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To cite this article: Rahmatsyah et al 2018 J. Phys.: Conf. Ser. 1120 012089

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Study of Distribution Metal From Shellfish at Coastal Beach in District of Central Tapanuli, Indonesia

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Abstract. The research of heavy metals spread in shellfish in the coastal area a zone of the high seas and zones of settlements waters in Central Tapanuli has done with the aim of knowing the content of heavy metals of Cu, Cr, Pb with parameters of the river water, sea water, shellfish and clamshell, basic sediments. Testing of river water, sea water, and shell meat was conducted using Atomic Absorption Spectrometer (AAS) by adsorption principle of light by atoms. Testing basic sediment and clamshell has done with XRD and TEM. The test results of river water showed are Cu <0,025 mg/l, Cr <0.006 mg/l - <0.025 mg/l, Pb <0.005 to 0.03 mg/l, in the conditions of under the river water quality standard. The test results on the sea water obtained are metal content of Cu. <0.006 mg/l, Cr <0,025 mg/l, Pb 0.13 to 0.24 mg/l. The test results show the shell meat are Pb. <0.005 to 2.34 mg /kg, Cu 0.85 to 14.4 mg/kg. The test results of clamshell with XRD showed peaks of CaCO₃ aragonite. With TEM showed that crystalline, by electron diffraction pattern formed by irregular dot, which means the elements contained in the various clamshells. Differences levels of heavy metals at every point stations predicted has their natural factors such as the direction of ocean currents, rainfall and sediment material and anthropogenic factors such as demographics residential waste pollution, industrial and port activity.

1. Introduction

Indonesia is a maritime country with an oceans area of 5.8 million km² consist of territorial waters, 12-mile sea waters and the EEZ waters of Indonesia stretches from Sumatra Island include Central Tapanuli district to New Guinea [1]. Geographically, Central Tapanuli district is located in the west coast of North Sumatra at coordinates 1°11'00"–2°22'00" north latitude and 98°07'–98°12' east longitude. With a coastline is 200 km directly facing the sea off, with oceans area of ± 400,000 ha, with a population density of 274 inhabitants / km², supported fairly rapid development of the industry, was fourth in 11.27% [2]. Industrial development has resulted potential of pollution from anthropogenic factors such as harbor waste, industrial waste, household waste that causes damage to marine biota, including shellfish. The abundance of pollutants represent a serious threat to the conservation of marine animals such as shellfish. Shellfish is the animals which eat with the filter feeders, which eat suspense especially plankton in the waters. Typically live in waters with sandy mud substrate or attached in a hard substrate such as rocks or wood [3]. The solubility from pollutants on the water bodys is controlled by the type, concentration of metal, mineral components oxidized [4]. Heavy metal components in the water can be influenced by oceanographic parameters, among others,
temperature, salinity, pH, flow velocity, turbulence and wave [5]. Heavy metals cannot be degraded by living organisms in the environment and accumulate into the environment, so they settle in the bottom waters forming complex compounds with organic materials and inorganic with adsorption and combinations. Heavy metals in waters affected by the current pattern [6]. The flow of water causes heavy metals dissolved in seawater surface can spread in all directions. High or low of heavy metals levels in a body of water is not only influenced by the remoteness of the beach, but also very dependent on seawater local conditions [7]. Presence of heavy metals in the water is actually not good for shellfish because of the bound heavy metals in the mucus tissue [8]. This condition would more increase the amount of mucus released, so it is by itself the respiration and filtration capabilities will decrease, so the amount of oxygen and food which can be absorbed by shellfish has diminish. Based of the trait of high accumulator to heavy metals, the shellfish are used as samples for monitoring heavy metal pollution in aquatic environments [9]. Food products manufactured, imported and marketed in The Indonesia territory must meet the requirements of the maximum limits of heavy metal contamination is allowed or recommended in food.

2. Method

Sampling of seawater and shellfish are conducted in the sea waters of Central Tapanuli, North Sumatra (Figure 1). Data retrieval starts from gridding the study site, taking the river water parameters in 5 stations, sea water sampling at 17 stations to analyze metals Fe, Cu, Pb, Cr which analyzed using Atomic Absorption Spectrophotometer equipment type Shimadzu AA-7000 (AAS). Taking samples shellfish with alive media such as sediments in 3 station, then patterning heavy metal pollution. The first, Samples of bottom sediments and shells in ballmill, then the sediment was analyzed by XRD, shells were analyzed by XRD and TEM, clam meat with the method of Atomic Absorption Spectrometry (AAS), which is based on the absorption of energy by atoms neutral on gaseous.

![Figure 1. Gridding Point Sea Water Samples.](image-url)

3. Result

The results of measurements of water quality in the county Central Tapanuli is the basis for the evaluation of the environmental effects of the watershed as trends analysis from water quality in the long time [10]; [11]; [12]; [13]; [17]. Data analysis from river water samples indicate the parameters heavy metals of river water is higher in station ST1 that Pb i.e. 0.03 mg/l and Fe 2.47 mg/l, Cu <0.025 mg/l, Cr <0.006 mg/l, DO amounted to 2, 68 mg/l, BOD is 5.86 mg/l, COD is 16.28 mg/l, pH 6, salinity 64.7 ppm, the lowest at station ST3 that heavy metals of Pb 0.02 mg/l, Cu <0.025 mg/l, Cr <0.006 mg/l. DO magnitude 7.11 mg/l, BOD is 1,61 mg/l, COD is 4.47 mg/l, Contour parameters of BOD, COD and DO at five rivers Station shown in Figure 2. Rivers in the category has not been
contaminated, especially content of heavy metals Pb showing value same with the river water quality standard i.e. 0.03 mg/l.

**Figure 2.** Contour BOD, COD, DO of five rivers.

The results of measurements of parameters of seawater at B3 station showed heavy metals Pb contained. 0.24 mg/l and the amount of DO 6.73 mg/l, BOD 1.51 mg/l, COD. 4.19 mg/l, conductivity 18.92 μs/cm, pH. 8.55, salinity. 9.30 ppm, turbidity. 3.57 NTU. Results show that the B3 station has been contaminated by heavy metals Pb which has passed through the sea water quality standard. 0.05 mg/l. Results lowest measurement in B1 station is observed Cu <0.006 mg/l and Cr <0.025 mg/l. DO 6.84 mg/l, BOD 1.36 mg/l, COD 3.77 mg/l, conductivity. 12.91 μs/cm, turbidity. 2.98 NTU [14].

**Figure 3.** Map of the contours of copper in sea water in Central Tapanuli

Results of analysis of shellfish samples testing were performed using an Atomic Absorption Spectrophotometer AA-7000 Shimadzu type. Observed heavy metals in shellfish. Pb <0.005 mg/kg – 2.34 mg/kg, Cu 0.85 mg/kg – 14.4 mg/kg, Fe 24.4 mg/kg – 168 mg/kg. Shell meat has dominated Pb. The test results of pattern mineral content samples from bottom sediment with XRD and shells obtained diffraction (Figure 4 and 5).
The results obtained for the shells was dominated of aragonite content of CaCO$_3$ in aragonite phase of the Joint Committee of Powder Diffraction Society (JCPDS) file no. 00-001-0628. Calcium carbonate (CaCO$_3$), which is one of the most abundant mineral in nature, exists in three polymorphs: calcite, aragonite and vaterite [15]. The content of heavy metals in sediment increasing concomitant increase of content of organic matter contained in water bodies and sediments, normally higher concentrations in molluscs because inability to regulate metal with age [3].

Result of Analysis by Transmission Electron Microscope using equipment JEOL / EO JEM-1400 source 120 kV, conducted in Bright field image in the form of illumination direct light, dark field image of the lighting comes from the result of reflection and electron diffraction observed in Figure 6a, b, and c. Showed the presence of crystals in the shells. Based of electron diffraction form a dot (dots) with irregular patterns, the elements contained in the shells vary. This is due to each measuring stations influenced by the form of natural factors such as ocean currents, precipitation, sedimentation material and anthropogenic factors such as demographics residential waste pollution, industrial and port activity.
Figure 6. TEM pattern on the clamshells of (a) Bright field (b) Dark Field and (c) diffraction.

4. Conclusions
The test results of river water showed that heavy metals Cu < 0.025 mg/l, Cr < 0.006 mg/l to < 0.025 mg/l and Pb <0.005 to 0.03 mg/l which in the conditions under the river water quality standard. The test results of heavy metals obtained in sea water Cu <0.006 mg/l, Cr < 0.025 mg/l, Pb 0.13 to 0.24 mg/l. The test results show the shell meat Pb <0.005 to 2.34 mg/Kg, Cu 0.85 to 14.4 mg/kg. Test results clamshells with XRD showed the peaks appeared corresponding Aragonite CaCO$_3$ and with TEM Indicates the presence of crystalline, with a pattern of irregular shape.

5. Acknowledgements
We would like to gratefully acknowledge to several people who helped us until this research completed. We would like to say our utmost gratitude to the Ministry of Research, Technology and Higher Education (RISTEKDIKTI) who funded this research. We also want to say our gratitude to the Rector and the Head of Research Institute of Medan State University.

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