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## Chemical Characteristics and Correlation of Heavy Metal Elements in Lumpue Beach, Parepare City

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**Abstract.** This study aims to analyze heavy metal elements in Lumpue Beach. Characterization of Lumpue Beach sediments in addition to the megaskopis and petrographic observation approach, determination of mineral chemical aspects using ICP-OES analysis was also done. This analysis done on 7 samples of very fine sand obtained from sieving and aimed to determine the level of heavy metal elements on the ppm scale. Based on ternary plotting diagrams, that the dominant Lumpue Beach is composed of sedimentary texture very fine sand - coarse sand. The ratio of Pb elements in the study area has an average level of 41.38 ppm and a trend line  $R^2 = 0.25$ , Cd has an average level of 1.65 ppm and a trend line  $R^2 = 0.12$ , Cu elements has an average level of 14.5 ppm and a trend line  $R^2 = 0.02$ imes and Zn element has an average level of 62.125 ppm and a trend line  $R^2 = 0.0022$ . They are indicated to exceed normal limits. Based on the use of Pearson method with two paired variables on metals Cu, Fe, Ni, Zn, Pb, Ti and Mn, it is known that Cu metal has a very weak correlation with Fe, Zn, Ni, Pb and Ti, while Fe metal has a strong correlation to Zn, Ti and Mn but have a weak correlation with Ni and Pb. Fe and Al metals are deposited with low values, this occurs in the concentrations of the two metals and follows the sediment fraction controlled by currents and tides.

### 1. Introduction

Increased levels of heavy metals in seawater occur due to the entry of waste containing heavy metals into the marine environment. Waste that contains a lot of heavy metals usually comes from industrial activities, mining, settlement and agriculture. In general, before going to the sea, heavy metals are affected by properties such as tides, sea breezes, water permeation and the geological conditions of the surrounding rocks. Lumpue Beach has quite high turbidity [1, 2].

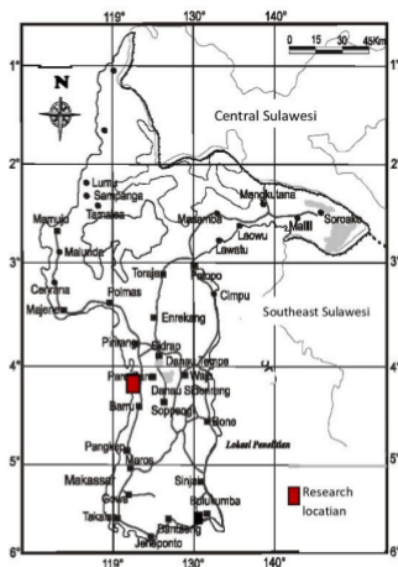
Turbidity that occurs in the Lumpue Beach area is affected by the presence of sediment resuspension [3]. Increasing ionic strength causes the pulling force between particles to become stronger and result in the accumulation of a material which is often called a floc. If the resultant attraction is large, the size of the floc will be even greater. In addition, the particles in Lumpue Beach have the ability to adsorb heavy metals, so that the dissolved metal content of water becomes reduced, then the content of this metal is deposited in the sediment.

Lumpue Beach is the largest tourist destination beach in the City of Parepare which is a gathering place for people to spend their holidays with family (Figure 1). Therefore, this research is important to determine whether Lumpue Beach is safe against harmful heavy metal elements. Because information about the analysis and distribution of heavy metals in Indonesia is still very limited, especially in the Lumpue Beach area, Parepare City, South Sulawesi.



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**Figure 1.** Map showing the location of the research area

The concentration of heavy metals will change during their time on the coast. The changes in metal concentrations are influenced by various processes in the coast such as dilution, flocculation, adsorption and desorption processes by particles. Based on geomorphological and petrography conditions of volcanic rocks regionally, it can be distinguished from south to north, namely Baturape, Lompobattang, Cindako, Camba, Soppeng and Parepare volcanic [4]. The process of heavy metal concentration occurs due to sedimentation from the geomorphological conditions of the original rock [5].

With the adsorption process, which is then followed by a flocculation process, the concentration of this metal will experience a reduction and vice versa if there is a desorption process or the dissolution of the particles, the concentration of heavy metals will increase [6]. This process can be seen by looking at the distribution of heavy metals in terms of the distribution of metal concentrations so that needs for heavy metal concentration data. The distribution of heavy metals that studied from sediment deposits in Lumpue Beach area are Pb, Cd, Cu, and Zn.

## 2. Geological of Study Area

The geomorphological group units in the study area consist of morphographic and morphometric approaches. Based on the morphographic approach, the dominant study area consisted of terrain, hills and mountains. This aspect of land formation is known by observing the parameters of each topography such as the shape of the peak, the shape of the slope and the shape of the valley. Based on the morphometry approach, the study area consists of land morphological units located in west of the Karajae River flow including the Kampungbaru, Watanbacukiki, Lumpue and Pekkae regions. This morphological unit occupies alluvial, tuff and intrusion trakit units (Figure 2).

Based on unofficial lithostratigraphy, the rock unit in the Lumpue Beach area can be divided into 2 rock units which are described sequentially from the youngest are alluvial and volcanic breccias units. The description of each rock unit contained in the study area will start from the oldest unit to the youngest.

Volcanic breccias units occupy about 25.1km<sup>2</sup> or about 28.33% from the total area of the mapping area. Lithology which composes units consists of volcanic breccias, agglomerate, lapili tuff, coarse tuff, ignimbrite and basalt. This unit occupies or around the total area of the study dominates from the southern to the north, including Latasiso, Bilalang, Jawi-Jawi, Lawalane, Lapance and Bacukiki.



**Figure 2.** The appearance of the morphology of the terrain in the Bacukiki area

The field appearance of the breccia unit that found in the study area has physical characteristics, namely fresh grayish brown color, brownish black weathered color, has a coarse clastic texture, grain size until coarse sand, with angular - subangular material shape, poorly sorted and open fabric. This rock is composed of components consisting of fragments from the igneous rock porphyry basalt and andesite porphyry, while the rock matrix is composed of volcanic material in the form of minerals which consists of plagioclase, orthoclase, biotite, and pyroxine, while the one that act as cement in rock is volcanic ash. Generally in difficult volcanic breccias outcrops there are a rock position or layered structure, but the layer of volcanic breccias can be generally measured if volcanic breccias are exposed together with other unit members, namely with coarse tuffs or lapilli tuff. Based on its constituent components, this rock is volcanic breccias [7].

In the study area exposed rocks in the form of porphyry trachyte which are igneous rock types with massive structures (Figure 3). Direct observation in the field that being study area shows igneous rock has a contact with porphyry trachyte rock. The distribution direction of rocks is N320°E or relatively southeast to northwest [8]. From the results of microscopic analysis, it found the brown absorption color, black interference color, hypocrySTALLINE crystallinity, porphyritic granularity (porphiroafanitic), anhedral-euhedral mineral form, mineral size <0.02–1.20 mm, mineral composition consisting of plagioclase, oligoclase, hornblende, biotite, quartz and groundmass (Figure 4).

Based on the lithology equation and its geographical distribution close to the type location, volcanic breccias units with Parepare volcanic rocks can be correlated with rocks deposited on land environment. In the regional stratigraphy relationship, the volcanic breccias unit of the study area is the same as the Parepare volcanic rock that is Pliocene [4, 9].

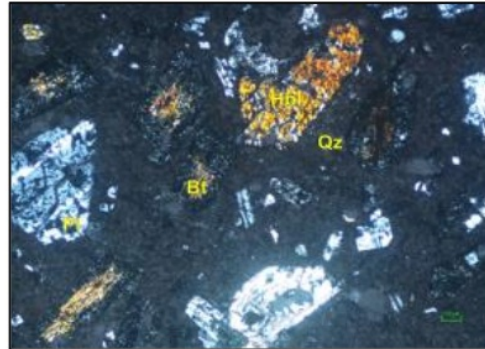
Alluvial units are spread along the Bojo river, forming river terrace or as active deposits in the Bojo river, which occupy an area of approximately 2.7 km<sup>2</sup> or around 2.9% of the entire study area. This alluvial unit is located in the southwest part of the study area.

The alluvial unit is composed of lumps of rock that come from igneous rocks, but sometimes there are also other rocks such as volcanic breccias but in very small quantities, the rest is sand-sized to clay, but this sand material is dominated by sand-sized material very coarse. As for the comparison group is the Qac group (alluvium, lake and beach deposits) composed of clay, silt, sand and gravel components along the large river.

The geological structure that developed in the study area was in the form of a sliding fault, which is the southwest-northeast direction, where there is a fault mirror or slickenslide, which was found in the Mangimpuru village. Age of Tolong fault, where the rock unit displaced is an old tuff unit between the Middle Miocene - Lower Pliocene, it can be concluded that the age of the Tolong fault is Lower Post-Pliocene [2, 4].



**Figure 3.** The appearance of porphyry trachyte rock outcrops at the Lumpue coast

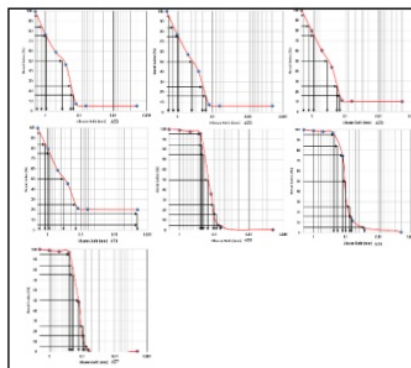


**Figure 4.** Photomicrograph of thin section showing the presence of plagioclase, hornblende, biotite and quartz minerals. Photographed with 50x magnification.

### 3. Analysis of Sediment Grain Size in Lumpue Beach

The grain size and distribution of Lumpue Beach sediment particles are identified and determined based on compilation of field observations in the form of descriptions of sediment samples in the form of wells test and results of laboratory data processing. The description of each layer of the well test is based on variations in sediment materials, color, structure or other sedimentary characteristics. The description results are then used to describe the main characteristics of each layer. The main characteristics of its components are sedimentary materials, texture and grain size of sediments, color of sediment material, thickness and slope of sediment distribution structure of sediments and layering fields [11]. Based on the results of compilation of the data, it is known that the dominant research area is composed of very coarse sand sediments to sandy silt.

Semi logarithmic curves (Figure 5) at stations 01 to stations 03 have in common the percentage of weight passes and grain size, while at station 04 there is a difference in weight passing by 20%. Sediment grain size distribution at stations 05, 06 and 07 are relatively smooth from station 4 with a grain size of  $\pm 0.51$  mm. It is interpreted that the direction of sedimentation is relative to stationary 04 or southeast. Based on ternary plotting diagram [10] in the form of abundance percentage and texture of sediment components (size of grains sediment), it is known that the dominant Lumpue Beach is composed of very fine sand sedimentary (Figure 6).



**Figure 5.** Semi-logarithmic curve of Lumpue Beach sediment distribution.

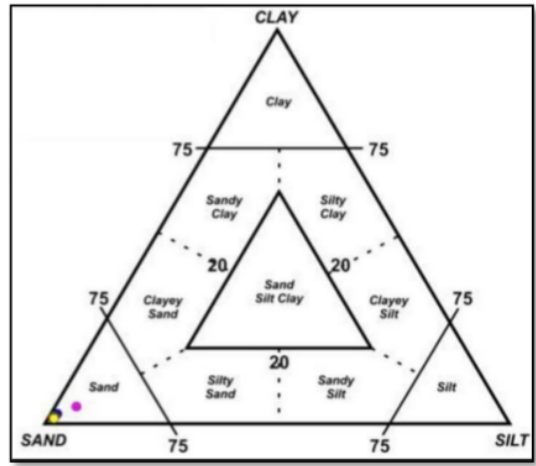


Figure 6. Distribution of Lumpue Beach sediments based on the texture and percentage of components

Based on the results of petrography analysis of mineral smear slides on sedimentary material in the study area, it is known that the composition of the constituent materials includes of rock fragments, plagioclase, hornblende, biotite and opaque minerals (Tabel 1 and Figure 7).

Table 1. Composition of the main components in Lumpue Beach sediments

Component	ST-01	ST-02	ST-03	ST-04	ST-05	ST-6	ST-7
Rock Fragment	40,00	25,00	45,00	45,00	10,00	25,00	25,00
Plagioclase	45,00	30,00	30,00	25,00	40,00	30,00	50,00
Hornblende	10,00	40,00	25,00	30,00	30,00	40,00	15,00
Biotite	5,00	0,00	0,00	0,00	5,00	0,00	5,00
Opaque Mineral	0,00	5,00	0,00	0,00	15,00	5,00	5,00

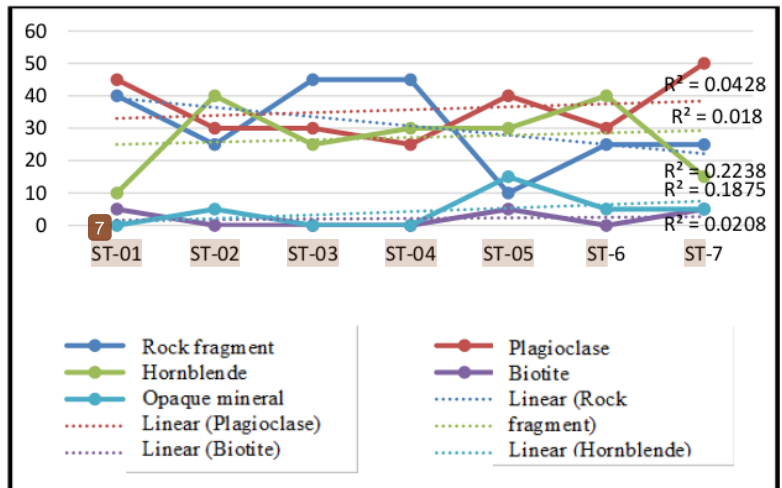


Figure 7. Trend line of petrography smear slide

#### 4. Chemical Characteristics and Correlation of Heavy Metal Elements in Lumpue Beach

Characterization of Lumpue Beach sediments in addition to the megaskopis and petrography observation approach, determination of mineral chemical aspects using ICP-OES analysis was also done [12]. This analysis done on 7 samples of very fine sand obtained from sieving and aimed to determine the level of heavy metal elements on the ppm scale.

Based on the use of Pearson method with two paired variables on metals Cu, Fe, Ni, Zn, Pb, Ti and Mn, it is known that Cu metal has a very weak correlation with Fe, Zn, Ni, Pb and Ti, while Fe metal has a strong correlation to Zn, Ti and Mn but have a weak correlation with Ni and Pb (Table 2a).

Ni metal has a strong correlation to Ti and Mn, and has a correlation of weaknesses against Fe, Zn and Pb. Zn has a strong correlation with Fe, Ti and has a weak correlation with Ni, Pb and Mn. Metal Pb is weakly correlated to the above elements.

Ti correlates strongly with Ni, Zn and Mn, while Mn correlates strongly with Fe metal, Ni and Ti. This correlation shows that there are fairly close relationship between heavy metals with alkaline compositions to other heavy metals, a strong correlation indicates that the higher level of a heavy metals will be followed by other metals.

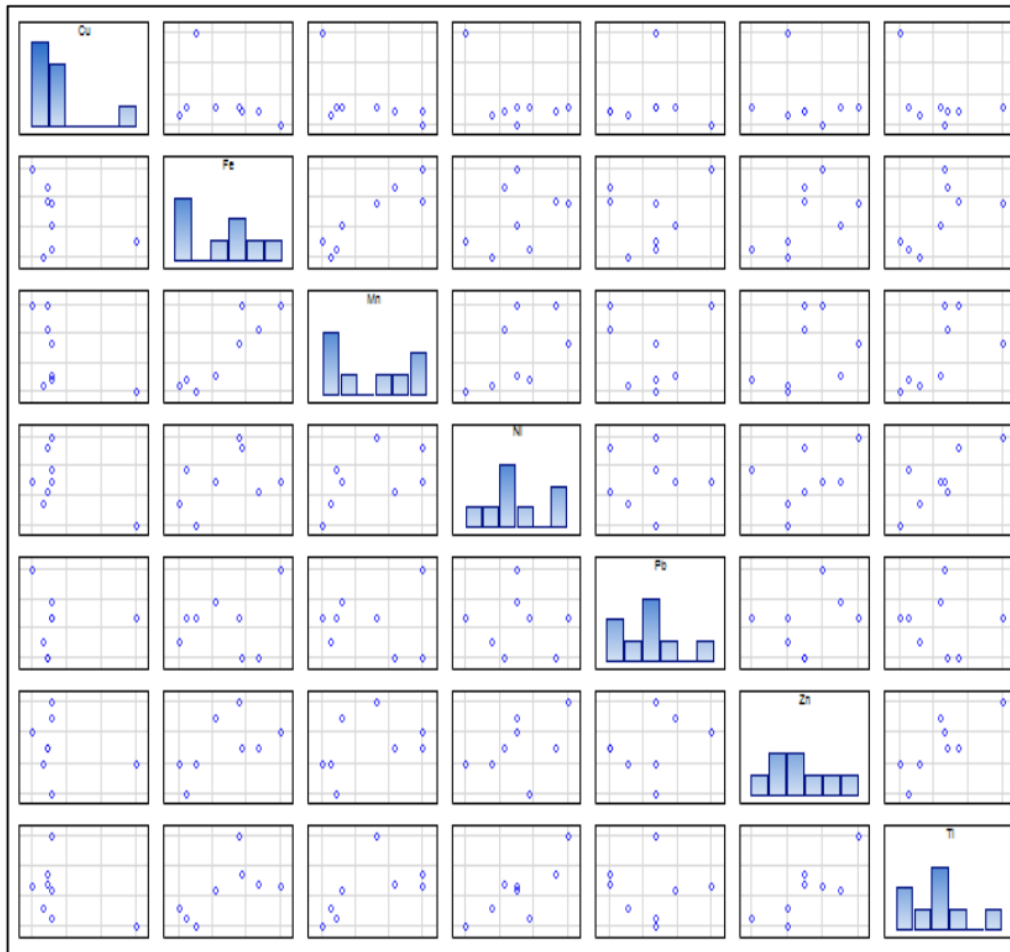
**Table 2a.** Elements correlation

		<b>Correlations</b>						
		<i>Cu</i>	<i>Fe</i>	<i>Ni</i>	<i>Zn</i>	<i>Pb</i>	<i>Ti</i>	<i>Mn</i>
<i>Cu</i>	<i>Pearson Correlation</i>	1	-.414	-.572	-.240	-.031	-.467	-.532
	<i>Sig. (2-tailed)</i>		.308	.138	.567	.942	.243	.174
	<i>N</i>	8	8	8	8	8	8	8
<i>Fe</i>	<i>Pearson Correlation</i>	-.414	1	.376	.570	.213	.609	.904**
	<i>Sig. (2-tailed)</i>	.308		.358	.140	.612	.109	.002
	<i>N</i>	8	8	8	8	8	8	8
<i>Ni</i>	<i>Pearson Correlation</i>	-.572	.376	1	.436	-.050	.800*	.532
	<i>Sig. (2-tailed)</i>	.138	.358		.281	.906	.017	.175
	<i>N</i>	8	8	8	8	8	8	8
<i>Zn</i>	<i>Pearson Correlation</i>	-.240	.570	.436	1	.279	.809*	.377
	<i>Sig. (2-tailed)</i>	.567	.140	.281		.503	.015	.357
	<i>N</i>	8	8	8	8	8	8	8
<i>Pb</i>	<i>Pearson Correlation</i>	-.031	.213	-.050	.279	1	-.055	-.017
	<i>Sig. (2-tailed)</i>	.942	.612	.906	.503		.897	.969
	<i>N</i>	8	8	8	8	8	8	8
<i>Ti</i>	<i>Pearson Correlation</i>	-.467	.609	.800*	.809*	-.055	1	.593
	<i>Sig. (2-tailed)</i>	.243	.109	.017	.015	.897		.121
	<i>N</i>	8	8	8	8	8	8	8
<i>Mn</i>	<i>Pearson Correlation</i>	-.532	.904**	.532	.377	-.017	.593	1
	<i>Sig. (2-tailed)</i>	.174	.002	.175	.357	.969	.121	
	<i>N</i>	8	8	8	8	8	8	8
** . Correlation is significant at the 0.01 level (2-tailed).								
* . Correlation is significant at the 0.05 level (2-tailed).								

In table 2b there is an element of Ca which strongly correlates with heavy metals Fe and Mn. This correlation shows that changes in heavy metal in the study area are influenced by Ca and Fe [13] and heavy metals Fe and Mn generally come from coastal material carried by currents. Statistical graph of the correlation of heavy metal elements on Lumpue Beach is shown in Figure 8.

**Table 2b.** Elements correlation

		<i>Correlations</i>							
		<i>Cu</i>	<i>Fe</i>	<i>Ni</i>	<i>Zn</i>	<i>Pb</i>	<i>Ti</i>	<i>Mn</i>	<i>Ca</i>
<i>Cu</i>	<i>Pearson Correlation</i>	1	-.414	-.572	-.240	-.031	-.467	-.532	-.336
	<i>Sig. (2-tailed)</i>		.308	.138	.567	.942	.243	.174	.416
	<i>N</i>	8	8	8	8	8	8	8	8
<i>Fe</i>	<i>Pearson Correlation</i>	-.414	1	.376	.570	.213	.609	.904**	.841**
	<i>Sig. (2-tailed)</i>	.308		.358	.140	.612	.109	.002	.009
	<i>N</i>	8	8	8	8	8	8	8	8
<i>Ni</i>	<i>Pearson Correlation</i>	-.572	.376	1	.436	-.050	.800*	.532	-.029
	<i>Sig. (2-tailed)</i>	.138	.358		.281	.906	.017	.175	.946
	<i>N</i>	8	8	8	8	8	8	8	8
<i>Zn</i>	<i>Pearson Correlation</i>	-.240	.570	.436	1	.279	.809*	.377	.176
	<i>Sig. (2-tailed)</i>	.567	.140	.281		.503	.015	.357	.677
	<i>N</i>	8	8	8	8	8	8	8	8
<i>Pb</i>	<i>Pearson Correlation</i>	-.031	.213	-.050	.279	1	-.055	-.017	.317
	<i>Sig. (2-tailed)</i>	.942	.612	.906	.503		.897	.969	.444
	<i>N</i>	8	8	8	8	8	8	8	8
<i>Ti</i>	<i>Pearson Correlation</i>	-.467	.609	.800*	.809*	-.055	1	.593	.124
	<i>Sig. (2-tailed)</i>	.243	.109	.017	.015	.897		.121	.769
	<i>N</i>	8	8	8	8	8	8	8	8
<i>Mn</i>	<i>Pearson Correlation</i>	-.532	.904**	.532	.377	-.017	.593	1	.700
	<i>Sig. (2-tailed)</i>	.174	.002	.175	.357	.969	.121		.053
	<i>N</i>	8	8	8	8	8	8	8	8
<i>Ca</i>	<i>Pearson Correlation</i>	-.336	.841**	-.029	.176	.317	.124	.700	1
	<i>Sig. (2-tailed)</i>	.416	.009	.946	.677	.444	.769	.053	
	<i>N</i>	8	8	8	8	8	8	8	8
		** . Correlation is significant at the 0.01 level (2-tailed).							
		* . Correlation is significant at the 0.05 level (2-tailed).							



**Figure 8.** Statistical graph of the correlation of heavy metal elements on Lumpue Beach

The geochemistry of Lumpue Beach sedimentary with the regression value shown Al: Fe in the linear regression graph shows that layer A has the correlation properties of Al and Fe, as follows that increased Fe and Al have similarities from the same source, Al and Fe concentrations in sediments change according to the size of the fraction and concentrated Al elements increase gradually compared to Fe.

Linear regression value B is shown by Al: Fe, where in this graph shows that the B layer of the study area has Al to Fe correlation properties and comes from different sources and deposited as part of the coastal sediment layer. Fe and Al metals are deposited with low values in layer A and slowly accumulate or element enrichment in layer B. This occurs in the concentrations of the two metals and follows the sediment fraction controlled by currents and tides [14].

The low value of Fe is seen in layer B but has a high value of Al in layer A. This shows that Fe is gradually deposited well from the sediment surface and then in the lower layer eroded by the influence of waves. Whereas Al occur the opposite, the more value increases in the lower layer (Figure 9).

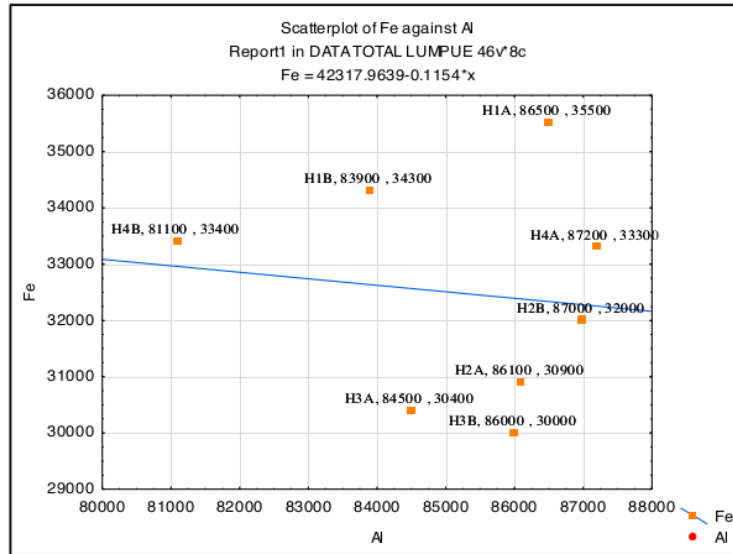


Figure 9. Total linear regression graph

Chemical characteristics of heavy metals in Lumpue Beach sediments were identified and determined based on the results of compilation of field observation data and geochemical results (ICP-OES). For the elements observed in the form of Pb, Cd, Cu, and Zn with a percentage of 1 ppm (Table 3). Based on the processing of statistical data and the distribution of heavy metal elements in the study area, there are relationship between the distribution of sediment particles, heavy metal elements to the influence of ocean wave currents on Lumpue Beach sediments.

Table 3. Lumpe Beach heavy metal elements content

Stasions	Heavy Metal Elements			
	Pb	Cd	Cu	Zn
H1A	48	2,8	8	63
H1B	37	1,4	12	62
H2A	42	1,2	34	61
H2B	44	2,0	13	64
H3A	42	1,4	13	59
H3B	39	1,0	11	61
H4A	42	1,4	13	65
H4B	37	2,0	12	62

Physical and chemical characteristics of Lumpue Beach sediment showed that the development of sedimentation in the study area is highly controlled by ocean waves, in addition changes from environmental conditions are identified to occur due to the development of geological activities in the form of sedimentation, changes in physiographic conditions and activities of local residents, especially those relating to household waste processing.

Based on the results of coastal sediment geochemical analysis (ICP-OES) which shows that the distribution of elements and changes in the composition of heavy metal elements are in the normal range and experience of element enrichment in the northern part of the research area. The distribution of Pb element at station 1 is relatively normal and tends to decrease, but at stations 2 - 4 there is an enrichment of Pb element with a trend line ratio that is R2 = 0.25. At stations 1 to 4 the level of Cd element is

relatively stable where the trend line ratio is  $R^2 = 0.12$ . The element Cu experienced a significant change at stations 1-2 and at stations 3-4 the elemental content was relatively stable with a trend line ratio of  $R^2 = 0.02$ . At stations 1 to 2 the increase in Zn element is relatively stable and regresses at station 3 and decreases again at station 4 with the trend line ratio that is  $R^2 = 0.0022$ .E (Figure 10).

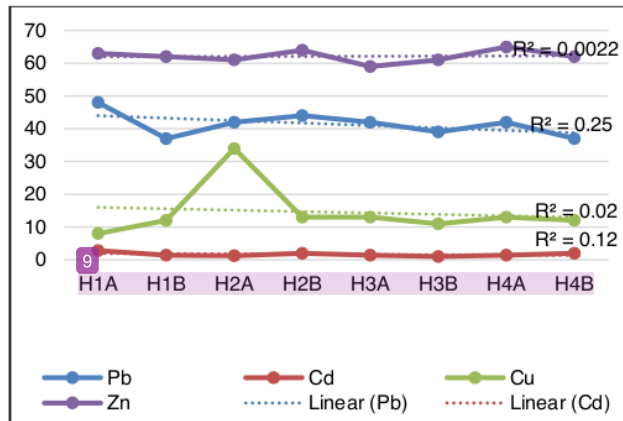


Figure 10. Trend line of Heavy Metal Elements Pb, Cd, Cu, Zn

### 5. Lumpue Beach Heavy Metals Distribution

The percentage of heavy metals Al and Fe are also poured in the graph below (Figure 11) where the elements of Al with a percentage of 50 ppm and the elements of Fe with a multiple of 0.01.

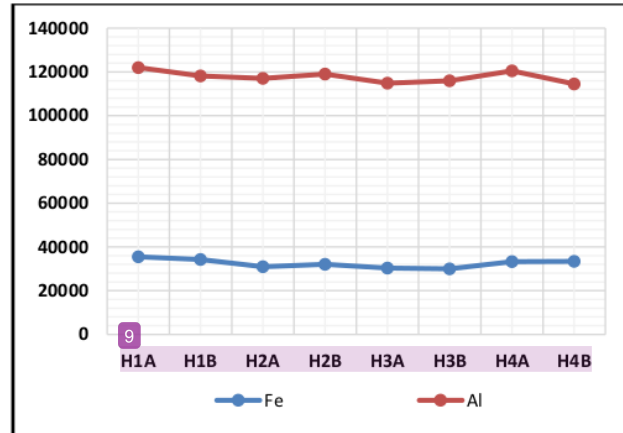


Figure 11. Trend line of heavy metal elements Fe and Al.

The distribution of heavy metals relative to the north caused by the direction of ocean currents in Lumpue Beach which is relatively south to north. The elemental abundance of Ca is found in station 1 with an average level of 53,636.96 - 60,049.89 ppm. The dominant Na element at stations 1 and 2 with an average level reached 26,108.69 ppm. The dominant Cu element is in station 2 with the element content reaching 17.17 - 23.49 ppm. The dominant Fe elements are found at station 1 and station 4 with an average level of 3.28 - 3.48%. Ti element is dominant at station 1 with the element content reaching 0.667 - 0.684 ppm. Pb elements are more dominant in stations 1 and 2 with the elements content reaching 42.24 - 42.99 ppm.

Based on the value from the maximum level of heavy metal types on the nature of conservative metals, it is known the ratio of the concentration of heavy metal elements (in ppm) in the study area are as follows:

1. The ratio of Pb elements in the study area has an average level of 41.38 ppm and a trend line  $R^2 = 0.25$ . This indicates that the presence of Pb element in the study area is indicated to exceed the normal threshold. Where the normal level of reference for Pb is 0.00003 and the maximum limit is 0.05 ppm.
2. The ratio of Cd element in the study area has an average level of 1.65 ppm and a trend line  $R^2 = 0.12$ . This shows that the presence of Cd element in the study area is indicated to exceed the normal threshold. Where the normal level reference for the Cd element is 0.00011 and the maximum limit is 0.01 ppm.
3. The ratio of Cu element in the study area has an average level of 14.5 ppm and a trend line  $R^2 = 0.02$ . This shows that the presence of Cu element in the study area is indicated to exceed the normal threshold. Where the normal level reference for Cu elements is 0.002 and the maximum limit is 0.05 ppm.
4. The ratio of Zn element in the study area has an average level of 62.125 ppm and a trend line  $R^2 = 0.0022$ . This shows that the presence of Pb element in the study area is indicated by a normal threshold. Where the normal level reference for Pb is 0.002 and the maximum limit is 0.01 ppm.

## 6. Conclusion

1. Distribution of Pb element at station 1 and tends to decrease, but at stations 2 - 4 enrichment occurs. At stations 1 to 4 the levels of Cd were relatively stable while Cu element experienced significant changes at stations 1-2 and at stations 3-4 the levels of elements were relatively stable. At stations 1 to 2 the increase in Zn element is relatively stable and regresses at station 3 and decreases again at station 4.
2. Abundance element of Ca is found in station 1 with an average level of 53,636.96 - 60,049.89 ppm. The dominant Na element at stations 1 and 2 with an average level reached 26,108.69 ppm. The dominant Cu element is in station 2 with levels of elements reaching 17.17 - 23.49 ppm. The dominant Fe element is found at station 1 and station 4 with an average level of 3.28 - 3.48%. The Ti element is dominant at station 1 with levels of elements reaching 0.667 - 0.684 ppm. The Pb element is more dominant at stations 1 and 2 with elemental levels reaching 42.24 - 42.99 ppm.
3. The characteristics of heavy metals in Lumpue Beach have ratio for each element where Pb, Cd, Cu and Zn are indicated to exceed normal limits.

## Acknowledgments

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