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Fraksinasi Logam Pb dalam Sedimen Laut Untuk Estimasi Nilai Potensial Biovaibility di Kepulauan Wilayah Perairan Provinsi Maluku Utara

Fractionation of Pb Metal In Marine Sediments for Estimation of Potential Value of Biovaibility in The Islands of Water Area in North Maluku Province

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ABSTRACT

Determination of the geochemical fractionation of metals is also important to identify sources of metal pollutants in waters, whether they originate from natural processes or originate from human activities. This study aims to analyze the potential availability of Pb metal in sediments for biota and analyze the relationship between sediment grain size and total organic matter with the geochemical characteristics of Pb metal. The research was carried out in the North Maluku Waters Region in March 2023. consisting of 4 stations namely Ternate Island (Bastiong Harbor and Waters around Pertamina Jambula), Tidore (PLTU Waters) and Halmahera (Waters around the NHM Gold Mining area). And each station consists of 3 points. Sample testing was carried out at the Chemical Oceanography Laboratory, Faculty of Maritime Affairs and Fisheries, Hasanuddin University. And metal analysis was carried out at the Agency for Standardization and Industrial Services Policy Testing Laboratory BBSP JIHPMM Makassar City. Metal concentrations in the sediment fraction were determined by the BCR Sequential Extraction method (Based on Sarkar et al., (2014) The results showed that the total fraction was unstable at station 1, 2 and 3 were higher than the non-labile fraction, while at station 4 it was found that the total non-labile fraction was higher than the labile fraction.

Keywords : metal pb, geochemical fractionation, sediment, BCR sequential extraction

Introduction

The marine waters area in North Maluku Province has been widely utilized with various forms of marine spatial utilization patterns such as sea transportation and ports, mining, coastal reclamation, marine recreation and tourism, settlements, capture fisheries and marine aquaculture. All of these anthropogenic activities can be found in every sea space in the North Maluku Province, both on a small and large scale.

Anthropogenic activities carried out around coastal areas have the potential to produce by-products in the form of solid waste (garbage) and liquid waste. In addition, activities in these coastal areas can cause changes in coastal and marine ecosystems which can lead to damage to coastal and marine ecosystems. Metal contamination is one of the impacts of waste. Metals are environmental pollutants that should be watched out for, because they have high toxicity, are abundant and easily accumulate in various organisms (Riba et al., 2004).

Anthropogenic sources that enter the aquatic environment accumulate in sediments through adsorption, precipitation, co-precipitation, and biological effects (Peng et al., 2018) so that the concentration of metals in sediments is much greater than in water bodies. This is in line with Werorilangi's statement (2019) saying that metals that enter the aquatic environment will eventually accumulate in sediments. When accumulated in sediments, metals can be absorbed by benthic biota and will eventually enter the food chain. The potential hazard due to metal exposure to biota is always associated with the total metal concentration in the media.

Lead (Pb) is soft and has a blackish brown color, and is easily purified from mining. These compounds are found in mining all over the world (Titin, 2010). This metal according to Yolanda et. al (2017) the benefits are unknown for aquatic organisms and can interfere with the survival of aquatic organisms as well as humans.

Organic matter content has a positive relationship with metal concentrations in sediments. where the higher the organic matter content, the metal content is also higher. Heavy metals have the property of easily bonding with organic matter in the water column and then precipitating at the bottom of the waters and uniting with sediments so that in general the levels of heavy metals in sediments are higher than in water.

One of the methods used to find out information on the availability of Lead (Pb) metal in sediments for biota (biovaibility) is by carrying out a fractionation process. Metal fractionation has a function, namely providing information about the behavior and characteristics of an element based on its mobility, function, bioavailability and toxicity (Purpasari et al. .al., 2014). The fractionation form is exchangeable (bonds that are very easy to exchange/break) binds to humic substances, binds to carbonates, binds to manganese and iron oxides, binds to organic matter, and binds to crystalline minerals (residue fraction) (Gao and Li, 2012). Therefore, determining the geochemical fractionation of heavy metals in sediments is very important to assess the potential toxicity and risks posed by heavy metals to ecosystems (Liu et al. 2015).

Determination of the geochemical fractionation of metals is also important to identify sources of metal pollutants in waters, whether they originate from natural processes or originate from human activities. The composition of the fraction in a resistant form indicates a source of heavy metal pollutants originating from natural processes, while the non-resistant fraction components indicate a source of heavy metal pollutants originating from human activities (Teixeira et al. 2003 and Rodrigues & Formoso, 2006).

Research Methods

Time and Place of Research

This research was conducted in March 2023. The research location is in North Maluku Waters, which consists of 4 stations namely Ternate Island (Bastiong Harbor and Waters around Pertamina Jambula), Tidore (PLTU Waters) and Halmahera (Waters around the NHM Gold Mining area). And each station consists of 3 points. Sample testing was carried out at the Chemical Oceanography

Laboratory, Faculty of Maritime Affairs and Fisheries, Hasanuddin University. And metal analysis was carried out at the Agency for Standardization and Industrial Service Policy Testing Laboratory for BBSP JIHPMM Makassar City.

Analysis of Total Pb Metal Concentration in Sediments

Heavy metals in sediments were analyzed based on APHA, AWWA, WEF, 2005 (Part 3000 Metals) with the following procedure; Weighed 5 grams of homogeneous sediment then dried in an oven at 60 ºC for 24 hours. The sediment was ground until smooth and put into a test tube then added 10 ml of HNO3 (1:1) and then heated at 95 ºC for 15 minutes. The sample was then cooled and then 5 ml of concentrated HNO3 was added and then heated for 30 minutes. After that, 5 ml of HNO3 was added repeatedly until the reaction was complete. Heated again until the volume reached 5 ml and then cooled again. Then added 2 ml of aquabidest and 3 ml of H2O2 (30%) then heated a few minutes then added another 1 ml of H2O2 and continued heating until the volume became 5 ml and then cooled. Another 10 ml of concentrated HCl was added and then heated at 95 ºC for 15 minutes, then filtered with whatman filter paper and ready to be analyzed by Atomic Absorption Spectrometry (AAS) variant of Shimudzu-AA7000.

Total Organic Matter (BOT) in sediments is analyzed based on APHA, AWWA, WEF, 2005 (Part 5000 Aggregate organic constituents) with the following procedure;

The cup is weighed and the weight is recorded (denoted by A). Then the wet sediment sample is put into the cup and then weighed and the weight is recorded (denoted by B). Then it was dried in an oven at 60 ºC for 24 hours and then the weight was again weighed and recorded (expressed by C). After that it was heated again in the furnace at 500 ºC for 4 hours then weighed and recorded the weight (expressed by D). The percentage of organic carbon in sediments is a component lost in the combustion process which is expressed as Loss on Ignition (LOI). To find out the percentage of organic carbon (LOI) in the sediment is calculated by the equation:

$$\%LOI = (C-D)/(B-A) \times 100$$

Where: LOI = organic matter content
A = weight of cup
B = weight of cup and wet sediment
C = weight of cup and dry sediment
D = weight of cup and sediment after heating (constant weight)

Sediment Weight and Grain Size Analysis

Samples that have been taken in the field are then followed by analyzing the samples in the laboratory. To determine the particle size of the sediment used dry sieving method and based on the Wenworth scale (Hutabarat and Evans, 1984). Sediment taken first is dried using an oven with a temperature of 1500C. Samples that had been dried using an oven were weighed as much as 100 grams, then sieved using a shieve shaker with constant motion to obtain a separation of sediment particles based on each sieve size. To calculate the percent (%) grain weight of sediment using the formula:

$$\% \text{ Weight} = (\text{sieved weight})/(\text{Initial weight}) \times 100$$

Metal Fractionation Process

The concentration of metals in the sediment fraction was determined by the BCR Sequential Extraction method (Based on Sarkar et al., (2014). The BCR (Community Bureau of Reference) method consists of four bonding phases analyzed. The extraction method can be seen in Table 1.

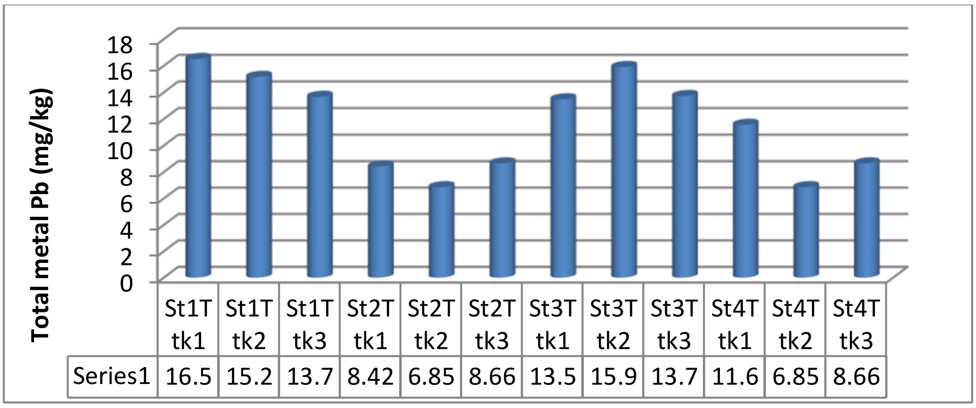
Table 1. Main extraction steps for the modified BCR sequential extraction procedure

Step	Sediment Phase	Extractant	Shaking Time and Temperature
F1	Water and acid soluble, and exchangeable (acid-soluble fraction –bound to carbonates)	40 ml of 0.11 mol L-1 CH3 COOH	16 h at room temperature at 22±5°C and speed 30±10 rpm. The extract was separated from the solid phase by centrifugation at 3000 rpm for 20 min.
F2	Reducible (iron / manganese oxyhydroxides) (reducible fraction – bound to Fe and Mn oxides)	40 ml of 0.5 mol L-1 HONH2 .HCl (pH 1.5)	16 h at room temperature 22±5°C and speed 30±10 rpm. The extract was separated from the solid phase by centrifugation at 3000 rpm for 20 min
F3	Oxidizable (organic matter and sulfides	10 ml of 8.8 mol L-1 H2O2 (two times), cool and add 50 mL of 1 mol L-1 NH4OAc (pH 2)	1 h at room temperature 1 h at 85°C 1 h at 85°c 16 h at room temperature 22±5°C and speed 30±10 rpm. The extract was separated from the solid phase by centrifugation at 3000 rpm for 20 min.
R	R Residual (insoluble compounds of metals inthe steps before) (residual fraction – strongly associated to the crystalline structures of minerals)	10 mL of aqua regia	Digesting in a mixture aqua regia in Microwave digestion

Results and Discussion

Concentration of Total Pb Metal in Sediments.

The total value of Pb metal can be seen in Figure 1 below.



	St1T tk1	St1T tk2	St1T tk3	St2T tk1	St2T tk2	St2T tk3	St3T tk1	St3T tk2	St3T tk3	St4T tk1	St4T tk2	St4T tk3
Series1	16.5	15.2	13.7	8.42	6.85	8.66	13.5	15.9	13.7	11.6	6.85	8.66

Figure 1. Total Pb Metal Value

The high concentration of Pb metal in sediments in fresh (riverine) and salt (marine) waters indicates that the source of heavy metal pollutants in sediments comes from two sources, namely from land and sea. Sources of heavy metal pollutants from the land are mainly in the form of particulates which enter river bodies and then settle to the bottom of the waters and then accumulate in sediments, while sources from the sea are in dissolved and particulate forms (Samawi, 2007; Werorilangi et al. 2013; Najamuddin, 2017). The total concentration of Pb metal in the sediment at several observation points ranged from 6.85-16.5 mg/kg. The highest value is found at Station 1, this phenomenon is in line with the designation. Where at station 1 this is where the fish market, speed port and ships and around these waters are used by the community as a tourist spot. This value is still below the quality standards set by the ANZECC/ARMCANZ Guidelines (2000) and CCME (2001).

This research was carried out in the rainy season, precisely in March, which is precisely called the western season. The concentration of heavy metal Pb in sediment particles is higher in the west monsoon than in the east monsoon due to the high input of particulate heavy metals from the erosion and weathering of rocks. The increase in the concentration of suspended particles in the West Monsoon in water bodies due to erosion of the topsoil and from surface runoff that enters the water bodies causes an increase in the concentration of particulate heavy metals that are deposited into the sediments.

Suspended particles that have the ability to bind heavy metals experience deposition to the bottom of the water when the movement of water masses weakens resulting in accumulation of heavy metals in sediments (Turekian, 2010). Another factor is that the increase in land erosion in the West Season also causes an increase in aluminum silicate minerals and iron oxide in particles, causing an increase in the binding of the heavy metal Pb to the surface of the particles (Bibby and Webster-Brown, 2006).

Fractionation of Pb Metal in Sediments.

Analysis of Pb metal in sediments in the waters of the North Maluku Islands Province used the BCR method and produced 4 types of fractions, which can be seen in Table 2.

Table 2. Fractionation Analysis Results

Stations and sampling points	Fractionation type % F1 (*Acid soluble*)	 % F2 (*Reducible)*)	 % F3 (*Oxidizable*)	 % F4 (*Residual*)
		Stations I		
1	2.996	7.6335	<0.0002	<0.50
2	1.4995	<0.0002	<0.0002	<0.50
3	1.8688	3.3638	<0.0002	<0.50
Total Result	6.3643	10.99749	<0.0006	<1.50
Average	2.12	3.66	<0.0002	<0.50
		Stations 2		
1	2.2249	0.7475	<0.0002	<0.50
2	<0.0002	<0.0002	<0.0002	<0.50
3	0.7453	6.7037	<0.0002	<0.50
Total Result	2.97	7.4512	<0.0006	<1.50
Average	0.99	2.48	<0.0002	<0.50
		Stations 3		
1	7.501	<0.0002	<0.0002	<0.50
2	11.567	3.3605	<0.0002	<0.50
3	<0.0002	<0.0002	1.6396	<0.50
Total Result	19.068	3.36	1.64	<1.50
Average	6.36	1.12	0.55	<0.50
		Stations 4		
1	<0.0002	<0.0002	<0.0002	30.3252
2	<0.0002	<0.0002	2.1202	<0.50
3	<0.0002	<0.0002	5.1766	<0.50
Total Result	<0.0006	<0.0006	7.3	31.3
Average	<0.0002	<0.0002	2.43	10.43

Based on the data in Table 2 for Station 1, the value of the F2 (Reducible) fraction dominates followed by the F1 (Acid soluble), F4 (Residual) and F3 (Oxidisable) fractions. For Station 2, the value of the F2 (Reducible) fraction dominates followed by the F1 (Acid soluble), F4 (Residual) and F3 (Oxidisable) fractions. This is in accordance with research from Sarkar et.al (2014) that metals such as Pb, Cr, and Zn, bind more to the Reducible, Residual and Oxidisable fractions.

According to several studies, the high concentration of Pb in Fraction 2 in the coastal area was due to the fact that the sediment fraction binds to iron and manganese oxides, consisting of metal adsorbed or coated with Fe-Mn oxides. According to Tessier et al (1979); Najamuddin, 2017) that this fraction has a relatively high mobility, depending on changes in redox conditions. This change causes the release of metal but some of it precipitates if there are sulfide minerals. Chunks or nodules of manganese (Mn) and iron (Fe) that form on the seafloor are forms of hydrogeneous sediments produced through chemical reactions in seawater.

The increase in the value of the F2 fraction at Station 1 was due to its association with the increasing size of the sediment particles. This was in accordance with Werorilangi's research (2012) that the Jeneberang and Tanjung Merdeka locations showed a high concentration of Pb metal in fraction 2 and had a small fine particle size.

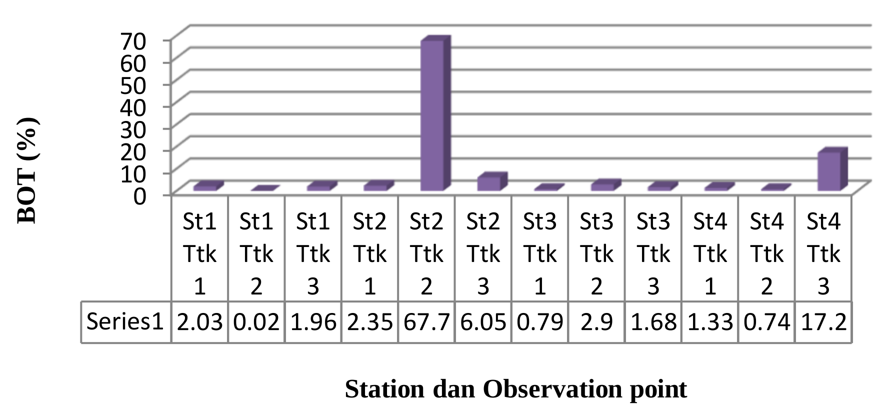
While the data at station 3, the value of the F1 (Acid soluble) fraction dominates followed by the F2 (Reducible), F3 (Oxidisable) and F4 (Residual) fractions. This is in line with Werorilangi's research (2019) which stated that there had been an increase in concentrations of Pb, Cd and Cu metals originating from anthropogenic sources and the detection of concentrations of Cd and Zn metals in fraction 1 indicated the potential for pollution and could cause biological and ecological impacts on aquatic biota and humans around it.

In station 4 data, the value of the F4 (Residual) fraction dominates followed by the F3 (Oxidisable) fraction, F1 (Acid soluble) and F2 (Reducible) fractions, this is in accordance with Najamuddin's research (2017) that the high percentage of the average residual fraction (fractions originating from natural processes) in the West Monsoon compared to the East Monsoon due to an increase in the input of natural sediment particles from the erosion and weathering of rocks on the mainland due to the high intensity of rainfall where these particles bind with heavy metals. This is reinforced by data on suspended particle concentrations and particle deposition rates in the West Monsoon which are higher than in the East Monsoon.

Estimation of the potential availability of metals in sediments for biota can also be known from the analysis of the fractionation of Pb metal in sediments. This determination can be seen from the value of the labile and non-labile fractions obtained from the analysis process. To get the presentation value of the labile fraction, the sum process of the Acid soluble, Reducible and Oxidisable fractions was carried out. The residual fraction will produce a non-labile (Resistant) component (Badri and Aston, 1983; Yap et.al, 2003; Selviana, 2016).

Total Organic Matter and Grain Size in Sediments

The value of Total Organic Matter can be seen in Figure 2 below.



BOT values in sediments at several observation points ranged from 0.74-17.2 mg/kg. The highest value is found at Station 2 Point 2. The percentage of sediment grain size can be seen in Table 3 below.

Table 3. Percentage of Sediment Grain Size

Station	Point	Sediment Grain Size (mm)	Identify the Wentworth Scale
S1	T1	0.7949	Coarse sand
	T2	0.5969	Coarse sand
	T3	0.9271	Coarse sand
S2	T1	0.2335	Fine Sand
	T2	2.3224	Very fine gravel
	T3	0.3879	Medium sand
S3	T1	0.693	Coarse sand
	T2	0.6994	Coarse sand
	T3	0.2521	Medium Sand
S4	T1	0.3372	Medium Sand
	T2	0.2521	Medium Sand
	T3	0.4606	Medium Sand

According to Maslukah (2013) that the total organic matter content is closely related to the grain size of the sediment. Water sediments that have different grain size percentages will have different organic matter content. In general, sediments that have a fine particle size will be followed by an increase in the amount of organic matter. The finer the sediment, the greater the ability to accumulate organic matter.

Based on Table 3, it can be seen that at all research stations the substrate type is mostly medium sand. The difference in the type of substrate is caused in S2T2 the sediment has been covered with coal spills, because this station is located at the Tidore PLTU pier. Whereas S3T3 is located in the waters where tofu waste is disposed of, and S4T2 is located in Kao Bay where the sediment grain size is very fine. This is in accordance with the opinion of Nugroho et.al (2014) that the difference in sediment grain size can be caused by the origin of the sediment source. The grain size of the sediment is finer as it gets deeper into the bay and coarser as it faces the open sea.

According to Huang and Lin (2003) in Yang et.al (2007) that generally sediments that have a finer size and have a lot of organic matter content contain a greater metal content than sediments that have a large type of sediment grain size.

Estimation of the potential availability of metals in sediments for biota can also be known from the analysis of the fractionation of Pb metal in sediments. This determination can be seen from the value of the labile and non-labile fractions obtained from the analysis process. To get the presentation value of the labile fraction, the sum process of the Acid soluble, Reducible and Oxidisable fractions was carried out. The residual fraction will produce a non-labile (Resistant) component (Badri and Aston, 1983; Yap et.al, 2003; Selviana, 2016). The presentation of fractional and non-labile values at 4 observation stations can be seen in Table 4.

Table 4. Results of Labile and Non Labile Fractions

Stations and sampling points	Fractination Type			
	% F1 (*Acid soluble*)	% F2 (*Reducible*))	% F3 (*Oxidizable*)	% F4 (*Residual*)
		Station I		
1	2.996	7.6335	<0.0002	<0.50
2	1.4995	<0.0002	<0.0002	<0.50
3	1.8688	3.3638	<0.0002	<0.50
Total Result	6.3643	10.99749	<0.0006	<1.50
Average	2.12	3.66	<0.0002	<0.50
		Station 2		
1	2.2249	0.7475	<0.0002	<0.50
2	<0.0002	<0.0002	<0.0002	<0.50
3	0.7453	6.7037	<0.0002	<0.50
Total Result	2.97	7.4512	<0.0006	<1.50
Average	0.99	2.48	<0.0002	<0.50
		Station 3		
1	7.501	<0.0002	<0.0002	<0.50
2	11.567	3.3605	<0.0002	<0.50
3	<0.0002	<0.0002	1.6396	<0.50
Total Result	19.068	3.36	1.64	<1.50
Average	6.36	1.12	0.55	<0.50
		Station 4		
1	<0.0002	<0.0002	<0.0002	30.3252
2	<0.0002	<0.0002	2.1202	<0.50
3	<0.0002	<0.0002	5.1766	<0.50
Total Result	<0.0006	<0.0006	7.3	31.3
Average	<0.0002	<0.0002	2.43	10.43

Based on the values in Table 4 at stations 1, 2 and 3, it was found that the total labile fraction was higher than the non-labile. Meanwhile, at station 4, the total value of the non-labile fraction was higher than that of the non-labile fraction.

The large total value of the non-labile fraction at station 4 indicates that the availability of Pb metal for biota is very small compared to the total concentration of Pb metal in the sediments. Meanwhile, the high value of the total labile fraction at stations 1, 2 and 3 indicates that there are anthropogenic inputs that can pollute the waters and can harm aquatic biota (Werorilangi, 2019). Meanwhile, according to Arifin (2004) that the high value of the non-resistant (labile) fraction characterizes that these metals come from human activities and have the potential to be accumulated by basic biota.

Correlation between textures and BOT in each fraction

The results of the correlation test between texture and BOT for each sediment fraction can be seen in Table 5.

Table 5. Correlation between texture texture and BOT

		Coarse sand	Medium sand	Content BOT
Fraksi 1	Pearson Correlation	-0.253	-0.047	-0.249
	Sig. (2-tailed)	0.428	0.885	0.435
	N	12	12	12
Fraksi 2	Pearson Correlation	0.363	0.181	-0.197
	Sig. (2-tailed)	0.247	0.574	0.540
	N	12	12	12
Fraksi 3	Pearson Correlation	0.000	0.399	0.047
	Sig. (2-tailed)	1.000	0.199	0.885
	N	12	12	12

The correlation table shows that the correlation of texture and BOT in each fraction has a very weak relationship and there is a significant relationship between texture and each fraction.

Conclusion

The results of the fractionation analysis show that for Station 1, the value of the F2 (Reducible) fraction dominates, followed by the F1 (Acid soluble), F4 (Residual) and F3 (Oxidisable) fractions. For Station 2, the value of the F2 (Reducible) fraction dominates followed by the F1(Acid soluble), F4 (Residual) and F3 (Oxidisable) fraction, Station 3, the F1(Acid soluble) value dominates followed by the F2 (Reducible) F3 (Oxidisable) fraction and F4 (Residual).

Based on the calculation of the number of labile and non-labile fractions, the high value of the non-resistant (labile) fraction indicates that these metals originate from human activities and have the potential to be accumulated by basic biota.

The correlation table shows that the correlation of texture and BOT in each fraction has a very weak relationship and there is a significant relationship between texture and each fraction.

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