

# Total and extractable copper, iron, manganese and zinc in major agricultural soils in the Lower Benue Valley, Central Nigeria and the concept of extractant efficiency

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## ABSTRACT

*As a contribution to the broader national effort to evaluate the fertility and management problems of Nigeria's major agricultural soils, total and plant-available concentrations of the micronutrients Cu, Fe, Mn and Zn were determined in six profiles, representing typical agricultural soils in the Lower Benue Valley, Central Nigeria. Total amounts of the elements ranged from 2.72-49.8 mg kg<sup>-1</sup> for Cu and 6.50-77.5 mg kg<sup>-1</sup> for Zn, and 0.52-12.7 % and 46.7-1340 mg kg<sup>-1</sup> for Fe and Mn, respectively. More total micronutrients occurred in the soil derived from metamorphic rocks, than in the soils with sedimentary parent materials. Although the amounts of the extractable micronutrients varied with the extractant employed, using critical limits established elsewhere in Nigeria, plant-available Cu, Fe and Mn may be considered adequate, while Zn deficiency problems may be expected in some of the soils in the region. Using the proportion of total elements extracted by each extractant, a new concept of "extractant efficiency" is introduced to aid in selecting candidate extractants for soil testing.*

## INTRODUCTION

Investigations into micronutrient levels and their crop requirements in Nigerian soils are still limited, and largely within academia<sup>1,2,3,4,5,6,7,8,9</sup>. This is probably due to the, hitherto, non-intensive use of agricultural land in much of the country. In the existing traditional farm-practice of shifting cultivation and rotational bush fallow, the assumption is that micronutrient deficiencies are probably not to be

expected, since under the system, recycling of nutrients through leaf and other organic residue decay during the fallow periods is believed to return adequate amounts of nutrients, including micronutrients, to the soil<sup>10</sup>. Moreover, incidental additions of these nutrients through generous applications of inorganic (largely NPK) fertilizers, a widespread practice, is considered an additional source which adequately addresses the micronutrient needs of common arable crops in Nigeria.

However, with a steadily growing population (currently estimated at ca. 160 million people), there is a corresponding pressure on farmland with the result that fallow periods are becoming shorter in some areas, while intensive agriculture is fast replacing the age-old peasant system. Indeed, a report in 1988 by the National Fertilizer Centre, Ibadan, suggested then, that Zn deficiency problems could increasingly be expected in the country<sup>11</sup>. This, indeed, became the case within ten years (and probably has worsened now), especially in the Southern Guinea Savanna ecological zone, requiring the inclusion of this nutrient in fertilizer formulations intended for use in the zone<sup>12</sup>.

The Lower Benue Valley (6° 15'E-10° 00'E and 6°15'N-8° 00'N) is a major part of Central Nigeria, most of which lies within the Southern Guinea Savanna. The entire area is generally considered the country's "food basket", because its agro-ecological characteristics permit the production of many of the country's staples, including root and tuber crops, cereals and legumes, fruits etc.; this is done, largely, under subsistent, rain-fed agriculture<sup>13</sup>. With the current population pressure, more of the agricultural land in the region has come under intensive cropping, with shorter fallow periods. Although high acidity and low available P are usually regarded as common soil factors that limit yields in tropical environments, the role of micronutrients cannot be downplayed<sup>14,15</sup>. At present little is known about the micronutrient status of the soils of this important agricultural region of Nigeria. Therefore, the overall objective of this study was to determine the total and

extractable (i.e. probable plant-available) concentrations and profile distributions of the micronutrients, Cu, Zn, Fe and Mn, in the main agricultural soils in the Lower Benue Valley, and relate these to any influence of their parent materials and other soil properties. This is expected to form a basis to anticipate any management needs regarding these nutrients in the area.

## MATERIALS AND METHODS

### *The Soils*

Six profiles were selected for this investigation, all of which lie within Kowal and Knabe's<sup>16</sup> Makurdi Polygon. This is an area subjected to very similar weathering conditions, so that the principal factor distinguishing the soils is their parent materials. Therefore, the profiles were chosen to reflect this, using the Geological Map of Nigeria<sup>17</sup> as guide. Details of their specific locations and sampling are reported elsewhere<sup>18</sup>.

### *Laboratory Analyses*

Only AnalaR grade reagents and chemicals were used in the following analyses.

### *Physico-chemical characteristics of soils*

Routine soil physico-chemical parameters, namely, texture, organic matter, pH, cation exchange capacity (C.E.C.) and sesquioxides (of Fe and Al) contents were determined on the < 2.0 mm soil fractions, using procedures described in the *International Institute of Tropical Agriculture Manual Series, No.1*<sup>19,20</sup>.

## RESULTS AND DISCUSSION

### *Extractable micronutrients (Cu, Fe, Mn and Zn)*

For extractable micronutrients, three soil testing extractants, namely 0.1 M HCl, 0.05 M Na<sub>2</sub> EDTA in neutral 1 M NH<sub>4</sub>OAc and 0.005 M DTPA + 0.01 M CaCl<sub>2</sub> + 0.1 M TEA, at pH of 10.9 (Dolar and Keeney, 1971) were employed. Duplicate 5.0g sub-samples of air-dried soil (< 2.0 mm diameter) at different profile depths (horizons) were transferred into 100-cm<sup>3</sup> acid-washed plastic bottles and extracted with 50cm<sup>3</sup> of extractant (0.1 M HCl, 0.05 M EDTA or 0.005 M DTPA) as described by Udo and Ogunwale<sup>20</sup>. The amounts of micronutrients extracted were determined by flame atomic absorption spectrophotometry using a *Perkin-Elmer AAS Model 2380* instrument fitted with Hamamatsu Hollow Cathode Lamps. For every determination, reagent blanks were prepared accordingly for quality assurance of the analytical data.

### *Total Cu, Fe, Mn and Zn.*

For total micronutrients, 5-10 g portions of < 2.0 mm air-dried soil samples were ground to pass through 100-mesh sieve. About 0.3 g sub-samples of this fraction, in duplicate, were transferred to 50 cm<sup>3</sup> capacity Teflon™ beakers and digested with 48% HF-70% HClO<sub>4</sub>-conc. HNO<sub>3</sub> mixture as described by Udo and Ogunwale<sup>20</sup>. The amount of the elements in the digest was also determined by flame atomic absorption spectrophotometry.

### *Physicochemical Characteristics of the Soils*

Table 1 summarizes some of the properties of the profiles, including their mineralogy, classification and parent materials. These soils are the major agricultural soils of the Lower Benue Valley in Central Nigeria. They have, in general, very low organic matter content and CEC and are only moderately acid. Their surface textures range from sandy loam (Profiles 1, 4, 5 and 6) to loam (Profile 2) and silty clay loam (Profile 3). Accumulation and profile trends of Fe and Al hydroxy-oxides along with the low CEC and kaolinitic clay mineralogy indicate that most of the soils are highly weathered, as might be expected of soils of the West African savanna<sup>22</sup>.

### *Concentrations and Distributions of the micronutrients in the profiles*

The concentrations of the total and extractable Cu and Zn are summarized in Table 2; similar data for Fe and Mn is contained in Table 3. Figures 1 and 2 show the distribution patterns of total concentrations of the elements (Cu, Zn and Fe, Mn, respectively) along with clay, in the profiles.

**Table 1.** Some physico-chemical properties of major agricultural soils in the Lower Benue Valley of Nigeria.

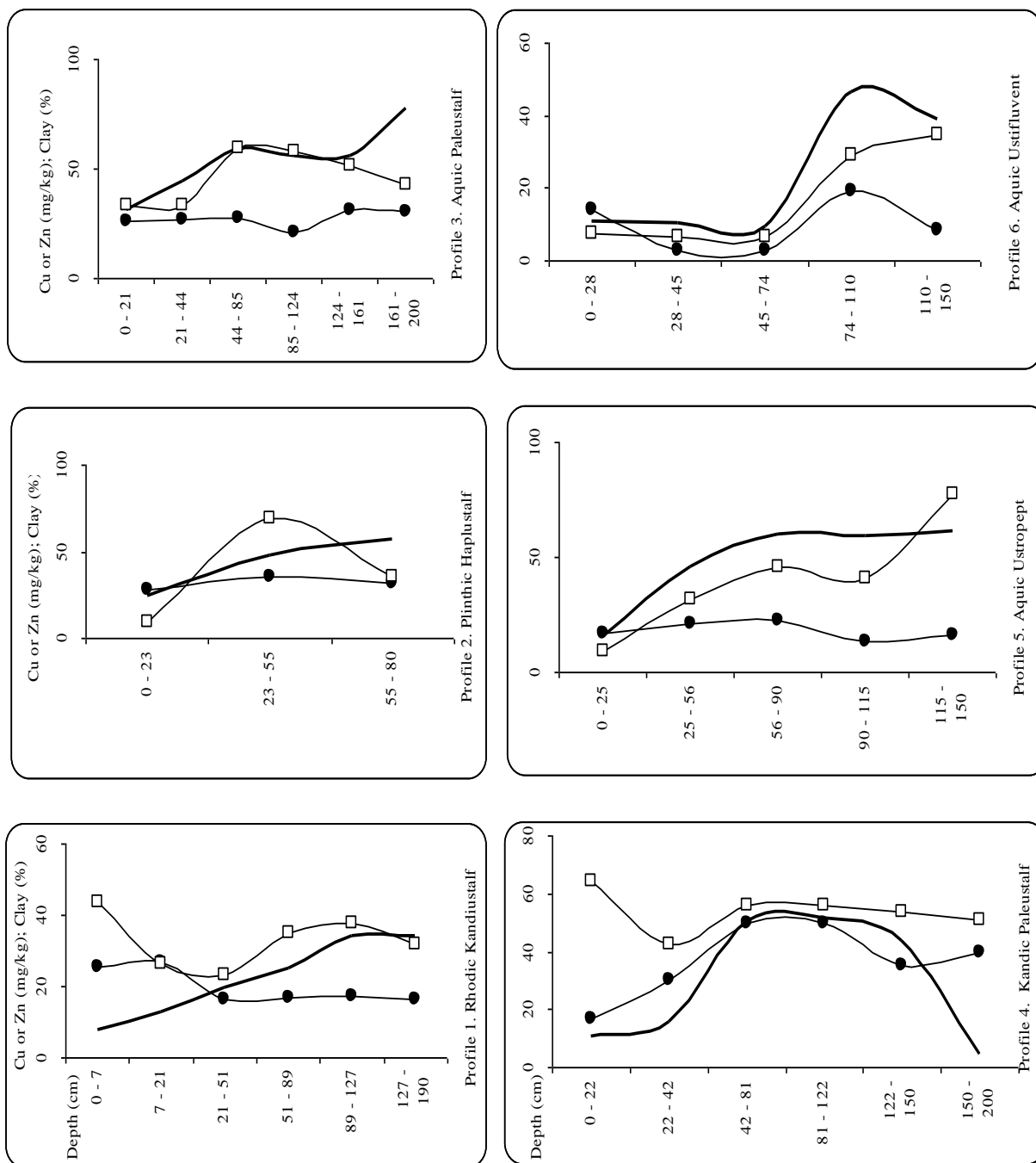
Depth (cm)	Particle Size Distribution			pH (H <sub>2</sub> O)	ECEC cmol (+) kg <sup>-1</sup>	O.M. %	Fe <sub>d</sub> %	Al <sub>d</sub> %	Mineralogy*
	Sand	Silt	Clay						
<b>Profile 1. Rhodic Kandiustalf on Cretaceous Sandstones/Upper Coal Measures</b>									
0-7	88	4.0	8.0	5.6	2.95	0.41	2.35	6.95	Q, K, f
-21	85	2.0	13	5.0	1.74	0.33	3.17	9.73	
-51	79	1.0	20	5.0	1.69	0.25	2.89	9.09	
-89	73	2.0	25	5.3	1.97	0.22	3.60	11.9	
-127	65	1.0	34	5.4	2.17	0.20	4.94	13.2	
-190	65	1.0	34	5.8	1.89	0.14	3.95	10.3	
<b>Profile 2. Plinthic Haplustalf on Cretaceous shale/siltstones</b>									
0-23	55	21	24	6.0	3.52	0.65	1.08	2.11	Q, K, f
-55	32	20	48	5.2	5.94	0.34	4.87	2.87	
-80	22	21	57	5.4	7.50	0.29	4.40	3.06	
>80	Thick Petroplinthite layer overlying shale saprolite								
<b>Profile 3. Aquic Paleustalf on Cretaceous shale/limestone</b>									
0-21	16	52	32	6.4	10.5	1.89	2.65	10.1	Q, K, s, f
-44	13	43	44	5.3	7.55	1.01	4.29	16.4	
-85	15	26	59	5.4	7.54	0.90	6.80	17.5	
-124	27	17	56	5.7	10.3	0.49	7.21	21.3	
-161	30	14	56	5.4	10.7	0.43	7.05	17.2	
-200	7.0	15	78	4.8	16.5	0.22	4.47	8.66	
<b>Profile 4. Kandic Paleustalf on Precambrian Basement Complex rocks (mainly Gneiss and Migmatites)</b>									
0-22	80	9.0	11	6.2	3.35	0.79	0.75	3.88	Q, K, f
-42	66	19	15	5.7	3.10	0.65	1.43	5.74	
-81	43	6.0	51	5.6	6.92	0.31	3.53	18.6	
-122	42	7.0	51	5.7	6.86	0.15	4.15	21.7	
-150	47	9.0	44	5.8	6.13	0.11	5.24	13.8	
-200	47	10	43	6.0	5.56	0.03	2.83	16.0	
<b>Profile 5. Aquic Ustropept on Quaternary (Benue River) alluvium</b>									
0-25	57	28	15	5.9	7.22	0.60	0.97	3.45	Q, K, I, s
-56	34	20	56	6.1	10.6	0.53	2.83	6.76	
-90	28	12	60	5.8	12.8	0.15	2.46	7.16	
-115	28	13	59	5.9	11.9	0.12	1.91	5.29	
-150	18	21	61	5.7	15.0	0.09	2.26	4.20	
<b>Profile 6. Aquic Ustifluent on Quaternary (Benue River) alluvium</b>									
0-28	74	15	11	5.6	5.66	1.2	0.45	0.14	Q, K, I
-45	78	11	11	5.7	3.49	0.55	0.31	0.14	
-74	80	10	10	5.8	3.90	0.15	0.27	0.14	
-110	40	14	46	6.7	11.0	0.23	1.65	0.44	
-150	41	21	38	7.2	12.4	0.10	0.91	0.17	

\*Based on XRD analysis of deferrated samples (< 100-Mesh) of soil taken from B or C horizons (Courtesy: Prof. Peter L. Van Reeuwijk, ISRIC, Wageningen, The Netherlands). Q = quartz; K = Kaolinite; F = feldspars; I = Illite; S = Smectite. Upper case = major component ; Lower case = minor component. O. M. = organic matter; Fe<sub>d</sub>, Al<sub>d</sub> = Citrate-Bicarbonate-Dithionite (CBD)-extractable hydrous oxides of Fe and Al.

**Table 2.** Profile averages and ranges of total and extractable Cu and Zn in major agricultural soils in the Lower Benue Valley of Nigeria

	0.1M HCl		0.005M DTPA		0.05M EDTA		Total	
	Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn
	mg kg <sup>-1</sup>							
<b><u>Profile 1. (Rhodic Kandistalf on Cretaceous Sandstones)</u></b>								
Mean:	0.80	0.76	0.93	0.24	0.54	0.35	19.9	33.0
Minimum:	0.36	0.31	0.64	0.12	0.39	0.25	16.2	23.1
Maximum:	1.11	1.14	1.28	0.38	0.71	0.46	26.9	43.7
Surface horizon:	1.11	1.14	1.13	0.25	0.71	0.46	25.4	43.7
<b><u>Profile 2. (Plinthic Haplustalf on Blackshale and Siltstones)</u></b>								
Mean:	1.52	1.11	2.89	0.48	1.94	0.35	31.7	38.1
Minimum:	0.96	0.46	2.44	0.24	1.73	0.17	27.8	9.37
Maximum:	1.85	1.65	3.29	0.68	2.18	0.57	35.2	69.5
Surface horizon:	1.85	1.65	2.94	0.68	1.73	0.57	27.8	9.40
<b><u>Profile 3. (Aquic Paleustalf on Shale and Limestone)</u></b>								
Mean:	2.94	2.22	4.45	1.54	3.37	1.87	27.2	46.3
Minimum:	2.20	0.72	3.71	0.34	2.82	0.64	21.2	33.1
Maximum:	3.63	3.22	5.42	2.33	4.06	2.85	31.1	59.4
Surface horizon:	2.20	3.22	3.71	1.74	3.27	2.23	25.8	33.1
<b><u>Profile 4. (Kandic Paleustalf on Basement Complex rocks)</u></b>								
Mean:	1.46	0.72	1.78	0.24	1.58	0.41	36.9	53.8
Minimum:	0.70	0.26	0.81	0.03	1.07	0.22	16.7	42.4
Maximum:	2.12	1.79	2.36	0.49	2.26	0.65	49.8	64.3
Surface horizon:	1.43	0.84	0.81	0.41	1.40	0.65	16.7	64.3
<b><u>Profile 5. (Aquic Ustropept on Quaternary alluvium)</u></b>								
Mean:	1.60	1.21	2.84	0.67	2.24	0.95	18.3	41.1
Minimum:	1.49	0.45	2.00	0.29	2.11	0.47	13.5	9.37
Maximum:	1.75	2.46	3.57	1.27	2.42	1.73	22.8	77.5
Surface horizon:	1.75	1.39	2.00	0.65	2.16	0.87	17.2	1.20
<b><u>Profile 6. (Aquic Ustifluent on Quaternary alluvium)</u></b>								
Mean:	0.49	0.70	1.72	0.29	1.32	0.45	9.5	17.0
Minimum:	0.29	0.39	1.25	0.14	0.86	0.29	2.72	6.50
Maximum:	0.77	1.27	2.22	0.37	1.65	0.62	19.4	34.8
Surface horizon:	0.77	0.47	1.33	0.30	1.65	0.62	14.2	7.43

Summary of within-profile (depth-wise) concentrations of the element



**Figure 1.** Profile distribution patterns of total Cu (●), Zn (□) and Clay (solid line) in major agricultural soils in the Lower Benue Valley, Central Nigeria

### **Total Levels**

Total Cu in the soils ranged from 2.72-49.8 mg kg<sup>-1</sup> soil with average of 23.8 mg kg<sup>-1</sup> soil, while total Zn ranged between 6.50 and 77.5 mg kg<sup>-1</sup> soil, with 38.8 mg kg<sup>-1</sup> soil as average. Considering profiles individually, Profile 4 derived from metamorphic (basement complex) rocks, had the highest average total profile concentrations of both elements, while the alluvial soil (Profile 6) had the lowest (Table 2).

Of the other sedimentary profiles, other hand, had low total Cu and Zn, although the latter element occurred in more or less comparable amounts as in the other profiles. The distribution trends of the total concentrations of the two micronutrients in the profiles showed accumulations of Cu in the genetic A horizon in Profile 1 and Zn in Profiles 1 and 4. There was accumulation of Cu also in the genetic A horizon of one alluvial soil (Profile 6, the Entisol). Apart from these, the general trend is one of subsurface accumulation of the elements in the profiles, more or less, matching the distribution of clay as shown in Figure 1.

Total Fe in the soils ranged from 0.52-12.7%, with average value of 3.86%, while total Mn occurred in the range 46.7-1360 mg kg<sup>-1</sup> soil with average 287 mg kg<sup>-1</sup> soil. On individual basis, Profile 3 on shale/limestone had the highest profile average total Fe of 7.05% followed by Profile 1 on sandstones with 4.13%, while the poorly developed alluvial Profile 6, had the lowest total Fe content at 1.48% Profile 3 overlying Cretaceous shale and limestone had more Zn, while Profile 2 overlying Cretaceous shale/siltstones had more Cu.

Together these may be considered to be next to the basement complex profile in especially, total Cu content. The sandstone-derived soil (Profile 1) on the average. With total Mn, the highest average profile concentration (603 mg kg<sup>-1</sup> soil) occurred in the Pre-Cambrian Basement Complex Profile 4, followed by Profile 3 on shale/limestone (with 327 mg kg<sup>-1</sup> soil), while the poorly developed Profile 6, on alluvium, had the lowest (113 mg kg<sup>-1</sup>). While total Fe showed some accumulation in the subsurface horizons (Figure 2) more total Mn was, generally, found in the surface and near-surface horizons. It is noteworthy that subsurface accumulations of both elements coincided with the Bt and Bs (i.e. sesquioxidic) horizons of Profiles 3 and 4.

### **0.1M HCl-Extractable Levels**

Taking all the soils together, the 0.1M HCl-extractable Cu ranged from 0.29-3.63 mg kg<sup>-1</sup> soil while the corresponding range for Zn was 0.26-3.22 mg kg<sup>-1</sup> soil, with average values of 1.49 mg kg<sup>-1</sup> and 1.13 mg kg<sup>-1</sup> respectively. Profile 3 (on shale/siltstones) had the highest profile average concentrations of Cu and Zn that were acid-soluble, while Profile 1 on sandstones and the alluvial Entisol (Profile 6) had the lowest. The other profiles had more or less comparable values as Table 2 shows.

The 0.1N HCl-extractable Fe and Mn varied widely in the soils, from as low as 19.5 to 249 mg kg<sup>-1</sup> for Fe and 3.15 to 423 mg kg<sup>-1</sup> for Mn; these gave corresponding average values of 78.7 mg kg<sup>-1</sup> and 60.4 mg kg<sup>-1</sup> soil for Fe and Mn, respectively (Table 3). Between the profiles, those on shales (i.e. Profiles 2 and 3) had the highest profile

average amounts of acid soluble Mn ( $104 \text{ mg kg}^{-1}$  and  $105 \text{ mg kg}^{-1}$ , respectively), while Profile 1 on sandstones had the lowest ( $11.0 \text{ mg kg}^{-1}$ ). Compared to the profiles on shale, the alluvial soils also had low amounts of acid soluble Mn ( $20.3\text{-}39.5 \text{ mg kg}^{-1}$ ). As for Fe, the poorly developed alluvial profile (i.e. Profile 6), had the highest profile average concentrations of 0.1M HCl-extractable Fe of  $160 \text{ mg kg}^{-1}$ , followed by Profile 3 on shale/limestone with  $134 \text{ mg kg}^{-1}$  soil. Again the sandstone soil (Profile 1) and the Basement Complex soil (Profile 4), had the lowest concentrations of acid soluble Fe: respectively,  $26.4 \text{ mg kg}^{-1}$  and  $37.8 \text{ mg kg}^{-1}$  soil.

#### ***0.005M DTPA-Extractable Levels***

The 0.005M DTPA-extractable Cu and Zn levels in the soils varied from  $0.64\text{-}5.42 \text{ mg kg}^{-1}$  and  $0.03\text{-}2.33 \text{ mg kg}^{-1}$ , respectively with corresponding average values  $2.40 \text{ mg kg}^{-1}$  and  $0.59 \text{ mg kg}^{-1}$ , respectively. Among the profiles, soils on shale and alluvium had more DTPA-extractable Cu and Zn than soils on basement complex and sandstones, with the soil overlying shale and limestone (Profile 3) having the highest profile average concentrations. In comparison, DTPA extracted more Cu than Zn from the soils while 0.1M HCl extracted more Zn than Cu.

The 0.005M DTPA-extractable Fe and Mn also varied widely among the soils. For Fe the range was  $3.77\text{-}131 \text{ mg kg}^{-1}$  with average  $31.3 \text{ mg kg}^{-1}$  soil and that for Mn was  $2.20\text{-}111 \text{ mg kg}^{-1}$  with average  $26.5 \text{ mg kg}^{-1}$  soil. Thus, this reagent extracted less

Fe and Mn in the soils compared to the mineral acid. Between profiles, Profile 3 had the highest concentrations of DTPA-extractable Fe and Mn, while Profile 4 had the lowest concentrations of DTPA-extractable Mn and Fe.

All considered, the shale/limestone soils had more DTPA-extractable Mn (with combined profile average of  $46.4 \text{ mg kg}^{-1}$  soil) while the alluvial and sandstone soils had the least ( $9.05\text{-}20.7 \text{ mg kg}^{-1}$ ). Profile 4 on Basement Complex had an amount ( $31.4 \text{ mg kg}^{-1}$ ), somewhat, intermediate between the other groups of soils. On the other hand, DTPA-extractable Fe was least in the Sandstone and Basement complex profiles (1 and 4, respectively;  $14.1 \text{ mg kg}^{-1}$  and  $10.7 \text{ mg kg}^{-1}$ , respectively), while the alluvial and shale profiles (3, 5 & 6) had more (with profile average, varying from  $19.3\text{-}56.6 \text{ mg kg}^{-1}$ ) as Table 3 shows.

#### ***0.05M EDTA-Extractable Levels***

0.05M EDTA extracted Cu from the soils in the range  $0.39\text{-}4.06 \text{ mg kg}^{-1}$  soil with average  $1.82 \text{ mg kg}^{-1}$  soil and Zn in the range  $0.17\text{-}2.85 \text{ mg kg}^{-1}$  with average  $0.77 \text{ mg kg}^{-1}$ . As with the other extractants, the soil overlying shale and limestone (Profile 3) had the highest profile average concentration of EDTA-extractable Cu and Zn. This is followed by the alluvial Inceptisol (Profile 5). Other profiles had more or less comparable concentrations, although the sandstone-derived soil (Profile 1.), again, had the lowest concentrations (especially of EDTA-soluble Cu). As with DTPA, the EDTA extractant removed more Cu, but less Zn than 0.1M HCl



**Table 3.** Profile averages and ranges of total and extractable Fe and Mn in major agricultural soils in the Lower Benue Valley of Nigeria\*

	0.1M HCl		0.005M DTPA		0.05M EDTA		Total	
	Mn	Fe	Mn	Fe	Mn	Fe	Mn	Fe
	mgkg <sup>-1</sup>						%	
<b><u>Profile 1. (Rhodic Kandistalf on Cretaceous Sandstones)</u></b>								
Mean:	11.0	26.4	9.05	14.1	10.6	30.6	191	4.13
Minimum:	5.20	23.1	2.73	3.77	4.96	17.3	145	2.59
Maximum:	36.0	34.7	32.4	29.2	33.5	46.4	337	4.49
<b><u>Profile 2. (Plinthic Haplustalf on Blackshale/Siltstones)</u></b>								
Mean:	104	41.9	43.6	19.3	73.2	66.0	168	2.20
Minimum:	3.15	19.5	2.20	11.4	2.36	24.1	73.3	0.89
Maximum:	292	67.3	111	32.0	200	119	318	3.01
<b><u>Profile 3. (Aquic Paleustalf on Shale and Limestone)</u></b>								
Mean:	105	134	49.2	56.6	73.1	175	327	7.05
Minimum:	13.0	98.4	17.5	14.9	13.3	17.0	58.8	2.97
Maximum:	423	184	101	99.8	174	239	536	12.7
<b><u>Profile 4. (Kandic Paleustalf on Basement Complex rocks)</u></b>								
Mean:	94.0	37.8	31.4	10.7	140	62.9	603	3.89
Minimum:	16.8	32.4	7.28	9.35	48.1	39.6	322	1.32
Maximum:	227	48.0	58.3	13.5	253	90.1	340	5.56
<b><u>Profile 5. (Aquic Ustropept on Quaternary alluvium)</u></b>								
Mean:	39.5	64.9	20.7	31.1	64.6	90.5	220	3.09
Minimum:	7.08	55.4	8.04	26.0	6.49	76.3	59.6	1.20
Maximum:	114	88.0	41.9	37.7	184	105	490	3.66
<b><u>Profile 6. (Aquic Ustifluent on Quaternary alluvium)</u></b>								
Mean:	20.3	160	9.87	53.9	23.4	112	113	1.48
Minimum:	12.8	57.1	4.78	5.27	8.45	25.2	46.7	0.52
Maximum:	29.8	249	18.5	131	62.0	202	166	2.85

\*Summary of within-profile concentrations of the elements.

On the whole, however, the DTPA extractant generally removed the highest amounts of Cu in essentially all the profiles, while 0.1M HCl gave the highest amounts of extractable Zn in the profiles.

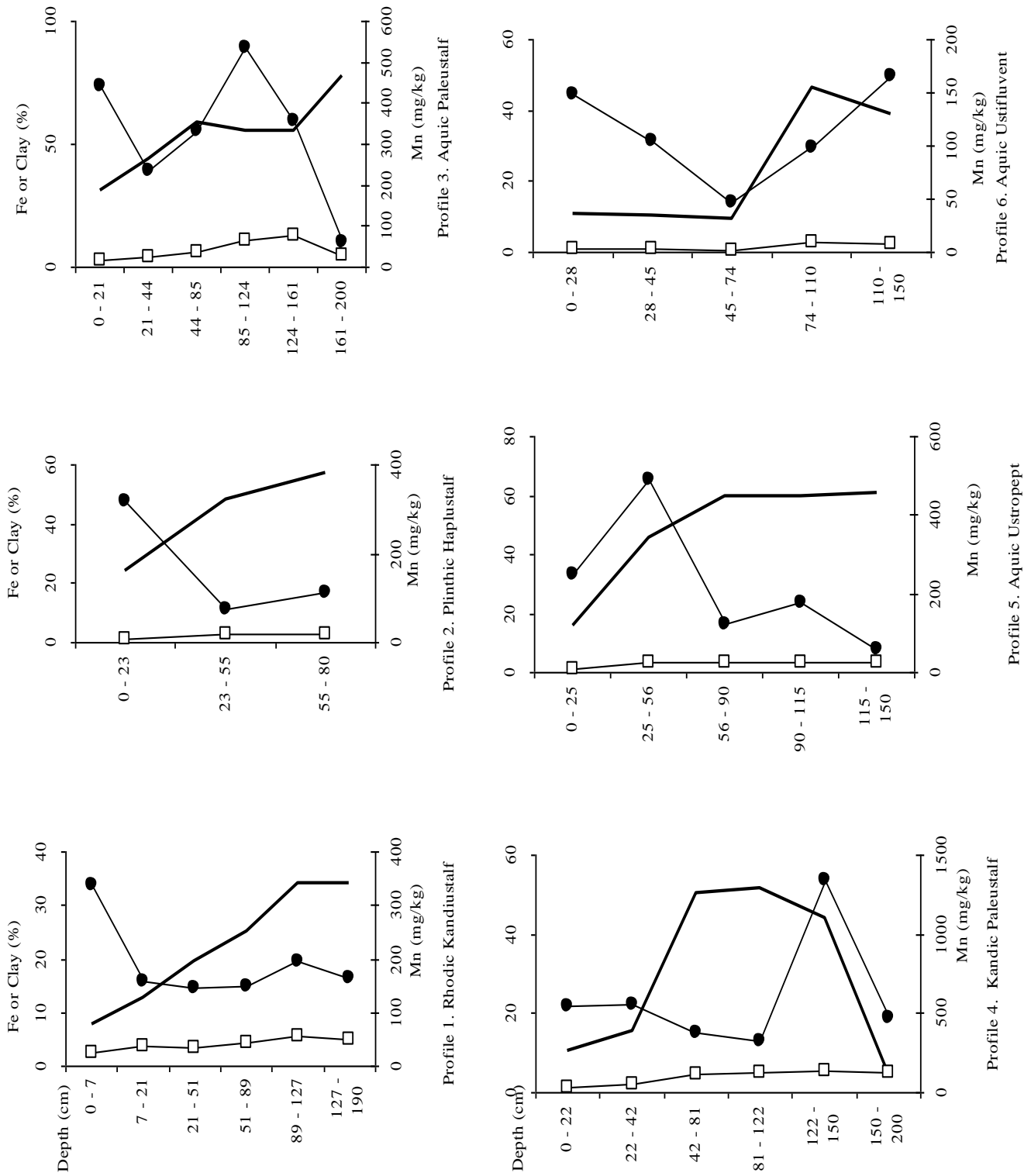
As with the other extractants, the amounts of Fe and Mn extracted with 0.05M EDTA extractant also varied widely. With regard to Fe, the range was from 17.3-239 mg kg<sup>-1</sup> soil with average 91.0 mg kg<sup>-1</sup>, while for Mn, the range and average were 2.36-253 mg kg<sup>-1</sup> and 64.6 mg kg<sup>-1</sup> soil, respectively. Similar to the DTPA reagent, 0.05M EDTA extracted the most Fe in the Profile 3 (average of 175 mg kg<sup>-1</sup>) followed again by the poorly developed alluvial profile (Profile 6) with profile average of 112 mg kg<sup>-1</sup>. The Sandstone soil had the lowest concentration of 30.6 mg kg<sup>-1</sup>.

As for Mn, the Basement Complex soil (Profile 4) gave the highest EDTA-extractable amount of 140 mg kg<sup>-1</sup>, while the Sandstone soil (Profile 1) and the poorly developed alluvial Profile 6 had the lowest (10.6 mg kg<sup>-1</sup> and 23.4 mg kg<sup>-1</sup> soil respectively). Comparing the three extractants, 0.005M DTPA extracted the most Fe in some of the soils (Profiles 1 and 2 and somewhat in Profile 6) and more less comparable amounts of Fe and Mn with 0.1M HCl in others. These observations are clearly illustrated in Figures 3 and 4, which show the profile distribution trends of extractable Fe and Mn extracted by the three reagents.

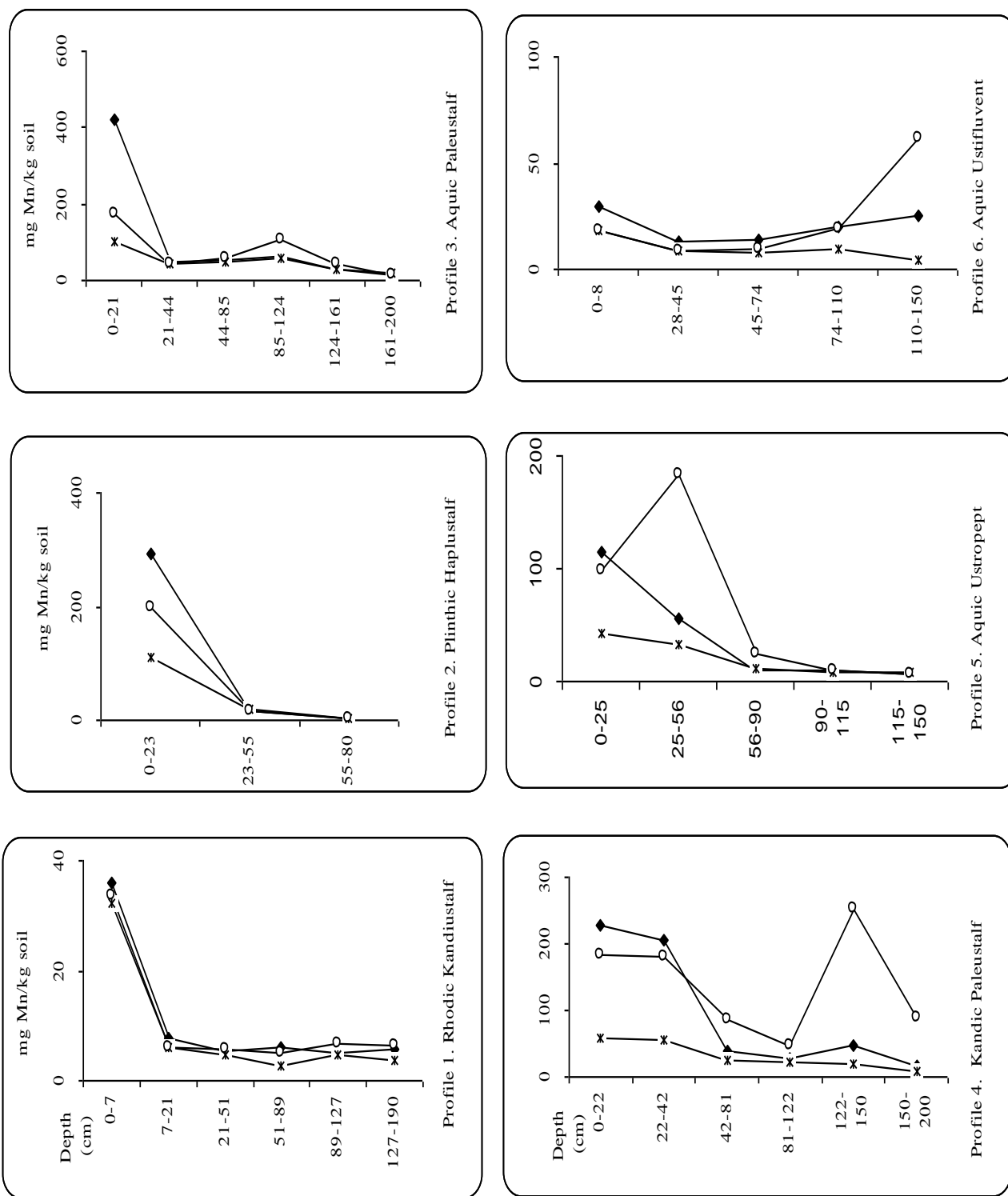
With the exception of Profile 4, all three extractants indicated similar distribution trends in extractable Fe within the profiles namely, a general decrease with increasing profile depth. Although less Fe was

extracted by all three reagents in the surface horizon at Profile 1 and less so at Profile 3, compared to the immediate subsurface horizons, still a decrease in the amounts of extractable Fe with increasing profile is clearly indicated. Similarly, most of the extractable Mn in the soils was concentrated in the surface (A) and near-surface (B) horizons of the profiles (Figure 2). All three extractants also indicated similar profile distribution patterns of extractable Mn in all with the probable exception of Profile 4, where EDTA-extractable Mn appeared to followed a different pattern.

Evaluation of the status of Cu, Fe Mn and Zn in the soils of the Lower Benue Valley, in this study, consisted only of analytical determinations of their total and chemically extractable amounts. No greenhouse experiments were conducted to obtain any correlations between amounts found and actual plant uptake. Still the concentrations of these elements, as extracted by 0.1M HCl, 0.005M DTPA and 0.05M EDTA, are considered good and valid estimates of the levels of their "available" forms in the these soils; confidence being built on general experience in the literature<sup>23,24</sup>. The interpretation and discussion of the results presented are, therefore, set within the limitations of this approach.



**Figure 2.** Profile distribution patterns s of total Fe (□), Mn (●) and Clay (solid line) in major agricultural soils in the Lower Benue Valley, Central Nigeria.



**Figure 3.** Profile concentrations and distributions of 0.10M HCl- (◆), 0.05M EDTA- (○) and 0.005M DTPA-extractable (\*) Mn in major agricultural soils in the Lower Benue Valley, Central Nigeria

### **Total Cu, Fe, Mn and Zn.**

The range of total Cu and Zn reported in this study may be considered low, but they are in agreement with their natural occurrence in soils, generally<sup>25</sup>. They are also typical of levels found in soils of the West African savanna. Similarly, the concentrations of total Fe and Mn in the soils may be considered typical<sup>2,26</sup>.

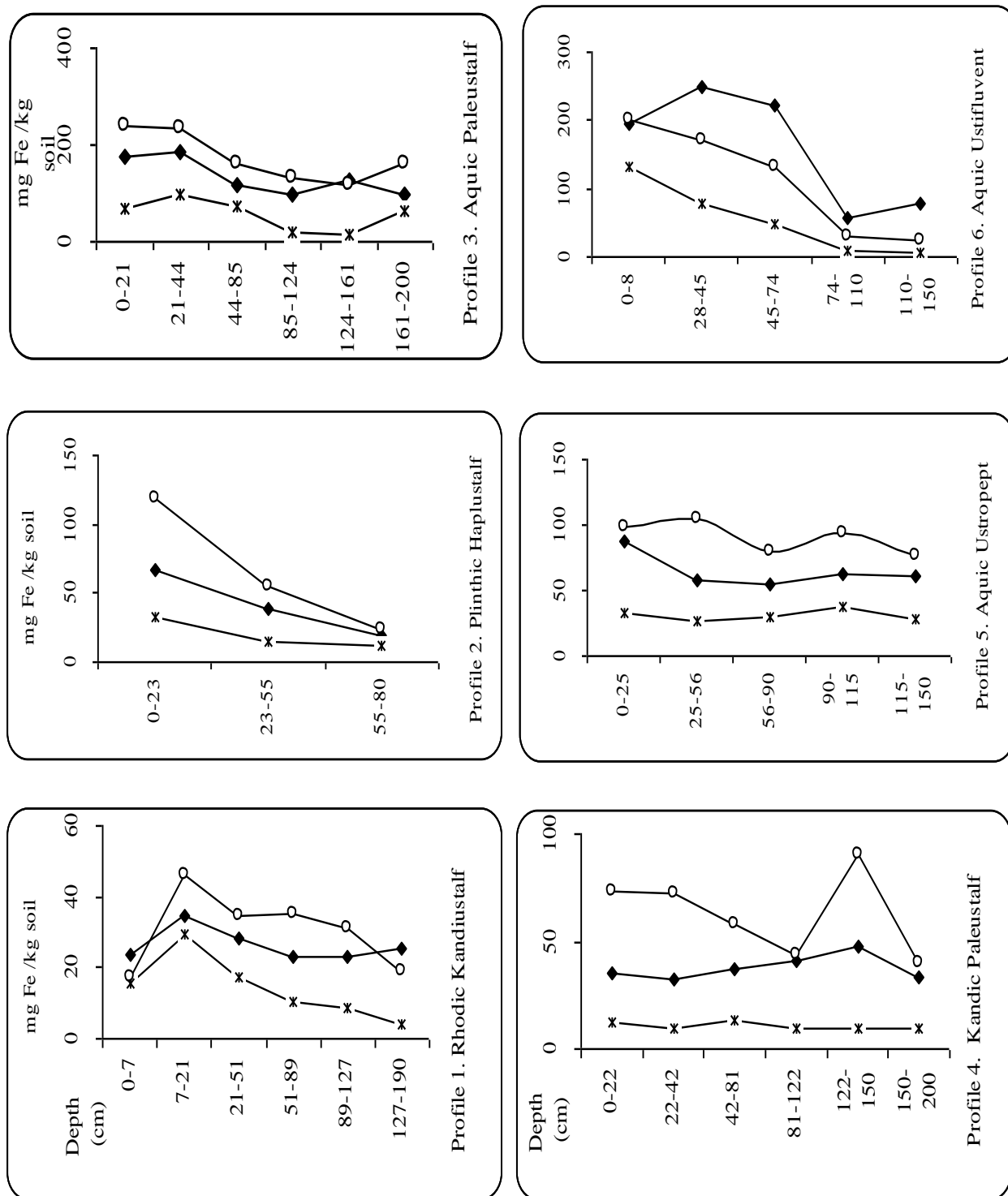
Although no clear-cut and consistent vertical patterns of variation of the total amounts with profile depth were observed, down-profile increase in the concentrations of Cu and Zn was definitely indicated. With Cu, and particularly Zn, this increase clearly coincided with clay distributions in the profiles, as also confirmed by simple correlation analysis (for Cu,  $r = 0.40$ ,  $P = 0.05$  and Zn,  $r = 0.60$ ,  $P = 0.01$ ). Cu and Zn are known to be the micronutrients most associated and translocated with clay in soils<sup>10,27</sup> although other workers did not find this relationship<sup>1,2,4</sup>. The present evidence, however, reinforces the more general observation of the positive Cu- and Zn-clay relationship.

Surface accumulations of these elements have also been widely reported. This is usually attributed to the influence of organic residues in surface horizons<sup>10</sup>, through the "pumping" action of vegetation, which returns nutrients to the surface from subsurface horizons. In the present case, surface accumulation of Zn was evident in the soils overlying sandstone and basement complex parent materials (i.e. Profiles 1 and 4, respectively). Only in the alluvial Entisol (Profile 6) and the sandstone soil (Profile 1) was any accumulation of Cu in the surface horizon observed. Generally, where Cu did

not parallel clay distribution, it showed little variation within the profile (Figure 1).

There is a consensus on the relationship between parent rocks and total concentrations of micronutrient elements in the overlying soils<sup>14,25,27</sup>. Results obtained in this study demonstrate this relationship, only to the extent that more total Cu, Mn and Zn are found in the Kandic Paleustalf (Profile 4), formed on a mosaic of Precambrian metamorphic (basement complex) rocks, made up mainly of gneisses and migmatites, when compared to the amounts in the profiles on Cretaceous and Quaternary sediments.

With regard to soil fertility, the total concentration of micronutrient elements in soils is of little significance<sup>28</sup>. Simple correlation analysis showed that total Cu correlated with the acid-extractable amounts ( $r = 0.41$ ,  $P = 0.05$ ) while total Zn did not correlate with any of the extractable forms considered plant-available. Since total Cu also correlated well with the (Fe and Al) sesquioxides content of the soils ( $r = 0.61$ ;  $P = 0.01$ ), correlation between HCl-extractable Cu and the total amount is expected, considering that the former also correlated with the sesquioxides content. Therefore, the acid (HCl) extractant may have removed Cu in the soils by desorption from oxidic surfaces, or by dissolution of sesquioxidic bodies harboring Cu in the soils<sup>29</sup>, which represents additional sources from which total amounts were estimated, amongst others.



**Figure 4.** Profile concentrations and distributions of 0.10M HCl- (◆), 0.05M EDTA- (○) and 0.005M DTPA-extractable (\*) Fe in major agricultural soils in the Lower Benue Valley, Central Nigeria

### ***Extractable Cu Fe, Mn and Zn.***

#### *Copper and Zinc*

Like their total amounts, the range of 0.1M HCl-extractable Cu and Zn in the soils may also be considered to be on the lower side of ranges reported for other Nigerian soils, especially in the Southwest. For example, Udo *et al*<sup>30</sup> found a range of 0.1-7.18 mg kg<sup>-1</sup> Cu in profiles selected from different parts of the country. This range is comparable to the 0.1-7.4 mg kg<sup>-1</sup> Aghimien<sup>33</sup> found in some hydromorphic profiles in Southern Nigeria. In soils on basement complex rocks in the drier rainforest in the Southwest, Fagbami *et al*<sup>10</sup> obtained even higher amounts and with a wide range of 0.4-17.0 mg kg<sup>-1</sup> Cu.

Still the range found here, is higher than what has been reported (0.54-1.6 mg kg<sup>-1</sup> Cu) in soils of the semi-arid northern parts of the country<sup>28</sup>.

In the case of Zn, Udo and Fagbami<sup>32</sup> found a range of 0.23-6.2 mg kg<sup>-1</sup> in some Nigerian soils, while much higher amounts and wider range of acid extractable Zn have also been reported by Fagbami *et al*<sup>10</sup>: 0.3-12.8 mg kg<sup>-1</sup> and Aghimien<sup>31</sup>: 0.3-12.8 mg kg<sup>-1</sup>. Unlike Cu, the levels of acid soluble Zn in soils of the drier northern savanna (Nigeria) were slightly higher (0.54-4.14 mg kg<sup>-1</sup>) than found in soils of the Lower Benue Valley in Central Nigeria, which is a region of higher rainfall compared to the northern savanna areas<sup>16</sup>. With the DTPA extractant, the levels of Cu and Zn obtained in the present study are comparable to what has been reported elsewhere, although values lower and higher than these are also

common. For instance, Oluwadare *et al.*,<sup>9</sup> reported average concentrations of 0.18, 0.1, 22.5 and 21.5 mg kg<sup>-1</sup> for Zn, Cu, Fe and Mn were respectively for some surface soils in

Nigeria's Guinea Savanna; Aghimien<sup>31</sup> and also Katyal and Sharma<sup>27</sup> found similarly comparable levels of 0.1-5.2 mg kg<sup>-1</sup> and 0.125-5.33 mg kg<sup>-1</sup> for some Nigerian and Indian soils, respectively. Higher concentrations of up to 11.7 mg kg<sup>-1</sup> have also been reported<sup>29,33,34</sup>. While lower levels have also been reported, for example 0.08-2.81 mg kg<sup>-1</sup> by Udo *et al.*,<sup>30</sup>. As for DTPA-extractable Zn, Singh and Sekhon<sup>33</sup> as well as Katyal and Sharma<sup>27</sup> have both reported comparable values in the range 0.4-2.1 mg kg<sup>-1</sup> and 0.12-2.89 mg kg<sup>-1</sup>, respectively, in some Indian soils. On the other hand Chude *et al*<sup>35</sup> found much lower concentrations (0.02-1.14 mg kg<sup>-1</sup>) of DTPA-extractable Zn in some soils supporting cacao plant in southwestern Nigeria, while wider ranges and higher concentrations have also been reported widely<sup>10,31,32,34</sup>. The foregoing shows that the concentrations of acid and DTPA-soluble Cu and Zn reported here are in the range of what is commonly found in soils, regardless of soil type and environment.

In contrast, the concentrations of EDTA-extractable Cu and Zn reported here are considerably lower than what have been reported to occur in Nigerian soils and elsewhere. For example Nyandat and Ochieng<sup>36</sup> found EDTA-extractable Cu of between 0.5-29.0 mg kg<sup>-1</sup> in some Kenyan soils of different parent materials (sedimentary, volcanic ash, metamorphic

and granitic materials), while Fagbami *et al*<sup>10</sup> obtained a range of 0.25-27.0 mg kg<sup>-1</sup> Cu and 0.30-12.8 mg kg<sup>-1</sup> Zn in soils formed on alluvium and basement complex rocks in southwestern Nigeria. Similarly Aghimien<sup>31</sup> found EDTA-extractable Cu of 0.3-11.1 mg kg<sup>-1</sup> and EDTA-extractable Zn of 1.3-25.6 mg kg<sup>-1</sup>, while in Bangladesh, Hassan<sup>37</sup> found EDTA-Cu and Zn of 0.3-12.9 and 0.6-10.9 mg kg<sup>-1</sup>, respectively. However, in the drier north of Nigeria, Lombin<sup>28</sup> found even much lower levels of EDTA-extractable Zn (0.49-1.50 mg kg<sup>-1</sup>) compared to what is reported here. Still the general picture is that the amounts of Cu and Zn the EDTA solution could remove from these soils were less than what is more usually reported.

Considered in perspective, while each extractant removed more Cu than Zn in the soils, using profile average concentrations as criterion, 0.005M DTPA consistently extracted more Cu than either 0.1 M HCl or 0.05 M EDTA. On the other hand, Zn was extractable more by the acid extractant than by DTPA or EDTA, notwithstanding that when only the surface soils are considered, 0.1M HCl or 0.05M EDTA were tended to extract more Cu than 0.005 M DTPA. In the case of Zn, 0.1M HCl generally gave the highest levels in all soils but one - the alluvial Entisol, where EDTA extracted the most Zn. Fagbami *et al*<sup>29</sup> found similarly that EDTA extracted more Cu than Zn in surface horizons (and in their case, the entire profile), while HCl extracted more Zn than Cu in the surface horizons (and about equal amounts of both in the entire profile) in southwestern Nigeria. Similar deductions

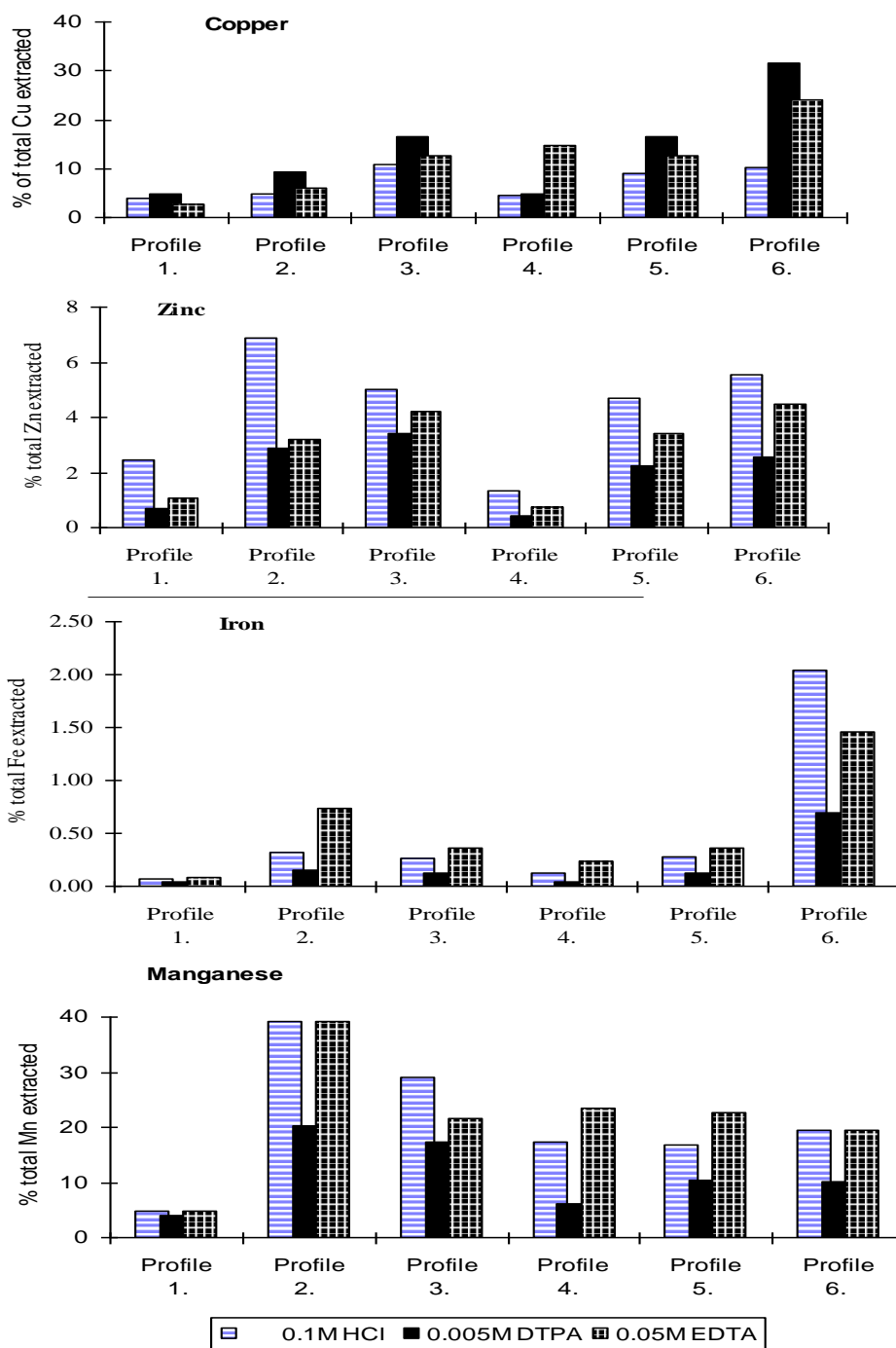
were made for hydromorphic soils in southern Nigeria by Aghimien<sup>31</sup>, while Jahiruddin *et al*<sup>38</sup> also found 0.1M HCl a better extractant for Zn than either EDTA or DTPA solutions, in Scottish soils. The present results therefore, conform to what may well be a general trend where the mineral acid solution extracts more Zn than the other reagents.

Why the DTPA and EDTA solutions should extract more Cu than HCl solution is not far-fetched. The former are both complexones whose affinity for Cu is rather high<sup>39</sup>, a feature which HCl lacks. On the other hand, while it may be plausible to expect the complexones to still extract more Zn than HCl for the same reasons, what is experienced is the opposite. This may be because, as earlier suggested, the acid removes not just non-specifically adsorbed and soil solution Zn, but also that adsorbed specifically at oxidic surfaces. It is also probable that the acid dissolves finely divided sesquioxide bodies in addition, releasing Zn occluded in such bodies<sup>29</sup>.

#### *Iron and Manganese*

The concentrations of Fe and Mn extractable with 0.1M HCl, 0.05M EDTA and 0.005M DTPA in these soils were far higher than the corresponding amounts of Cu and Zn. However since 0.1M HCl is not a common soil test for Fe and Mn, the following discussion dwells more on their DTPA- and EDTA- extractable levels, the latter two being the more usual soil tests for these nutrients.





**Figure 5.** Profile average proportions (%) of total Cu, Fe, Mn and Zn extracted by 0.1 M HCl, 0.05 M EDTA and 0.005 M DTPA from major agricultural soils in the Lower Benue Valley, Central Nigeria. These proportions are used to assess each reagent’s “efficiency” to estimate plant-available nutrient.

It is worthwhile to state here that, pH which is supposed to be an important soil property as far as micronutrient availability is concerned, did not seem to influence the extractable (i.e. plant available) amounts of Cu, Fe, Mn and Zn in the profiles studied. The levels of DTPA-extractable Fe and Mn (3.77-131.0 mg kg<sup>-1</sup> and 2.20-111.0 mg kg<sup>-1</sup>, respectively) fall well within literature reports for a wide range of soils. For instance Indian workers<sup>27,33,40</sup> found concentrations, of DTPA-extractable Fe ranging from 1.20-199.1 mg kg<sup>-1</sup> and DTPA-Mn of 1.6-341 mg kg<sup>-1</sup>. In Nigeria, Okpidi<sup>43</sup> obtained a range of 1.6-128 mg kg<sup>-1</sup> DTPA-Mn in soils of the Oil-Palm belt (in Southern Nigeria). On average, these reports show that DTPA-extractable Fe and Mn occur in soils more in units of tens of parts per million, and only rarely, in hundreds of parts per million. Therefore what was found in the profiles, as reported here, is not uncommon. But on the contrary, the range of concentrations of EDTA-extractable Mn found (2.36-253 mg kg<sup>-1</sup>) is rather high, compared to literature records. Okpidi<sup>41</sup> found concentrations ranging only between 1.6 and 145 mg kg<sup>-1</sup> in soils supporting oil palms in southern Nigeria, while even lower concentrations (1.4-4.7 mg kg<sup>-1</sup>) were reported in soils of the semiarid savanna in the north of the country<sup>28</sup>. In Bangladesh, Hassan<sup>37</sup> found a range of 1.0-17.40 mg kg<sup>-1</sup> EDTA-extractable Mn. Although extractable (i.e. plant available) Mn is not necessarily correlated with the total amounts in soil<sup>42</sup> the relatively high amounts of Mn extractable with EDTA, in these soils may be related to the high total concentrations of the element (47-1340 mg kg<sup>-1</sup> with average 287 mg kg<sup>-1</sup>) in the profiles. This notion is

supported by the very significant and positive correlation between the two ( $r = 0.83, P < 0.01$ ). Apart from this relation, the amounts of both Fe and Mn extractable with all three extractants had no relationship to their total amounts. With regard to other soil properties, no significant relationships were found between the extractable levels of Fe and Mn and the sand, clay and sesquioxide contents or the C.E.C of the soils.

However, this lack of correlations may only be apparent and only due to the narrow range of pH values encountered in the soils (profile average values 5.4- 5.6 with population variability, as coefficient of variation (C.V.) of only 8.7%). It is possible that samples with a wider range of pH values might show correlations between available micronutrients and pH.

#### ***Lability of Cu, Fe, Mn and Zn in the Soils***

Viets<sup>43</sup> conceptualized what he termed "chemical pools" within which micronutrient cations maybe found in soil. These are, in increasing concentric order (i.e. the next level encompassing the lower levels):

- A. Water-soluble cations.
- B. Cations exchangeable by a weak exchanger like NH<sub>4</sub><sup>+</sup>.
- C. Adsorbed, chelated, or complexed ions exchangeable by other cations possessing high affinities for exchange sites or extractable with stronger chelating agents.
- D. Micronutrient cations held in secondary clay minerals and insoluble metal oxides.
- E. Cations held in primary minerals.

These pools collectively hold the **total** amount of any given element in the soil.

The concentric relationship implies that each outer pool includes all others within, using common extraction schemes. Pools A, B, C are considered to be in rapid and reversible equilibrium with one another. *Micronutrient cations in these pools are the more readily available to plants and which may be estimated by the use of mild chemical extractants.* Against this background, we hypothesize that a micronutrient which resides predominantly in pools A to C is "labile". Such micronutrients, therefore, stand greater chance of rapid depletion, for example under intensive cropping. Thus, the more labile a nutrient is in the soil, the quicker would deficiency levels be attained once a fallow is opened, especially where pool E is very small or absent, as may be the case in highly weathered soils.

The "lability" of Cu, Fe Mn and Zn in these soils was estimated as the percentage of the total amount of each, which was extractable with 0.1M HCl, 0.05M EDTA and 0.005M DTPA. Overall assessment of the results (Figure 5) shows that more Cu, Mn and Zn than Fe exists in the available pools (A to C) in these soils, implying they are relatively labile in these soils.

### ***Extractant Efficiency***

An essential part of micronutrient fertility management protocol is the choice of extractant(s), as "Soil Test(s)" for the nutrients of interest. This choice is guided largely by such considerations as the crop (and variety), soil nutrient capacity and the soil factors that control this on the one hand, and actual correlations between the "soil test" value obtained and crop uptake, on the other. Nevertheless, we consider it plausible that the correct choice of

extractant or "Soil Test" may be made in a semi-empirical way if it is remembered that all nutrients ions in pools A to C may be readily available for uptake by plants. In this regard, the extractant that removes the greater proportion of the total nutrient reserves in the soil, under mild conditions, is most likely to draw on all the possible available pools (A to C and probably D and E). Such an extractant would be considered "efficient" in estimating plant-available nutrient, and is likely to give good correlations with plant uptake data. With this in mind, the efficiency of the three reagents (0.1M HCl, 0.05M EDTA and 0.005M DTPA) as extractant for Fe and Mn in the soils was determined, by comparing the percentage of the total element each reagent was able to extract in the soils. The profile averages are summarized in Figure 5. From this figure the following deductions may be made:

(1) DTPA first, and then EDTA, are the choice extractants for available Cu in most of the soils, irrespective of parent material. The only possible exception is the sandy, sandstone-derived soil (Profile 1), where 0.1 M HCl appears to be superior to EDTA after DTPA.

(2) For available Zn, 0.1M HCl is consistently superior to both DTPA and EDTA. Between the latter two, EDTA appears to be a better choice than DTPA for most of the soils.

(3) For available Fe, EDTA is the most efficient reagent for its extraction in all the profiles, allowing for the comparable efficiency with 0.1M HCl in Profile 1 and the reverse trend in Profile 6.

(4) For available Mn, 0.1M HCl and 0.05M EDTA show a more or less comparable efficiency (Profiles 1,2 and 6). But

0.1M HCl is better than 0.05M EDTA in the Profile 3, while EDTA is better in Profiles 4 and 5. There is, therefore no clear agreement on the superiority in performance between these two reagents, with respect to Mn; they may be used alternately.

The importance of the foregoing observations and deductions is that, in developing soil tests for these micronutrients in these soils, a less arbitrary choice of extractant may be made, bearing in mind that the most efficient extractant for a particular element is most liable to extract most of the plant available forms of the element in soils.

## CONCLUSION

In this study, the occurrence of total and extractable (i.e. plant-available) Cu, Fe, Mn and Zn in the major agricultural soils of the Lower Benue Valley, in Central Nigeria, showed a relationship to their parent materials. Association of Cu and Zn contents in the profiles with soil clay and sesquioxides was also, indicated especially for Zn. While total Fe showed accumulation in the subsoil, more total Mn was found in the surface horizons of the soils. The common soil nutrient extractants, 0.1M HCl, 0.05M EDTA and 0.005M DTPA, returned different concentrations of the elements. However, all three extractants indicated similar profile distribution trends of Fe and Mn i.e. a decrease with increasing profile depth. While actual nutrient availability is a function both of the soil and the plant or crop considered, various critical limits have been established with different crops and in different soil types<sup>44</sup>. On the

whole and based on critical limits set elsewhere for a variety of crops, the major soils of the Lower Benue Valley have adequate concentrations of plant-available Cu, Fe and Mn at present, whereas Zn deficiency problems are to be expected in most of the soils, especially if brought under intensive cropping, as it is beginning to be the case in the area. On the basis of the proportion of the total element extracted by the various extractants, we introduced the concept of nutrient 'lability' in soil as well as nutrient "extractant efficiency" to serve as guide to choosing a soil testing extractant. Using this concept, Mn was adjudged the more labile nutrient element in these soils, followed by Zn, Cu and Fe in that decreasing order; it is therefore, more likely to suffer rapid depletion, once a fallow is opened and the soils come under intensive cultivation. This is the subject of future investigations.

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