UNIVERSITI PUTRA MALAYSIA

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By

AWAD AHMED AL-ZAHRANY

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

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DEDICATION

I would like to dedicate this thesis to my parents, brothers, and sisters. I am especially dedicating this thesis to my ever supportive wife Mrs. Fatima Saleh. Finally, I would like to dedicate this thesis to my daughters Rawabi, lamya, my sons Abdul-Allah, Zead and Osama.

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

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Chairman: **Professor Elias Saion, PhD**

Faculty: **Science**

The horizontal and vertical distributions of concentrations of major, minor, and trace elements from the grap and core marine sediment samples along the West Coast of Peninsular Malaysia were investigated. All together there are 35 elements including the following 27 elements namely Al, As, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Mg, Mn, Na, Rb, Sb, Sc, Sm, Ta, Th, U, V, Yb, and Zn were studied by using Instrumental Neutron Activation Analysis (INAA) and the following 8 elements namely Cd, Cu, Mo, Pb, Ni, Sr, Ba, and Ti were studied by using Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) technique. The obtained elemental concentrations were evaluated by various methods including by comparing the

concentrations to that of the mean crustal materials and average shales, the national studies, and the international guidelines for marine sediments of Canada, Netherlands and USA-New York State. The enrichment factor method was used to determine whether the elements belong to anthropogenic and non-anthropogenic sources. In addition, different statistical analysis methods including the linear regression analysis and the cluster analysis were used to determine the correlation of concentrations between the measured elements. To ensure the accuracy and precision of the generated data, proper quality control and quality assurance procedures have been incorporated in the INAA analysis including 'blank', duplicate sample analysis, application of certified reference materials, and quantification using K_0-NAA procedure. The data generated using ICP-MS were subject to the same quality control and quality assurance procedures as the INAA analysis without K_0-NAA procedure.

For the horizontal elemental distributions the grab sediment samples were used. The non-anthropogenic elements identified by the enrichment factor calculation were Al, Ba, Ca, Cd, Co, Cr, Cu, K, Mg, Mn, Mo, Na, Ni, Rb, Sr, Ta, Ti, V, and Zn. The concentrations of Al, Ba, Cd, Co, Cr, Cu, K, Mn, Mo, Ni, Sr, Ta, Ti, V, and Zn are lower than those of the average shales and the mean crustal materials. This may be due to high solubility of these elements in the tropical weathering. The concentrations of Ca, Mg and Na are lower than the mean crustal materials but higher than the average shales. The concentration of Rb is slightly greater than that of the mean crustal materials but lower than the average shales. Also, this may be due to high solubility of Ca, Mg, Na, and Rb in the tropical weathering. The anthropogenic elements in the grab sediment samples were As, Br, Cs, Fe, Hf, Pb,

Sb, Th, and U. The concentrations of As, Br, Cs, Hf, Pb, and Sb are greater than those of the mean crustal materials. This indicates that there were external inputs of anthropogenic sources such as industrial and mining activities at the inland area along the Straits of Melaka. The concentration of Pb is approximately twice of the average shales and three times than the mean crustal materials. Higher concentration of Pb in the grab sediment samples may be due to industrial activities such as manufacture of batteries and automotive emissions from cities along the rivers flowing into the Straits of Melaka.

For the vertical elemental distributions the core sediment samples were used. The non-anthropogenic elements Al, Ba, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Rb, Sr, Ta, Ti, V, and Zn in the core sediment samples are lower than the concentrations of the mean crustal materials and average shales. The anthropogenic elements in the core sediment samples were As, Br, Ca, Cs, Hf, Pb, Sb, Th, and U, where the concentrations of Br, Ca, Cs, Hf, Th, and U are greater than the concentrations of the mean crustal materials and average shales. This indicates that there were external inputs of anthropogenic sources such as industrial and mining activities at the inland area along the Straits of Melaka. The concentration of Pb is greater than the concentration of the mean crustal materials but lower than the average shales. For toxic elements such as As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb, and Zn the mean concentrations are either lower than or equal to the mean concentrations for the Straits of Johor and the Penang Island. Moreover, the mean concentrations of most elements were found lower than the international guidelines for marine sediments from Canada, Netherland and USA-New York State, except for the concentrations of Cr and Ni, which are greater than the international guidelines.

The depth profile of As/Al, Cd/Al, Cr/Al, Cu/Al, Fe/Al, Mn/Al, Sb/Al, and U/Al of the core sediment samples normalized to aluminum metal revealed the general trends that the concentration level in the upper layer is higher than the bottom layer. The explanation for the higher concentrations of As, Cd, Cr, Cu, Fe, Mn, Sb, and U in the upper layers may be due to the lower oxygen level in an anoxic sediment which caused digenesis process in which the multi-oxidations state in those elements tend to be higher for concentration level at the surface sediment layer. This indicates that the core marine sediments in the Straits of Melaka are having enough oxygen level and remain healthy for marine ecosystem.

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

TABURAN KEPEKATAN UNSUR DALAM SEDIMEN MARIN DI SELAT MELAKA DENGAN MENGGUNAKAN KAEDAH ANALISIS PENGAKTIFAN NEUTRON DAN SPEKTROMETRI JISIM.

OLEH

AWAD AHMED AL-ZAHRANY

March 2007

PENGERUSI: **Profesor Elias Saion, PhD**

FAKULTI: **Sains**

Taburan kepekatan mengufuk dan mencacang bagi unsur major, minor dan surih dalam sedimen marin secara pesampelan cekup dan teras di sepanjang perairan Selat Melaka, Pantai Barat Semenanjung Malaysia telah diselidiki. Kesemuanya 37 unsur termasuk 27 unsur berikut Al, As, Ba, Br, Ca, Cd, Ce, Co, Cr, Cs, Cu, Eu, Fe, Hf, K, La, Lu, Mg, Mn, Mo, Ni, Pb, Rb, Sb, Sc, Sm, Sr, Ta, Th, Ti, U, V, Yb and Zn telah dikaji dengan menggunakan kaedah instrumentasi analisis pengaktifan neutron (INAA) dan 8 unsur berikut Cd, Cu, Mo, Pb, Ni, Sr, Ba, and Ti telah dikaji dengan mengunakan teknik aruhan gandingan plasma-jisim spektroskopi (ICP-MS). Keputusan analisis kepekatan diinterpretasikan dengan pelbagai kaedah, termasuklah membandingkan keputusan dengan nilai purata bahan kerak bumi dan purata kepekatan dalam batuan, membandingkan dengan kajian peringkat kebangsaan, dan

membandingkan dengan penunjuk antarabangsa untuk penilaian tahap pencemaran sedimen marin daripada Kanada, Netherlands dan USA-Negeri New York. Kaedah factor pengayaan telah digunakan untuk menentukan sama ada sesuatu untur itu berasal daripada kegiatan manusia iaitu antropogenik atau sebaliknya bukan antropogenik. Di samping itu pelbagai kaedah statistik seperti kaedah analisis regresi linear dan analisis kelompok telah juga digunakan untuk menentukan korelasi kepekatan antara unsur-unsur yang dikaji. Untuk memastikan ketepatan dan kejituan data yang dijana dalam kajian ini, beberapa kaedah kawalan kualiti dan ketentuan kualiti telah disertakan dalam analisis K_0-INAA termasuk penggunaan sampel kosong atau 'blank, analisis penduaan sampel, menggunakan penilaian kepekatan unsur rujukan piawai dan menggunakan kaedah K_0-NAA. Data yang dijana dengan kaedah ICP-MS juga telah dipastikan kualitinya dengan cara yang sama tetapi tanpa menggunakan kaedah K_0-NAA.

Untuk taburan kepekatan mengufuk pesampelan cekup telah digunakan. Unsur bukan antropogenik yang dikenal pasti menggunakan factor pengayaan ialah Al, Ba, Cd, Co, Cr, Cu, K, Mg, Mn, Mo, Ni, Rb, Sr, Ta, Ti, V, and Zn yang mempunyai kepekatan lebih rendah berbanding dengan kepekatan kedua-dua bahan dalam batuan dan kerak bumi. Kepekatan Mg lebih rendah berbanding purata kepekatan dalam batuan tetapi lebih tinggi sedikit berbanding purata kepekatan dalam kerak bumi. Sementara kepekatan Rb lebih tinggi sedikit berbanding purata kepekatan kerak bumi tetapi lebih rendah berbanding purata kepekatan dalam batuan. Keadaan ini mungkin disebabkan oleh Mg, Na, and Rb lebih mudah larut dalam cuaca panas iklim tropika seperti di kawasan perairan Selat Melaka. Unsur antropogenik yang telah di kenal pasti dalam sampel sedimen cekup ialah As, Br, Cs, Fe, Hf, Pb, Sb, Th,

dan U. Kepekatan As, Br, Cs, Hf, Pb, dan Sb lebih besar daripada purata kepekatan bahan kerak bumi. Ini mungkin disebabkan terdapatnya input bahan pencemaran daripada aktiviti perindustrian dan perlombongan di kawasan daratan sepanjang Selat Melaka. Kepekatan Pb didapati menghampiri dua kali kepekatan dalam batuan dan tiga kali lebih tinggi daripada bahan kerak bumi. Kepekatan Pb yang tinggi dalam sampel cekup mungkin disebabkan aktiviti industri seperti kilang bateri dan pencemeran kenderaan di bandar-bandar sepanjang sungai yang mengalirkan airnya ke Selat Melaka.

Untuk taburan kepekatan mencacang pesampelan teras telah digunakan. Unsur bukan antropogenik yang dikenal pasti menggunakan factor pengayaan ialah Al, Ba, Cd, Co, Cr, Cu, K, Mg, Mn, Mo, Ni, Rb, Sr, Ta, Ti, V and Zn yang didapati lebih rendah berbanding purata kepekatan dalam bahan kerak bumi begitu juga berbanding dengan purata dalam batuan. Unsur antropogenik yang di kenal pasti dalam sample sedimen teras pula ialah As, Br, Ca, Cs, Hf, Pb, Sb, Th and U yang mana kepekatan Br, Ca, Cs, Hf, Th and U adalah lebih besar daripada purata kepekatan dalam bahan kerak bumi dan juga berbanding purata dalam batuan. Ini mungkin disebabkan terdapatnya input bahan pencemaran daripada aktiviti perindustrian dan perlombongan di kawasan daratan sepanjang Selat Melaka. Di samping itu kepekatan Pb di dapati lebih besar berbanding purata dalam kerak bumi tetapi lebih rendah berbanding dengan kepekatan dalam batuan. Untuk unsur toksik seperti As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb dan Zn, menunjukkan purata kepekatan sama ada lebih rendah atau setara dengan purata kepekatan dalam sedimen daripada perairan Johor dan Pulau Pinang. Dalam pada itu juga, kepekatan purata untuk semua unsur berkenaan didapati kepekatannya lebih rendah berbanding dengan nilai penunjuk

pencemaran antarabangsa daripada Canada, Netherlands dan USA-Negeri New York kecuali bagi kepekatan Cr dan Ni dimana kepekatannya lebih tinggi daripada penunjuk pencemaran antarabangsa.

Profil kepekatan unsur As/Al, Cd/Al, Cr/Al, Cu/Al, Fe/Al, Mn/Al, Sb/Al dan U/Al yang dinormalisasikan terhadap kepekatan logam aluminium menurut kedalaman teras sampel sedimen menunjukkan bahagian lapisan teratas lebih tinggi kepekatannya berbanding lapisan bawah. Tingginya kepekatan As, Cd, Cr, Cu, Fe, Mn, Sb, and U mungkin boleh dijelaskan oleh kurangnya kepekatan oksigen di antara lapisan sedimen dan kolom air, menyebabkan terbentuknya sedimen permukaan yang anoksik. Ini mengakibatkan berlakunya proses diagenesis yang menyebabkan unsur-unsur multi-oksidan berhijrah daripada sedimen bahagin bawah ke permukaan. Ini menunjukkan bahawa dalam sedimen marin teras kandungan paras oksigen adalah mencukupi dan masih sesuai untuk ekosistem marin.

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I certify that an Examination Committee has met on 28 March 2007 to conduct the final examination of Awad Ahmed Al-Zahrany on his Doctor of Philosophy thesis entitled "Elemental Distributions in Marine Sediments in the Straits of Melaka Using Neutron Activation and Mass Spectroscopic Analyses" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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This thesis submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee are as follows:

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

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AWAD AMED AL-ZAHRANY

Date: 2007

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