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Heavy metal content in pumpkin pond of Kutaraja Fishing Port Banda Aceh

Muhammad Muhammad[1], Pratiwi Shelly Anggie[1], Thaib Rizwan[1,*], Zulkarnain Jalil[2]

[1] *Fisheries Resource Utilization Departement, Marine and Fisheries Faculty, Universitas Syiah Kuala, Banda Aceh, Indonesia.*
[2] *Physics Departement, Mathematics and Natural Science Faculty, Universitas Syiah Kuala, Banda Aceh, Indonesia.*

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ABSTRACT

Fishing port scan support fishery resources management by incorporating social-economic activities to improve the local community's welfare; however, it can also negatively impact the environment by increasing waste pollution to the surrounding waters. Kutaraja Fishing Port, Banda Aceh, is one of the active fishing ports that conduct multiple activities, such as industrials, transportations, and domestic activities threatening the environment through the production of pollution such as heavy metals. The purpose of this study is to determine the concentration of heavy metals Zinc (Zn) and Chromium (Cr) and the sediment contamination level in the Kutaraja Fishing Port, Banda Aceh. This research was conducted in February 2021 at the water site of Samudra Kutaraja Fishing Port, Banda Aceh, and sampled sediments using the purposive sampling method. Samples were then analyzed for heavy metal concentration using the Atomic Absorption Spectrophotometer (AAS) instrument in the laboratory of the Aceh Industrial Research and Standardization Center (BARISTAND). The results showed that the concentration of heavy metal Zn ranged from 15.6507 - 27.2939 mg/kg. The majority of heavy metal Cr concentrations were below the test limit of <0.000, except at station 2, which was 9.1212. Both heavy metal concentrations are still categorized as low contamination criteria and still below the Australian and New Zealand Environment and Conservation Council (ANZECC, 2000) and the Canadian Council of Ministers for the Environment (CCME, 2002). This research proved that both heavy metals do not threaten the biota and have a low contamination level in the waters.

Introduction

The socio-economic activities that occur in the fishing port area contribute to improving the economy and welfare of the community (Schipper *et al.,* 2017). Fishing Port of Kutaraja is one of the international fishing ports managed by Aceh Province located in Banda Aceh city. This perspective opens up development opportunities related to infrastructure that will support the increased activity in the port area. Some of the activities that are concentrated in Kutaraja Fishing Port include the processing industry, sea transportation, domestic businesses, and settlements. However, generally, the activities at the port threatened the environmental conditions due to the increase in the amount of waste, both in the form of gas, solid, and liquid which polluted the environment (Shen *et al.,* 2017). Therefore, the port is one of the primary producers of pollutants into the waters from various activities in the area. One of the major wastes that potentially reduce the environment's carrying capacity is the presence of heavy metals (Salleh and Halim, 2018).

The source of heavy metal concentrations in the coastal areas can be divided into two factors: natural factors, such as geological activities or microbial synthesis (Zhang *et al.,* 2019b), and factors caused by human activities resulting in the release of heavy metals into the waters. Increasing use of heavy metals on land or the surrounding areas was carried towards the ocean and significantly contributes to the high concentration of these heavy metals in the coastal areas (Nurhamiddin and Ibrahim, 2018). According to Farzingohar *et al.* (2020), heavy metals in waters

* Corresponding author.
Email address: rizwanthaib@unsyiah.ac.id

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are derived from anthropogenic activities in the port area, such as spreading fishing gear, oil spills from ships, repairing and building ports, and modernization such as industrial development. Heavy metals are toxic, persistent, *biodegradable* pollutants and can accumulate through biological chains such as soil, plants, seawater, and marine organisms. These characteristics threaten and pollute the environment; hence, heavy metals in the coastal areas become the main problem (Abdelhafez *et al.,* 2015).

Research on heavy metals in Aceh waters has been carried out in various ways, ranging from heavy metal content in sharks (Zulfahmi *et al.,* 2020) to heavy metals in dissolved and sedimentary forms (Rizkiana *et al.,* 2017). Research conducted by Warni *et al.* (2017) stated that the heavy metal concentration in the sediments at the Jetty Meulaboh Port had passed the quality standards set by ANZECC (2000). The same study was also conducted by Pratama *et al.* (2019) at Kutaraja Fishing Port by testing the dissolved concentration of heavy metals (Pb), which showed that the presence of heavy metal lead (Pb) in the water was in low concentrations. Thus, it is concluded that the heavy metal concentration in Aceh waters and some of them have passed the predetermined quality limits. Regularly monitoring the concentration of heavy metals is necessary to evaluate the contamination status of the aquatic environment (Al-Naggar *et al.,* 2018) and prevent threats to ecological sustainability. Indra (2018) added that the ecological condition of Kutaraja Fishing Port still has a low index value. These considerations encouraged to conduct of research investigating the heavy metal content of Zn and Cr in the waters of Kutaraja Fishing Port, Banda Aceh. This assessment was carried out due to heavy metals, which could threaten the balance of the aquatic environment. Therefore, this research is needed to investigate the pollution status of the Kutaraja Fishing Port by assessing the heavy metal concentration in the sediments in the Kutaraja Fishing Port pumpkin pond.

Materials and Methods

Location and time of research

The research was conducted on February-March 2021 in the waters of Kutaraja Fishing Port Banda Aceh. Data were sampled using *purposive sampling,* which is adjusted based on the determined criteria according to the research objectives. The research sample was taken in the form of sediment obtained from 5 (five) observation points (Figure 1). Station (1) is located close to the drainage connecting the main wharf, and the two ports, station (2) is at the mooring boat and cleaning station for materials and ships area, station (3) is at the estuary, station (4) is at the edge of the estuary, and station (5) is close to the edge of the *breakwater* which is about 600 m from the station (1). The bottom sediment samples were collected using the *coring* method with a PVC pipe of Ø 3.5 inches in diameters inserted vertically up to a thickness of 30 cm. Approximately 1 kg of the sediment was collected and put in a polyethylene bag and stored in a cool container.

Laboratory materials and equipment

The sediment samples were analyzed for the heavy metal concentration using the spectrophotometric method performed in the *Atomic Absorption Spectrophotometry* (AAS) (Figure 2). In principle, the AAS absorbed a certain wavelength spectrum by a metal atom. This tool started with the evaporation of the sample solutions, then transformed into the free atom and absorbed by radiation from the cathode-emitted light source. Analysis was conducted in Aceh Industry Research and Standardization Center (*Balai Riset dan Standarisasi Industri Aceh – BARISTAND*). Materials used in the laboratory analysis were sediment samples, standard solution of 1000ppml metal (Zn) and (Cr), nitric acid (HNO 3), hydrochloric acid (HCl), aquabidest, and standard *Whatman* filter paper. Meanwhile, the tools used in this research are *hot plate*, cathode lamp, digital scale, glassware, volume pipette, *microwave*, and digital camera.

Research procedure

The collected sediment samples were placed in a *shuffle* (container) for drying using the *microwave* at a temperature of 105 ^{0}C for 5 hours. After completely dried, the samples were mashed and weighed using 5 grams scale digital and then put into a beaker. The samples were then continued with the digestion process carried out by adding 5 ml of HNO 3 and 15 ml of HCl and heated for 15 minutes using a *hot plate* at temperature 100 0 ^{0}C until the sediment dissolves. The samples were then cooled at room temperature, transferred into a volumetric flask, and added aquabidest until they reached the boundary mark. The digestion results that have been diluted were filtered with medium size *Whatman* paper. The results of this phytase were measured for its heavy metals level in the AAS by using an air-acetylene flame.

The calibration curve was determined by making a standard solution in a series of analytes called concentrations. A calibration curve was made by taking a standard solution of 1000 ppm pipette about 0.01, 0.002, 0.005, 0.1, 0.2, 0.5 ml and then were diluted using aquabidest until the limit mark. The solution concentration was analyzed using the atomic absorption of radiant light at a certain wavelength according to the metal that was being analyzed. The wavelength for Zn metal is 213.9 nm and for Cr metal is 357.9 nm. The results of the standard solution absorption process (absorbance) and the concentration of standard solution substances formed a linear relationship with the correlation value and the regression equation y = ax + b.

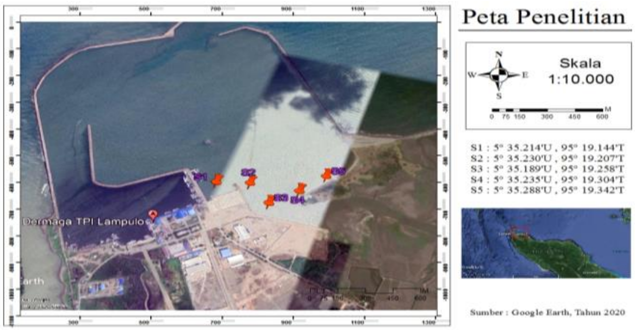

Figure 1. Map of the sampling sites in Kutaraja Fishing Port.

Figure 2. Atomic Absorption Spectrophotometry instrument.

Data analysis

The AAS provides values of the calibration curve to obtain the tested metal concentration value in the form of the regression concentration. Based on the regression concentration, the metal concentration levels was be determined by following the equation:

$$\text{Heavy Metals} = {mg}/{Kg} = \frac{Creg\ X\ P\ X\ V}{W}$$

Where: C = Heavy metal concentration read as AAS (mg / L); P = dilution factor; V = Volume of sample used (L); W = sample weight (Kg).

The results obtained from the heavy metal levels measurements were tabulated and compared to the reference quality standards by the *Australian and New Zealand Environment and Conservation Council* (ANZECC) and the *Canadian Council of Ministers for the Environment* (CCME) (Macdonald, 2018). The use of these quality standards references due to the unavailability of Indonesia's definite quality standard guidelines for sediment.

Contamination Factor (CF) described the sediment contamination level by heavy metals with the ratio between the concentration of heavy metals in the sample and the average concentration of heavy metals in the natural environment (*background value*). The *background* concentration of heavy metal Zn is 70 mg/kg, and Cr is 100 mg/kg (El-Amier *et al.*, 2017) with the following equation:

$$CF = \frac{c\ (Heavy\ Metal)}{C\ (Heavy\ Metal)}$$

Where: c metal = Concentration of heavy metals; C background = Metal concentration in nature.

The CF interpretation valuesrange are: (CF <1) = low contamination, 1 <CF <3 = moderate contamination, 3 <CF <6 = high contamination, CF> 6 = very high contamination.

Results

Based on the results of these measurements, the heavy metals Zn and Cr levels in the sediments at PPS Kutaraja Banda Aceh were obtained for each observation station. Zn metal varied at each station; meanwhile, almost all heavy metal Cr was below the detection limit of the test equipment, except at station 2. The results showed the heavy metals concentration status in each station. The highest Zinc (Zn)concentration was found at station 5 with 27.2939 mg/kg, and the lowest level was 15.6507 mg/kg at station 4. Cr concentration was found at very low levels in all stations, except in station 2, where the Cr concentration reached 9.1212 mg/kg.

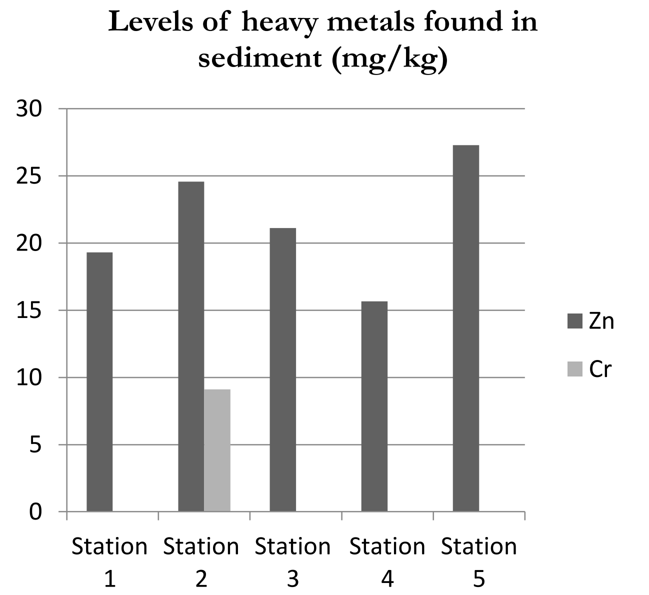

Figure 3. The heavy metals (Zn and Cr) concentration at each station.

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The heavy metal concentrations in this study were compared with the sediment quality standard guidelines by ANZECC (2000) from Australia and CCME (2002) from Canada. These guidelines were used as a comparison because there is no definite guideline for sediment quality published by Indonesia. Results showed that the range of heavy metal Zn and Cr concentrations was below the low value of the ANZECC quality standard and the ISQG value of the CCME quality standard. This comparison value revealed that the heavy metals Zn and Cr concentrations in Kutaraja Fishing Port are considered safe for the aquatic ecosystem (includes literature review). The comparison values are presented in Table 2.

Table 2. Comparison of Zn and Cr metal concentration in sediments with ANZECC and CCME quality standards.

Sediment Samples		Zn (mg / kg)	Cr (mg / kg)
	Min.	15,650	<0.0001
	Max.	27,293	9,1212
ANZECC Guidelines (2000) *	Low	200	80
	High	410	370
CCME (2002) *	ISQG [1]	124	52.3
	PEL [2]	271	160

(Note: [1] ISQG, interim sediment quality guidelines; [2] PEL, probable effect levels)

Table 3. Contamination factors (CF) in sediments (mg / kg) in the PPS Kutaraja area.

Location	Contamination Factor (CF) Zn	Contamination Factor (CF) Cr	Criteria
ST.1	0.2031	*)	
ST.2	0.2585	0.1013	CF <1 'Low
ST.3	0.2233	*)	1<CF<3 'Moderate
ST.4	0.1647	*)	3<CF<6 'Sufficient
ST.5	0.2873	*)	CF>6 'Very high
Natural mean	95	90	

Note: *) indicated that no calculation was performed due to the level of heavy metal that is smaller than the

Heavy metal contamination assessment in sediments is necessary to monitor its *natural level* in the environment, regardless of the sources of these heavy metals to the environment. Heavy metals have similar criteria as other metals; the difference lies in their effects when in contact with living organisms, especially in high concentrations (Sonone *et al.*, 2020). High concentrations of heavy metals in the environment will change the ecosystem's structures and functions. Table 3 shows the calculation of the *background value* ratio with the value of the heavy metal concentration in the test samples. Overall, the heavy metal contamination level from each observed station indicated that the heavy metal concentration of Zn and Cr is in the low contamination zone.

Discussion

The heavy metal concentration of Zn and Cr in sediments

Heavy metals in sediments are one of the primary pollutants used as an indicator for assessing the environmental quality and anthropogenic activities (Liu *et al.*, 2015). Heavy metals have the characteristic that easily settles or binds organic matter to the sediments that resulted in a higher concentration of heavy metals in the sediment than in the dynamic seawater; therefore, sediment is commonly used in assessing the status of heavy metals in aquatic ecosystems (Sojka *et al.*, 2018). Wastes from anthropogenic activities that were released directly to the waters significantly contribute to the high concentration of heavy metals in the aquatic environment. Generally, heavy metals in the waters are found in two forms, which are in the form of dissolved and particulate. Dissolved heavy metals are distributed in the water column and follow the water flow pattern. Meanwhile, heavy metals in particulates tend to be deposited and transferred to the water bodies through adsorption and absorption processes. In addition, heavy metals altered the bioaccumulation and bio magnification processes in a biota (Asare *et al.*, 2018).

The heavy metal zinc (Zn) exists naturally from the earth's crust, and it is widely used in various industries. Heavy metal Zn is an essential metal for organisms' metabolism; however, excessive Zn concentration in the water will lead to toxicity such as organ dysfunction and poisoning (Yadav *et al.*, 2017). Meanwhile, heavy metal chromium (Cr) is toxic, carcinogenic, and mutagenic in its hexavalent form. It is produced from anthropogenic activities such as the leather tanning industry, agriculture, mining, and fishing activities (Pratiwi, 2020).

The analysis results in this study indicated an accumulation of heavy metals Zn and Cr in the sediment at the observation sites. The range of heavy metal values found in this study was much lower than the heavy metals Zn and Cr concentrations found in the study area (Anbuselvan, 2018; Wang *et al.*, 2020). The highest Zn concentration was found in station 5, where it is located near the *breakwater*. The *breakwater* infrastructure combined with oceanography factors inhibits the spread of these substances and allows the substance to be trapped and accumulated within the area. Therefore, visually, the sediment type in station 5 is dominated by mud. Sediment size composition influences the distribution of the heavy metals in the sediment, where the heavy metals concentrations are higher in muddy sediments than in sandy sediments. The fine fraction tends to stronger bind heavy metals (Ernawati and Cahyadi, 2019). The presence of a sediment fraction supports the binding of heavy metals so that the concentration of heavy metals will keep increasing for an extended period (Susantoro *et al.,* 2015). However, no related study confirmed the relationship between the duration and distribution of heavy metals Zn and Cr in sediments. Heavy metals concentration in stations 2 and 3 were sourced from anthropogenic activities, such as ship cleaning and maintenance, further distributed by the oceanographic factors.

The second highest Zn heavy metal concentration was found at station 2, reaching 24.5577 mg/kg. The high concentration of Zn in station 2 was mainly derived from the drops of ship lubricants from ships maintenances, operation, and cleaning, and peeling off the electroplating coated ship parts (Enguito *et al.,* 2018) and the use of hull paint that contains Zn and Cr for *anti-fouling* on a ship (Yin *et al.,* 2015). Naturally, Zn enters the aquatic environment through abrasion and runs off of mineral and metal residuals. The difference in Zn concentration in stations 2 and 5 is still uncertain; however, the distribution pattern of heavy metals in the water is highly influenced by the Physico-chemical conditions of the waters.

The presence of heavy metal Zn at station 3 might be influenced by its position close to the river mouth. Zn concentration at station 3 is lower than station (5,2) and higher than station (4,1), presumably caused by mangroves that dominated the areas. Mangroves have an ecological function of trapping, absorbing, and transporting natural toxic material from the surrounding environment (Setiawan, 2015); hence a small portion of heavy metals are scattered to station 3. The low levels of heavy metals at stations 1 and 4 can be suspected caused bypassive activities, which can cause heavy metal waste. Even though station 1 is in the drainage that connects the loading and unloading of the ship at the dock area, it lacks heavy metal permeability processes. Thus, the low Zn concentration level in station 1.

The sediment analysis for Cr concentration showed low concentration (below the detection of the AAS test equipment) of heavy metal Cr in the sediment. All stations reaching <0.0001 mg/kg, however, station 2 is an exception with Cr concentration reaching 9.1212 mg/kg. The presence of Ct metal at station 2 is suspected derived from ship activities, including peeling paint and fuel spills (Jupp *et al.,* 2017) while the ships were berthed at that location. The Cr concentration at stations 1,3,4, and 5 are below the detection of the test equipment as shown in (table 1) and can be categorized as not present at the stations. Generally, industrial waste is the most potent source that produces heavy metals. Heavy metal Cr is used as a component in the metal coating industry, leather tanning, paint, and textile industry (Shahid *et al.,* 2017). In the Kutaraja PPS area, there is only a fish processing industry and *cold storage,* while potential industries that can produce heavy metals such as Cr are not found in this port area.

The metal content of Zn and Cr in sediments at PPS Kutaraja ranged from 15,650 - 27,293 and <0.0001 - 9,1212 (table 2). Based on the quality standards of the *Australian and New Zealand Environment and Conservation Council* (ANZECC, 2000), the two metal levels found were within the range *low* (<200) for heavy metals Zn and *low* (<80) for heavy metal Cr. Hence, the presence of these heavy metals at the observed locations is still classified as safe for the environment and does not pose potential threats to aquatic biota. The comparison with the quality standards set by the *Canadian Council of Ministers for the Environment* (CCME, 2002) obtained the same results, which are under the "ISQG" value limit. ISQG value limit is the limit of the heavy metals concentration that potentially adversely affects the biota. Based on the heavy metal concentration assessment in the sediment, Zn and Cr concentrations are considered low contamination status with values CF <1 (Table 3). The process of accumulation and absorbance of heavy metals in sediments will not be bound continuously with the supporting substances. These particles will occasionally resuspend into the pool of water and spread following the movement of the water body (Jahan and Strezov, 2018). The distribution of these heavy metals in the water bodies can result in accumulation in aquatic organisms. Therefore, the low concentrations of Zn and Cr found in the sediments could be due to the dissolving process in the water bodies. The analysis showed that each metal concentration in the sediment is still at tolerable limits in the aquatic environment.

The ecological implications of metals

Human activities have an impact on the presence of waste problems in the waters. One of the problems is due to the deposition and absorption of heavy metals in the environment and caused harm to the environment, and have been shown to cause

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disease risk to humans (Liu *et al.*, 2018), such as induced oxidative stress, DNA damage, carcinogenicity, and cell death (Matos *et al.*, 2020). Generally, all heavy metals can cause adverse effects at certain concentration limits depends on the type of metal, the form of metal ions, and the level of tolerance of the organism exposed. The metals such as Zn, Cu, Fe, and Mn are required for metabolic activity in organisms to a certain extent, while metals such as Cd, Cr, Pb, and As tend to show their toxicity even though they are found at low concentrations (Lestari, 2017). Water contaminated with heavy metals will decrease the environment's carrying capacity (Briffa *et al.,* 2020), and uncontrolled metal pollution impacts living biota, especially biota that is sedentary and challenging to move, and further exacerbate the bioaccumulation process.

The existence of heavy metals for a long time in the environment poses a serious and significant threat to the environment and accumulates in the food chain. Heavy metals potentially absorbed by organisms that forage at the bottom of the sea, called benthic organisms, which is the basis for biomagnifications that potentially become a metal transfer agent from low trophic levels to higher levels. This process indirectly impacts humans as they consume seafood contaminated with heavy metals, such as from direct observation. The sampling location is close to the location used by local people to collect shellfish. Heavy metals can cause serious problems when they reach into the metabolic system of organisms. Another example is fish as a source of food that is impacted by the bioaccumulation of heavy metals (Ali *et al.*, 2019; Gashkina *et al.*, 2020). A high concentration of metals in the environment will be absorbed by the aquatic organism in the ionic phase and influenced by pH and temperature. Heavy metal contaminations will be absorbed by fish through their gills and skin, transferred to their organs and blood, and attached to protein inside the fish. The concentration of heavy metal absorbed will be controlled within the fish body and released to the water through its gills, skin, and feces. Biological and environmental factors highly influence a species' heavy metals bioaccumulation process (Rubalingeswari *et al.*, 2021).

The presence of heavy metals in waters results from the activities that can produce heavy metals, such as ports and industries. These activities are continuously operating and result in difficulties in decomposing the heavy metals; hence the concentration will be more abundant over time. Ports are classified as carrying out sustainable activities in optimizing their functions and tasks. In contrast, the development needs to be carried out by considering economic, political, and ecological aspects. Ecologically sustainable means the activities that occur must maintain the integrity of the ecosystem, maintain the carrying capacity of the environment, and conserve natural resources (biodiversity). In this case, analyzing the heavy metal concentration is important to understand the potential dangers it poses to organisms. The potential bioavailability of metals in sediment is also needed to support monitoring and evaluating metal pollution in a location that will be planned for construction. The concentrations of Zn and Cr in this study are classified as low; however, these metal residues must be monitored because, through time, these metals increase. The pollution in the port contributes to reducing environmental quality, damaging the quality of seawater, and affecting the ecological environment and even harmful organisms to humans.

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