



UNIVERSITI PUTRA MALAYSIA

**ASSESSMENT OF HEAVY METALS CONTAMINATION IN SURFACE
SEDIMENT AND BLACK TILAPIA (*Oreochromis mossambicus*) AS A
MONITORING ORGANISM IN THE KLANG RIVER**

ABOLFAZL NAJI

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By

ABOLFAZL NAJI

**Thesis submitted to the school of Graduate Studies, Universiti Putra Malaysia in
Fulfillment of the Requirements for the Degree of Doctor of Philosophy**

January 2012

DEDICATION

To the memory of my caring late elder brother Sadroddin Naji

To my beloved parents Hassan and Sarah Khaton

and

*To the most patient and thoughtful persons that I love more than ever Hamideh,
Amir Hussein and Hanieh*

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

**ASSESSMENT OF HEAVY METALS CONTAMINATION IN SURFACE
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Chairman: Professor Ahmad Ismail, PhD

Faculty: Science

Concentrations of Cd, Zn, Ni, Cu, Pb, Fe, T-Hg and Me-Hg in the surface sediments and *Oreochromis mossambicus* were evaluated to determine the concentration, distribution, overall classification and risk associated with trace metals connected with urban and industrial discharge in the Klang River. Some parameters such as pH, total organic carbon (TOC) and particles sizes in sediment were measured to assess of their impact on metals behavior in the studied area. The concentration of metals (all in µg/g, except for Fe in % and Me-Hg in ng/g, dry weight) were as follows: 0.57- 2.19 Cd; 31.89-272.33 Zn; 5.96-24.47 Ni; 10.57- 52.87 Cu; 24.23-64.11 Pb; 1.56-3.03 Fe; 0.02-0.45 T-Hg and 0.12-12.57 Me-Hg. The highest ($p < 0.05$) concentration of metals was found in those stations along the vicinity of industrial parks (e.g., Shah Alam industrial area) and highly populated centers (e.g., Klang Valley and Kuala Lumpur). Pearson's

correlation indicated that effectiveness of TOC in controlling the distribution and enrichment of metals was a more important factor than that of the grain size ($< 63\mu\text{m}$).

Sequential extraction technique (SET) was used to evaluate the four fractions (exchangeable, acid-reducible, oxidisable-organic and resistant) in surface sediment. Sequential extraction technique (SET) showed that mean anthropogenic portions of metals were in the order of $\text{Zn} (60.22) > \text{Cu} (56.01) > \text{Cd} (45.63) > \text{Ni} (42.08) > \text{Pb} (33.22) > \text{Fe} (10.26)$. The fractionation of metals in most stations were in the order of resistant $>$ acid-reducible $>$ oxidisable-organic $>$ exchangeable fraction. Since highest concentrations of the metals were found in the residual fraction which indicated that the mobility of these metals in the Klang River was quite low.

The degree of sediment contaminations were computed with sediment quality guidelines (SQGs) of threshold effect level (TEL) and probable effect level (PEL), enrichment factor (EF), geoaccumulation index (I_{geo}) pollution load index (PLI). The results suggested that enrichment factor and geoaccumulation values of Cd were greatest among the studied metals. Likewise, highest PLI were found at the station with high anthropogenic activities. The study revealed that on the basis of computed indexes, Klang River is classified as moderately polluted river. The result also determined that none of studied metals concentrations in the sediments were as high as the PEL value, whereas the concentrations of metals in some stations exceeded the TEL value.

The mean concentrations of the metals in fish from six stations along the Klang River ranges from 2.66-251.6 in the gill; 1.43-117.4 in the operculum; 0.31-173.1 in the muscle; 0.50-873.92 in the kidney, 2.01-2062.2 in the liver; 0.8- 111.69 in the scale; 1.73-114.54 in the bone; 0.78-197 in the caudal fin; 1.42-75.82 in the skin; for Cd, Zn, Ni, Cu, Pb, Fe, T-Hg and Me-Hg (all in $\mu\text{g/g}$, except for T-Hg and Me-Hg in ng/g), respectively.

The result of the present study showed that relationships of metals between each fraction of sediment and metal concentrations in different organs of the fish were found between Ni, Cd and Fe in the different organs (except operculum), kidney and all organs of *O. mossambicus*, respectively.

Metallothionein (MT) concentrations in gill and liver tissues of *O. mossambicus* were determined to assess the biological response of fish to level of some metals. The concentrations of Cd, Zn, Cu and Hg ($\mu\text{g/g}$ wet weight) in the fish tissues were correlated with MTs content. The increases of MTs level from Puchong Tengah as reference area to Kampung Seri Kenangan as polluted area were 3.4- and 3.8-fold for gills and liver, respectively. The result determined that MTs concentration was tissue-specific, with highest levels in liver. Therefore, liver can be as a tissue indicator in *O. mossambicus* in the study area.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan ijazah Doktor Falsafah

**PENILAIAN LOGAM PENCEMARAN BERATA DALAM SEDIMEN
PERMUKAAN DAN KESAN PADA IKAN (*Oreochromis mossambicus*)
SEBAGAI ORGANISMA BIOMONITORING DALAM SUNGAI KLANG**

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Januari 2012

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Kepekatan Cd, Zn, Ni, Cu, Pb, Fe, T-Hg dan Me-Hg dalam sedimen permukaan dan *Oreochromis mossambicus* dinilai untuk menentukan kepekatan, pengedaran, klasifikasi keseluruhan dan risiko yang berkaitan dengan logam surih yang berkaitan dengan Bandar dan perindustrian sekitar Sungai Klang. Dan juga, beberapa parameter seperti pH, enapan jumlah karbon organik (TOC) dan saiz zarah diukur untuk menilai kesannya terhadap tingkah laku logam di kawasan yang dikaji. Kepekatan logam ($\mu\text{g/g}$, untuk Fe dalam unit peratus dan Me-Hg dalam ng/g berat kering) adalah seperti berikut: 0.57- 2.19 Cd; 31.89-272.33 Zn; 5.96-24.47 Ni; 10.57- 52.87 Cu; 24.23-64.11 Pb; 1.56-3.03 Fe; 0.02-0.45 T-Hg and 0.12-12.57 Me-Hg. Kepekatan tertinggi ($p < 0.05$) logam didapati di stesen mereka disepanjang sekitar taman-taman perindustrian (contohnya, kawasan perindustrian Shah Alam) dan kawasan berkepadatan penduduk yang tinggi (contohnya, Lembah Klang dan Kuala Lumpur). Korelasi Pearson

menunjukkan bahawa keberkesanan TOC dalam mengawal pengedaran dan pengayaan adalah satu factor yang lebih penting daripada saiz partikel tanah ($<63\mu\text{m}$).

Teknik pengekstrakan berurutan (SET) telah digunakan untuk menilai empat pecahan (ditukar, asid-dikurangkan, organik yang dioksidakan dan sisa) dalam sedimen permukaan. Teknik pengekstrakan berurutan (SET) menunjukkan bahawa pecahan purata logam adalah dalam seperti $\text{Zn} (60.22) > \text{Cu} (56.01) > \text{Cd} (45.63) > \text{Ni} (42.08) > \text{Pb} (33.22) > \text{Fe} (10.26)$. Pemeringkatan logam dalam kebanyakan stesen adalah dalam susunan pecahan residu $>$ pecahan asid-dikurangkan $>$ pecahan organik yang dioksidakan $>$ pecahan ditukar. Kepekatan tertinggi logam yang ditemui dalam pecahan residu menunjukkan bahawa mobility logam ini dalam Sungai Klang agak rendah.

Darjah pencemaran sedimen telah dikira dengan garis panduan kualiti sedimen (SQGs) tahap kesan ambang (TEL) dan tahapkesan yang berkemungkinan (PEL), faktor pengayaan (EF), Indeks Pengumpulan Geo (I_{geo}) dan Indeks Beban Pencemaran (PLI). Keputusan mencadangkan bahawa faktor pengayaan dan nilai-nilai pengumpulan geo bagi logam Cd adalah tertinggi di kalangan logam yang dikaji. Didapati PLI tertinggi ditemui di stesen yang banyak aktiviti-aktiviti antropogenik. Kajian ini menunjukkan bahawa pada asas indeks dikira, Sungai Klang diklasifikasikan sebagai sungai yang sederhana tercemar. Hasilnya juga ditentukan bahawa tidak ada kepekatan logam yang

dikaji dalam mendapan setinggi nilai PEL, manakala kepekatan logam di beberapa stesen melebihi nilai TEL.

Kepekatan purata logam dalam ikan dari enam stesen di sepanjang banjaran Sungai Klang dari 2.66-251.6 dalam insang; 1.43-117.4 dalam operkulum; 0.31-173.1 dalam otot; 0.50-873.92 dalam buah pinggang, 2.01-2062.2 di dalam hati; 0.8- 111.69 dalam sisik; 1.73-114.54 dalam tulang; 0.78-197 dalam sirip kaudal; 1.42-75.82 dalam kulit; untuk Cd, Zn, Ni, Cu, Pb, Fe, T-Hg and Me-Hg (semua dalam $\mu\text{g/g}$, kecuali untuk T-Hg dan Me-Hg dalam ng/g), masing-masing.

Hasil kajian ini menunjukkan bahawa hati adalah organ sasaran bagi Zn, Cu and Fe. Secara signifikan ($p < 0.05$) tertinggi T-Hg dan kepekatan Me-Hg ditemui di dalam buah pinggang manakala kepekatan Cd ketara tertinggi telah dijumpai dalam insang. Dan juga, sisik sebagai organ sasaran bagi Ni dan Pb, kerana logam ini adalah signifikan ($p < 0.05$) tertinggi di organ.

Hubungan logam antara pecahan setiap sedimen dan kepekatan logam di dalam organ-organ yang berlainan ikan ditemui antara Ni, Cd dan Fe dalam organ-organ yang berbeza (kecuali operkulum) buah pinggang dan semua organ-organ *O.mossambicus*, masing-masing. Oleh itu, *O.mossambicus* boleh sebagai ejen biomonitoring berguna bagi Ni, Cd dan Fe dalam Sungai Klang.

Kepekatan metallothionein (MT) dalam insang dan tisu hati *O.mossambicus*, telah ditentukan bahawa kepekatan Cd, Zn, Cu dan Hg ($\mu\text{g/g}$ berat basah) dalam tisu ikan berkait rapat dengan kandungan MTs. Peningkatan paras dari Puchong Tengah MTs sebagai kawasan merujuk kepada Kampung Seri Kenangan sebagai kawasan 3.4 tercemar dan 3.8 kali ganda untuk insang dan hati, masing-masing. Hasilnya ditentukan bahawa kepekatan MTs tisu tertentu, dengan paras tertinggi di dalam hati. Oleh itu, hati boleh sebagai penuding tisu di *O.mossambicus*, di kawasan Kajian.

Kajian ini adalah kajian pertama mengikut pemeringkatan kimia logam dalam sedimen permukaan Sungai Klang. Sebaliknya, ia terletak di kawasan yang paling sensitive Malaysia. Oleh itu, data kandungan logam berat adalah amat berguna untuk mengawal dan mengurangkan pencenaran di Sungai Klang.

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APPROVAL

I certify that an Examination Committee has met on 16 January 2012 to conduct the final examination of Abolfazl Naji on his Doctor of Philosophy thesis entitled “ASSESSMENT OF HEAVY METALS CONTAMINATION IN SURFACE SEDIMENT AND FISH (*Oreochromis mossambicus* Peters) AS A MONITORING ORGANISM IN THE KLANG RIVER’ in accordance with Universiti Putra Malaysia (High Degree) Act 1980 and Universiti Putra Malaysia (High Degree) Regulations 1981. The committee recommends that student be awarded the Doctor of Philosophy Degree.

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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 degree at Universiti Putra Malaysia or at any other institutions.

ABOLFAZL NAJI

Date: 16 January 2012

TABLE OF CONTENTS

	Page
DEDICATION	ii
ABST	iii
ACKNOWLEDGEMENTS	x
APPROVAL	xi
DECLARATION	xiii
LIST OF FIGURES	xx
LIST OF ABBREVIATIONS	xxii
 CHAPTER 1	 1
INTRODUCTION	1
1.1 General	1
1.2 Objectives of the study	5
 LITERATURE REVIEW	 7
1.3 Heavy metal pollution	7
1.3.1 Cadmium (Cd)	9
1.3.2 Zinc (Zn)	11
1.3.3 Nickel (Ni)	12
1.3.4 Copper (Cu)	13
1.3.5 Lead (Pb)	14
1.3.6 Mercury (Hg)	16
1.3.7 Iron (Fe)	18
1.3.8 Monitoring of heavy metal in river environment	18
1.3.9 Fish as a metal biomonitor of contamination	26
1.3.10 Metallothionein (MT) as biomarker	27
1.3.11 Black Tilapia (<i>Oreochromis mossambicus</i>)	31
 MATERIALS AND METHODS	 34
1.4 Study area and sampling locations	34
1.5 Sampling and storage	37
1.5.1 Sediment	37
1.5.2 Water	38
1.5.3 Biological	39
1.6 Sample Digestion	42
1.6.1 Sediment: Total metal content	42

1.6.2	Sediment: Sequential extraction technique (SET)	42
1.6.3	Total Mercury (T-Hg) in sediment and biological samples	44
1.6.4	Methyl-mercury (Me-Hg) in surface sediments	44
1.6.5	Methyl-mercury (Me-Hg) in biological samples	45
1.6.6	Metallothionein (MT)	46
1.7	Determination of heavy metal concentrations	47
1.7.1	Flame Atomic Absorption Spectrophotometer (FAAS)	47
1.7.2	Direct Mercury Analyser	48
1.7.3	Quality control	49
1.7.4	Blank procedure	49
1.7.5	Recovery test	50
1.8	Pollution indices	52
1.8.1	Sediment Quality Guideline (SQG)	52
1.8.2	Enrichment Factor (EF)	53
1.8.3	Geoaccumulation Index (I_{geo})	54
1.8.4	Contamination factors (CFs)	55
1.8.5	Pollution Load Index (PLI)	56
1.8.6	Individual and global contamination factor	57
1.9	Sediment characteristics	58
1.9.1	Determination of sediment pH	58
1.9.2	Particle size analysis	58
1.9.3	Total organic matter analysis	60
1.10	Statistical analysis	60
RESULT AND DISCUSSION		62
1.11	General sediments characteristics	62
1.12	The concentration and distribution of trace metals	64
1.13	Metal speciation	67
1.13.1	Cd speciation	67
1.13.2	Zn speciation	70
1.13.3	Ni speciation	73
1.13.4	Cu speciation	76
1.13.5	Pb speciation	80
1.13.6	Fe speciation	82
1.13.7	Risk Assessment Code (RAC)	86
1.14	Metal concentration in water	88
1.15	Mercury and methyl mercury distribution in the surface sediments	91
1.16	Mercury methylation potential	93
1.17	Correlation Matrix	97
1.17.1	Correlation between total metals content	97
1.17.2	Relation between total metals content and total Fine grains (<63 μ m)	98
1.17.3	Relation between total metals content and total organic carbon	101

1.18	Contamination assessment	104
1.18.1	Enrichment Factor (EF)	104
1.18.2	Geoaccumulation Index (I_{geo})	107
1.18.3	Contamination factors (CFs)	111
1.18.4	Pollution Load Index (PLI)	111
1.18.5	Individual and global contamination factor	114
1.19	Sediment quality guidelines (SQGs)	117
1.20	Comparison with literature values	118
1.21	Heavy metal assessment in black tilapia (<i>O. mossambicus</i>) from the Klang River	121
1.21.1	Metal concentrations in different organs of black tilapia (<i>O. mossambicus</i>)	121
1.21.2	Bioconcentration factor (BCF)	133
1.21.3	Public health concern	135
1.22	Relationship between different chemical speciation of heavy metal and their accumulation in different organs of <i>O. mossambicus</i>	137
1.23	Assessment of Metallothionein content as biomarker in <i>O. mossambicus</i>	152
1.23.1	Metals (Cd, Zn, Cu and T-Hg) concentrations ($\mu\text{g g}^{-1}$ wet weight) in liver and gill of <i>O. mossambicus</i>	152
1.23.1	Metallothionein (MT) content in the gills and livers of <i>O. mossambicus</i>	155
5	SUMMARY, CONCLUSION AND RECOMMENDATIONS FOR FUTURE RESEARCH	160
	REFERENCES	166
	BIODATA OF STUDENT	198
	LIST OF PUBLICATIONS	199