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

Margaret Abat

B. Sc. (Hons.) Industrial Chemistry

Loagan Bunut Lake, Miri, Sarawak

Don't cry because it's over,

smile because it happened (Dr Suess)

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Abstract

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

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Acknowledgements

List of Abbreviations

AF	Alan forest
ANOVA	Analysis of variance
AR	Analytical reagent
B	Boron
$^{\circ}C$	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

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1.1 General Introduction

In many developing countries, there is an increasing demand for agriculture to develop new land, often caused by population pressures, deterioration of existing land as a result of farming, and competition for land from industry and urbanisation (Andriesse, 1988). For many countries, self-sufficiency in food may either necessitate intensification of food cropping on existing land, or the conversion of new land for agriculture (Andriesse, 1988; Tie and Kueh, 1979). Most land not yet developed for agriculture has limitations on its suitability for crop production, and peat soil in tropical areas is a good example of this.

Peat soil covers more than 200 million hectares (Mha) worldwide and about 32 Mha are found in Southeast Asia. About two-thirds of the peat in Southeast Asia are found in Indonesia with the remaining areas located in Malaysia and Thailand (Attanandana et al., 1995; Purwanto et al., 2002). In Malaysia, which comprises Peninsular Malaysia, Sabah and Sarawak, peat soils cover an area of 2.7 Mha (Mutalib et al., 1991; Tie and Kueh, 1979). Sarawak has the largest area of peat in the country, covering about 1.7 Mha, which is equivalent to 13% of the total land area (Tie and Kueh, 1979). Peat soils in Malaysia occur both in the highland and lowland areas. The lowland peats are found almost entirely in low-lying, poorly drained land or basins in the coastal plains (Mutalib et al., 1991).

Peat soil is an important natural resource and large areas have been cleared for agriculture. Approximately 0.9 Mha of peat soils in Malaysia have been reclaimed and in Sarawak alone about 0.6 Mha of peats are being cultivated (Jamaludin, 2002). The major crop being planted is oil palm because of the expected high economic return. In Sarawak the target is

to plant at least 1 Mha of peat soils with oil palm in the next 5 years (beginning 2008) in order to drive economic development (Melling et al., 2007). Assuming this target can be reached, the total economic impact on the State's economy will be about RM10.8 billion annually (Melling et al., 2007). Other crops which have been planted on peat soils are sago (Purwanto et al., 2002; Yanbuaban et al., 2007), pineapple (Ahmed et al., 2007; Tay et al., 1969; Tay et al., 1968), barley (Ambak and Tadano, 1991), rice (Ambak and Tadano, 1991; Attanandana et al., 1995), maize (Ambak et al., 1991; Kanapathy, 1972) and tomatoes (Adams et al., 1978; Ambak et al., 1991; Graves et al., 1978). Vegetables such as French bean, brinjal and angled loofah (Chew and Yeong, 1974), carrots (LeBlanc and Gupta, 1994) lettuce (Adams et al., 1978; Stone et al., 1999) and cucumber (Adams et al., 1978) have also been planted on peat soils.

The agricultural use of peat soils is often viewed with great concern. Many problems are encountered in the development of peats, such as waterlogging, peat subsidence and poor structural stability. Reclamation disturbs the existing equilibrium, which leads to rapid chemical exhaustion of the soils and increased compaction and decomposition of the peat (Andriesse, 1988). Early attempts to farm these soils, especially those undertaken by smallholders, were disappointing, often ending in the abandonment of the farms (Mutalib et al., 1991).

The poor physical and chemical properties of peat soils indicate a very low suitability for any agricultural use (Tie and Kueh, 1979). The water table is always high in areas of peat soils, and occurs at or near the surface with tree roots in peat areas exposed to allow them to obtain sufficient oxygen (Melling et al., 2007). Peat soils are generally unsuitable for the cultivation of most crops because of their extreme acidity (pH < 4.0) (Cheong and Ng, 1977). Liming is therefore a prerequisite prior to planting of most crops on peat soils,

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usually to raise the soil pH to 5.0-5.5, because most crops require soil pH over 4.5 for their optimum growth (Andriesse, 1988).

One of the most important factors that prevented large scale use of peat soils in the tropics was their low chemical fertility. Peat soil generally has low levels of available nutrients, and these are often unbalanced compared to crop requirements. Micronutrient deficiencies, especially of copper (Cu) and zinc (Zn), are a problem in the agricultural utilisation of peat soils (Tie and Kueh, 1979). The low availability of Cu and Zn in peat soils has been attributed to the low native amounts of these essential elements, or strong complex formation with solid-phase soil organic matter (Stevenson, 1994). Application of Cu and Zn fertilisers on peat often fail to ameliorate the deficiency (Husni et al., 1993). Although it has been hypothesised that sorption reactions of Cu and Zn with solid-phase soil organic matter reduces the availability of added micronutrients (Ambak and Tadano, 1991), research on the adsorption and desorption reactions of Cu and Zn in these soils is limited.

Generally, peat soils require fertilisation in order to become productive. In Sarawak, due to the lack of research conducted on the micronutrient requirements of crops grown in peat, an attempt was made to provide general fertiliser guidelines and principles for peat soils to suit the local environment, based on results of research work conducted elsewhere. In addition, research on peat soils in Malaysia has focused more on crop agronomy and screening of crops and cultivars that are likely to generate income and produce high yield rather than on soil chemistry and fertility. Thus, the adsorption-desorption reactions and fertiliser requirements of Cu and Zn for crops grown in these soils is important and should be investigated. With a good understanding of the sorption/desorption behaviour of micronutrients in peat soils and how this affects the micronutrient requirements of crops

grown in these soils, agricultural activities in tropical peat soils will have a better chance to succeed and sustain local communities.

1.2 Thesis Outline

This thesis will first review the available information on peat soils in general and tropical peat soils in particular (Chapter 2). The information regarding the physical and chemical properties of the peat soils selected, responses to lime and NPK fertiliser in tomato (an important horticultural crop) growth are reported in Chapter 3. Micronutrient reactions with the peat soils in both natural and limed states were examined in adsorption and desorption experiments, and these are reported in Chapter 4. Information obtained from the adsorption and desorption studies (Chapter 4) is useful for the estimation of micronutrient availability for plant uptake. A field trial to evaluate micronutrient uptake by plants would have been more relevant, but because of time and logistical constraints, a pot experiment was carried out to study Cu and Zn uptake by tomato plants in these soils. This study is reported in Chapter 5. Finally, general discussion, future research and conclusions are presented in Chapter 6. Chapters 4 and 5 were prepared in manuscript style and therefore some information has been repeated to make them stand-alone chapters.

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2.1 Introduction

Peats are technically defined as organic soils of at least 0.5 metres deep, one hectare in aerial extent and with a maximum mineral content of 35% (Tie and Kueh, 1979). Peats have also been defined as a turf with partly carbonised vegetable tissues formed in wet conditions by decomposition of various plants and mosses (Andriesse, 1988). In addition, tropical peats are defined as all organic soils in the wetlands of the tropics and subtropics lying within latitudes 35° North and South, including those at high altitudes (Andriesse, 1988).

In the past, chemists and geologists have studied peats because of their potential for industrial or energy purposes, and not as a medium for plant growth, especially in their natural states (Andriesse, 1988). Research on peats for agricultural purposes is relatively more recent than that for other soil types. In Peninsular Malaysia, studies on peat soils commenced in the 1950s (Coulter, 1957). In Sarawak, initial research work began in 1966, was abandoned a few years later, and re-initiated in the 1970s (Tie and Kueh, 1979). Since then, research and development on peat soils has intensified. However, extensive exploitation of peat soils is not permitted by the governing authority because of various factors. In particular, development of peat soils for agricultural activities requires a high degree of management to minimise undesirable impacts that could lead to a drastic subsidence and a rapid disappearance of the peats (Andriesse, 1988).

2.2 Morphology, and Physical and Chemical Properties of Peat Soils

2.2.1 Morphology

Peat soils consist of partly decomposed plant materials in addition to mineral fractions such as clay, silt and sand (Andriesse, 1988; Tie and Kueh, 1979). Unexploited peat soils consist of dark reddish brown to black, loose, partially decomposed leaves, branches, twigs and tree trunks with low mineral contents (Mutalib et al., 1991). The water table is always high and occurs at or near the surface. In drained areas, the peats are transformed into a compact mass consisting of partially and well-decomposed plant remains with large wood fragments and tree trunks embedded in it, as a result of decomposition, shrinkage and consolidation of the virgin peat (Melling et al., 2007; Mutalib et al., 1991). The common soil profile of the drained peat consists of three distinct horizons (Mutalib et al., 1991; Tie and Kueh, 1979; Wong, 1991):

(a) an upper horizon, 20 to 30 cm thick, consisting of well-decomposed organic materials of the sapric type,

(b) a middle horizon, 30 to 40 cm thick, containing semi-decomposed organic materials belong to the hemic type,

(c) a lower horizon of fibric peat which is made up of a large quantity of relatively undecomposed organic materials consisting of tree trunks, large wood fragments and branches.

2.2.2 Physical properties

The physical characteristics of peat soils are important to explain the need for adequate drainage, compaction and nutrient requirements for crops grown in these soils (Andriesse, 1988). The moisture content of peats is generally more than 80% (w/v) and maximum water holding capacity (MWHC) is usually 15 to 30 times higher than their dry weight (Tay et al., 1969). The ash content in most of the peat of Sarawak is less than 10% and loss of ignition

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(LOI) is more than 90%, indicating very high organic matter contents (Wong, 1991). The bulk density for the top 30 cm of the peat is low and varies from 0.1 to 0.2 g/cm^3 (Tie and Kueh, 1979).

Peat soils are prone to subsidence due to the removal of water upon drainage and compression due to agricultural activities. The peat level drops due to the collapse of the loose fibric materials followed by subsequent decomposition and compaction of hemic and sapric materials (Mutalib et al., 1991; Tie and Kueh, 1979). In Sarawak, a subsidence rate of 6 cm/year has been reported for peat with a water table at 75-100 cm (Tie and Kueh, 1979).

2.2.3 Chemical properties

In their natural state, peat soils are very acidic with pH values between 3.0 and 4.0 (Tie and Kueh, 1979; Wong, 1991). Variations within this range are caused either by the parent materials which generally will increase the pH or by the specific location in the peat swamp (Andriesse, 1988). In some peat soils, where sulphidic materials are found within the profile, pH values drop below 3.0 (Mutalib et al., 1991). The cation exchange capacities (CEC) at pH 7.0 are high, between 40 and 143 cmol(+)/kg soil. The variability in the CEC values is due to the stage of decomposition and nature of the soil organic matter (Wong et al., 1986).

The organic carbon (C) contents of peat soils are between 40 and 60%. The differences in organic C contents reflect the type of organic materials present, the decomposition stage and probably the analytical method being used (Andriesse, 1988). The total nitrogen (N) contents of peat soils are relatively high with values greater than 1% (Tie and Kueh, 1979). The C/N ratio of peat soils are usually high resulting in low mineralisation potentials, and a

large amount of nitrogenous fertiliser is often required for crop production (Mutalib et al., 1991).

Peat soils have low micronutrient contents, which may cause crop failures after reclamation. Deficiencies of micronutrients, particularly Cu and Zn, have been recorded in crops grown in peat soils (Andriesse, 1988; Mutalib et al., 1991; Tie and Kueh, 1979). These micronutrient deficiencies were attributed to either the low native amounts of Cu and Zn in the soils, or strong complex formation with the solid phase of soil organic matter (Stevenson, 1994).

2.3 Copper and Zn Chemistry in Soils

2.3.1 Copper and Zn in mineral dominated soils

Copper and Zn are required for normal plant growth and biochemical functions (Fageria, 2001; Sommer, 1931). Plant available Cu and Zn is governed by mineral solubility, soil organic matter, and Cu or Zn adsorbed on clay and organic matter (Havlin et al., 2005). Normal Cu concentrations in plant tissues are between 5 and 15 mg/kg and for Zn between 30 and 200 mg/kg (Reuter and Robinson, 1997). Thus, deficiencies of Cu and Zn are probable at plant concentrations <5 mg/kg and <20 mg/kg, respectively (Havlin et al., 2005; Reuter and Robinson, 1997).

The mean Cu concentration in various surface soils of the world ranges between 13 and 34 mg/kg and for Zn between 17 and 125 mg/kg (Kabata-Pendias and Pendias, 2001). In the surface horizon of Histosols and other organic soils of different countries, the mean concentrations for Cu are 6-15 mg/kg, and for Zn 27-80 mg/kg (Kabata-Pendias and Pendias, 2001) (Table 2.1).

Table 2.1 Copper and Zn concentrations of surface horizons of Histosols and other organic soils of different countries[a]

Metal	Country	Range (mg/kg)	Mean (mg/kg)
Copper	Denmark	4 -24	15
	Israel	27 - 41	-
	Ivory Coast	1 - 3	-
	Poland	1 -113	6
	U.S.A	1 - 100	15
	Russia	5 - 23	12.5
Zinc	Bulgaria	-	80
	Denmark	48 – 130	72.5
	New Zealand	21 – 34	27
	Poland	13 – 250	60
	U.S.A	5 - 108	34
	Russia	7.5 - 74	34

[a] Source: Kabata-Pendias and Pendias (2001)

Copper and Zn in soil can occur in soil solution in both ionic and complexed forms; as an exchangeable cation on the exchange complex; as a specifically adsorbed (non-exchangeable) ion; in organic matter; in occluded oxides; and in minerals (Barber, 1995; Reed and Martens, 1996; Shuman, 1985). In soil solution, most of the soluble Cu^{2+} exists in complexed forms with organic acids (He et al., 2006; Hodgson et al., 1965; Jeffery and Uren, 1983), and solid-phase Cu consists of exchangeable Cu^{2+} on mineral and organic surfaces, as well as Cu-containing minerals. Zinc is predominantly present as Zn^{2+} in the soil solution but may also complex with dissolved organic matter. Solid-phase Zn consists of exchangeable Zn^{2+} on the cation-exchange sites and organically complexed Zn in the soil solid phase (Barber, 1995; Jeffery and Uren, 1983; Nolan et al., 2003). Copper and Zn become less available as soil pH increases above pH 5.5-6.5 because the adsorption of Cu and/or Zn increases with increasing pH, and high pH also promotes the formation of solid-phase Cu and Zn precipitates (Sauchelli, 1969). Copper and Zn form stable complexes with organic matter that may be soluble or insoluble (Barrow, 1993; Havlin et al., 2005). With

insoluble complexes, Cu and Zn availability to plants will be reduced; this is the case in Cu and/or Zn-deficient peats and organic soils (Havlin et al., 2005).

2.3.2 Copper and Zn in peat soils

Copper and Zn deficiencies frequently occur in soils of high organic C content, particularly in peat soils, including alkaline peat soils which have appreciable amounts of ferrous iron (Andriesse, 1988; Sauchelli, 1969). Copper deficiency in plants was first recognised as 'reclamation disease' in crop grown in newly reclaimed peats in Holland and later in crops grown in some sandy and gravelly soils in Florida and Australia (Sauchelli, 1969). Zinc deficiency is apparent in highly leached sands, on soils with a pH greater than 6.5 or on peat soils which have been heavily limed and those receiving large applications of phosphorus (P) fertiliser (Andriesse, 1988). The negative effect of liming or high natural soil pH on Cu and Zn availability occurs due to the increase in soil cation exchange capacity, which relies on the presence of pH-dependent charges in the soils (Alloway, 1990). As the soil solution pH increases, metal adsorption increases due to a decrease in competition with H^+ for binding sites and an increase in the negative charge of the soil surfaces, so that metal availability to plants will decrease as pH increases. Precipitation of metal hydroxides or carbonates may also reduce the solubility of metals after liming. Zinc deficiency had been observed in rice grown in peat soils in some Asian countries, for example in the Philippines (Havlin et al., 2005).

The behaviour of Cu and Zn in soils is of great interest to researchers from both the agricultural and environmental standpoints because both micronutrients are important for plant and animal health. In peat soils, Cu and Zn concentrations are low, and deficiencies have been reported in many crops. Progress has been made in diagnosing and correcting the deficiencies of both Cu and Zn in plants grown in these soils. However, there is little

information on the sorption behaviour of Cu and Zn in tropical peat soils and how this affects crop response to applied Cu and Zn fertilisers. Such information is useful in estimating the availability of Cu and Zn uptake to plants and the management of peat soils.

2.4 Adsorption and Desorption of Metals in Soils

2.4.1 Adsorption and desorption of metals in mineral-dominated soils

The behaviour of metals in soils is controlled by a number of processes, including adsorption-desorption or precipitation-dissolution (Bruemmer et al., 1988; Brummer et al., 1983; Tiller and Hodgson, 1962; Zhang et al., 2006). When the retention mechanism is not known the term sorption is used (Buchter et al., 1989). Initially, in the first few minutes and hours after metal addition (fast reaction kinetics), both adsorption (and precipitation reactions at high concentrations) will reduce the fraction of added metal that remains labile (Lindsay, 1979; McLaughlin et al., 2002). Adsorption transfers metal from soil pore water to soil mineral and organic surfaces and precipitation reactions may create new solid mineral phases in soil (Lindsay, 1979; McLaughlin et al., 2002). The balance between adsorption and precipitation will depend on the concentrations of metal added, the pH and the presence in soil solution of anions which form poorly soluble solid phases with metals (e.g. phosphate, carbonate) (Lindsay, 1979; McLaughlin et al., 2002).

In neutral to alkaline soils precipitates of copper hydroxide ($Cu(OH)_2$) or copper hydroxide bicarbonate ($Cu_2(OH)_2CO_3$) may form, with clay or carbonate mineral surfaces acting as nucleation sites (Cavallaro and McBride, 1978; Lindsay, 1979). However, precipitation phenomena generally do not control soil solution metal concentrations, rather control is by adsorption-desorption processes (Cavallaro and McBride, 1978; McBride, 1981). Adsorption is strongest at low coverage of adsorption sites (low metal concentrations), when the majority of adsorption is by way of specific adsorption processes (McLaren and

Crawford, 1973b). As the concentration increases (with increased added metal), increasing amounts are adsorbed via weaker, non-specific processes (i.e. cation exchange on clay minerals), from where the metals are more easily desorbed (Atanassova, 1995).

The adsorption and co-precipitation of metals by aluminium (Al) and iron (Fe) oxides and clay minerals have been demonstrated in many studies (Bruemmer et al., 1988; Martinez and McBride, 2001; Padmanabham, 1983a; Padmanabham, 1983b; Tiller et al., 1984a; Tiller et al., 1984b). The oxidation-reduction processes in soils serve to dissolve and reform hydrous ferric oxides and create the potential for co-precipitation of metals into the solid phase (Martinez and McBride, 2001). Bruemmer et al. (1988) studied the sorption reactions of cadmium (Cd), nickel (Ni) and Zn with goethite over a range of initial metal concentrations. They reported that the initial rapid adsorption of metals on goethite (within the first few hours) was followed by a much slower reaction called diffusion-controlled penetration. The reactions of metals with goethite involve (i) adsorption of metals on external surfaces, (ii) solid-state diffusion of metal from external to internal binding sites and (iii) metal binding and fixation at positions inside the goethite particles (Bruemmer et al., 1988). Brummer et al. (1983) studied the adsorption-desorption and precipitation-dissolution reactions as a function of pH and determined Zn concentration in soil clay fractions. The concentrations of Zn in equilibrium solutions with soil clay fractions and whole soil samples at pH below 7 were determined by adsorption-desorption reactions and at neutral to alkaline pH values, precipitation-dissolution reactions were likely to occur (Brummer et al., 1983).

While the concentrations of micronutrients in soil solutions and their availability to plants are controlled by adsorption reactions at the surfaces of soil colloidal materials, it is desorption processes that are likely to control the amount and rate of release of

micronutrients into solution for plant uptake (Brummer et al., 1983; Hogg et al., 1993; Kuo and Mikkelsen, 1980; Tiller et al., 1984a). While many studies have been conducted to determine the adsorption of metals by soils and soil components (Jarvis, 1981; McLaren and Crawford, 1973a; McLaren et al., 1981), less studies have examined the desorption of the metals into solution and the factors affecting desorption reactions (Hogg et al., 1993). Nutrient uptake by plants is a continuous process that leads to nutrient depletion in the root zone and thus requires desorption of nutrient from soil surfaces (Dang et al., 1994). Consequently, the greatest cause of error in predicting potential deficiency and/or toxicity of metals is due to the limited understanding of desorption processes (Covelo et al., 2004).

Desorption reactions of metals often occur at a slower rate than adsorption reactions (Barrow et al., 1989; Kuo and Mikkelsen, 1980). The slower rate of desorption reactions is probably due to the transformation of sorbate from one state to another i.e. conversion from adsorbed species to a surface precipitate. It may also be due to other reactions with soil minerals, e.g. diffusive penetration of the ion into the mineral surface as noted above (Singh et al., 2006; Strawn and Sparks, 2000). The ability of adsorbed Cu and Zn to desorb from soil surfaces back into solution is important to ensure the availability of these nutrients for plant uptake (Schnitzer and Skinner, 1966).

Since Cu and Zn are required by plants in amounts greater than those available in soil solution, the desorption rate of adsorbed Cu or Zn is an important factor regulating their plant availability (Kuo and Baker, 1980). The rate of Zn desorption in six Californian soils was initially rapid and gradually declined with time, hence the amount of metal desorbed into soil solution also decreased (Kuo and Mikkelsen, 1980). Desorption of Cu and Zn from the surfaces of soil particles has been investigated using various chemical extractants, with DTPA being the most widely used extractant (Kuo and Baker, 1980; Lindsay and Norvell,

1978; McBride, 1981). Knowledge of desorption reactions is required in order to improve our ability to predict the release of native metals from soils and the release of fertiliser-derived metals added to soils.

2.4.2 Adsorption and desorption of metals in peat soils

The physical and chemical behaviour of Cu and Zn in soils, including sorption reactions have been extensively studied (Arias et al., 2005; Brummer et al., 1983; McBride, 1981; McLaren and Crawford, 1973a; McLaren and Crawford, 1973b; McLaren et al., 1981; Singh et al., 2006; Tiller and Hodgson, 1962), but many of these studies were conducted on mineral soils. Information regarding the sorption reactions and behaviour of Cu and Zn in organic soils is limited to a few studies. For example, Naganuma et al. (1993) investigated the effects of solution pH, and Cu and Zn equilibrium concentrations on the surface charge and the sorption of Cu and Zn on tropical peat soils of Malaysia and Thailand. They found that the sorption of Cu and Zn increased with the increasing solution pH and equilibrium metal concentrations. In addition, more Cu was adsorbed on the peat soils than Zn (Naganuma et al., 1993). Yonebayashi et al. (1994) studied the chemical fractionation of Cu, Fe, Mn and Zn of tropical peat soils under natural conditions and their changes after reclamation. Their study showed that most of Cu and Fe present were strongly chelated to organic matter and in non-extractable forms. The strength of binding (based on sequential chemical extraction) of metal ions to humic substances in the tropical peats followed the order Cu > Fe > Zn > Mn (Yonebayashi et al., 1994).

The organic matter in peat has the following functional groups: carboxylic (COOH), phenolic (OH), hydroxylic (OH), carbonyl (C=O) and amine (NH) (Bunzl, 1974; Bunzl et al., 1976; Villaverde et al., 2009). These functional groups are responsible for the chelation and complexation of metal ions from soil solution (Bloom and McBride, 1979; Gosset et

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al., 1986; Stevenson and Ardakani, 1972). Reactions with organic matter frequently involve the interaction with carboxylic and phenolic functional groups (Gamble et al., 1970). Infrared (IR) spectroscopy has been used to confirm the involvement of carboxylic functional groups in the complexation of Cu by sewage sludge (Boyd et al., 1979) and in soil humic substance (Piccolo and Stevenson, 1982). Carboxylic and phenolic groups have been found to be important in the complexation of Zn in soil organic matter (Himes and Barber, 1957).

Organic matter plays a major role in soil retention for both Cu and Zn (Kabata-Pendias and Pendias, 1984; McLaren and Crawford, 1973a; McLaren et al., 1981). Soils higher in organic matter content and with high CEC were found to have greater sorption capacities for Cu and Zn (Kuo and Baker, 1980). Soil organic matter sorbs metals by ion exchange, surface adsorption, chelation and complex coagulation and peptization reactions (Mortensen, 1963). Organic matter has been found to specifically sorb Cu in soil, perhaps because the Cu^{2+} ion is unique in its ability to form inner-sphere complexes under a wide range of pH conditions (McBride, 1981; McLaren and Crawford, 1973a). Soil organic matter binds Zn in coordination complexes, but the Zn may be displaced by Cu, which has a higher stability constant (Barber, 1995). Copper has greater affinity than Zn for functional groups of soil organic matter; carboxylic and phenolic groups are hard Lewis bases, Cu is a borderline hard Lewis acid and Zn is a soft Lewis acid. Additionally Cu has higher electronegativity than Zn (2.0 and 1.6 for Cu and Zn, respectively), making Cu a better candidate than Zn for electrostatic and inner-sphere surface complexation reactions (Sparks, 1994), which will decrease Cu availability in soil.

In acid-washed peat, the strong affinity of Cu to organic matter was attributed to functional groups that form strong complexes with the metal, and not due to ion exchange reactions (Bunzl et al., 1976). The selectivity and strength of metal binding by organic matter

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depends on the amount of metal available for binding and the amount of metal bound (Davies et al., 1969). The binding strength of Cu^{2+} to sedge peat was increased when the added Cu concentration decreased (Davies et al., 1969). The binding strength of Zn^{2+} to synthetic organic material such as polymers was also greater at lower Zn concentration (Zunino et al., 1979). The adsorption and desorption rates were found to be influenced by the electronegativity of organic matter (Bunzl et al., 1976) with ions having greater electronegativity being adsorbed faster and, *vice versa* for desorption (Bunzl et al., 1976). The electronegativity of metals and their affinity for organic matter is shown in Table 2.2.

Table 2.2 Electronegativity of divalent metal ions and sequence of affinity (from high to low) for organic soil at pH 5 (Schnitzer and Skinner, 1966)

NOTE:
This table is included on page 18
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2.4.3 Factors affecting adsorption and desorption reactions of metals in soils

Metal sorption reactions are influenced by the soil pH, organic matter content, CEC, concentration and type of clay minerals, sesquioxides, redox potential, and amount of metal added (Jalali and Khanlari, 2008; Kabata-Pendias and Pendias, 2001; Kuo and Baker, 1980; Kuo and Mikkelsen, 1980; McLaren and Crawford, 1973a; Msaky and Calvet, 1990). Co-precipitates of Cd, Cu, lead (Pb) and Zn with Fe oxides can reduce the solubility of these metals, depending on the pH at which the co-precipitates form (Martinez and McBride, 2001).

Bruemmer et al. (1988) studied the reactions of Cd, Ni and Zn with goethite and found that the adsorption of these metals increased with pH (4 to 8), reaction time (2 hours to 42 days) and temperature (5 ^{o}C to 35 ^{o}C). Adsorption of Cu, Mn and Zn on oxides and clay minerals

had been reported to result in a drop in the pH of the solution, indicating the release of protons from the adsorbate surface (Padmanabham, 1983a). The proportions of Cd, Ni and Zn sorbed to soil clay fractions increased with increasing pH and time (Tiller et al., 1984a).

The adsorption of Cu and Zn by peat and other soil types was increased with increasing pH (McLaren and Crawford, 1973a; Villaverde et al., 2009). Adsorption and desorption of Zn in four surface soils of New Zealand were found to vary widely with soil pH and both the amounts of adsorbed and desorbed Zn increased with the increasing pH (Singh et al., 2008). Kuo and Baker (1980) reported the sorption of Cu, Cd and Zn in three acid soils increased with increasing pH and Cu was preferentially sorbed over Cd and Zn. In addition, the adsorption of Cu in three Malaysian soils in rice growing areas increased with increasing soil pH (Choudhury and Khanif, 2000). Thus, soil pH is the most important factor in relation to sorption reactions, hence bioavailability of metals in soils.

The CEC of peat soils is mainly derived from organic matter, so the CEC values depend on pH. The soil CEC is low at acidic pH values and moreover, the CEC of peat soils are lower than those of mineral soils on a volumetric basis (Funakawa et al., 1996). As a result, cations that have dissolved into the soil solution cannot be retained easily and are susceptible to leaching (Purwanto et al., 2002). A shallow ground water table might inhibit leaching losses of nutrients, but the decrease of the ground water level as a result of natural outflow or artificial drainage removes dissolved nutrients from peat soils (Laiho et al., 1998).

The availability of metals is low in soils with a high content of sesquioxides (Brennan et al., 1980). High contents of sesquioxides are associated with soil horizons having high pH-dependent charge and high metal fixing capacity (McKeague and Day, 1966). Following

the removal of oxides by ammonium oxalate and dithionite-citrate extractions, sorption and fixation of Cu and Zn were reduced considerably, indicating a significant role of the oxides in metal retention (Cavallaro and McBride, 1984). Metal sorption is also influenced by soil clay minerals. High clay content is likely responsible for high metal adsorption capacity in soils (Kuo and Mikkelsen, 1979), hence reduced its availability for plant uptake. Different types of minerals in soil exhibit different charges and potential behaviour that affects the metal adsorption (Majidi et al., 2010).

Oxidation-reduction (redox) reactions can effect changes in metal speciation (Cherry et al., 1979). This effect is important because metals tend to be mobile under oxidising or reducing conditions. Calmano et al. (1993) examined the binding and mobilisation of Cd, Cu, Pb and Zn in contaminated sediments affected by pH and redox potential and found that more metals are mobilised in the oxidising than in reducing conditions. Thus, redox reactions may influence the adsorption and/or desorption of metals in soils.

2.4.4 Adsorption equations

The adsorption of metal cations by soils can be described by an equilibrium-type model, which assumes rapid or instantaneous reactions of the metals with the soil matrix (Buchter et al., 1989). Metal adsorption mechanisms at solid surfaces have been described by either linear or non-linear Langmuir or Freundlich equations (Amacher et al., 1998; Diatta et al., 2003; Harter, 1991; Schlebaum et al., 1999), with the latter preferred (Sposito, 1984; Travis and Etnier, 1981).

The Langmuir equation is not suitable to describe the reaction of ions in soil (Barrow, 2008). Veith and Sposito (1977) reported that the Langmuir equation cannot differentiate between adsorption and secondary precipitation, and concluded that the Langmuir

parameters will have no particular chemical meaning unless it is independently shown that only adsorption occurs. Hendrickson and Cory (1981) found that selectivity coefficients or binding strengths of surfaces are concentration dependent unless the concentration of adsorbate in solution is low compared to concentrations of competing ions. The Langmuir equation has been found to describe phosphate sorption reactions only under conditions of low P concentrations (Barrow, 1978; Cole et al., 1953; Kuo and Lotse, 1972; Olsen and Watanabe, 1957). Similar findings had been reported for Zn in two alkaline soils where the Langmuir equation could describe Zn sorption only at extremely low concentrations (between 0.10 and 0.23 mg/kg) (Kuo and Mikkelsen, 1979). In comparison, the Freundlich equation was used to effectively describe Zn sorption in the same soils, both at low and high Zn concentrations (Kuo and Mikkelsen, 1979).

The parameters obtained from Freundlich equations such as the partition (distribution) coefficient, K_F and the affinity constant, n are important in the understanding of the sorption processes involved, and can assist the estimation or prediction of the amount of fertiliser required for crops (Arias et al., 2005; Barrow, 1978). The non-linear Freundlich equation is an empirical equation given by

$$Q \text{ (mg/kg)} = K_F (C_{Equil})^{1/n} \qquad (1)$$

where Q is the concentration of Cu or Zn adsorbed on the solid phases (mg/kg); and C_{Equil} is the Cu or Zn concentration in solution at equilibrium (mg/L); K_F is the Freundlich isotherm coefficient, n is the affinity value of the Freundlich isotherm coefficient. The constant n can range between 0 and 1, with a linear C-type isotherm produced when $n = 1$ (McBride and Martinez, 2000).

The linear form of the Freundlich equation is represented by

$$\text{Log } Q \text{ (mg/kg)} = \log K_F + n \log C_{Equil} \qquad (2)$$

where C_{Equil}, Q and K_F are as previously defined. The K_F coefficient can give an estimation of the amount of adsorbed metal in mg/kg at a solution concentration of 1 mg/L (Welp and Brummer, 1999).

2.5 Ageing of Cu and Zn in Soils and Effects on Plant Uptake

2.5.1 Ageing of Cu and Zn in mineral-dominated soils

After a metal such as Cu or Zn is added to soil in dissolve form, several reactions may occur that will change the concentration of the metal in the soil pore water and the fraction of added metal available to organisms (Ma et al., 2006; McLaughlin et al., 2002). The initial rapid adsorption of metals within a few hours is followed by a much slower reactions that are related to time (Bruemmer et al., 1988). These reactions are called 'ageing' or 'fixation' reactions and will slowly reduce the availability of metals to organisms over time (McLaughlin et al., 2002). These reactions result in hysteresis in adsorption–desorption curves. With increasing reaction time and also with elevated temperature the bound metals become less and less mobile (Kuo and Mikkelsen, 1980; McKenzie, 1980; Nelson and Melsted, 1955).

Ageing processes in soils can significantly affect the potential biological availability of introduced metals through diffusion into surface pores, solid phase diffusion, occlusion of metals through precipitation of other phases, precipitation of new metal solid phases or occlusion in organic matter (Ma et al., 2006; McLaughlin et al., 2002; Wendling et al., 2009). Over time, metals in contact with the soil solid phase are less freely exchangeable with the soil solution and, hence, less available to soil biota (Wendling et al., 2009). The possible reactions occur during the adsorption and ageing processes in soils are shown in Figure 2.1.

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Figure 2.1 Adsorption and ageing processes in soils. Adsorption moves metals from solution to soil surfaces. Ageing moves metal from soil surfaces to deeper in the solid phase through (a) surface pore diffusion, (b) solid state diffusion, (c) occlusion of metals through precipitation of other phases, (d) precipitation of new metal solid phases, and (e) occlusion in organic matter (McLaughlin et al., 2002).

Where ageing of Cu and Zn in soils over time has been examined through sorption studies using soils and soil minerals, a decrease in extractability/availability has been observed (Bruemmer et al., 1988; Hogg et al., 1993; Kuo and Mikkelsen, 1980; Singh et al., 2006). Results of several studies suggest that metal retention processes are not completely reversible, so that desorption fails to remove all the adsorbed metal, a phenomenon known as hysteresis. In several Cu adsorption studies, hysteresis in the adsorption-desorption curves for Cu have been observed i.e. a portion of the added Cu becomes bound strongly to the soil solid phase and is not easily desorbed (Atanassova and Okazaki, 1997; Bunzl et al., 1976; Hogg et al., 1993; Padmanabham, 1983a; Padmanabham, 1983b; Wu et al., 1999). Bunzl et al. (1976) demonstrated adsorption-desorption hysteresis with peat, while

Padmanabham (1983a) found desorption hysteresis using goethite to be both time and pH dependent – increasing at longer goethite-Cu contact times and at lower pH values, when the oxide surface would be expected to have a predominantly positive charge. Working on whole soils, Hogg et al. (1993) studied the desorption in 0.01M $Ca(NO_3)_2$ of added Cu at a small addition rate (+7 mg/kg) with times of soil-Cu contact varying from 24 hours to 12 weeks and found increasing the period of soil-Cu contact reduced desorption of added Cu. Cavallaro and McBride (1984) studied Cu and Zn sorption and fixation by clay fractions of two acid soils from New York. They reported the amount of Cu and Zn adsorbed increased with increasing pH and at high pH (high sorption) as much as 95% of the sorbed metal could not be desorbed by several extractions with 0.05 M $CaCl_2$ solution and thus could be considered fixed by Al and Fe oxides (Cavallaro and McBride, 1984). Figure 2.2 shows an example of Cu adsorption-desorption hysteresis.

NOTE:
This figure is included on page 24
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Figure 2.2 Diagrammatic representation of adsorption-desorption hysteresis. Addition of soluble Cu to a soil suspension followed by incubation causes some of the added Cu to be strongly bound to the surfaces (McLaughlin et al., 2002).

Hysteresis of Zn sorption has also been reported (Elrashidi and O'Connor, 1982; Singh et al., 2006). Elrashidi and O'Connor (1982) observed that desorption of sorbed Zn from nine soils by 0.05 M calcium chloride ($CaCl_2$) was extremely hysteretic after five desorption

periods and only soils with low CEC exhibited measureable Zn desorption. Singh et al. (2006) reported hysteresis effect in the sorption of Zn in New Zealand soils after ten desorption periods using 0.01M calcium nitrate $(Ca(NO_3)_2)$. An investigation of Zn desorption in six Californian soils showed that the amount of Zn desorbed by DTPA continue to decrease with increasing aging time and elevated temperature further enhanced Zn aging and reduced Zn extractability (Kuo and Mikkelsen, 1980). Following 100 days of aging time, the total amount of Zn extractable by DTPA was estimated at 46 to 49% of the initial amount of Zn adsorbed (Kuo and Mikkelsen, 1980). Barrow (1993) observed longer reaction times transform added soluble Zn into stable forms, likely through diffusion into crystalline oxides, thus decreasing Zn availability. Thus, due to the hysteresis effect, the added nutrient fertilisers will be made less available in the soils for plant uptake, thus leading to possible nutrient deficiency for crop growth.

Brennan et al. (1980) found Cu availability to wheat plants decreased with increasing incubation time after application of the metal to various types of soil. Following 120 days of aging, Cu was up to 70% less available than when freshly applied (Brennan et al., 1980). This reduction in effectiveness of incubated Cu compared to that freshly applied Cu is interpreted as evidence of 'slow' reactions converting Cu into unavailable forms (Brennan et al., 1983). Tests under field conditions have shown that Cu added to soil is gradually transferred from the more labile fractions (e.g. soluble and exchangeable Cu) into less labile fractions (McLaren and Ritchie, 1993). Added Cu initially decreased the pH of the soil through an acidifying effect and lowered its cation exchange capacity (McLaren and Ritchie, 1993). With regard to Cu fractions, the most labile (exchangeable Cu) was found to decrease with increasing incubation time; also, the moderately labile fractions (organically bound Cu) evolved to forms more strongly bonded to soil colloids (McLaren and Ritchie, 1993).

The ageing of Cu and Zn in soils over time has also been examined through fractionation studies using soils and soil minerals, a decrease in extractability/availability has been observed over time. For example, ageing had a significant effect on Cu fractionation in spiked soils incubated from 3 to 56 days; Cu tended to transform from the exchangeable to more stable fractions such as the reducible and oxidisable fractions (Lu et al., 2009). Sayen et al. (2009) demonstrated that following 60 days of incubation of vineyard soil with added Cu, the amount of available Cu was reduced during a $Ca(NO_3)_2$ leaching of soil columns, which suggests a redistribution of a weakly-bound Cu fraction to a more strongly-bound fraction. The availability of applied Cd, Cu, Pb and Zn in five calcareous soils of Iran were decreased with increasing contact time and a large proportion of the added metals rapidly became non-exchangeable in the first hours due to fixation (Jalali and Khanlari, 2008). Arias-Estevez et al. (2007) examined the effects of adding $Cu(NO_3)_2$ to a soil developed on amphibolites and found that the proportions of Cu in the exchangeable and organically bound forms decreased with increasing incubation time. The DTPA-extractable concentrations of Zn in three tropical soils of Taiwan incubated with biosolids, decreased over a period of one year (Hseu, 2006). Therefore, the ageing effect influences not only the mobility and bioavailability of metals in soils but is also responsible for converting the exchangeable metal form into reducible and oxidisable fractions.

2.5.2 Ageing of Cu and Zn in peat soils

Few studies have reported ageing of metals in organic or peat soils even though the process plays an important role in influencing the availability of metals in soils. However, a study using organic substances such as humic acid (HA) has been reported. Using a sequential extraction procedure and a parabolic diffusion equation, the ageing of added Cu in bentonite with and without HA was investigated as a function of incubation time over one year (Zhou et al., 2009). At the same time, the effect of pH on Cu ageing in bentonite with

HA was also studied. The most labile Cu fractions (water-soluble Cu, Cu extracted by

NH_4NO_3 and EDTA) gradually transformed into less extractable forms (Zhou et al., 2009).

The modelled diffusion equation suggested that the ageing processes were controlled by

surface nucleation/precipitation and diffusion. In the presence of HA, the contribution from

surface nucleation/precipitation increased significantly, whereas that from diffusion

decreased, this indicated the addition of HA significantly enhanced the short-term ageing

by complexation with Cu ions, but strongly inhibited the further diffusion of Cu ions into

interlayers of bentonite during long-term ageing owing to the more stable complexes

formed on solid surface (Zhou et al., 2009). With increasing pH in bentonite with HA, the

apparent diffusion rate coefficient (D/r^2) increased greatly, which showed that during long-

term ageing, pH played an important role in reducing the extractability as a result of the

significant increase in residual Cu (RES-Cu), the most inert fraction, due to micropore

diffusion (Zhou et al., 2009). Therefore, based on this study, ageing is likely to reduce the

mobility and bioavailability of metals in organic or peat soils.

2.6 Deficiencies and Effects on Crop Growth of Cu and Zn Addition to Peat Soils

2.6.1 Copper and Zn deficiencies in peat soils

There are many limitations to the agricultural use of peat soils. However, some crops

respond well when grown in these soils with proper management, and thus the soils

constitute a tremendous potential for food production (McKay et al., 1966). Developed peat

soils could provide a good structure for crop cultivation but their growth has been limited

by soil nutrient deficiencies, particularly Cu and Zn (Kanapathy, 1972; Lim et al., 1973; Tie

and Kueh, 1979).

Copper deficiencies are widespread on acidic sandy and organic soils (Hodgson et al.,

1966; Lucas and Davis, 1961). Copper deficiency of crops grown in peat has been

identified in oil palm (Matsumoto et al., 1998; Ng and Tan, 1974), sago palm (Matsumoto et al., 1998; Purwanto et al., 2002), sorghum and groundnut (Chew et al., 1979), tapioca (Kanapathy, 1974; Kanapathy and Keat, 1970), maize (Kanapathy, 1972), oats and soybeans (Roth et al., 1971) and tomatoes (Adams et al., 1978; Graves et al., 1978). In addition, Cu and Zn deficiencies contributed to sterility in rice and the failed formation of tomato fruit grown in peat soils (Ambak and Tadano, 1991). Copper deficiency in annual crops grown in highly weathered acidic soils has also been reported due to the intensive cropping systems and the use of lime to raise the soil pH (Fageria, 2001).

Zinc deficiency in soils is also common. About 30% of the agricultural soils of the world are Zn deficient (Silanpaa, 1982), and the problem is more prevalent on calcareous soils (Hodgson et al., 1966) and organic soils (Lucas and Davis, 1961). Zinc deficiency is a problem in rice production in some countries in the world (Quijano-Guerta et al., 2002; Yoshida et al., 1973). Severe Zn deficiency symptoms with corresponding low yields in cereals were reported in crops grown in calcareous soils of arid and semi-arid regions in India, Australia and China (Takkar and Walker, 1993). The deficiency of Zn in crops grown in organic soils may be caused by low Zn concentrations in the soils and/or by low Zn availability (Alloway, 1990; Lucas and Davis, 1961). High clay and P supply and low soil temperatures are also known to promote Zn deficiency (Marschner, 1985).

Restricted plant growth observed in crops grown in peat soils are likely to be at least partly due to the low concentrations of total and available Cu and Zn in the soil (Lucas and Davis, 1961). Liming of the soils may exacerbate the deficiency by increasing the amounts of Cu or Zn complexed by soil organic matter, adsorbed on surfaces of inorganic soil components and occluded by soil hydroxides and oxides (Martens and Westermann, 1991) and consequently reducing the available Cu and Zn in the soil (Alloway, 1990; Graves et al.,

1978). For example, Nascimento et al. (2007) examined the effect of liming on the plant availability and forms of Cu and Zn in soil and observed decreases in concentrations of exchangeable Cu and Zn, and increases in concentrations of Cu and Zn in the organic matter and the Fe oxide fractions, which decreased the plant accumulation of Cu and Zn.

Copper deficiency limited the yield of tomatoes, lettuce and cucumbers, and resulted in low leaf Cu concentration in all plant types (Adams et al., 1978). In the absence of micronutrient application, the tomato yield was reduced by 20-65% and the leaf B, Cu and Mn concentrations were less than when a micronutrient mixture was applied (Graves et al., 1978). Although liming is important to alleviate the acidity of peat soils, increasing the soil pH to > 6.0 depressed the concentration of B and Cu (Graves et al., 1978).

Deficiency of Cu and Zn in peat soils are typified by stunted plant growth, reduced yield and low Cu and/or Zn concentrations in plant shoots, roots or leaves (Adams et al., 1978; Ambak et al., 1991; Graves et al., 1978; Kanapathy, 1972). The need for Cu and/or Zn by crops grown in peat has been attributed to the low concentration and low availability of Cu and/or Zn in peat and its fixation by humic acid (organic matter) rendering the soil Cu and/or Zn unavailable to plants (Szalay, 1969).

2.6.2 Effects on crop growth of Cu and Zn additions to peat soils

Addition of Cu and Zn to peat soils has been found to be either beneficial or to have no effect on crops (Table 2.3). These contrasting results could be due to various factors such as the types of peat soils, plant species, addition of lime, interactions with other micronutrients and the forms of Cu and Zn used in the studies. For example, while application of Cu increased yield in maize (Kanapathy, 1972), carrots (LeBlanc and Gupta, 1994) and rice (Attanandana et al., 1995), application of Zn had little or insignificant effect on yield in

carrots (LeBlanc and Gupta, 1994) and rice (Attanandana et al., 1995) (Table 2.3). However, addition of Cu did not have any significant effect on the dry weights of plant tops in oats and soybean grown in muck in California, and a high level of Cu addition (2,000 mg/kg) induced deficiencies of Fe and P causing a decline in dry weights of the plants (Roth et al., 1971).

Addition of Cu and/or Zn has been reported to increase growth and yield of maize (Ambak et al., 1991; Kanapathy, 1972), tomato (Ambak et al., 1991; Graves et al., 1978), carrots (LeBlanc and Gupta, 1994), lettuce and cucumber (Adams et al., 1978) (Table 2.3). The addition of Cu and/Zn fertilisers also generally increases Cu and/or Zn concentrations in plants. For example, the addition of Cu enhanced the absorption of Cu, Fe, Mn and Zn by sorghum and groundnut as determined by the plant leaf analysis (Chew et al., 1979). The effects of Cu and/or Zn addition on crops grown in peat soils are summarised in Table 2.3.

Table 2.3 Effects of micronutrient additions on plant growth and nutrient uptake on peat soils

Type of Peat Soil	Plant Species	Treatments	Results	References
Peat soil, Malaysia	Maize	Cu application Nine cropping seasons	• ~13.5 kg Cu/ha, an optimum rate for maximum yield, after seven successive crops. • Significant increases in [Cu] in cob leaves at the 3rd and 4th seasons compared to control. • Cu had a very high residual effect, therefore economical to apply once. • Initial application of 13.5 kg Cu/ha, followed by another 13.5 kg/ha in area which still showed signs of Cu deficiency, may last 5-10 years.	Kanapathy (1972)
Virgin sphagnum peat, New Brunswick	Carrots	Cu and Zn application	• 30 kg Cu/ha significantly increased the root yield and leaf [Cu] from 5.3 (untreated) to 12.0 mg/kg • 10 kg Zn/ha Zn did not significantly increase the root yield and leaf [Zn]. • Leaf [Zn] in all treatments was 44-53 mg/kg, within the sufficiency range. • Lack of response to Zn indicates the presence of sufficient amount of Zn in the sphagnum peat during the study period.	Le Blanc & Gupta (1994)
Two organic soils (Histosols).	Hard spring wheat	Banded and broadcast applications of different rates of $CuSO_4$ and Cu chelate (CuHEDTA) Field trials	• Grain yields increased as Cu rate increased in both broadcast and banded applications. • Broadcast application of $CuSO_4$ after planting was effective in correcting Cu deficiency to that of banded application.	Varvel (1983)

Table 2.3 Effects of micronutrient additions on plant growth and nutrient uptake on peat
        soils: Continued

Type of Peat Soil	Plant Species	Treatments	Results	References
Peat muck, California	Oats and soybean	Cu and Ni application	• Cu and Ni treatments had no significant effect on the dry weights of plant tops. • 2,000 mg/kg Cu and 1,800 mg/kg Ni induced deficiencies of Fe and P causing the decline in dry weights of the plants.	Roth et al. (1971)
Peat soils, the United Kingdom	Tomatoes, lettuce and cucumber	Cu & lime application $CuSO_4$	• Application of Cu increased yields by 11% (tomatoes),53% (lettuce) and 48% (cucumbers). • Cu application increased [Cu] in leaves .	Adams et al. (1978)
Peat	Tomatoes	Fritted B, Cu, Fe, Mn, Zn & lime application	• Tomato yield increased by 20-65% with addition of micronutrients. • Leaf [B], [Cu] and [Mn] increased with the amount of micronutrient mixture applied. • Liming to pH > 6.0 depressed the [B] and [Cu].	Graves et al. (1978)
Deep peat soil, Malaysia	Maize and tomato	B, Cu, Fe, Mn, & Zn application	• Growth of maize and tomato was extremely retarded and the yield was very low in the treatment without micronutrient application, probably due to the deficiency in B and/or Cu. • Both [B] (maize shoot: 5.6-6.2 mg/kg; tomato shoot: 15.1-20.4 mg/kg) and [Cu] (maize shoot: 1.2-3.7 mg/kg; tomato shoot: 1.7-4.0 mg/kg) were low or lower than the critical levels (B: 7-30 mg/kg; Cu: 4-5 mg/kg) reported (Adams et al., 1978; Graves et al., 1978).	Ambak et al. (1991)

Table 2.3 Effects of micronutrient additions on plant growth and nutrient uptake on peat
soils: Continued

Type of Peat Soil	Plant Species	Treatments	Results	References
Peat soils, Thailand	Rice	B, Cu, Zn & lime application Pot experiments	• B, Cu, Zn and lime application markedly increased the grain yield and decreased sterility. • Similar straw and grain weights were recorded between single addition of Cu at 40.9 mg/kg and B+Cu+Zn (40+40.9+40 mg/kg, respectively) indicating that [B] and [Zn] in the soils probably sufficient for rice growth. • Mineral dressing with peat, 7.5 cm of mineral soils and NPK fertilisers gave the highest grain yield and the lowest unfilled grain.	Attanandana et al. (1995)
Peat soil, Malaysia	Sorghum & groundnut	B, Cu, Fe, Mn, & Zn application	• Only crops treated with 8.0 kg/ha Cu had a significant increase in dry weight, indicating that the peat soil was able to supply adequate amounts of Fe, Mn, Mo and Zn to meet normal crop requirements. • Cu application enhanced the absorption of Cu, Fe, Mn and Zn by sorghum and groundnut as determined by the plant leaf analysis.	Chew et al. (1979)

[B] – B concentration, [Cu] – Cu concentration, [Mn] – Mn concentration, [Zn] – Zn concentration

Application methods and the form of micronutrients used are also important factors to be considered. The broadcast application of $CuSO_4$ and CuHEDTA after planting was more effective in correcting Cu deficiency in hard spring wheat than banded application at the same rates (Varvel, 1983) (Table 2.3). Varvel's results contradict other reports, perhaps

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because the banded Cu remained in a small zone near the seed and became less available to the growing wheat plant as the actively absorbing roots grew out of that zone (Varvel, 1983). Thus, the effectiveness and the rate of Cu fertiliser needed depend to a large extent on the method of application and the amount of incorporation.

The above studies showed that peat soils are generally deficient in Cu, Zn and other nutrients, and the application of balanced nutrient fertilisers may improve crop yields. The responses obtained on crops grown in peat soils with the addition of Cu and/or Zn fertilisers may indicate that Cu and/or Zn could be the main limiting factor limiting crop growth (Table 2.3). Therefore, Cu and Zn fertiliser application appears to be essential for healthy crop growth on limed peat soils.

2.6.3 Copper and Zn requirements of crops grown in peat soils

Copper and Zn fertiliser requirements for some crops grown in organic soils compared to other soil types are given in Table 2.4. The Cu and Zn fertiliser requirements for crops grown in peat soils are much higher than those for the same crops grown in other soil types. For example, rice grown in peat needs about 8 to 13 kg Cu/ha, more than ten times higher than rice grown in Oxisols, which only requires about 0.8 kg/ha (Table 2.4). Rice grown in peat soils required between 8 to 13 kg Zn/ha, while rice grown in other soils needs 0.9 kg/ha (Table 2.4).

The large differences between Cu and Zn fertiliser requirements for crops grown in peat soils versus other soil types may be due to stronger adsorption capacities of Cu and Zn in peat than in mineral-dominated soils, especially after liming. The high fertiliser requirements could also be due to low mineral concentrations in the available form

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(Andriesse, 1988; Funakawa et al., 1996; Yonebayashi et al., 1994) and low clay contents

in tropical peat soils (to retain nutrients against leaching) (Stevenson, 1994).

Table 2.4 Copper and Zn fertiliser requirement for different crops grown in peat soil and other soil types

Fertiliser	Crop	Fertiliser rate (kg Cu/ha or kg Zn/ha)	
		Peat soils	Other soil types
Copper	Brinjal, French bean and Luffa	4.0 (Chew and Yeong, 1974)	NA
	Tomato	5.1 (Ambak et al., 1991)	NA
	Rice	8.0 (Ambak and Tadano, 1991) 13.6 (Attanandana et al., 1995)	0.8 (Fageria, 2001)
	Barley	8.0 (Ambak and Tadano, 1991) 2.7 to 5.3 (Broadcast) (Varvel, 1983)	0.12 (Foliar) (Varvel, 1983)
	Sorghum and groundnut	8.0 (Chew et al., 1979)	NA
	Cassava	8.8 to 13.5 (Anon, 1975)	NA
	Carrot	11.9 (LeBlanc and Gupta, 1994)	NA
	Oil palm	13.0 (Mutert et al., 1999)	NA
	Maize	13.5 (Kanapathy, 1972) 13.2 (Hochmuth et al., 1999)	0.8 (Fageria, 2001)
Zinc	Tomato	4.5 (Ambak et al., 1991)	NA
	Rice	8.0 (Ambak and Tadano, 1991) 13.3 (Attanandana et al., 1995)	0.90 (Fang et al., 2008)
	Maize	4.5 (Ambak et al., 1991) 8.8 (Hochmuth et al., 1996)	NA
	Barley	8.0 (Ambak and Tadano, 1991)	NA

Note: Method of application – banded onto the soil or otherwise specified. NA, not available

2.7 Summary

Peat soils occupy 13% of the State of Sarawak's total land area. They occur extensively in the easily accessible lowlands. Interest in the agricultural development of these organic soils arose because of their extensive nature, close proximity to population centres and flat topography, limited area of fertile land and the need to increase food production. There are several problems associated with the agricultural reclamation of peat soils, such as subsidence and irreversible drying upon drainage, acidity and micronutrient deficiencies.

Peat soils are low in total and extractable concentrations of Cu and Zn, and deficiencies of both Cu and Zn have been observed in many crops grown in these soils. High rates of Cu and Zn fertilisers need to be applied to ensure sustainable and optimum crop production on these soils. The high requirements Cu and Zn on these soils for are likely due to the strong sorption of these metals by organic matter, particularly in those soils that are limed prior to crop production. Therefore, a study on the sorption and desorption reactions of Cu and Zn in peat soils is important for a better understanding of the potential availability of fertiliser Cu and Zn to crops, and for the estimation of effective rates of fertiliser use. The interaction between added Cu and Zn in fertilisers and the indigenous Cu and Zn in the soils also deserves more study due to the relative affinities of organic matter for these micronutrients.

I therefore developed a series of experiments to examine the retention characteristic of Cu and Zn in a range of peat soils of Sarawak, and examined the response of a representative crop to addition of Cu and Zn fertilisers to these soils in relation to the micronutrient retention characteristics of the soils.

2.8 Aims and Objectives

This thesis had two main objectives; firstly, to determine the adsorption and desorption reactions of Cu and Zn in three tropical peat soils of Sarawak. Experiments were carried out to compare the amounts of Cu and Zn adsorbed and desorbed in natural (unlimed) and limed peat soils. Adsorption data were summarised using the Freundlich equation. In the desorption study, the amounts of Cu and Zn desorbed were compared between two extractants differing in desorption strength, namely diethylene triamine pentaacetic acid (DTPA) and dilute calcium nitrate ($Ca(NO_3)_2$) solutions. Secondly, in a pot experiment, the effects of added Cu and Zn to correct the micronutrient deficiency problems in peat soils were evaluated. Tomato (*Solanum lycopersicum* L.) var. Tiny Tom was used as the test plant.

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Physico-chemical Characterisation, and Response to Lime Addition and NPK Fertilisation

of Three Tropical Peat Soils of Sarawak, Malaysia

3.1 Introduction

3.1.1 Soil characterisation

Despite their many limitations and constraints on crop growth, there has been an increasing demand to develop peat soils for agriculture (Mutalib et al., 1991). Peat soil is very acidic and deficient in nutrients, particularly boron (B), copper (Cu), manganese (Mn) and zinc (Zn) (Mutalib et al., 1991; Tay, 1969; Tie and Kueh, 1979; Yonebayashi et al., 1994a). Under natural conditions, peat soil is flooded and requires drainage before crop cultivation. However, uncontrolled and excessive drainage of peat may result in subsidence and irreversible shrinkage of the peat (Andriesse, 1988; Yonebayashi et al., 1994a). Initial subsidence is mainly caused by compaction and shrinkage due to removal of water by free drainage. Subsequent subsidence is due to decomposition, loss of soluble organic matter through leaching, burning and wind erosion (Tie and Kueh, 1979). The degree of decomposition of organic materials is a very important characteristic that determines the properties of peat soils (Tie and Kueh, 1979).

Peat materials can be characterised in various ways depending on the purpose for which they are being described (Andriesse, 1988). Reclamation of peat requires knowledge of the soil physical and chemical properties, the nature of the peat swamps and peat materials (Andriesse, 1988). An understanding of the peat soil characteristics is important in assisting to maximise yield of crops grown in these soils and improving peat soil management. The characteristics of the surface horizon of the soils are often used to differentiate the

components and properties that will most influence the adsorption-desorption capacity and mobility of metals and their retention by soils (Sparks, 2002).

3.1.2 Liming requirement

Peat soils in Sarawak are very acidic with pH values less than 4.0 and have low nutrient concentrations (Cheong and Ng, 1977; Tie and Kueh, 1979). The high acidity in peats required the use of lime to raise the soil pH because many crops require a pH of over 4.5 for optimum growth and good yield (Andriesse, 1988). Maize, groundnut and cassava grown in a limed peat soil at pH 4.6 had a significantly better yield than those grown in control soils having pH of 3.2 (Tie and Kueh, 1979). The ideal pH value for crops to grow in organic soils is about pH 5.5; higher pH decreases the availability of B, Mn, phosphorus (P) and Zn, while very acidic soils tend to be deficient in B, calcium (Ca), Cu, potassium (K), nitrogen (N) and molybdenum (Mo) (Lucas and Davis, 1961).

The lime requirement of a soil, as measured by most buffer-pH methods, is the amount of liming material required to raise the pH of a given layer to a desired level. In peat soils, a pH rise of 0.1 unit is generally achieved by thoroughly mixing 0.7 tonnes/ha of limestone to a depth of 15 cm (Andriesse, 1988). In Sarawak, an application of 5.0 tonnes/ha of lime was reported to raise the pH from 5.7 to 6.6 (Tie and Kueh, 1979). However, the amount of lime required per unit change of pH varies for different soils depending on exchange characteristics, mineral contents and the depth to which the pH increase is effective (Andriesse, 1988). Therefore, it is necessary to determine lime requirements for each peat soil.

The method commonly used to determine lime requirement is by measuring the changes in pH of a buffer solution in contact with soil (Barrow and Cox, 1990). Many testing

laboratories use buffer solutions to estimate lime requirements, however some of these solutions are not suitable for organic soils as they were developed for mineral soils with different exchange characteristics (Andriesse, 1988). A suitable test using a pH 6.6 buffer containing triethanolamine, acetic acid, ammonium chloride and sodium glycerophosphate has been developed by Mehlich (1942) and liming was recommended if soil pH in the buffer solutions was less than 5.5. Nevertheless, lime recommendations also depend on the crops grown in the soils. Groundnut, soya bean and sweet potato responded to the application of ground magnesium limestone at the rate of 5 to 10 tonnes/ha (Chew, 1971). An application of 7.5 tonnes/ha of ground magnesium limestone had doubled the fresh yield of Napier grass (Kueh, 1972).

Another method of determining lime requirement is the batch method, in which calcium carbonate ($CaCO_3$) is added to simulate field liming. It has often been used to calibrate buffer methods (Bache, 1988). This method has not been tested in laboratories because of the slow lime reaction which may take months to complete and the long term incubation is likely to lead to accumulation of mineral N (Bache, 1988). A quick and simple method of improving the usefulness of lime incubation is to increase the incubation temperature, which minimises microbial activity and increases the rate of the reaction (Barrow and Cox, 1990).

3.1.3 Response to nitrogen, phosphorus and potassium (NPK) fertilisers

Peat soils are known for their extremely low chemical fertility and require adequate fertiliser application in order to be productive (Andriesse, 1988; Tie and Kueh, 1979). Deficiencies of N, P and K in crops grown in these soils have been reported. Crops require adequate amounts of NPK fertilisers to grow and for good yield. Although the total N concentrations in peat soils are generally higher than mineral soils, the amount of available

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N is low (Andriesse, 1988). The low total and available P concentrations in peat soils contribute to P deficiency in crops. Most of the P present in peat is in organic forms and only available for crop uptake after mineralisation (Andriesse, 1988). Most of the K found in peat soils is in available forms but due to the low total concentration, K deficiency becomes severe once several crops have been grown (Andriesse, 1988). In addition, K is easily leached from the soils because of the high rainfall in the tropics (Tie and Kueh, 1979). Based on the situation given above, NPK fertilisers are required for crops grown in peat soils.

The NPK fertiliser requirements of crops vary according to crop type and also the type of peat soils. Application of 140 kg N/ha, 12 kg P/ha and 116 kg K/ha increased tobacco yield grown in peat soils significantly (Anon, 1972). For cassava, applications of 140 kg N/ha and 58 kg K/ha produced significant yield responses while no effect was observed for P at the same rate (Anon, 1975). Legumes respond differently to NPK treatments. In a field experiment, cowpea planted on Sarawak peat soils and treated with inoculants did not respond to N application while plants treated with 24 kg P/ha and 116 kg K/ha had marked responses (Anon, 1973). In a pot experiment, Joseph et al. (1970) obtained responses in tomato grown in peat soils to the application of NPK fertilisers applied at the rates of 72, 40 and 76 mg/kg, respectively. The NPK fertiliser requirements for other crops grown in peat soils are showed in Appendix 1. Based on the published data, the NPK fertiliser rates used for tomato grown in the three peat soils in this study were 50:50:50 kg/ha of N, P and K, respectively.

The basic information currently available on peat soil properties and characteristics are of limited use. Peat soils in most part of Sarawak have not been thoroughly studied in term of their physical and chemical properties. The objectives of this study were:

1. to analyse the physico-chemical characteristics of three tropical peat soils of Sarawak under natural conditions;

2. to determine the rate of $CaCO_3$ required to raise the soils pH to 5.5, which will be used in subsequent adsorption/desorption and fertiliser response experiments; and

3. to determine the growth response of tomato to the application of NPK fertilisers to verify whether basal fertilisation of the soils is required in subsequent growth chamber experiments examining growth responses of tomato plants to the addition of Cu and Zn fertilisers.

3.2. Materials and Methods

3.2.1 Location of soils sampled

Loagan Bunut is located in Miri, Sarawak, covers an area of 10,736 hectares and at the centre of the park is a lake that occupies about 650 ha surrounded by tropical peat swamps to the east, north and south and the Tinjar River to the west (Figure 3.1). The three studied sites, namely Mixed swamp forest (MSF), Alan forest (AF) and Padang Alan forest (PF) sites were located along a traverse line across this same peat basin (Figure 3.2). The site is located between latitudes 3º 47'31.0''N and 3º 47'50.6''N and longitudes 114º 14'06.7''E and 114º 13'32.4''E (Melling et al., 2008).

Figure 3.1 Map showing the location of Loagan Bunut , Miri, Sarawak.

NOTE:
This figure is included on page 54
of the print copy of the thesis held in
the University of Adelaide Library.

Figure 3.2 The cross-section of three different forest types of peat at Loagan Bunut, Miri, Sarawak (Melling et al., 2008).

3.2.2 Peat soil samples

At each site, a pit was dug to a depth of one metre (m) and the peat profiles are shown in Figure 3.3. The surface layers (0-25 cm depth) of three deep peat soils (Mixed swamp forest (MSF), Alan forest (AF) and Padang Alan forest (PF), named after the sites) were collected. This depth was chosen because it is the important root growth depth and the most

decomposed layer of the peat. The peat samples for the determination of soil physical and chemical characteristics were air-dried to approximately 70% moisture, ground and sieved to < 2 mm and then stored prior to analysis. For the pot experiments, the soils were moistened to 50% field capacity.

NOTE:

This figure is included on page 55 of the print copy of the thesis held in the University of Adelaide Library.
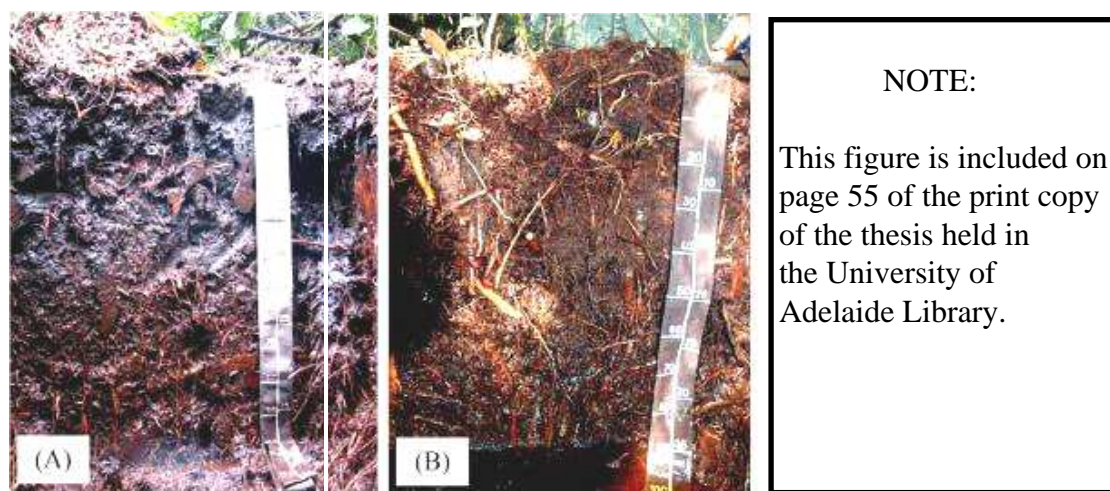
Figure 3.3 Soil profiles of Mixed swamp forest (A), Alan forest (B) and Padang Alan forest (C) (Melling et al., 2008).

3.2.3 Peat soil physical and chemical analyses

All of the following analyses, except for bulk density were carried out in the laboratory in the University of Adelaide, Australia. The bulk density was determined at the Tropical Peat Soil Research Unit Laboratory in Sarawak, Malaysia. The soil has not been sterilised before importation, thus assuming no major implication on nutrient transformations and uptake. Appropriate import permit was obtained from the Australian Quarantine and Inspection Services (AQIS) before bringing in the soils to Australia.

Undisturbed core samples (100 cm^3) were taken in duplicate from the profile face by horizontal insertion for the determination of bulk density (Melling et al., 2008). Maximum water holding capacity (MWHC) was measured using the tension plate method at 10 Kpa (Marshall and Holmes, 1979). Moisture content in the soils was determined by drying the

samples in the oven at 105 ℃ until constant weight was reached. The loss of ignition was determined by heating the oven-dried samples to 1,000 ℃ for one hour. Soil pH was determined with a pH electrode in 1:5 soil-to-water ratios. The organic carbon (C) content was determined by the LECO Carbon Analyzer. Total N was measured using a LECO Nitrogen Analyzer. The cation exchange capacity (CEC) was determined by leaching the soil with 1M ammonium acetate (NH_4AOc) at pH 7.0 (Thomas, 1982). Concentrations of aluminium (Al) and iron (Fe) oxides were determined using a sodium dithionite-citrate (NaDC) and ammonium oxalate (NH_4Ox) methods (McKeague and Day, 1966). The soils were digested in a 1:3 mixture of concentrated nitric acid (HNO_3) and hydrochloric acid (HCl) and analysed for total metal concentrations using inductively coupled plasma-optical emission spectroscopy (ICP-OES) or inductively coupled plasma-mass spectroscopy (ICP-MS). Iron, Al and Mn were determined in the extract by ICP-OES.

3.2.4 Liming requirement experiment

The liming material used in the incubation was pure $CaCO_3$. Approximately 100 g of < 2 mm air dried soil was weighed into a 500 ml plastic container. Eight lime treatments were added to the three soils (in triplicate) at rates of 0, 0.10, 0.25, 0.50, 1.0, 1.50, and 2.50 g $CaCO_3$ per 100 g soil, and mixed thoroughly (equivalent to $CaCO_3$ rates of 0, 0.4, 1.0, 2.0, 4.0, 6.0 and 10 tonnes/ha, assuming soil at 0 – 25 cm depth). The soils were then moistened to 50% water holding capacity or to about the sticky point. The soils were then incubated in an incubator at 40 °C for 14 days. Soil pH was determined on 10 g subsamples by suspending in 50 ml of deionised water and shake for one hour. One ml of 0.5 M calcium chloride ($CaCl_2$) were then added, shake for 30 seconds to resuspend the soil and then allow the solids to settle for 20 minutes and measure the pH in the supernatant solution using an Orion pH meter and a glass electrode. Values for 'Zero' time were obtained by adding 0.5 M $CaCl_2$ solution to air-dried soil and $CaCO_3$ at different levels and measuring the pH immediately.

3.2.5 NPK requirement study procedure

A pot experiment was conducted in a controlled growth chamber using tomato (*Solanum lycopersicum* L.) variety Tiny Tom as a test plant. The chamber temperature was set at 22 ºC day and 16 ºC at night. The tomato variety used in this experiment was suitable for late winter to early spring climatic conditions. Therefore, this temperature regime was deemed appropriate. Nitrogen, P and K were applied to the soils as analytical reagent (AR) grade ammonium sulphate [$(NH_4)_2SO_4$], ammonium phosphate [$(NH_4)HPO_4$], and potassium phosphate [(K_2HPO_4)], respectively. Nitrogen, P and K were applied to all soils at the rates of 125, 167 and 154 mg/kg soil, respectively. Each pot was filled with 250 g of soil. The soils were pre-treated with $CaCO_3$ at the rates of 18.7, 16.9 and 18.3 g $CaCO_3$ per kg for MSF, AF and PF soil, respectively. All treatments were replicated three times. The selected lime rates were based on a pilot liming study and aimed to raise soil pH to 5.5 (see Section 3.2.4).

The limed peat soils were incubated at 50% MWHC for two weeks at 40 ºC. Seeds of tomato var. Tiny Tom were germinated in between moist filter papers for four days before sowing (Appendix 2). The germinated seedlings were transplanted to individual pots just below the soil surface at a sowing density of three seedlings per pot and thinned to two plants per pot after one week. Throughout the experiment, the soil moisture was maintained at approximately 50% field capacity by daily addition of deionised (DI) water. The tomato plants were harvested once they showed deficiency symptoms such as the yellowing of the leaves and stunted growth, which happened about 14 to 21 days after planting. Plant shoots were cut off one centimetre above the soil surface, rinsed three times with distilled water and dried in an oven at 70 ºC to a constant weight. Dried shoots were ground to pass through a 0.5 mm sieve and digested in concentrated nitric acid (HNO_3). Total metal concentrations in the digest solutions were determined by ICP-OES or ICP-MS. Soil

samples were taken from the pots, air-dried, ground and sieved through a 2 mm sieve. The sieved soils were digested in a 1:3 mixture of concentrated HNO_3 and HCl and total elemental concentrations in the digest solutions analysed by ICP-OES or ICP-MS.

3.2.6 Statistical analysis

Analysis of variance (ANOVA) and tests of least significant difference were conducted using Genstat (10th edition). The relationship between the soil pH and lime rates were described by regression analysis. The amounts of $CaCO_3$ required to raise the soil pH to 5.5 were estimated using the regression equations.

3.3 Results and Discussion

3.3.1 Peat soil physical and chemical properties

The three peat soils used in this study were classified as deep peat, as peat depth was more than 2.5 m (Melling et al., 2008). The bulk density of the three soils was very low, between 0.12 and 0.16 g/cm^3 (Table 3.1). The reported mean bulk densities for Sarawak peat soils are between 0.09 and 0.12 g/cm^3 (Driessen and Rochimah, 1976). The bulk densities are low compared to mineral soils because of the low particle density and high porosity. Bulk density measurements are important in interpreting soil analytical data, particularly those indicating concentrations of available nutrients, and the values depend on the amount of compaction, composition of the materials, the degree of decomposition and the mineral and moisture contents at the time of sampling (Andriesse, 1988).

Table 3.1 Physical and chemical properties of the peat soils (0 -25 cm depth)

Parameter	Soil Type[a]		
	MSF	AF	PF
pH (H_2O)	3.37	3.40	3.33
Bulk density (g/cm^3)	0.16	0.12	0.13
Loss of ignition (%)	96.45	97.30	96.52
Moisture content (%)	69.80	71.80	71.25
Maximum water holding capacity (%)	272	303	322
Total organic carbon (%)	60	59	63
Total nitrogen (%)	1.94	1.90	1.83
C/N ratio	30.9	31.1	34.4
Cation exchange capacity (cmol(+)/kg)	46.0	45.0	50.0
Total P (mg/kg)	194.5	149.0	115.0
Total K (mg/kg)	55	73	68
Total Ca (mg/kg)	241	195	204
Total Mg (mg/kg)	191	144	160
Total Cu (mg/kg)	3.19	2.77	2.19
Total Zn (mg/kg)	10.97	10.68	10.08
Total Fe (mg/kg)	296	106	131
Total Mn (mg/kg)	4.21	1.77	3.10
Total B (mg/kg)	5.00	5.50	5.00
Total Na (mg/kg)	32.0	23.5	28.5
Total S (mg/kg)	440	314	296
Total Mo (mg/kg)	<LR	<LR	<LR
Sodium dithionitecitrate (NaDC)			
Al oxides (mg/kg)	<300	<300	<300
Fe oxides (mg/kg)	<300	<300	<300
Mn oxides (mg/kg)	<300	<300	<300
Ammonium oxalate (NH_4Ox)			
Al oxides (mg/kg)	683	504	742
Fe oxides (mg/kg)	683	400	344
Mn oxides (mg/kg)	<150	<150	<150

[a] Mixed swamp forest (MSF), Alan forest (AF), Padang Alan forest (PF)

The moisture contents and maximum water holding capacities in the soils in this study were high, ranging from 69 to 72%, and 272 and 322%, respectively (Table 3.1). The reported water holding capacity for peat in Borneo is between 275 and 322%, which is considered low relative to cultivated peat (Andriesse, 1988). The moisture content of organic soils is influenced by the structure of the peat profile and is important in the reclamation of the soils, especially in designing efficient drainage layouts (Andriesse, 1988; Tie and Kueh, 1979).

All three peat soils were very acidic with the pH of the soils ranging from 3.33 to 3.40 (Table 3.1). Most lowland tropical peats are acidic with a pH range in water of 3.0 to 4.5 and in the presence of pyritic material the pH can reach values of less than 2.0 (Mutalib et al., 1991; Tie and Kueh, 1979). The pH of organic soils is related to the presence of organic compounds, the exchangeable hydrogen and aluminium (Al), iron (Fe) sulphide and other oxidisable sulphur (S) compounds (Anderson, 1964; Andriesse, 1988). The organic matter content of the three peat soils was between 96 and 97% as indicated by the values for loss on ignition (LOI). Loss on ignition has been established as a quick method to determine the amount of mineral matter in an organic soil. For tropical peats consisting of pure organic materials, an ash percentage of around one percent is common (Andriesse, 1988). The cation exchange capacity (CEC) of the three peat soils was between 45 cmol(+)/kg and 50 cmol(+)/kg (Table 3.1). The high CEC value in peat soils depends on the soil pH (Andriesse, 1988).

The Al and Fe oxide contents determined using NH_4Ox varied between 504 and 683 mg/kg, and 344 and 683 mg/kg, respectively (Table 3.1). The Mn oxide contents were less than 150 mg/kg when this extractant was used. Less than 300 mg/kg Al, Fe and Mn oxides were measured when NaDC was used as the extractant. The NH_4Ox extracted more Al and Fe

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than NaDC, indicating lower levels of non-crystalline oxides than crystalline oxides in the peat soils. The comparison of NH_4Ox and NaDC extractable Al and Fe has been useful in distinguishing Bf horizons in Canadian soils (McKeague and Day, 1966). Iyengar et al. (1981) found that in six Virginia soils treated with NH_4Ox in the dark, lesser amounts of Al and Fe oxides were extracted than soils treated with NaDC. The concentrations of Al and Fe oxides in the peat soils were lower than the reported concentrations for Al and Fe oxides in other soil types. For example, the concentrations of Al treated with NH_4Ox in the dark in six Virginia soils ranged from 1,000 to 2,200 mg/kg and for Fe the concentrations were between 500 and 5,000 mg/kg (Iyengar et al., 1981). Buchter et al. (1989) investigated metal sorption in eleven soils includes spodosols and found that for a given solution metal concentration, soils with high pH or high CEC or those that contained high concentrations of Al and Fe oxides retained more metal than did low pH or low CEC or soils with low concentrations of metal oxides. Khan et al. (2005) had reported that oxide components contributed significantly to retention of Cu in three out of five pasture soils. Based on those studies, the concentrations of Al and Fe oxides in peat soils is likely to influence Cu and Zn sorption reactions.

The total organic C and total N content ranged from 59 to 63% and 1.83 to 1.94%, respectively. Determination of organic C and N content in peat soils is of considerable importance to agriculture, particularly for calculating the C/N ratio of the peat (Andriesse, 1988). The C/N ratio indicates the degree of humification of the peat and the likelihood of N consumption by micro-organisms when the peats are fertilised on reclamation (Tie and Kueh, 1979). Generally, residues with low N content or wide C/N ratios have slow decomposition rates (Anderson, 1964). The C/N ratio of deep tropical peat is low compared to temperate peat due to the high lignin content derived from tree remains (Tie and Kueh, 1979). The C/N ratio for the three soils used in this study ranged from 30.9 to 34.4. The

reported C/N ratios for peat soils in Sarawak are between 20.1 and 35.0 (Tie and Kueh, 1979). In tropical organic soils, C/N values greater than 16 are regarded as indicative of soils where nitrogen stress will form a constraint to crop growth (Andriesse, 1988).

The total P contents of the three peat soils ranged from 115 to 194 mg/kg (Table 3.1). The reported total P concentrations in peat soils of Sarawak ranged between 400 and 1,000 mg/kg (Tie and Kueh, 1979). Total P concentrations in tropical peat soils have been found to decrease with increasing depth, and with distance from the coast (Andriesse, 1988). Concentrations of trace elements in peat soils are generally low, and low in nutrient availability for most crops. The peat soils of Sarawak were classified as oligotrophic peat because of their low nutrient concentrations (Andriesse, 1988; Yonebayashi et al., 1994b). Ahmed and Ng (1973) reported mean concentrations of Cu, Fe, Mn and Zn in a selection of peat soils in Sarawak to be 1, 49, 43 and 14 mg/kg, respectively (Ahmed and Ng, 1973). The concentrations of total sulphur (S) in the three peat soils ranged from 296 to 440 mg/kg. Total S concentration up to 1,000 mg/kg have been reported in oligotrophic peats (Lucas, 1982). Sulphur concentrations are often high because of the presence of sulphidic materials e.g. pyrite (FeS_2) and other Fe sulphides (Andriesse, 1988).

Calcium and Mg are usually not deficient in tropical peats. However, high levels of K and sodium (Na) may induce Ca and Mg deficiencies (Andriesse, 1988; Tie and Kueh, 1979) probably due to competition for uptake by plants. In the three peat soils studied, the concentrations of total Ca ranged from 195 to 241 mg/kg and total Mg between 144 and 191 mg/kg. In peat soils of Malaysia, the concentrations of total Ca ranged from 40 to 2,600 mg/kg and total Mg between 110 and 3300 mg/kg (Funakawa et al., 1996; Yonebayashi et al., 1994a). The concentrations of K in these peat soils ranged from 55 to 73 mg/kg. The concentrations of K reported previously were between 200 and 5,280 mg/kg (Funakawa et

al., 1996; Lucas, 1982; Yonebayashi et al., 1994a). The Na concentrations in the three soils were between 24 and 32 mg/kg. These values are relatively low compare to the published data of 800 to 1000 mg Na/kg soil due to distance from coast (Funakawa et al., 1996; Lucas, 1982). As can be seen, there is a wide variation in the total mineral concentrations in these peat soils. These differences could probably due to the soil type, sampling depth and types of vegetation. Andriesse (1988) attributed the variation in the mineral concentrations to environmental conditions which change the various layers of peat deposits during peat formation.

3.3.2 Liming requirements of the peat soils

The effect of liming on the soil reaction of the surface layers of the three peat soils is given in Figure 3.3. The pH increased significantly ($P \leq 0.05$) with the increased lime rates. The relationships between the soil pH and rate of $CaCO_3$ added were generally linear with correlation coefficients (R^2) between 0.98 and 0.99. All three peat soils showed the same response to lime addition. The amount of lime required to attain pH 5.5, as determined from the regression equations were 18.7, 16.9 and 18.3 g $CaCO_3$/kg soil which are equivalent to 7.48, 5.07 and 5.94 tonnes/ha for MSF, AF and PF soils, respectively, assuming 0 to 25 cm depth. These values are within the range with some of the data reported previously for peat soils. It had been reported that an application of 5 tonnes/ha of lime raised the soil pH from pH 5.7 to 6.6 of some peat soils of Sarawak (Andriesse, 1988). Similar rates of lime application (5 – 10 tonnes/ha) have given substantial yield responses in many plants grown in peat soils (Ambak et al., 1991; Chew, 1971; Tie and Kueh, 1979).
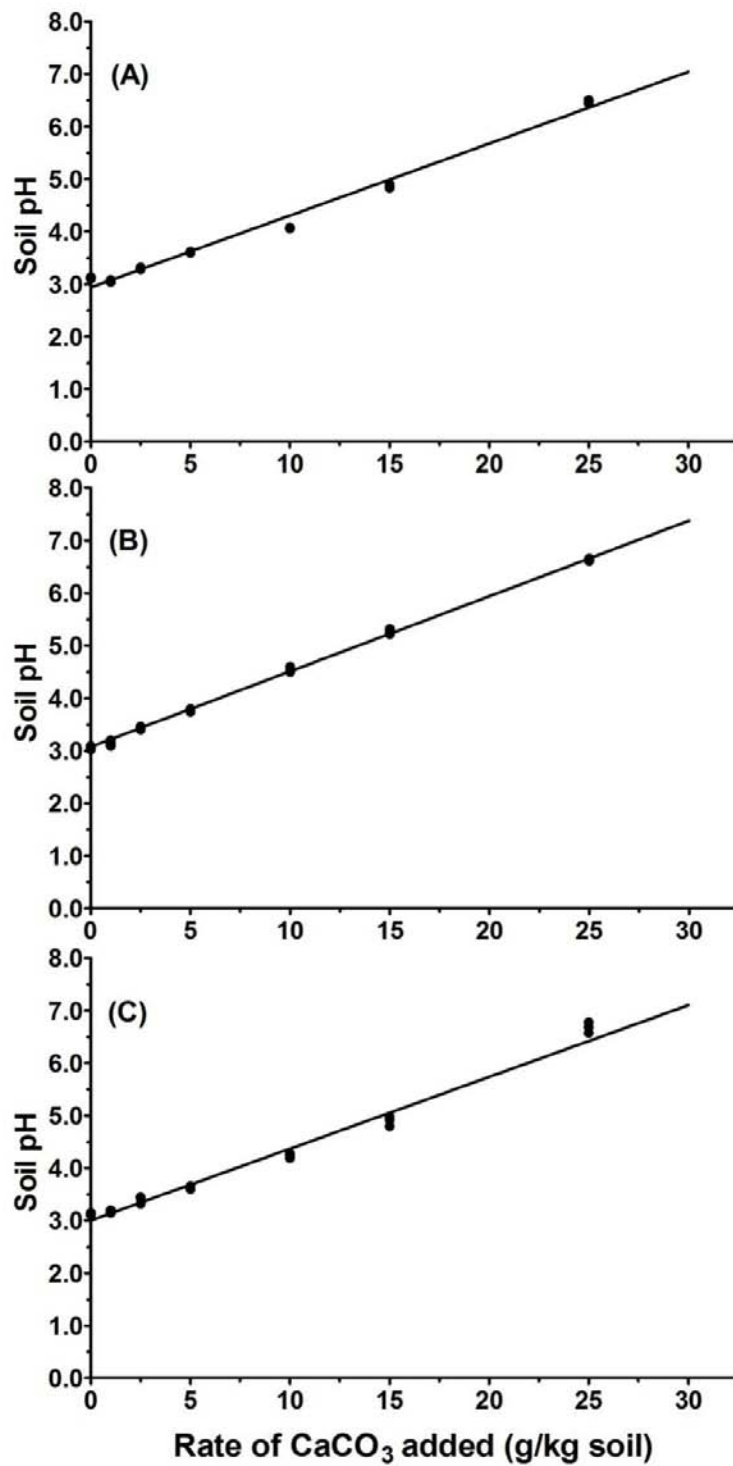
Figure 3.4 Changes in soil (0-25 cm depth) pH values as a function of the rate of applied lime. The peat soils were A (Mixed swamp forest; $y = 0.136x + 2.96$, $R^2 = 0.987$), B (Alan forest; $y = 0.145x + 3.05$, $R^2 = 0.998$) and C (Padang Alan forest; $y = 0.14x + 2.99$, $R^2 = 0.985$).

3.3.3 Responses of tomato to NPK fertilisers

Deficiency symptoms were observed in control limed soils between eight and 14 days after emergence, but not in the NPK-treated pot (Figure 3.4). Without the application of NPK, deficiencies became so acute that plants failed to tiller and their growth was stunted. Even plants receiving NPK fertiliser had slow growth and the leaves were small and light green to yellowish green to pale yellow.

Figure 3.5 Comparison between tomato plants without NPK fertilisers (A) and with NPK fertilisers (B) application at two weeks after transplanting.

Plants receiving NPK fertilisers produced significantly greater shoot dry weights ($P \le 0.05$) than those in unfertilised control soils (Figure 3.5). In the absence of NPK fertilisers, shoot dry weights were 13, 15 and to 17 times lower than those receiving NPK treatments in MSF, AF and PF soils, respectively. The results from this study indicated that without the application NPK fertilisers, plant growth on peat soils is poor and will result in crop failure.
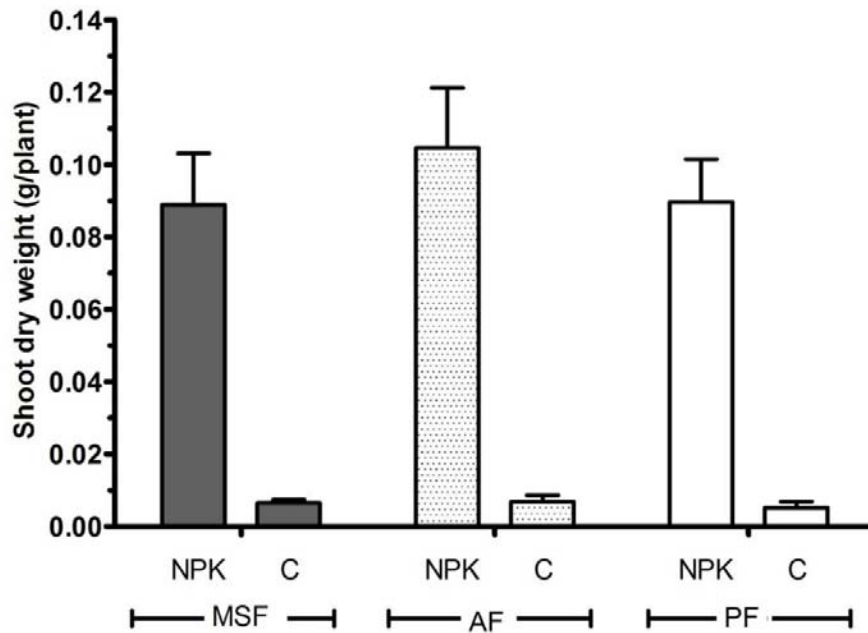
Figure 3.6 Comparison of shoot dry weights in three peat soils in different treatments. Data represent mean ± SD (standard deviation) of shoot dry weights. The soils were Mixed swamp forest (MSF), Alan forest (AF), Padang Alan forest (PF). NPK denotes nitrogen, phosphorus, and potassium application and C denotes control (without NPK).

Nutrient analysis of the leaf tissue provided clues as to the likely deficiencies. The concentrations of K in the tomato leaves in two of the soils (MSF and PF) were marginal (Table 3.2) and indicate that the K rate applied on these two soils was not sufficient for healthy growth. Boron, Cu, Mn and Zn concentrations in the leaves were also marginal, suggesting deficiencies of these nutrients. Although there were relatively large variations in leaf concentrations of Ca, Fe, Mg and P (Table 3.2), the concentrations were adequate and did not suggest any deficiencies.

Table 3.2 Nutrient concentrations in tomato leaves

Element	Soil types[a]			Adequate level[b]
	MSF	AF	PF	
Phosphorus, P (%)	0.87	0.76	0.63	0.65 - 1.20
Potassium, K (%)	2.50	3.33	4.08	4 - 6
Calcium, Ca (%)	3.08	1.51	1.62	1.5 – 2.5
Magnesium, Mg (%)	0.38	0.50	0.63	0.4 – 0.8
Copper, Cu (mg/kg)	3.1	2.7	6.1	5 -15
Zinc, Zn (mg/kg)	27.9	26.2	20.6	30 - 200
Manganese, Mn (mg/kg)	35.2	41.8	41.0	50 - 500
Iron, Fe (mg/kg)	119.3	157.6	147.1	100 - 300
Boron, B (mg/kg)	36.7	39.5	70.2	40 - 100

[a] MSF – Mixed swamp forest, AF – Alan forest, PF – Padang Alan forest; [b] Source: Reuter and Robinson (2002); Not enough samples for N determination.

3.4 Conclusions

The peat soils used in this study had low bulk densities and high water holding capacities compared to mineral-dominated soils. The organic matter content was high (> 90%) and mineral content low, compared to other types of soils. The soils were very acidic and had low concentrations of nutrients and alkaline earth cations and high C/N ratios. For organic soils, the soil properties are of particular relevance to the reclamation, development and management of the soils. Based on the soil physical and chemical properties determined, the capability of reclaimed peat land to support cropping was considered to be rather limited, especially under low input management.

Liming is required to bring soil pH values up to desired levels in these soils. Due to the low pH of the peat soils used in this study, large amounts of lime were required to substantially increase the pH. The liming rates required to raise the pH to 5.5 were between the

equivalent of 5.07 and 7.48 tonnes/ha. These liming rates will be used in subsequent adsorption/desorption (Chapter 4) and fertiliser response (Chapter 5) studies.

The addition of NPK fertilisers at the rates equivalent to 50:50:50 kg/ha produced dramatic growth responses in tomato, indicating the very poor macronutrient status of all three soils. Basal dressings with NPK fertilisers are evidently a pre-requisite for crop growth in these soils. Chemical analysis of soils indicated high concentrations of total N, but due to the wide C/N ratio and/or the type of organic-N, the N was not available for plant uptake. Concentrations of Cu and Zn in leaf tissue were especially lower, indicating the poor availability of these elements in peat soils. Additions of Cu and Zn fertilisers are likely to be essential in the reclamation and agricultural use of these soils.

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Sorption and Desorption of Copper and Zinc in

Tropical Peat Soils of Sarawak, Malaysia

Chapter 4 was written in a manuscript style and submitted to Geoderma. The format for the

journal is attached in Appendix 3.

SORPTION AND DESORPTION OF COPPER AND ZINC IN THREE TROPICAL PEAT SOILS OF SARAWAK, MALAYSIA

M. Abat, M.J. McLaughlin, J.K. Kirby, S.P. Stacey

Soil Science, School of Agriculture, Food and Wine,
Waite Research Institute, University of Adelaide,
PMB 1, Glen Osmond, SA 5064, Australia

Text in manuscript

STATEMENT OF AUTHORSHIP

SORPTION AND DESORPTION OF COPPER AND ZINC IN THREE TROPICAL PEAT SOILS OF SARAWAK, MALAYSIA

Text in manuscript

ABAT, M. (Candidate)
Planned and carried out the experiment, analysed and interpreted the data, wrote the manuscript and acted as the corresponding author

I hereby certify that the statement of contribution is accurate

Signed: ……………………………………….. Date: ……………….

McLAUGHLIN, M.J.
Provided comments on the planning of the experiment, assisted in the data interpretation and provided critical evaluation on the manuscript

I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the manuscript in the thesis

Signed: ……………………………………….. Date: ……………….

KIRBY, J.K.
Provided comments on the planning of the experiment, assisted in the data interpretation and provided critical evaluation on the manuscript

I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the manuscript in the thesis

Signed: ……………………………………….. Date: ……………….

STACEY, S.P.
Provided comments on the planning of the experiment, assisted in the data interpretation and provided critical evaluation on the manuscript

I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the manuscript in the thesis

Signed: ……………………………………….. Date: ……………….

Sorption and Desorption of Copper and Zinc in Tropical Peat Soils of Sarawak, Malaysia

Margaret Abat[a,*], Michael J. McLaughlin[a,b], Jason K. Kirby[b], and Samuel P. Stacey [a]

[a]Soil Science, School of Agriculture, Food and Wine, University of Adelaide, PMB 1, Glen Osmond, SA 5064, Australia.
[b]CSIRO Sustainable Agriculture Flagship, PMB 2, Glen Osmond, SA 5064, Australia.

[*]Corresponding Author: Margaret Abat
Address: Soil Science, School of Agriculture, Food and Wine, University of Adelaide, PMB 1, Glen Osmond, SA 5064, Australia.
Telephone number: +61 8 8303 6519
Fax number: +61 8 8303 6511
Email: margaret.abat@adelaide.edu.au

Abstract

Tropical peat soils are inherently deficient in micronutrients, particularly copper (Cu) and zinc (Zn). In addition, limited information is available on the sorption and desorption of these micronutrients in these soils, which are important factors governing nutrient concentrations in the soil solution and nutrient availability to plants. A study was carried out to quantify sorption and desorption of Cu and Zn in three untreated and limed tropical peat soils of Sarawak, Malaysia. Copper and Zn sorption increased gradually with increasing levels of added Cu and Zn in both control and limed soils. The sorption of Cu and Zn in limed soils was 50 and 67 fold, respectively, that of control soils. The Freundlich coefficient (K_F) values for Cu in both control and limed peat soils were higher than for Zn indicating that Cu is more strongly sorbed to the soil solid phase than Zn. The K_F values for Cu and Zn in this study were higher than those reported for other soil types. The percentage of sorbed Cu and Zn susceptible to desorption into 5 mM DTPA was higher than that desorbed by 10 mM $Ca(NO_3)_2$ in all soils. A higher percentage of Cu than Zn was desorbed by DTPA than Zn because Cu has a higher critical stability constant with DTPA. Liming is necessary to increase the pH of peat soils but it also inevitably decreases the solubility and hence the bioavailability of Cu and Zn. This study provides evidence on the importance of sorption and desorption data for estimating nutrient availability for plant uptake in tropical peat soils.

Keywords: Sorption, Desorption, Copper, Zinc, Tropical Peat Soils

1.0 Introduction

Tropical peat soils occupy an area of 2.7 million hectares (Mha) in Malaysia, which account for about 8% of the country's total land area (Mutalib et al., 1991). About 1.7 Mha of these peat soils are found in the State of Sarawak, which is equivalent to 13% of the State's total land area (Tie and Kueh, 1979). The soils are an important natural resource, which has been earmarked for future development. Large areas have been, and are being cleared for agricultural activities such as oil palm plantations because of their expected high economic returns (Melling et al., 2007), and a number of short-term cash crops, such as watermelon, honey dew and vegetables.

However, peat soils have been regarded as problematic soils. Generally, the soils in their natural state are not suitable for the cultivation of most crops because of high acidity, ranging from pH 3.0 to pH 4.0 (Wong, 1991), and low levels of available nutrients (Cheong and Ng, 1977). The application of lime prior to planting helps to reduce the acidity problem but it might also affect the availability of essential nutrients, especially micronutrients. Deficiencies of micronutrients, in particular copper (Cu) and zinc (Zn), are a problem in agricultural peat soils (Tie and Kueh, 1979), and are attributed to either low native amounts of these essential elements, or strong complex formation with the solid phase of soil organic matter (Stevenson, 1982). Andriesse (1988) has suggested that humified organic matter in these soils might form solid-phase complexes with metal ions and make the nutrients less available, leading to micronutrient deficiencies in crops. Thus, both Cu and Zn fertilisation is important to meet the nutrient requirements of crops planted in peat soils, especially those limed to overcome the inherent acidity. However, application of Cu and Zn as trace elements in peats has failed to ameliorate the deficiency problem because the applied Cu and Zn may react with inorganic and organic compounds within the soils (James and Barrow, 1981; McBride, 1981). Adsorption and/or sequestration of these micronutrients

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with soil organic matter is a likely cause of the low availability of the added micronutrients (Brennan et al., 1983; Khan et al., 2005; Spathariotis and Kallianou, 2007).

Adsorption reactions are important as they determine micronutrient availability to plants and their mobility throughout the soil (Covelo et al., 2006). These reactions, rather than precipitation reactions, are most likely to control concentrations of micronutrients in soil solution of soils amended with soluble micronutrients, and hence their bioavailability and toxicity (Swift and McLaren, 1991). Adsorption reactions of Cu and Zn in soils have been widely studied (Covelo et al., 2004; Covelo et al., 2006; McLaren and Crawford, 1973; McLaren and Crawford, 1983; McLaren et al., 1981; Spathariotis and Kallianou, 2007). However, most of these studies have focused on mineral-dominated soils in temperate countries. Limited information is available on the adsorption of Cu and Zn in tropical peat soils (Naganuma et al., 1993; Yonebayashi et al., 1994; Zhang et al., 2006) which determines the rates of these micronutrients that need to be applied to overcome inherent deficiencies.

The availability of micronutrients in soils is also affected by desorption, and the extent to which added micronutrients are strongly retained against subsequent desorption. Desorption has been studied using extractants such as acids or complexing agents to simulate the possible physico-chemical reactions involved in micronutrient acquisition by plants (Marschner, 1997), and using weak salt solutions. Hysteresis of adsorption/desorption relationships provides an indication of the strength of retention of micronutrients by soil surfaces (Brummer et al., 1983; Wu et al., 1999). For example, diethylene triamine pentaacetic acid (DTPA) appears to be the most widely used desorption agent to measure bioavailable micronutrient cations in soil (Lindsay and Norvell, 1978). However, Lindsay and Norvell (1978) found that DTPA was an ineffective chelator for Cu and Zn in soils between pH 5.8 and 6.2, but became more effective with rising pH. The Cu-DTPA and Zn-DTPA complexes were expected to be stable in alkaline and calcareous

soils, moderately stable in slightly acid soils, and unstable in acid soils (Norvell and Lindsay, 1972). In addition, the use of high concentrations of organic extractants is likely to substantially enhance the amount and rate of desorption and faster desorption than would be likely under normal soil conditions (McLaren et al., 1998). Desorption into a weak electrolyte solution such as calcium nitrate ($Ca(NO_3)_2$) is likely to simulate metal desorption into soil solution by plant uptake more than the use of strong chelators. While we know that organic matter can strongly retain Cu and Zn, there have been limited studies to determine if Cu and Zn sorbed to organic matter is easily desorbed, and hence potentially available for plant uptake.

Hence, the objectives of this study were to

1) measure the sorption of Cu and Zn in three untreated and limed tropical peat soils of Sarawak, and

2) evaluate the ease of desorption of these micronutrients once sorbed.

2.0 Materials and Methods

2.1 Soil collection

The soil samples were collected from the Loagan Bunut National Park in Miri, Sarawak, Malaysia. The park covers an area of 10,736 hectares (ha) and at its centre is a lake, which occupies about 650 ha, surrounded by tropical peat swamps to the east, north and south, and the Tinjar River to the west. The surface layers (0–25 cm) of the three peat soils, identified as Mixed swamp forest (MSF), Alan forest (AF) and Padang Alan forest (PF) (Melling et al., 2008), were used in this study. The soil samples were air-dried to approximately 30% moisture content, ground, sieved to < 2 mm, and stored at 25 ^{o}C prior to analysis.

2.2 Soil analysis

Soil pH was measured with a glass electrode in calcium chloride ($CaCl_2$) using a 1:1 v/v (soil:solution suspension) (Rayment and Higginson, 1992). Moisture content was determined by drying the soil overnight at 105 ℃ (Rayment and Higginson, 1992). Maximum water holding capacity was determined using the tension plate method at 10 kPa (Marshall and Holmes, 1979). Bulk density was determined by taking undisturbed core samples for measurement of volume at the laboratory using a soil volume analyzer (Model DIK-1110, Daiki Rika Kogyo Co. Ltd) (Melling et al., 2007). Total organic carbon was measured by a Leco Carbon Analyzer. Total nitrogen was analysed using a Nitrogen Analyzer. Cation exchange capacity (CEC) was determined using the 1 M ammonium acetate method at pH 7.0 (Thomas, 1982). Available Cu and Zn were determined by extracting 10 g of soils with 30 mL 5 mM DTPA buffered to pH 7.3, shaken for two hours then centrifuged at 2,500 RCF for 10 minutes, filtered through Whatman No. 42 filter paper (Lindsay and Norvell, 1978; Rayment and Higginson, 1992) and quantified using inductively coupled plasma-optical emission spectroscopy (ICP-OES) or inductively coupled plasma-mass spectroscopy (ICP-MS). Total metal concentrations were determined by digesting the soils in an *aqua regia* mixture of concentrated nitric acid (HNO_3) and hydrochloric acid (HCl) at the ratio of (1:3 ratio) and analysed by ICP-OES or ICP-MS (Zarcinas et al., 1996). Aluminium (Al), iron (Fe) and manganese (Mn) oxides were extracted using both the ammonium oxalate and dithionite-citrate methods (McKeague and Day, 1966). Soil particle size was determined by the wet sieving and the pipette methods (Gee and Bauder, 1986). All analyses were performed in triplicate.

2.3 Sorption procedures

Both natural pH (control) and lime-amended peat soils were compared. Calcium carbonate ($CaCO_3$) was used to raise the soil pH from pH 3.3 to a pH of 5.5 because the acidic condition of the tropical peat soils is not suitable for most economically important crops. In fact, many crops require a soil pH of over 4.5 for their optimum growth (Andriesse, 1988).

Sorption isotherms for Cu and Zn were obtained on the three selected soils using batch equilibrium experiments at 25 ^{o}C. The spiking solutions were prepared in 0.01 M $Ca(NO_3)_2$ as a background electrolyte, with increasing additions of Cu (control: 0 to 2.5 mg Cu/g soil and limed: 0 to 11 mg Cu/g soil) as copper nitrate ($Cu(NO_3)_2$) and Zn (control: 0 to 2.5 mg Zn/g soil and limed: 0 to 12.5 mg Zn/g soil) as zinc nitrate ($Zn(NO_3)_2$). Soil (2.5 g) was placed in 50 mL centrifuge tubes and 25 mL of Cu or Zn spiking solution was added, a drop of toluene was added to each tube to inhibit microbial activity and then the tubes were shaken end-over-end for 72 hours. After this equilibration period, the samples were allowed to settle for 30 minutes and pH was measured. Samples were then centrifuged for 15 minutes at 3500 RCF and supernatants filtered through 0.2 µm filters (Sartorius). The concentrations of Cu and Zn in the filtrates were determined using ICP-OES or ICP-MS. All samples were prepared in triplicate.

2.4 Sorption curves

The sorption data for Cu and Zn were summarized using the Freundlich relationship (Bolster and Hornberger, 2007; Fitter and Sutton, 1975; McBride and Martinez, 2000). The non-linear Freundlich isotherms were calculated using the Microsoft Excel spreadsheet developed by Bolster and Hornberger (2007). The Freundlich equation is

$$Q \text{ (mg/kg)} = K_F(C_{Equil})^{1/n} \qquad (1)$$

where K_F is the Freundlich coefficient and n is the affinity value of the Freundlich coefficient; Q is the concentration of Cu or Zn adsorbed on solid phases (mg/kg); and C_{Equil} is the Cu or Zn concentration in solution at equilibrium (mg/L). The coefficient n can range between 0 and 1, with a linear C-type relationship produced when $n = 1$ (Fitter and Sutton, 1975; McBride and Martinez, 2000). The K_F and n are coefficients that determine the steepness and curvature of the isotherm (Akgerman and Zardkoohi, 1996). The K_F coefficient can give an estimation of the amount of adsorbed metal in mg/kg at a solution concentration of 1 mg/L (Welp and Brummer, 1999).

2.5 Desorption procedures

Desorption of Cu and Zn from the soils was estimated using 10 mM $Ca(NO_3)_2$ and 5 mM DTPA on selected soil samples from the sorption experiments. Samples selected were, for the control soils, the 0.05 and 2.50 mg/g initial spike samples, and for limed soils, the 0.75 and 11.1 (Cu) or 12.5 (Zn) mg/L initial spike samples. The desorption of Cu and Zn was determined on individual samples by three successive extractions with approximately 20 ml $Ca(NO_3)_2$ or DTPA (1:10 dry mass to solution ratio, DTPA pH 7.3). The soil suspensions were shaken for 2 hours on an end-over-end shaker, centrifuged for 15 minutes at 3,500 RCF, and the supernatants filtered through a 0.2 µm filter (Sartorius). The three $Ca(NO_3)_2$ or DTPA extracts were then combined and total Cu or Zn concentrations in solutions determined by ICP-OES or ICP-MS. Copper or Zn desorbed were calculated as a percentage of that sorbed. The amount of Cu and Zn in the entrained solution after the sorption experiment was corrected for.

2.6 Data Analysis

Sorption data for Cu and Zn were fitted to the Freundlich equation. Differences among the treatments were determined by analysis of variance (ANOVA) using Genstat software (Genstat 10th edition).

3.0 Results and Discussion

3.1 Soil physical and chemical properties

The soil characteristics of the three peat soils are shown in Table 1. The soils were very acidic with soil pH between 3.33 and 3.40. Bulk densities were very low ranging from 0.12 to 0.16 g/cm^3. Organic carbon contents were between 59 and 63% and CEC ranged from 45 to 50 cmol(+)/kg. Generally, the concentrations of Al extracted using ammonium oxalate were higher than those of Fe and Mn in the three peat soils (Table 1). The mean total concentrations of Cu and Zn were 2.7 and 10.6 mg/kg, respectively.

3.2 Sorption of Cu and Zn in the peat soils

In this study, non-linear relationships were observed between sorbed (mg/kg) and equilibrium (mg/L) solution concentrations of Cu and Zn in all soils. The sorption data for Cu and Zn were adequately described by the Freundlich equation (Figure 1 and Table 2). The higher K_F values observed for Cu (control: 701-818 L/kg and limed: 6,025- 6,750 L/kg) suggest a stronger bonding affinity compared to Zn (control: 103-116 L/kg and limed: 1,023-1,159 L/kg). In addition, both Cu and Zn were found to have a stronger bonding affinity in limed soils than in the controls (Table 2). The concentrations of sorbed Cu and Zn in the three peat soils at an equilibrium concentration of 1 mg/L (K_F) were estimated to be 8.4 and 10.1 times (average) higher in the limed soils than in the control soils (Table 2). Values of *n* were always considerably less than 1, indicating a decreasing

strength of binding as metal concentrations in solution increased – this is strongly indicative of adsorption rather than precipitation reactions dominating sorption in these soils.

The K_F values for Cu and Zn obtained from this study are higher than published values for other soil types. These results indicate that the strong Cu and Zn sorption capacity of peat soils may lead to potential deficiencies of these micronutrients in the soils. The reported K_F values for Cu and Zn in an acidic Haplic podzol soil (pH 3.2) were 30.0 and 1.8 L/kg, respectively (Welp and Brummer, 1999). The K_F values for Cu and Zn in 11 soils, including Spodosols, ranged from 56.2 to 6,309 and 2.1 to 776.3 L/kg, respectively (Buchter et al., 1989). The mean K_F value for Cu from a compilation of 70 different studies was reported to be 4,799 L/kg (Sauve et al., 2000). The mean K_F values for Zn in loamy sand, sandy loam and loam soils were 19.3, 247.1 and 427.3 L/kg, respectively (Diatta et al., 2003). The variation in the magnitude of the K_F values for Cu and Zn are influenced by the soil and element properties (Buchter et al., 1989) with soils having high K_F values in that study being high in pH and having high CEC.

The Freundlich affinity values, *n*, for Cu and Zn in both control and limed peat soils, were all lower than 0.60, although they were slightly higher for control (0.44-0.60) than for limed soils (0.29-0.47) (Table 2). The *n* values obtained for Zn were greater than those of Cu in both control and limed soils (Table 2). Similar to K_F, *n* values are also related to the soil and element properties (Buchter et al., 1989). The magnitude of *n* values depends on how strong the retention of cation is by the soils and the stability and solubility constants of the given cation for ion complexes of a given ligand in solution (Buchter et al., 1989). A value of *n* less than unity (one) is an indication that significant adsorption takes place at low concentration but the increase in the amount adsorbed as solution concentrations increase becomes less, and *vice versa* (Teng and Hsieh, 1998). This suggests a decreasing affinity of the organic matter surfaces for Cu and Zn as the concentration of metal in the equilibrium solution increase. In another study, the *n* values for Cu and Zn in

11 different soils were reported to range from 0.471 to 1.420 and 0.510 to 1.011, respectively (Buchter et al., 1989). For loamy sand, sandy loam and loam soils, the mean n values for Zn were found to be 0.592, 0.398 and 0.320, respectively (Diatta et al., 2003). The n values for four New Zealand soils were found to be between 0.89 and 1.34 (Singh et al., 2006).

The greater sorption of Cu over Zn has been reported in acid (HCl) washed peat (Bunzl et al., 1976), in three acid soils from Washington (Kuo and Baker, 1980), and in solid goethite, Al-substituted goethite and a system of kaolinite goethite (Spathariotis and Kallianou, 2007). This preference may be due to the greater affinity of Cu for functional groups of soil organic matter, which are hard Lewis base-carboxylic and phenolic groups (Cu is a borderline hard Lewis acid and Zn is a soft Lewis acid) as well as the higher electronegativity of Cu (2.0 and 1.6 for Cu and Zn, respectively), making Cu a better candidate than Zn for electrostatic and inner-sphere surface complexation reactions (Sparks, 1994).

The pH of control soil solutions became more acidic with increasing Cu or Zn addition to the peat soils (initial pH: 2.70 to 2.90; final pH: 2.45 to 2.60). The observed decrease may be due to the release of protons (H^+) associated with organic matter functional groups in the peat soils that can be displaced into solution following Cu or Zn adsorption (Sparks, 1994). In this study, increases in sorption of Cu (50 times increase at 0.25 mg/g initial spike rate) and Zn (67 times increase at 0.25 mg/g initial spike rate) were recorded following the lime amendment of control soils (initial pH: 2.6 to 2.7; final pH: 5.4 to 5.6). Recently, similar increases in adsorption of Cu^{2+} with increasing pH in an ombrotrophic peat have been reported (Villaverde et al., 2009). The reason for this enhanced metal sorption with increased soil solution pH is due to a decrease in competition with H^+ for binding sites and an increase in the negative charge of the peat surface. Naganuma (1993) reported that the relationship between the H^+ release and Cu and Zn adsorption was in the range of 1 to 2,

suggesting that Cu and Zn replaced one or two H^+ ions from the sites with H^+ adsorption of tropical peat soils, although H^+ consumption by hydrolytic Cu and Zn ions in the solution and dissociated carboxyl groups of tropical peat soils caused the decrease in the ratios of apparent release of the H^+ ions for Cu and Zn adsorption.

The tropical peat soils in this study contained more than 90% organic matter. It is well known that increasing organic matter in soil increases cation exchange capacity (CEC), and consequently may increase Cu sorption (Arias et al., 2005)A similar finding was documented by Singh et al. (2006) for Waimakariri soil of New Zealand, which also has a relatively high CEC, due to the high organic matter content of the soil. The increased sorption of Cu and Zn after liming in the present study is likely due to increased CEC, which depends on the presence of pH-dependent charges in the soil and the decreased competition with H^+ for complexation onto soil organic matter (SOM) (Alloway, 1990). Soil organic matter can influence the mobility of metals in soils by two different mechanisms: 1) as an adsorption site on particulate organic matter decreasing Cu mobility; and 2) through complexation as soluble organic matter thus increasing Cu concentrations in solution (Adriano, 2001; Krishnamurti and Naidu, 2002; Stevenson, 1991). The high sorption of divalent metals, especially Cu, on solid phase soil organic matter (SOM) has previously been reported (Kabata-Pendias and Pendias, 1992; McBride and Martinez, 2000; McLaren et al., 1981; Shuman, 1975; Stevenson and Ardakani, 1972). In addition, high Al and Fe oxide contents in soils may increase Cu and Zn sorption (Table 1). Khan et al. (2005) observed that oxide components contributed significantly to retention of Cu in three out of five pasture soils.

Using the Giles et al. (1974) classification, the sorption of Cu and Zn on these peat soils was found to follow an L-type isotherm and possibly an H-type for Cu on the limed soils, as they were characterised by a slope that decreased with increasing metal concentration in solution (Figure 1). This result is in agreement with a study on four humic

Umbrisol soils of Spain by Covelo et al. (2004). They found that the adsorption isotherms of Cu were similar to L- or H-type curves, suggesting that a high affinity exists between the Cu and the soil, especially at low solution concentrations. Singh et al. (2008) determined the effect of pH on Zn sorption and desorption on four New Zealand soils and reported that three out four of the soils studied had L- or H-type curves.

The results from this study indicate that in limed peat soils a high proportion of the added Cu or Zn will become associated with the solid phase. However, the lability and hence the potential bioavailability of Cu or Zn in limed peat soils cannot be accurately estimated from K_F values alone, since adsorbed metal may still remain in the exchangeable pools on the solid phase. Metals may also form stronger associations with the solid phase over time, which means that sorption K_F values may not accurately represent solid-solution partitioning for metal desorption, and this divergence may increase with time (Brummer et al., 1983; Wu et al., 1999). The amount of labile and hence potentially bioavailable adsorbed Cu or Zn on the solid phases was be estimated by desorption experiments using dilute $Ca(NO_3)_2$ or DTPA.

3.3 Desorption of sorbed Cu and Zn from soils

Data for the desorption of Cu and Zn using $Ca(NO_3)_2$ and DTPA are shown in Figure 2. Using $Ca(NO_3)_2$, low percentage of sorbed Cu was found to be desorbed from both control (0.79-16.5%) and limed (0.64-7.91%) peat soils (Figure 2A). The increase in percentage of Cu desorbed by $Ca(NO_3)_2$ with increasing initial spike concentration on both control and limed soils may be due to weaker associations at higher metal concentrations when the binding strength was lower . High percentages of sorbed Cu were desorbed using DTPA from control (79.6-92.3%) and limed (61.4-80.0%) soils (Figure 2A). Since $Ca(NO_3)_2$ is a neutral salt, Cu or Zn cannot easily precipitate from the solution. However, DTPA can decrease solution pH and solubilise precipitates. Low desorption of Cu from substrates

containing humic acids has been attributed to the formation of complexes with high binding energies (Arias et al., 2005). The high solid phase partitioning of Cu and its strong binding with SOM in this study (Table 2) suggests that fertiliser Cu added into limed tropical peat soils will have a low lability and hence low potential availability to crops.

The percentages of Zn desorbed by $Ca(NO_3)_2$ were higher in control (15-35%) than limed (12-20%) peat soils (Figure 2B). This suggests that at lower soil pH, Zn adsorbed to control soils was weakly associated with soil solid phases. In contrast to control soils, a high percentage of Zn in limed peat soils was found to be desorbed using DTPA (Figure 2B). The greater desorption of Zn by DTPA in limed soils confirms that DTPA is more effective in complexing Zn at higher pH values.

In comparison to Cu, higher percentages of Zn were desorbed by $Ca(NO_3)_2$ at the same initial spiked concentrations in both control and limed peat soils (Figure 2). Hence, Zn is more likely to be displaced by calcium (Ca) than is Cu (Cu is more strongly held by the organic matter in the soil than Zn). In contrast, higher percentages of Cu than Zn were desorbed than Zn when DTPA was used as an extracting solution. This higher desorption of Cu is due to its higher critical stability constant to DTPA; the stability constant for Cu-DTPA is about 3 units higher than that for Zn (Martell and Smith, 1989). The lower solid phase partitioning of Zn and its weaker association with solid phases in this study (Figures 1-2 and Table 2) suggests that fertiliser Zn added into limed tropical peat soils will have a higher lability and hence higher bioavailability than Cu for plant uptake. However, despite having higher bioavailability than fertiliser Cu, Zn deficiencies in some crops may still be more prevalent, for example in oil palm, where the critical level for Zn is 2 to 3 times higher than for Cu (Reuter and Robinson, 1997).

4.0 Conclusions

In the three tropical peat soils studied, sorption of both Cu and Zn increased with increasing pH following lime amendment of the soils. The Freundlich equation was fitted to the sorption data of Cu and Zn. The K_F values were greater for Cu than Zn in both control and limed peat soils, indicating that Cu is much more strongly held by the soils than Zn. Thus, the Cu ion is likely to be less mobile in these soils. The K_F values for both Cu and Zn obtained in this study were higher than those published for other soil types. Therefore, application of Cu and Zn fertilisers into limed peat soils could result in a significant amount of the fertiliser Cu and Zn being sorbed strongly onto organic matter, and losing its effectiveness for crop growth.

The desorption study using $Ca(NO_3)_2$ and DTPA showed significant proportions of the sorbed Cu and Zn could not be readily desorbed back into solution, indicating that efficiency of micronutrient Cu and Zn fertilisers will be low. Approximately 60% more Cu and Zn was desorbed by DTPA than by $Ca(NO_3)_2$. This clearly has implications for the bioavailability of Cu and Zn applied to the soils as fertilisers. However, further research is necessary to examine the forms of Cu and Zn in soil solution that would assist us to comprehend the loading capacity and distribution of Cu and Zn species in these soils.

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Table 1

Physical and chemical properties of the three peat soils (0-25 cm depth)

Properties	Soil type[a]		
	MSF	AF	PF
pH ($CaCl_2$)	3.37	3.40	3.33
Bulk density (g/cm^3)	0.16	0.12	0.13
Maximum water holding capacity (%)	272	303	322
Total organic carbon (%)	60	59	63
Total nitrogen (N)	1.94	1.90	1.83
Cation exchange capacity (cmol/kg)	46	45	50
Total copper (Cu) (mg/kg)	3.19	2.77	2.19
Total zinc (Zn) (mg/kg)	10.97	10.68	10.08
Available Cu (mg/kg)	0.20	0.16	0.30
Available Zn (mg/kg)	1.50	1.70	2.20
Ox-Al- oxide (mg/kg)	< 300	< 300	< 300
Ox-Fe- oxide (mg/kg)	<300	< 300	< 300
Ox-Mn- oxide (mg/kg)	< 300	< 300	< 300
DC-Al-oxide (mg/kg)	683	504	742
DC-Fe-oxide (mg/kg)	683	400	344
DC-Mn-oxide (mg/kg)	< 150	< 150	< 150

[a]MSF (Mixed swamp forest), AF (Alan forest), PF (Padang Alan forest). Available Cu and Zn were extracted using 5 mM DTPA (Lindsay and Norvell, 1978). Ox and DC denote ammonium oxalate and dithionite-citrate , respectively (McKeague and Day, 1966).

Table 2

The Freundlich values for Cu and Zn adsorbed to three Sarawak tropical peat soils

Soil types	Metal	Freundlich coefficient, K_F (L/kg)	Affinity value, *n*	Model efficiency, E
Mixed swamp forest (MSF)	Cu control	760	0.469	0.987
	Cu limed	6750	0.337	0.770
	Zn control	110	0.598	0.880
	Zn limed	1023	0.468	0.974
Alan forest (AF)	Cu control	818	0.443	0.992
	Cu limed	6337	0.298	0.980
	Zn control	116	0.560	0.916
	Zn limed	1159	0.439	0.986
Padang Alan forest (PF)	Cu control	701	0.482	0.995
	Cu limed	6025	0.286	0.992
	Zn control	103	0.569	0.919
	Zn limed	1123	0.433	0.988

E = model efficiency that represents the proportion of variance accounted for by the regression (calculated from the ratio of error of sum of squares to the total sum of squares). When E = 1, the data fit the model ideally (Komarek et al., 2009)

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Figure 1

Freundlich isotherms for Cu in control (A) and limed (B), and Zn in control (C) and limed (D) peat soils. Closed square, circle and diamond symbols represent mean ± SD (n = 3) of adsorbed Cu and Zn for Mixed swamp forest (MSF), Alan forest (AF) and Padang Alan forest (PF), respectively

Figure 2

Desorption of Cu (A) and Zn (B) from tropical peat soils of Sarawak by $Ca(NO_3)_2$ and DTPA. Open bars represent DTPA desorbed Cu or Zn whereas closed bars represent $Ca(NO_3)_2$ desorbed Cu or Zn. Data are mean ± SD (n = 3
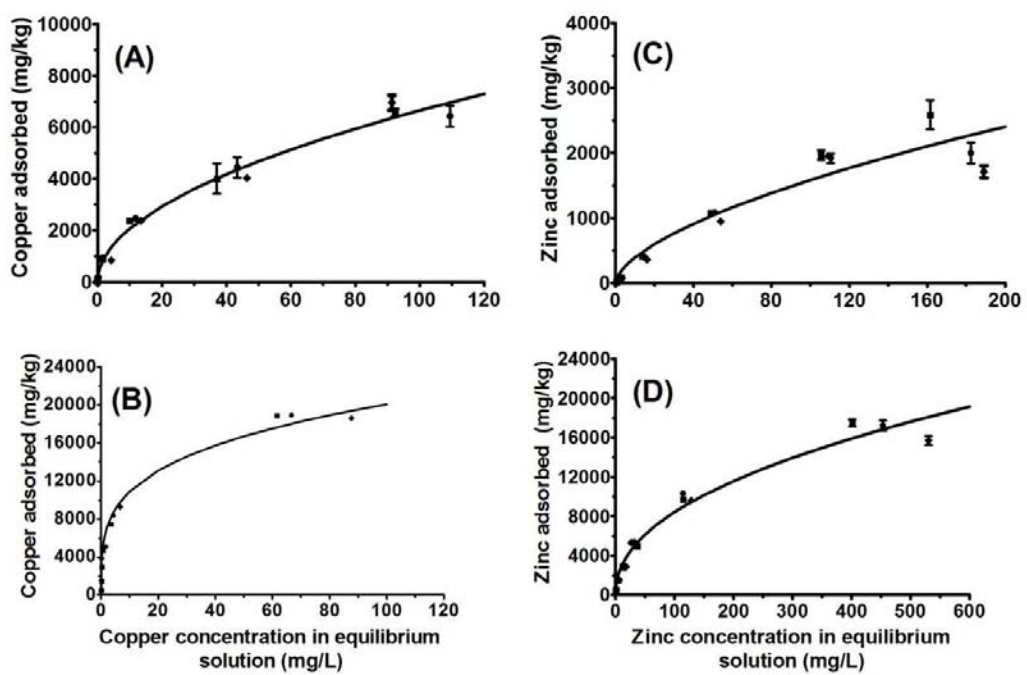
Figure 1
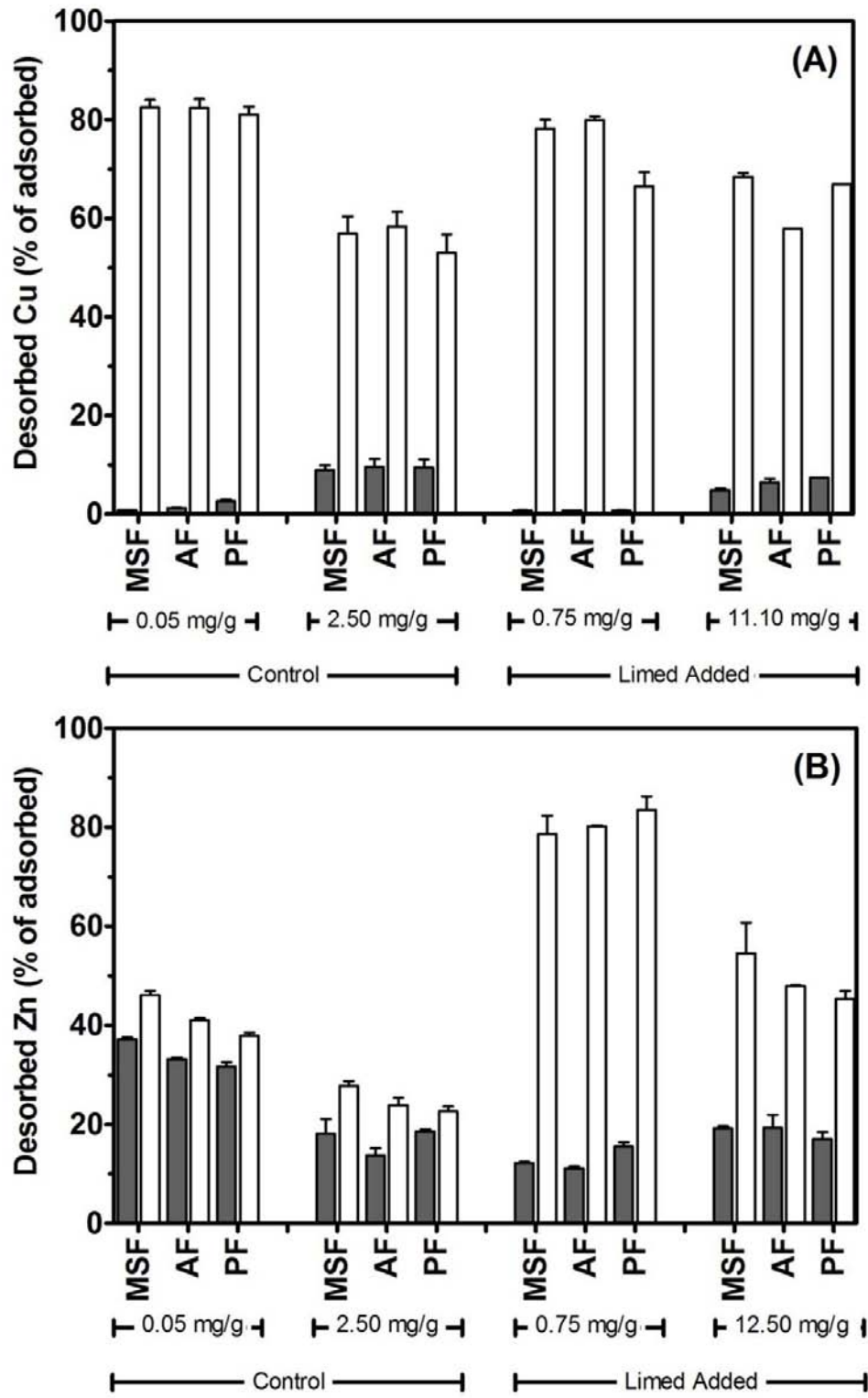
Figure 2

Responses of Tomato (*Solanum lycopersicum* L.) var. Tiny Tom to

Application of Copper and Zinc Fertilisers in

Three Limed Tropical Peat Soils of Sarawak

Chapter 5 was written in a manuscript style and submitted to Geoderma. The format for the journal is attached in Appendix 3.

RESPONSES OF TOMATO (*Solanum lycopersicum* L.) VAR. TINY TOM TO APPLICATION OF COPPER AND ZINC FERTILISERS IN THREE LIMED TROPICAL PEAT SOILS OF SARAWAK

M. Abat, M.J. McLaughlin, S.P. Stacey, J.K. Kirby

Soil Science, School of Agriculture, Food and Wine,
Waite Research Institute, University of Adelaide,
PMB 1, Glen Osmond, SA 5064, Australia

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STATEMENT OF AUTHORSHIP

RESPONSES OF TOMATO (*Solanum lycopersicum* L.) VAR. TINY TOM TO APPLICATION OF COPPER AND ZINC FERTILISERS IN THREE LIMED TROPICAL PEAT SOILS OF SARAWAK

Text in manuscript

ABAT, M. (Candidate)
Planned and carried out the experiment, analysed and interpreted the data, wrote the manuscript and acted as the corresponding author

I hereby certify that the statement of contribution is accurate

Signed: ……………………………………….. Date: …………………

McLAUGHLIN, M.J.
Provided comments on the planning of the experiment, assisted in the data interpretation and provided critical evaluation on the manuscript

I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the manuscript in the thesis

Signed: ……………………………………….. Date: …………………

KIRBY, J.K.
Provided comments on the planning of the experiment, assisted in the data interpretation and provided critical evaluation on the manuscript

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Signed: ……………………………………….. Date: …………………

STACEY, S.P.
Provided comments on the planning of the experiment, assisted in the data interpretation and provided critical evaluation on the manuscript

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Responses of Tomato (*Solanum lycopersicum* L.) var. Tiny Tom to Application of Copper and Zinc Fertilisers in Three Limed Tropical Peat Soils of Sarawak

Margaret Abat[a,*], Michael J McLaughlin[a,b], Samuel P Stacey[a] and Jason K Kirby[b]

[a]Soil Science; School of Agriculture, Food and Wine; University of Adelaide, PMB 1, Glen Osmond, SA 5064, Australia.

[b]CSIRO Sustainable Agriculture Flagship, PMB 2, Glen Osmond, SA 5064, Australia.

[*] Corresponding Author: Margaret Abat

Address: Soil Science, School of Agriculture, Food and Wine, University of Adelaide, PMB 1, Glen Osmond, SA 5064, Australia.

Telephone number: +61 8 8303 6519

Fax number: +61 8 8303 6511

Email: margaret.abat@adelaide.edu.au

Abstract

We assessed the response of the tomato variety "Tiny Tom" to the application of copper (Cu) and zinc (Zn) fertilisers in three tropical peat soils of Sarawak: Mixed swamp forest, Alan forest and Padang Alan forest. Limed soils were used because peat soils in their natural condition are unsuitable to sustain healthy growth of most crops. Yield responses were correlated with the added Cu and Zn using the Mitscherlich model. Adequate levels of applied Cu and Zn were calculated as those which resulted in 90% of the maximum obtainable shoot dry weight. Application of Cu and Zn significantly ($P \leq 0.05$) increased the shoot dry weight and the leaf Cu and Zn concentrations of tomato. Application of the equivalent of 8.3 kg Cu and 5.2 kg Zn per ha was required to achieve 90% of the maximum shoot dry weight. In tomato shoots, the critical concentration for Cu was 18 mg/kg and for Zn, 92 mg/kg. The corresponding concentrations of DTPA extractable Cu and Zn in the soil were 2.3 mg Cu/kg and 3.6 mg Zn/kg. However, the addition of Cu fertiliser also increased Zn uptake by tomato, probably by displacing native Zn that was weakly sorbed to the soil solid phase. This study confirms that Cu and Zn fertilisers are essential for maximum crop production on tropical peat soils of Sarawak.

1.0 Introduction

Sustainable agricultural activities are limited by the availability of fertile land. This limitation has led to reclamation of problematic areas such as peat soils in many parts of the world. However, the reclamation of these soils for agricultural purposes is restricted by various problems associated with their characteristics such as low soil pH, low bulk density and high water holding capacity (Mutalib et al., 1991). Sorption to soil organic matter commonly reduces the availability of essential nutrients (Andriesse, 1988). For example, micronutrient deficiencies have been observed in crops grown in peat soils, which inevitably limits crop productivity (Tie and Kueh, 1979). Among the micronutrients, copper (Cu) and zinc (Zn) appeared to be the most deficient elements for crops grown in tropical peat soils (Andriesse, 1988; Ng and Tan, 1974; Tie and Kueh, 1979).

In West Malaysian peat soils, several researchers have reported Cu deficiency in maize (Kanapathy, 1972), cassava (Kanapathy, 1974), sorghum and groundnut (Chew et al., 1979) and pineapple (Tay, 1969), and deficiencies of both Cu and Zn in oil palm (Ng and Tan, 1974). Without the application of Cu and Zn, the growth of tomato and maize were found to be severely retarded, resulting in sterility in maize and no fruit formation in tomato (Ambak et al., 1991). Deficiencies of micronutrients, particularly of Cu, have been linked to sterility in rice grown in peat soils in Thailand (Attanandana et al., 1995). The low contents of Cu and Zn in peat soils have been considered as the main factors contributing to the slow growth and low productivity of sago palm grown in peat soils of Riau, Indonesia and Sarawak, Malaysia (Purwanto et al., 2002).

Although deficiencies of micronutrients in tropical peat soils are widespread, research is limited on the micronutrient requirements of crops grown in deep peat soils in Sarawak. In most studies to date, researchers have focused on the requirements for major nutrients such as nitrogen (N), phosphorus (P) and potassium (K), and on screening of crops and cultivars that are well adapted to peat soils. A systematic protocol for studying

micronutrient deficiencies, particularly of Cu and Zn, in crops has not been well established. In addition, most information on fertiliser use on tropical peat soils has been obtained from studies carried out in the Everglades, Florida (euthrophic and mesotrophic peats) and oligotrophic coastal peats of Indonesia (Andriesse, 1988). However, this information may not be suitable to Sarawak, due to the climatic conditions, geographic aspects and the nature of the peat itself.

Peat soils of Sarawak are very acidic, with soil pH ranging from 3.0 to 4.0 (Wong, 1991), conditions not suitable for most agricultural crops. The soils need to be limed to raise the soil pH before planting, although liming has been found to decrease micronutrient availability in peat (Haynes and Swift, 1985). Soil organic matter contents in peat soils are generally ~90% and the soils generally have low nutrient contents. Furthermore, these peat soils strongly sorb added micronutrients, especially after liming, (Abat et al., submitted) so that micronutrient fertiliser requirements may be significantly higher than for mineral soils. Information on the amounts of fertilisers required for optimum plant growth in the peat soils of Sarawak is important for their sustainable utilisation.

The study reported here used three limed Sarawak peat soils and tomato as the experimental plant, both because of its short growing period and the importance of tomato production in Sarawak. The Sarawak government is interested in promoting tomato production in the tropics because it has great potential to improve farm income and living standards. The objectives of the study were to determine:

 i.   the rates of Cu and Zn fertiliser required for optimal growth; and
 ii. the relationship between the amounts of Cu and Zn added and their concentrations in soil (DTPA extractable) and in tomato shoots.

2.0 Materials and Methods

2.1 Soil samples

The surface layers (0-25 cm) of three peat soils were used, namely Mixed swamp forest (MSF), Alan forest (AF) and Padang Alan forest (PF) (Melling et al., 2008). The soils are located within the same basin but the composition of trees and vegetation are different (Melling et al., 2008). The methods used for analysing the soil properties have been previously described (Abat et al., submitted).

2.2 Experimental procedures

A pot experiment was conducted in a controlled growth chamber using tomato (*Solanum lycopersicum* L.) variety Tiny Tom as the model plant. The chamber temperature was set at 22 ^{o}C during the day and 16 ºC at night. Copper and Zn were applied separately to the soils as analytical reagent (AR) grade copper sulphate ($CuSO_4.5H_2O$) and zinc sulphate ($ZnSO_4.7H_20$), respectively. There was no Zn applied as a basal fertiliser to the Cu treatments and *vice versa*. Nine rates of the fertilisers were evaluated. These were 0, 0.5, 1.0, 2.0, 4.0, 8.0, 16.0 32.0 and 64.0 mg Cu per kg of soil, and 0, 0.1, 0.2, 0.4, 0.8, 1.0, 2.5, 5.0 and 10.0 mg Zn per kg of soil (approximately equivalent to 0, 0.17, 0.34, 0.68, 1.37, 2.73, 5.47, 10.93, 21.87 kg Cu/ha and 0, 0.03, 0.07, 0.14, 0.27, 0.34, 0.85, 1.71 and 3.42 kg Zn//ha, assuming soil at 0 -25 cm depth). The rates were chosen based on the amounts needed to reach critical concentrations of Cu and Zn in soil solutions of untreated soils as determined from sorption experiments (Abat et al., submitted). Each pot (90-mm diameter) was filled with 250 g of the soils. Nitrogen, P and K were applied to all soils as AR grade $(NH_4)_2SO_4$, $(NH_4)HPO_4$ and K_2HPO_4, respectively, at the rates of 125 mg N/kg soil, 167 mg P/kg soil and 154 mg K/kg soil. The soils were pre-treated with calcium carbonate ($CaCO_3$) at the rates of 18.7, 16.9 and 18.3 g $CaCO_3$ per kg for MSF, AF and PF soils, respectively, (approximately equivalent to 7.48, 5.07 and 5.95 tonnes $CaCO_3$/ha for MSF,

AF and PF, respectively) prior to the application of Cu, Zn and NPK fertilisers. The selected $CaCO_3$ rates were chosen to increase soil pH to 5.5, based on a preliminary liming rate experiment (data not shown). The ideal pH value to grow crops on organic soils has been reported to be about pH 5.5 (Andriesse, 1988; Lucas and Davis, 1961). The experiment was arranged as a randomized complete block design (RCBD) with three replications. Seeds were germinated for four days in the dark. Germinated seedlings were transplanted to individual pots just below the soil surface at a planting density of three seedlings per pot and thinned to two plants per pot after one week. Throughout the experiment, the soil moisture content was maintained at approximately 50% field capacity by daily addition of deionised (DI) water. The moisture content at field capacity was determined using tension plates at 10 kPa (Marshall and Holmes, 1979).

The tomato plants were harvested eight weeks after transplanting. Shoots were cut about one centimetre above the soil surface, rinsed three times with distilled water and dried in an oven at 70 °C to constant weight. Dried shoots were ground and then digested in concentrated nitric acid (HNO_3). Soil samples were taken from each pot, air dried, ground and sieved through a 2 mm sieve. The sieved soils were digested in a 1:3 *aqua regia* mixture of concentrated HNO_3 and hydrochloric acid (HCl) and analysed for total metal concentrations. Diethylene triamine pentaacetic acid (DTPA) extractable Cu and Zn in the treated soils were also measured by extracting 10 g of soils with 30 mL of 5 mM DTPA buffered to pH 7.3, shaken for two hours, centrifuged at 2,500 RCF for 10 minutes and filtered through Whatman No. 42 filter paper (Lindsay and Norvell, 1978; Rayment and Higginson, 1992). Copper, Zn and other elements were analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES) or inductively coupled plasma mass spectroscopy (ICP-MS) depending on the concentration of the elements in the solutions.

The critical Cu and Zn concentration in tomato shoot, calculated as the Cu and Zn concentration in the shoot corresponding to 0.90 maximum shoot dry weights, were

determined from the relationship between relative yield of shoot dry weight and Cu and Zn concentrations in shoots (Dang et al., 1993). The Mitscherlich model was used to examine the relationship between yield response and DTPA-extractable Cu and Zn in the soils, and to calculate critical values based on 0.90 maximum shoot dry weights.

2.3 Statistical analysis

Analysis of variance (ANOVA) and tests of least significant difference ($P \leq 0.05$) were conducted using Genstat (10th edition). A diminishing-return Mitscherlich equation was used to describe the relationship between the tomato shoot dry weight and the rate of applied Cu and Zn in the soils:

$$Y = A(1 - Bexp^{CX}) \qquad (1)$$

where Y is the actual yield obtained after any given quantity of nutrient X, is applied, A is the asymptote value (maximum possible yield obtained by supplying the nutrient element in optimum amount), B is the proportional yield responsiveness to applied nutrient, and C is the curvature coefficient (McLaughlin et al., 1999; Sinclair et al., 1994; Sonar and Babhulkar, 2002).

3.0 Results and Discussion

3.1 Soil physical and chemical properties

The chemical properties of the three peat soils are shown in Table 1. The pH of the soils varied from 3.3 to 3.4, which are typical levels for untreated peats in Malaysia. Bulk density was very low ranging from 0.12 to 0.16 g/cm^3. The low bulk density and high water content of peat soils impede the development of plant root systems and restrict the use of heavy machinery. The contents of exchangeable calcium (Ca), K, magnesium (Mg) and sodium (Na) were low compared with the cation exchange capacity (CEC) value measured at pH 7 (Table 1). Total organic carbon (C) content was between 59 and 60% and total

nitrogen content ranged between 1.83 and 1.94%. Mean values for total Cu and Zn concentrations in the three soils were 2.7 and 10.6 mg/kg, respectively. These values are slightly lower than the reported average concentrations of Cu and Zn in peat soils of Peninsular Malaysia which were 4.1 and 15.0 mg/kg, respectively (Yonebayashi et al., 1994). The differences between the mean values for total Cu and Zn concentrations obtained in this study and the previously published data are probably due to the differences in peat types and origin as well as the method of determination. Yonebayashi et al. (1994) measured Cu and Zn concentrations using atomic absorption spectroscopy (AAS) after the soils were digested by a dry combustion technique.

3.2 Growth response and shoot dry weight

The growth of tomato plants in unfertilised soils was poor. The growth was slow, plants were stunted and leaves were very small and chlorotic compared to plants in soils fertilised with Cu or Zn. Shoot dry weight of tomato plants increased significantly ($P \leq$ 0.05) with increasing addition of Cu and Zn, but the response diminished as the yield approached the maximum yield or asymptote (Figure 1). The maximum yield was taken as 100% relative yield (RY). For the Mitscherlich model, critical values were defined as concentrations at a RY of 90%. There was no significant difference in the maximum yield of tomato grown in the three peat soils. The mean maximum yield obtained in soils fertilised with Cu or Zn was 0.09 and 0.11 g, respectively. The spread of yields around the fitted Mitscherlich curves was quite large, making it difficult to predict accurately the rates of Cu and Zn fertilisers required for any specified yield. The percentage of variation accounted for by the fitted models of shoot dry weights ranged from 43 to 65% in Cu treatments and from 69 to 90% in Zn treatments. The parameters of Mitscherlich response curves for the three peat soils are given in Table 2. Standard errors of C (curvature

coefficient) were generally small relative to C, indicating that the model accurately predicted yield response to varying Cu and Zn rates.

Based on 90% of maximum shoot dry weight, average adequate application rates were addition rates of 24.3 mg Cu/kg and 15.3 mg Zn/kg soils. These amounts were approximately equivalent to 8.3 kg Cu and 5.2 kg Zn per ha, assuming the soil bulk densities in Table 1 and a 25 cm soil depth. Limited studies have measured tomato response to Cu and Zn fertilisers on peat soils. Ambak et al. (1991) reported that the Cu and Zn requirements for tomato grown in peat soils in the field were 5.1 and 4.5 kg/ha, respectively. In a field experiment on peat from Selangor, West Malaysia using maize as an indicator plant, application of 13.5 kg Cu/ha had a marked effect on maize growth (Kanapathy, 1972). It was recommended that another 13.5 kg Cu/ha should be added into the soil if the deficiencies persisted (Kanapathy, 1972). Application of 8.8 to 13.5 kg Cu/ha induced a marked yield response for tapioca grown in peat (Anon, 1975). A significant increase in straw and grain weight of rice grown in Thailand peat soils was observed when Cu and Zn were added at the rates of 40.9 and 40.0 mg/kg, respectively (Attanandana et al., 1995). Few of these studies however examined responses of crops to a wide range of addition rates of Cu and Zn, or were able to define critical Cu and Zn addition rates for optimal crop growth. Field studies in temperate regions have shown that the application of 0.7 to 2.9 mg Cu/kg of soil as a broadcast application can correct Cu deficiency in annual crops (Martens and Westermann, 1991). Similarly, broadcast applications of 0.9 to 6.9 mg Zn/kg soil are used for correcting Zn deficiencies (Martens and Westermann, 1991). Differences in recommended Cu and Zn rates between studies are likely due to differences in soil properties, such as organic matter content, soil pH and soil mineralogy (Andriesse, 1988, ; Funakawa et al., 1996; Stevenson, 1994; Yonebayashi et al., 1994) and differences in plant requirements. It is evident that peat soils have a high requirement for Cu and Zn compared to mineral soils in temperate regions.

3.3 Copper and Zn concentrations in tomato shoots

Shoot nutrient concentrations can be used as a diagnostic tool to identify nutrient deficiencies (Jones, 1991; Melsted et al., 1969). The concentrations of Cu and Zn in shoots of control plants were 0.86 and 15.83 mg/kg respectively (Table 2). These values were lower than published critical values (Reuter and Robinson, 1997), indicating severe deficiencies. The shoot concentrations of Cu and Zn grown in fertilised soils were significantly different from that of unfertilised peat soils ($P \leq 0.05$). The concentrations of Cu and Zn in the shoots increased progressively with the addition of Cu and Zn soils. Copper concentrations in tomato shoots plateaued in all three soils at around 12.5 mg/kg, indicating strong regulation of Cu uptake by the plants (Norvell and Welch, 1993; Welch et al., 1993) (Figure 2). In contrast, there was less evidence for a strongly regulated uptake of Zn, as shoot Zn concentrations increased well above the critical concentration, suggesting a luxury uptake of Zn by the plant (Figure 2). The spread of values around the fitted Mitscherlich curves was quite large, reducing the precision of determination of critical fertiliser addition rates. The percentage of variation accounted for by the fitted models ranged from 40 to 63% in Cu treatments and from 66 to 85% in Zn treatments.

The critical concentrations in tomato shoot were 18 mg/kg Cu and 92 mg/kg Zn. In 4 of the 6 cases (Figure 3), the shoot critical concentrations involved extrapolation. This reduced the reliability of the critical valued obtained. The critical concentration of Cu in tomato shoots grown in various soil in temperate regions was reported to be 5 mg/kg (Jones, 1991). The critical concentration of Zn in whole tomato shoots at the 13 leaves growth stage was previously reported to be between 20 and 30 mg/kg (Reuter and Robinson, 1997). The critical Zn concentrations in tomato leaf obtained in our study were thus 2 to 3 times higher than those previously reported. However, the robustness of the critical value is unclear as the source of the data is a personal communication. In this study, the addition of Cu to peat soils significantly ($P \leq 0.05$) increased Zn concentration in the

tomato shoots (Table 3). Similarly, the addition of Zn to the soils also increased Cu concentrations in tomato shoots. Copper fertiliser may have desorbed Zn that was sorbed to the soil organic matter, thus increasing Zn availability for uptake by the plants.

3.4 DTPA-extractable Cu and Zn in soils

In these three Sarawak peat soils, 2.3 and 3.6 mg/kg of DTPA-extractable Cu and Zn, respectively, was required to produce 90% maximum shoot dry weight (Figure 4) with no significant difference in critical value between soils. Below these critical values tomato plants are likely to suffer from Cu and Zn deficiencies. In 3 of the 6 cases (Figure 4), the critical concentrations determined involved extrapolation outside the experimental dataset. This reduced the reliability of the critical values obtained. The critical concentrations of soil DTPA-extractable Cu for tomato in a field study of various soil types were previously reported to range from 0.1 to 5.0 mg/kg (Brennan and Best, 1999) and the general recommendation made for critical concentrations of soil DTPA-extractable Zn in 'all crops' grown in Queensland soils were between 0.3 and 0.8 mg/kg at pH > 7, or between 0.2 and 0.5 mg/kg at pH < 7 (Armour and Brennan, 1999). Our values for DTPA-extractable Cu were within the range reported by Brennan and Best (1999). However, the results obtained for Zn were higher than those reported in the literature. The differences between the values obtained from this study and the previously published results are probably due to differences in soil properties, plant requirements, stage of growth and the environment where the study was conducted; whether in a controlled environment (glasshouse) or in the field.

In this study, the high organic matter content of the peat soils in relation to other soil types was probably responsible for the higher critical value for DTPA-extractable Zn in peat soils. It has been reported that organic matter can significantly increase the critical value for DTPA-extractable Zn in soil but not for DTPA-extractable Cu (Li et al., 2007). In

the present study, it was also observed that the amounts of DTPA-extractable Zn in soils increased as the level of added Cu increased (Table 3). The Cu added into the soils displaced Zn from soil exchange sites, which may have helped alleviate the Zn deficiency and enhanced the growth of tomato plants in peat soils fertilised with Cu.

4.0 Conclusions

Micronutrient deficiencies limit plant growth and crop yields in Sarawak peat soils. Without the application of Cu and Zn, the growth of tomato in these three peat soils was severely depressed. In the unfertilised soils, the concentrations of Cu and Zn in tomato shoots were critically low, thus indicating severe deficiencies. The concentrations of Cu and Zn in tomato shoots increased progressively with the addition of increasing amounts of Cu and Zn to the soils. The application of Cu and Zn fertilisers significantly increased the shoot dry weight of tomato, with fertiliser applications equivalent to 8.3 kg Cu and 5.2 kg Zn per ha found to be sufficient to attain maximum tomato growth. Subsequent trials would be necessary to confirm these values under field conditions. Soil application of Cu displaced native Zn in the peat soils and increased Zn uptake by tomato shoots. Therefore, the response to Cu fertiliser may have, in part, been due to improved Zn nutrition. Consequently, the application of Cu and Zn fertilisers are essential to sustain crop productivity on tropical peat soils of Sarawak.

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Table 1

Physical and chemical properties of the three peat soils used in the experiment

Properties	Soil type[a]		
	MSF	**AF**	**PF**
pH ($CaCl_2$)	3.37	3.40	3.33
Bulk density (g/cm^3)	0.16	0.12	0.13
Maximum water holding capacity (%)	272	303	322
Total organic carbon (%)	60	59	63
Total nitrogen (%)	1.94	1.90	1.83
Cation exchange capacity (cmol(+)/kg)	46	45	50
Exchangeable K (cmol(+)/kg)	0.38	0.73	0.52
Exchangeable Ca (cmol(+)/kg)	1.47	0.82	0.72
Exchangeable Mg (cmol(+)/kg)	2.82	2.50	1.15
Exchangeable Na (cmol(+)/kg)	0.50	0.69	0.47
Total P (mg/kg)	194	149	115
Total K (mg/kg)	55	73	68
Total Ca (mgkg)	241	95	42
Total Mg (mg/kg)	91	44	60
Total Cu (mg/kg)	3.19	2.77	2.19
Total Zn (mg/kg)	10.97	10.68	10.08
Total Fe (mg/kg)	296	106	131
Total Mn (mg/kg)	4.21	1.77	3.10
Total B (mg/kg)	5.00	5.50	5.00
Total Na (mg/kg)	32.00	23.50	28.50
Total S (mg/kg)	440	314	296
Total Mo (mg/kg)	<LR	<LR	<LR
Available Cu (mg/kg)	0.20	0.16	0.30
Available Zn (mg/kg)	1.50	1.70	2.20

[a]MSF (Mixed swamp forest), AF (Alan forest), PF (Padang Alan forest), LR (limit of reporting). Maximum water holding capacity was determined using the tension plate method (Marshall and Holmes, 1979), cation exchange capacity (CEC) and exchangeable K, Ca, Mg and Na were determined using the 1 M ammonium acetate (NH$_4$OAc) method at pH 7.0 (Thomas, 1982).

Table 2

Parameters of fitted Mitscherlich curves for three tropical peat soils

Metal	Soil type[a]	A (g/pot)	B	C	Standard errors in A	Standard errors in B	Standard errors in C
Copper (Cu)	MSF	0.0991	-0.0457	0.9484	0.0076	0.0077	0.0251
	AF	0.0873	-0.0303	0.9426	0.00873	0.0090	0.0446
	PF	0.0742	-0.0344	0.8423	0.0042	0.0061	0.0697
Zinc (Zn)	MSF	0.1051	-0.0794	0.8680	0.0096	0.0108	0.0543
	AF	0.116	-0.0968	0.8930	0.0448	0.0433	0.0417
	PF	0.1014	-0.0715	0.8585	0.0143	0.0144	0.0557

[a]MSF, Mixed swamp forest; AF, Alan forest; PF, Padang Alan forest

A, asymptote; B, proportion of yield response to applied nutrients; C, curvature coefficient

Table 3

Mean Cu and Zn concentrations in tomato shoot, and DTPA-extractable concentrations in the soils in relation to added Cu and Zn

Metal added	Total metal in soils (mg/kg)	Cu in shoot (mg/kg)	Zn in shoot (mg/kg)	DTPA Cu (mg/kg)	DTPA Zn (mg/kg)
Copper (Cu)	3.00	0.86	3.70	0.098	0.444
	3.52	1.24	4.82	0.114	0.499
	4.90	2.44	7.22	0.103	0.570
	6.48	4.14	7.82	0.161	0.560
	8.15	8.05	11.84	0.314	0.651
	14.06	8.95	10.70	0.677	0.783
	23.06	10.57	14.98	1.708	0.971
	39.83	11.57	18.19	2.790	0.819
	73.18	12.87	19.21	4.746	0.916
Zinc (Zn)	10.53	1.76	15.83	0.124	0.42
	11.58	1.73	14.08	0.138	0.62
	12.75	3.31	22.40	0.128	0.64
	13.38	3.32	27.23	0.119	0.78
	14.58	3.43	26.41	0.128	0.92
	16.06	4.14	31.79	0.106	1.07
	17.57	3.96	34.85	0.168	1.57
	20.71	4.10	39.06	0.135	2.47
	26.77	4.36	50.82	0.119	2.79

List of figures

Figure 1

Relationships between added Cu (A, B, C) and Zn (D, E, F) in three peat soils and relative yield of tomato shoots. The peat soils were Mixed swamp forest (A & D), Alan forest (B & E) and Padang Alan forest (C & F). The lines are best-fit Mitscherlich response curves. (R^2 for A = 0.74, B = 0.73, C = 0.67, D = 0.81, E = 0.84, F = 0.83)

Figure 2

Relationship between added Cu (A, B, C) and Zn (D, E, F) and concentration of copper and zinc, in leaves of tomato grown in three peat soils. The peat soils were Mixed swamp forest (A & D), Alan forest (B & E) and Padang Alan forest (C & F). The lines are best-fit Mitscherlich response curves. (R^2 for A = 0.45, B = 0.58, C = 0.58, D = 0.76, E = 0.86, F = 0.88)

Figure 3

Relationship between concentration of Cu (A, B, C) and Zn (D, E, F) in shoots and the relative yield in three peat soils. The peat soils were Mixed swamp forest (A & D), Alan forest (B & E) and Padang Alan forest (C & F). The lines are best-fit Mitscherlich response curves. (R^2 for A = 0.79, B = 0.80, C = 0.80, D = 0.79, E = 0.81, F = 0.80)

Figure 4

Relationship between DTPA-extractable Cu (A, B, C) and DTPA-extractable Zn (D, E, F) in soil and relative shoot yield of tomato grown in three peat soils. The peat soils were Mixed swamp forest (A & D), Alan forest (B & E) and Padang Alan forest (C & F). The lines are best-fit Mitscherlich response curves. (R^2 for A = 0.52, B = 0.71, C = 0.56, D = 0.81, E = 0.80, F = 0.82)
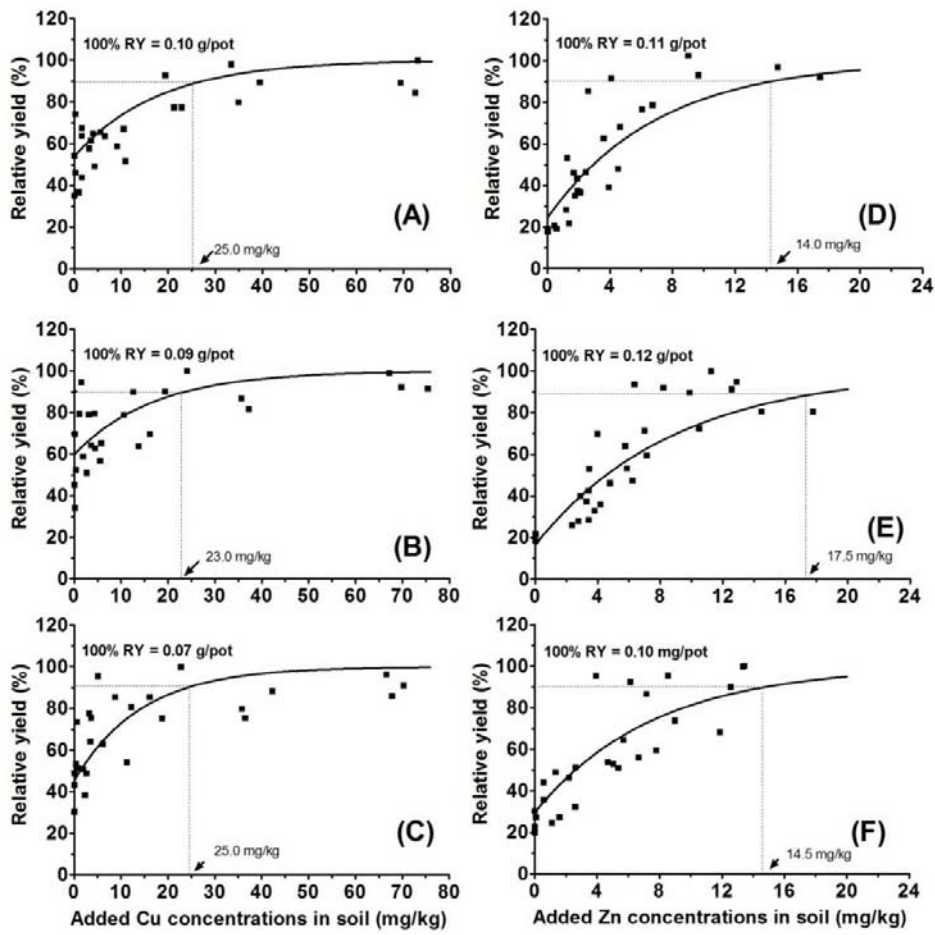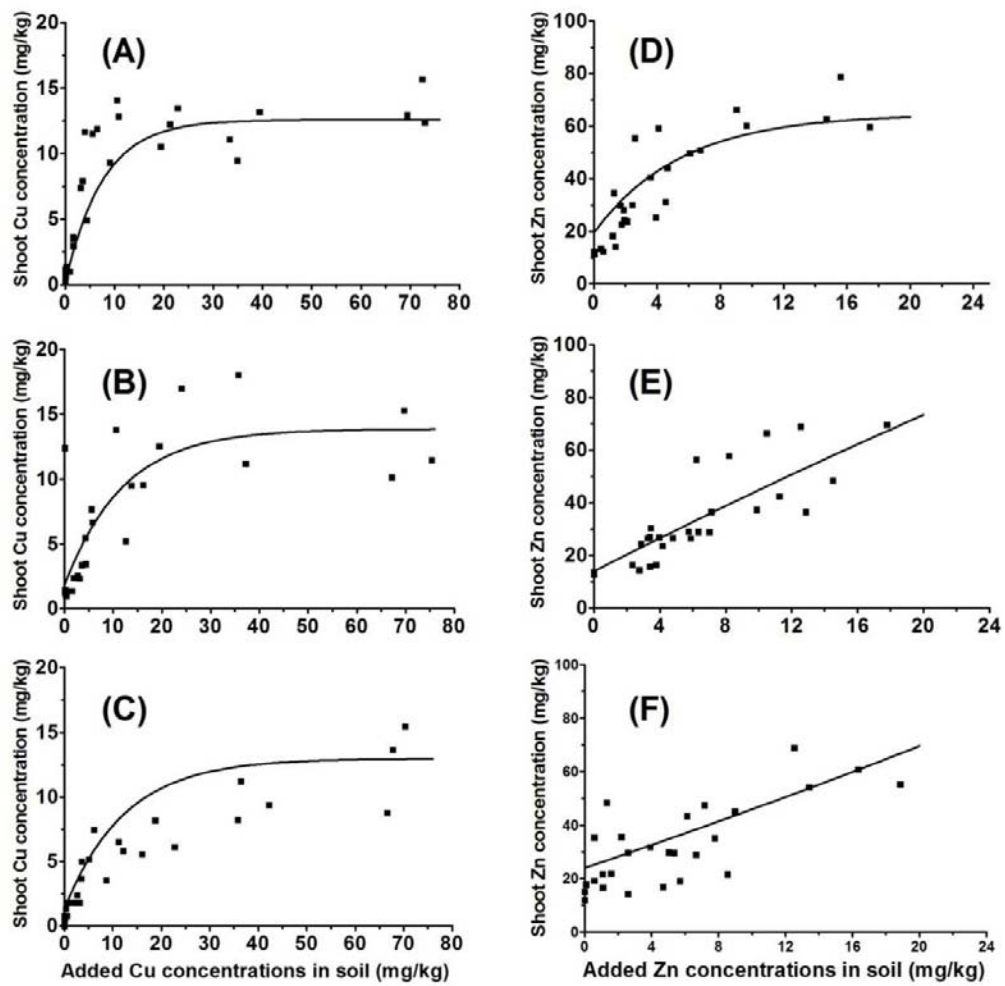
Figure 1

Figure 2
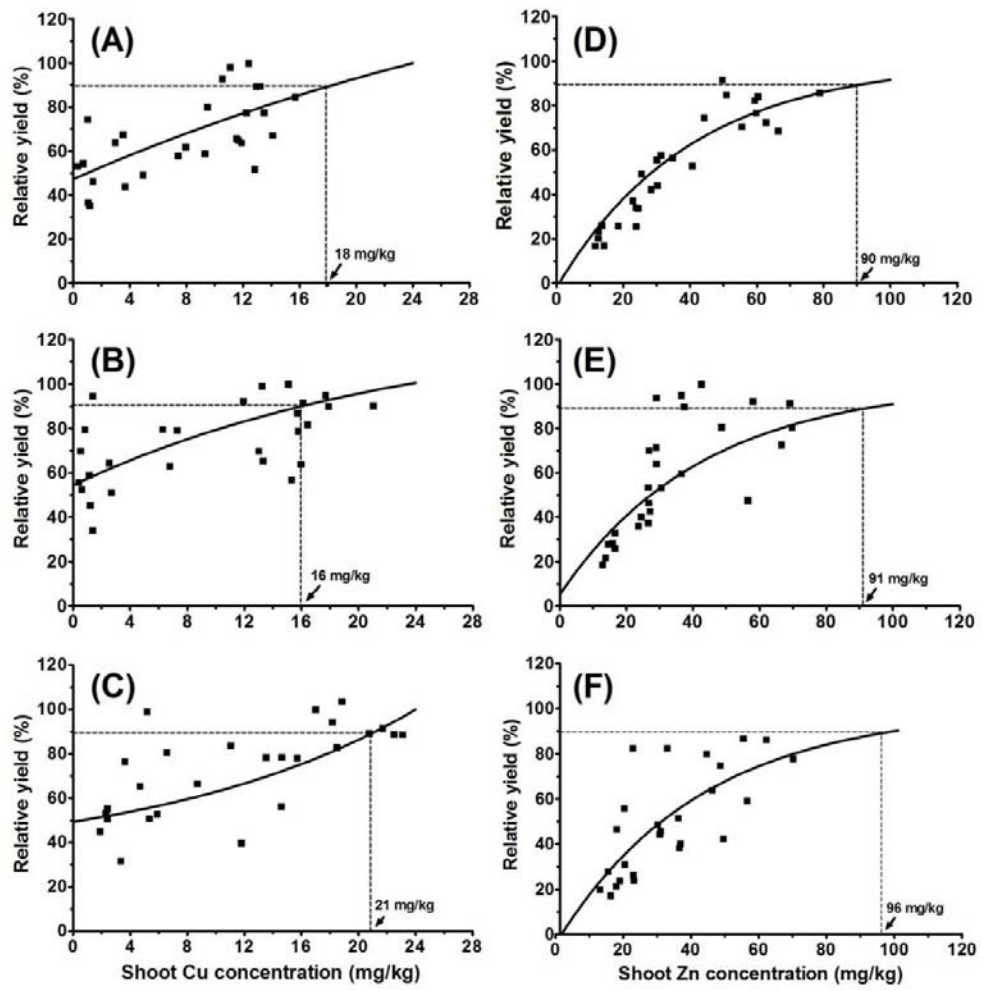
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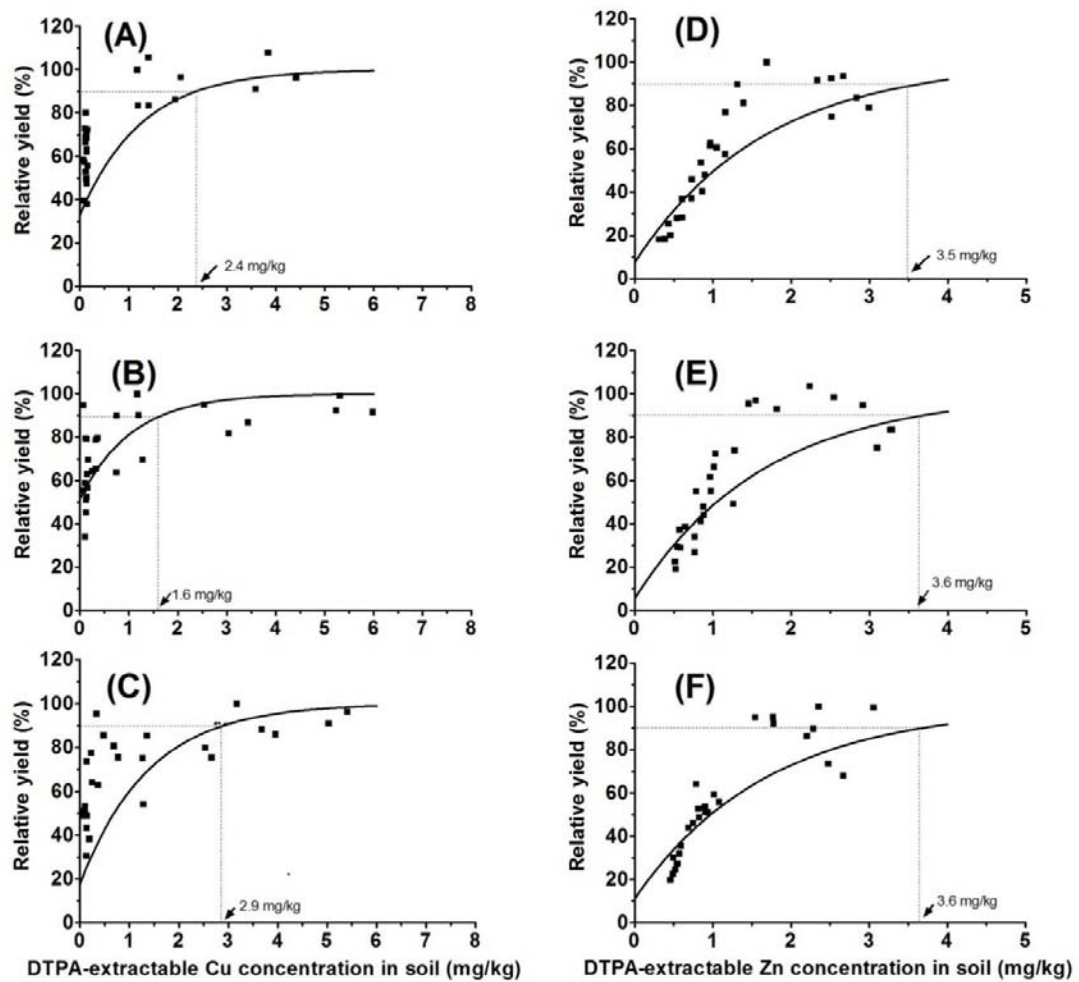
Figure 4

6.1 General Discussion

Tropical peat soils are an important natural resource which inevitably have been, and will be, exploited for agricultural purposes. Sound knowledge of the physico-chemical properties and nutrient availability to plants of nutrient in peat soils is therefore a prerequisite for their sustainable use. In the preceding chapters, I have quantified

(1) the physico-chemical properties of the soils, and assessed their pH buffer capacity and fertility (Chapter 3),

(2) the sorption and desorption of Cu and Zn (Chapter 4), and

(3) the fertiliser Cu and Zn response of tomato plants (Chapter 5).

In this Chapter, I will consolidate and summarise the major findings from Chapters 3, 4 and 5 and suggest areas for future research.

6.1.1 Natural tropical peat soils are unsuitable for growing commercial crops

Peat soil is classified as having a very low potential for agriculture because of its physical and chemical properties (Yanbuaban et al., 2007). Physically, the soils have high moisture contents and low bulk densities (Chapter 3, Table 3.1). Chemically, the soils are very acidic, have high organic matter content and a low nutrient status (Chapter 3, Table 3.1). Chemical analysis of the soils found high concentrations of total N, but the N was not available for plant uptake presumably at least partly due to the wide C/N ratio and crops grown in such soils readily responded to applied N.

All three peat types had similar physical and chemical properties although different vegetation grows in the three peat areas. For organic soils, the soil properties are of

particular relevance to the reclamation, development and management. Based on the soil physical and chemical properties determined, the use of reclaimed peat land was considered to be rather limited, especially under low input management (Chapter 3, Table 3.1).

Liming is required to raise soil pH values to desired levels in these soils due to their acidity. Due to the low pH of the peat soils used in this study, large amounts of lime were required to substantially increase the soil pH. The liming rates required to raise the pH to 5.5 were equivalent to between 5.07 and 7.48 tonnes/ha. These liming rates were used in the subsequent adsorption/desorption (Chapter 4) and fertiliser response (Chapter 5) studies. Although liming is necessary for the successful cultivation of crops on tropical peat soils, increases in pH inevitably enhance the sorption of micronutrient cations and hence increase the likelihood of micronutrient cation deficiencies (as reviewed in Chapter 2, Table 2.2).

The addition of NPK fertilisers at 50:50:50 give rates kg/ha produced dramatic growth responses in tomato, indicating the very poor macronutrient status of all three soils. In the preliminary study (Chapter 3), it was observed that tomato plants could not grow on limed peat soils without the application of NPK fertilisers. Thus, basal dressings of NPK fertilisers are a pre-requisite for crop growth in these soils.

6.1.2 Both sorption and desorption data are crucial for estimating available Cu and Zn in tropical peat soils

The availability of micronutrients in soil is likely to affect the growth, production and quality of crops. Thus, it is important to study the sorption reactions of these nutrients in soil to assist estimates of their availability for plant uptake. We observed that the adsorption capacities of Cu and Zn in peat soils increased with liming, which is similar to results previously reported in pure peats (Gosset et al., 1986; Naganuma et al., 1993).

Copper and Zn adsorption by these peat soils was satisfactorily described by the non-linear Freundlich equation. The Freundlich coefficients, K_F, for Cu in both untreated and limed peat soils were higher than those for Zn, indicating stronger solid phase sorption of Cu than Zn. Thus, the Cu ion is likely to be less mobile in these soils. The K_F values for both Cu and Zn obtained in this study were higher than those published for other soil types. The difference in K_F values indicates that the strong Cu adsorption capacity in these soils will likely lead to crop deficiencies of Cu, especially in limed soils. Therefore, application of Cu fertiliser into limed peat soils could result in a significant amount of the fertiliser Cu being adsorbed strongly onto organic matter. Although Zn was less strongly retained by Cu in these soils, retention was still strong and additions of Zn fertilisers will be required to maximize crop production. Although the peat soils were of three different types with different vegetation, the soils physical and chemical properties were not significantly different ($P \leq 0.05$). This probably explained why the adsorption isotherms for Cu and Zn in these soils were similar.

The results from the desorption study showed that significant proportions of Cu and Zn added to the peat soils were strongly retained by the soil solid phase. About 60% more adsorbed Cu and Zn was desorbed by DTPA than $Ca(NO_3)_2$. The substantial adsorption-desorption hysteresis observed for both Cu and Zn suggested that both Cu and Zn form high energy bonds with the organic matter in these soils. Evidence for adsorption desorption hysteresis in peat soils has been reported by other researchers (Bunzl et al., 1976; Naganuma et al., 1993; Yonebayashi et al., 1994). In addition, sorption of Cu and Zn by a range of soil components has been shown to be only marginally reversible (McLaren and Crawford, 1983; Padmanabham, 1983).

The desorption study using $Ca(NO_3)_2$ and DTPA showed significant proportions of the adsorbed Cu and Zn cannot readily desorb back into solution, indicating that efficiency of micronutrient Cu and Zn fertilisers will be low. However, further research is necessary to examine the forms of Cu and Zn in soil solution, to assist us to comprehend the loading capacity and distribution of Cu and Zn species in these soils.

In summary, it is important to study the sorption behaviour of Cu and Zn in tropical peat soils. The information on the adsorption and desorption of Cu and Zn is important to improve our ability to estimate the release of both naturally-occurring Cu and Zn from soils and the release of Cu and Zn added to soils as fertilisers. In soils with higher adsorption capacities, more Cu and Zn fertiliser may be needed to elicit a crop response. Results from Chapter 4 showed that adsorption of both Cu and Zn were higher in the studied soils than most mineral soil types, suggesting that Cu and Zn fertiliser requirements for tomato grown in peat soils will be higher than other soil types.

6.1.3 Application of Cu and Zn fertilisers is necessary for optimum plant growth in tropical peat soils

There is little information concerning the micronutrient status of tropical peat soils, yet such information is required for agricultural development of these soils. The difficulties encountered in the management of peat soils are often due to the binding of cationic micronutrients by organic matter, thus decreasing their availability to plants (Andriesse, 1988). Therefore, cationic micronutrient supply needs special attention within the context of peat soil productivity.

The results from the pot experiment (Chapter 5) indicated that both Cu and Zn supply are limiting factors for tomato (and perhaps other crops) grown in tropical peat soils. In the

absence of Cu and Zn fertiliser addition, plant growth was slow and deficiency symptoms appeared within 10 to 14 days after transplanting. The addition of Cu and Zn both significantly increased tomato shoot dry weight which is interesting as it might have been expected that alleviating Cu deficiency would not improve Zn nutrition, and vice versa, but indeed this is what was observed. The added Cu probably displaced native Zn that was weakly sorbed to the soil solid phase. Copper ions are well known to complex strongly with soil organic matter whereas Zn ions associate more weakly with the soil organic matter (Cavallaro and McBride, 1978; Cavallaro and McBride, 1984; Hodgson et al., 1966). Thus, Zn ions may be readily removed from the adsorption sites while Cu less easily replaced. Therefore, the response to Cu fertiliser may have, in part, been due to improved Zn nutrition. To some extent, Zn had a similar effect although it does not bind strongly to organic matter.

Micronutrient deficiencies, particularly of Cu and Zn have become a problem in peat soils, perhaps due to their low total content and the strong bonding with organic matter in these soils. The mean value for total Cu concentrations in the three soils studied was 2.7 mg/kg and for Zn, 10.6 mg/kg. The critical concentrations of DTPA extractable Cu and Zn in soil were 2.3 and 3.6 mg/kg, respectively. In the present study, it was also observed that the amounts of DTPA-extractable Zn in soils increased as the level of added Cu increased. The Cu added into the soils probably displaced Zn from soil exchange sites, which may have helped alleviate the Zn deficiency and enhanced the growth of tomato plants in peat soils fertilised with Cu.

Application of the equivalent of 8.3 kg Cu and 5.2 kg Zn per ha was required to achieve 90% of the maximum shoot dry weight of tomato. Subsequent trials would be necessary to confirm these values under field conditions. The amount of Cu fertiliser required by tomato

grown in the peat soils is higher than a previously reported value of 5.1 kg/ha (Ambak et al., 1991). However, the Zn fertiliser requirement was lower than published data of 4.5 kg/ha (Ambak et al., 1991). The differences in the amount Cu and Zn fertiliser requirements for tomato are likely due to experimental conditions (glasshouse vs field), crop growth stage, crop variety and peat soil types and properties. The Cu and Zn fertiliser requirements for tomato grown in peat soils reported by Ambak et al. (1991) were from field experimentation. Generally, Cu and Zn fertiliser requirements for crops grown in peat soils are much higher than those compared to crops grown in other mineral soil types (Chapter 2, Table 2.3).

The results obtained from the study in Chapter 5 revealed the importance of lime, NPK, Cu and Zn applications for the cultivation of tomato in peat soils and perhaps for other crops for improvement of crop yield as well as nutritional quality. Should Cu and Zn deficiencies be suspected in peat soils, Cu and Zn fertilisers could be applied to the soils at the rates of ~8 and ~5 kg/ha, respectively.

6.2 Future Research

Total concentrations of metals in soils are a poor indicator of metal bioavailability since metals exist in different solid-phase forms that can vary greatly in terms of their bioavailability (Nolan et al., 2003). In sorption reaction studies, the species of metal present in solution is deemed important. It is well known that the metal affinity to the surface is a function of its chemical form in solution (Arias et al., 2002). The bioavailability of metals, their uptake and toxic effects on soil organisms can be better understood in terms of their chemical speciation (Nolan et al., 2003). Therefore, speciation studies of Cu and Zn in soil solution is important in providing a better understanding of Cu and Zn mobility and bioavailability in tropical peat soils.

Isotope dilution can be a useful technique to measure the labile pool of Cu and Zn in peat soils, and this technique has not been applied to tropical peat soils. Isotope dilution techniques have been widely applied in research investigating the reactivity and bioavailability of different elements in soils (Ahnstrom and Parker, 2001; Hamon et al., 2002). The isotope dilution technique could be useful to determine the relative and residual effectiveness of Cu and Zn fertiliser utilisation in peat soils, and thus improve the management of these soils.

The effects of NPK fertilisers on Cu and Zn also need to be studied, as these elements might induce deficiencies of Cu and Zn by diluting the absorbed Cu and Zn to deficient concentrations and inhibiting Cu and Zn transport from plant roots to shoots by the formation of protein complexes (Gilbert, 1951; Ozanne, 1955). It has been reported that N fertiliser severely depressed the concentrations of Cu and Zn in plant shoots and roots of wheat grown in Australian soils (Chaudhry and Lonegaran, 1970).

To obtain further information on crop responses to fertilisation on tropical peat soils, I recommend that future research should include other application methods such as foliar sprays or broadcasting (LeBlanc and Gupta, 1994; Varvel, 1983). Broadcast application of $CuSO_4$ was found effective and superior than banded application in correcting Cu deficiency in hard red spring wheat grown in Histosols. The effectiveness of the broadcast $CuSO_4$ was probably due to the amount and/or distribution of rainfall which moved the surface applied material into the root zone, and/or kept the surface root system actively absorbing (Varvel, 1983). Thus, by comparing the methods of fertiliser application, we may be able to find the most effective way to manage the fertiliser requirements of crops grown in peat soils.

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Research into different types of fertiliser such as liquid fertilisers, granular, single versus compound and Cu/Zn chelated with DTPA or EDTA would be beneficial. Copper chelated with EDTA was significantly better than $CuSO_4$ in correcting Cu deficiency in wheat grown in Histosols (Varvel, 1983). In the desorption studies, the percentage of adsorbed Cu and Zn susceptible to desorption into 5 mM DTPA was higher than that desorbed by 10 mM $Ca(NO_3)_2$ in the peat soils. Therefore, chelating Cu or Zn with DTPA may help to prevent Cu and Zn from being immobilised by soil organic matter and other soil components.

6.3 Conclusions

Results indicate that tropical peat soils (MSF, AF and PF) have low availability of the essential nutrients, are highly acidic and have other characteristics that will not be able to support normal growth of the majority of economically important crops. The need for liming to increase the soil pH to reasonable values, basal dressing with NPK fertilisers and Cu and Zn fertilisers is unquestionable. Of interest is the ability of Cu application to enhance Zn uptake by plants. More research is required to further elucidate the suitability of tropical peat soils for agricultural activities to bring optimum benefits with low negative environmental impacts.

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Appendix 1 Estimated NPK fertiliser requirements for selected crops grown in peat soils (Andriesse, 1988)

NOTE:
This table is included on page 137
of the print copy of the thesis held in
the University of Adelaide Library.

Appendix 2 Seed sterilisation and pre-germination methods

Methods

The seeds were sorted first by sieving to remove seeds that were too large, too small or damaged. The seeds were then surface washed using 1% sodium hypochlorite (NaOCl) solution for ten minutes to remove any bacteria, rinsed three times with sterile reverse osmosis (RO) water, washed with 70% ethanol to remove fungi, rinsed three times with sterile RO water, washed with 2% sodium thiosulphate ($Na_2S_2O_3$) for 5 minutes and rinsed again in sterile RO water. About 50 washed seeds were placed into sterilized glass Petri dishes. Each dish had 2 x 9 cm filter paper lining in the bottom and 1 x 9 cm paper on top of the seeds. Seeds were pre-germinated by adding about 3-4 ml water and placed in the growth chamber at 25 ºC for three to four days.

Appendix 3 Guide for authors. *Geoderma.*

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ISSN: 0016-7061
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