UNIVERSITI PUTRA MALAYSIA

DISTRIBUTION AND CONCENTRATION LEVELS OF SELECTED HEAVY METALS AND NUTRIENTS IN SUNGAI TENGI DUE TO PADDY PLANTATION ACTIVITIES

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By

NURUL ADILAH MOHD BADROLDIN

Thesis submitted to the school of Graduate Studies, Universiti Putra Malaysia, in fulfilment of the requirements for the degree of Master of Science

January 2012

DEDICATIONS

This thesis is especially dedicated to:

My mother and father,

Thanks for the never ending love

My brothers and sister,

Hope the future holds something wonderful for all of you

Mia and family,

Your help and encouragement has been so valuable to me

All my friends,

I'll never get this far without your support, thanks for the friendship.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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NURUL ADILAH MOHD BADROLDIN

January 2011

Chairman : Prof. Ahmad Ismail, PhD

Faculty : Science

Monitoring of river water quality is one way of assessing the quality of environment. In this study, Sungai Tengi was chosen as the sampling site to assess the input of heavy metals and nutrients due to agricultural and other activities in the vicinity area into the river system and finally to the estuary. The water from Sungai Tengi was also used to irrigate the paddy fields in the Sekinchan, Sungai Besar and Tanjung Karang areas which are known as the biggest rice production areas in Selangor district. Therefore, the objectives of this study are to investigate the concentration levels of heavy metals (Cu, Zn, Fe, Pb, Ni and Cd) and nutrients (nitrate and phosphate) in water column and sediment obtained from Sungai Tengi. Besides that, the levels of heavy metals in various tissues of black tilapia in Sungai Tengi were determined. Then, the pollution status of heavy metals in sediment along Sungai Tengi was estimated using the geochemical index. A total of 16 stations were set up along the river and 3 sample types of water, sediment and fish were taken. The samplings were carried out in four stages of paddy planting processes.

The ranges of heavy metals in water were Cu (0.01-0.07 mg/l), Zn (0.02-3.57 mg/l), Fe (0.17-12.96 mg/l), Pb (0.03-0.80 mg/l), Ni (0.03-0.58 mg/l) and Cd (0.00-0.07 mg/l) respectively showed significant difference ($p<0.05$). The ranges of heavy metals in sediment were Cu (5.24-38.55 µg/g), Zn (23.46-81.05 µg/g), Fe (6876.50-18579.01 µg/g), Pb (9.00-50.22 µg/g), Ni (5.91-22.90 µg/g) and Cd (0.06-0.85 µg/g) respectively showed significant difference ($p<0.05$). The ranges of nitrate in water and sediment were 0.019-0.917 mg/l and 0.132-0.877 µg/g respectively. While, the ranges of phosphate in water and sediment were 0.0101-0.0713 mg/l and 0.0303-0.2953 µg/g respectively.

The levels of heavy metals in tilapia were higher compared to previous studies. The ranges are below the permissible limit except for Pb and Ni. The ranges of heavy metals in muscle of tilapia were Cu (0.86-1.91 µg/g), Zn (0.90-2.93 µg/g), Fe (2.20-7.68 µg/g), Pb (1.54-6.62 µg/g), Ni (0.69-2.00 µg/g) and Cd (0.10-0.29 µg/g) respectively showed significant difference ($p<0.05$).

Based on geochemical fraction, the level of heavy metals are 10% due to anthropogenic loading during ploughing stages. While 100% due to natural occurring during growing stages, 13% due to anthropogenic loading during fertilizing stages and 14% due to anthropogenic loading during harvesting stages respectively. However, present study showed low range of heavy metals in surface sediment from Sungai Tengi compared to others studies.

The study showed Sungai Tengi is not really contaminated by heavy metals, nitrate and phosphate in water, sediment and tilapia since it were localize due to vicinity activities. The data obtained could serve as a reference to evaluate the heavy metals, nitrate and phosphate in agricultural area.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah master sains

TABURAN DAN KEPEKATAN LOGAM BERAT DAN NUTRIEN YANG TERPILIH DIDALAM SUNGAI TENGI BERDASARKAN AKTIVITI PENANAMAN PADI

Oleh

NURUL ADILAH MOHD BADROLDIN

Januari 2011

Pengerusi : Prof. Ahmad Ismail, PhD

Fakulti : Sains

Pemantauan kualiti air sungai adalah satu cara untuk menilai kualiti alam sekitar. Dalam kajian ini, Sungai Tengi telah dipilih sebagai lokasi persampelan untuk menilai kadar kemasukan logam berat, nitrat dan fosfat yang di sebabkan oleh aktiviti-aktiviti pertanian dan sebagainya di kawasan sekitar yang mengalir ke dalam sungai dan akhir sekali ke muara. Air dari Sungai Tengi juga digunakan untuk mengairi kawasan sawah padi di sekitar Sekinchan, Sungai Besar dan Tanjung Karang yang dikenali sebagai daerah pengeluaran beras terbesar di Selangor. Oleh itu, objektif kajian ini adalah untuk mengetahui aras logam berat (Cu, Zn, Fe, Pb, Ni dan Cd) dan nutrient (nitrat dan fosfat) di dalam air, sedimen dari Sungai Tengi. Malah, aras logam berat di dalam beberapa jenis tisu tilapia hitam turut di tentukan. Kemudian, tahap pencemaran logam berat di dalam sedimen turut dikira menggunakan indek geokimia. Terdapat 16 stesen di sepanjang sungai dan 3 jenis sampel diambil iaitu air, sedimen, dan tilapia hitam. Persampelan di jalankan dalam empat peringkat penanaman padi.

Julat logam berat di dalam air menunjukkan perbezaan yang signifikan ($p<0.05$) bagi Cu (0.01-0.07 mg/l), Zn (0.02-3.57 mg/l), Fe (0.17-12.96 mg/l), Pb (0.03-0.80 mg/l), Ni (0.03-0.58 mg/l) dan Cd (0.00-0.07 mg/l). Julat logam-logam berat di dalam sedimen menunjukkan perbezaan yang signifikan ($p<0.05$) bagi Cu (5.24-38.55 µg/g), Zn (23.46-81.05 µg/g), Fe (6876.50-18579.01 µg/g), Pb (9.00-50.22 µg/g), Ni (5.91-22.90 µg/g) dan Cd (0.06-0.85 µg/g). Julat nitrat di dalam air dan sedimen adalah seperti yang berikut 0.019-0.917 mg/l dan 0.132-0.877 µg/g. Manakala, julat fosfat di dalam air dan sedimen adalah 0.0101-0.0713 mg/l dan 0.0303-0.2953 µg/g.

Aras logam berat dalam tilapia adalah lebih tinggi berbanding kajian-kajian sebelum ini. Walaubagaimanapun, ia masih berada dalam had yang di benarkan kecuali Pb dan Ni. Julat logam berat di dalam tisu tilapia menunjukkan perbezaan yang signifikan ($p<0.05$) bagi Cu (0.86-1.91 µg/g), Zn (0.90-2.93 µg/g), Fe (2.20-7.68 µg/g), Pb (1.54-6.62 µg/g), Ni (0.69-2.00 µg/g) dan Cd (0.10-0.29 µg/g).

Berdasarkan taburan geokimia, aras logam berat semasa peringkat membajak adalah 10% di sumbangkan oleh faktor antropogenik, 100% di sumbangkan oleh faktor semulajadi semasa peringkat membesar, 13% di sumbangkan oleh faktor antropogenik semasa peringkat membaja dan 14% di sumbangkan oleh faktor antropogenik semasa peringkat menuai. Bagaimanapun, Kajian ini juga menunjukkan julat logam berat di permukaan sedimen di Sungai Tengi adalah rendah berbanding kajian lain.

Kajian ini menunjukkan Sungai Tengi tidak dicemari oleh logam berat, nitrat dan fosfat didalam air, sedimen dan tilapia kerana ia bersifat setempat dan turut di pengaruhi oleh aktiviti persekitaran. Diharap data yang di perolehi dapat dijadikan sebagai rujukan untuk menentukan logam berat, nitrat dan fosfat yang terdapat di kawasan pertanian.

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I certify that an Examination Committe has met on 27 January 2012 to conduct the final examination of NURUL ADILAH MOHD BADROLDIN on her Master of Science thesis entitled “Distribution and Concentration Levels of Selected Heavy Metals and Nutrients in Sungai Tengi Due to Paddy Plantation Activities” in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The committee recommends that the student be awarded the Master of Science.

Members of the Examination Committee were as follows:

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This thesis was submitted to the senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the supervisory Committee were as follows:

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BUJANG BIN KIM HUAT, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

NURUL ADILAH MOHD BADROLDIN

Date: 27 January 2012

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LIST OF ABBREVIATIONS

µm	micrometer
µg/g	microgram per gram
µg/L	microgram per liter
mg/l	miligram per liter
ppm	part per million
TDS	Total dissolved solid
DO	Dissolved oxygen
TSS	Total suspended solid
S1	ploughing stage
S2	growing stage
S3	fertilizing stage
S4	harvesting stage
SE	standard error
n	Number of individual in the area

CHAPTER 1

INTRODUCTION

1.1 Background of the study

Recently, most of world communities have been discussing on environmental issues such as water pollution. The unique thing about water resource is that any activity or form of pollution from air and land eventually ends up here. Identified activities such as vehicle emission, factory and residential waste, agricultural activities and land clearing have caused direct and indirect pollution to water. Natural weathering process can also affects the state of water.

In general, heavy metals enter the aquatic environment naturally through geological weathering (Millward and Turner, 1995). However, human activities have also introduced large amounts of metals to the water bodies and caused the changes in the natural steady state balance (Chen *et al*., 2002). The hazardous chemical elements released into the environment accumulate in the sediments (Foo *et al*., 2008) and can transfer or dissolve into the water.

Later on, lower aquatic organisms will absorb and transfer the heavy metals elements through the food chain to higher trophic levels which include fish. Based on previous studies, heavy metals that accumulated in tissue of aquatic animals can reflect past exposures (Yilmaz, 2003, 2005). However, under certain environmental conditions, heavy metals may accumulate to a toxic concentration (Oehlenschlager, 2002) and cause ecological damage (Freedman, 1989). Hence, heavy metals become one of the serious pollutants in the natural environment due to the toxicity,

persistence and bioaccumulation (Cravo and Bebianno, 2005; Upadhyay *et al*., 2006).

The use of water and sediment for heavy metals measurement has increased significantly (Thompson *et al*., 1984; Fichet *et al*., 1998). Since, the previous data shows that the level of bioavailable metals could directly reflect the potential hazard to human health and the potential heavy metal pollutions in water (Beiras *et al*., 2003; Adamo *et al*., 2005).

The presence of biota in the aquatic ecosystem can be used as biological indicator to monitor the heavy metal contamination in certain areas. The uses of biological indicator are well documented (Philips, 1977; Philips, 1980; Bryan *et al*., 1985; Langston *et al*., 1998; Ismail and Asmah, 1999; Ismail *et al*., 2000; Szefer *et al*., 2002). These biomonitor organisms can be classified in several groups such as fish, bivalve, gastropod and many more. Hence, this study has used the sediment, water and black tilapia as the samples to measure the level of heavy metals.

Khaled (2004) has highlighted that studies on heavy metals can be important in two main aspects. The first aspect is from the perspective of public health, where the attention has been drawn to the necessity of measuring the accumulation of heavy metals that pose serious health hazards to humans. The second aspect is from the aquatic environment, the main problem has been to prevent biological deterioration and to identify the sources which threaten ecological equilibrium. In this regard, the more abundant metals such as copper, zinc and manganese may sometimes represent greater hazard than lead, mercury and cadmium (Kinne, 1984). Meanwhile, concentrations of heavy metals in the organs of fish are determined primarily by the level of pollution in water and food (Farkas *et al*., 2000).

Beside heavy metals pollution, nutrients pollution such as nitrate and phosphate can also degrade the river water quality. This pollution is derived from many sources, for example from fertilizer, wastewater, runoff from agriculture and animal husbandry.

The Third National Agricultural Policy or NAP3 for 1998 - 2010 (Department of Agriculture, 2003) have highlighted paddy and oil palms are the major food crop in Malaysia. According to Food and Agriculture organization (FAO) (2004), approximately, 90% of all types of farming systems in Malaysia used fertilizers. Paddy plantations are the main crops in Tanjung Karang. Appoximately 19, 700 hectare area was used to generate the production of paddy which is 137, 258 metric tonne per season or 274,515 metric tonne per year (DOA, 2010). Paddy plantation activities in Tanjung Karang were monitored by Integrated Agricultural Development Area (IADA) Barat Laut.

Sungai Tengi is one of the rivers in Selangor that has rapid development in agriculture, light industry and expansion of urbanization. With this rapid activity, it can cause heavy metal and nutrient pollution (Othman *et al*., 2006). The surface runoff from land, released effluent, evaporation and atmospheric deposition entered the river system and estuary. These activities have attracted a great concern of environmental studies since heavy metals and nutrients pollution can affect mankind, coastal wildlife and shore birds' health directly and indirectly.

1.2 Significance of the study

All of those factors mentioned in the previous section were related to rivers. River plays important roles in our daily activities. River supplies water for domestic uses, irrigation, recreational activities, industrial sector, habitat for aquatic organisms and plants. The Department of Environment, Malaysia reported that in 2007, 638 rivers in Malaysia (60%) were found to be clean, 376 (35%) slightly polluted and 50 (5%) polluted. Sungai Tengi was recognized as among the cleanest. But, recent human activities in aquaculture, agriculture, light industry, oil palm plantation and others have the potential to pollute the Sungai Tengi by hazardous chemicals such as heavy metals including nutrients such as nitrate and phosphate. Therefore, monitoring is a good move to ensure that the river remain at its best quality and to prevent deterioration of water quality.

Sungai Tengi is located in Tanjung Karang, Selangor. The river plays vital role for irrigation of paddy field in Tanjung Karang, Sekinchan and Sg. Besar. These areas were the largest rice cultivation producer in Selangor. Besides, there was a water treatment plant that processes the water from Sungai Tengi for domestic uses. The main activities that concentrated in this area were based on agriculture and fisheries, which include paddy and oil palm plantation and aquaculture. Many of such activities have been found to contaminate water supplies, due to insecticide and herbicide runoff into surface waters (Manahan, 2000).

Environmental impacts on fish farming activities have been well documented and received increasing attention in the last two or three decades. One of the most significant effects of fish farming are the enrichment of aquatic bodies with nutrients such as nitrate, phosphate, ammonia, organic matter and decreasing dissolved oxygen (Wu *et al*.,1994; Leung *et al*., 1999). The end points of Sungai Tengi flows to

the Straits of Malacca. The Straits of Malacca is one of the busiest routes for shipping activities in the world and there are possibilities that these two factors can be a threat for marine ecosystem. The Straits of Malacca has been studied extensively on the impact of heavy metals (Ismail *et al*., 1993, 2003; Ismail and Ramli, 1997; Chua *et al*., 2000; Law *et al*., 2001; Yap *et al*., 2002, 2003, 2006).

In order to evaluate the water quality of aquatic systems, many countries have introduced a plan to monitor and assess the pollution effects (Stambuk, 1999; Pesce and Wunderlin, 2002; Zampella *et al*., 2006). Parameters for chemical, physical and biological constituents are quantified in all rivers around the world.

In order to resolve this problem, Regulatory Agencies have established a general index as a management tool. One of these tools is the Interim National Water Quality Standards for Malaysia (INWQS) developed by the Department of Environmental (DOE) of Malaysia which is based on biological measurement and chemical measurements. Biological measurement comprise of (i) the abundance and variety of aquatic plant and animal lives, (ii) the ability of test organisms to survive in water sample. Meanwhile, chemical measurement involves pH, Conductivity, Salinity, Total suspended solids (TSS), Dissolved oxygen (DO), Chemical oxygen demand (COD), Biochemical oxygen demand (BOD), Fecal coliform, Nitrate and Phosphate.

The Water Quality Index Ranges from 0 to 100, where 100 represents water perfect quality conditions, while zero indicates water that is not suitable for the intended use without further treatment (Bordalo *et al*., 2001, 2006). In Malaysia, the water quality indices are shown in Table 1, 2 and 3.

Table 1 : Water Quality Index Ranges

Range	Level
90 – 100	Excellent
70 - 90	Good
50 – 70	Medium
25 – 50	Bad
0 – 25	very bad

*source: DOE Malaysia

Table 2 : Interim National Water Quality Standards for Malaysia (INWQS)

Parameters	Unit	I	IIA	IIB	III	IV	V
BOD	mg/l	1	3	3	6	12	>12
COD	mg/l	10	25	25	50	100	>100
DO	mg/l	7	5-7	5-7	3-5	<3	<1
pH		6.5-8.5	6-9	6-9	5-9	5-9	-
Conductivity	µS/cm	1000	1000	-	-	6000	-
TSS	mg/l	25	50	50	150	300	300
Temperature	°C	-	29	29	29	-	-
Turbidity	NTU	5	50	50	-	-	-
Total coliform	counts/100mL	100	5000	5000	50000	50000	>50000

*source: DOE Malaysia

Table 3 : Water Quality Classification

Class	Description
I	Conservation of natural environment water supply 1 - practically no treatment necessary.
	Fishery 1 - very sensitive aquatic species
IIA	Water Supply II - conventional treatment required
	Fishery ll - sensitive aquatic species
IIB	Recreational use with body contact
III	Water Supply lll - extensive treatment required
	Fishery lll - common, economic value, and tolerant species livestock drinking
IV	Irrigation
V	None of above

*source: DOE Malaysia

1.3 Objectives of the study

Based on previous studies, data on water quality are still sparse in Malaysia and no data were reported on the level of heavy metals, nitrate and phosphate in the Sungai Tengi yet. Therefore, this study will elucidate the condition of Sungai Tengi because this area is vital for the farmers, fishermen and public. Thus, the objectives of this study:

1. To investigate the concentration levels of heavy metals (Cu, Zn, Fe, Pb, Ni and Cd) and nutrients (nitrate and phosphate) in water column and sediment obtained from Sungai Tengi.
2. To determine the levels of heavy metals in various tissues of black tilapia in Sungai Tengi.
3. To estimate the pollution status of heavy metals in sediment along Sungai Tengi using the geochemical index.

It is hoped that the data obtained could serve as a reference to evaluate the heavy metals, nitrate and phosphate in the Sungai Tengi and monitoring is one of the ways to help the management and ensure that Sungai Tengi still remains as non polluted river. All the information provided is important to reduce the deterioration of our environment.

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