Faculty of Resource Science and Technology

Impact of Aquaculture on Water Quality and Heavy Metals in the Water and Sediment of Selang Sibu River

Nuraminah Bt Jaafar (21973)

Bachelor of Science with Honours
Resource Chemistry
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DECLARATION

I hereby declare that this thesis is based on my original work except for citations which have been properly acknowledged. No portion of the work referred to in this study has been submitted in support of an application of another degree of this or any other university or institution of higher learning.

Nuraminah Binti Jaafar

Programme of Resource Chemistry

Faculty of Resource Science and Technology

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List of Abbreviations

$(NH_4)_2S_2O_8$	Ammonium Persulfate
Cd	Cadmium
Cr	Chromium
Cu	Copper
Fe	Iron
g	Gram
km	Kilometre
M	Molarity
m	Metre
mg/kg	Milligram per kilogram
mg/L	Milligram per litre
mL	Millilitre
N	Normality
Ni	Nickel
Pb	Lead
ppt	Parts per thousand
Zn	Zinc

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ABSTRACT

Aquaculture is the farming of aquatic plants and animals. Aquatic farming such as shrimp farming in the tributary, Selang Sibu River, generates income and provides food. The objectives of this study were to evaluate the impacts of aquaculture on the water quality and sediment of Selang Sibu River. Samplings were conducted in six stations. Results indicated that the total phosphorus (TP), and ammonia-nitrogen (NH_3-N) in water were recorded high in shrimp farm discharge due to shrimp farm effluent. pH of water and sediment samples were in alkaline conditions and fall in Class I according to INWQS. Total organic carbon (TOC) values were in decreasing order of S2>S1>S3>S4>S5>S6. In sediment quality, the TP concentration was high at shrimp farm discharge. The textures of the sediment among the stations were sandy clay and sandy clay loam. Concentrations of Iron (Fe) were higher at station S1 near shrimp farm discharge in water and sediment samples. Concentrations of Cadmium (Cd) were under detection limit for water and sediment samples.

Keywords: shrimp aquaculture; water quality; sediment quality; heavy metal

ABSTRAK

Akuakultur ialah penternakan haiwan dalam sistem perairan. Penternakan akuatik seperti penternakan udang di kawasan anak sungai Selang Sibu adalah sumber pendapat dan makanan. Tujuan penyelidikan ini adalah untuk menilai kesan daripada aktiviti akuakultur in pada kualiti air dan lumpur pada anak sungaiSelang Sibu. Sampel diambil pada enam kawasan pada hilir dan hulu sungai. Hasil menunjukkan jumlah fosforus dan ammonia nitrogen dalam air mencatatkan jumlah tertinggi pada tempat pembuangan penternakan udang berdasarkan pengaliran pembuangan tersebut. pH air dan lumpur adalah dikatogerikan dalam kelas pertama dalam INWQS. Nilai jumlah organik karbon adalah ditunjukkan dalam susunan menurun seperti S2>S1>S3>S4>S5>S6. Kepekatan fosforus dalam lumpur adalah dicatatkan tinggi di tempat pembuangan penternakan udang. Tekstur lumpur pada setiap sampel menunjukkan tanah liat berpasir dan campuran tanah liat berpasir. Kepekatan besi (Fe) dalam air dan lumpur adalah tinggi pada kawasan S1 yang berhampiran dengan tempat pembuangan penternakan udang. Manakala, kepekatan kadmium (Cd) adalah dibawah tahap pengesan yang rendah untuk sampel air dan lumpur.

Kata Kunci: Akuakultur udang; kualiti air; kualiti lumpur; logam berat

CHAPTER ONE

GENERAL INTRODUCTION

1.1 Introduction

Marine aquaculture is an important development around the world including Malaysia. Aquaculture refers to the reproduction of aquatic organisms in an artificial system and this has been done for a long time in some Asian countries. Selang Sibu River a tributary of Sibu Laut River is located near Kuching in the state of Sarawak, Malaysia. This river supplies the income for fishermen. Due to the relatively clean water and extensive coastline and high world market demand, Sarawak has developed into an important state for shrimp culture in Malaysia (Ling *et al.*, 2010a).

Aquaculture activities may give an impact on the concentration of heavy metal in the water. Furthermore, activities of aquaculture such as shrimp culture could modify the concentration of heavy metal in the water of a river. The high nutrients such as nitrogen, phosphorus and organic matter were reported near shrimp farm discharge (Ling *et al*., 2010b). But more exhaustive studies in this topic are required. In this study, the influence of aquaculture activities on the concentrations of different heavy metals Lead (Pb), Copper (Cu), Chromium (Cr), Zinc (Zn), Iron (Fe) and Cadmium (Cd) in the sediment and water was investigated.

The water and sediment quality are important measures because the aquaculture activities influence water quality. Water quality parameters such as pH, temperature, salinity, dissolved oxygen and BOD in the water is important to measure how polluted is the water caused by aquaculture activities and effects of some land use such as agriculture and industries. Without proper management, shrimp aquaculture can give rise to environmental deterioration (Michelle *et al.*, 2009; Boyd and Green, 2002; Latt, 2002; and WRM 2001). Wastewater discharges from shrimp farm contains high loads of nutrients and suspended solids (Michelle *et al.*, 2009; Boyd and Tucker, 1992; Latt, 2002; and Paez-Osuna *et al.*, 1998). Nutrients such as phosphorus and nitrogen in the shrimp farm effluent will promote the growth of phytoplankton and contribute to eutrophication. As reported by Ling *et al.*, (2009a) and Buda *et al.*, (2008) the Semariang Batu River water quality indicated phosphate was the highest at the station downstream of shrimp farm discharge and ammonia-nitrogen was highest at the station near the residential area. Other than that, a study of river sediment indicated that the station near shrimp farm recorded the highest organic carbon, phosphorus and nitrogen (Ling *et al.*, 2009a).

The problem statement in this study was how shrimp farming discharge can impact water quality and sediment quality at different distances from the shrimp farming discharge.

1.2 The objectives of the study

This study was carried out according to the following objectives:

a) To determine the concentration of Zn, Cu, Cr, Cd, Fe, Ni and Pb in the water and sediment,

b) To measure the water and sediment quality parameters,

c) To study the relationship between water and sediment quality and the distance from the shrimp farm discharge.

CHAPTER TWO

LITERATURE REVIEW

2.1 Aquaculture and Shrimp Farm

Aquaculture can be defined as the high-density production of fish, shellfish and plant forms in a controlled environment (Neospark, 2006). Aquaculture industry is expanding in many regions of the world including Malaysia. This industry plays a vital role in the economy, market and nutritional requirements (Amaranemi, 2006; Hashmi*et al.*, 2002). An aquaculture project is often located on or near estuaries and coastal area because these waters often provide for salt water aquaculture (Amaranemi, 2006). In addition, the water quality in the water is a major factor in aquaculture sustainability (Hashmi *et al.*, 2002). The Semariang Batu River is a tidal influenced river and due to the bloom in shrimp industry and became a site for shrimp aquaculture (Ling *et al*., 2009a). Impacts of shrimp aquaculture on the water quality have been reported in different parts of the world (Cole *et al.*, 2009; Paez-Osuna*et al.*, 2003; Senarath and Visnanathan, 2001).

The shrimp farming industry has often been promoted in term of the possibility of increasing rural employment and generating foreign exchange, especially in developing countries (Kongkeo, 1995; Xie and Yu, 2007). China has been one of the world's largest shrimp producers since 1988 and has recently seen a rapid expansion (Xie and Yu, 2007). As estimated, the big cities and industrial zones in the coastal areas dispose billions of tons of wastes and sewage, causing gradual worsening of the offshore waters and endangering marine farming (Xie and Yu, 2007). Instances of shrimp mortality in large areas caused by bad water quality are not rare. Another important element is organic contamination caused by the shrimp farming itself such as the use artificial feed of bad quality by the wrong ways, which does not reach the required stability in the water. Consequently, large amount of feeds escape from the intake by shrimps, and become the organic contaminants harmful to shrimps (Xie and Yu, 2007).

There are two main categories of water supply for aquaculture, groundwater and surface water. Groundwater also called well water or spring water often differs substantially from surface water in many characteristics. Groundwater is commonly considered the most desirable water source for aquaculture because, at a given site, it is usually consistent in quantity and quality, and free of toxic pollutants and contamination with predator or parasitic living organisms (Summerfelt, 1998).

A culture process typically requires a large amount of water resources and land area, sometimes produces a polluted effluent, adversely impacting the environment. Additionally, water quality in aquatic culture become worst or deteriorate because of accumulated feed residue and fish excreta. In many cases the metal source has been related to the food used (Uotila, 1991; Chou *et al*., 2002; Belias *et al*., 2003). The input of shrimp aquaculture farm into the river and coastal areas include nutrients and organic matter (Jones, 2001). The organic matter contents influences many of soil properties such as in supplying plant available nitrogen and deactivating pesticides. Other than that, according to Cole *et al*., (2009), negative effects for aquaculture include organic pollution and eutrophication due to excessive build-up of nutrients and waste. Too much nutrient salt and organic matter in the shrimp producing system leads to the eutrophication and worsening of the environment (Sun *et al*., 1997). The negative impacts of aquaculture are those related with higher loads of nutrients, suspended solids and organic matter (Uotila, 1991), giving rise to increased biochemical oxygen demand, excessive algae growth, etc. In addition, sediment composition can be effected by organic matter that acts as metal trap.

Wastes generated by aquaculture activity such as feces and unconsumed feed first settle in the bottom, as a consequence of organic waste and metabolites of degraded organic matter accumulated in sediment and water. Part of the waste is flushed out of the ponds immediately or after the organic matter has been degraded (Neospark, 2006).

2.1 Heavy metal in Water and Sediment

Heavy metal is accumulated in marine sediments, where they are incorporated in several biological and chemical cycles, affecting the water column and biota. On the other hand, chemical reactions can change the concentration of heavy metals in sediments and, as a consequence in the overlying water (Luoma, 1990). Besides that, heavy metals are of particular concern due to their environmental persistence and biogeochemical recycling and ecological risks (Abbas *et al.*, 2008). Furthermore, aquaculture activities could also modify the concentration of heavy metals in adjacent sediment by introducing high loadings of metals contained in the particulate matter present in the effluents, which may be up to several tons per day (Tovar *et al.*, 2000). The heavy metal sources from the municipal waste, food, fertilization and bottom liming are potential sources (Carbonell *et al.*, 1997). The fate and consequences of metals in the aquatic environment depend largely on the physical and chemical conditions of the water (Kamaruzzaman *et al., 2010*)

Sediments are mixture of several components including different mineral species as well as organic debris. It also represent one of the ultimate sinks for heavy metals discharged into environment (Luoma and Bryan, 1981; Bettinetti *et al.,* 2003; Hollert *et al.,* 2003) and also sink for organic materials, nutrient and sediment condition affected the overlying water (Ling *et al.,* 2009a). The total analysis of heavy metals such as Cd, Cr, Cu, Ni, Pb, and Zn in sediments and soils is commonly done to evaluate the degree of contamination of aquatic and terrestrial environments.

2.3 Water Quality

Water quality during culture is influenced by rates of photosynthesis and respiration, water temperature, levels of fertilization and feeding, mechanical aeration and the amount of water exchanged in the culture enclosure daily (Lovshin and Manomaitis, 2000).

The pH of water is an index of hydrogen ion (H^+) activity of water. The pH scale (range from 0 to 14) is logarithmic (base 10), an important fact to remember because a drop of 1 pH unit indicates a 10 fold increase in hydrogen ions (H^+) present in water. A pH value may fall anywhere on a scale from 0 (strongly acidic) to 14 (strongly basic or alkaline), with a value of 7 representing neutrality. The pH of most productive natural waters that are unaffected by pollution is normally in the range of 6.5 to 8.5 at sunrise, typically closer to 7 than 8 (Summerfelt, 1998).

Dissolved oxygen (DO) is by far, the most important parameter in aquaculture (Samantha, 2008). Oxygen consumption is directly linked to size, feeding rate, activity level and temperature, and it will surprise some that large fish consume less oxygen than their smaller counterparts which have higher metabolic rates. The amount of dissolved oxygen in water increases as temperature reduces, but decreases when salinity and altitude increases

(Samantha, 2008). Biochemical oxygen demand (BOD) is a measure of the amount of oxygen that bacteria will consume while decomposing organic matter under aerobic conditions (NGRGC, 2001).

According to Lovshin and Monamaits, (2000), total ammonia nitrogen is commonly measured in water used for aquaculture. Total ammonia nitrogen is the sum of unionized and ionized ammonia in the water. Unionized-ammonia is very toxic to aquatic animals while ionized ammonia has slight toxicity. Unionized-ammonia (NH_3) is a nitrogenous excretory product of most aquatic animals.

Phosphorus and nitrogen nutrients can cause eutrophication and are potential sources of pollution in natural waters (Gross and Boyd, 1998). In many nations, regulations are being implemented to limit pollution of natural waters by aquaculture pond effluents (Boyd *et al.*, 1998). Total phosphorus and total nitrogen concentrations can be used as indicators for the pollution potential of pond effluents. A standard way to measure total phosphorus and total nitrogen in water is to convert all forms of phosphorus and nitrogen to orthophosphate and nitrate, respectively, by digestion and persulfate oxidation (APHA, 2005).

Table 1 show the classes of water quality standard that was proposed for Malaysia.

Table 1 Interim National Water Quality Standard for Malaysia

Parameter/Classes	I	II	III	IV	V
Ammonia-Nitrogen (mg/L)	< 0.1	0.1 – 0.3	0.3 – 0.9	0.9 – 2.7	> 2.7
BOD (mg/L)	< 1	1 – 3	2 – 6	6 – 12	> 12

Dissolved Oxygen (mg/L)	> 7	5 – 7	3 – 5	1 – 3	< 1
pH	> 7.0	6.0 – 7.0	5.0 – 6.0	< 5.0	> 5.0
Phosphate (mg/L)	0.0 – 1.0	1.1 – 4.0	4.1- 9.9	> 10.0	-

Source: Department of Environment (http://www.jas.sains.my)

Class	Category
I	Represents water body of excellent quality
II	Represents water bodies of good quality
III	Is defined with the primary objective of protecting common and moderately tolerant aquatic species of economic value
IV	Defines water quality required for major agricultural irrigation activities which may not cover minor applications to sensitive crops
V	Represents other waters which do not meet any of the above categories.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Study Site and Sample Collection

The study site was at the Selang Sibu River tributary of Sibu Laut River, located near to Telaga Air village, Kuching state of Sarawak, Malaysia. Station S1 was located about 200 m downstream from the shrimp farm effluent discharge point (Figure 1). Station S2 was located 500 m upstream from the shrimp farm discharge but downstream of the Selang village; station S3 was located 500 m downstream of shrimp farm discharge; station S4 and station S5 were located about 1.50 km and 1.80 km downstream of shrimp farm discharge; station S6 was located about 2.50 km downstream of shrimp farm discharge and near at tributary Trombol River.

Water samples and sediment samples were collected three times, that is, 13 August 2010, 8 December 2010, and 20 January 2011 during low tide. Water and sediment samples were collected at six stations (S1, S2, S3, S4, S5 and S6). Water samples were collected on the surface. Prior to the sampling, the bottles were soaked in 10% nitric acid overnight and washed with deionized water and dried (Muzawina, 2005). The water samples were filtered (Advantex GA-100) except water for BOD_5 analysis before they were preserved at 4°C.

Sediment samples were collected from the river during low tide and were packed using plastic bags. The water and sediment samples were packed in the cooler box with ice. The sediment samples were air dried for one week.

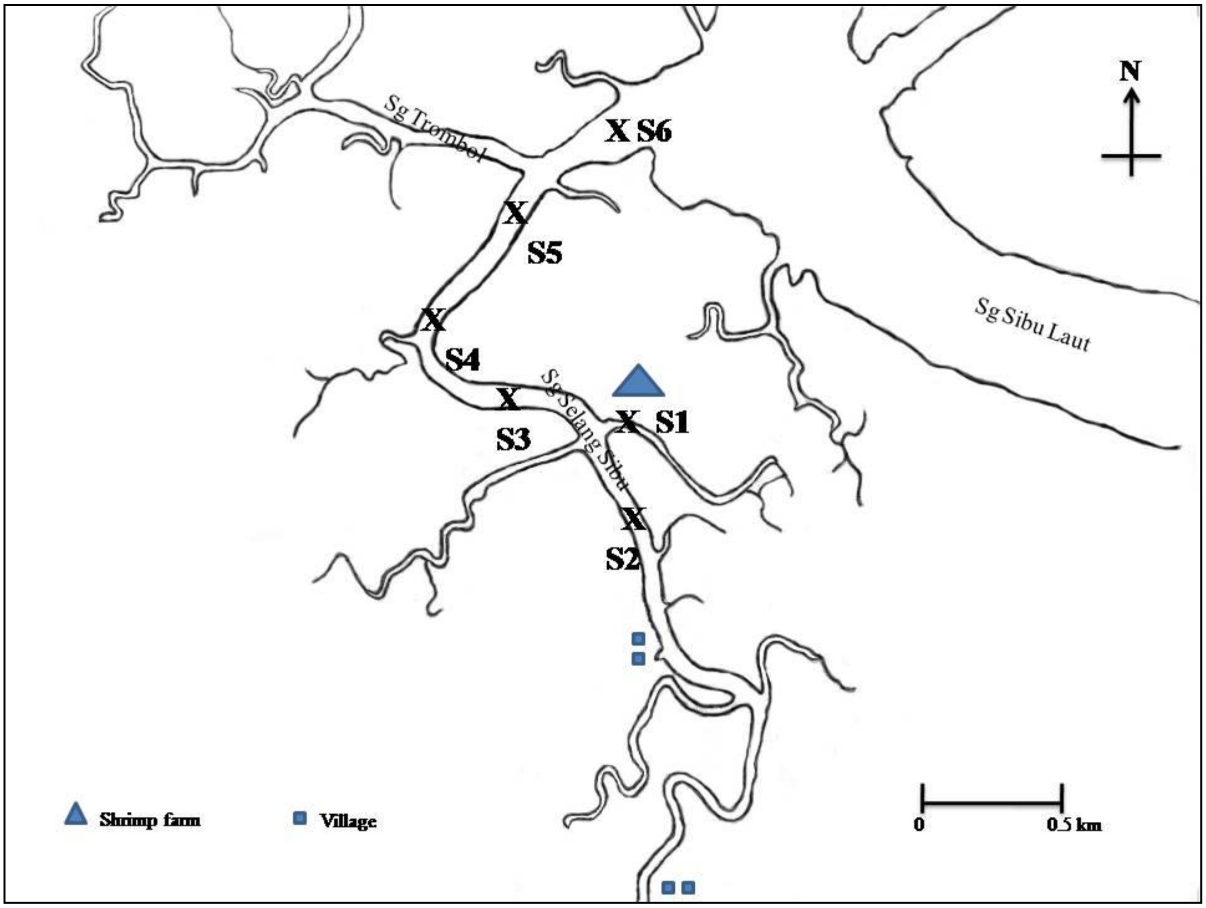

Figure 1 Map of sampling stations at tributary Selang Sibu River

3.2 Water Quality Parameters measured *in-situ*

River water quality parameters were measured *in-situ*. They were dissolved oxygen (DO) using a DO meter (Cyberscan 100^{DO}), pH and temperature using pH meter (Thermo Orion), salinity using portable refractometer (Apago), depth of water was measured using a depth finder (PS-7, Hondex) and transparency of water using measuring tape and secchi disc. The readings were taken in triplicates.

3.3 Parameters Analyzed in the Laboratory

Water samples were analyzed for 5-days biochemical oxygen demand (BOD_5), ammonia-nitrogen (NH_3-N), total phosphorus (TP), total Kjeldahl nitrogen (TKN) and heavy metals (Zn, Cu, Cr, Cd, Pb, Fe and Ni). All parameters were analyzed according to Standard Method (APHA, 2005) and HACH (1996). NH_3-N was analyzed using two method according to Standard Method (Phenate Method) (APHA, 2005) and (Nessler Method) (HACH, 1996) to make a comparison of the values of concentration.

The sediment samples were grounded using mortar and pestle before the analysis in the laboratory. Sediment analysis included moisture content, pH, particle size analysis (PSA), total organic carbon (TOC), total Kjeldahl nitrogen (TKN), total phosphorus (TP) and heavy metals(Zn, Cu, Cr, Cd, Pb, Fe and Ni).

A. Water Analysis

3.3.1 Heavy metal analysis in the water

Nitric Acid Digestion (3030 E)

Heavy metal was analyzed using Flame Atomic Absorption Spectrophotometer (AAS) according to standard method (APHA, 2005). The water samples were collected using the polyethylene bottles. The water samples were filtered through a 0.45 micropore membrane filter or filter paper (Whatman No. 41) for estimation of dissolved metal content. Filtrate of 500 mL water samples was preserved with 2 mL concentrated nitric acid (HNO_3) to pH < 2 to prevent the precipitation of metals.

One hundred millilitres of well-mixed, acid preserved sample appropriate for the expected metals concentration was transferred to a beaker. In a hood, 5 mL concentrated $HNO_3$was added. The beaker was covered with a ribbed watch glass to minimize contamination. It was brought to slow boil and evaporated on a hot plate to the lowest volume possible about 10 to 20 mL before precipitation occurs. Heating was continued and concentrated HNO_3 was added as necessary until digestion was complete as shown by a light-colored, clear solution. During digestion, the samples were not dried. The down flask or beaker walls were washed with metal-free water and then filtered. The filtrate was transferred to a 100 mL volumetric flask with two 5 mL portions of water and these rinsing was added to the volumetric flask. It was cooled, diluted to mark and mixed thoroughly before bring analyzed using Atomic Absorption Spectrophotometer (AAS) (Thermo Scientific, ICE 3500). The concentration unit was in the mg/L. The detection limits for heavy metals are shown in the Table 2.

Table 2 Detection limits for heavy metals in concentration mg/L for water

Elements	Detection limits (mg/L)
Cadmium (Cr)	0.0028
Chromium (Cd)	0.0054
Copper (Cu)	0.0045
Iron (Fe)	0.0043
Lead (Pb)	0.0130
Nickel (Ni)	0.0080
Zinc (Zn)	0.0033

3.3.2 **Total Phosphorus**

Persulfate Digestion (4500 P) (APHA 2005)

Total Phosphorus in the water was analyzed using Persulfate Digestion Methods according to standard methods (APHA, 2005). Fifty millilitres of mixed samples were used and 1 drop phenolphthalein indicator solution was added. If a red color develops, dropwise sulphuric acid, H_2SO_4 solution was added to discharge the color. One mL H_2SO_4 solution and 0.5 g solid potassium persulfate, $K_2S_2O_8$ was added. Then, the solution is boiled gently on a preheated hot plate for 30 to 40 minutes or until a final volume of 10 mL is reached. It was cooled, and diluted to 30 mL with deionized water. One drop of phenolphthalein indicator solution was added. One normality, *N*, of sodium hydroxide, NaOH was used to neutralize to faint pink color and it was made up to 100 mL with deionized water. The digestion step was completed and phosphorus was determined by Ascorbic Acid Method (4500 P-E) (APHA, 2005).