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ADSORPTION–DESORPTION AND BIOAVAILABILITY OF SELECTED MICRONUTRIENTS IN TROPICAL PEAT SOIL IN SARAWAK, MALAYSIA

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By

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Tropical peatland has a distinctive bio-sequence of concentric forest zones with different forest types. Mature peat swamps in Sarawak comprised of mixed peat swamp forest (MPS), Alan Batu forest (A.Bt), and Alan Bunga forest (A.Bg). These forest types may differ in their decomposition of soil organic matter (SOM) contents, thus affect the availability of micronutrients, since peat soils are generally oligotrophic. This study investigated the availability of copper (Cu), zinc (Zn) and boron (B) to the plants under different forest types. The adsorption and desorption batch experiment were performed using soil samples collected from MPS, A.Bt and A. Bg forests. Further relationship between adsorption and desorption with Cu, Zn and B availability in highly decomposed peat soil type (MPS) were examined in a polybag experiment using Napier grass (*Pennisetum purpureum*) as the test crop. The adsorption data of Cu were fitted better on the Langmuir's model while Zn adsorption data were comparable between the model used and B adsorption data was fitted better in the Freundlich's model. Generally, the K_f and b values were observed in order of Cu > Zn > B. This shows that Cu has a high affinity towards the peat soils surface compare to Zn and B. The MPS forest soils were observed to have slightly high adsorption capacity for Cu, Zn and B. This could emphasize that more decomposed peat materials would influence the affinity of Cu, Zn and B towards peat soil surface. Release of Cu, Zn and B was evaluated with different extractants to determine the available, exchangeable and complex form of micronutrients. The complex form of Cu and Zn is significantly different for MPS soil compare to exchangeable and available form. Copper and Zn were observed to highly bind to the surface of peat soils and the stronger chelating agent needed to desorb them into the soil solution. Release of B has shown no significant differences among extractants used, since B has low affinity towards the soil surface and easily leach out from the soil system. The application of Cu, Zn and B solution with different concentration (0, 1, 3, 5, 10, 20, 30 mg L^{-1}) to the Napier grass planted in peat soils showed that mean dry matter yield has no significant difference among the treatment. The polynomial plot showed the optimum uptake of Cu and Zn (in

range of 10 – 20 mg L^{-1}) and B (up to 5 mg L^{-1}). The mean uptake of Zn (0.52 mg $plant^{-1}$) was higher than Cu (0.11 mg $plant^{-1}$) and B (0.064 mg $plant^{-1}$) because Cu has a high affinity towards the soil surface, while B easily leaches out to the soil solution system. Therefore, considering 4R (right source, right rate, right time and right place) nutrient stewardship is important to the improved nutrient use efficiency of the plant.

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

PENJERAPAN-PENYAHJERAPAN DAN KETERBIOSEDIAAN MIKRO NUTRISI TERPILIH DALAM TANAH GAMBUT TROPIKA DI SARAWAK, MALAYSIA

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Tanah gambut tropika mempunyai rangkaian urutan-bio hutan berpusat yang tersendiri dengan jenis hutan yang berlainan. Tanah gambut berpaya yang matang di Sarawak terdiri daripada hutan gambut campuran (MPS), hutan Alan Batu (A.Bt) dan hutan Alan Bunga (A.Bg). Jenis-jenis hutan ini mempunyai perbezaan tahap penguraian dalam kandungan bahan organik tanah, lalu mempengaruhi keterbiosediaan mikro nutrisi memandangkan tanah gambut kebiasaannya oligotropik (nutrisi yang rendah). Penyelidikan ini mengkaji keterbiosediaan unsur Kuprum (Cu), Zink (Zn) dan Boron (B) terhadap tumbuh-tumbuhan di bawah jenis hutan yang berlainan. Eksperimen penjerapan dan penyahjerapan telah dilakukan menggunakan sampel tanah yang diambil dari hutan MPS, A.Bt dan A.Bg. Hubungan proses penjerapan dan penyahjerapan dengan keterbiosediaan unsur Cu, Zn dan B dalam tanah gambut yang mempunyai kadar penguraian tertinggi iaitu tanah MPS ditentukan dengan penanaman *Napier grass* (*Pennisetum purpureum*) sebagai tumbuhan ujian. Data penjerapan untuk Cu lebih sesuai dalam model Langmuir manakala data penjerapan Zn sebanding di antara model yang digunakan dan data penjerapan B lebih sesuai dalam model Freundlich. Secara umum, nilai K_f dan *b* dilihat dalam urutan Cu > Zn > B. Ini menunjukkan Cu mempunyai pertalian yang tinggi terhadap permukaan tanah berbanding dengan Zn dan B. Tanah hutan MPS dilihat mempunyai kapasiti penjerapan yang agak tinggi untuk Cu, Zn dan B. Ini boleh ditekankan bahawa bahan gambut yang lebih terurai akan mempengaruhi pertalian Cu, Zn dan B terhadap permukaan tanah gambut. Pelepasan unsur Cu, Zn dan B telah diuji dengan larutan ekstrak yang berlainan untuk menentukan mikro nutrisi dalam bentuk ketersediaan, kebolehtukaran dan kompleks. Bentuk kompleks Cu dan Zn mempunyai perbezaan ketara dalam tanah MPS berbanding dengan bentuk kebolehtukaran dan ketersediaan. Kuprum (Cu) dan Zn telah diperhatikan mempunyai ikatan yang kuat terhadap permukaan tanah gambut dan memerlukan ejen pengikat yang kuat untuk dilepaskan dari permukaan tanah

ke dalam larutan tanah. Pelepasan unsur B telah menunjukkan tiada perbezaan ketara di antara larutan ekstrak yang digunakan memandangkan ikatan terhadap permukan tanah sangat lemah dan mudah larut ke dalam larutan tanah. Purata jirim kering *Napier grass* menunjukkan tiada perbezaan ketara antara rawatan unsur Cu, Zn dan B (0, 1, 3, 5, 10, 20, 30 mg L^{-1}) yang ditambah ke dalam tanah gambut dalam penanaman *Napier grass*. Plot polynomial menujukkan pengambilan optimum untuk Cu dan Zn dalam 10 – 20 mg L^{-1} dan B sampai 5 mg L^{-1}. Purata pengambilan Zn (0.52 mg $plant^{-1}$) adalah tertinggi berbanding Cu (0.11 mg $plant^{-1}$) dan B (0.064 mg $plant^{-1}$) kerana Cu mempunyai ikatan yang tinggi terhadap permukaan tanah, manakala B mudah larut ke dalam system larutan tanah. Oleh itu, mengambilkira pengawasan prinsip 4R (Kesesuaian punca, kadar, masa dan tempat) sangat penting untuk meningkatkan keberkesanan penggunaan nutrisi oleh tumbuhan.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

A.Bg	Alan Bunga
A.Bt	Alan Batu
ANOVA	Analysis of Variance
Al	Aluminium
B	Boron
BS	Base Saturation
$B(OH)_4^-$	Tetrahydroborate
C	Carbon
Ca	Calcium
$CaCl_2$	Calcium Chloride
$CaCO_3$	Calcium Carbonate
CEC	Cation Exchange Capacity
CH_3COONH_4	Ammonium Acetate
cm	centimeter
cmol	centimole
CRD	Complete Randomized Design
Cu	Copper
CuCl	Copper Chloride
CuOH	Copper Hydroxide
$CuSO_4.5H_2O$	Copper (II) Sulfate Pentahydrate
DF	Dilution Factor
DM	Dry matter
DNA	Deoxyribonucleic
DOC	Dissolve Organic Carbon

DTPA	Diethylenetriaminepentaacetic acid
ET/P	Evapotranspiration/Precipitation
EDTA	Ethylenediaminetetraacetic acid
Fe	Iron
H	Hydrogen
HCl	Hydrochloric Acid
HNO_3	Nitric Acid
HSD	Honestly Significant Difference
HWOM	Hot-Water Extractable Organic Matter
H1 – H10	Humification Level
$H_3BO_3^-$	Boric Acid
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectrometry
K	Potassium
KCl	Potassium Chloride
K_2SO_4	Potassium Sulphate
kg	Kilogram
LOI	Loss on Ignition
m	meter
MARDI	Malaysian Agricultural and Development Institute
Mg	Magnesium
mg kg^{-1}	Miligram per kilogram
mg L^{-1}	Miligram per liter
Mha	Million hectares
Mn	Manganese
Mo	Molybdenum

MPS	Mixed Peat Swamp
N	Nitrogen
NaOH	Sodium Hydroxide
$Na_4P_2O_7.10H_2O$	Tetrasodium Pyrophosphate Decahydrate
O	Oxygen
OH^-	Hydroxide ion
P	Phosphorus
PC	Phasic community
ppm	Part per million
PSI	Pyrophosphate Solubility Index
RNA	Ribonucleic Acid
S	Sulphur
SAS	Statistical Analysis System
SOM	Soil organic matter
TOC	Total Organic Carbon
Zn	Zinc
ZnS	Zinc Sulfide
$ZnSO_4.7H_2O$	Zinc Sulphate Heptahydrate

CHAPTER 1

INTRODUCTION

1.1 Context

Elements and chemical compounds required for plant growth and metabolism comprise both macro and micronutrients. The important micronutrients for plant growth are copper (Cu), zinc (Zn), manganese (Mn), iron (Fe), molybdenum (Mo) and boron (B). They are needed in much smaller amounts than the macronutrient elements, nitrogen (N), phosphorus (P), sulphur (S), potassium (K), calcium (Ca) and magnesium (Mg) (Krauskopf, 1972; Fageria et al., 2002). Even though plant tissues contain less micronutrients than macronutrients, their influence are crucial within the vegetation cycle as they are directly engaged in metabolism (Fageria et al., 2002) and growth factors of plant (Rydin and Jeglum, 2006). Other functions of micronutrients are as parts of prosthetic groups fractions in metalloproteins and act as a catalyst in enzyme reactions. The plant enzyme systems would merely be an inert mass of protein without micronutrients (Gupta et al., 2008).

In recent years the prevalence of micronutrient deficiencies in crops has increased notably due to loss through leaching and top soil loss by erosion, the over-liming practice of acid soils, dependency on chemical fertilizers instead of farmyard manure application, intensive farming in order to increase yields per unit area to increase food production (Baligar et al., 2001) and the use of marginal lands that contain low levels of essential nutrients for production of crop (Fageria et al., 2002). One of the soils that have marginal agriculture capabilities in their natural state is tropical peat soil (Mutalib et al., 1991).

In Malaysia, tropical peat soils occupy about 8% (2.7 Mha) of the country's total land area with 1.7 Mha in Sarawak (13% of the state's land area (Mutalib et al., 1991; Abat et al., 2012). Approximately 1.5 Mha (89%) of Sarawak's peatswamp are classified as deep (>1.5 m) and usually ombrogenous peat. Ombrogenous peat develops a convex or biconvex morphology and therefore receives water and nutrient input solely through precipitation (Phillips, 1998) which lead to the nutrient deficiencies. Rydin and Jeglum (2006) state that nutrient deficiencies are typical on peatlands and the productivity of trees may be limited by lack of N, P or K, individually or in some combination. Deficiencies of other major nutrients, e.g. Mg, and micronutrients such as Cu, Zn, Fe, Mn, B, and Mo can develop on peat soils. The lack of these micronutrients may become nutritional limiting factors for crop production particularly in most tropical deep peat soils with woody layers (Ambak et al., 1991). However, the expansion of agriculture development by utilizing peat soil area was inevitable due to a shortage of good agriculture land, especially in the state of Sarawak where the largest area of peat soils located.

In their natural condition, lowland peat swamps in Sarawak locally known as peatswamp forest was subdivided into six 'phasic communities' (PC) on the basis of floristic composition and forest structure, which varies from the outer edges of the peat dome to its centre (Anderson, 1961; Tie and Esterle, 1991). According to Anderson (1961) ecological survey works, PC1 forest type located at the edge of the peat dome and known as Mixed Peat Swamp forest (MPS). PC2 (Alan Batu forest), PC3 (Alan Bunga forest), PC4 (Padang Alan forest), PC5 (Padang Selunsor) and PC6 (Padang Keruntum) were located successively towards the centre of peat dome. The PC1 (MPS) has the most decomposed peat profile and generally more fertile than the other phasic communities which leads to the richer in species composition (Melling, 2016). As the degree of peat decomposition differs from the edge to the centre of the peat dome, so the soil organic matter (SOM) quality also differs. The quality of SOM in term of different decomposition stages is one of the factors affecting micronutrients availability for plant uptake (Mortvedt, 2000). Johnson (1995) states that the decomposition level of organic matter exerts a significant control over nutrient availability and productivity in forest ecosystems. Therefore, interaction and mobility of micronutrients particularly Cu, Zn and B in peat soils with different phasic communities as they have a different SOM quality need to be investigated in order to recognize their availability for plant uptake.

1.2 Justification

Sarawak's tropical peatland is a potential land resource for crop production for the continuous supply of food, even though its SOM quality varies across the peat dome (Miyamoto et al., 2013). Peat soils have been regarded as problematic and unsuitable for cultivation due to various problems including low pH and low nutrient content in their natural condition or undisturbed forest condition (Abat et al., 2012) and issues regarding fertilizer application (amounts, timing, interaction and efficiency), irreversible drying out, root anchorage in the case of top-heavy perennial crops and micronutrient deficiencies (Andriesse, 1991).

The most critical micronutrients deficiencies are Cu, Zn and B (Ambak et al., 1991; Yonebayashi et al., 1994; Abat et al., 2012). A study done by Abat et al. (2012) on the differentiation of peat soil type has shown that the adsorption capacity of both Cu and Zn were increased with increasing of pH after the addition of calcium carbonate ($CaCO_3$) as a liming material. The discussion on her study was emphasized more on the difference of pH that influencing the adsorption capacity of Cu and Zn. The result also showed that a significant proportions of the adsorbed Cu and Zn could not be readily desorbed back into solution. It was indicated by extracting adsorbed Cu and Zn with a strong chelating agent such as diethylenetriaminepentaacetic acid (DTPA). Melo et al. (2014) also conducted the adsorption-desorption experiment using tropical peat soil collected from Sergipe State, Brazil and manipulated the soil pH and multi-elements as the factors in the differentiation of adsorption-desorption capacity of six micronutrients, namely Cu, Fe, Co, Ni, Zn and Mn. To date, not many studies have been conducted regarding the reaction of micronutrients particularly Cu, Zn and B with different quality of SOM on tropical peat soil. Furthermore, the fraction of readily available, exchangeable and the complex form of Cu, Zn and B also have not been properly quantified. The magnitude of micronutrient availability and SOM quality of peat soils may vary from region to region due to the difference in physiographic and geomorphological of peat swamps. Therefore, this study was conducted by using peat soils collected from Maludam Peninsular as a largest single peat swamp in Sarawak and Brunei (Anderson, 1961). The Maludam Peninsular also has the complete bio-sequence of major phasic communities, namely Mixed Peat Swamp (MPS), Alan Batu (A.Bt) and Alan Bunga (A.Bg) forest which reflects the different SOM quality as the decomposition level may differ among themselves. As far as we know, there is no available data of the adsorption –desorption batch experiment on tropical peat soils collected from three major different phasic communities of Maludam Peninsular.

1.3 Research Objectives

The primary objective of this study was to investigate the availability of selected micronutrients, i.e., Cu, Zn and B on tropical peat soils collected from three different phasic communities of tropical peat swamp forest. A second objective was to investigate how available is the added Cu, Zn and B for plant uptake in tropical peat soils. The specific objectives of this study were:

1. To evaluate the adsorption and desorption behaviour of Cu, Zn and B in three different types of tropical peat soils.

2. To examine the uptake of different concentration of Cu, Zn and B in Napier grass (*Pennisetum purpureum*) planted in polybag containing peat soils.

3. To determine the optimum dry matter yield and uptake of Cu, Zn and B by Napier grass in polybag experiments.

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