



**UNIVERSITI PUTRA MALAYSIA**

***COPPER STATUS IN TROPICAL SOILS AND CRITICAL LEVELS  
FOR BRASSICA RAPA L. VAR. PARACHINENSIS***

**NURUL WAHIDA BINTI HANI**

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*BRASSICA RAPA L. VAR. PARACHINENSIS***

**By**

**NURUL WAHIDA BINTI HANI**

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

**January 2014**

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## DEDICATION

*For my beloved grandmother, Haminah Kadir*

*And*

*The late Assoc. Prof. Dr. Anuar Abd Rahim*

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

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**Chair: Anuar Abd Rahim, PhD**

Copper is one of the essential micronutrients required in small amounts however it will impair plant growth and cause toxicity when present in high concentrations. The use of agrochemicals in intensive agricultural land causes Cu build up in the soils. The availability of Cu to plants depends on its mobility which partly controlled by its association with soil constituents. The goals of this study were to assess the Cu concentration and phase associations in intensive vegetable farms; to evaluate Cu sorption-desorption in Oxisol, Inceptisol and Histosol; to evaluate *Brassica rapa* response to increasing soil Cu concentration and phase associations in the mineral soils.

Soil sampling took place in selected conventional and organic farms in Cameron Highlands, Pahang while one organic farm was chosen in Bangi, Selangor. Copper phase associations were analyzed using Cu sequential extraction (Salas *et al.*, 1998) while soil pH, CEC, total carbon and free Fe, Al and Mn oxides were determined too. Assessment of soils in vegetable farms showed that soil Cu content in conventional (33.61 mg Cu kg<sup>-1</sup>) and organic (11.91 mg Cu kg<sup>-1</sup>) vegetable farms in the highland contained higher Cu than the forest soil (2.72 mg Cu kg<sup>-1</sup>). There was no significant

difference in Cu content between soil of organic farms of highland (11.91 mg kg<sup>-1</sup>) and lowland (12.79 mg kg<sup>-1</sup>). This study found that the increase in Cu content was associated with higher pH, CEC and total carbon. Organic matter was found to be the main component that controls the fate of Cu in the cultivated soil under study. Longer operation farm period, routine application of fungicides and chicken manure leads to higher Cu concentration in conventional farm.

The Cu sorption isotherm was carried out in a batch experiment where 1:10 ratio of soil to solution equilibrated with 0.01M CaCl<sub>2</sub> solution containing 5, 10, 15, 20, 30, 60 and 100 mg L<sup>-1</sup> Cu as CuCl<sub>2</sub>, followed by desorption of Cu. Uncultivated soils from Oxisol (Munchong Series), Inceptisol (Selangor Series) and Histosol (peat) were used in this study. Results showed that Histosol had the highest sorption capacity followed by Oxisol and Inceptisol. The Freundlich model was found to be better in describing the sorption isotherms of Oxisol (74.82 L kg<sup>-1</sup>, R<sup>2</sup>=0.99) and Histosol (688.65 L kg<sup>-1</sup>, R<sup>2</sup>=0.99). Copper sorption in Inceptisol was well described (R<sup>2</sup>=0.98) by the Langmuir model which provides the maximum adsorption value of 384.62 mg kg<sup>-1</sup>. Histosol had the least tendency to desorb Cu followed by Oxisol and Inceptisol at 100 µg mL<sup>-1</sup> Cu loading. The sorption-desorption capacity is influenced by the CEC, organic matter content, Fe and Al oxides and clays.

A factorial pot experiment was carried out to determine the Cu critical and toxicity threshold levels for *Brassica rapa* in Oxisol, Inceptisol and Histosol. Copper sulphate solution was applied at the rates of 0, 5, 10, 15, 20, 30 and 60 mg Cu kg<sup>-1</sup> soil. The yield response of plant on Oxisol, Inceptisol and Histosol are expressed in quadratic equations of  $y^{-1} = 1.422 \pm 0.244x + 0.014x^2$ ,  $y^{-1} = 0.626 \pm 0.084x + 0.005x^2$  and  $y = 1.678 + 0.198x - 0.007x^2$ , respectively. The soil Cu critical level in Oxisol, Inceptisol and Histosol is 7.34, 5.96 and 7.40 mg kg<sup>-1</sup>, respectively; and threshold toxicity level is 10.63, 10.92 and 21.64 mg kg<sup>-1</sup>, respectively. Both Cu levels are in consistence with the soils desorption capacity and the concentration of Cu mobile fraction as defined as summation of water soluble and exchangeable fractions. Height of plants and the SPAD value of leaves decreased with increasing Cu concentration. Copper phase associations in Oxisol and Inceptisol were determined using sequential extraction method. Both soils were found to have the same order of Cu fractions of organic > residual > Fe/Mn oxides > carbonates > exchangeable > water soluble.

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

**STATUS KUPRUM DALAM TANAH TROPIKA DAN PARAS KRITIKAL  
UNTUK *BRASSICA RAPA* L. VAR. *PARACHINENSIS***

Oleh

**NURUL WAHIDA BINTI HANI**

**Januari 2014**

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Kuprum (Cu) ialah salah satu mikronutrien penting yang diperlukan dalam kuantiti yang kecil. Tetapi ia boleh menjejaskan pertumbuhan tanaman dan menyebabkan ketoksikan dalam kuantiti tinggi. Penggunaan bahan kimia secara intensif dalam penanaman menyebabkan peningkatan konsentrasi Cu di dalam tanah. Ketersediaan Cu untuk tanaman bergantung kepada mobiliti yang dipengaruhi oleh ikatannya bersama komponen tanah. Objektif kajian ini ialah menilai kandungan dan sebaran Cu dalam tanah di kebun sayur  $\pm$  sayuran; menilai keupayaan erapan-penyaherapan Cu dalam Oxisol, Inceptisol dan Histosol; menilai tindak balas *Brassica rapa* ke atas peningkatan konsentrasi Cu dan pecahan Cu dalam tanah mineral.

Pensampelan tanah dilakukan di sebuah kebun sayur konvensional dan organik di Cameron Highlands, Pahang manakala di Bangi, Selangor sebuah kebun sayur organik dipilih untuk penilaian kandungan Cu dalam tanah. Analisis fasa pecahan Cu dilakukan melalui kaedah pengekstrakan bersiri (Salas *et al.*, 1998). Selain itu, analisis pH tanah, keupayaan penukaran kation, jumlah karbon dan oksida Fe, Al dan Mn juga dijalankan. Kandungan Cu di dalam tanah kebun sayur konvensional (33.61 mg kg<sup>-1</sup>) dan organik (11.91 mg kg<sup>-1</sup>) di kawasan tanah tinggi adalah lebih tinggi



daripada tanah hutan. Kandungan Cu di dalam tanah kebun sayur organik di kawasan tanah tinggi ( $11.91 \text{ mg kg}^{-1}$ ) tiada perbezaan ketara dengan tanah kebun sayur organik di kawasan tanah pamah ( $12.79 \text{ mg kg}^{-1}$ ).

Pemerhatian menunjukkan peningkatan konsentrasi kuprum ada perkaitan dengan peningkatan pH tanah, keupayaan penukaran kation dan jumlah karbon. Kajian ini mendapati bahan organik merupakan komponen utama dalam pecahan Cu dalam tanah kebun sayur - sayuran. Kandungan Cu dalam tanah kebun sayur konvensional adalah disebabkan oleh tempoh operasi kebun yang lebih panjang yang disertakan dengan penggunaan racun kulat dan aplikasi baja tahi ayam secara rutin.

Isoterma erapan Cu dijalankan melalui kaedah eksperimen bersiri di mana nisbah 1:10 tanah kepada larutan yang diseimbangkan dengan  $0.01\text{M CaCl}_2$  mengandungi 5, 10, 15, 20, 30, 60 dan  $100 \text{ mg L}^{-1}$  Cu dalam  $\text{CuCl}_2$ , kemudian diikuti dengan isoterma penyahherapan. Tanah Oxisol (Siri Munchong), Inceptisol (Siri Selangor) dan Histosol (gambut) digunakan dalam eksperimen ini. Keputusan eksperimen keupayaan erapan-penyahherapan Cu di dalam Oxisol, Inceptisol dan Histosol menunjukkan Histosol mempunyai kadar erapan paling tinggi diikuti dengan Oxisol dan Inceptisol. Model Freundlich didapati lebih tepat dalam menunjukkan sifat erapan isoterma Oxisol ( $74.82 \text{ L kg}^{-1}$ ,  $R^2=0.99$ ) dan Histosol ( $688.65 \text{ L kg}^{-1}$ ,  $R^2=0.99$ ) manakala model Langmuir pula didapati lebih bersesuaian dengan sifat erapan Inceptisol, yang menganggarkan maksimum erapan sebanyak  $384.62 \text{ mg kg}^{-1}$ . Pada konsentrasi  $100 \text{ mg L}^{-1}$ , Histosol menyahherap Cu paling rendah, diikuti dengan Oxisol dan Inceptisol.

Keupayaan erapan-penyaherapan dipengaruhi oleh keupayaan penukaran kation, bahan organik, Fe dan Al oksida serta lempung.

Sebuah faktorial eksperimen telah dijalankan untuk menentukan paras kritikal dan ketoksidan ambang Cu untuk Brassica rapa yang ditanam dalam Oxisol, Inceptisol dan Histosol. Larutan kuprum sulfat dicampurkan dengan tanah pada kadar 0, 5, 10, 15, 20, 30 dan 60 mg Cu kg<sup>-1</sup> tanah. Respon hasil tanaman Oxisol, Inceptisol dan Histosol adalah kuadratik;  $y^{-1}=1.422 \pm 0.244x+0.014x^2$ ,  $y^{-1} = 0.626 \pm 0.084x+ 0.005x^2$  and  $y = 1.678+0.198x \pm 0.007x^2$ , bagi setiap order tanah. Paras kritikal Cu dalam tanah untuk Oxisol, Inceptisol and Histosol masing-masing ialah 7.34, 5.96 dan 7.40 mg kg<sup>-1</sup> ; manakala tahap ketoksidan ambang ialah 10.63, 10.92 and 21.64 mg kg<sup>-1</sup>, bagi setiap order tanah. Kedua  $\pm$  dua tahap Cu adalah konsisten dengan keupayaan penyaherapan dan kepekatan pecahan mobil Cu. Ketinggian pokok dan nilai SPAD daun menurun dengan peningkatan kepekatan Cu. Pecahan Cu di dalam Oxisol dan Inceptisol ditentukan melalui pengekstrakan bersiri. Kedua  $\pm$  dua tanah didapati mempunyai pecahan Cu mengikut turutan yang sama iaitu organik > sisa baki > Fe/Mn oksida > karbonat > pertukaran > larut air.

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I certify that a Thesis Examination Committee has met on 3 January 2014 to conduct the final examination of Nurul Wahida binti Hani on her thesis entitled "Copper Status in Tropical Soils and Critical Levels for *Brassica rapa* L. var. *parachinensis*" 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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## DECLARATION

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## LIST OF ABBREVIATIONS

ANOVA	Analysis of Variance
CEC	Cation Exchange Capacity
CRD	Complete Randomized Design
EDTA	Ethylene-diamine-tetra-acetic acid
GML	Ground Magnesium Limestone
RCBD	Randomized Complete Block Design
SEP	Sequential Extraction Procedure
SNK	Students-Newman-Keuls

# CHAPTER 1

## INTRODUCTION

After World War II, the use of chemical fertilizers has increased worldwide. Ammonia-based fertilizers were new to the old-time farmers which was one of the drivers of the process of development in agriculture. Back then, farmers and scientists were told by the modern science that growing plants need at least 17 nutrients important to crops. They are nitrogen, phosphorus, potassium, calcium, magnesium and sulfur (macronutrients) and chlorine, boron, iron, manganese, zinc, copper and molybdenum (micronutrients).

One of the essential micronutrients needed by plants is copper (Cu). Copper plays a vital role in a large number of enzymes that are involved in cell metabolism. Thus, it is important for plant growth and development. Nevertheless, it is toxic to plants and soil biota when present in excess. The obvious visual symptoms of Cu toxicity are chlorosis followed by necrosis. The sources of Cu introduced to the cultivation area are such as chemical and organic fertilizers, sewage sludge and fungicides.

In 2009, the total vegetable area in Malaysia were 41, 078 ha with 623, 457 tonnes production. The area increased in 2010 to 52, 793 ha and total production of 870, 251 tonnes vegetables (Statistik Tanaman, 2012). In the near future, there will be limited land for agricultural use due to increasing urbanization, commercial plantations and others. Indirectly, this will have implications on soil sustainability. More application of fertilizers, pesticides and other anthropogenic input will be used to grow large scale of crops in order to meet demand. These practices are common soils of where vegetables are grown intensively. Heavy use of these materials with time, would lead to depletion in soil quality, groundwater contamination and direct exposure to human health.

Copper is widely known for its specific adsorption with soil constituents. It is very tightly held with both inorganic and organic exchange sites. The processes that control its association with soil constituents are such as adsorption, occlusion and co-precipitation, organic chelation and complexation and microbial fixation. Therefore, Cu distribution varies with soils in accordance with the type and amount of each soil components present. Copper association with the soil components has direct influence on the equilibrium concentration between soils solid and liquid phases. In other words, Cu availability and toxicity to plants is controlled by sorption-desorption mechanisms.

Large application of anthropogenic sources elevate Cu concentration in soil with time. Hence, it is important to assess the Cu content in soils under intensified vegetable cultivation in order to know the degree of Cu contamination and Cu phase association. Different sorption-desorption capacity of Cu and its versatility to bind onto various

soil constituents gives impact on Cu forms, plant availability and toxicity especially on tropical soils of varying physico-chemical properties. Therefore, it is interesting and a good concern to study Cu behaviour in term of its sorption-desorption capacity, phase association in soil and its toxicity to plant grown on selected tropical soils. This will provide information of concentration of Cu available for plant with respect to type of soil system under study. Besides that, one is able to estimate required rates of Cu fertilizer to avoid the wastage of resources and avoid soil, plant and water contamination.

The specific objectives of this study were to:

1. evaluate and compare Cu status and phase associations in soil of highland and lowland vegetable farms
2. evaluate sorption and desorption behaviour of Cu in Oxisol, Inceptisol and Histisol
3. evaluate *Brassica rapa* growth response and to determine the Cu critical, threshold toxic level of soil in Cu amended Oxisol, Inceptisol and Histisol; and to evaluate the Cu phase associations in Oxisol and Inceptisol.



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