



UNIVERSITI PUTRA MALAYSIA

ASSESSMENT, DISTRIBUTION AND SPECIATION OF HEAVY METALS (Zn, Cu, Pb, Ni, Cd and Fe) IN SURFACE SEDIMENT AND DIFFERENT PARTS OF *Dreissena polymorpha* ALONG THE SOUTH COAST OF THE CASPIAN SEA AND ANZALI WETLAND, IRAN

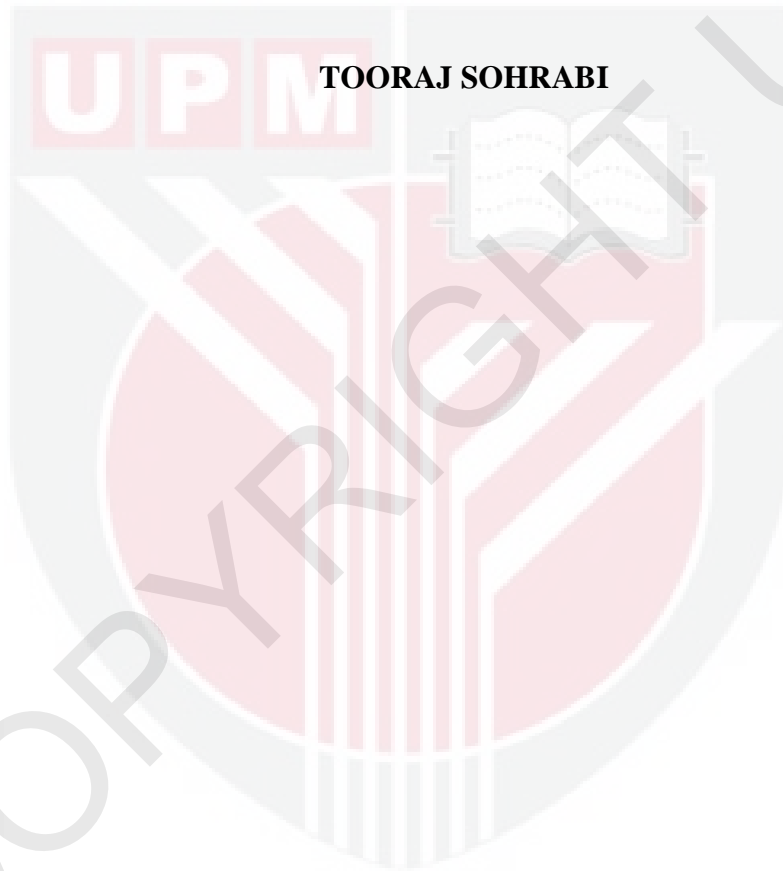
TOORAJ SOHRABI

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By

TOORAJ SOHRABI



**This thesis submitted to the School of Graduate Studies, Universiti Putra Malaysia
in Fulfilment of the requirements for the Degree of Doctor of Philosophy**

November-2011

DEDICATION

To

This thesis dedicated to my dear and lovely daughter Mahtab, to my beloved wife, Tooba Mirzapour, to my dear mother Tooba Sohrabi and my lovely father Teimour Sohrabi and brother Shahrokh Sohrabi that I owe them all of success in my life



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

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This study was concentrated on speciation and fractionation of heavy metals (Pb, Ni, Cd, Zn, Cu and Fe) on surface sediments of the south Caspian Sea as a biggest Lake in the world and Anzali wetland as an international important wetland registered in the Ramsar convention during 2008-2009. Concentrations of heavy metals in bivalve *Dreissena polymorpha* also were determined to assess the status of heavy metals pollution in the south of the Caspian Sea. There was no study before about the speciation, fractionation of heavy metals in the surface sediment of south Caspian Sea and Anzali wetland. Because of living more than 10 million people in this area, assessment of anthropogenic input on surface sediment and influence of that on bivalve as a food of sturgeons can be important. The Aqua Regia method and sequential extraction technique "easily, freely, leachable and exchange-able (EFLE)", "acid-reducible", "oxidisable organic" and "resistant" were

used for analyses of total concentration and geochemical fraction of heavy metals from 14 sites of south Caspian Sea and 6 sites of Anzali wetland. The air-acetylen flame atomic absorption spectrophotometer (AAS) Perkin-Elmer Model 4100 was used for determination of heavy metals. The metal levels were evaluated according to the Enrichment Factor (EF), Pollution Index (PLI) and Geoaccumulation Index (I_{geo}) analyses. Total Metal concentrations ($\mu\text{g/g}$; except Fe%) showed variations with Pb, 13.06-33.48; Ni, 18.01-69.63; Cd, 0.62-1.5; Zn, 30.11-87.88; Cu, 5.86-38.89; Fe, 1.8-4. Concentration of heavy metals in surface sediment were found to be higher in some sites close to ports, urban areas and ship transport areas in the west and east of the Caspian Sea with anthropogenic activities. Measured EF and PLI for all metals in the west of Caspian Sea were higher than other sites. Cadmium showed higher EF and PLI when compared to other metals. The average enrichment factor of cadmium (8.71 ± 2.86) was determined to be higher than 5 in surface sediment of the south Caspian, which indicated that Cd contamination, had moderately severe enrichment. I_{geo} value for Cd in most stations which was classified as moderately contaminated and moderately to strongly contaminated, as well as the average of I_{geo} of Cd (1.77 ± 0.35) suggested that surface sediments of Caspian coast were moderately polluted by this metal. All of the metal concentrations in sediments for 14 sampling Stations (Pb, Ni, Zn, Cu and Fe) except Cd were dominated by the resistant fractions. The non-resistant fractions were lower than the resistant fractions for the whole duration of the study, which indicated that there were no significant anthropogenic inputs of Pb, Ni, Zn, Cu and Fe to the surface sediments of south Caspian Sea. The high percentages of non-resistant geochemical fractions of Cadmium indicated that sources of Cd in surface sediments of the south Caspian Sea were mainly contributed from anthropogenic

sources. Results revealed that heavy metal pollution is mainly localized in the west of the Caspian Sea in port areas devoted to shipping, agriculture and Azerbaijan activities and in the east, which is under the influence of industrial activities. The mean concentrations of each metal varied for the soft tissue, shell and byssus of *D. polymorpha*. Concentrations of Ni, Cd, Cu and Fe were found to be highest in byssus, whilst highest concentrations of Pb and Zn were recorded in shell and soft tissue, respectively. This suggested that, the byssus of *D. polymorpha* can be used as biomonitoring agent for Ni, Cu, Fe and especially Cd because of a high positive correlation of Cd in the byssus with fractions of sediments. For Anzali wetland, generally, Shanbe Bazar showed the highest level of Pb (69.10 µg/g dw); Ni (71.79 µg/g dw); Cd (1.81 µg/g dw); Zn (830.95 µg/g dw); Cu (89.54 µg/g dw). Shanbe bazaar is located in the urbanized area of Anzali city and may receive heavy pollution through municipal effluents. Also highest concentration of EFLE and oxidisable organic fractions of heavy metals (Pb, Ni, Cd, Zn, Cu and Fe) in comparison with other sampling sites was recorded in Shanbe Bazar. Most of the metals were strongly and positively correlated. The strong positive relationships between the Pb, Cd, Zn and Cu indicated that the sources of both natural and anthropogenic inputs were similar. Higher percentages of heavy metals in the non-resistant fraction reflect a greater tendency to become bioavailable. Studying the effects of metal concentration on the gill of the zebra mussel collected from special sites of the Caspian Sea by transmission electron microscopy showed that ultramorphology technique is good tool to study cell alterations used as biomarkers, being efficient in the analysis of environment. It was clear that the zebra mussel in polluted sites suffered changes related to the respiratory system.

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

PENILAIAN, AGIHAN DAN PEWUJUDAN SPESIES LOGAM-LOGAM BERAT (PB, NI, CD, ZN, CU AND FE) DI ENDAPAN PERMUKAAN DAN BAHAGIAN-BAHAGIAN BERLAINAN *DREISSENA POLYMORPHA* DI PANTAI SELATAN LAUT CASPIAN DAN TANAH BASAH ANZALI, IRAN

Oleh

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Kajian ini telah tertumpu pada pewujudan spesies dan pemeringkatan logam-logam berat (Pb, Ni, Cd, Zn, Cu dan Fe) ke atas endapan permukaan di selatan Laut Caspian yang merupakan suatu tasik terbesar di dunia (yang disempadani oleh Azerbaijan, Russia, Iran, Kazakhstan dan Turkmenistan), dan tanah basah Anzali yang merupakan satu tanah basah penting yang didaftarkan di persidangan Ramsar pada 2008-2009. Tumpuan logam-logam berat di dalam dwicangkerang *Dreissena polymorpha* juga dipastikan untuk menilai status pencemaran logam berat di selatan Laut Caspian. Sebelum ini tiada kajian mengenai pewujudan spesies, pemeringkatan logam-logam berat dan pemasukan pencemar di endapan permukaan Laut Caspian dan tanah basah Anzali. Oleh sebab wujudnya lebih dari 10 juta

penduduk di kawasan ini, penaksiran input antropogeni ke atas endapan permukaan dan pengaruhnya ke atas dwicangkerang sebagai makanan bagi ikan sturgeon mungkin penting. Kaedah Aqua Regia dan teknik pengekstrakan berurutan bagi contoh-contoh “mudah, sering, melarut resap dan boleh ditukar” (EFLE), “boleh dikurangkan oleh asid”, “organik yang boleh dioksidakan” dan “merintang” digunakan untuk analisis penumpuan keseluruhan dan pecahan geokimia logam-logam berat dari 14 tapak di selatan Laut Caspian dan 6 tapak tanah basah Anzali. Spektrofotometer nyala asetilena-udara serapan atom (AAS) Perkin-Elmer Model 4100 digunakan untuk menentukan logam-logam berat. Logam-logam berat dinilai mengikut Faktor Pengayaan (EF), Indeks Pencemaran (PLI) dan analisis-analisis Indeks Geotumpukan (I_{geo}). Kepekatan-kepekatan Logam Keseluruhan ($\mu\text{g/g}$; kecuali % Fe) menunjukkan variasi dengan Pb, 13.06-33.48; Ni, 18.01-69.63; Cd, 0.62-1.5; Zn, 30.11-87.88; Cu, 5.86-38.89; dan Fe, 1.8-4. Kepekatan logam-logam berat di endapan permukaan didapati lebih tinggi di beberapa tapak berdekatan dengan pelabuhan, kawasan-kawasan bandar dan kawasan-kawasan pengangkutan kapal di barat dan timur Laut Caspian dengan aktiviti-aktiviti antropogeni. Kepekatan-kepekatan ini sebanding dengan kepekatan logam di perairan pantai, dan lebih tinggi dari kepekatan-kepekatan yang didapati di dalam endapan-endapan dari bahagian-bahagian lain Laut Caspian di Russia, Kazakhstan dan Azerbaijan yang masing-masing terletak di utara, timur dan barat Laut Caspian. EF dan PLI yang disukat untuk semua logam di barat Laut Caspian lebih tinggi berbanding dengan tapak-tapak lain. Cadmium menunjukkan EF dan PLI yang lebih tinggi dari logam lain. Faktor pengayaan purata Cadmium (8.71 ± 2.86) didapati lebih tinggi dari 5 di endapan permukaan Caspian selatan, yang menunjukkan bahawa pencemaran Cd mempunyai pengayaan yang sederhana teruknya. Adalah diketahui bahawa

kepekatan-kepekatan tertinggi besar kemungkinannya berlaku berdekatan industri-industri besar di pantai (contohnya semenanjung Absheron di Azerbaijan Astara dan di Iran) dan juga muara-muara sungai yang terdapat perlombongan, industri kimia dan pertanian di kawasan tadahannya. Nilai I_{geo} untuk Cd di kebanyakan tempat tugas dikelaskan sebagai sederhana teruk tercemarnya dan sederhana hingga teruk tercemarnya, dan purata I_{geo} Cd sebanyak (1.77 ± 0.35) menunjukkan bahawa endapan-endapan permukaan di pantai Caspian telah dicemari dengan sederhana oleh logam ini. Semua kepekatan di dalam endapan untuk 14 Stesen percontohan (Pb, Ni, Zn, Cu dan Fe) kecuali Cd didominasi oleh pecahan-pecahan yang merintang. Pecahan-pecahan tidak-merintang adalah lebih rendah dari pecahan-pecahan merintang di keseluruhan jangkamasa kajian, yang menunjukkan bahawa tiada input antropogeni yang penting bagi Pb, Ni, Zn, Cu dan Fe ke atas endapan permukaan di selatan Laut Caspian. Peratusan-peratusan pecahan geokimia tidak-merintang yang tinggi bagi Cadmium menunjukkan bahawa sumber-sumber Cd di endapan permukaan selatan Laut Caspian kebanyakannya disumbangkan oleh sumber antropogeni. Keputusan-keputusan menunjukkan bahawa pencemaran logam berat kebanyakannya tertumpu di barat Laut Caspian di kawasan pelabuhan yang dikhaskan untuk perkapalan, pertanian dan kegiatan Azerbaijan dan juga di timur, yang di bawah pengaruh kegiatan-kegiatan industri. Nilai-nilai pertengahan kepekatan setiap logam berbeza untuk tisu lembut, cangkerang dan 'byssus' *D. polymorpha*. Kepekatan Ni, Cd, Cu dan Fe didapati paling tinggi di 'byssus', sementara kepekatan tertinggi Pb dan Zn didapati masing-masing di cangkerang dan tisu lembut. Ini menunjukkan bahawa 'byssus' *D. polymorpha* boleh digunakan sebagai agen biomonitor untuk Ni, Cu, Fe dan terutama sekali Cd oleh sebab korelasi positif yang tinggi Cd di dalam 'byssus' dengan pecahan-pecahan

endapan. Untuk tanah basah Anzali, secara amnya, Shanbe Bazar menunjukkan paras tertinggi Pb (69.10 $\mu\text{g/g dw}$); Cd (1.81 $\mu\text{g/g dw}$); Zn (830.95 $\mu\text{g/g dw}$); dan Cu (89.54 $\mu\text{g/g dw}$). Bazar Shanbe terletak di kawasan bandar kota Anzali dan mungkin tercemar teruk oleh efluen perbandaran. Kepekatan tertinggi EFLE dan pecahan-pecahan organik yang boleh dioksidakan logam berat juga (Pb, Ni, Cd, Zn, Cu dan Fe) berbanding dengan tapak-tapak persampelan yang lain dicatatkan di Shanbe Bazar. Kebanyakan logam-logam tersebut berkorelasi positif dengan kuat. Pertalian positif yang kuat di antara Pb, Cd, Zn dan Cu menunjukkan bahawa sumber-sumber input semula jadi dan antropogeni adalah sama. Peratusan logam berat yang lebih tinggi di pecahan tidak-merintang mencerminkan kecenderungan yang lebih untuk menjadi biosedia. Berkenaan amaun-amaun kepekatan tidak-merintang Cd di kedua-dua kawasan Anzali (Pelabuhan dan tanah basah) dan, berlainan dari kajian-kajian sebelum ini, nampaknya tidak pula kepekatan Cd yang tinggi di Anzali dipengaruhi oleh kawasan tanah basah Anzali. Pengkajian kesan penumpuan logam di insang kupang zebra yang dikutip dari tapak-tapak khas Laut Caspian secara kemikroskopan elektron penghantaran menunjukkan bahawa teknik ultramorfologi ialah alat yang baik untuk mengkaji perubahan-perubahan sel, yang digunakan sebagai biopenanda, oleh sebab ia efisien di dalam analisis persekitaran. Adalah jelas bahawa kupang zebra di tapak-tapak yang tercemar telah mengalami perubahan berkaitan dengan sistem pernafasan.

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I certify that a Thesis Examination Committee has met on ... to conduct the final examination of Tooraj Sohrabilangaroudi on his thesis entitled “assessment, distribution and speciation of heavy metals (Pb, Ni, Cd, Zn, Cu and Fe) in surface sediment and different parts of *Dreissena polymorpha* along the south coast of the Caspian Sea and Anzali wetland ” in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia[P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy Degree. Members of the Thesis Examination committee were as follow:

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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.

TOORAJ SOHRABI LANGAROUDI

Date: 23 November 2011



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