The Effect of Carbon Organic Total and Salinity on The Discharge of Heavy Metals Pb and Cu in Lapindo Mud into the Aloo River

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ABSTRACT

The research attempts to examine the effect of waters salinity and carbon organic total in the Lapindo Mud on the fluctuation of heavy metals Cu and Pb in the waters of Aloo Rivers. Sample is taken from Lapindo Mud from four different locations. Result of the characterization of Lapindo Mud shows that the clay and dust contents are 34-35 % and 39-46 %. Lapindo Mud texture is clay loam. The organic matter in Lapindo Mud is not surely increasing the concentration of heavy metal because there is oxide compound with great contribution to the increase of heavy metal concentration in Lapindo Mud. Result of TOC analysis indicates that the organic carbon ranges from 54.7 % to 55.47 %, Pb rate ranges from 0.27-0.34 mg/L, and Cu rate ranges from 0.83-1.31 mg/L. Indeed, Pb has higher metal flux in salt water at AL from $5x10^{-5}$ mg/cm².hour to $9x10^{-5}$ mg/cm².hour. Cu has higher metal flux in freshwater at SA1 $2.3x10^{-6}$ mg/cm².hour to $8.71x10^{-5}$ mg/cm².hour

Key word: Lapindo mudflow, TOC (Total Organic Carbon), Salinity, fluctuation

INTRODUCTION

Sidoarjo mud flood or Lapindo Mud is a spurt event of hot mud at a drilling location of PT Lapindo Brantas in the Renokenongo village, Porong, Sidoarjo Regency, East Java, since May 27, 2006. Lapindo mud in Sidoarjo is composed of 70% water and 30% solids [1]. Salt content (salinity) of mud is very high $(38-40^{\circ}/_{oo})$, so it is salty [2]. This hot mudflow has inundated agricultural land (fields), industrial, residential, public facilities, vacant land and others. Source of hot mud from the leakage of drilling wells on the exploration activities of oil and gas by PT. LapindoBrantas.Exploration activities of oil and gas conducted by PT Lapindo Brantas, Inc. are seismic survey and exploration activities.

Oxide minerals dominated the clay content of the Lapindomud. According [3], Lapindo mud content is SiO₂, AI₂O₃, Fe₂O₃, TiO₂, CaO, MgO, Na₂O, K₂O and SO₂ with alumina (AI₂O₃) of 18.27%. Statements that are not much different given by [4], that AI₂O₃ was classified as major element, because AI₂O₃ content amounting to 17.08 -18.95%. The aluminum content in Lapindo mud is potential asaluminum supply source besides bauxite.

The existence of mineral deposits and Total Organic Carbon in Lapindo mud is also expected play a role in the adsorption process. Whereinsilica, alumina, and organic carbon compound in the Lapindo mud may act as ion binding groups of heavy metal so if Lapindo mud into the waters then the heavy metals in the sludge will moved to waters body and cause environmental pollution. Salinity in the waters of the river waters also affects the heavy metals distribution. At the river mouth where there is a mass gathering of fresh water (low The journal homepage www.jpacr.ub.ac.id

salinity and has low ionic strength) with seawater (high salinity and has higher ionic strength) led to instability suspended solid particles, forming aggregations that followed the deposition due to gravity [5].

Based on the results of preliminary tests conducted by the UNDAC toward Lapindo mud is known that it contain Cu heavy metal content of 24.5 ppm, while for Pb heavy metal content of 17.8 ppm [6]. Cu is an element of heavy metal that is essential. The certain amount of Cu is needed by living organisms, but if in the excess amount, can cause toxic effects. While Pb, including one class of heavy metal is not essential so if it get into the bodies of living organisms will be able to be toxic.

This article will review the characterization of the Lapindo mud and the influence from waters salinity and total organic carbon toward the release of heavy metals Cu and Pb in the in Lapindo mud into the waters. This heavy metal pollution is related to the impact on aquatic body ecosystems of Aloo River.

EXPERIMENT

The equipment used is a set of tools glasses, porcelain plate, analytical weight, biuret 100 mL, furnaces (Memmert 854 Schwabch), clamp, filter paper, shakers (SM25, Edmund buhler), centrifuges (Hettich, D-7200 Tuttlingen), Conductometry (Wtw, LF91), pH meter (CG 820, Schott Gerate)) and AAS AA-6200 (Shimadzu, japan).

The materials needed is a solution of concentrated HNO₃ (65%, ρ 1.39 Kg / L, Merck), concentrated HCl (37%, ρ 1.19 Kg / L, Merck), concentrated H₂SO₄(98%, Merck), concentrated H₃PO₄ (85%, Merck), 0.5 M K₂Cr₂O₇ from 36.77 g K₂Cr₂O₇ (Merck) was dissolved in 250 mL distilled water, 0.5 M FeSO₄.7H₂O from 69.50 g FeSO₄.7H₂O (99,5%, Merck) was dissolved in 500 mL distilled water, solid Pb (NO₃) ₂(Merck), CuSO₄(Merck), distilled water, Lapindo mud samples and samples of freshwater, brackish and salty.

	No	Sample Code	LS"	BT"	
			(south latitude)	(east longitude)	
	1	A (Location Near of Aloo River I	7"31'00.52"	112°42'43.03"	
	2	B (Location Near of AlooRiverII)	7"31'08.90"	112°43'12.32"	
	3	C (Location Near of Porong River I)	7"32'05.82"	112°42'27.40"	
	4	D (Location Near of Porong River II)	7"31'56.92"	112°43'07.31"	

Table 1. Sampling Location of Lapindo Mud

Sampling of Lapindo Mud

The sample of Lapindo Mud is taken from 4 points (A, B, C and D). The sample point coordinates are shown in Table 1 and Figure 1, and the Characterization of Lapindo Mud, Determination of Carbon Organic Total and calculated fluctuation of Pb and Cu metals.

Flux =
$$\frac{\text{metal mass diffused in the water (mg)}}{A (cm^2) x t (hour)}$$
$$= \frac{(m_{\text{final}} - m_{\text{initial}})}{A (cm^2) x t (hour)}$$

Where: $m_{initial} = mass of metal in the water early (mg)$ $m_{final} = mass of dissolved metal after contact with mud (mg)$ A = surface area of sludge sample (cm²)t = contact time (hours)

Determination of water salinity was undertaken with EC (Electrical Conductivity). This determination begins by measuring a temperature and EC of water sample. It is followed by the determination of salinity of the sample using the following equation

$$S = a_0 + a_1 R_t^{1/2} + a_2 R_t + a_3 R_t^{3/2} + a_4 R_t^2 + a_5 R_t^{5/2} + \Delta S$$

Where:
$$\Delta S = \left[\frac{T - 15}{1 + 0.0162 (T - 15)}\right] (b_0 + b_1 R_t^{1/2} + b_2 R_t + b_3 R_t^{3/2} + b_4 R_t^2 + b_5 R_t^{5/2})$$
[2]

Notes:

 $\begin{array}{ll} S = salinity \\ R_t = Electrical \ conductivity \ (EC) \\ T = Temperature \ of \ solution \\ a_0 = 0.0080 \qquad b_\circ = 0.0005 \\ a_1 = -0.1692 \qquad b_1 = -0.0056 \\ a_2 = 25.3851 \qquad b_2 = -0.0066 \\ a_3 = 14.0941 \qquad b_3 = -0.0375 \\ a_4 = -7.0261 \qquad b_4 = 0.0636 \\ a_5 = 2.7081 \qquad b_5 = -0.0144 \end{array}$

Note:

• 1 dS m⁻¹= 1 mS cm⁻¹= 1 mmhos cm⁻¹ = 1000 μ S cm⁻¹ = 1000 μ mhos cm⁻¹

RESULT AND DISCUSSION The Salinity of Aloo River

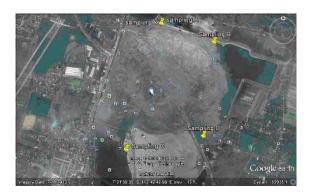
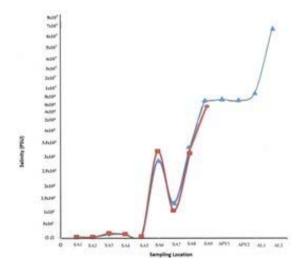


Figure 1 Map Sampling Location of Lapindo Mud

Each sampling location is determined for its EC (electrical conductivity) rate. Based on EC data, salinity rate can be known mathematically. The salinity of the bank of river water is relatively greater than of the middle of river. It is apparent because the river bank has smaller

stream mobility such that the dissolution of salts such as NaCl, MgCl, CaCl, NaCO₄, NaHCO₄, and KBr, and its effect on the salinity, are increasing. Temperature also influences the salinity. The riverbank area has relatively higher temperature because the adsorption of sunlight intensity by river surface is not changed. It is happening because the mobility of riverbank water is smaller such that the evaporation is relatively higher. However, the temperature at the middle of river is relatively smaller because the mobility of river stream is very high such that it may reduce the temperature of river surface, thus causing the lower rate of water evaporation as shown in Figure 2.



The salinity in the area of Aloo River which is approaching to the sea is increasing. However, the exception is occurring at points SA6 and SA7 where the salinity changes. At location SA6, the salinity is higher than SA7 because SA6 experiences the increase of dissolved salt. It is indeed the main cause of salinity increase. There are 7 main ions dissolved into water: natrium (Na), potassium (K), calcium (Ca), magnesium (Mg), chloride (Cl), sulfate (SO₄), and bicarbonate (HCO₃). Such increase is apparent because the area around the sampling location is mostly land for planting field rice. The accumulation of salinity in this rice area is triggered from fertilization. The fertilizer may contain macro and micro dry matters. The macro is Nitrogen, Phosphor, and Potassium, while the micro is MgO, Ca and S. Some of these dry matters are absorbed by the soil, while some others dissolve into waters. Dry matters such as Ca, K, Mg and S will increase EC rate in the waters such that the salinity can also increase

Lapindo Mud Content

The observed parameters in Lapindo Mud are physical and chemical parameters. The physical characterization involves texture and porosity. Chemical characterization is involving pH, KTK, humat acid, Pb rate, Cu rate, water content and Organic-C. The result of the characterization of Lapindo Mud is shown in Table 2.

Na	Parameter -		Sample Code			
No		А	В	С	D	
1.	Physical					
	- Weight (Cm.cm ⁻³)					
	1. Contents	1,25	-	2,35	-	
	2. type	1,3	-	2,34	-	
	- Porosity%	46,75	-	44,5	-	
	- Sand%	8	-	20	-	
	- Dust%	39	-	46	-	
	- Clay%	53	-	34	-	
	- Texture	Clay	-	Medium	-	
2.	Chemical	-		Clay		
	- pH 1:1			-		
	$1. H_2O$	6,9	-	7,0	-	
	2. KCl 1N	6,6	-	6,6	-	
	- KTK (NH ₄ OAC 1 N pH ; 7					
	Me/100g)	3,89	-	35,42	-	
	- Humic Acid %	Nd	-	Nd	-	
	- Pb (mg/Kg)	0,34	0,34	0,29	0,27	
	- Cu(mg/Kg)	0,83	0,85	1,31	0,83	
	- water content (%)	51,11	45,27	60,73	40,41	
	- C-Organik total (%)	54,75	55,47	54,82	55,02	

Tabel 2. Content of Lapindo Mud

^{*}Nd : not detectable

Physical parameter of Lapindo Mud is recognized from mass test showing that the mud is relatively heavy (from 2.34 to 2.35 cm.cm⁻³) because of its oxide content. The oxides of silica, calcium, natrium and potassium have great density which is then causing the heavy dense mud. Result of analysis over Lapindo Mud texture indicates that the composition of Lapindo Sample A is 8 % Sand, 39 % Dust, and 53 % Clay, while the composition of Lapindo Sample C is 20 % Sand, 46 % Dust, and 34 % Clay. The analysis over physical nature indicates that Lapindo Mud A has *clay* mud texture, while Lapindo Mud C has *clay loam* texture.

Result of analysis over the porosity of Lapindo Mud shows that the porosity of Lapindo Mud A is 46.75 %, while that of Lapindo Mud C is 44.5 %. It means that Lapindo Mud A has higher porosity rate than Lapindo Mud C because percentages of sand, dust and clay fractions are in balance at Lapindo Mud C. In addition, sand fraction is greater in Lapindo Mud C and therefore, it produces few sand pores. Few pores will narrow the touching surface such that the water touching ability is weakened. This condition makes air and water easily to go into and out of the mud, leaving few waters behind. It can be inferred that Lapindo Mud can attach some waters because the pore space percentage is very high in the mud such that it is easier for the water molecules to attach into the mud.

Chemical parameters of Lapindo Mud include heavy metal contents, KTK, pH, water content, and total organic carbon. Soil colloid with great negative load may capture high number of cation. This captured cation is exchangeable at certain pH. Therefore, the colloid

has cation exchange capacity (KTK-kapasitas tukar kation). Functional cluster in the mud/soil which is acting as cation exchanger is -COOH cluster with the contribution to cation exchange capacity (KTK) for 54 %. Phenol cluster also exists. Acetate and phenol clusters contribute to mud/soil KTK in the range of 85-90 %. In addition, COOH and phenol clusters, enol cluster (-COH-OH) and imida cluster (= NH) also provides significant contribution to soil KTK rate. In the Lapindo Mud, Pb and Cu metals clusters may attach with Lapindo Mud mineral particle which is attached by organic matters in Lapindo Mud, or is absorbed at Lapindo Mud metal oxides such as SiO_2 and alumina Al_2O_3 . Based on the Lapindo Mud characterization data, cation exchange capacity (KTK) is 34.89-35.42 Me/100 g. The cation exchange capacity in Lapindo Mud reflects the ability of Lapindo Mud in attaching heavy metal cation. KTK in Lapindo Mud is classified as high. This high rate leads to the greater levels of the organic matter and the organic mineral with its important function to absorb heavy metal in Lapindo Mud. Both organic matter and organic mineral have negative content which is easily neutralized by cations such as Pb^{2+} and Cu^{2+} such that Pb^{2+} and Cu^{2+} metal ions which are absorbed in the Lapindo Mud were also high resulting in very high concentration of Pb and Cu heavy metals. Indeed, pH rate of Lapindo Mud in Table 2 is from 6 to 7, thus remaining in the neutral category.

Result of analysis against some locations where Lapindo Mud sample is taken indicates that Cu rate in the sample of Lapindo A is 0.83 mg/kg, while that of Lapindo B, C, and D are 0.85 mg/kg, 1.31 mg/kg, and 0.83 mg/kg. Meanwhile, Pu rate in sample of Lapindo A is 0.34 mg/kg, while that of Lapindo B, C and D are 0.34 mg/kg, 0.29 mg/kg and 0.27 mg/kg. Cu concentration is greater than Pb in Lapindo Mud because the abundance of Cu in the earth crust is 50 mg/kg, while Pb is only 15 mg/kg [6] In such, the presence of Cu in the nature is relatively greater than Pb. The concentration of Pb and Cu at each proximate location is different because the squirt of Lapindo Mud has different depth. The decomposition process is different in the earth belly. One reason of stone decomposition is temperature. The greater depth of the mud is related to greater temperature in the earth belly such that the heavy metal content is also bigger.

Total organic carbon at Lapindo Mud can be ordered as follows: Lapindo A = 54.75 %; Lapindo B = 55.47 %; Lapindo C = 54.82 %; and Lapindo D = 55.02 %. Lapindo A and B are near Aloo River, while Lapindo C and D are near Porong River. The organic carbon source in the Lapindo Mud comes from the decomposition of plant remnant and dead animal when the mud inundates the rice field in the village. The organic carbon is buried in the soil and sediment in any forms such as leaf, twist and branch, as well as the decomposed matter likes humus [7]. An organic carbon possibly found is humat acid. However, result of analysis shows that humat acid is not presented in Lapindo Mud.

The presence of Pb and Cu heavy metals in Lapindo Mud is affected by physical absorption process in Lapindo Mud surface. Physical absorption is happening if there is adhesive force between adsorbents (in Lapindo Mud) due to Van der Walls force, or if there is interaction between dipoles at short-term hydrogen bond. The absorption of Pb and Cu depends on the acidity of solution (pH). At pH < 4.4, monomeric complex is established through electrostatic interaction with silica surface, while covalent dimeric complex of Pb and Cu on silica surface is made at pH > 6. Data of characteristic test against pH of Lapindo Mud show that pH is between 6 and 7, such that there is a bond between heavy metals and SiO₂. In the Lapindo Mud, this bond represents a covalent attachment which is establishing a dimeric complex. It seems that the effectiveness of SiO₂ in retaining Pb²⁺ and Cu²⁺ is very depending on the condition of the mud which contacts with SiO₂ surface.

The dissolution and mobility of metals in the environment is affected by metal absorption through some mechanisms. It covers an electrostatic interaction between positive loaded metal ions and mineral surface cluster. The direct chemical bonding of metal ions on the surface is established through the coordinative bond with surface ligands and the metal settlement on mineral surface. Complex compounds with electrostatic attachment are usually having weaker bonding than chemically-bonded complex compounds. Therefore, former compounds are easier to be transferred and dissolved in the solution. Meanwhile, settlement is very resistant to metal remobilization. If Lapindo Mud is removed into rivers, it is possible that Pb and Cu make a covalent bonding with SiO₂. This bonding is so mobile, thus possibly polluting the rivers.

The Relationship Between Total Organic Carbon and Heavy Metals in Lapindo Mud

The research is reviewing the relationship between the total organic carbon and the heavy metals in Lapindo Mud. This relationship is shown in Figure 3.

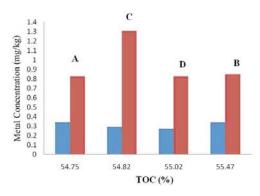


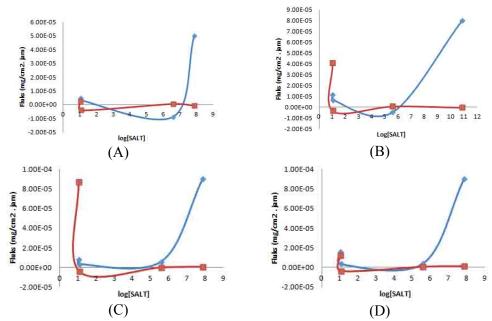
Figure 3. Relationship between TOC to lead and copper metal concentration in Lapindo Mud (Blue Pb, red Cu)

The diagram indicates that the highest Total Organic Carbon (TOC). The highest TOC rate is at Location B with 55.47 %, near Aloo River. A source of carbon containing in Lapindo Mud is coming from the decomposition of plant and animal. The organic carbon in Lapindo Mud remains in the form of humat and fulvat acids. Both acids are representing hydrophilic colloid. These acids have negative load because of a dissociation of functional clusters of –COOH and –OH [8]. The presence of these clusters –COOH and –OH allows the organic matter in Lapindo Mud to produce electrostatic bonding with metal ions such as Cu²⁺ and Pb²⁺.

In Figure 3, it is seen that at TOC = 54.75 %, Lapindo Mud A has Pb and Cu rates for 0.34 mg/kg and 0.83 mg/kg. At TOC = 54.82 %, Lapindo Mud C has Pb and Cu rates for 0.29 mg/kg and 1.31 mg/kg. At TOC = 55.02 %, Lapindo Mud D has Pb and Cu rates for 0.27 mg/kg and 0.83 mg/kg. At TOC = 55.47 %, Lapindo Mud B has Pb and Cu rates for 0.34 mg/kg and 0.85 mg/kg. Based on this data, it is summarized that TOC in Lapindo Mud is not surely increasing the presence of heavy metals within the mud [9]. The metal cation which is absorbed or bonded by soil particle is remaining in the form associated with metal oxide and/or with soil organic matter through absorption, complexing, and *chelation* mechanisms. The presence of metals is determined by the presence of metal oxide compound

in Lapindo Mud. The highest metal oxide in Lapindo Mud is SiO_2 with 53.08 % [1] The metals in Lapindo Mud have covalent bonding with SiO_2 and have electrostatic bonding with organic compound at –COOH and –OH clusters. These bonding are resulting in the presence of Pb and Cu heavy metals in Lapindo Mud.

It is said that Cu has highest rate (content) compared to Pb. It also seems that organic carbon in Lapindo Mud tends to attach Cu than Pb. Greater concentration of Cu than P is because Cu ionic radius is smaller than Pb, which is precisely 74 pm for Cu and 108 pm for Pb. The greater atomic radius of the metal will reduce the strength of metal bonding. Therefore, it is not surprising to find small concentration of Pb in the mud.



The Relationship Between Metal Flux and Salinity at Aloo River

In Figure 4, Pb and Cu fluxes in Lapindo Mud A, as contacting with waters in Aloo River, can be explained as follows. The highest Pb flux is $5x10^{-5}$ mg/cm².hour and found at AL site in rate of Log [SALT] of 7.86 psu. At SA1 site, Log [SALT] is 1.03 psu with flux of $5x10^{-6}$ mg/cm².hour. At SA2 site, Log SALT is 1.06 psu where Pb flux is decreased. At APY site, Log SALT is 6.59 psu where Pb flux is decreased again. The metal flux increases at AL site with Log SALT of 7.86 psu. It means that the increased salinity improves Pb flux in Lapindo Mud A. The flux trend for Cu at SA1 to SA2 sites is decreasing, while at APY and AL sites, this trend is decreasing.

Lapindo Mud B, which contacts with the waters of Aloo River, shows some conditions. At SA1 and SA2 sites, Pb flux decreases, so does at APY site. At AL site, Pb flux increases again. The trend of Cu flux from SA1 to SA2 sites is decreasing, while at APY and AL sites, this trend is decreasing.

For Lapindo Mud C, which contacts with Aloo River, there is a significant flux trend. From SA1 to SA2 sites, Pb flux decreases but increases at APY and AL sites. Meanwhile, Cu

flux from SA1 to SA2 sites is decreasing, but decreasing at APY site and increasing again at AL site.

For Lapindo Mud D which is contacted with Aloo River, it has also distinctive flux trend. From SA1 to SA2 sites, Pb flux is decreasing, but increasing at APY and AL sites. Moreover, Cu flux trend is decreasing from SA1 to SA2 sites, but decreasing at APY and increasing again at AL site.

The flux rate of heavy metals that diffuses from mud into river water is positive (+) because the metal concentration in the river water is increasing. In contrast, the flux rate of heavy metals that diffuses from river water into mud is negative (-) because the metal concentration in the river water is decreasing. Such condition is happening because pH of river water is neutral, which is about 6 to 7. At fresh water with low salinity, the ion affecting the metal dissolvability is bicarbonate ion, or HCO⁻₃, while at brackish water and salt water with high salinity, the influential ion is Cl⁻ ion. At freshwater with low salinity, metal fluctuation is positive (+) because bicarbonate ion will increase the dissolvability of heavy metal, and therefore, the heavy metals are always in the dissolvable form. At brackish water and salt water with high salinity, metal fluctuation is negative (-) because the presence of Cl⁻ chloride ion stimulates the establishment of settlement and heavy metal complex. Therefore, the dissolvability of the metal is decreased. A complex compound of heavy metals tends to have a bonding with organic compound in Lapindo Mud. It is then reasonable to see the presence of heavy metals in Lapindo Mud.

CONCLUSION

- The characteristic of Lapindo Mud shows some indications. Specific weight of the mud is 1.25-2.35 cm.cm⁻³. The clay and dust contents are 34-35 % and 39-46 %. Lapindo Mud texture is clay loam species. The pH of the mud is between 6.6 and 7, with KTK of 3.89-35.42 Me/100g, Pb rate between 0.27 and 0.34 mg/L and Cu rate between 0.83 and 1.31 mg/L. Humic acid is not identified. Water content is 40.41-60.73 %, while total organic carbon is 54.75-55.47 %.
- 2. The highest Cu flux is found at SA1 site in Lapindo Mud which contacts with Aloo River at fresh water region. The highest Pb flux is apparent at AL site in salt water region. Of both metals, the highest flux is shown by Cu in the range from 2.3x10⁻⁶mg/cm².hour to 8.71x10⁻⁵mg/cm².hour and the highest flux is shown by Pb in the range 5x10⁻⁵mg/cm².hour to 9x10⁻⁵mg/cm².hour.
- 3. The organic matter content in Lapindo Mud is not surely increasing the concentration of heavy metals in Lapindo Mud because there is also oxide compound of metals in Lapindo Mud with the role of increasing the concentration of heavy metals in Lapindo Mud. If the organic content and metal oxide content are high, then the concentration of metals in Lapindo Mud is also higher such that the heavy metal content released into waters is also greater.

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