Determination Of Heavy Metals (Pb, Zn, Cd, Cu) of Coastal Urban Area of Semarang Indonesia

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Abstract. This research aimed to determine the concentrations of heavy metals (Cu, Zn, Pb, Cd) pollutants in coastal sediment, Semarang. This research would be conducted in 2017 with the location of sampling and water quality measurement conducted at Usman Janatin Street, Semarang. The sample analysis would be conducted at the Diponegoro University Integrated Laboratory. In this research was focused on deep and width. According to some previous studies such as study done by Mancuso and Green (2010) that stated the TAL metals analysis results gave a wide scope of the concentration of metals in coastal urban area. Based on the analysis and result, the conclusion as follows: There was relationship between levels of heavy metals and external environment. The relationship was positive, it means the higher levels of heavy metals, the external environment would be more polluted. The lower levels of heavy metals, the external environment would be low polluted. The internal levels of coastal sediment could be used as an index to infer the state of the environment. This heavy metals determination tool could be used to support policy and decision-making.

Keywords: **Pb; Zn; Cd; Cu**

1. Introduction

Nowadays, there is increasing development among industries sectors and another sectors, whereas in urban area and rural area. The consequences of this situation or conditions, so in the urban areas, this come with the higher rate of urbanization. These things also make the increasing activities of housing, industry and another operational sectors. The negative impact of these things are the higher waste or garbages. As we know, the waste can be solid waste or municipal waste. Waste or the solid waste can be divided as organic and inorganic waste. This arises from human activities and this waste must be managed well so the environment cannot endanger. According to data, the municipal waste condition has been the majority of proportion or composition from organic waste.

In the last decades, in Indonesia the heavy metals is the major problems because the heavy metals can accumulate in waters and not biodegradable [1]. Heavy metals are very dangerous and the heavy metals can pollute the environment include mercury, lead (Pb), arsenic (As), cadmium, chromium and nickel that dangerous for human and animals [2]. Increased levels of heavy metals in water will result in heavy metals originally required for various metabolic processes may turn toxic and cause toxic effects on the biota [7].

Based on the background above, so this research will analyze about the determination of heavy metal (Pb, Zn, Cd, Cu) of coastal sediment in urban Semarang, Indonesia. The objective of this study to determine the concentrations of heavy metals (Cu, Zn, Pb, Cd) pollutants in coastal sediment, Semarang, create a statistical model based on the result of test that will be obtained from coastal sediments samples, and to make permit statements about pollution and change that occurs on the state of the environment in the urban catchment, creating database on pollution control in the region and in the future to maintain biodiversity (to give the industrial activities-pollution permits-by official bodies for the protection of the environment in the state).

The benefit of this research is to find out the efforts in realizing low carbon development or low carbon communities in the development process.

2. LITERATURE REVIEW

2.1. Heavy metal

As we know, the heavy metals can be defined as the metal group that have the same criteria as the other metals. These heavy metals can be live in the living life.

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2.2. Heavy Metal Characteristics

Naturally heavy metals exist throughout nature, but at very low levels. The origin of heavy metal ingredients into the waters is naturally divided by three, namely (a) coming from the coast including rivers and the erosion by wave and weathering of rocks, (b) coming from oceans resulting from volcanic activity in the sea, and) [6].

2.3. Marine pollution by Heavy Metal

[3] defines that pollution or pollution is a condition that has changed from the original form to a worse state. "Shifting form from the original form to this bad condition can occur as a result of the entry of pollutants or pollutants. Pollutants have toxic forces that can create adverse conditions from their original conditions, thus triggering pollution. "

2.4. Heavy Metal Resources in the Waters

"Heavy metals which are initially dissolved in river water are adsorbed by fine particles (suspended solids) and by the flow of river water is brought to the estuary. River water meets the tidal flow at the mouth of the river, so that fine particles settle in the mouth of the river. This is what causes the levels of heavy metals in the sediment estuary to be higher than the high seas".

2.5. The Influence of Heavy Metals to aquatic Organisms

Elements of heavy metals can enter into the body of marine organisms through food chains, gills, and diffusion through the skin surface. Heavy metals can accumulate in the body of the organism and will remain in the body for a long time as the accumulated poison [3]

2.6. The Effect of Heavy Metal on Humans

In addition to the negative effects of heavy metal toxicity, the most important and the main concern is its effect on humans. Several cases of metal poisoning in humans have been widely reported, so there is a special name against certain metal poisoning, for example in Japan, namely: "minamata disease" due to methyl mercury poisoning, "itai-itai disease" due to poisoning Cd acute poisoning from harmful metal It usually occurs in people who consume foods containing metals or because of the effect of drug administration [8].

3. METHODOLOGY

3.1. Location and Period

This research will be conducted in 2017 with the location of sampling and water quality measurement conducted at Usman Janatin Street, Semarang. The sample analysis will be conducted at the Diponegoro University Integrated Laboratory.

Figure 1.Location Research Detailed (Usman Janatin, Semarang)

- A= 0
- B= 100 meter from A
- C= 100 meter from B
- D= 100 meter from C
- E= 100 meter from D
- F = Ocean 1 (100 meter from E)
- G = Ocean 2 (100 meter from F)

3.2. Variables

3.2.1. Dependent Variables

1. Deep and Width

In this research will focused on deep and width. According to some previous studies such as study done by Mancuso and Green (2010) that stated the TAL metals analysis results gave a wide scope of the concentration of metals in the soil sample locations.

3.2.2. Independent Variables

1. Location: Usman Janatin Street, Semarang in five location, that are A,B,C,D, E, F and G. Location A will be mark as 0 point, location B is 100 meter from A, location C will be 100 meter from B, location D will be 100 meter from C, location E will be 100 meter from D, location F will be 100 meter from E, location G will be 100 meter from F.

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2. Lead(Pb)

Lead (Pb) is a bluish-white metal with a bright jet. It is very soft, easy to form, ductile, and not a good electrical conductor.

3. Zinc(Zn)

Zinc is a bluish-white metal, a metal that is easy to forge and tough at temperatures between 110-1500C.

4. Cadmium(Cd)

Metal Cd is found in rocks calamine (zinc carbonate). Cadmium name itself is taken from the Latin name "calamine" is "cadmia".

5. Cupper(Cu)

In general, the entry of Copper into the environmental order can occur naturally and can also be non-natural. Naturally, copper enters into the environmental order as a result of various natural events.

6. Fish

In this research also add fish and muscles as the samples, that are 3 kinds ocean fish and 3 kinds of fresh water fish.

3.3.Sampling and Handling of Sediment Samples

Cutting of samples starting from the surface of the sample on the thickness of 0-2 cm, 9-11 cm and 18-20 cm [4]

Figure 2. Handling of Sediment Samples

1. Measurement of Water Quality Parameters
2. Analysis of sediment samples
3. Analysis of Heavy Metals in Sediments
4. Total Heavy Metal Content

3.4.Data Analysis

The data obtained are presented in the form of tables, graphs and compared with a predefined

quality standard. Water quality data compared to seawater quality standard for marine biota based on Ministry of Environment Decree No. 51 of 2004 Attachment III. The content of heavy metals of Pb and Cd in sediments is compared with the standards of quality of the Australian and New Zealand Environment and Conservation Council (ANZECC), Netherlands, National Oceanic and Atmospheric Administration (NOAA); Swedish Environmental Protection Agency (SEPA). The standard standard of heavy metals Pb and Cd can be seen in Table 1.

Table 1.Standard quality standards of heavy metals Pb, Zn,Cd, Cu in sediments

Heavy Metals in Sediments (mg / kg)	Quality standards
Lead (Pb)	ANZECC ISQG-Low (50 mg/kg) Netherland (85 mg/kg) NOAA 218 ppm SEPA year 2000 (≤ 50 - Class 1- very low)
Zinc (Zn)	ANZECC ISQG-Low (200 mg/kg)
Cadmium (Cd)	ANZECC ISQG-Low (1.5 mg/kg) Netherland (0.8 mg/kg) NOAA 9,6 ppm SEPA year 2000 (≤0.8 - Class 1- very low)
Cupper (Cu)	ANZECC ISQG-Low (65 mg/kg) Netherland (35 mg/kg) SEPA year 2000 (25-100 - Class 3- moderate high conc.)

4. RESULT AND ANALYSIS

After make experiment, in 7 location, so the result as follows:

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Table 2. Heavy Metals Sedimentation in 7 Locations

Deep (m)	Heavy Metals			
	Pb (ppm)	Zn (ppm)	Cd (ppm)	Cu (ppm)
Location A:				
2	0,054	0,107	<0.001	0,485
4	0,043	0,101	<0.001	0,312
6	0,022	0,006	<0.001	0,224
Location B:				
2	0,115	0,143	<0.001	0,556
4	0,095	0,128	<0.001	0,342
6	0,023	0,106	<0.001	0,102
Location C:				
2	0,19	0,067	<0.001	0,303
4	0,104	0,055	<0.001	0,223
6	0,009	0,043	<0.001	0,106
Location D:				
2	0,012	0,115	<0.001	0,347
4	0,01	0,102	<0.001	0,225
6	0,005	0,008	<0.001	0,194
Location E:				
2	0,146	0,147	<0.001	0,039
4	0,102	0,122	<0.001	0,022
6	0,004	0,103	<0.001	0,014
Location F:				
2	0,113	0,05	<0.001	0,025
4	0,102	0,034	<0.001	0,012
6	0,007	0,012	<0.001	0,008
Location G:				
2	0,056	0,03	<0.001	0,013
4	0,044	0,012	<0.001	0,01
6	0,02	0,008	<0.001	0,009

From Table 2. It can be said that Cu at location A is the highest sedimentation level than Pb and Zn. While Cd is the lowest because <0.001mg /

l. At a depth of 2 meters the level of heavy metals shows the highest level of 4 meters deep and 6 meters is the lowest. The thickness of the heavy metal to the 6 meters will deepen and the lower the pollution especially for Pb. Zn at location A is lower than 4 meters and 2 meters. For Cd there is no difference because it has the same number of all.

In Location B Cu is the highest sedimentation level than Zn and Pb. While Cd is the lowest because <0.001mg / l. At a depth of 2 meters the level of heavy metals shows the highest level of 4 meters deep and 6 meters is the lowest. For the lowest Pb (0.0023) is at 6 meters and the highest (0.115) is at 2 meters. Zn in the dominant heavy metals that found in Semarang.

In location C the Cu is the highest levels of sedimentation rather than Pb and Zn. Pb is the second highest levels of heavy metals and the third rank is Zn. Meanwhile Cd is the lowest one because < 0.001mg/l. In the deep 2 meters the levels of heavy metals showed the highest levels rather than the deep 4 meters and 6 meters is the lowest.

In location D the Cu is the highest levels of sedimentation rather than Zn and Pb. Zn is the second highest levels of heavy metals and the third rank is Pb. Meanwhile Cd is the lowest one because < 0.001mg/l. In the deep 2 meters the levels of heavy metals showed the highest levels rather than the deep 4 meters and 6 meters is the lowest.

In location G the Pb is the highest levels of sedimentation rather than Zn and Cu. Zn is the second highest levels of heavy metals and the third rank is Cu. Meanwhile Cd is the lowest one because < 0.001mg/l. In the deep 2 meters the levels of heavy metals showed the highest levels rather than the deep 4 meters and 6 meters is the lowest.

The number of Pb because it is more widely used by manufacturing companies in Usman Janatin Street. The highest Pb content is in location C and location E, because in Usman Janatin road at location C and E is 100 meters and close to the population, a lot of fiber there is waste of factory waste.

Table 3. Fresh Water and Ocean Fish in Different Depth

Fish	Sample	Cu (ppm)	Zn (ppm)	Cd (ppm)	Pb (ppm)
Fresh Water	Gouramis	2,57	10,98	<0,01	2,66
	Cat Fish	1,38	10,59	<0,01	1,3

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	Tiger barb	3,15	2,5	0,17	2,32
Ocean	Red Snapper	<0,005	12,35	0,125	2,5
	Tuna	1,89	7,27	0,435	3,14
	Cod	<0,005	7,12	0,014	5,72

From the Table 3. it can be said that the fresh water fish (Gouramis, catfish and tiger barb) including in the area that fulfilled by Cu, Zn and Pb. The highest is Zn in this area. From the Table 4.2. it can be said that the ocean fish (Red snapper, tuna and cod) including in the area that fulfilled by Cu, Zn and Pb. The highest is Zn in this area. For water type in fresh water for Cu content has a value below the standard of 3.15, for Zn has a value of 12.35 which is still below the standard, for Cd has a value of 0.434 which means still below the standard, and Pb also has a value dibawah standard 5.75. When Cu falls into 3.15 then many tigerbarb live there. For the highest Zdungan Zn (12,35) many red snapper fish. For Cd when the highest content of 0.434 lots of fish una live there, while for Pb when entering the highest number of 5.72 many cod live there. Gurmai can survive in high BP while tigerbarb can survive in high Cu.

4.1. The relationship between levels of heavy metals and external environment

The average Pb metal content vertically shows a value that is not much different between the sediment layers. The highest average metal content of Pb was found in the top layer 2 meters deep and lowest in 6 meters deep. The high content in the upper layer, suspected because the top layer of sediment directly related to pollution inputs derived from activities around the water. The high content of heavy metal Pb at the bottom layer of sediment sampling was suspected due to the high dominance of the influence of the ballast water input derived from the shipping activity, related to the position of the sampling point A Location in which is the center of the voyage both locally and internationally. Increasing industrial activity around these waters, making the shipping activity also higher, in the end the entry of metal into the waters will vary, depending on the pattern of current and time at the deposition of ballast water containing heavy metals.

The relationship between the leacy metal level with the external environment as follows, the deeper in the sea, so will affect the lower level of sedimentation and the more far away from the coastal region indicated the lowest sedimentation.

4.2. The internal levels of coastal sediment be used as an index to infer the state of the environment

The river flow affects the increase of the number of parcels of water column and sedimentation caused by the erosion of land and wastes that are transported and carried to the estuary by the river. The concentration and vertical distribution of metals in sediments can be controlled by various factors such as particle size (granulometric composition), sediment mineral composition, carrier (eg hydroxide, carbonate, sulphide), sediment surface area, organic matter content, individual and Eh combined and pH, and other factors. The efficiency of various factors that affect the bonding and enrichment of heavy metals in sediments depends on the sedimentation environment, which is characterized by chemical composition, salinity, pH, redox potential and hydrodynamic conditions [5]. The internal levels of coastal sediment be used as an index to infer the state of the environment because the lower level of coastal sediment it will affect the state to make better environment and lower pollutions.

4.3. The heavy metals determination tool be used to support policy and decision-making

According to [5], the metals in the sediments can be in various forms and bonds, inter alia, as free ions and binding to carbonates, this form of metal is called a highly volatile metal that is easily released into the waters and easily absorbed by the organism (bioavailable). Metals can also bind to the Fe / Mn oxide and are referred to as reducible forms. The results of monitoring data should also be processed in a good database and standard format, given the many environmental problems that exist require speed in the process of searching files and the process of updating or adding data. The development of technology, monitoring process can be done on line or directly, especially in areas or areas that are considered critical and need continuous monitoring. Measurements on line monitoring can be done regularly at specified intervals or during critical events where the parameters measured far exceed the standard set. The results of monitoring data are very useful for evaluation of activities or programshas been and is running, whether there is improvement of environmental conditions or not. For example, on

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a stream that is being carried out the net program is measured in its initial condition, after the program has completed whether any improvements can be seen from the results of monitoring whether there are significant changes from the implemented program.

5. Conclusion

Based on the result and analysis, the conclusion in this research as follows:

1. There is relationship between levels of heavy metals and external environment. The relationship is positive, it means the higher levels of heavy metals, the external environment will be more polluted. The lower levels of heavy metals, the external environment will be low polluted.
2. The internal levels of coastal sediment can be used as an index to infer the state of the environmet.
3. This heavy metals determination tool can be used to support policy and decision-making

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