UNIVERSITI PUTRA MALAYSIA

ASSESSMENT OF HEAVY METALS IN SOILS AND TUBER CROPS ON EX-MINING LAND OF SOUTHERN PERAK, MALAYSIA

KAMSHARY MENDER.

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By

KAMSHARY MENDER

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

March 2004

DEDICATION

Specially dedicated to my beloved…

Father…

Mother….

Wife….

Son….
&

To all my family members…

Lastly

To all my best friends

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 HEAVY METALS IN SOILS AND TUBER CROPS ON EX-MINING LAND OF SOUTHERN PERAK, MALAYSIA.

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March 2004

Chairman: Associate Professor Siti Zauyah Bte Darus, Ph.D.

Faculty: Agriculture

Large areas of ex-mining lands in Southern Perak, Malaysia, are used for the cultivation of vegetables, fruits and tuber crops due to the shortage of land for agricultural productions. These areas have been cultivated for more than 20 years. Recent studies have reported that ex-mining land used for the cultivation of tuber crops and some fruits were found to be contaminated by heavy metals. Heavy metals concentrations may be high due to the use of high amounts of organic fertilizers (chicken dung) and agrochemicals (fertilizers, pesticides). There is a growing concern and awareness amongst consumers that long term addition of fertilizers may accumulate heavy metals in soil and taken up by tuber crops grown in the ex-mining lands. Heavy metals are known to cause detrimental health effects to human. Thus, a study concerning heavy metals contamination on tuber crops cultivated on ex-mining lands had been conducted.

Four major cultivation areas were selected for this study namely; Kg. Baharu Bikam, Tapah Road, Pekan Pasir and Kg. Baru Cold Stream. The farms in these areas were found to be the largest tuber crops production in southern Perak. In the cultivated areas, sampling sites were chosen where the tuber crops were ready for harvest. Each sampling site, 3 soil samples and tuber crops were sampled. The three soil samples from each point were combined to form a composite sample. The soils were collected by using a stainless steel auger. An hundred eighty soil samples were collected from the cultivated soils which is 60 soil samples for each 3 depths (0-20 cm, 20-40 cm and 40-60 cm). While only 60 soil samples were collected on topsoil (0-20 cm) from the uncultivated ex-mining lands. The uncultivated soils were collected for the determination of heavy metals and used as background values (control). An overall total of 240 soil samples were taken from the cultivated and uncultivated soils. The crops selected were tuber crops such as tapioca, yam bean, sweet potatoes and Chinese radish. For each sampling site, geographic coordinates were recorded using global positioning system (GPS). The soils were air-dried, crushed, sieved to pass 2 mm sieve and analysed for the texture, mineralogy, pH, total organic carbon (OC), cation exchangeable capacity (CEC), total heavy metals content (Pb, Ni, Zn, Cd and Cu) and available heavy metals extracted with three different extractants i.e. 0.1 N HCl, EDTA and DTPA. While heavy metals in tuber crops were extracted using dry-ashing method. The heavy metals (Pb, Ni, Zn, Cd and Cu) were determined by Atomic Absorption Spectrophotometer (AAS).

From this study, it was found that, the uncultivated soils in the study areas can be categorized according to their texture i.e sand, sandy clay loam and sandy loam. Sand texture consists of 89.5 to 91.5% sand and very low clay content (7-10%). Sandy clay loam texture consists of 15.5 to 18.4 % sand and very high in clay content which is 41.8 to 42 %. Sandy loam consists of 12 to 19.5 % clay, 70 to 75.5% of sand and 15.5 to 18 % of silt.

The pH of topsoils in the cultivated ex-mining soils of southern Perak had a mean value of 6.08. The mean cation exchange capacity of the cultivated ex-mining soils was 0.77 $cmol_c kg^{-1}$ soil. The soils have a mean organic carbon content of 0.66 %. On the other hand, soils in the uncultivated lands have pH, CEC, OC, with the values of 4.56, 0.35 $cmol_c kg^{-1}$ and 0.31 %, respectively. Generally, there is a significant increase at $p \leq 0.05$ of pH, OC and CEC in the cultivated soils.

Mean concentration of Zn in the cultivated soil was the highest followed by Pb, Cu, Ni and Cd, with values of 15.84 $mgkg^{-1}$, 10.43 $mgkg^{-1}$, 4.20 $mgkg^{-1}$, 3.07 $mgkg^{-1}$, and 0.84 $mgkg^{-1}$, respectively. In the uncultivated soil, a similar trend in heavy metal concentrations was observed for Zn, Pb, Cu, Ni and Cd with mean values of 8.09 $mgkg^{-1}$, 5.78 $mgkg^{-1}$, 1.19 $mgkg^{-1}$, 1.00 $mgkg^{-1}$ and 0.69 $mgkg^{-1}$, respectively. T-test analysis showed that metal concentrations in cultivated soils are significantly higher at $p \leq 0.05$ level than in uncultivated soil except for Cd. However, both levels are still below the critical heavy metal concentrations limits in agricultural soils of Peninsular Malaysia and the concentration ranges (using the 95^{th} percentile), except for Cd.

Total Pb and Cd concentration in soil were significantly positive correlated with available Pb using 0.1N HCl extractant (r = 0.41*, n= 60) available Cd using DTPA (r= 0.23*, n=60). On the other hand, total Ni in soil was significantly negative correlated with available Ni using DTPA (r=-0.38, n=60). Regardless of the extraction methods used (0.1N HCl, EDTA or DTPA), no significant correlation was found between total Cu and Zn in soil and available Cu and Zn. Correlation analysis between heavy metals in tuber crops with available heavy metals indicates that, there was no relationship between total heavy metals in the tuber crops and available heavy metals in soil using different extraction methods except for Zn and Cu, which have a negative correlation using 0.1 N HCl (r = -0.25*, n= 60) and DTPA (r=-0.22*, n=60), respectively.

Amongst all of the crops studied, Chinese radish, tapioca and sweet potato contains the highest concentration of 15.33 $mgkg^{-1}$ Zn, 0.85 $mgkg^{-1}$ Pb and 0.12 $mgkg^{-1}$ Cd, respectively. On the other hand, yam bean showed that the lowest concentration of Zn, Cd, Cu and Ni with values of 2.41 $mgkg^{-1}$, 0.07 $mgkg^{-1}$, 0.63 $mgkg^{-1}$ and 0.56 $mgkg^{-1}$, respectively.

Lead is significant higher at $p \leq 0.05$ in yam bean than in sweet potato and Chinese radish. There is no significant difference in the concentrations of Cd in all tuber crops studied. Copper show significant higher in tapioca than in sweet potato followed by Chinese radish and yam bean. Zinc concentration is significantly higher in Chinese radish than in tapioca, sweet potato and yam bean, while Ni is significantly higher in Chinese radish than in yam bean.

Results from this study show an increased concentration of heavy metals in Chinese radish followed by tapioca, sweet potato and yam bean, but the heavy metals levels of all the tuber crops studied were still below the Maximum Permissible Concentration (MPC) as stated in the Malaysia Food Act (1983) and Food Regulation (1985).

Spatial distribution map is useful to detect the spatial area, which are low, optimum or high in heavy metal concentration. Tapah Road areas have the highest concentration of heavy metals in all elements studied with Zn value of 17.41 $mgkg^{-1}$, followed by Pb, Cu, Ni and Cd. On the other hand, Kg. Baharu Bikam has the lowest concentration for all elements. Statistical analyses indicate that there is no significant difference at $p \leq 0.05$ of heavy metals content in soil among those areas.

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

PENILAIAN TERHADAP LOGAM BERAT DALAM TANAH DAN TANAMAN UMBISI DI TANAH BEKAS LOMBONG DI SELATAN PERAK, MALAYSIA

Oleh

KAMSHARY MENDER

Mac 2004

Pengerusi: Profesor Madya Siti Zauyah Bte Darus, Ph.D.

Fakulti: Pertanian

Kawasan tanah bekas lombong yang luas di Selatan Perak, Malaysia digunakan untuk tanaman sayur-sayuran, buah-buahan dan tanaman umbisi disebabkan kekurangan kawasan untuk pengeluaran pertanian. Kawasan ini telah digunakan untuk pertanian lebih daripada 20 tahun yang lalu. Kajian terbaru mendapati kawasan tanah bekas lombong untuk tanaman umbisi dan buah-buahan telah dicemari oleh logam berat. Kepekatan logam berat yang tinggi ini mungkin disebabkan oleh penggunaan baja organik (tahi ayam) yang berlebihan dan penggunaan bahan berasaskan kimia (baja, racun perosak). Terdapat kesedaran dikalangan pengguna dan mereka mengambil berat bahawa penggunaan baja dalam jangkamasa yang lama akan menyebabkan pengumpulan logam berat dalam tanah dan diserap oleh tanaman umbisi yang ditanam pada tanah bekas lombong. Logam berat dipercayai berupaya mendatangkan masalah kesihatan kepada manusia. Oleh itu, kajian tentang pencemaran logam berat ke atas tanah dan tanaman umbisi di kawasan tanah bekas lombong telah dijalankan.

Empat kawasan penanaman utama dipilih untuk kajian ini, iaitu Kg. Baharu Bikam, Tapah Road, Pekan Pasir dan Kg. Baru Cold Stream. Ladang-ladang ini telah dikenalpasti sebagai kawasan pengeluaran tanaman umbisi yang terbesar di kawasan selatan Perak. Di kawasan penanaman, tempat persampelan dipilih pada kawasan yang mempunyai tanaman umbisi yang sedia untuk dituai. Pada setiap kawasan persampelan, 3 sampel tanah dan umbisi diambil. Sampel tanah ini digabung untuk membentuk satu unit komposit. Sampel tanah diambil menggunakan auger (anti karat). Sebanyak 180 sampel tanah diambil pada tanah bertanaman (cultivated soil) iaitu 60 sampel untuk setiap 3 kedalaman (0-20 cm, 20-40 cm dan 40-60 cm). Manakala hanya 60 sampel tanah tanpa tanamam (uncultivated soil) pada tanah bahagian atas sahaja (0-20 cm) diambil. Tanah tanpa tanaman disampel untuk mengesan kandungan logam berat dan digunakan sebagai perbandingan (kawalan). Secara keseluruhan sejumlah 240 sampel tanah telah disampel pada kawasan tanah bertanaman dan tanpa tanaman. Tanaman umbisi yang dipilih ialah ubi kayu, sengkuang, keledek dan lobak putih. Pada setiap titik persampelan, koordinat kedudukan diambil menggunakan sistem penentu lokasi (GPS). Sampel tanah dikering udara, dikisar dan diayak menggunakan pengayak bersaiz 2 mm dan dianalisis untuk tekstur, mineralogi, pH, jumlah karbon organik, keupayaan pertukaran kation, jumlah kandungan logam berat (Pb, Ni, Zn, Cd dan Cu) dan logam berat tersedia yang menggunakan tiga bahan pengekstrak yang berbeza iaitu 0.1 N HCl, EDTA dan DTPA. Manakala logam berat dalam tanaman umbisi pula diekstrak menggunakan kaedah pengabuan kering. Bagi setiap logam berat (Pb, Ni, Zn, Cd and Cu) yang telah diekstrak, ia dibaca menggunakan Spektrofotometer Penyerapan Atom.

Daripada kajian ini, didapati bahawa, kawasan bekas lombong terbiar boleh dibahagikan kepada kategori berdasarkan tekstur iaitu berpasir, lom lempung berpasir dan pasir berlom. Tekstur berpasir mempunyai peratusan sebanyak 89.5 sehingga 91.5 % pasir dan mempunyai kandungan lempung yang sangat sedikit (7-10 %). Tekstur lom lempung berpasir mengandungi 15.5 hingga 18.4 % pasir dan sangat tinggi kandungan lempung iaitu 41.8 hingga 42 %. Lom berpasir pula mengandungi 12 hingga 19.5 % lempung, 70 ke 75.5 % pasir dan 15.5 hingga 18% kelodak.

Purata pH tanah bahagian atas pada tanah bertanaman ialah 6.08. Nilai purata KPK ialah 0.77 $cmol_ckg^{-1}$ dan purata karbon organik pula ialah 0.66 %. Sebaliknya bagi tanah tanpa tanaman pula, purata pH, KPK dan karbon organik masing-masing ialah 4.56, 0.35 $cmol_ckg^{-1}$ dan 0.31 %. Secara amnya, terdapat peningkatan pada $p \leq 0.05$ pada tanah bertanaman bagi pH, karbon organik dan KPK.

Purata kepekatan Zn pada tanah bertanaman adalah yang tertinggi diikuti oleh Pb, Cu, Ni and Cd dengan nilai masing-masing 15.84 $mgkg^{-1}$, 10.43 $mgkg^{-1}$, 4.20 $mgkg^{-1}$, 3.07 $mgkg^{-1}$ dan 0.84 $mgkg^{-1}$. Pada tanah tanpa tanaman pula, corak yang sama juga didapati pada kepekatan logam beratnya iaitu Zn, Pb, Cu, Ni dan Cd dengan nilai purata masing-masing 8.09 $mgkg^{-1}$, 5.78 $mgkg^{-1}$, 1.19 $mgkg^{-1}$, 1.00 $mgkg^{-1}$ dan 0.69 $mgkg^{-1}$. Melalui analisis ujian-T, menunjukkan kepekatan logam pada tanah bertanaman lebih tinggi pada paras $p \leq 0.05$ untuk semua elemen berbanding dengan tanah tanpa tanaman, kecuali Cd. Walaubagaimanapun, didapati kedua-dua tanah masih berada dibawah paras kritikal yang dibenarkan kecuali Cd, dengan kepekatan bagi tanah pertanian di semenanjung Malaysia dan julat kepekatan peratusan ke-95.

Jumlah kepekatan Pb dan Cd dalam tanah mempunyai hubungan korelasi bererti yang positif dengan Pb dan Cd yang tersedia dengan menggunakan bahan pengekstrak masing-masing 0.1 N HCl (r=0.41*, bil=60) dan DTPA (r=0.23*, bil=60). Sebaliknya, kepekatan Ni dalam tanah mempunyai hubungan korelasi yang Negatif dengan Ni yang tersedia dengan menggunakan DTPA (r=-0.38*, bil=60). Merujuk pada bahan pengekstrak (0.1N HCl, EDTA or DTPA), tidak terdapat korelasi bererti diantara jumlah Cu dan Zn dalam tanah dengan Cu dan Cd yang tersedia. Analisis korelasi diantara logam berat dalam tanaman umbisi dengan logam berat dalam tanah, menunjukkan bahawa tiada perhubungan diantara jumlah logam berat dalam tanah dengan kandungan logam berat pada tanaman umbisi kecuali Zn dan Cu, di mana ia mempunyai hubungan korelasi negatif dengan menggunakan bahan pengekstrak masing-masing 0.1N HCl (r=-0.25*,n=60) dan DTPA (r=-0.22*, n=60).

Di antara tanaman yang dikaji, didapati lobak putih, ubi kayu dan keledek mempunyai kepekatan yang tinggi masing-masing bagi 15.33 $mgkg^{-1}$ Zn, 0.85 $mgkg^{-1}$ Pb dan 0.12 $mgkg^{-1}$ Cd. Sebaliknya, sengkuang menunjukkan kepekatan yag paling rendah untuk Zn, Cd, Cu dan Ni dengan nilai masing-masing 2.41 $mgkg^{-1}$, 0.07 $mgkg^{-1}$, 0.63 $mgkg^{-1}$ and 0.56 $mgkg^{-1}$.

Kepekatan Plumbum lebih tinggi pada $p \leq 0.05$ dalam sengkuang berbanding keledek dan lobak putih. Bagi kepekatan Cd pula, tidak terdapat perbezaan bererti di antara kesemua umbisi yang dikaji. Kuprum menunjukkan lebih tinggi pada ubikayu berbanding dengan keledek dengan diikuti oleh lobak putih dan sengkuang. Bagi kepekatan Zn pula, lebih tinggi bagi lobak putih berbanding ubikayu, keledek dan sengkuang. Sementara itu, kepekatan Ni lebih tinggi pada lobak putih berbanding dengan sengkuang.

Keputusan daripada kajian ini menunjukkan terdapat peningkatan kepekatan logam berat dalam lobak putih diikuti dengan ubi kayu, keledek dan sengkuang, namum kesemua tanaman ini adalah masih berada di bawah paras kepekatan penyerapan maksima yang diperuntukkan oleh Akta Makanan (1983) dan Peraturan Makanan (1985).

Peta taburan logam berat, adalah berguna untuk mengesan kawasan mengikut ruang samada mengandungi kepekatan logam berat yang rendah, optima ataupun tinggi. Kawasan Tapah Road mempunyai kepekatan logam berat yang tertinggi dalam semua elemen yang dikaji dengan nilai Zn iaitu 17.41 $mgkg^{-1}$, dengan diikuti oleh Pb, Cu, Ni dan Cd. Sebaliknya, Kg. Baharu Bikam mempunyai kepekatan yang terendah bagi kesemua elemen. Analisis statistik menunjukkan tidak terdapat perbezaan bererti pada $p \leq 0.05$ dalam kandungan logam berat pada tanah diantara kawasan tersebut.

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I certify that an Examination Committee met on 4th March 2004 to conduct the final examination of Kamshary Mender on his Master of Science thesis entitled "Assessment of Heavy Metals in Soils and Tuber Crops on Ex-mining Land of Southern Perak, Malaysia" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulation 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 fulfillment of the requirement for the degree of Master of Science. The members of the Supervisory committee are as follows:

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Date: 15 SEP 2004

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.

KAMSHARY MENDER

Date: 13 . 06 . 2004

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LIST OF ABBREVIATIONS

AAS	- Atomic Absorption Spectrophotometer
ANOVA	- Analysis of variance
CEC	- cation exchange capacity (usually measured in meq/100g of dry soil ; SI equivalent= $cmol_c kg^{-1}$)
DOA	- Department of Agriculture
DOE	- Department of Environment
DTPA	- Diethhylene diamine tetracetic acid
EDTA	- Ethylene diamine tetra acetic acid
EPA	- Environment Pollution Act
GIS	- Geographical Information System
GPS	- Global Positioning System
GS+	- Computer software for geostatistical analysis
LSD	- Least Significant Different
MOA	- Ministry of Agriculture
MOP	- Muriate of Potash
MPC	- Maximum Permitted Concentration
NAP	- National Agriculture Policy
NH_4OAc	- Ammonium acetate
NPK	- Nitrogen/Phosphorus/Potassium
OC	- Organic Carbon
POME	- Palm Oil Mill Effluent
PTEs	-Potential Toxic Elements
RM	- Malaysian Ringgit
SAS	- Statistical Analysis System
TSP	- Triple Super Phosphate