

HYDROCARBONS AND HEAVY METALS POLLUTANTS IN AQUACULTURE

Ananth Retnam*, Mohamad Pauzi Zakaria

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1.0 INTRODUCTION

The increasing of human population has increased the need for food supply. This with the need for quality fish protein has increased the demand for fish and fish products. The global consumption of fish and derived fish products has generally increased during recent decades (Wim et al., 2007). The cage aquaculture sector has grown very rapidly during the past 20 years and is presently undergoing rapid changes in response to pressures from globalization and growing demand for aquatic products in both developing and developed countries. It has been predicted that fish consumption in developing countries will increase by 57 percent, from 62.7 million metric tons in 1997 to 98.6 million in 2020 (Delgado *et al.*, 2003). In Malaysia, government agricultural policy is actively encouraging investment in aquaculture, and there has been increasing number of marine and brackish water aquaculture operations. Total fish production from aquaculture has increased from 100 thousand tons in 1997 to 200 thousand tons by 2006 (MOF, 2007).

PROBLEM STATEMENT

Fish enjoys a good reputation as a nutritious and healthy food. The consumption of fish is recommended because it is a good source of omega-3 fatty acids which has been associated with health benefits due to its cardio-protective effects (Castro et al., 2008). Fish also contains vitamins, mineral and proteins which play essential role in human health (Wim et al., 2007). However, the levels of contaminants in fish and poor management of fisheries are of particular interest because of the potential risk to humans who consume them. In June 2008 European Union (EU) ban on Malaysian seafood products. The ban was due to health concern where the seafood industries in the country failing to meet the standards set by the agriculture audit authorities of the EU. The seafood producers failed to maintain quality and safety of their products. The seafood industry suffered losses of almost RM600 million (Bernama, 2008). Malaysia's export of fish and crustaceans to the EU was worth €102 million (\$131 million) in 2007 (International Herald Tribunal, 2009).

The aquaculture industries are exposed to many chemical, biological and other pollutants. The use of antibiotic, agrochemicals formulated feed resulted in presence of many chemical and biological pollutants beside the anthropogenic inputs like heavy metals and PAHs also contributed to pollutants in aquaculture facilities.

In Malaysia, there have been many researches on contaminants in fish but from the toxicological point of view, excessive consumption of PAH and metal contaminated seafood may cause toxicity to humans. Polycyclic aromatic hydrocarbons (PAHs) are organic compounds known for their mutagenic and carcinogenic effects, bioaccumulate in animal and human tissue. Heavy metals are inorganic chemicals that are non-

biodegradable, cannot be metabolized and will not break down into harmless forms. This marks the measurement of levels of PAHs and heavy metals in the tissues of fish and other aquatic organism becoming more significant. There is a lack of research work on PAHs and heavy metals contamination in cultured fish. However, extensive survey of PAHs contamination in Malaysian environment has been conducted by Zakaria et al, 2001; 2002; Isobe, et al., 2004; Isobe, et al., 2007; Chandru, et al., 2008; Saha, et al., 2009. For heavy metals so far only one of such study conducted in cultured fish in Linggi estuary. In this study high concentration of Pb and Cd were found in the tissue of cultured fish. The concentrations of these elements are above than the permissible level set by the Malaysian Government (Shahrizat, 2005).

High level of PAHs and heavy metals can accumulate in cultured fish to such a degree that it becomes toxic to human when ingested. In Malaysia data on PAHs and heavy metals in aquaculture area and cultured organism are lacking. The safety and health state of the fish consumed are not aware of. The study of the presence of PAHs and heavy metals in the aquaculture environment is important because they play toxic roles in cultured especially when they passed on to human being through the consumption of fish and fish products.

SIGNIFICANCE OF THE STUDY

This study is believed to be able to provide some information on the status of pollutant contamination in fish from aquaculture site in Malaysia and the safety of the aquaculture products for human consumption.

RESEARCH OBJECTIVES

1. To evaluate the levels of polycyclic aromatic hydrocarbons (PAHs) and heavy metals in water, sediments and fish from aquaculture fish ponds
2. To evaluate PAHs and heavy metals concentration in different organs of cultured fish gain sight into distribution in fish
3. To assess the impact of these pollutants on the aquaculture ponds and the surrounding aquatic environment
4. To assess the quality of the fish for human consumption
5. To document the chemicals and other products used in the aquaculture facility

2.0 LITERATURE REVIEW

Contribution of fish to the daily dietary energy supply is very important. World wide fish is considered to be an essential part of the diet. In Asia annual per capita consumption is mostly above 25 kg (FAO, 2006).

Polycyclic aromatic hydrocarbons (PAHs) are wide spread organic pollutant in the environment. The sources of PAHs are both from natural and anthropogenic mainly from incomplete combustion of organic materials, fossil fuel and petroleum (Liang, 2007). PAHs are persistence to degradation and lipophilic therefore they tend to accumulate in organic tissues of animals and human (Vives & Grimalt, 2002). These compounds may show the toxic effects on organisms at a very low concentration, some at even in $\mu\text{g/g}$ levels (Deb, 2000). PAHs have been detected in many aquatic organisms like fish, prawn and mussels. In Hong Kong PAHs have been detected in tilapia fish muscle at 184-194 ng/g and viscera at 505-854 ng/g. In this study, the accumulation of PAHs are higher in

viscera 3.5 times than in muscles (Liang, 2007). In France a study conducted to evaluate the PAHs concentration in fishes from natural reserve. They have detected PAHs in fish gall bladder and liver with concentration varying from 5-30ng/g (Pointet, 2000). PAHs not only detected in the wild catch and natural reserve but also in aquaculture organisms. In India, PAHs detected in prawns with compounds benz(ghi)perylene in highest concentration with 220 ng/g and this exceed the FOA/WHO permissible levels (Amaraneni, 2006). In China, fish from aquaculture cages in coastal waters were analysed for PAHs. Naphthalene and phenanthrene were detected in fish bile (Klumpp, Huasheng, Humphrey, Xinhong, & Codi, 2002). This is the scenario of PAHs detected in fishes from wild catch and also aquaculture but there is reported case for PAHs in fish from Malaysian waters.

Heavy metals leave biological cycles very slowly. Elements such as mercury, cadmium, copper and zinc are considered most dangerous in the ecotoxicological aspect (Golovanova, 2008). Aquatic organisms are able to accumulate heavy metals up to concentration that are tenth and even thousands of times higher than the concentration in the environment. Heavy metals accumulate in many important organs (Golovanova, 2008). Supporting structures and gill mostly accumulate waterborne heavy metals, while stomach and intestines accumulated food-associated elements. Most often highest concentration of heavy metals found in fish liver, kidney and gills (Golovanova, 2008). Diet is the main route of exposure to heavy metals in the case of population no-exposed to them. Heavy metals have been one of the important pollutants in the coastal waters because of their toxicity and capacity to accumulate in marine organism. Heavy metal contamination has been identified as a concern in coastal environment due to discharge from industrial waste, agricultural and urban sewage (Asyum et al., 2009). Water metals concentration correlates positively with concentrations in fish tissue (Castro et al., 2008). Increased concentration of metals mainly mercury, cadmium and lead have been observed in cultured fish. In Hong Kong, metals pollution problems in the fish culture sites were serious as reflected by high metal concentration recorded in seawater, sediments and biomonitor *Perna viridis* and concentration of zinc and copper are higher in fish tissues (Wong et al., 2001). Another study conducted in estuary in Spain indicated high level of zinc and copper in water and high concentration of zinc, copper, arsenic and lead in sediments. High copper and zinc concentration observed in liver tissue and correlates with metal levels in fraction of water and sediments (Juan et al., 2009).

In Malaysia, a preliminary study conducted on heavy metals in fish from Terengganu river basin East Coast Malaysia found high concentrations of Fe, Pb and Cu. The high concentration of Pb and Cu found at the downstream stations could be attributed to sewage effluents from domestic sources (Suratman et al., 2009). Another study conducted on heavy metals in edible fish from Paka estuary Terengganu showed highest accumulation of Cu and Zn in liver followed by stomach and lowest in gill (Kamaruzzaman et al., 2007). Most of the study carried out focused on wild catch fish.

3.0 RESEARCH METHODOLOGY

3.1 Study Area

Samples will be collected from Penang (figure 1). Penang has the highest number of brackishwater cages (24,235). Siakap (*Barramundi*) selected for the study because of it is the mostly rare species and likely the highly consumed fish species in Malaysia.

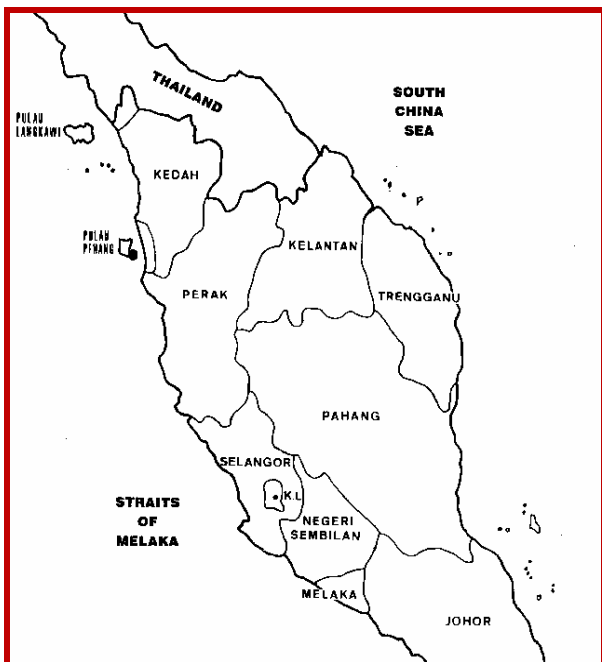


Figure 1: Sampling location

3.2 Research Instrument: Inductively coupled plasma- Mass Spectrometer (ICP-MS) and gas chromatography-mass spectrometer (GCMS)

3.3 Sampling and sampling materials

Sampling will be conducted twice throughout the study period.

Samples collection for water, sediments, Fish, fish feed and phytoplankton

3.4 Research procedure:

Objective 1 and 2

PAHs in samples (water, sediment, fish, fish feed and phytoplankton) determined by solvent extraction using SPE and soxhlet. The extracts go through volume reduction and clean up procedures before injecting into GCMS. For heavy metals determination, the samples will be acid digested before introduced into ICP-MS.

Fish tissue dissection, the gill, liver, bile and muscle will be dissected stored separately prior to sample preparation. Necessary quality control steps will be taken to ensure the accuracy of the results.

Objective 3

Water samples will be analysed for physio-chemical parameters like pH, Dissolved Oxygen (DO), Total Suspended Solids (TSS), Phosphorous, Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD) and compared with standards for aquatic organism.

Objective 4

The concentration of PAHs and heavy metals in fish, water and sediment will be compared with standards and guidelines for PAHs and heavy metals in fish, water and sediment for human consumption like FOA/WHO

Objective 5

The chemicals like antibiotics, feed additives, soil and water treatment etc that used in the aquaculture site will be documented through questionnaire and interviews

3.5 Data analysis:

ANOVA

REFERENCES

FAO, 2006. Food and Agriculture Organization Technical paper 500. State of world aquaculture

MOF, 2007. Ministry of Fishery, Malaysia. <http://www.mof.moa.my>. Accessed on 17 February 2009.

BERNAMA, 2008. Malaysian National News Agency. www.bernama.com. Assessed on 23 March 2009.

S. Focardi, I. Corso, E. Franchi. 2005. Safety issues and sustainable development of European aquaculture: new tools for environmentally sound aquaculture. *Aquaculture International* 13: 3-17

International Herald Tribunal. 2009. www.iht.com assessed on 23 march 2009

Wim, V., Issabelle, S., Karen., Stefan, D. H., John, V. C. 2007. Consumer perception versus scientific evidence of farmed and wild fish: exploratory insights for Belgium. *Aquaculture International* 15: 121-136

Castro-Gonzalez, M. I., Mendez-Armenta, M., 2008. Heavy metals: Implications associated to fish consumption. *Environmental Toxicology and Pharmacology* 26: 263-271

Wong, C. K., Wong, P. P. K., Chu L. M. 2001. Heavy metal concentration in marine fishes collected from fish culture sites in Hong Kong. *Archives of Environmental Contamination and Toxicology* 40:60-69

Juan, J. Vicente-Martorell, Maria, D. Galindo-Riano, Manuel, Garcia-Vargas, Maria, D. Granado-Castro. 2009. Bioavailability of heavy metals monitoring water, sediments and fish species from polluted estuary. *Journal of Hazardous Material* 162: 823-836

Asyum, Turkmen., Yalcin, Tepe., Mustafa, Turkmen. 2009. Heavy metals contamination in tissues of the Garfish, *Belone belone* L., 1761, and the Bluefish, *Pomatomus saltatrix* L., 1766, from Turkey waters. *Bulletin Environmental Contamination and Toxicology* 82:70-74

Golovanova, I. L. 2008. Effects of heavy metals on the physiological and biochemical status of fishes and aquatic invertebrates. *Inland Water Biology* 1(1):93-101

Suratman, S., Hang, H., C. Shazili, N., A., M. Mohd Tahir, N. 2009. A Preliminary Study of the Distribution of Selected Trace Metals in the Besut River Basin, Terengganu, Malaysia. *Bulletin of Environmental Contamination Toxicology* 82:16–19

Kamaruzzaman, B., Y. Zaleha, K. Ong, M. C., Wilson, K., Y., S. 2007. Copper and Zinc in Three Dominant Brackish Water Fish Species from Paka Estuary, Terengganu, Malaysia. *Malaysian Journal of Science* 26 (2): 65-70

Shahrizat, Y. 2005. Distribution and Accumulation of Heavy Metals in Fish Cage System in Linggi Estuary, Malaysia. Master Thesis. Faculty of Science Universiti Putra Malaysia

Amaraneni, S. (2006). Distribution of pesticides, PAHs and heavy metals in prawn ponds near Kolleru lake wetland, India. *Environment international*, 32(3), 294-302.

Chandru, K., Zakaria, M. P., Anita, S., Shahbazi, A., Sakari, M., Bahry, P. S., et al. (2008). Characterization of alkanes, hopanes, and polycyclic aromatic hydrocarbons (PAHs) in tar-balls collected from the East Coast of Peninsular Malaysia. *Marine pollution bulletin*, 56(5), 950-962.

Deb, S. C., Araki, Taro., Fukushima, Takehiko. (2000). Polycyclic Aromatic Hydrocarbons in fish organs. *Marine pollution bulletin*, 40(10), 882-225.

Isobe, K. O., Zakaria, M. P., Chiem, N. H., Minh, L. Y., Prudente, M., Boonyatumanond, R., et al. (2004). Distribution of linear alkylbenzenes (LABs) in riverine and coastal environments in South and Southeast Asia. *Water Research*, 38(9), 2448-2458.

Isobe, T., Takada, H., Kanai, M., Tsutsumi, S., Isobe, K. O., Boonyatumanond, R., et al. (2007). Distribution of polycyclic aromatic hydrocarbons (PAHs) and phenolic endocrine disrupting chemicals in South and Southeast Asian mussels. *Environmental Monitoring and Assessment*, 135(1-3), 423-440.

Klumpp, D., Huasheng, H., Humphrey, C., Xinhong, W., & Codi, S. (2002). Toxic contaminants and their biological effects in coastal waters of Xiamen, China. I. Organic pollutants in mussel and fish tissues. *Marine pollution bulletin*, 44(8), 752-760.

Liang, Y., Tse, M.F., Young, L., Wong, M.H. (2007). Distribution pattern of polycyclic aromatic hydrocarbons (PAHs) in the sediments and fish at Mai Po Marshes Nature Reserve, Hong Kong. *Water Research*, 41, 1301-1311

Pointet, K. a. M., Arielle (2000). PAHs analysis of fish whole gall bladders and livers from the Natural Reserve of Camargue by GCMS. *Chemosphere*, 40, 293-399.

Saha, M., Togo, A., Mizukawa, K., Murakami, M., Takada, H., Zakaria, M. P., et al. (2009). Sources of sedimentary PAHs in tropical Asian waters: Differentiation between

pyrogenic and petrogenic sources by alkyl homolog abundance. *Marine pollution bulletin*, 58(2), 189-200.

Vives, I., & Grimalt, J. (2002). Method for integrated analysis of polycyclic aromatic hydrocarbons and organochlorine compounds in fish liver. *Journal of Chromatography B*, 768(2), 247-254.

Zakaria, M. P., Okuda, T., & Takada, H. (2001). Polycyclic aromatic hydrocarbon (PAHs) and hopanes in stranded tar-balls on the coasts of Peninsular Malaysia: Applications of biomarkers for identifying sources of oil pollution. *Marine pollution bulletin*, 42(12), 1357-1366.

Zakaria, M. P., Takada, H., Tsutsumi, S., Ohno, K., Yamada, J., Kouno, E., et al. (2002). Distribution of polycyclic aromatic hydrocarbons (PAHs) in rivers and estuaries in Malaysia: A widespread input of petrogenic PAHs. *Environmental Science and Technology*, 36(9), 1907-1918.