SELECTED HEAVY METAL AND WATER QUALITY PARAMETERS AROUND BUNTAL COASTAL WATER SARAWAK

Nurhidayah binti Samsuddin

(38137)

Bachelor of Science with Honours
(Aquatic Science and Resource Management)
2015

UNIVERSITI MALAYSIA SARAWAK

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(Name of the supervisor)

Dr Farah Akmal Idrus
Lecturer
Department of Aquatic Science
Faculty of Resource Science & Technology
UNIVERSITI MALAYSIA SARAWAK
94300 Kota Samarahan

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Dr Farah Akmal Idrus
Lecturer
Department of Aquatic Science
Faculty of Resource Science & Technology
UNIVERSITI MALAYSIA SARAWAK
94300 Kota Samarahan

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SELECTED HEAVY METAL AND WATER QUALITY PARAMETES AROUND BUNTAL COASTAL WATER SARAWAK

Nurhidayah binti Samsuddin

(38137)

This project report is submitted in partial fulfillment of the Final Year Project 2(STF3015)

Faculty of Resource Science and Technology
UNIVERSITI MALAYSIA SARAWAK
2015

ACKNOWLEDGEMENTS

Alhamdulillah, all praise to Allah, God of The Universe for giving me this opportunity, strength and guidance to finish my thesis for Bachelor of Aquatic Science. I want to express my appreciation to my supervisor Dr. Farah Akmal Idrus, for motivation, guidance and supervised me to complete the requirement for my final year project as well as my thesis .A special thanks to the Department of Aquatic Science and Resource Management of Universiti Malaysia Sarawak, for giving me the opportunity to experience priceless experiences in pursuing my degree. Not forgetting Mr.Tommy, laboratory assistance for assisting me to do my lab work, my senior, course mate and others whom I not mentioned, big thanks for all of your help and support while the thesis is in progress. Last but not least, to my supportive parents and my siblings, who always there for me give me strength when I face the difficulty during my work and support me mentally and financially.

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I hereby declare that no portion of this dissertation has been submitted in support of an application for another degree of qualification of this or any other university or institution of higher learning.

Nurhidayah Binti Samsuddin

_____

Aquatic Resources Science and Management
Aquatic Science Department

Faculty of Resources Science and Management
University Malaysia Sarawak

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List of Abbreviations

GPS	Global Position System
FAAS	Flame Atomic Spectrophotometer Absorption
FIMS	Flow Injection Mercury System
Cd	Cadmium
Cu	Copper
Hg	Mercury
Pb	Lead
Mn	Manganese
Zn	Zinc

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Selected Heavy Metals and Water Quality Parameter around Buntal Coastal Water Sarawak

Nurhidayah Binti Samsuddin

Aquatic Resources and Management Programme
Faculty of Resource Science and Technology
Universiti Malaysia Sarawak

ABSTRACT

Heavy metals are the natural component of the earth. Anthropogenic activities have significantly altered their compositions; geochemical cycles and biochemical balance of these heavy metals and might give negative impacts to the aquatic ecosystem. Therefore, the objective of this study is to determine the concentration of Manganese (Mn), Zinc (Zn), Cadmium (Cd), Copper (Cu), Lead (Pb) and Mercury (Hg) and selected water parameter were investigated. The results showed the concentration of metals in the Buntal coastal water were Zn (0.097-0.247mg/L), Hg (0.0012-0.369mg/L), Mn (0.0518mg/L), Cd (0.004-0.025mg/L), Cu (0.01mg/L),Pb (below detection limit). The results of concentration of heavy metals showed that Buntal coastal waters are higher than Malaysia Marine Water Quality Criteria and Standard by Department of Environment.

Keywords: Heavy metals, anthropogenic, water parameter

ABSTRAK

Logam berat adalah komponen semulajadi bumi. Aktiviti antropogenik telah banyak mengubah komposisi ,kitaran geokimia dan keseimbangan biokimia logam berat dan berkermungkin akan member kesan negatif kepada ekosistem akuatik. Oleh itu , objektif kajian ini adalah untuk menentukan kepekatan Mangan (Mn), zink (Zn), Kadmium (Cd), tembaga (Cu), Plumbum (Pb) dan Mercury (Hg) dan parameter air dipilih disiasat. Hasil kajian menunjukkan kepekatan logam dalam Buntal air pantai adalah Zn (0.097-0.247mg/L), Hg (0.0012-0.36 mg/L),Mn (0.0518 mg/L), Cd (0.004-0.025 mg/L), Cu (0.01 mg/L), Pb (dibawah paras ukuran). . Keputusan kepekatan logam berat menunjukkan bahawa perairan pantai Buntal adalah lebih tinggi daripada Kriteria Kualiti Air Marin Malaysia dan Standard oleh Jabatan Alam Sekitar.

Kata kunci: Logam berat ,antropogenik, parameter air

1.0 Introduction

The term "heavy metals" refers to any metallic element that has a relatively high density and is toxic or poisonous even at low concentration (Lenntech, 2004). According to Singh *et al.* (2011), heavy metals are a member of an ill-defined division of elements that exhibit metallic properties. These include the transition metals, some metalloids, lanthanides, and actinides. Heavy metals also known as one of the common transition metals, such as copper, lead, and zinc. Heavy metals include lead (Pb), cadmium (Cd), zinc (Zn), mercury (Hg), arsenic (As), silver (Ag) chromium (Cr), copper (Cu) iron (Fe), and the platinum group elements (Duruibe *et al.*, 2007). Heavy metal does play important roles in aquatic living organism. It involves in photosynthesis photosystem, redox reaction, and even act as nutrient for some organisms. There are two types of nutrients present in water column; macronutrient such as nitrogen, phosphorus and potassium and micronutrient such as trace metals. According to Banerjee *et al*. (2000), states that some trace metals elements like zinc, copper, boron, molybdenum and etc may acts as micronutrients to certain plants but become very toxic if the levels concentration were high. The uptake amount for macronutrient nutrients by plants were usually high compared to micronutrients.

Heavy metals occur as natural constituents of the earth crust, but recently, the amount of heavy metal increased directly and indirectly due to human activities (Ghorade *et al*., 2014). Seawater contains a variety of trace metals at concentrations which rarely exceed 1 µg1-^{l} in open oceans. Excess amount of heavy metals that contain in water can cause water pollution. A pollutant is any material in the environment, which causes offensive effects, impairing the interests of the environment, reducing the quality of life and may eventually cause death. According to Peng *et al.* (2008), heavy metal is usually distributed as follows in aquatic

environment: water-soluble species, colloids, suspended forms and sedimentary phases.However, the removal of these heavy metals can be occurred through biological activities, residences time and seasonal changes.

The concentration of heavy metal also can be affected by the physicochemical parameters such as pH, temperature, turbidity, and salinity (Li *et al*., 2013). Lawson *et al*. (2011) state that the pH of a water body does influences the concentration of many metals by altering their availability and toxicity. Metals like Zn and Cd are most likely to have increased negative environmental effects as a result of lowered pH. Temperature affects solubility of gasses in water, gas solubility decreases as temperature increases. High temperatures may increase the toxicity of many substances such as trace metals in water. In addition pH and temperature are two important factors for microbial activities within an aquatic medium (Lawson *et al.*, 2011).

There are fewer study on heavy metals conducted in Sarawak coastal area particularly in Buntal coast. Therefore, the objectives of this study were (1) to determine the concentration of selected of heavy metals (Mn, Zn, Cd, Cu, Hg, and Pb) around Buntal coastal area and (2) to determine the selected water quality parameters around Buntal coastal waters.

2.0 Literature Review

2.1 Heavy Metals

Heavy metals are natural constituents of Earth's crust and exist in various concentrations in all ecosystems. A continuous increase in amount of anthropogenic heavy metals for both, inorganic and organic heavy metals has derived over the last decades since industrial revolution happened (Komarnicki, 2005). According to Castro *et al.* (2009), coastal zones can be considered as an area of interaction between marine ecosystems and terrestrial which is important for the survival of large variety of marine organisms. Over the years, the coastal pollution has been increasing as well as the level of environmental problems in developing countries, thus this results an increase of concentration of heavy metals present in water body. Heavy metals are divided into two categories; essential and non-essential. According to Valavanidis and Vlachogianni (2010), many metals are essential to living organisms but some of them become toxic at high concentration. An essential metal such as Mn, Cu and Zn plays an important role in aquatic ecosystem meanwhile non-essential metals such as Hg, Pb and Cd which are generally not required in metabolic activity and are toxic to living organism at quite low concentrations.James *et al*., (2005), states that the concentration of metals that present in seawater were approximately; Mn ($2x10^{-5}$mg/L), Cu ($1x10^{-1}$mg/L), Zn ($4x10^{-4}$mg/L), Hg ($3x10^{-7}$mg/L), Pb ($2x10^{-6}$mg/L) and Cd ($1x10^{-1}$mg/L). However, the concentrations of elements were slightly higher in the coastal area due to intrusion of water and other anthropogenic activity that has been carried out in that particular area.

2.2 Importance of Essential Metals

Each element of heavy metals has its own role in aquatic organism especially to phytoplankton since it related to photosynthesis. Redfield ratio shows the atomic ratio of carbon, nitrogen and phosphorus in phytoplankton and throughout the oceans. According to James *et al.* (2005), the average molar ratio of carbon to two principal nutrients element in organic matter were nitrogen and phosphorus is close to 106:16:1 (C:N:P) and this is the basic of Redfield ratios. The Redfield ratios then were extended to: $\mathbf{(C_{124}N_{16}P_1S_{1.3}K_{1.7}Ca_{0.5})_{1000}(Sr_{5.0}Fe_{7.5}Mn_{3.0}Zn_{0.80}Cu_{0.38}Co_{0.19}Cd_{0.21}Mo_{0.03})}$ as scientific study showed that trace element does need by aquatic organism as micronutrient. The amount of carbon, nitrogen, phosphorus, silicate, potassium and calcium were high in the Redfield ratio because those elements are macronutrient. From the extended Redfield ratio it shows that small concentration of trace metals are needed for phytoplankton.However, Twining *et al.* (2004), states that the extended ratio may vary depends on the phytoplankton species.Phytoplankton conduct photosynthesis process to create their ownfoodand some of heavy metals are needed in order to ensure that the process goes well. During photosynthesis process, Mn plays important role in O_2 release by photosystem II and largely results from the association of the metal with a few enzymes and proteins (Silva and Williams, 1991). Zn was required by the enzymes in cytoplasm for release of peptides and reaction of extracellular matrix. According to Riddle (2012), Cu is important for plant because it involve in electron transfer. Cu also necessary for maintain the appropriate membrane fluidity to ensure the mobility of plastoquinone molecules to transfer electrons between two photosystems (Droppa *et al.*, 1984).

2.3The harmful of metals

Heavy metals has been contaminated coastal water by anthropogenic sources of heavy metal, cadmium for examples, including industrial emissions, the application of fertilizer and sewage sludge to farm land. According to Jarup (2003), cadmium occurs naturally in ores together with zinc, lead and copper. Long-term high cadmium exposure may cause skeletal damage, first reported from Japan, where the itai-itai disease (a combination of osteomalacia and osteoporosis) was discovered in the 1950s. Severe mercury exposure may give rise to Minamata diseases. Minamata disease is a methylmercury poisoning with neurological symptoms that associated with daily consumption of large quantity of fish or shellfish that has been contaminated with toxic chemical; mercury (Hachiya, 2006).Headache, irritability, abdominal pain and various symptoms which related to the nervous system will cause poisoning. These prove that excess heavy metal will contaminate the water coastal and give a bad impact to human health.

2.4 Bioaccumulation and biomagnifications of metals

Bioaccumulation is a process in which certain toxic substances (such as heavy metals) accumulate and keep on accumulating in living organisms, posing a risk to health, life, and to the environment. The chemicals were uptake from any of those potential sources such as substrate, food, air and water. Heavy metals can be bioaccumulated and biomagnified via the food chain and finally assimilated by human consumers resulting in health risks (Agah *et al*., 2009). As a consequence, fish are often used as indicators of heavy metals contamination in the aquatic ecosystem because they occupy high trophic levels and are important food source (Blasco *et al.,* 1998; Agah *et al*., 2009)

2.5 Water quality

The physical-chemical controls on seawater can be attributed to the effect of composition of the major components on the thermodynamics and kinetics of processes in the oceans. The effect of the major components on the physical-chemical properties of seawater, the carbonate system in the oceans, the solubility of iron in seawater and the redox reactions of iron and copper in natural water were examined. The amount of heavy metal concentration does affect the water quality. According to Li *et al.* (2013), in the low pH (4–7) condition, the heavy metals release rates were affected to a much superior level than in high pH (8–10) condition. At higher temperature (30–35°C), the metals were released more rapidly than at low temperature. The flow rate significantly affected the release amount of Zn, Pb, and Cr, while it slightly affected the concentration of Cu and Cd. From these evidence, it reflects that any change of pH, temperature, dissolved oxygen, and flow rate of overlying water all cause the different variations of the concentrations of heavy metals (Li *et al.*, 2013).

3.0 Materials and Methodology

3.1 Sampling sites

The sampling site for this project is around Kampung Buntal Coastal areas. There are 8 stations (Figure 1 and Table 1) proposed in this sampling areas and the coordinate were recorded by using Global Positioning System (GARMIN, 62S). In each sampling areas the water sampling were divided into two types; Chlorophyll-*a* and nutrient analysis, and heavy metals analysis**.**

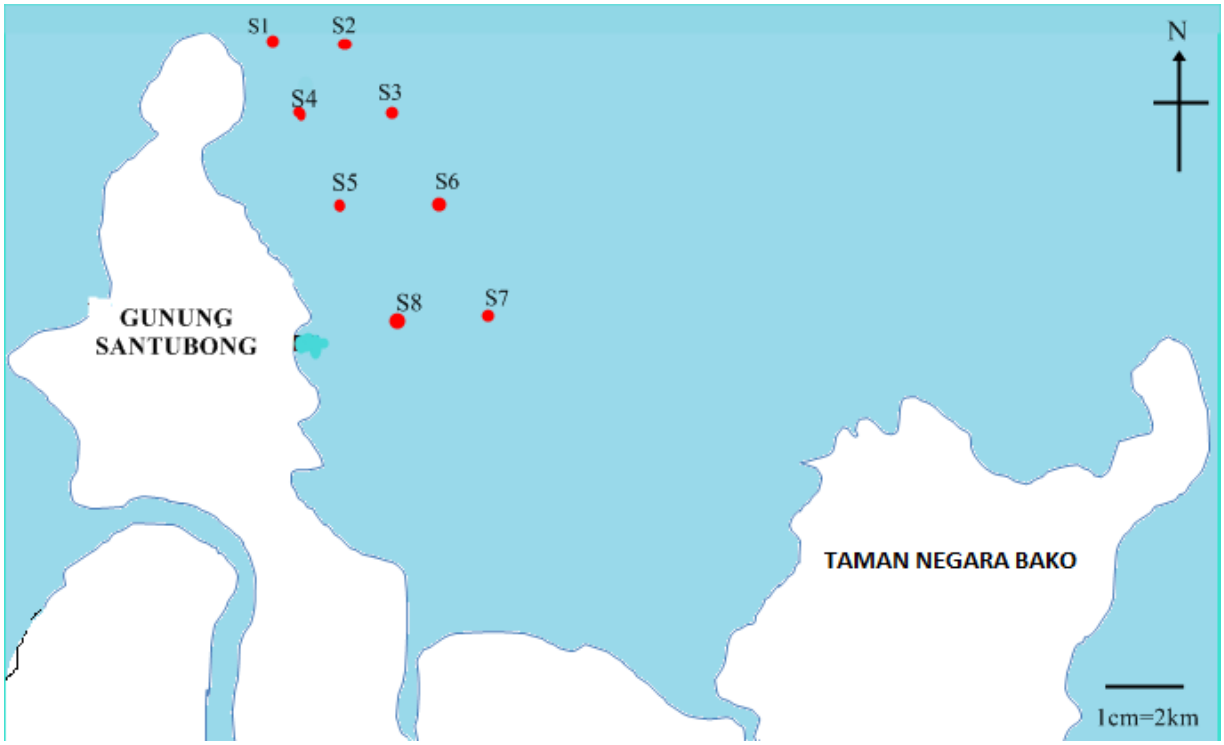

Figure 1: Location of the sampling sites at part of Kampung Buntal, Sarawak

Table 1: Coordinates of sampling sites

STATION	COORDINATES	TOTAL DEPTH
S 1	N 1˚ 48.543’ E 110˚ 20.006’	8.3
S 2	N 1˚ 49.361’ E 110˚ 19.621’	8.1
S 3	N 1˚ 47.860’ E 110˚ 21.130’	6.6
S 4	N 1˚ 46.928’ E 110˚ 20.994’	4.2
S 5	N 1˚ 46.032’ E 110˚ 21.263’	3.9
S 6	N 1˚ 46.018’ E 110˚ 21.928’	4.4
S 7	N 1˚ 43.927’ E 110˚ 21.702’	1.0
S 8	N 1˚ 44.378’ E 110˚ 22.540’	2.4

3.2 Pre-sampling

3.2.1 Acid wash procedure

All 32 water sample bottles (0.5L) were acid wash before sampling in order to prevent contamination. All the bottles were washed by using phosphate-free detergent and rinsed with tap water. Then all the bottles were acidified overnight by using 10% of hydrochloric acid, HCl. All the bottles were rinsed with deionized water, and dried in laminar flow bench. Each of bottles then was stored in the sealed plastic bag prior to sampling.

3.3 Sampling

3.3.1 Physicochemical analysis

For every station, the water column samples were collected by using a Van-Dorn Water Sampler (Wildco), 1 meter depth from the surface of the water column were measured by

using depth finder (SPEEDTECH), for chlorophyll-*a* analysis, nutrient analysis and heavy metal analysis. Then the samples were stored in 0.5L acid-washed bottles. The physicochemical parameters for temperature, salinity, pH, transparency and depth were taken in each station by using appropriate instrument as pH and temperature; pH meter (EXTECH, SDL 100), salinity; salinometer (ATAGO_PAL-06S), turbidity; turbidity meter (LT Lutron, TU-2016) and water transparency; Secchi disc and measuring tape.

3.4 Post-sampling

3.4.1 Chlorophyll-*a* nutrients and heavy metals

The water samples were collected using a Van-Dorn Water Sampler at 1 meter depth from the surface of the water column for each station. The water samples were stored in a labeled acid wash sample bottles and were placed in the sealed plastic bags. All water samples were stored in cooler box to be transported back to UNIMAS.

3.4.2 Sample preservations and storage

The preservation of water samples was done within 24 hours after water sampling collection to stabilize the metal composition in the solution. Water sample were acidified to ~pH 2 at volume of 1 ml of 12M HCl per 1L of water sample. This is due to prevent the loss of trace elements by the adsorption of the water bottles. The preservation of the water sample could last up to 2 months before water analysis. The water samples that have been preserved are located at clean container or box to reduce the contamination. In the laboratory, the acidified water samples were filter by using filtration set with 0.45µm glass fiber filter (Advantec, Japan) to remove suspended.

3.5 Laboratory analysis

3.5.1 Chlorophyll-*a* procedure

The water samples were filtered by using filtration set with glass fibers filter paper (size 47mm). The water that has been filtered, were stored into the bottle that has been acid wash in order to prevent contamination. The filter paper will be grind by using mortar and pastel with addition of 5ml of 90% acetone. Then filter papers were transferred into centrifuge tube and acetone was added until it reaches 10ml. All the samples were centrifuged for 20 minutes with speed 300rpm in order to separate the supernatant and the filter paper. All the centrifuge tubes were put into its rack, covered with aluminum foil and stored into refrigerator for 24 hours. Rinsed the cuvette with acetone and the supernatant were transferred into the cuvette. The spectrophotometer reading based on 4 wavelengths absorbance; 630λ, 647λ, 664λ and 750λ were recorded. These procedures were done in dim light. Chlorophyll a concentration was calculated based on the equation that stated by ESS Method 150.1: Chlorophyll - Spectrophotometric

$$\text{Chlorophyll a } (\mu g/L) = \frac{[11.85\ (Abs_{664}) - 1.54\ (Abs_{647}) - 0.08\ (Abs_{630})]\ (V)}{Vw(L)} \quad \text{.....Equation 1}$$

Where,

V, volume of acetone used in mL

Vw, volume of water filtered in L

L, cell/cuvette path length in cm (1cm)

3.5.2 Nutrient analysis

Nutrient analyses (nitrate, nitrite, orthophosphate and silicate) were performed by using spectrophotometer and method as described by Hach (2010).

3.5.2.1 Nitrate analysis

The standard method 351 N, Nitrate LR were used, Cadmium Reduction Method to measure the concentration of nitrate in each water samples. 10mL of graduated cylinder were filled with 50ml of water sample. The contents of one NitraVer 6 were added into the cylinder and shaken vigorously for 3 minutes. Then, the cylinder left for two minutes to allow the settlement of cadmium. 25mL of water sample then will be transferred into another cylinder and mix with NitraVer 3. After 15 minutes, the blank sample was inserted into spectrophotometer and 'Zero' button was pressed. 10mL of water sample were used as blank sample. The blank sample then replaced with sample cell and the absorbance reading displays for both samples were recorded.

3.5.2.2 Nitrite analysis

Nitrite analysis was done following Diazotization Method. The standard method 371 N, Nitrite LR PP were used, a sample cell were filled with 10mL of sample. NitriVer 3 Nitrite Reagent Powder Pillow and swirled into it dissolved. The solution was left for 20 minutes for reaction period. 10mL of water sample were filled into another cell and were used as blank sample. The blank sample was inserted into spectrophotometer and 'Zero' button was pressed. 10mL of water sample were used as blank sample. The blank sample then replace with sample cell and the absorbance reading display for both samples will be recorded.

3.5.2.3 Orthophosphate analysis

The standard methods 8048, (Ascorbic Acid) Method were used with range from 0 mgL^{-1} to 2.5 mgL^{-1} PO_3^{2}-. For sample cell preparation, PhosVer 3 was added into 10mL of sample. The sample cell will be inverted until it dissolved. 10mL of water were used as blank sample. Shift + Timer were pressed for two minutes reaction period. The blank sample was inserted into spectrophotometer and 'Zero' button was pressed. Then, blank sample were replaced with sample cell and then both absorbance reading display were recorded.

3.5.2.4 Silicate analysis

The standard method, Heteropoly Blue Method; 651 Silica LR was used. Two sample cells were filled up with 10mL of water sample. 14 drops of Molybdate 3 Reagent were added, swirled and left for 4 minutes for reaction period. Citric Acid Reagent Powder Pillow were added into each samples, swirled to mix and left for 1 minute. Then, Amino Acid F Reagent Powder Pillow into one the sample cells, swirled to mix and left for 2 minutes. The blank sample was inserted into spectrophotometer and 'Zero' button was pressed. Then, the blank sample was replaced with sample cell and then both absorbances reading display will be recorded.

3.5.3 Heavy metals analysis

The concentration of manganese (Mn), cadmium (Cd), zinc (Zn), copper (Cu) and lead (Pb) were determined by using atomic absorption spectrophotometer (Thermo Scientific, AAS iCE3500) while mercury (Hg) was determined by using flow injection mercury system (Perkin Elmer, FIMS 400)