+} ion concentrations

Location	Ion Concentration (mg/L)	
	Cd^{2+}	Pb^{2+}
1	0.0225	0.0074
2	0.0059	0.0101
3	0.0178	0.0155

Based on the data obtained in Table 5, it is known that the concentration of ions accumulated in the binding gel with the calculation results of each location is 0.0225 mg/L at location 1, as much as 0.0059 mg/L at location 2. and 0.0178 mg/L at location 3. According to Purba *et al.*, (2014), the levels of Cd^{2+} ions in sediment range from 2.145 mg/L to 7.121 mg/L. Meanwhile, Pb^{2+} ions are bioavailable and have the potential to migrate from sediment into seawater zonally, namely from location 3 to location 2 and to location 1 which follows the distribution of Pb^{2+} metal ions in sediment using the sequential extraction method. According to Khairuddin *et al.*, (2017). the concentration of Pb^{2+} ions in the waters of Palu Bay before the Earthquake and Tsunami ranged from 0.024 mg/L to 0.048 mg/L. The concentration of Pb successfully absorbed by DGT is much greater because this tool is only able to absorb labile metal ion species or complexes with weak bonds. However, if associated with the history of mining by communities along the river basin that flows into Palu Bay. It is strongly suspected that this is the result of sedimentation that has long occurred due to traditional gold mining by the surrounding community.

Based on the results of the analysis of metal concentrations in the sequential extraction fraction. there is a difference between the easily released (available) fraction and the Pb^{2+} metal ion absorbed by DGT. This is because measurements with DGT can be carried out in situ so that it can minimize changes that occur in each metal species. Speciation techniques cannot be carried out in situ which can result in changes in the sample due to the period between the sampling time and the sample characterization time.

CONCLUSION

The results of the speciation analysis of Cd^{2+} ions and Pb^{2+} ions at 3 locations using the fractionation method obtained the highest concentration of Cd^{2+} ions of 1.4492 mg/L at location 1 and the highest concentration of Pb^{2+} ions of 0.0200 mg/L at location 3. The results of ion analysis at 3 locations using the DGT method obtained the highest elution concentration of Cd^{2+} ions of 0.0225 mg/L at location 1 and the highest elution concentration of Pb^{2+} ions of 0.0155 mg/L at location 3.

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