SCHOOL OF AGRICULTURE, FOOD AND WINE

THE UNIVERSITY of ADELAIDE

Retention, Release and Plant Availability of Copper and Zinc in Three Tropical Peat Soils of Sarawak, Malaysia

Margaret Abat

B. Sc. (Hons.) Industrial Chemistry

A thesis submitted to the University of Adelaide
in fulfilment of the requirement
for the degree of Master of Agricultural Science

Soil Science Discipline
School of Agriculture, Food and Wine
Faculty of Sciences, Waite Research Institute
University of Adelaide

December 2010

Loagan Bunut Lake, Miri, Sarawak

Don't cry because it's over,

smile because it happened (Dr Suess)

Table of Contents

Natural tropical peat soils are unsuitable for cultivation of commercial crops because of their innate high acidity, high organic matter contents and low concentrations of essential nutrients. Lime is commonly applied to increase the soil pH prior to planting but this practice may affect the availability of nutrients. Deficiency of micronutrients, in particular copper (Cu) and zinc (Zn), has been reported, but there is still a lack of information on the behaviour and bioavailability of these micronutrients in tropical peat soils. The aims of this thesis were therefore to study the adsorption and desorption reactions of Cu and Zn in tropical peat soils of Sarawak, Malaysia and evaluate the effects of added Cu and Zn to correct the micronutrient deficiency problems in the soils.

The adsorption and desorption of Cu and Zn in three untreated (control) and limed soils were studied. The soils were sampled from three locations in Sarawak and were all characterised by low pH, low bulk density, high organic matter content and low concentrations of available macro- and micronutrients. For the limed soils, calcium carbonate ($CaCO_3$) was used to increase the soil pH to 5.5. Both Cu and Zn adsorption followed a curvilinear (Freundlich) trend with binding affinity decreasing with concentrations of added Cu and Zn in all soils. At the same initial spiked concentrations, the adsorption of Cu and Zn were 50 and 67 times higher, respectively, in limed soils compared to that of controls.

The three soils behaved similarly in relation to sorption of both Cu and Zn. The Freundlich coefficients (K_F values) for Cu in control and limed soils were higher than those of Zn, indicating stronger solid phase sorption of Cu than Zn. The K_F values for Cu and Zn were higher than those reported for mineral soils, but were similar to those reported for other tropical peat soils, suggesting that the efficiency of micronutrient Cu and Zn fertilisers

would be low, and therefore fertiliser requirements for optimal crop production would be high.

Desorption of adsorbed Cu and Zn was assessed using 10 mM calcium nitrate ($Ca(NO_3)_2$) and 5 mM diethylene triamine pentaacetic acid (DTPA). DTPA solution desorbed about 60% more Cu and Zn than $Ca(NO_3)_2$ solution. Copper was more effectively desorbed by DTPA than Zn, as Cu has a higher critical stability constant with DTPA. The percentage of adsorbed Cu desorbed by DTPA was lower in limed soils than in control soils, indicating that added Cu in limed soils will be less labile and bioavailable. By contrast, the percentage of adsorbed Zn desorbed by DTPA was higher in limed soils than in control soils. This is likely due to the possible changes in Zn speciation with increasing soil pH.

The response of a tomato (*Solanum lycopersicum* L.) var. Tiny Tom to application of Cu and Zn as basal fertilisers was also assessed. Using the Mitscherlich model, yield responses were found to correlate well with the rates of added Cu and Zn. The shoot growth of tomato plants in fertilised soils was significantly ($P \leq 0.05$) enhanced by the application of Cu and Zn fertilisers in all three soils. Leaf Cu and Zn concentrations were also significantly ($P \leq 0.05$) increased. Responses to applied Zn were greater than those to applied Cu, and addition of Cu also increased Zn concentrations in tomato leaves and *vice versa*. This suggests a Zn 'hidden' response may exist when Cu fertiliser is added to these soils, since the addition of Cu probably displaces native Zn adsorbed to soil surfaces in these peat soils.

As the rate of added micronutrients increased, concentrations of Cu in plant shoot material were much more regulated than those of Zn. Critical Cu and Zn concentrations in plant shoot to achieve 90% maximum yield were 16-21 mg/kg and 90-96 mg/kg, respectively, greater than those reported for tomato grown in other soil types. Critical concentrations for

DTPA-extractable Cu and Zn in soil to achieve 90% maximum yield in the three soils were 1.6-2.9 and 3.5-3.6 mg/kg, respectively. The values for DTPA extractable Cu were within the range of the published critical values in other soil types. However, the critical concentrations of DTPA-extractable Zn were higher than the published critical values. These values can be used as a guide for fertiliser Cu and Zn recommendations on tropical peat soils in Sarawak.

Declaration

This work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution to Margaret Abat and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text.

I give consent to this copy of my thesis, when deposited in the University Library, being made available for loan and photocopying, subject to the provisions of the Copyright Act 1968.

I also give permission for the digital version of my thesis to be made available on the web, via the University's digital research repository, the Library catalogue, the Australasian Digital Theses Program (ADTP) and also through web search engines, unless permission has been granted by the University to restrict access for a period of time.

....

(Margaret Abat)

Date: ....

Acknowledgements

Wonderful are the ways of God and thanks to Him for what He has done, been doing and going to do.

I am really grateful to all my supervisors: Prof Mike McLaughlin; Dr Jason Kirby and Dr Samuel Stacey. Thank you for the guidance, comments, suggestions and encouragement given to me throughout my study. Thank you for never giving up on me. Your kindness, support and care for my family and I, forever we will treasure and appreciate.

Thank you to the Sarawak State Government, Malaysia for awarding the scholarship to pursue my study. I am very grateful to Mr Paul Ritom (DA, DOA, Sarawak), Mr Lai Kui Fong (SADR) and Ms Chin Siew Phin (Head of Chemistry Section) for allowing me to take study leave. To Dr Lulie Melling and her staff, thank you for your help and efforts with the peat soils and to have the samples delivered.

Thank you to Margaret Cargill for commenting and editing my work. I enjoyed the sessions that we had. Thank you to Jia Wen, Anna McBeath, Gill Cozen, Cathy Fiebieger, Claire Wright, Margaret Yam and Becci Heeps for helping me with the things in the laboratory and the friendship that we have. Thanks for those wonderful moments.

To Pat, Pishen, Angie, Matthew, Narelle, Chris, Judy, Peter, Kay, David, Rose, Nigel and all the Holy Trinity congregation, thank you for those prayers, love and assistance. Thank you for being part of my family.

To all my many friends out there, thank you very much for your wishes, help and support.

To my parents, siblings and in laws, thank you for just being there for us.

Last but not least, to my husband, Maclin and my special people Callysta, Charmaine, Ceinlys, Emmanuel and Edmund, my love for you all keep me going. Thank you for loving me and always be there for me.

List of Abbreviations

AF	Alan forest
ANOVA	Analysis of variance
AR	Analytical reagent
B	Boron
^{o}C	Degree Celsius
Ca	Calcium
$CaCl_2$	Calcium chloride
$CaCO_3$	Calcium carbonate
$Ca(NO_3)_2$	Calcium nitrate
CEC	Cation exchange capacity
Cu	Copper
$CuSO_4$	Copper sulphate
DA	Director of Agriculture
DI	Deionised water
DTPA	Diethylene triamine pentaacetic acid
DOA	Department of Agriculture Sarawak
EDTA	Ethylene diamine tetraacetic acid
Fe	Iron
HA	Humic acid
HCl	Hydrochloric acid
HNO_3	Nitric acid
ICP-MS	Inductively couple plasma – mass spectroscopy
ICP-OES	Inductively couple plasma – optical emission spectroscopy
K	Potassium
K_F	Freundlich constant
K_2HPO_4	Potassium phosphate
LOI	Loss of ignition
M	Molarity
Mg	Magnesium
$MgCO_3$	Magnesium carbonate
Mha	Million hectares
Mn	Manganese
Mo	Molybdenum

MSF	Mixed swamp forest
MWHC	Maximum water holding capacity
N	Nitrogen
Na	Sodium/Natrium
NaDC	Sodium dithionite citrate
NaOCl	Sodium hypochlorite
$Na_2S_2O_3$	Sodium thiosulphate
$(NH_4)_2HPO_4$	Ammonium phosphate
NH_4Ox	Ammonium oxalate
$(NH_4)_2SO_4$	Ammonium sulphate
OC	Organic carbon
OM	Organic matter
P	Phosphorus
P	Probability
PF	Padang Alan forest
RCBD	Randomized complete block design
S	Sulphur
SD	Standard deviation
S_{max}	Maximum adsorption
SOM	Soil organic matter
[x]	x concentration, eg. [Cu]
Zn	Zinc
$ZnSO_4$	Zinc sulphate

List of Tables

List of Figures

Page

Chapter 2

Chapter 3

Chapter 4

Chapter 5

List of Appendices

Page