Determination of Heavy Metals (Pb, Zn, Cd, Cu) in Coastal Sediments and Fish 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, to create a statistical model based on the result of test that would be obtained from costal sediments samples, to make permite 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). 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 et al. 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: Heavy metals; Coastal sediments; Urban area; Indonesia

Introduction

In line with the increasing pace of development in all sectors in the current and future conditions in urban areas, has triggered an increase in the rate of urbanization. The logical consequence of all this is the increase in urban activity in various sectors, both housing, industry, trade and other sectors. One of the impacts of such activity is solid waste or garbage. Waste is a solid waste comprised of organic or inorganic materials from residues or residues arising from human activities that are deemed to be useless and must be managed in order not to endanger the environment and protect development investment. In general, municipal solid waste conditions exhibit characteristic characteristics. Municipal waste condition has the largest composition of organic waste with an average value of 79.164%, while inorganic waste is only 20.836% with standard deviation of 9.5%. Over the past few years water pollution by heavy metals has become a worldwide problem including in Indonesia, because heavy metals are indestructible and can accumulate in waters [1]. Heavy metals that are dangerous and often pollute the environment include mercury (Hg), lead (Pb), arsenic (As), cadmium (Cd), chromium (Cr) and nickel (Ni) [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 [3]. Cd or cadmium metal (cadmium) has a molecular weight (BM) of 112.4 with white: white, bluish-shiny, solid and odorless. The use of Cd is generally as a stabilization. The utilization of Cd and its compounds is used as dyestuff, battery industry, photography world of cadmium bromide and cadmium ionide compounds, tetraethyl-Pb manufacture, polyvinyl chloride (PVC) manufacturing industry [4]. Cd can enter the body through inhalation and digestion. The heavy metal content in the waters can reduce the diversity of aquatic species and cultivated productivity. In addition, the consumption of cultured fish that has been contaminated will cause human exposure to heavy metals. Previous studies have shown that Cd metal can cause italite and Pb metals to decrease hemoglobin synthesis, impaired renal function, joints, reproductive and cardiovascular systems and damage to the central and peripheral nervous system [5,6].

Heavy metals can move from environment to organism and from one organism to another through the food chain. The heavy metals that exist in the waters, will someday drop and settle on the bottom of the waters, forming sedimentation and this will cause marine biota to find food in the bottom waters such as shrimp, shellfish and crabs will have an enormous opportunity for contaminated heavy metals. If the marine biota that has been contaminated by heavy metals are consumed in a certain period of time, it can be a toxic substance that will poison the body of living things [4]. The toxicity of heavy metals in the marine environment has become a major concern because it has a high potential risk for a number of flora and fauna, including humans, through the food chain [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.

Research questions

- What is the relationship between levels of heavy metals and external environment?
- Can the internal levels of coastal sediment be used as an index to infer the state of the environmet?

- Can this heavy metals determination tool be used to support policy and decision-making?

Research objectives

The objective of this study as follows:

- 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 costal sediments samples.
- To make permite statements about pollution and change that occurs on the state of the environment in the urban catchment, creating databae 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).

Benefit of the study

- For the development of environmental sciences to be able to know and examine more about the heavy metal content that is around the coast of Semarang city.
- For researchers is to contribute literature on heavy metals (lead Pb, zinc Zn, cadmium Cd, copper Cu).
- For the government to determine heavy metal (lead Pb, zinc Zn, cadmium Cd, copper Cu) on sediment beach in urban Semarang, Central Java Indonesia.

Literature Review

Heavy metal

Heavy metals still belong to the metal group with the same criteria as the other metals. The difference lies in the effects it produces when these heavy metals enter or are fed into living organisms. The term heavy metal has been widely used, especially in scientific libraries, as an element that describes the shape of a particular metal. Characteristics of heavy metal groups are as follows:

- Has a very large gravitation specification (more than 4).
- Has atomic number 22-23 and 40-50 as well as lactanide and actinide elements.
- Having a specific (specific) biochemical response to living organisms.

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) Comes from the atmosphere in the form of particles or dust that fall into the sea [8]. The concentration of heavy metal elements in sea water ranges from 10-5-10-2 ppm. Under these conditions, heavy metals are required by the organism for growth and development in life. This concentration will increase when urban, agricultural and industrial wastes containing heavy metals enter into marine waters and settle to the bottom of the waters which eventually become toxic to marine organisms [9]. According to Rahman et al. [10] the meaning of heavy metals are elements with atomic numbers 22 to 92 and lie in periods 3 to 7 in the periodic system. The heavy metal element is an element having a density greater than 5 g/cm^3. Hg has a density of 13.55 g/cm^3. Among all heavy metal elements, Hg ranks first in terms of toxicity, compared with other heavy metals, followed by heavy metals such as Cd, Ag, Ni, Pb, As, Cr, Sn, Zn.

Marine pollution by heavy metal

Palar et al. [4] defines that pollution or pollution is a condition that has changed from the original form to a worse state. The shifting of the shape form from the original form to these adverse conditions can occur as a result of the entry of pollutants or pollutants. Pollutants have a toxic power that can create a bad state of the original condition, thus triggering the occurrence of pollution. Notohadiprawiro et al. [11] said that Pollution of heavy metals Pb and Cd is one of the various kinds of heavy metal pollution that many found in big cities. Metal Pb and Cd can enter the waters naturally by crystallization, in the air with the help of rain water and from human activities such as through industrial waste associated with Pb and Cd. The most important source of Pb in the environment is motor vehicle wastewater. Cd sources are widely available in the dyeing, photography and electroplating industries.

Heavy metal resources in the waters

The heavy metals which were originally dissolved in the river water adsorbed by the fine particles (suspended solid) and by the flow of river water carried to the estuary. The river water meets the tidal stream at the mouth of the river, so that the fine particles settle in the mouth of the river. This is what causes heavy metal levels in the estuary sediments higher than the high seas. In general, the estuary of the river undergoes sedimentation process, where the metal is difficult to dissolve the dilution process that is in the water column over time will come down to the bottom and settle in the sediment. The high metal content can be seen from the base pH value (pH=7.40-8.59) at the location where the metal is difficult to dissolve and settles to the bottom of the water [12].

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 [13]. According to Amin et al. heavy metal pollution of the marine environment is closely linked to the essential and non-essential use of metals by humans that are naturally found in marine environments, but they are generally below the threshold value that endangers organism life Increased levels of heavy metals in seawater will result in heavy metals originally required for various metabolic processes will turn into toxins for marine organisms. In addition to turning into heavy metal toxins that will accumulate in sediments and biota through the process of gravity, bioconcentration, bioaccumulation and biomagnification by marine biota. Increased levels of heavy metals in continuous seawater will be followed by increased levels of heavy metals in the biota bodies within the environment [12].

One example of research conducted by Nurrachmi et al. [14] about the bioaccumulation of metal Cd, Cu, Pb and Zn on some parts of fish body gulama (Sciaena russelli) in Dumai waters, obtained the result that the metal content entering the fish body, distributed to all parts of the body through the gills. Gill organs are the body parts of fish that have the highest heavy metal content for all metals, because the gills

are the active and passive exchange organs that occur between the fish and its environment. Heriyanto et al. [15] says that in general the largest accumulation of magnesium (Mg) in the leaves and roots, zinc (Zn) accumulates on the root and leaves, cadmium (Cd) on the leaves and roots, while arsenic (As) on the leaves and Mangrove stems close to the source of pollutants. Content of pollutant Mg biggest accumulated on shrimp that is equal to 82.63 ppm, fish blanak equal to 60.30 ppm. The accumulation of Mg on shrimp is larger (ten times) than that of shrimp found in Alas Purwo National Park (TNAP), the content of Mg contaminant in fish blanak 4.5 times larger in Cilacap compared with TNAP.

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. This usually occurs in certain groups of individuals or individuals. But on the chronic toxicity caused by people who consume a small amount of metal but lasts longer, it usually occurs in the community or residents living in a polluted environment [16].

Heavy metals directly or indirectly harm human beings, such as Pb can lead to inhibition of hemoglobin formation system (Hb) causing anemia, depending on the central and peripheral nervous system, kidney system, reproductive system, idiot in children, convulsions (epilepsy) Skeletal defects and damaging somatic cells [16]. Although the amount of Pb absorbed by the body is small, this metal turns out to be very dangerous. This is because Pb compounds can have toxic effects on many organs contained in the body [13].

Previous study

Jenyo et al. stated that Rapid urbanization and industrialization in developing countries have been associated with product ion and deposition of hazardous wastes in aquatic environments. Heavy metals are major components of these wastes which have been implicated in several metal-related diseases and food poisoning in man. This study evaluated iron, lead, cobalt, nickel, chromium and cadmium concentrations in water, sediment, Nile Tilapia (*Oreochromis niloticus*) and African river prawn (*Macrobrachium vollenhovenii*) samples of Lake Asejire, Oyo State, Nigeria. The concentration of these metals was determined spectrophotometrically in three locations along the course of the lake. Results revealed that only iron and lead were detected in water samples. However, all the metals were found in sediments, Nile Tilapia and African river prawn. Iron had the highest mean concentrations (mg kg^{-1}) of 2.392 ± 0.015, 7.4314 ± 1.184, and 1.6100 ± 0.099 in sediments, fish and prawn respectively. Significant differences was found across each sample type for the metals determined. The detection of these metals in Lake Asejire call for close environmental monitoring and adequate public awareness. This is necessary to discourage further pollution which could lead to high metal concentration and metal poisoning.

Herngren et al. [17] stated that Road-deposited sediments were analysed for heavy metal concentrations at three different land uses (residential, industrial, commercial) in Queensland State, Australia.

The sediments were collected using a domestic vacuum cleaner which was proven to be highly efficient in collecting sub-micron particles. Five particle sizes were analysed separately for eight heavy metal elements (Zn, Fe, Pb, Cd, Cu, Cr, Al and Mn). At all sites, the maximum concentration of the heavy metals occurred in the 0.45-75 μm particle size range, which conventional street cleaning services do not remove efficiently. Multicriteria decision making methods (MCDM), PROMETHEE and GAIA, were employed in the data analysis. PROMETHEE, a non-parametric ranking analysis procedure, was used to rank the metal contents of the sediments sampled at each site. The most polluted site and particle size range were the industrial site and the 0.45-75 μm range respectively. Although the industrial site displayed the highest metal concentrations, the highest heavy metal loading coincided with the highest sediment load, which occurred at the commercial site. GAIA, a special form of Principal Component Analysis, was applied to determine correlations between the heavy metals and particle size ranges and also to assess possible correlation with Total Organic Carbon (TOC). The GAIA-planes revealed that irrespective of the site, most of the heavy metals are adsorbed to sediments below 150 μm. A weak correlation was found between Zn, Mn and TOC at the commercial site. This could lead to higher bioavailability of these metals through complexation reactions with the organic species in the sediments.

Singh et al. [18] stated that The objective of the study is to reveal the seasonal variations in the groundwater quality with respect to heavy metal contamination. To get the extent of the heavy metals contamination, groundwater samples were collected from 45 different locations in and around Goa mining area during the monsoon and post-monsoon seasons. The concentration of heavy metals, such as lead, copper, manganese, zinc, cadmium, iron, and chromium, were determined using atomic absorption spectrophotometer. Most of the samples were found within limit except for Fe content during the monsoon season at two sampling locations which is above desirable limit, i.e., 300 lg/L as per Indian drinking water standard. The data generated were used to calculate the heavy metal pollution index (HPI) for groundwater. The mean values of HPI were 1.5 in the monsoon season and 2.1 in the post-monsoon season, and these values are well below the critical index limit of 100.

Widianarko et al. [19] stated that Elevated environmental concentrations of metals are usually associated with the impact of urbanization. The present study is focused on metal contamination in urban sediments. A field survey was carried out to determine the distribution of four metals, i.e., cadmium (Cd), lead (Pb), copper (Cu), and zinc (Zn), in the coastal urban area of Semarang, Central Java, Indonesia. Sediment samples were collected from 101 grids of 2]2 km. To map the spatial distribution of these metals, concentrations of each metal were plotted against the corresponding grid coordinate. Cd was below the detection limit ((0.03 lg/g) in all samples, whereas concentrations of Pb, Zn, and Cu fell into a wide range. Frequency distributions of Pb, Zn, and Cu concentrations indicated a similar pattern, in which the major proportion of the sites had a low metal concentration. Some sites, however, had extremely high metal concentrations, Zn up to 1257 lg/g, Pb up to 2666 lg/g, and Cu up to 448 lg/g. The data were used to define background concentrations for sediments in coastal zones of Indonesia (99 reference values::). The proposed reference values are 25.6 lg/g, 132.2 lg/g, and 40.7 lg/g, respectively, for Pb, Zn, and Cu. The degree of metal contamination of each individual site was classified according to the calculated value of a combined pollution index, W. Four categories of the degree of metal contamination were proposed, i.e., unpolluted, slightly polluted,

polluted, and heavily polluted. Based on this classification, from 101 sites investigated in the greater Semarang area, 51 are unpolluted, 36 slightly polluted, 9 polluted, and 5 heavily polluted.

Abdulrahman et al. [20] stated that study was carried out at fish laboratory of Animal Production Department, Faculty of Agricultural Sciences, University of Sulaimaniya using commercial dry yeast in three concentration (0%, 3%, and 5%) for 12 weeks to study their effects on concentration of some heavy metals (namely Cr, Cd, Co, Pb, Cu, Fe, Zn, and Mg) of common carp fingerlings (*Cyprinus carpio*). The experiment was included three treatments each in three replicates (plastic tanks) in which 10 fingerlings common carp of the same size and average weight (3.5 gram) were stocked in each aquarium. The actual experimental feeding trials lasted three months. Results indicated that the concentrations of heavy metals differ among the treatments.

Hervé et al [21] stated that was undertaken to evaluate the heavy metals contamination of copper, zinc, manganese, iron, chromium, nickel, lead and cadmium, to assess the environment quality of the coastal area from town activities. Nickel, lead and cadmium are used in different kind of current accumulators and they are dangerous for sea wild life and for human food resources. The five others metals are usual and at a high concentration they are able to threat environment system. Six samples had been choice at two town of Madagascar north-western coast: Nosy Be and Mahajanga, in February, 2007. These sampling points stand in front of each mean sewage mouths in each locality. Tables 1 and 2 give us same descriptions of each sampling points. These two sampling area are among the principal fishing area of Madagascar. Three kinds of analytical method were used for metals determination and quantification: flame spectrophotometer atomic absorption, UV spectrophotometer, and voltammeter method. The flame spectrophotometer atomic absorption gives the best result by testing with certified reference materiel. Our data suggested that Mahajanga's stations have higher values of admium (1 mg/kg) and lead (91 mg/kg) than the non-contaminated sediments. However, the concentrations of other metals such as copper, zinc, manganese, iron and chromium in Nosy Be sediments, were twice as higher than in those of Mahajanga. In compiling our data obtained at the same stations in the vertical water column, we would like to confirm the growing order of potential absorption between metals and sediments, nickel, copper, cadmium and lead. According to the results of determinations, we suggested that more determination should have done in open sea to assess metals in a wide scale.

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.)

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

Methodology

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).

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).

Variables

Dependent Variables-Deep and Width: In this research will focused on deep and width. According to some previous studies such as study done by Mancuso et al. that stated the TAL metals analysis results gave a wide scope of the concentration of metals in the soil sample locations. The main metals focused on were aluminum, calcium, magnesium, and mercury. It was predicted that trends would show correlation between magnesium, calcium, and aluminum. Aluminum characteristically increases with depth and calcium and magnesium decrease.

Park et al. statet that the root growth of transgenic lines was better than that in the wild-type plant under heavy metal stress (for Cd, Pb, and Zn). In particular, the transgenic lines showed enhanced Pb tolerance in a wide range of Pb concentrations. Furthermore, the Pb and Zn content in the shoots of the transgenic lines were higher than those in the wild-type plant. These results suggest that overexpression of $CsHMA_3$ might enhance Pb and Zn tolerance and translocation. Also, the transgenic lines displayed a wider leaf shape compared with the wild-type plant due to an induction of genes related to leaf width growth and showed a greater total seed yield compared to the wild type under heavy metal stress.

Independent variables

- 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.
- 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.
- Zinc(Zn): Zinc is a bluish-white metal, a metal that is easy to forge and tough at temperatures between 110- 150°C.
- Cadmium(Cd): Metal Cd is found in rocks calamine (zinc carbonate). Cadmium name itself is taken from the Latin name "calamine" is "cadmia".

- 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.
- 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.

Sampling and handling of sediment samples

Sediment sampling is done once on each station using gravity core, then the sample is put into a tightly sealed container and then labeled, and then the sample is taken to the laboratory for analysis. The samples analyzed were sediment samples as deep as 20 cm divided into three layers (top, middle and bottom). Cutting of samples starting from the surface of the sample on the thickness of 0-2 cm, 9-11 cm and 18-20 cm [22] (Figure 2).
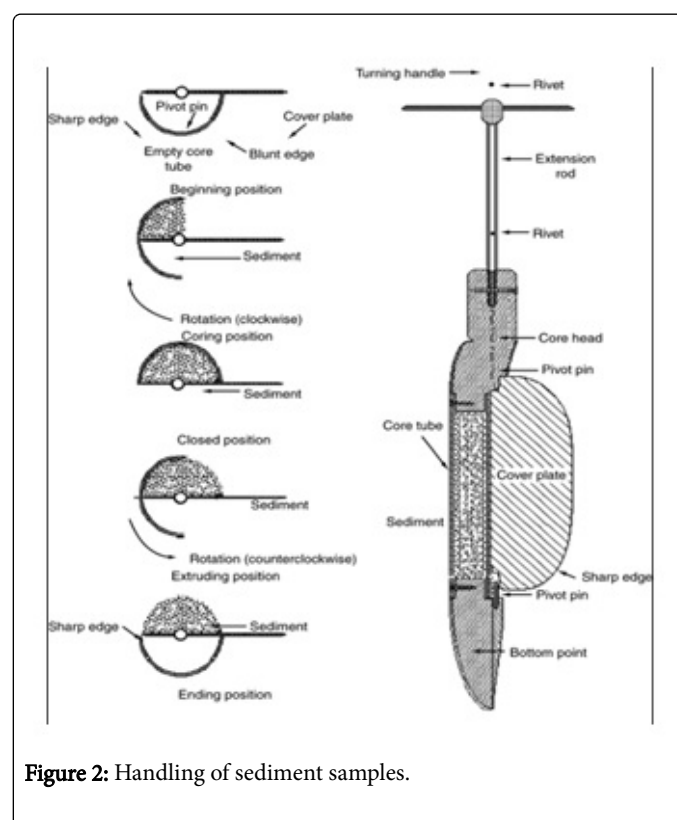
Figure 2: Handling of sediment samples.

Measurement of water quality parameters

Aquatic environmental parameters measured include temperature, pH, salinity, depth, brightness and current velocity. Measurements are performed once at each sampling point. The aim is to describe the condition of the waters at the time of the study.

Analysis of sediment samples

Analysis of sediment samples for sedimentary fractions, sediment composition and organic materials, was conducted at the Diponegoro University Laboratory, Semarang.

Analysis of heavy metals in sediments

Analysis of heavy metals in sediments was performed using spectrophotometric method based on SNI 06-6992.3-2004 procedure for Pb metal and SNI 06-6992.5-2004 for Cd by using Atomic Absorption Spectrophotometer (AAS) measurement instrument, where cathode lamp as source of radiation. Analysis of heavy metal content of Pb and Cd using mixture of air and acetylene as energy source, with wavelength Pb is 283.3 nm and Cd 228.8 nm. The result obtained from AAS is the absorbance value which is then calculated to obtain the actual heavy metal content value of the sample.

Total heavy metal content

The procedure of analysis of heavy metal content of Pb and Cd in the sediment is as follows: the existing sediment sample is dried in the oven at Temperature of 110°C and then dried sediments are destroyed by means Mortal (mortal). As much as 1 gram of dry sediment is weighed and inserted Into a beaker glass, add 5 ml of concentrated HNO_3, 3 ml of concentrated HCl and water 100 ml flask, heated on a hot plate at a temperature of 105°C to the rest Volume to 20 ml, added 5 ml of concentrated H_2SO_4, and closed beaker glass With a watch glass and heated until all dissolved, visible from the color The precipitate in the test sample becomes white or the test sample becomes clear. Watch glass rinsed with distilled water and put water into beaker glass, water Distilled and added to 100 ml volume, the solution is filtered into 200 ml of 200 ml flask, then the test sample is checked with AAS.

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.

Results and Analysis

After make experiment, in 7 locations, so the result as follows (Table 2):

Deep	Heavy Metals			
	Pb	Zn	Cd	Cu
Location A:				
1:2 meters	0.054	0.107	<0.001	0.485
2:4 meters	0.043	0.101	<0.001	0.312
3:6 meters	0.022	0.006	<0.001	0.224
Location B:				
1:2 meters	0.115	0.143	<0.001	0.556
2:4 meters	0.095	0.128	<0.001	0.342
3:6 meters	0.023	0.106	<0.001	0.102
Location C:				
1:2 meters	0.19	0.067	<0.001	0.303
2:4 meters	0.104	0.055	<0.001	0.223
3:6 meters	0.009	0.043	<0.001	0.106
Location D:				
1:2 meters	0.012	0.115	<0.001	0.347
2:4 meters	0.01	0.102	<0.001	0.225
3:6 meters	0.005	0.008	<0.001	0.194
Location E:				
1:2 meters	0.146	0.147	<0.001	0.039
2:4 meters	0.102	0.122	<0.001	0.022
3:6 meters	0.004	0.103	<0.001	0.014
Location F:				
1:2 meters	0.113	0.05	<0.001	0.025
2:4 meters	0.102	0.034	<0.001	0.012
3:6 meters	0.007	0.012	<0.001	0.008
Location G:				
1:2 meters	0.056	0.03	<0.001	0.013
2:4 meters	0.044	0.012	<0.001	0.01
3:6 meters	0.02	0.008	<0.001	0.009

Table 2: Heavy Metals Sedimentation in 7 Locations.

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 <0.001 mg/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 <0.001 mg/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.

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 <0.001 mg/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 <0.001 mg/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 E the Zn is the highest levels of sedimentation rather than Pb and Cu. Pb is the second highest levels of heavy metals and the third rank is Cu. Meanwhile Cd is the lowest one because <0.001 mg/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 F 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 <0.001 mg/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 <0.001 mg/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 Ph 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, the abanyak fiber there is waste of factory waste.

Fish	Sample	Cu	Zn	Cd	Pb
Fresh Water	Gouramis	2.57	10.98	<0.01	2.66
	Cat Fish	1.38	10.59	<0,01	1.3
	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

Table 3: Levels of heavy metals in different fish samples.

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 3. 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 dibawha standard 5.75. When Cu falls into 3.15 then many tiger barb 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. This is supported by research conducted by Widianarko et al. [19] stated that Elevated environmental concentrations of metals are usually associated with the impact of urbanization (Figure 3).
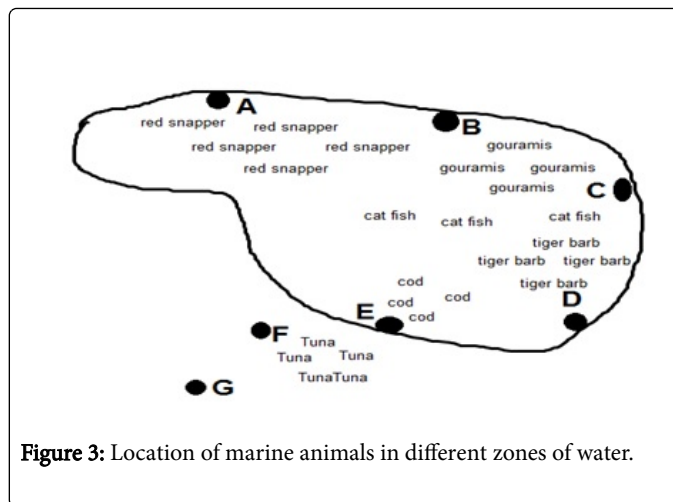
Figure 3: Location of marine animals in different zones of water.

Discussion

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 vertical profile is characterized by increasing the concentration of inputs in the upper layers of the sediment for the sediment loading process from the surrounding area. However, the highest concentration of Pb does not exceed normal Pb levels on the surface of the earth. Mohiuddin et al. [7] said that normal Pb levels on the surface of the earth is <12.5 ppm. 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.

According to Pb metals enter much into the aquatic bodies through the discharge of ballast water, asphalt and fuel oil engine emissions are used as an anti-knock on the machine. The low metal content of Pb in the middle layer of sediment sampling point 1 is suspected because the input of waste is more dominated by domestic waste coming from the settlement. According to Doraja et al. wastewater from household waste, such as water used by laundry, kitchen, bathroom and toilet. Domestic liquid waste contains 99.9% water and 0.1% solids. Solid substances consist of proteins, carbohydrates, fats and the remaining inorganic substances especially sand grains, salts and metals. Pb metals may come from non-source sources such as atmospheric, transport and rainfall caused by coal combustion in industrial activity. Difference of metal content of Pb and Cd in West Dumai waters is very high. The high concentration of Pb metal, indicating the increasing mobility occurring in the western Dumai Waters containing Pb metals. In

accordance with the statement of Yang et al. [23], high concentrations of Pb metals indicate high Pb metal mobility compared to Cd metals.

The average content of metal Cd vertically tends not much different between layers of sediment. The metal content of Cd were <0.001 mg/l is found in the all layer of sediment sampling point. The Cd metal content in the west Dumai waters, below the average value of natural Cd metal content, indicating the dominance of Cd metal sources in sediments derived from nature [7]. That is, the content of metal Cd in sediments in the waters of Usman Janatin western part is still categorized as unpolluted waters and can be tolerated for the life of benthic organisms [23].

Low cadmium concentrations suggest that Cd metals come from natural or negligible anthropogenic influences. The presence of Cd in the sediments is thought to have been influenced by anthropogenic activities as well as inputs derived from river flow around the coastal and Usman Janatin Waters, both from industrial waste, ship painting and agriculture. Because Cd metal is essentially derived from the influence of external discrete sources such as industrial activity, agricultural runoff, and other anthropogenic inputs. Agricultural waste containing fertilizers and pesticides carries heavy metal content such as Cd and Pb into the waters. 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.

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 (e.g., 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. Smooth current movements affect the characteristics of sediment and the speed of sedimentation. The high sedimentation speed causes heavy metal movement to spread throughout the bottom of the water and is assisted with patterns of current movement that occur during two times a day. Riani et al. [24] said that the movement of metals is strongly influenced by the shape and type of metal engagement and its availability (bioavailability) in aquatic environments. Sediments which are the ends of compounds in aquatic environments play an important role in determining metal forms in waters.

According to Rifardi et al. [22], the movement of coastal sediments or coastal sediment transport is a sedimentary movement in the coastal region caused by the waves and currents it generates. In coastal areas there are two directions of sediment transport, ie cross-shore transport or onshore-offshore transport of sediments and sediment movements along coastal or parallel shores commonly termed by longshore transport. Flows and waves are the main factors that determine the direction and distribution of sediments. This strength also causes different sediment characteristics so that on the bottom of the waters is composed by various groups of sediment population.

Sedimentation is influenced by anthropogenic and geological activities that occur around the river. These anthropogenic activities include shipping, harbor vessels, trade, settlements and industry along streams that can lead to erosion along river banks. Such conditions may provide sediment supply to the study site. The geological characteristics of the research area can lead to run-off and erosion by the rain stream and the flow of the river itself.

Surface, base and wave currents strongly influence the pattern of sediment distribution in the study sites. Differences of morphological type of waters as well as the fractional sediments scattered in this area also give effect to sedimentation speed. The waters of the river mouth are the waters located around the mouth of the river. The influence of land through the river and the influence of the ocean through tidal events makes these waters have their own characteristics, fertile and vulnerable. Estuary of the river is generally a fertile waters and an important fishery area because of the abundance of nutrients carried by the river. The hydrological mechanism of river water in addition to supplying nutrients supporting the life of aquatic organisms, also bring ingredients that can inhibit the growth of even killer organisms or causes of declining quality of aquatic environment [22]. The waters of the estuary receive a lot of organic matter from the land and all the activities that occur along the river flow and greatly affect the waters of the estuary.

Estuary waters are ecosystems that are closely related to the physical chemistry of the land and the ocean. There are several environmental factors determining the quality of water at the mouth of the river such as physical factors include brightness, temperature, velocity, color and suspended substances. Then chemical factors include dissolved oxygen, degree of acidity (pH) and water hardness as well as biological factors including competition among organisms, predation prey relationships and food chain dependence [22].

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.

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

According to Yu et al. [23], 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. Branding with organic materials and sulphides can also produce metals in an oxidizable form. The metal in the form of a strong engagement with the mineral crystal structure in the sediment is called residual form. Riani et al. [24] states that metals that are bioavailable will accumulate in aquatic animals that have metallic receptors and are toxic to the aquatic animal and may even kill sensitive individuals.

Metals interact with the sediment matrix through different binding mechanisms, including adsorbed to organic materials as well as mineral surfaces, associated with carbonates, Fe-Mn oxides, sulphides and mineral refractory crystal lattices [25]. The accumulation and mobility of heavy metals in sediments as well as in the upper water column with low concentration is highly dependent and controlled by various factors, including the properties of sediment particles, the properties of absorbing compounds, and the prevailing physical-

chemical conditions. These conditions give rise to sediment content and characteristics containing Pb, Zn, Cu and Cd metals differently between each sampling point.

Monitoring is an activity to observe the progress of development plan implementation, to identify and anticipate problems that arise and or will arise to be taken as early as possible. Monitoring is the checking of an activity whether it is in accordance with the planning, and supporting activities that are very important in evaluating environmental conditions and law enforcement. Avoiding prolonged disputes over environmental issues, data centers are needed. Charging data is needed monitoring, especially the waters considered to be vulnerable or industrial areas that allegedly pollute the aquatic environment. Given the vastness of activities and the amount of costs incurred for monitoring, not every region can be routinely monitored water quality. Under normal circumstances non-routine monitoring does not pose a problem, but the situation may be exploited by a naughty industry to dispose of its waste when it is off guard. As a result, the target of activities for environmental improvement has never been achieved. Law enforcement cannot be done without firmly supported by supporting data of accurate and continuous monitoring result.

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 programs has been and is running, whether there is improvement of environmental conditions or not. For example, on 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.

The government plays a very important role, especially in enforcement of Laws, Government Regulations, Local Regulations. Environmental regulations change a lot and increase from year to year. Therefore, it needs to be socialized both directly and indirectly to the community and industry players. Environmental violations occur because some people have not read or understand the existing regulations, given the environmental issues, especially marine pollution that is still considered normal in Indonesia, and law enforcement is still very minimal compared to other cases. Enforcement of regulations should be followed by reliable monitoring to support pollution data. Evidence of pollution case is one of the most common disadvantages, and this condition makes it difficult in enforcing environmental law in Indonesia. Therefore, an independent environmental laboratory is required to support law enforcement. The accuracy of data and information is valid and impartial to anyone.

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