# ASSESSMENT OF HEAVY METAL CONCENTRATIONS IN VEGETABLES AND DIFFERENT SOIL TYPES IN THE KLUANG-KOTA TINGGI AREA, JOHOR, MALAYSIA

**By**

**JULIANA BINTI BOKHARI**

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirement for the Degree of Master of Agricultural Science**

**April 2006**

# DEDICATION

This thesis is specially dedicated to:

**My beloved parents,**

*Bokhari Hitam*

*and*

*Hjh. Beah Hj. Salleh*

**Sisters,**

*Hazreena*
*Marlina*

**& lastly**

*Muhammad Hafizan Sharudin*

Who always supported and encourage me to do the best

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the Degree of Master of Agricultural Science

**ASSESSMENT OF HEAVY METAL CONCENTRATIONS IN VEGETABLES AND DIFFERENT SOIL TYPES IN THE KLUANG-KOTA TINGGI AREA, JOHOR, MALAYSIA**

By

**JULIANA BINTI BOKHARI**

**April 2006**

**Chairman : Associate Professor Siti Zauyah Bte Darus, PhD**

**Faculty : Agriculture**

The vegetables in Johore are grown on several soil types. Heavy metal contents in Johore soils and vegetables have not been fully studied although it is known that the concentration of heavy metals in soils under vegetable cultivation was affected by excessive use of fertilizers, agrochemical and addition of chicken dung. The quality of these vegetables and the soils from heavy metals perspective is important lately. The knowledge of both the total concentration and chemical speciation is necessary to understand the behavior of heavy metals in soil. This study was conducted to determine heavy metal contents in organic and mineral soils cultivated with vegetables and the relationship between heavy metal concentration and some physico-chemical properties. Heavy metal speciation study is also necessary for evaluating the mobility and bioavailability of heavy metals in the soils.

Soil and vegetable samples were collected from several vegetable plots in Kluang and Kota Tinggi. A total of 177 soil samples were collected comprising of 42 organic soil samples, 81 Rengam series, 27 Telemong series and 27 Batang Merbau series soil. The soil samples were taken from 3 depths (0-20 cm, 20-40 cm and 40-60 cm) using a stainless steel auger. Top soil samples (0-20 cm) from the surrounding area, werealso collected in order to determine the background values of heavy metals in the soil as compared to the vegetable cultivated areas. GPS reading was taken at every sampling point. The crops selected were leafy vegetables (39 samples) and fruit vegetables (17 samples).

Soil samples were analyzed for the pH, organic C, cation exchange capacity (CEC) and texture. Available heavy metals were extracted with EDTA, DTPA and 0.1 N HCl extractants. Total heavy metal contents were determined by the aqua regia-method. The heavy metal concentrations were extracted through dry ashing of the vegetable tissues. For the speciation study, 24 cultivated and 12 uncultivated Rengam series samples were extracted using sequential extraction procedures (exchangeable, carbonate, Fe-Mn oxides, organic and residual fractions) as outline by Abollino *et al.,* (2001) which is a modified method from Tessier (1979). The heavy metal (Cd, Cr, Zn, Pb, Cu and Ni) contents in soil and vegetables were determined using Atomic Absorption Spectrophotometer (FAAS). The geographical distribution maps were produced using GIS software (MapInfo).

From the t-test analysis, the pH, OC and CEC values in the top layers of cultivated

organic and mineral soils were significantly higher when compared to background soils. Pearson correlation analysis indicates that the mineral soil pH significantly correlated with Cu (r=0.435**, n=45) and Zn (r=0.450**, n=45) concentrations. Only Cu concentration showed significant correlation with carbon percentages of mineral soils with value of r=0.457**, n=45. Copper, Pb and Zn correlated positively with CEC with values of r=0.176*, r=0.242** and r=0.219* (n=45), respectively. Correlation analysis showed that all heavy metals in organic soil correlated positively with soil pH.

The difference between means of heavy metals of mineral soils showed by t-test indicated that metal concentrations at the top layers of cultivated soils were significantly higher compared to the background soils. Data from organic soils showed that only Cd, Cu, Pb and Zn were significantly higher compared to the background soils. Heavy metals such as Cu, Cr, Pb and Ni in organic and minerals soils were still within the normal range of Malaysian soils. The concentrations of these metals were still lower than the 95$^{th}$ Percentile and Dutch target values except for Cd in the all soil types and Zn (138.11 mgkg$^{-1}$) in Telemong series. From speciation study, the percentages of mobile Cd (32%) was found to be high in cultivated Rengam series compared to other metals. However, the percentages of mobile fractions for all metals in the cultivated soils were lower compared to the uncultivated soils. The majority of metals present were in the residual form (immobile fraction).

Among the vegetables, Indian Pennyworth exhibited the highest mean concentrations of Cd (0.02 mgkg$^{-1}$), Cr (0.8 mgkg$^{-1}$), Pb (0.29 mgkg$^{-1}$) and Zn (10.16 mgkg$^{-1}$) compared to

the other vegetables species. Fruit and leafy vegetable tissues contain highest Zn and the least Cd concentrations. Results of the transfer coefficients showed that leafy vegetables tend to accumulate higher concentration of metals in edible tissue compared to the fruit vegetables. Pearson correlation analysis indicated that total Ni in vegetables grown on Rengam series correlated positively with available Ni in soil using EDTA (r=0.408*, n=27), while Cd in vegetables correlated significantly with available Cd using 0.1N HCl extraction (r=0.615**, n=27). Positive correlation was only obtained between Cr content in vegetables grown on organic soil with available Cr (r=0.566*, n=14) using 0.1N HCl. Results showed that the heavy metal concentrations in fruit and leafy vegetables were still below the maximum permissible concentration (MPC) as stated in the Malaysian Food Act (1983) and Food Regulations (1985).

Distribution maps of heavy metals in Kluang and Kota Tinggi showed that Cd concentrations in vegetable areas were higher than the 95$^{th}$ percentile, which is proposed by Zarcinas *et al.,* (2004) to be Malaysian soil investigative level. One of the vegetable areas in Kluang (C5) showed high concentration of Zn (157 mgkg-1), which is higher than the 95$^{th}$ percentile. This farm had been actively producing leafy vegetable for almost 20 years. It is evident that the vegetable areas in Kluang and Kota Tinggi showed higher content of metal concentration compared to the surrounding areas. The pollution index (PI) values in the vegetable areas in Kluang and Kota Tinggi are still below 1.0, indicating that metal concentrations are below tolerable level. However, these vegetable growing areas must be continuously monitored due to some indication of possible heavy metal contamination.

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

**PENILAIAN KEPEKATAN LOGAM BERAT DALAM SAYURAN DAN JENIS TANAH BERBEZA DI KAWASAN TANAMAN SAYURAN SEKITAR KLUANG-KOTA TINGGI, JOHOR, MALAYSIA**

Oleh

**JULIANA BINTI BOKHARI**

**April 2006**

**Pengerusi : Profesor Madya Siti Zauyah Bte Darus, PhD**

**Fakulti : Pertanian**

Kawasan penanaman sayur di Johor didapati terdiri daripada jenis tanah yang berbeza. Logam berat dalam tanah dan sayuran di Johor tidak dikaji secara mendalam walaupun secara amnya, sudah sedia maklum bahawa pengumpulan logam berat dalam tanah adalah disebabkan oleh penggunaan bahan-bahan berasaskan kimia (baja, racun perosak) serta baja organik (tahi ayam) yang berlebihan di kawasan penanaman sayur. Kualiti tanah dan sayuran dari sudut perspektif logam berat menjadi semakin penting sejak akhir ini. Pengetahuan tentang jumlah kandungan dan bentuk kimia logam berat adalah penting untuk memahami sifat logam berat dalam tanah. Kajian ini dijalankan untuk menentukan tahap kepekatan logam berat di dalam tanah mineral dan tanah organik yang ditanam

dengan pelbagai sayuran serta mengenalpasti hubungan diantara logam berat dengan sifat-sifat kimia dan fizikal tanah. Kajian penentuan bentuk logam berat dalam tanah yang dijalankan adalah untuk mengenalpasti bentuk logam berat yang mudah diserap oleh tanaman sayuran.

Sampel tanah dan sayuran diambil daripada kawasan tanaman sayur di sekitar Kluang dan Kota Tinggi. Sebanyak 117 sampel tanah yang merangkumi 42 sampel tanah organik, 81 sampel siri Rengam, 27 sampel siri Telemong dan 27 sampel siri Batang Merbau . Sampel- sampel tanah diambil pada tiga kedalaman berbeza iaitu 0-20 cm, 20-40 cm dan 40-60 cm menggunakan auger anti karat. Sampel tanah permukaan (0-20 cm) daripada sekitar kawasan kajian diambil untuk digunakan sebagai perbandingan (kawalan). Bacaan GPS diambil di setiap lokasi sampel. Sebanyak 39 sampel sayur jenis daun dan 17 sampel sayur jenis buah dipilih untuk dianalisa.

Sifat kimia dan fizik tanah yang dianalisis adalah pH, karbon organik, kadar pertukaran kation (KPK), tekstur tanah dan kandungan logam berat. Kadar logam berat tersedia di dalam tanah diekstrak menggunakan 3 bahan pengekstrak iaitu EDTA, DTPA dan 0.1N HCl. Jumlah kandungan logam berat dalam tanah pula ditentukan dengan menggunakan kaedah aqua-regia. Kandungan logam berat dalam sayur diekstrak menggunakan kaedah pengabuan kering. Untuk kajian bentuk logam berat dalam tanah, sebanyak 36 sampel tanah siri Renggam (tanah sayuran 24 sampel, tanah kawalan 12 sampel) ditentukan menerusi prosedur pengekstrakan yang terdiri daripada 5 peringkat yang diubahsuai oleh Abollino *et al.,* (2001) daripada kaedah Tessier *et al.,* (1979). Lima bentuk logam berat

yang dikenalpasti melalui prosedur ini iaitu bentuk tukarganti, karbonat, Fe-Mn oksida, organik, dan sisa baki. Kadar logam berat dalam tanah ekstrak dan sayuran ditentukan dengan menggunakan Spektrofotometer Penyerapan Atom Nyalaan (FAAS). Peta geografi taburan logam berat dihasilkan dengan menggunakan maklumat dari GPS dan perisian MapInfo.

Daripada kajian ini, didapati terdapat peningkatan pH, karbon organik dan KPK dalam tanah yang ditanam dengan sayuran berbanding dengan tanah kawalan. Kajian korelasi Pearson di antara sifat kimia tanah dan logam berat menunjukkan bahawa pH tanah mempunyai korelasi dengan kepekatan Cu ($r=0.435^{**}$, $n=45$) dan Zn ($r=0.450^{**}$, $n=45$) dalam tanah mineral. Peratus karbon menunjukkan korelasi positif dengan kepekatan Cu ($r=0.457^{**}$, $n=45$) dalam tanah yang sama, manakala KPK tanah mineral mempuyai korelasi dengan Cu, Pb dan Zn dengan nilai $r=0.176^{*}$, $r=0.242^{**}$ and $r=0.219^{*}$ ($n=45$). Analisis yang sama menunjukkan logam berat dalam tanah organik mempunyai korelasi positif dengan pH tanah.

Analisis t-test min logam berat dalam tanah mineral pada kedalaman 0-20 cm adalah lebih tinggi berbanding tanah kawalan dalam kedalaman yang sama. Sebaliknya tanah organik menunjukkan hanya Cd, Cu, Pb dan Zn yang mempunyai min kepekatan lebih tinggi berbanding tanah kawalan. Kepekatan semua logam berat yang dikaji (Cu, Cr, Pb, Zn dan Ni) di dalam setiap tanah masih berada dalam julat kepekatan normal, manakala kepekatan Cd dalam semua jenis tanah dan kepekatan Zn (138.11 $mgkg^{-1}$) dalam tanah siri Telemong didapati telah melebihi julat kepekatan peratusan ke-95 iaitu tahap

penyiasatan untuk Malaysia yang dicadangkan oleh Zarcinas *et al.,* (2004) dan nilai sasaran Dutch. Analisis penentuan bentuk logam berat dalam tanah menunjukkan peratusan Cd (32%) dalam bentuk mudah diserap adalah tinggi dalam tanah yang ditanam dengan sayur berbanding dengam logam berat yang lain, walaubagaimanapun peratusan setiap logam dalam bentuk mudah diserap dalam tanah sayuran semakin berkurangan berbanding tanah yang tidak ditanam dengan sayuran. Majoriti logam berat berada dalam bentuk sisa baki (tidak diserap).

Antara semua jenis sayur yang dikaji, sayur pegaga didapati mempunyai kandungan Cd (0.02 mg $kg^{-1}$ ), Cr (0.8 mg $kg^{-1}$), Pb (0.29 mg $kg^{-1}$) dan Zn (10.16 mg $kg^{-1}$) yang paling tinggi berbanding dengan jenis sayuran yang lain. Tisu sayur daun dan sayur buah menunjukkan kepekatan Zn yang tinggi manakala kepekatan Cd adalah yang paling rendah. Koefisien pemindahan logam berat daripada tanah kepada tumbuhan menunjukkan bahawa sayur daun mengumpul kepekatan logam dalam tisu lebih tinggi berbanding sayur buah. Analisis korelasi Pearson menunjukkan bahawa kepekatan Ni dalam sayuran yang ditanam di atas tanah siri Rengam mempunyai kolerasi bererti yang positif dengan Ni tersedia dengan menggunakan bahan pengekstrak EDTA (r=0.408*, n=27), manakala kepekatan Cd dalam sayuran yang ditanam di atas siri tanah yang sama mempunyai kolerasi bereerti dengan Cd (r=0.615**, n=27) tersedia menggunakan bahan pengekstrak 0.1N HCl. Bahan pengekstrak yang sama (0.1N HCl), menunjukkan korelasi positif diantara Cr dalam sayuran yang ditanam atas tanah organik dengan Cr tersedia (r=0.566, n=14). Walau bagaimanapun, kepekatan logam berat dalam tisu kedua-dua

jenis sayuran masih di bawah kepekatan penyerapan maksimum yang dibenarkan oleh Akta Makanan (1983) dan Peraturan Makanan (1985).

Peta taburan logam berat di Kluang dan Kota Tinggi menunjukkan bahawa kepekatan Cd di dalam kawasan tanaman sayuran adalah lebih tinggi daripada julat kepekatan peratusan ke-95. Salah satu kawasan penanaman sayur di Kluang (C5) menunjukkan kepekatan Zn (157mg $kg^{-1}$) melebihi julat kepekatan peratusan ke-95. Aktiviti penanaman sayur daun dilakukan secara aktif di kawasan ini dalam jangkamasa 20 tahun. Terbukti bahawa kawasan tanaman sayuran mempunyai kandungan logam berat yang lebih tinggi berbanding kawasan lain di sekitarnya. Indeks pencemaran (PI) di kawasan sayur sekitar Kluang dan Kota Tinggi didapati masih kurang dari 1.0. Nilai indeks pencemaran kurang daripada 1.0 menunjukkan kepekatan logam berat di kawasan tersebut belum mencapai tahap tercemar.

## ACKNOWLEDGEMENT

First of all, I thank Allah S.W.T for giving me the strength to complete this study. I am also sincerely grateful to Assoc. Prof. Siti Zauyah Darus, the chairman of my Supervisory Committee for her guidance, advise, support and patience during the course of this study and in the preparation of this thesis. I am also grateful to Assoc. Prof. Che Fauziah Ishak, for her supervision, comments, and suggestions during the course of this study.

I would also like to thank all the laboratory staff of the Department of Land Management, Faculty of Agriculture, UPM for their kind assistance and corporation, especially En. Alias Tahar, En. Rahim, En. Jamil, En. Ramli, Pn. Hashimah, Pn. Pouziah, Pn. Fauziah, Pn. Hjh. Faridah, Pn. Nomi, and En. Linggam. Special thanks to Dr. Osmanu Haruna, En. Roslan Asri, staff of the Department of Land Management, to En. Asari from Department of Agriculture Kluang and En. Zailan from Wisma Tani, for their help on statistical analysis and preparation of maps. To my friends, Cik Noorhafizah, En. Roslan, En. Azizi, Cik Nurhanani and Cik Nooreehan, my sincere thanks for their help and co-operation during the course of my study.

I would like to express my heartfelt thanks to En. Muhamad Hafizan Sharudin for his patience, support, encouragement, and understanding. To my beloved parents and sisters, for their support and love during my study. Finally, my sincerely thanks to all those who have helped me in my way to make this study success.

I certify that an Examination Committee has met on 12th April 2006 to conduct the final examination of Juliana Binti Bokhari on her Master of Agricultural Science thesis entitled "Assessment of Heavy Metal Concentrations in Vegetables and Different Soil Types in the Kluang-Kota Tinggi Area, Johor, Malaysia" 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 follow:

**Shamsuddin Jusop, PhD**
Professor
Faculty of Agriculture
Universiti Putra Malaysia
(Chairman)

**Aminuddin Hussin, PhD**
Associate Professor
Faculty of Agriculture
Universiti Putra Malaysia
(Internal Examiner)

**Rosenani Abu Bakar, PhD**
Associate Professor
Faculty of Agriculture
Universiti Putra Malaysia
(Internal Examiner)

**Yahya Mohd Nor, PhD**
Associate Professor
Science and Biology
Universiti Sains Malaysia
(External Examiner)

_____
**HASANAH MOHD. GHAZALI, PhD**
Professor/Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

This thesis submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Master of Agricultural Science. The members of Supervisory Committee are as follows:

**Siti Zauyah Darus, PhD**
Associate Professor
Faculty of Agriculture
Universiti Putra Malaysia
(Chairman)

**Che Fauziah Ishak, PhD**
Associate Professor
Faculty of Agriculture
Universiti Putra Malaysia
(Member)

_____

**AINI IDERIS, PhD**
Professor/ Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

## DECLARATION

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

_____

**JULIANA BINTI BOKHARI**

Date:

# TABLE OF CONTENTS

# LIST OF TABLES

# LIST OF FIGURES

# LIST OF ABBREVIATIONS

| | |
|---|---|
| ANOVA | Analysis of variance |
| CEC | Cation exchange capacity |
| DTPA | Diethylene diamine tetracetic acid |
| EDTA | Ethylene diamine tetra acetic acid |
| GIS | Global Information System |
| GPS | Global Positioning System |
| MOP | Murate of Potash |
| MPC | Maximum Permitted Concentration |
| NPK | Nitrogen/Phosphorus?Potassium |
| OC | Organic carbon |
| PI | Pollution Index |
| SAS | Statistical Analysis System |
| TSP | Triple Super Phosphate |