MICRONUTRIENTS IN PEAT: 1 PRELIMINARY ANALYSIS BY DIFFERENT EXTRACTION METHODS

ZULKIFLI HASHIM, MOHD. TAYEB DOLMAT AND HAMDAN ABU BAKAR* icronutrients especially Zn and Cu, are normally present in too low a concentration in peat to be adequately available to a crop.

This study was conducted to compare the characteristics of several classes of peat and to do a preliminary assessment on the actively and potentially plant-available forms of micronutrients as a guide to the use in peat of fertilizers containing micronutrients.

Five different extractants, namely ammonium acetate-EDTA, 'double acids' $(0.05 \text{ N HCl/}0.025 \text{ N H}_2\text{SO}_4)$, 0.5 M HNO_3 , 0.1 M HCl and 0.2 N NaOH, were investigated on six different classes of peat.

The amounts of micronutrients extracted differed with the extractants used, depending on the nature of the peat, its drainage status and its agricultural utilization. Ammonium acetate-EDTA and NaOH were effective in extracting Cu and Fe: for example NaOH removed about 70%–93% of total Cu from peat. Ammonium acetate-EDTA, double acids, HCl and nitric acid were comparable, and appeared to be good extractants to displace Zn and Mn from peat. However, all the extractants studied merit further investigation to correlate the micronutrients extracted with the actual uptake by crops to obtain more useful and meaningful information on their availabilities in peat.

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INTRODUCTION

P eat covers approximately 2.5 million hectares or 7% of the land area of Malaysia. Its fertility is considered poor because of characteristic physical and chemical constraints. It is very acidic, with a pH usually less than 4, low in base saturation and available nutrients, and very low in bulk density or bearing capacity. A proper understanding of these constraints is required for successful and economic exploitation of peat for agriculture.

Copper (Cu), iron (Fe), manganese (Mn) and zinc (Zn) are essential micronutrients for plant growth. However, deficiency in one or more of these micronutrients usually occurs in peat. The micronutrients in peat are either present in low concentrations or retained too strongly by organic matter to be adequately available to a crop. Hence, soil test methods are needed to assess both the actively and potentially plant-available forms of Cu, Fe, Mn and Zn in peat. The information should be useful as a guide to the use of fertilizers containing these micronutrients for successful crop planting on peat.

The extractable levels of these micronutrients in soils are known to be affected by soil aeration (Swaine and Mitchell, 1960), soil moisture (Parr, 1969; Hutchinson, 1970), soil micro-organisms (Mulder and Geretson, 1952), soil organic matter (Walsh and Lamb, 1952), soil pH (Lucas and Davis, 1961) soil texture (Lucas and Knezek, 1972) and soil temperature (Rufty et al., 1979). Several recent studies have suggested that the distribution of Cu, Fe, Mn and Zn and their availabilities are influenced by time (Mathur, et al., 1985) and by soil properties (Mathur, et al., 1988).

There are several test methods for micronutrients, designed mainly for mineral soils, but although they are effective and reliable for some soils, none of them is satisfactorily applicable to all soils (Katyal and Randawa, 1983). A recent review of the literature (Mathur and Levesque, 1988) also revealed a lack of soil testing methods primarily designed or extensively tested for peat soil. An ideal soil test extract should remove both the active, immediately available form of the nutrient in question, and a constant proportion of the reserve form that replenishes the former. This

paper compares several commonly used soil tests for mineral soils applied to peat collected from different locations.

MATERIALS AND METHODS

Soils

Peat samples used in this study were collected from six different locations in the Pontian district of Johor as follows:-

- 1. Raw peat from virgin jungle, undrained.
- 2. Raw peat from felled jungle, drained to a small extent.
- 3. Raw peat from felled and burnt jungle, moderately-drained.
- 4. Developed peat, planted with oil palm, drained.
- 5. Developed peat, planted with rubber, drained.
- 6. Developed peat, planted with pineapple, drained.

Soil Analyses

Chemical analyses were performed on air-dried peat samples that were ground to pass through a 2-mm sieve. Parameters analyzed included pH, organic carbon (C), total nitrogen (N), total and available phosphorus (P), exchangeable potassium (K), exchangeable magnesium (Mg), exchangeable calcium (Ca), aluminium (Al) and hydrogen (H), and total and extractable copper (Cu), iron (Fe), manganese (Mn) and zinc (Zn).

Soil pH was determined using a glass electrode, organic carbon by Walkley and Black's method, total and available P by HClO₄-H₂SO₄ digestion and Bray and Kurtz's No. 2 method respectively, total N by the Kjeldahl method, extractable Ca, Mg and K by an NH₄OAc shaking method, exchangeable Al and H using a NaF extractant, and total micronutrients using an aqua regia method, whilst extractable Cu, Fe, Mn and Zn were determined using five different extractants namely ammonium acetate-EDTA, 'double acids', HNO₃, HCl and NaOH.

Total Micronutrients

Fifty ml of aqua regia solution (3 parts HCl to 1 part HNO₃) were added to 10 g soil and the mixture was allowed to stand overnight. It was then heated on a hot plate for about 2 hours,

filtered into a 100 ml volumetric flask and made up to the mark with distilled water. Total Fe, Cu, Mn and Zn were determined with an Atomic Absorption Spectrophotometer.

Extractable Micronutrients

a. Ammonium acetate-EDTA (pH 4.65)

Twenty grams of soil were shaken for 30 minutes with 100 ml of the extracting solution (0.5 M ammonium acetate, 0.5 M acetic acid and 0.02 M EDTA) and filtered. The filtrate was analyzed for Fe, Cu, Zn and Mn using the Atomic Absorption Spectrophotometer.

b. Double acids (0.05 N HCl/0.025 N H,SO)

Twenty-five ml of extraction solution were added to 5 g soil and the mixture was shaken for 15 minutes, then filtered. The filtrate was analyzed for Fe, Cu, Zn and Mn using the Atomic Absorption Spectrophotometer.

c. 0.1 M HCI

Fifty ml of 0.1 M HCl were added to 5 g soil and the mixture was shaken for 30 minutes and filtered. The filtrate was analyzed for Fe, Cu, Zn and Mn using the Atomic Absorption Spectrophotometer.

d. 0.5 M HNO₃

Twenty grams of soil were shaken mechanically with 100 ml of 0.5 M HNO₃ for 30 minutes and the mixture was filtered. The filtrate was analyzed for Fe, Cu, Zn, and Mn using the Atomic Absorption Spectrophotometer.

e. 0.2 N NaOH

Ten grams of soil were shaken with 50 ml of 0.2 N NaOH for 30 minutes on a mechanical shaker and the mixture was filtered. The filtrate was analyzed for Fe, Cu, Zn and Mn using the Atomic Absorption Spectrophotometer.

RESULTS AND DISCUSSION

The peat samples were analyzed for various chemical properties as shown in *Table 1*. There was wide variation among the six peat samples in the values for most of the parameters investigated.

The low pH values obtained, ranging from 3.15 to 3.87, indicate the very acid nature of peat. The lowest pH value of 3.15 (extractable H 3.63 meg/100 g), found in the peat planted with oil palm, is a reflection of the relatively higher fertilizer input in this area, particularly of the ammonium form. It is a well-known fact that oil palm requires relatively more nutrients than rubber, pineapple and most other crops. It is suprising that the pH value of peat planted with pineapple was 3.61. This could be attributed to the lime (in Bordeaux mixture) normally used in the cultivation of pineapple. However, the highest pH value, 3.87. was obtained from the raw peat area where the trees had been felled and burnt. The ash formed contributed substantial quantities of bases, as also seen in the high values of extractable K. Ca and Mg obtained from the analyses. Total P, and especially available P, were also highest in this peat area because of the release of organic-P in the ash.

Compared with most mineral soils, peat samples from the six sites were very high in total N, somewhat low, in total P and low in available P (except those from virgin peat and from raw peat that had gone through the processes of felling and burning, i.e. samples 1 and 3 respectively), moderate to high in extractable K and Ca, and high to very high in extractable Mg. It is evident (Table 1) that raw peat from felled and burnt jungle had the highest values for all these parameters except total N.

The C values obtained were obviously very high, with fairly wide C/N ratios ranging from 31.9 to 56.2. Sample 1 (raw peat from undrained virgin jungle) had the second highest C/N ratio of 52.2 and was found to be still in the fibric stage. Intermittent inundation with water had greatly retarded the decomposition of the woody (organic) materials and kept most of them in the original undecomposed state. The highest C/N ratio was obtained in the peat samples from the pineapple area. The peat there had been drained for a number of years and developed, and was probably in a hemic to sapric stage. The C/N ratio should be lower than that in fibric peat, but the return and accumulation of vegetative matter from the earlier crops of pineapple could probably have pushed up the C/N ratio. Samples 2, 3 and 4 were

TABLE 1. CHEMICAL ANALYSIS OF PEAT

Property			Classes	of peat		
•	1	2	3	4	5	6
рН	3.3	3.4	3.9	3.2	3.3	3.6
%C	33.4	33.6	30.0	36.3	35.8	32.6
Total N (%)	0.64	0.68	0.74	0.78	1.12	0.58
C/N	52.2	49.4	40.5	46.6	31.9	56.2
Total P (ppm)	263	183	320	103	280	105
Available P (ppm)	57	15	225	11	8	23
Extractable K (meq/100g)	0.47	0.26	1.64	0.27	0.34	0.21
Extractable Ca (meq/100g)	7.4	7.9	16.2	2.5	3.9	7.4
Extractable Mg (meq/100g)	5.2	2.2	7.2	3.3	1.8	5.0
Extractable H (meq/100g)	0.4	0.6	1.0	0.8	2.9	0.9
Total Cu (ppm)	2.1	4.0	2.1	7.4	2.6	4.3
Total Zn (ppm)	5.3	4.5	6.2	5.2	4.5	6.0
Total Mn (ppm)	6.1	3.8	4.6	6.8	9.0	4.8
Total Fe (ppm)	110	126	141	145	136	101

mostly grouped as hemic while the drained and developed peat from the rubber area had the lowest C/N ratio of 31.9, and was classified as sapric. Significant loss in peat depths owing to subsidence was evidenced in this area by the observed exposure of most of the rubber roots.

The extractable Al levels were considered low except for the peat sample taken from the rubber area (2.92 meq/100g soil). This could not be explained by any of the agronomic or cultural practices normally carried out in a rubber holding. The advanced state of development of the peat and the subsequent subsidence and the approach of the soil top layer to the silty clay subsoil could have played a role. Extractable H was lowest in the peat sampled from the felled and burnt

area (1.59 meq/100 g soil) and the pineapple field (1.69 meq/100 g soil). This could have been largely due to the release of bases in the burnt peat (as seen from the higher pH value) and the heavy use of lime commonly practised in the cultivation of pineapple.

Total micronutrients (Fe, Mn, Cu and Zn) were generally low in all the peat samples analyzed. The values obtained varied according to the nature of the peat and the crops being cultivated. The total micronutrients were in the orders of Fe > Mn > Zn > Cu for samples 1 and 5, Fe > Zn > Mn > Cu for samples 3 and 6, Fe > Zn > Cu > Mn for sample 2, and Fe > Cu > Mn > Zn for sample 4. In all, Fe was the micronutrient present in the largest quantity in peat. The orders also suggest that Cu was the most limiting micronutrient in peat.

TABLE 2. THE CONTENT OF CU, ZN, AND FE IN PEAT USING FIVE DIFFERENT EXTRACTANTS

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acid 1.20 1.09 2.85 2.26 1.75 1.24 5.40 3.72 5.40 3.97 4.00 45.50 41.36 43.10 34.21 58.40 41.42 128.40 88.55 128.00 94.12 43.00 110.00 126.00 141.00 145.00 145.00 161.00	c. HCl	9.40	8.55	17.50	13.89	16.75	28.53	21.5	52.21	3 5	21.T8	CT-7	F 7 • 7
45.50 41.36 43.10 34.21 58.40 41.42 128.40 88.55 128.00 94.12 43.00 110.00 126.00 141.00 145.00 145.00 136.00	d. Nitric acid	1.20	1.09	2.85	2.26	1.75	1.24	5.40	3.72	3 4	3 97	400	9 0
110.00 126.00 141.00 145.00 136.00 101.00	e. NaOH	45.50	41.36	43.10	34.21	58.40	41.42	128.40	88.55	128.00	94.12	43.00	42.57
	lotal Fe	110.00		126.00		141.00		145.00		136.00		101.00	

SIMPLE LINEAR CORRELATION BETWEEN THE MICRONUTRIENTS IN VARIOUS EXTRACTS TABLE 3.

	Total Micronutrient	onutrient	Ammonium ac	ium acetate EDTA	Double Acids	Acids	HCI	5	Nitri	Nitric Acid
Ammonium acetate -EDTA	Cu = 0.86* Zn = 0.99***	Mn = 0.73 Fe = 0.63								
Double Acids	Cu = 0.48 Zn = 0.99***	Mn = 0.73 Fe = 0.36	Cu = 0.54 Zn = 0.99***	Mn = 0.99*** Fe = 0.48						
HCI	Cu = 0.75 Zn = 0.99***	Mn = 0.71 Fe = 0.59	Cu = 0.96** Zn = 0.99***	Mn = 0.99*** Fe = 0.63	Cu = 0.45 Zn = 0.99***	Mn = 0.99*** Fe = 0.87**				
Nitric Acid	Cu = 0.51 Zn = 0.99***	Mn = 0.71 Fe = 0.33	Cu = 0.84* Zn = 0.99***	Mn = 0.99*** Fe = 0.50	Cu = 0.36 Zn = 0.99***	Mn = 0.99*** Fe = 0.99***	Cu = 0.95** Zn = 0.99***	Mn = 0.99*** Fe = 0.91**		
NaOH	Cu = 0.99*** Zn = 0.99***	Mn - 0.73 Fe = 0.69	Cu = 0.83* Zn = 0.99***	Mn = 0.98** Fe = 0.65	Cu = 0.45 Zn = 0.99***	Mn = 0.99*** Fe = 0.76	Cu = 0.71 Zn = 0.99***	Mn = 0.98*** Fe = 0.97***	Cu = 0.47 Zn = 0.99***	Mn = 0.98*** Fe = 0.80

% Level of Confidence

%0.9% . *** %0.9% . **

As would be expected, the amounts of Cu, Mn. Fe and Zn extracted differed according to the extractants used. Lombin (1983) evaluated several micronutrient soil test methods and concluded that 0.1 M EDTA in 1 N NH, OAc, 0.1 N HCl and double acids (0.05 N HCl in 0.025 N H,SO,) were the most suitable extracting reagents for plantavailable Cu, Mn, Fe and Zn in the semi-arid West African savanna, Dolar and Keeney (1971) reported that 0.1 N HCl extracted more of these micronutrients than 0.1 M EDTA-NH₂OAc. However, Osiname et al. (1973), working with the savanna and forest soils of southern Nigeria, reported contrasting results. In general, the mineral acid extracted more of the metals than did the chelating agent EDTA in the semi-arid savanna soils (Lombin, 1983).

Table 2 shows the amounts of Cu. Zn. Mn and Fe in peat extracted by the five reagents used in the exercise. In the case of Cu, chelating agent EDTA and NaOH removed more than the mineral acids. Extractant 'e' removed about 70%-93% of total Cu from the peat. Compared with other elements, the proportion of Cu was the highest in the NaOH-extractable fraction, probably because it forms the most stable complexes with soil organic matter compared to Zn, Mn and Fe (Stevenson and Ardakani 1972), Interestingly, the amounts of Cu extracted by NaOH were highly correlated with total Cu (Table 3). The use of NaOH may lead to an overestimation of plantavailable Cu in peat. However, this fraction is considered to be the 'potentially available' form for plants because it is believed to be in equilibrium with the easily soluble form within a short period of time. Extractants 'a' and 'c' were also found to be quite effective, removing about 15%-75% of total Cu, depending on the nature of the peat. The values obtained by extractant 'a' also correlated well with total Cu.

Similar observations were made for Fe; about 34%-94% of total Fe was removed by extractant 'e'. Extractants 'a' and 'c' were also found to be effective in removing a relatively high percentage of Fe. However, the amounts obtained by these extractants did not correlate well with total Fe, suggesting that the distribution of Fe in peat was not influenced by its total quantity. The amounts extracted by double acids and nitric acid were less than 4% of the total Fe, which could have

been due to the concentration of H⁺ in these two extractants not being enough to prevent reabsorption or chelation of the dissolved Fe.

For zinc, it was found that the amounts obtained ranged quite widely among the six peat samples analyzed, depending on the extractants used. However, total Zn evidently had a strong influence on the distribution of Zn in soil, since all forms of Zn extracted were highly correlated with total Zn. Suprisingly, all forms of Zn were also found to be well correlated with each other. This suggests that all the extractants used could be considered as efficient for testing the concentration of Zn in peat, except perhaps for NaOH, which extracted relatively less Zn than the other reagents.

The same trend was observed for Mn where extractants 'a', 'b', 'c' and 'd' displaced Mn quite effectively, with more than 60% of the total Mn being removed. Extractant 'e' removed less than 50% of the total Mn. The values obtained using the other four extractants correlated well with each other. Total Mn however, did not correlate well with the values obtained with any of the five extractants tested.

The data in *Table 4* reveal that, in general, the concentrations of micronutrients obtained by the various extractants were independent of the soil properties, except for Cu extracted by the double acids, which showed slight correlations with pH. exchangeable Ca, exchangeable K and available P. Interestingly, Zn extracted by all the extractants tested was highly correlated with exchangeable Al, suggesting that the amount of Zn in peat is very much dependent on the level of the latter. The reason may be the complexation of Zn by aluminium in the soil solution. Cu removed by several extractants was found to be negatively correlated with the amount of total P, indicating that there was some relationship between Cu and P in the peat soil.

CONCLUSIONS

The micronutrients Cu, Zn, Mn and Fe in peat were found to occur in different concentrations depending on the nature of the peat, its drainage status and its agricultural utilization. These points were clearly shown by the analyses

TABLE 4. SIMPLE LINEAR CORRELATION BETWEEN MICRONUTRIENTS IN VARIOUS EXTRACTS AND OTEHR SOIL PARAMETERS.

	Total Micronutrient	onutrient	Ammonium acetate	nium acetate -EDTA	Double Acids	Acids	HCI		Nitric Acid	Acid	NaOH	НС
Hd	Cu = 0.53 Zn = 0.29	Mn = 0.66 Fe = 0.11	Cu = 0.34 Zn = 0.30	Mn = 0.72 Fe = 0.45	Cu = 0.85* Zn = 0.31	Mn - 0.74 Fe - 0.42	Cu - 0.24 Zn - 0.29	Mn = 0.71 Fe = 0.49	Cu - 0.09 Zn - 0.32	Mn = 0.7 Fe = 0.56	Cu = 0.54	Mn-0.69
Organic Carbon	Cu = 0.64	Mn = 0.65	Cu - 0.40	Mn = 0.73	Cu = 0.81	Mn - 0.76	Cu = 0.30	Mn = 0.73	Cu = 0.12	Mn = 0.72	Cu - 0.61	Mn-0.75
	Zn = 0.45	Fe = 0.23	Zn - 0.45	Fe = 0.51	Zn = 0.46	Fe - 0.70	Zn = 0.45	Fe = 0.79	Zn = 0.45	Fe = 0.75	Zn - 0.47	Fe - 0.74
Exchangeable Ca	Cu = 0.68	Mn - 0.62	Cu - 0.54	Mn = 0.64	Cu = 0.91*	Mn - 0.67	Cu - 0.41	Mn = 0.63	Cu - 0.24	Mn = 0.63	Cu = 0.64	Mn=0.64
	Zn = 0.36	Fe - 0	Zn - 0.37	Fe = 0.44	Zn = 0.38	Fe - 0.68	Zn - 0.37	Fe = 0.69	Zn - 0.37	Fe = 0.74	Zn = 0.38	Fe = 0.61
Exchangeable Mg	Cu = 0.43	Mn - 0.15	Cu = 0.38	Mn = 0.55	Cu = 0.71	Mn = 0.59	Cu = 0.43	Mn = 0.56	Cu = 0.40	Mn = 0.56	Cu = 0.36	Mn=0.56
	Zn = 0.53	Fe - 0.16	Zn = 0.55	Fe = 0.17	Zn = 0.56	Fe = 0.66	Zn = 0.54	Fe = 0.60	Zn = 0.55	Fe = 0.66	Zn = 0.55	Fe = 0.50
Exchangeable K	Cu = 0.60 Zn = 0.20	Mn - 0.25 Fe - 0.38	Cu - 0.72 Zn - 0.17	Mn = 0.32 Fe = 0.12	Cu = 0.96* Zn = 0.19	Mn - 0.35 Fe - 0.50	Cu = 0.66 Zn = 0.18	Mn = 0.32 Fe = 0.53	Cu = 0.59 Zn = 0.16	Cu - 0.32 Fe - 0.19	Cu = 0.55	Mn-0.30
Exchangeable AI	Cu = 0.2	Cu = 0.2 Mn = 0.25	Cu = 0.36	Cu = 0.36 Mn = 0.68	Cu = 0.1	Mn - 0.68	Cu - 0.39	Mn = 0.69	Cu = 0.37	Mn 0.71	Cu - 0.28	Mn - 0.73
	Zn = 0.97**	Zn = 0.97*** Fe = 0.38	Zn = 0.97***	Zn = 0.97*** Fe = 0.14	Zn = 0.16	Fe - 0.82*	Zn - 0.15	Fe = 0.57	Zn = 0.14	Fe 0.81	Zn - 0.14	Fe - 0.43
Total N	Cu = 0.79	Mn = 0.26	Cu = 0.75	Mn = 0.01	Cu = 0.38	Mn - 0.02	Cu = 0.59	Mn = 0.01	Cu - 0.41	Mn = 0.01	Cu = 0.73	Mn=0.07
	Zn = 0.05	Fe = 0.02	Zn = 0.05	Fe = 0.48	Zn = 0.07	Fe - 0.82*	Zn = 0.06	Fe = 0.57	Zn - 0.06	Fe = 0.81	Zn = 0.05	Fe = 0.42
Total P	Cu = 0.87* Zn = 0.38	Mn = 0.1 Fe = 0.26	Cu = 0.98** Zn = 0.37	Cu = 0.98*** Mn = 0.26 Zn = 0.37 Fe = 0.46	Cu = 0.50 Zn = 0.35	Mn - 0.23 Fe - 0.36	Cu = 0.88* Fe = 0.22	Mn = 0.27 Zn = 0.36	Cu - 0.73 Fe - 0.50	Mn = 0.27 Zn = 0.37	Cu = 0.86* Dw = 0.06	Mn-0.23
Available P	Cu = 0.60	Mn = 0.29	Cu = 0.67	Mn = 0.42	Cu = 0.96**	Mn = 0.45	Cu = 0.61	Mn - 0.42	Cu - 0.53	Mn = 0.42	Cu = 0.55	Mn -0.41
	Zn = 0.25	Fe = 0.27	Zn = 0.28	Fe = 0.17	Zn = 0.30	Fe = 0.56	Zn = 0.28	Fe - 0.44	Zn - 0.29	Fe = 0.61	Zn = 0.28	Fe - 0.30

carried out using the five extractants in this study. The results seemed to suggest that:

- Ammonium acetate-EDTA and NaOH were the most effective extractants for Cu in peat.
- ii. Ammonium acetate-EDTA, double acids, HCl and nitric acid were found to be good extractants in removing Zn and Mn in peat.
- iii. Ammonium acetate-EDTA, HCl and NaOH were found to be effective in extracting Fe in peat.

However, all the extractants studied merit further investigation since the amounts of Cu, Zn, Mn and Fe extracted need to be correlated with the actual uptake of these elements by the crop to provide more meaningful information on their availabilities. This work is in progress.

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