



UNIVERSITI PUTRA MALAYSIA

***ASSESSMENT OF CONCENTRATION AND DISTRIBUTION OF HEAVY METALS
IN WATER-SEDIMENT FACIES IN LANGAT RIVER, MALAYSIA***

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FPAS 2013 10

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By

LIM WAN YING

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

April 2013

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

ASSESSMENT OF CONCENTRATION AND DISTRIBUTION OF HEAVY METALS IN WATER-SEDIMENT FACIES IN LANGAT RIVER, MALAYSIA

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April 2013

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The release of pollutants such as heavy metals into aquatic environment attributed to dense development bears a direct effect to river ecosystem and becomes an emerging issue nowadays. This thesis discusses the heavy metals variation and their pollution magnitude status in Langat River, based on heavy metal concentrations, comparison with different standard guidelines, application of different indices and indicator, statistical and modelling analyses. In general, this study aimed to provide data on the spatial and temporal variation of heavy metals in river water and sediment, their potential pollution sources and ecological risk area. The metal speciation and saturation indices based on PHREEQC modelling was also presented. A total of 30 sampling stations (LY 1 to LY 30) were selected and the samplings were conducted during the wet (December 2010) and dry (July 2011) seasons. Triplicate of water and sediment

samples were collected simultaneously and subjected to analyses. Both water and sediment samples were analyzed for heavy metals concentration (aluminium (Al), arsenic (As), barium (Ba), cadmium (Cd), cobalt (Co), copper (Cu), chromium (Cr), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), and zinc (Zn)) using an Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Based on measurement, each metals were found varied significantly among sampling stations and seasons ($p < 0.05$). In general, the concentration levels of heavy metals were more likely to be high in wet season and this statement was supported by the calculation of degree of contamination. Most of the water samples were within the drinking water quality standards stipulated by the World Health Organization (WHO) and the Malaysia Ministry of Health (MOH), except for Al, As, Fe, Ni and Mn at certain sampling stations. For sediment samples, most of the studied metals did not exceed the Interim Sediment Quality Guidelines (ISQG-high values), except for As and Pb. Based on the environmental forensic investigation via the use of analytical analyses, water and sediment quality standards, different indicators and geochemical indices, as well as multivariate analyses, it can be summarized that the pollution sources responsible for both sediment and water are anthropogenic (agricultural and industrial activities) and natural (seawater intrusion and geological weathering) processes. In addition, the significant relationships between certain parameters (pH, *Eh*, salinity, and CEC) with metals identified the intrinsic factors contributing to the mobility of metal in Langat River and their tendency to depict a similar trend of distribution pattern. The hierarchical cluster analysis (HCA) renders the sampling stations into two clusters for both wet and dry seasons. Both seasons yield a similar cluster where Cluster 1 (LY 15 to LY 30) was mainly influenced by the

agricultural and industrial pollution while Cluster 2 (LY 1 to LY 14) was affected by seawater. Meanwhile, the mineral saturation indices and the distribution of aqueous species in river water were performed using hydrochemical model, PHREEQC. Heavy metals were divided into three groups: (i) Ba^{2+} , Mn^{2+} , Zn^{2+} , and Cu^{2+} which dominated by free ions; (ii) Fe^{3+} and Al^{3+} which dominated by hydroxyl species; (iii) Cd^{2+} and Pb^{2+} which dominant by sulfate and chloride species. The saturation indices revealed that the samples were mostly under-saturation or close to saturation with respect to analyzed minerals, except gibbsite, goethite, and hematite. Thus, this study recommends an environmental forensics research approach to illustrate the degree of metal pollution in the Langat River as well as the origin of these metals. The outcomes of this approach provide a better understanding on the pollution magnitude, evaluation of potential ecological risks and contamination status of the river.

Keywords: Hydro-geochemistry, heavy metals, Langat River, water and sediment interaction

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

**PENILAIAN KEPEKATAN DAN TABURAN LOGAM BERAT DI
PERMUKAAN AIR-SEDIMEN DI SUNGAI LANGAT, MALAYSIA**

Oleh

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Pelepasan bahan pencemar seperti logam berat dalam persekitaran akuatik dikaitkan dengan pembangunan padat menanggung kesan langsung terhadap ekosistem sungai dan menjadi satu isu baru yang muncul pada masa kini. Tesis ini membincangkan perihal taburan logam berat dan kadar magnitud pencemaran di Sungai Langat, berdasarkan kepada kepekatan logam berat, perbandingannya dengan beberapa garis panduan piawaian, dan aplikasi terhadap beberapa indeks dan petunjuk yang berbeza, serta permodelan analisis dan statistik. Secara umumnya, kajian ini bertujuan untuk menghasilkan variasi data dari segi ruang dan masa bagi logam berat di dalam air sungai dan juga sedimen, beserta potensi sumber pencemarannya dan juga kawasan yang berisiko dalam konteks ekologi. Kajian spesis logam dan indeks ketepuan berdasarkan permodelan PHREEQC telah juga dipersembahkan. Sebanyak 30 stesen persampelan

(LY 1 hingga LY30) telah dipilih dan aktiviti persampelan telah dijalankan semasa musim hujan (Disember 2010) dan musim kering (Julai 2011). Tiga sampel air dan sedimen masing-masing telah diambil serentak tertakluk kepada analisis. Kedua-dua sampel air dan sedimen telah dianalisis untuk kepekatan logam berat (aluminium (Al), arsenik (As), barium (Ba), kadmium (Cd), kobalt (Co), kuprum (Cu), kromium (Cr), ferum (Fe), manganat (Mn), nikel (Ni), plumbum (Pb), dan zink (Zn)) dengan menggunakan spektrometri jisim-plasma gandingan induktif (ICP-MS). Berdasarkan kepada penilaian yang dibuat, setiap logam didapati mempunyai kadar variasi yang signifikan antara stesen persampelan dan musim ($p < 0.05$). Secara amnya, kadar kepekatan logam berat adalah lebih tinggi dalam musim hujan dan kenyataan ini telah disokong oleh pengiraan terhadap tahap pencemaran. Kebanyakan sampel air berada dalam julat piawaian kualiti air minum yang telah ditetapkan oleh Pertubuhan Kesihatan Sedunia (WHO) dan Kementerian Kesihatan Malaysia (MOH), kecuali Al, As, Fe, Ni, dan Mn di beberapa stesen persampelan tertentu. Manakala bagi sampel sedimen pula, kebanyakan darinya tidak melebihi Panduan Interim Kualiti Sedimen (ISQG-nilai tinggi), kecuali As dan Pb. Berdasarkan kepada kajian forensik alam sekitar dengan menggunakan kaedah analisis analitikal, piawaian kualiti air dan sedimen, penunjuk dan indeks geokimia berbeza, serta analisis multivariat, dapat disimpulkan bahawa sumber pencemaran air dan sedimen boleh dibahagikan kepada sumber antropogenik (aktiviti pertanian dan perindustrian) dan proses semulajadi (kemasukan air laut dan keadaan geologi). Di samping itu, perkaitan signifikan di antara beberapa parameter (pH, *Eh*, kemasinan, dan CEC) dengan logam telah dikenal pasti sebagai faktor-faktor dalaman yang menyumbang kepada pergerakan logam di Sungai Langat dan kecenderungannya

untuk menghuraikan corak agihan yang serupa. Analisis kelompok hierarki (HCA) menterjemahkan stesen persampelan kepada dua kelompok untuk musim hujan dan musim kering. Kedua-dua musim menghasilkan kelompok yang sama di mana Kelompok 1 (LY15 hingga LY30) dipengaruhi oleh pencemaran daripada aktiviti pertanian dan perindustrian, manakala Kelompok 2 (LY1 hingga LY 14) pula dipengaruhi oleh air laut. Sementara itu, indeks ketepuan mineral dan juga taburan spesies logam dalam air sungai telah dijalankan menggunakan model hidrokimia, PHREEQC. Logam berat telah dibahagikan kepada tiga kumpulan: (i) Ba^{2+} , Mn^{2+} , Zn^{2+} , dan Cu^{2+} yang didominasi oleh ion bebas; (ii) Fe^{3+} dan Al^{3+} yang didominasi oleh spesies hidroksil; (iii) Cd^{2+} dan Pb^{2+} yang didominasi oleh spesies sulfat dan klorida. Indeks ketepuan telah mendedahkan bahawa kebanyakan sampel berada dalam keadaan dibawah-ketepuan atau hampir kepada ketepuan, berdasarkan analisis mineral, kecuali bagi mineral gipsit, goetit dan bijih besi. Oleh itu, kajian ini menyarankan satu pendekatan penyelidikan forensik alam sekitar bagi menggambarkan tahap pencemaran logam di Sungai Langat, serta asal usul logam tersebut. Hasil daripada kajian ini memberikan kefahaman yang lebih baik berkenaan magnitud pencemaran, penilaian potensi risiko ekologi, dan tahap pencemaran sungai.

Kata kunci: Hidrogeo-kimia, logam berat, Sungai Langat, interaksi air dan sedimen

ACKNOWLEDGEMENTS

There were many individuals who contributed directly or indirectly in some ways towards the completion of this work. First of all, I would like to extend the greatest appreciation to my worthy supervisor, Dr. Ahmad Zaharin Aris, for his professional insight, skilful guidance, encouraging attitude, and contribution of time and energy, reviewed my initial writing and providing valuable suggestions for improving the text. Thanks a lot for his patience and kindness. I also would like to express my sincere appreciation to my co-supervisor, Professor Dr. Mohamad Pauzi Zakaria for his valuable comments, precious suggestions, and encouragement in the whole study. This research was funded by Research University Grant Scheme (RUGS) vot no. 9199751, no. project 03-01-11-1142RU from Universiti Putra Malaysia (UPM) and The Academy of Sciences for the Developing World (TWAS) project number 09-09 RG/EAS/AS_C/UNESCO FR:3240231216. I acknowledge the support from Graduate Research Fellowship Scholarship awarded by UPM and also the World Federation of Scientists for my study. Co-operation from Department of Drainage and Irrigation, Malaysia for the rainfall data and field services provided is highly acknowledged. Part of this thesis is already published. Thus, I would also like to take this opportunity to thank anonymous reviewers who gave valuable comments and positive feedbacks prior to publication. Last but not least, this thesis would never come into completion without the continuous encouragements, enlightens, advises, cares, and nurture from my beloved parents, Lim Chai Hoo and Toh Lee Boy, my family members, staffs, and students from the Faculty of Environmental Studies upon their field assistance, friendship, and support.

I certify that a Thesis Examination Committee has met on 3 April 2013 to conduct the final examination of Lim Wan Ying on her Master of Science thesis entitled “Assessment of Concentration and Distribution of Heavy Metals in Water-Sediment Facies in Langat River, Malaysia” 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 Master of Science.

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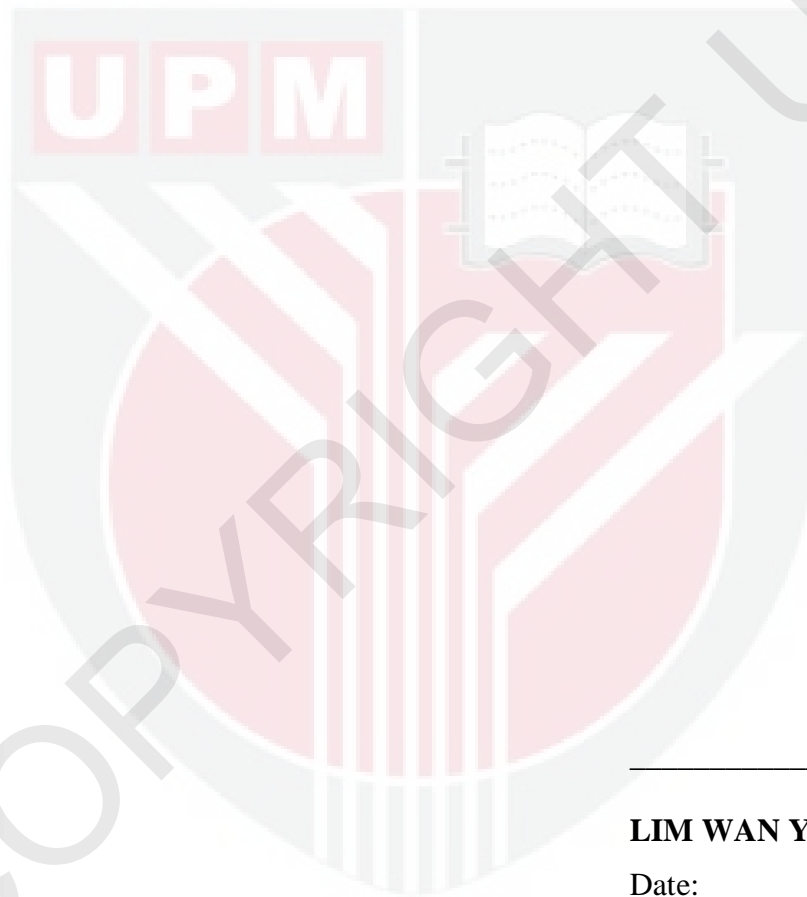
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DECLARATION

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 its not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.



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