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Analysis of Heavy Metals in Water and Sediment in Singkep Island Coastal Waters

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Abstract.
Analysis of the content of heavy metals Cu, Pb and Zn in seawater, sediment and snails (C. obtusa) in Singkep island was held on June – July 2022. All parameters measured water quality is still within tolerable limits for the survival of the aquatic organism . Samples of sea water, sediment and snails (C. obtusa) were taken from five stations with three replicates at each station. Heavy metals were analyzed in the KLH Pekanbaru laboratory using an Atomic Abortion AA-7000 Shimadzu spectrophotometer. The results showed that the average content of heavy metals in Singkep waters was 0.0724 mg/l (Cu), 0.1285 mg/l (Pb)) and 0.11525 mg/l (Zn), the sediment was 10.7513 ug/g (Cu), 25.7750 ug/g (Pb) and 34.1493 mg/g (Zn). Simple linear regression analysis indicates negative correlation between metals content in seawater and in sediment with Y = 12.864 –29.178X, r = 0.1616 (Cu), Y = 26.181 – 3.1564X, r = 0.0632(Pb) ; and Y=45.479 - 61.286X, r = 0.2689 (Zn).

Keywords:*Heavy metals, water, sediment, Snail and Singkep Island*.

I. INTRODUCTION

Coasts and oceans become recipients of waste with an increase in population and technological advances in the fields of industry, transportation, tourism, agriculture and mining. This will eventually be followed by an increase in the amount of waste entering the sea both through human activities on land and at sea.

Almost all waste generated from human activities contains metal elements. Naturally, heavy metal elements are found throughout nature, but in very low levels, however, the levels will increase if urban, mining, agricultural, industrial waste contains a lot ofmetals enter the marine environment (Darmono, 1995). Singkep Island, Riau Archipelago is one of the oldest former tin mining areas in Indonesia, where this mining operation began from 1887 to 1992. Even though this tin mining is no longer operating, it is strongly suspected that the impact of this tin mining will still have an impact on water pollution, including in it water pollution by heavy metals which will ultimately affect the life of marine biota.

Since 1992 until now mining activities have been continued by several private mining companies, but are engaged in the sand and bouxite mining sector. Sand and bouksite mining activities are also suspected to have the same impact as tin mining, namely in the form of waste materials from mining, including those that will cause water pollution.

The impact of general mining activities is an increase in heavy metal compounds in waters due to mining erosion. Increased levels of heavy metals in seawater will cause heavy metals that were originally needed for various metabolic processes to turn into poison for marine organisms. Besides being toxic, heavy metals will also accumulate in sediments and biota. Heavy metals that enter the marine environment will dissolve in water and will accumulate in sediments and also be accumulated by organisms including shellfish (Dahuri, 2003).

II. RESEARCH METHODS

This research was conducted in June - July 2022. Water, sediment and C. Obtusa samples were taken from the waters around the former tin mining.

The location of the sampling point is determined purposively which represents the condition of coastal waters
Singkep Island which is described as in Table 1.

Table 1. Sampling Area Description

Station	Station Location	Sampling coordinates	pointCommunity Activity Specifications
1	taker	00 23' 15,79" S 1040 25' 27.77" E	Residential settlements, Sand mining
2	Kuala Raya	00 24' 31.99" S 1040 24' 07.36" E	Residential settlements, Singkep tin mine, mine
3	Old Moroccan	00 32' 10.04" S 1040 19' 05.65" E	Residential settlement with mangrove vegetation, active bouksit mine PT. Hermina Jaya, Fishing Boat Harbor, former tin mining PT. Mine Sigkep tin
4	Little Morocco	00 38' 45.87" S 1040 23' 07.86" E	Residential area, plantation, ex-tin mine of PT. The Singkep Tin Mine and bouksite mine are active
5	insects	00 29' 07.83" S 1040 35' 31.86" E	Residential settlement, near the Sergang Tourism Beach area

Samples of surface sea water were taken as much as 500 ml using bottles at each sampling point. The seawater sample that has been taken is then put into a polyethylene plastic bottle which has been rinsed three times with seawater. Then added with concentrated nitric acid (HNO3) so that the pH becomes ≤ 2 (1/500ml), then put into an ice box and taken to the laboratory for analysis.

Sediment samples were taken from each station using the Eckman grab, approximately 500 grams of wet weight that was on the surface and not in contact with the grab. At each station, surface sediment was taken with a thickness of about 10 cm using a plastic spoon and then put into a plastic bag labeled by station. Then put in an ice box and after that brought to the laboratory for analysis.

The procedure for analyzing the levels of Cu, Pb and Zn metals in seawater was carried out based on Hutagalung's (1997) procedure as follows: The test seawater sample was shaken and measured 50 ml in duplicate, then put each into a 100 ml beaker. Then 5 ml of concentrated HNO3 nitric acid was added and heated slowly until the remaining volume was 15-20 ml. Then another 5 ml of concentrated HNO3 was added and the beaker was covered with a watch glass, then heated again. The addition of acid and heating is carried out until all the metals dissolve, this can be seen from the formation of a precipitate in the seawater sample which becomes slightly white and the solution becomes clear. Then another 2 ml of concentrated HNO3 nitric acid was added and heated for about 10 minutes. The watch glass is rinsed with distilled water and the rinse water is put into the beaker.

The test solution was transferred each into a 50 ml volumetric flask and distilled water was added until it was exactly marked, then the test solution was transferred to a test bottle for analysis of seawater samples that had been labeled. The test seawater samples are ready to be analyzed using an Atomic Absorption Spectrophotometer (AAS).

To find out the correlation between heavy metal content in water and sediment, a linear regression test was performed (Sudjana, 1992). Statistical analysis (Anova) was carried out with the help of Microsoft Software and Statistical Package For Social Science (SPSS) version 16.0 to determine differences in concentrations of heavy metals Cu, Pb and Zn in seawater and sediments from each station. The environmental parameters measured included temperature, pH, salinity, brightness, and current velocity during sampling.

III. RESULTS AND DISCUSSION

Singkep Island is part of Lingga Regency which is located between 0o 31' 0.49"S and 104o 26' 20.64"E with an area of 757km²(292miles²). This island is separated from the east coastSumatrabyIdol

Strait.This island is surrounded by Posik Island in the west, Serak Island in the southwest, Lalang Island in the south, and Selayar Island in between.Phallusand Singkep. The results of measuring water quality in this study are presented in Table 2.

Table 2. Average Measurement Results of Water Quality Parameters

Parameter / Station	Temperature (°C)	pH	Salinity (‰)	Brightness(cm)	Current Speed (m/s)
1	30	6	20	0.75	0.60
2	29	6	19	0.65	0.50
3	27	7	18	0.70	0.55
4	28	6	18	0.75	0.65
5	29	7	20	0.80	0.70
Average	28,6	6,4	19	0.73	0.60

Based on the results of measurements of water quality parameters during the study, it can be stated that the aquatic environment of Singkep Island Beach is still within the permitted limits in accordance with Kep. No. 51/MENKLH/2004 Concerning Sea Water Quality Standards. In Table 2 it can be seen that among the five (5) research stations, in general there is no significant difference in each of the water quality parameters. For temperatures ranging from 270-300C, the pH of the waters ranges from 6 – 7, Salinity ranges from 180/00 - 200/00, the brightness of the waters ranges from 0.65cm – 0.80 cm and the current velocity ranges from 0.5m/s – 0.70 m /s.

Content of Cu, Pb and Zn Metals in Water

The content of Cu, Pb and Zn metals in the water at each station from Singkep Island coastal waters can be seen in Table 3.

Table 3. Content of Cu, Pb and Zn Metals in Seawater (Mean ± Std.Deviation)

Station	Heavy Metal Content (μg/g)		
	Cu	Pb	Zn
1	0.1285±0.0068	0.3121±0.0461	0.2423±0.0497
2	0.0393±0.0072	0.1136±0.0309	0.1923±0.0246
3	0.0642±0.0018	0.0307±0.0219	0.1155±0.0058
4	0.0458±0.0094	0.1340±0.0012	0.0759±0.0134
5	0.0843±0.0030	0.0523±0.0232	0.1364±0.0269

Source: Primary Data 2021

Based on the Test of Normality with the Kolmogorov-Smirnova test, it shows that the content of heavy metals Cu, Pb and Zn in water has a normal data distribution because it has a p value > 0.05 so the statistical test used is the ANOVA test and because the ANOVA test results show that no If the p value is significant > 0.05 then no further tests are carried out, except for metal Pb where p <0.05 then it is further tested with Turkey HSD. For more details can be seen in Table 4.

Table 4. Tukey HSD Test Results Average Heavy Metal Pb Content in Water Between Research Stations

Station	1	2	3	4	5
1	-				
2	0.000**	-			
3	0.000**	0.033*	-		
4	0.000**	0.901ns	0.009 **	-	
5	0.000**	0.139 ns	0.880ns	0.036 *	-

Description: ns = not significant

* = p < 0.05 (significant)

** = p < 0.01 (very significant)

From Table 4 it can be seen that 50% of Pb metal (5 out of 10 comparisons) is very significantly different (very significant), namely the sampling points (1-2), (1-3), (1-4), (1-5) and (3-4) with $p<0.01$. As many as 20% were significantly different, namely the sampling points (2-3) and (4-5) with a value of $p<0.05$ and 30% were not significant ($p>0.05$) namely the sampling points (2-4), (2- 5) and (3-5).

The results of measurements of Cu, Pb and Zn content in water at all stations in the coastal waters of Singkep Island can be seen in Table 3. The highest Cu, Pb and Zn content was found at Station 1 (0.1285 µg/g, 0.3121 µg/ g and 0.2423 µg/g). The lowest Cu was at Station 2 (0.0393 µg/g), the lowest Pb was at Station 3 (0.0307 µg/g) and the lowest Zn was at Station 4 (0.0759). At Station 1 (Taking) there are the highest Cu, Pb and Zn content compared to other stations. This is presumably due to the input of residential waste along the river, the input of water from the former tin mine excavation of PT. Singkep Timah Mine (TTS) and sand mining PT. Singkep Alat Perkasa and PT. Citra Bumi Mulya especially when it rains. In accordance with the opinion of Darmono (1995) that naturally heavy metal elements are found throughout nature, but at very low levels. This level increases if there is an increase in the amount of waste entering the sea. This waste can come from human activities at sea and on land, including residential waste.

In addition, this station is also facing Selayar Island with residential and bouksite mining activities, so it is suspected that metal inputs were carried by the currents. Unlike the other stations (2, 3, 4 and 5), even though the station is located at the mouth of a river, it is suspected that there is no metal input from other areas except for input from local area activities. When compared with the heavy metal quality standards for sea water from Kep.MENLH No. 51 of 2004 (Cu and Pb<0.008 mg/L and Zn<0.05 mg/L) it can be said that the levels of heavy metals Cu, Pb and Zn in the coastal waters of Singkep Island are still below the established quality standard values.

Content of Cu, Pb and Zn metals in sediments

The metal content of Cu, Pb and Zn in the sediments at each station from the waters of the Singkep Island coast can be seen in Fig.Table 5.

Table 5. Content of Cu, Pb and Zn Metals in Sediments (Mean ± Std. Deviation)

Station	Heavy Metal Content (µg/g)		
	Cu	Pb	Zn
1	7.8117±1.1451	26.1533±4.1495	16.5933±4.5658
2	8.3850±0.5574	22.7333±2.4798	26.1733±2.7026
3	21.4900±6.1898	31.3933±6.1177	96.3883±2.5129
4	8.2233±1.3885	27.8267±5.2846	14.1650±11.5102
5	7.8467±0.6280	20.7683±1.1537	17.4267±6.0690

Source: Primary Data 2021

Based on the Test of Normality with the Kolmogorov-Smirnova test, it shows that the content of heavy metals Cu, Pb and Zn has a normal data distribution because it has Sig. > 0.05 so the statistical test used is the ANOVA test, because the ANOVA test results show that the p value is significant > 0.05 for the heavy metals Cu and Pb so no further tests are needed except for metals with significant Zn p values <0.05 so continue with Tukey HSD test to see comparisons between stations.

Table 6. Tukey HSD Test Results Average Zn Heavy Metal Content in Sediments Between Study Stations

Station	1	2	3	4	5
1	-				
2	0.996 ns	-			
3	0.037*	0.063ns	-		
4	1,000ns	0.991ns	0.032*	-	
5	1,000 ns	0.997 ns	0.039 *	1,000 ns	-

Description: ns = not significant
* = p < 0.05 (significant)

Tukey HSD test results for Zn metal in sediments between research stations showed that the p value was significant <0.05 at sampling points (1-3), (3-4) and (3-5). While not significant indicated by the sampling point (1-2), (1-4), (1-5), (2-3), (2-4), (2-5) and sampling points (4-5).

In general, the content of heavy metals in sediments is higher than that found in seawater. Heavy metals have the property of binding organic matter and precipitating at the bottom of the waters and uniting with sediments so that the levels of heavy metals in sediments are higher than those in water (Connell and Miller in Priyanto et al., 2008). This is in line with what was stated by Bhosale and Sahu (1991) heavy metals that settle on the seabed will accumulate in the sediments, so that their amounts are higher than those found in the waters. Heavy metals that enter the waters will experience precipitation, dilution and dispersion.

The results of measuring the content of Cu, Pb and Zn metals in sediments at each observation point for all stations in the coastal waters of Singkep Island can be seen in Table 5. The highest concentrations of Cu, Pb and Zn metals were at Station 3 (21.4900 μg/g, 31.3933 μg/g) and 96.3883 μg/g).

The high concentrations of Cu, Pb and Zn at Station 3 are thought to be closely related to the velocity of the river estuary currents and human activities both on land and at sea. This station is still covered by mangrove vegetation so that it is slightly under pressure from sea waters. When associated with the current speed, Station 3 is classified as low when compared to Stations 1, 4 and 5 and differs slightly by 0.05 m/s from Station 2 so that more dissolved metals in the waters accumulate to the bottom of the waters.

Judging from human activities, Station 3 is a former tin mining area, a fishing boat port and also an area adjacent to an active bouksite mine (PT. Hermina Jaya). Unlike the other stations, although the human activities are almost the same as Station 3 with the exception of Station 5 (a tourist area), the waters are under a lot of pressure from sea waters such as tides so that the metals in the waters are more likely to be carried away by the currents rather than settle to the bottom of the waters. According to what Waldichuk (1974) said, heavy metal pollutant materials usually come from land. The biggest part is carried by river flow, when entering the sea, the levels of heavy metals are greatly influenced by the tides.

Relationship of Heavy Metal Content in Water with Sediments

Based on the content of Cu, Pb and Zn metals in water and sediment, the results of the regression analysis showed a negative correlation with each of them being Cu metal (Y = 0.12,864 – 29.178X, R2 = 0.0261 and r = 0.1616), Pb metal (Y = 26.181 – 0.3.1564X, R^2 = 0.004 and r = 0.0632) and Zn metal (Y = 45.479 – 61.286X, R2 = 0.0723 and r = 0.2689) with the relationship between the variables weak.

Pollution Status of Singkep Island Coastal Waters

To determine the level of contamination that occurred in the coastal waters of Singkep Island, the heavy metal content in the sediment was compared with the ERL and ERM standards as proposed by Long et al. (1995). Comparison of the metal content of Cu, Pb and Zn obtained during the study with standard ERL (Effect Range Low) and ERM (Effect Range Median) values can be seen in Table 7.

Table 7. Comparison of Heavy Metal Content (µg/g) in Sediment in Singkep Island Coastal Waters with ERL and ERM Standard Values

Metal	Concentration (μg/g)		
	This research	ERL*	ERM*
Cu	10.7513	34.00	270.00
Pb	25.7750	46,70	218.00
Zn	34.1493	150.00	410.00

* Long et al. (1995)

As can be seen in Table 7, the metal content of Pb, and Zn and Cu is still far below the ERL and ERM, which means that the metal content of Cu, Pb and Zn in the coastal waters of Singkep Island has not had a negative impact on the organisms in these waters. Thus, it is estimated that there will be no real biological effects on the organisms in these waters. This is also indicated by the large number of fishery products (fish, shellfish and snails) found in the waters of Singkep Island Beach.

Pollution index (PLI) values for Cu, Pb and Zn metals in the coastal waters of Singkep Island are based on their content in sediment and can be seen in Table 8.

Table 8. Results of Calculation of the PLI (Pollution Load Index) Value of Heavy Metals (Sediments) in the coastal waters of Singkep Island

Station	PLI (Pollution Load *Index*)*	Status Description Waters
1	0.3847	Low pollution level
2	0.4375	Low pollution level
3	1.0297	Low pollution level
4	0.3789	Low pollution level
5	0.3626	Low pollution level
Average	0.5187	Low pollution level

* Based on Salomon and Forstner (1984): Pb = 19, Cu = 33, Zn = 95

Based on the calculation results as shown in Table 8, it is known that of the five sampling points the highest pollution index is Station 3 (PLI = 1.0297) which is a fishing boat port area, a former tin mining area and also an active bouxite mining area. While the lowest pollution index is Station 5 (PLI = 0.3626) which is a tourist beach area where most of the input of waste into the waters only comes from community settlements. From the five stations, it shows that the level of pollution is low, so there is no need for rectification or fast recovery.

IV. CONCLUSION

In general, the environmental conditions of Singkep Island's coastal waters are still within the limits allowed in accordance with Kep. No. 51/MENKLH/2004 Concerning Sea Water Quality Standards. The highest heavy metal content in water is Pb, followed by Zn and Cu. The highest heavy metal content in the highest sediments is Zn metal, followed by Pb and Cu.

The results of linear regression analysis of the metal content of Cu, Pb and Zn in water with sediments produced a negative correlation with a weak correlation between variables. The pollution index (PLI) value in the coastal waters of Singkep Island at all sampling points is still low, which indicates the low level of pollution in these waters.

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