CONCENTRATION OF HEAVY METAL IN WATER, SEDIMENT AND AQUATIC LIFE AT STRAITS OF JOHOR

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ABSTRACT

In this study, marine water quality at Johor Straits along Kampung Pasir Putih was investigated. Changes in land use and increased discharge of domestic, agricultural and industrial waste into the coastal water have severely affected the water condition and threatened fishes and green mussels aquaculture activities. The study investigated on the distribution concentration levels of heavy metals, which are Zn, Cu, Cd and Pb in crabs and mussels with addition to sediment samples that were collected. The mean heavy metals concentration level in whole body of crabs and mussels were found in range of 60.4-256.5 mg/g, 21.8-50.3 mg/g, 1.6–4.5 mg/g and 8.2-23.7 mg/g dry weight for Zn, Cu, Cd and Pb, respectively. The patterns of heavy metals distribution in crabs and mussels of the different sampling stations were found to be Zn > Cu > Pb > Cd, where the highest were usually indicated by Zn and Cu which were not consistent in their order, and the lowest were indicated by Cd and Pb. This was due to the different function of heavy metals in crabs and mussels such as for essential purpose, sequestration and even to be excreted. As for sediments, the mean heavy metals concentration level were found in range of 17.7-147.1 mg/g, 17.7-155 mg/g.2, 2.4-5.3 mg/g and 9.8-14.5 mg/g dry weight for Zn, Cu, Cd and Pb, respectively. As the development increase, the quality of water will be decrease, thus, the accumulation of heavy metals in green mussels and crabs will increase. This is proven by the low dissolved oxygen (DO) concentration which was between 1.36 to 6.71 mg/L. The heavy metals concentration in marine water along Kampung Pasir Putih were between 0.01 to 0.6 mg/L for Zn, 0.04 to 0.22 mg/L for Cd, 0.01 to 0.08 mg/L for Cu, and 0.03 to 0.33 mg/L for Pb. Based on the selected parameters conducted, Kampung Pasir Putih is classified as Class 3 according to Malaysia Marine Water Quality Standard (MMWQS). Overall the water quality was affected along the study thus classified as slightly polluted. With that proper management and prevention planning should be carried out to preserve the food environment.

ABSTRAK

Dalam Kajian ini, kualiti air laut di selat Johor sepanjang Kampung Pasir Puteh telah dikaji. Perubahan kepada penggunaan tanah dan peningkatan pelepasan domestik , pertanian dan sisa industri ke dalam laut telah menyebabkan perubahan pada keadaan air dan mengancam aktiviti akuakultur ikan dan kupang. Kajian ini menyiasat kepekatan taburan logam berat Zn, Cu, Cd dan Pb di dalam ketam dan kupang disamping sampel sedimen yang telah dikumpulkan. Kepekatan purata logam berat di dalam keseluruhan ketam dan kupang adalah dalam linkungan 60.4-256.5 mg/g, 21.8-50.3 mg/g, 1.6-4.5 mg/g dan 8.2-23.7 mg/g berat kering untuk Zn, Cu, Cd dan Pb setiap satu. Corak taburan logam berat di dalam ketam dan kupang pada setiap lokasi kajian mendapati Zn > Cu > Pb > Cd, di mana nilai kepekatan tertinggi ditunjukkan oleh Zn dan Cu tidak konsisten dengan corak taburannya yang tidak konsisten manakala nilai Cd dan kepekatan terendah ditunjukkan oleh Pb. Ini disebabkan oleh perbezaan fungsi logam berat di dalam ketam dan kupang iaitu sama ada digunakan untuk tujuan kemandirian, pengasingan dan penyingkiran. Bagi sedimen, purata kepekatan logam berat adalah dalam linkungan 17.7-147.1 mg/g, 17.7-155.2 mg/g, 2.4-5.3 mg/g dan 9.8-14.5 mg/g berat kering untuk Zn, Cu, Cd dan Pb setiap satu. Apabila pembangunan meningkat, kualiti air akan berkurang dan kandungan logam berat di dalam kupang dan ketam akan meningkat. Secara keseluruhan kualiti air di kawasan kajian diklasifikasikan sebagai tercemar. Dengan itu, perancangan serta pelan pemulihan perlu dilaksanakan bagi memelihara sumber makanan. Ini dibuktikan oleh kandungan oksigen terlarut (DO) yang rendah iaitu antara 1.36 hingga 6.71 mg/L. Kepekatan logam berat dalam air laut di sepanjang Kampung Pasir Puteh pula adalah antara 0.01 hingga 0.6 mg/L untuk Zn, 0.04 hingga 0.22 mg/L untuk Cd, 0.01 hingga 0.08 mg/L untuk Cu, dan 0.03 hingga 0.33 mg/L untuk Pb. Berdasarkan parameter yang dijalankan, Kampung Pasir Puteh diklasifikasikan sebagai Kelas 3 mengikut Piawaian Kualiti Air Marin Malaysia (MMWQS). Secara keseluruhan, kualiti air terjejas sepanjang kajian ini dikelaskan sebagai sedikit tercemar. Dengan perancangan pengurusan dan pencegahan yang sewajarnya perlu dilakukan untuk memelihara persekitaran makanan.

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LIST OF ABBREVIATIONS

JPT	Johor Port Terminal
MMHE	Malaysian Marine and Heavy Engineering
Hg	Mercury
As	Arsenic
Zn	Zinc
DO	Dissolved Oxygen
GIS	Geographic Information System
GPS	Geographic Positioning System
DOE	Department of Environment Malaysia
˚C	Celsius
ppt	Part per thousand
mS/cm	MilliSiemens per centimeter
mg/L	Milligram per liter
µg/L	Microgram per liter
µg/g	Microgram per gram
MMWQS	Malaysia Marine Water Quality Standard
CSQG	Canadian Sediment Quality Guideline
AAS	Atomic Absorption Spectrometer
HNO_3	Nitric acid
H_2O_2	Hydrogen Peroxide
HCL	Hydrochloric Acid
FAAS	flame atomic absorption spectrometer
ANOVA	analysis of variance
ERL	effects range-low
ERM	effects range-high

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CHAPTER 1

INTRODUCTION

1.0 Introduction.

Heavy metals contamination in water may arise in many ways. Some of them are being mobilized by man to the atmosphere and sometimes exceeding those by weathering process. Human activities that may result to water pollution include agriculture, irrigation, fire, urbanization, mining and industrialization (Goudie, 1990). The Straits of Johor is a semi-enclosed formation and heavy discharges from the surrounding industries have been on-going for many decades. Discharge of industrial wastes also constitute about 62% of total source of heavy metal such as lead (Pb), zinc (Zn), copper (Cu), nickel (Ni), cadmium (Cd), chromium (Cr) and manganese (Mn) which are responsible not only for degrading the water quality of a river or sea but for killing a number of aquatic organisms(Abubakar and Garba, 2006). These metals are toxic after large accumulation in the body of flora and fauna and later pass on through the food chain from fish to man (Ayodele and Abu Bakar, 2001).

Human population residing along coastal areas give raise to the building of many infrastructure, land reclamation for port, industrial, tourism and recreational activities, agriculture and other economic expansion, etc, leading to various environmental and ecological implication including habitat modification, erosion, sediment deposition of natural resources and environmental degration. Futhermore, outfalls of domestic effluent and pollutants such as heavy metals created from these ongoing activities ae usually discharge and incorporated to the surrounding areas particularly in local sediments, water and organism of the near shore intertidal regions.

The Straits of Johor has been the subject of past and present studies on heavy metal pollution involving different uses of organics including fishes, bivalves, gastropods, crustaceans and their surrounding habitat like sediments and water. It is an area given much of considerable attention due to its population density, rapid urbanization, and industrial development (Olowu *et al.*, 2010). The study area is located near Johor Port (JPT) which is an international shipping lane. In general, the Straits of Johor is a principle repository for domestic effluent and pollutant originating from land-based and sea-based activities (Abdullah, 1995 ; Abdullah et al., 1999). Local studies on heavy metal pollution undoubtedly address the importance and potential input of this toxicant to intertidal coastal ecosystems brought about by various anthropogenic activities occurring within the west coast region.

Crabs are crustaceans that are abundant in the sea, and few are common in moist land environments (Cubbage, 1991). They are part of invertebrate organisms in aquatic environment, and are also benthic organism. Crabs are consumed by many animals including humans and are rich in protein (Ghiselin, 2009). Crabs take in hazardous materials such as heavy metals, chlorinated paraffin, pesticides (Sea On Screen, 1988). The body either stores or excretes it. By storing it the concentrations of toxic materials in the body can increase and become greater than in the surrounding environment. This phenomenon is called bioaccumulation (Olowu *et al.*, 2010). Heavy metals accumulate in organisms as a result of direct uptake from the surroundings across the body wall, from respiration and from food (Heip,1997). There is an increasing concern about the health effect in human due to continuous consumption of food contaminated with heavy metals (Chukwujindu *et al.*, 2008). Heavy metals are introduced in an aquatic environment through domestic and industrial waste discharge into water body. It is rather of great concern that over 80% of the industries in Malaysia discharge their solid, liquid and gaseous effluents containing toxic concentration of heavy metals into the environment without any prior treatment while just only 18% undertake rudimentary recycling prior to disposal.

Though monitoring of sediments and water should not be neglected, living organisms should be used to monitor environmental contamination as they can better reflect the contamination history of a sample location through their exposure to contaminants that accumulate over their lifetime. The levels of heavy metals in living organisms are often considerably higher than that in other constituents of the marine environment, signifying an organism's capability to accumulate and uptake metals in their tissues in proportion to the degree of environmental metal contamination and altogether be a bio monitor of metal pollution (Rainbow and Philips. 1993; Rainbow, 1995). Biomonitoring programs for instance the 'Mussel Watch' program, were first initiated by Goldberg *et al*. (1975) in which bivalves were used as biomonitors for global marine pollution monitoring. Thereof many studies have focused on using different organisms (e.g. fishes, gastropods and crustaceans) to monitor heavy metal pollution in the marine environment.

However, there has been little research to access heavy metal levels in crustacean, crab species which represent the most abundant crustaceans found in intertidal coastal ecosystems of the Straits of Johor, apart from mussels that are often submerged in water and have less contact to sediments of the marine environment where metals can accumulate. This much justify the interest in finding another bioindicator organism for the monitoring of heavy metals in Malaysia plus comparing a bottom dweller to aquaculture bivalves.

Crab was one of the important aquatic biota in marine environments which can be used as an indicator to assess and evaluate the level of heavy metals in water. Usually, the most abundant and common crab to be found in Malaysia water was flower crab which can be known as *Portunus Pelagicus.* There were two types of flower crab which normally can be found in coastal environments. An attractive blue pattern and markings on their body can be identified as males while females tend to have a dark brown pattern on their body and carrying egg. During low tides, it was quite difficult to identify females crab because of their camouflage due to their body colour that was almost similar to sand or mud.

Flower crab also can be used as an indicator which it can accumulate high amount of heavy metal in their bodies and muscle. A study conducted by Heidarieh *et al*. (2013) showed the level of heavy metal concentration in flower crab at Persian Gulf, Kuwait. In this study, the heavy metal assessment was measured in the whole body of the flower crab where zinc measured as the highest metal concentration compared to the other metals such as manganese, ferum, arsenic and cobalt. The zinc recorded a value of 66.64 ppm per dry weight. By comparing to a study conducted by Sadiq *et al*. (1982), the concentration of zinc ranges from 35.94 to 46.09 ppm. This showed that the zinc recorded almost a higher metal reading compare to the other metal because zinc was originated from the surrounding anthropogenic activities such as the sewage effluent. In another study, heavy metals accumulation was measured in different parts of *Portunus Pelagicus.* By measuring through different parts of crab, it can show whether a higher metal concentration were accumulated in claw or their bodies.

Figure 2.5 showed the metal concentration in different features of *Portunus Pelagicus.* The result depicts that a higher metal was accumulated in claw rather than in body for zinc and copper. But the results were different for ferum and manganese where it shows a higher accumulation in body than claw meat. However, there were several factors which can affect the heavy metal accumulation in crab. Heidarieh *et al.* (2013) discussed on factors which can affect the accumulation of heavy metal such as effect or organs, sex, size of crabs as well as the location of sampling and the season. A bigger size of crabs tends to accumulate higher heavy metals in their body.

	Zn	Fe	Mn	Cu
Callinectes sapidus				
Claw meat	6.99±0.9	1.04 ±0.13[a]	0.39±0.07[a]	2.53±0.16
Body meat	4.7±0.03	1.13±0.07[a]	0.37±0.04[a]	3.13±0.06
Portunus pelagicus				
Claw meat	4.68±0.1	0.45±0.02[b]	0.06±0.02[b]	2.08±0.05
Body meat	3.72±0.4	0.68±0.03[b]	0.16±0.03[b]	1.49±0.09

Apart from that, crabs were selected as an indicator to evaluate the heavy metal accumulation because of various reasons. First, crabs is one type of common benthic organism that can be easily to find. Moreover, their habitat which was located in contaminating surface sediments and feed on benthic prey items living among contaminated sediments also can adding up more heavy metal accumulation in their tissue and bodies. A relationship between the condition of aquatic environments and the heavy metal concentration by measuring it in crabs also can provide additional correlation (Zhao *et al*., 2012). Ololade *et al*. (2011) also discussed on the selection of fish and shellfish to be used as an indicator to assess the heavy metal concentration in coastal environments. Through the study, it reported that fish and shellfish which can inhabit in different trophic levels and showed large bioaccumulation factors were the reason it can be a good indication to assess metal contamination in aquatic environments.

1.2 Background of Study

Industrialized and urbanized estuaries and coastline receive effluent discharge which contain conservative contaminants, i.e. those with long half-life, are likely to bio-accumulate (remain with the food chain) and thus have a toxic effect (Clark, 2004). Such contaminants include heavy metals both essential e.g. Cu, Zn and toxic e.g. Hg, Cd, radio nuclides and synthetic organic compounds e.g. dieldrin and polychlorinated biphenyls. The hazard associated with heavy metal cannot be over emphasized as they are highly toxic to practically all form of life. In human they can cause skin, kidney, birth defect and even death etc.

The danger of mercury in seafood was demonstrated by the appearance in the 1950s and1960s of a crippling neurological disorder among the inhabitants of Minamata Bay in southern Japan. The victims were poisoned by eating fish and shellfish that had concentrated mercury discharge at sea by a chemical plant (Peter and Micheal, 2005; Spiro and Stighani, 2008). Heavy metals pollution represents a serious problem for human health and for life in general. The disposal of heavy metals is a consequence of several activities like chemical, manufacturing, painting, coating, mining, extractive metallurgy, nuclear and other industries. These metals exert a deleterious effect on fauna and flora of lake streams (Sayari *et al.,* 2005). The presence of trace metals in aquatic systems originates from the natural interactions between water, sediments and atmosphere with which the water is in contact. The concentrations fluctuate as a result of natural hydrodynamic chemical and biological forces. Man, through industrialization and technology, has developed the capacity to alter these natural interactions to the extent that the very waters and the aquatic life herein have been threatened to a devastating point (Tam and Wong, 2000).The activity of trace metals in aquatic systems and their impact on aquatic life vary depending upon the metal species. The major importance in this regard is the ability of metals to associate with other dissolve and suspended components. Most significant among these associations is the interaction between metals and organic compounds in water and sediment.

These organic species, which many originate naturally from process such as vegetable decay or result from pollution through organic discharge from municipal and industrial sources, have a remarkable affinity and capacity to bind metals. This phenomenon would naturally alter the reactivity of metals in the aquatic environment (Singer, 1974). Many human activities (e.g. mining, overuse of chemicals, industries waste from ports and refineries) have negative impact on several biological processes and there is no doubt that these will continue to affect the functioning of highly productive coastal ecosystems. Contamination caused by trace metals affects ocean waters, those of continental shelf and the coastal zone where, besides having longer residence time, metal concentrations are highly due to input and transport by river runoff and the proximity to industrial and urban zones (Ajiwe *et al.,* 2002; Guzman and Garcia, 2002). Rivers appear to be the most important sources of heavy metals into the sea as they carry much larger quantities of elements as particulate than they do as solutes (Bryan and Langston, 1992).

1.3 Problem Statement

In the past century there has been rapid expansion in the chemical industry. This has led to an increase in the complexity of toxic effluents at Johor Port which release waste materials into Sungai Laloh (Ajiwe *et al.,* 2002). Several industrial processes generate metal containing wastes (Forstner, 2003). Again, it is very important to have a more definite and clear understanding of the effects of a given pollutant on an aquatic ecosystem, and to be made aware of this problem from as many perspectives as possible. Crab can be used as an ideal and reference candidate for monitoring the intensity of pollution in general or in a given area as they are consumed by a large percentage or section of human population without knowing the sources of the organisms ,i.e., if they were from polluted or non-polluted areas (Ajiwe and Okonkwo, 2007). Johor Straits is a highly productive ecosystem supporting rich supply of food, and serving as necessary ground for a variety of fish and shellfish species. They serve not only as food and natural resources on which human depends.

This output can be sustained only if the ecosystems on which they survive are not abused, and the organisms are not overexploited. The environmental health of these waters calls for immediate attention as the changes are immediately reflected on the health of the organisms. Pollution along the Johor Strait is notable. The area is also a source of environmental contention between Malaysia and Singapore, due to land reclamation projects on both sides of the causeway. There have been suggestions that the ongoing land reclamation projects may impact the maritime boundary, shipping lanes and water ecology of the Malaysia side. Environmental Impact Assessments are requested before any reclamation is carried out such as the Forest City Project. Reclamation project may also endanger the habitat and food sources of dugongs, which are native to the strait.

Heavy metals are normal constituents of aquatic environment in trace quantities. When the levels increase they act as cumulative toxic to estuarine and marine organisms. Pollution monitoring carried out in recent years have revealed elevated levels of many heavy metals in the marine environment. Therefore, the deleterious effects should be studied more seriously so that corrective or defensive methods could be developed. Though numerous toxicological studies have been carried out on finfishes in general and crabs in particular, a scrutiny of literature clearly reveals the gap in our understanding of the biochemical changes taking place in the organism exposed to heavy metals, which pollute the estuarine and marine habitats of the crabs.

Heavy metal contamination has been a critical problem mainly because metals tend to persist and accumulate in the environment (Forstner, 2003). The tremendous increase in the use of heavy metals over the past few decades has inevitably resulted in an increased flux of metallic substance in aquatic environment. Mine drainage, industrial and domestic effluent, agricultural run-off, acid rain etc. have all contributed to some extend to the metal loads in the water bodies. The effect of metals in water range from beneficial or toxic, depending on concentration.

Lead (Pb) is a serious cumulative body poison where natural waters seldom contains more than 5 µg/L. Lead is generated in effluents from the production of storage batteries, pigments, petroleum, fuel, photographic materials, mining, smelting, painting, etc. zinc is a bluish white metal with an atomic weight of 65.37. Zinc is chemically active and alloys readily with other metals. Therefore, this study was set out to explore and exploit the potential of crabs and mussels as a bioindicator and to see the difference of accumulation in both species since they are located at different water levels in the same area. Mussels at aquaculture are usually hanging from surface to 3 meter depth whereas crabs are bottom dwellers near sediments or inter-tidal.

1.4 Aim and Objectives

The aim of this present study is to investigate heavy metal contents in water, sediment and aquatic life from Straits of Johor. The objectives incorporated in this study are :

i. To investigate the distribution concentration of Zn, Cu, Cd and Pb in water and sediment at the different study area.

ii. To investigate the level of heavy metal deposits in the aquatic life i.e crab and mussels

iii. To estimate and calculate the bioconcentration factor in the crabs at the different areas as a insitu biomonitor indicator.

1.5 Scope of Study

The study covered a period of 18 months sampling both wet and dry season periods from six selected locations along Straits of Johor. Determination of heavy metal concentration was carried out in the seawater, sediment and aquatic sample namely crab and mussels. This project aims to determine the concentration of heavy metals, Cu, Pb, Cd and Zn, in the water as well as the sediment in two of the sources. Apart from laboratory analysis insitu was also conducted for DO, pH, conductivity, salinity and temperature.

1.6 Significance of Study

This study is important to assess the concentration of heavy metal in water, sediment, crab and mussels since Cu, Pb and Cd are considered very toxic in aquatic life wheres Zn is needed for aquatic life. Each of this heavy metal has their consequences to the aquatic life at Kampung Pasir Puteh. As the number of aquatic life keep decreasing due to rapid development and poor water quality, this study assessed on the level of pollution at the study area through analysis of heavy metals by following the guidelines provided. Apart from that, sources of water pollution were also identified along the study area. This is crucial to check whether the sources greatly affects the level of pollution and at the same time to compare the heavy metal concentration at different sampling stations.

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