UNIVERSITI PUTRA MALAYSIA

HEAVY METAL CONCENTRATIONS IN SURFACE SEDIMENTS AND GIANT MUDSKIPPERS, Periophthalmodon schlosseri PALLAS FROM WEST COAST OF PENINSULAR MALAYSIA AND THEIR METALLOTHIONEIN INDUCTION TOWARDS METAL TOXICITY

TIJJANI RUFA'I BUHARI

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By

TIJJANI RUFA'I BUHARI

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

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DEDICATION

In memory of my beloved elder brother Umar Faruk and my nephew Muhammad Sunusi Rufa'i may their souls rest in perfect peace

and

to my patient, caring and good understanding parents that

I cherish always;

Alhaji Rufa'i Buhari and Hajiya Hawwa Muhammad Mahi

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

HEAVY METAL CONCENTRATIONS IN SURFACE SEDIMENTS AND GIANT MUDSKIPPERS, *Periophthalmodon schlosseri* PALLAS FROM WEST COAST OF PENINSULAR MALAYSIA AND THEIR METALLOTHIONEIN INDUCTION TOWARDS METAL TOXICITY

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Assessment of heavy metals concentrations; Cu, Zn, Pb, Cd and Ni in surface sediment and giant mudskipper *P. schlosseri* and its metallothionein induction towards metals toxicity in the west coast of Peninsular Malaysia was conducted in the year 2008 and 2010. Surface sediments and giant mudskippers were collected in August and September 2008 and in March and June 2010 at six sampling sites. Top 3-5 cm surface sediments were collected in triplicates from each sampling sites using plastic scoop and placed in separate plastic bags which was instantly placed on ice. Fish samples were collected using trap net at the same locations were sediments were collected and placed in plastic aquarium containing some sediment and water. The surface sediments and fish samples were brought to laboratory until further analyses. Total metals concentrations and geochemical fractionation of metals in surface sediments were determined by direct aqua – regia and modified sequential extraction procedures respectively. Metallothioneins assay was conducted to determine metals induction in liver, gills and muscle.

The concentrations of heavy metals in the surfaces sediment ranged from 12.79 – 65.39, 60.83 – 442.19, 8.46 – 53.73, 0.6 -1.65 and 10.09 – 29.25 µg/g dry weight for Cu, Zn, Pb, Cd and Ni respectively. These values were comparable to metals concentrations in the west coast of Peninsular Malaysia and some part of the south eastern Asia. Based on fractionation analysis, effective range low (ERL), effective range medium (ERM), index of geoaccumulation (I*geo)* and enrichment factor (EF) shows that metals concentrations were found higher than background concentration of world average shale, continental crust and world average sediment which might suggest anthropogenic input of metals in the study areas. Geochemical fractionation of metals revealed that of more than 66 % of Cu, Pb, Cd and Ni in surface sediments of west coast of Peninsular Malaysia were associated with resistant fraction which indicates the mobility of these metals was low. The non-resistant fraction of Zn dominated 50 % of the sampling sites suggesting anthropogenic input of Zn at these sampling sites.

Heavy metals concentrations in the tissues of *P. schlosseri* ranged from 0.04 – 18.61, 12.79 – 152.63, 0.04 – 37.71, 0.04 – 4.42 and 0.04 – 121.84 for Cu, Zn, Pb, Cd and Ni µg/g dry weight respectively. The concentrations of metals in the tissues showed a significant difference between the sampling sites, except Cu concentration in gill which showed non-significant difference between the sampling sites. Results of Pearson's correlation analyses showed metal concentrations in the tissues of *P. schlosseri* were significantly correlated with some geochemical fraction of metals in the sediment which suggest that *P. schlosseri* could be used as a biomonitoring agent for heavy metals pollution in the west coast of Peninsular Malaysia.

The bioconcentration factor (BCF) revealed that most of the tissues of *P. schlosseri* were classified as macro concentrators. Liver and intestine have highest average BCF values for Cu and Zn respectively while cartilage recorded the highest BCF for Pb, Cd and Ni. These tissues might be suggested as good accumulators of the metals observed in them.

The metallothioneins (MT) content in the tissues of *P. schlosseri* showed a significant difference between the sampling sites. The order of MT content was in the decreasing order of: liver > gill > muscle. Results of heavy metals concentrations, geochemical fractionation and pollution indices in the surface sediments revealed that the sampling sites in the present study could be classified as unpolluted, to moderately to strongly polluted. Sediment quality guideline quotient (SQG – Q) and Potential ecological risks index (RI) further indicated that the sampling sites were moderately polluted and exhibited low to moderate potential ecological risk respectively.

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

KEPEKATAN LOGAM BERAT DALAM SEDIMEN PERMUKAAN DAN MUDSKIPPER YANG GERGASI MUDSKIPPER, *Periophthalmodon schlosseri* DARI PANTAI BARAT SEMENANJUNG MALAYSIA DAN INDUKSI METALLOTHIONEIN YANG KE ARAH KETOKSIKAN LOGAM.

Oleh

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Penilaian kepekatan logam berat Cu, Zn, Pb, Cd dan Ni dalam sedimen permukaan dan gergasi mudskipper *P. schlosseri* dan induksi metallothionein yang ke arah ketoksikan logam di pantai barat Semenanjung Malaysia telah dijalankan pada tahun 2008 dan 2010. Sedimen permukaan dan ikan tembakul gergasi telah dikumpulkan dalam bulan Ogos dan September 2008 dan pada bulan Mac dan Jun 2010 di enam kawasan persampelan.

Gasing 3 -5 sedimen permukaan cm dikumpulkan dalam triplicates dari setiap kawasan persampelan menggunakan sudu plastik dan diletakkan di dalam beg plastik yang berasingan yang serta-merta diletakkan di atas ais. Sampel ikan telah dikumpulkan menggunakan bersih perangkap di lokasi yang sama adalah sedimen telah dikumpulkan dan diletakkan di dalam akuarium plastik yang mengandungi beberapa sedimen dan air. Sedimen permukaan dan sampel ikan telah dibawa ke makmal sehingga membuat analisis selanjutnya.

Kepekatan total logam dan pemeringkatan geokimia logam dalam sedimen permukaan telah ditentukan oleh langsung aqua - regia dan diubahsuai prosedur pengekstrakan berjujukan masing-masing. Asai metallothioneins telah dijalankan untuk menentukan induksi logam di dalam hati, insang dan otot.

Kepekatan logam berat di permukaan sedimen adalah dari12,79 - 65,39, 60,83 - 442,19, 8,46 - 53,73, 0.6 -1,65 dan 10,09 - 29,25 µg / g berat kering untuk Cu, Zn, Pb, Cd dan Ni masing-masing. Nilai-nilai ini adalah setanding dengan kepekatan logam di pantai barat Semenanjung Malaysia dan beberapa bahagian Asia tenggara.Berdasarkan analisis pemeringkatan, rendah pelbagai berkesan (ERL), sederhana pelbagai berkesan (ERM), faktor indeks geopengumpulan (I*geo*) dan pengayaan (EF) menunjukkan bahawa kepekatan logam didapati lebih tinggi daripada kepekatan latar belakang dunia purata syal, kerak benua dan duniasedimen purata yang mungkin mencadangkan input antropogenik logam di kawasan kajian. Pemeringkatan geokimia logam mendedahkan bahawa lebih daripada 66% Cu, Pb, Cd dan Ni dalam sedimen permukaan pantai barat Semenanjung Malaysia telah dikaitkan dengan pecahan tahan yang menunjukkan mobiliti logam tersebut adalah rendah. Pecahan yang tidak tahan Zn menguasai 50% daripada kawasan persampelan mencadangkan input antropogenik Zn di kawasan persampelan ini.

Kepekatan logam berat dalam tisu *P. schlosseri* adalah antara dari 0,04 - 18,61, 12,79 - 152,63, 0,04 - 37,71, 0,04 - 4,42 dan 0,04 - 121,84 untuk Cu, Zn, Pb, Cd dan Ni µg/g berat kering masing-masing. Kepekatan logam dalam tisu menunjukkan perbezaan yang signifikan antara kawasan persampelan, kecuali kepekatan Cu dalam

insang yang menunjukkan bukan bererti perbezaan di antara kawasan persampelan. Keputusan analisis korelasi Pearson menunjukkan kepekatan logam dalam *tisu P. schlosseri* telah mempunyai hubungan yang signifikan dengan pecahan beberapa geokimia logam dalam sedimen yang mencadangkan bahawa P. schlosseri boleh digunakan sebagai ejen 'biomonitor untuk pencemaran logam berat di pantai barat Semenanjung Malaysia.

Faktor biopemekatan (BCF) mendedahkan bahawa kebanyakan tisu *P. schlosseri* telah diklasifikasikan sebagai makro concentrators. Hati dan usus mempunyai nilai BCF tertinggi purata untuk Cu dan Zn masing-masing manakala rawan mencatatkan BCF tertinggi bagi Pb, Cd dan Ni. Tisu ini mungkin akan mencadangkan sebagai penumpuk baik logam yang diperhatikan pada mereka.

Kandungan metallothioneins (MT) dalam tisu *P. schlosseri* menunjukkan perbezaan yang signifikan antara kawasan persampelan. Perintah kandungan MT adalah dalam perintah itu menurun: hati> otot insang.Keputusan kepekatan logam berat, pemeringkatan geokimia dan indeks pencemaran dalam sedimen permukaan mendedahkan bahawa kawasan persampelan dalam kajian ini boleh dikelaskan sebagai tidak tercemar, sederhana kuat tercemar. Sedimen darjah garis panduan kualiti (SQG - Q) dan risiko ekologi Potensi indeks (RI) seterusnya menunjukkan bahawa kawasan persampelan sederhana tercemar dan dipamerkan rendah hingga sederhana risiko ekologi potensi masing-masing

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I certify that an Examination Committee has met on 13th June 2012 to conduct the final examination of Tijjani Rufa'i Buhari on his Doctor of Philosophy thesis entitled "Heavy Metals Concentrations in Surface Sediment and Giant Mudskipper *Periopthalmodon schlosseri* From West Coast of Peninsular Malaysia and Its Metallothionein Induction Towards Metal Toxicity" 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 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 other degree at Universiti Putra Malaysia or at any other institution.

_____

TIJJANI RUFA'I BUHARI

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