

Determination of Potential Heavy Metal Contents in Peat in Selected Agriculture areas in Sepang, Selangor, Malaysia

Kabir Kayode Adebayo, Roslan Bin Ismail, Olatunji Olayinka, Eliza Azura Azman, Monsuru Adekunle Salisu

Abstract— Peat soils are acidic in nature and deficient in nutrients particularly Cu, Zn, Fe and B. Liming materials and agro-chemicals are widely used as soil amelioration to enhance the growth of crops. Therefore, the study was conducted to determine the concentration and distribution status of some selected heavy metals (Cu, Zn, Pb, Mn, Fe, As and Cd), sources, possible effect on crops when compared with the permissible concentration in any agricultural land. This study was conducted on a farm located in Sepang district Selangor, Malaysia. The soil type comprises of peat and a mixture of peat and mineral soil underlying the peat. Soil samples were collected using a systematic grid (3 m by 3 m). 150 soil samples were collected at 5 different depths (0-20 cm, 20-40 cm, 40-60 cm, 60-80 cm and 80-100 cm) across the farm using a hand auger. Soil analysis for Soil pH, Soil Organic Carbon and Soil Heavy metals were conducted using appropriate methods. Results showed that the soil in the study area is very strongly acidic to a strong acidic (3.03- 4.46). Soil Organic Carbon ranged from 9.30 % to 17.64 % with a decreasing value down the soil profile. The total content of Zn and Mn were above the WHO permissible limit at 60 cm (53.59 mg/kg), (52.66 mg/kg) respectively. The available micronutrients were all above the critical limit at all depths, and the concentration of the available micronutrients was in the following decreasing order i.e Fe>Mn>Zn>Cu. The results showed a significant difference with varying depth and the source of the heavy metals were related to the natural and anthropogenic sources. Results also revealed that the soil in the study area does not indicate serious contamination by heavy metals.

Index Terms— Peat Soil; Heavy Metals; Anthropogenic; Agrochemicals; WHO..

I. INTRODUCTION

Soil is the reservoir of nutrients, minerals, organic and inorganic matters (1). Peat soils also are important ecosystem which provides a significant contribution to the agriculture

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sector in Malaysia. The peat soils are formed through decomposition of organic matter which has accumulated over years. Peat soils are generally very acidic in nature and deficient in soil nutrients particularly Cu, Zn, Fe and B. Liming materials and agro-chemicals are widely used as soil amelioration to enhance the growth of crops in this soil for better yields. Unfortunately, these activities have contributed to the accumulation of heavy metals. The contamination of the peat soil with heavy metals is related to the natural source which is derived from parent rocks (2) and anthropogenic input which could be mobile sources like emissions from the automobile exhausts (3;4) and stationary sources including power plants, industrial waste incinerators and land disposal of waste products, use of agricultural inputs such as agrochemicals, organic amendments, animal manure, mineral fertilizer, sewage sludge and industrial wastes (5, 6, 7,8). These sources (natural and anthropogenic) releases heavy metals into the environment mostly in soils. Heavy metals are referred to as those metals whose density is greater than 5 g/cm³(9), and they are considered as one of the major sources of soil pollution or contamination. Heavy metal pollution or contamination of the soil is usually caused by various metals, especially Copper (Cu), Nickel (Ni), Cadmium (Cd), Zinc (Zn), Chromium (Cr) and Lead (Pb) (10). These metals are found in the earth's crust and can remain in the environment for a long time without any biodegradation (1).

Presently, soil pollution by heavy metals in soils meant for agriculture has become a great global environmental concern due to the crucial importance of food production and security (11; 12,13), and for this, there should be a constant monitoring program to develop a database regarding the contamination status of heavy metals in the soil. Previous reports (14;15), shows that some of the heavy metals like Arsenic (As), Cadmium (Cd), Mercury (Hg), Lead (Pb) or Selenium (Se) are not essential for plant growth, and others like Cobalt (Co), Copper (Cu), Iron (Fe), Manganese (Mn), Molybdenum (Mo), Nickel (Ni) and Zinc (Zn) are essential elements required for normal growth and metabolism of plants. The accumulation of the heavy metals in soil may induce nutrient antagonism between and other nutrients like copper, iron and manganese can inhibit plant uptake of zinc, which could have been due to competition for the same carrier site in the soil-water system and plants root. Other metals such as Fe, Mn, Co, Cu and Ni are micronutrients and thus, their permissible limits are quite low in living organisms, but when they (heavy metals) accumulate above the limit, then they

become toxic to biological systems (16).

The accumulation of these heavy metals in the soil will increase the concentration of the metals in the soils and may eventually cause a soil and plant nutrient deficiency thereby having effect on the health of such plant consumer (17, 18). (19) reported that the contamination of heavy metals will not only portends the human health but also deteriorates the surface water, groundwater, and quality of atmosphere. The accumulation of heavy metals will reduce soil quality, crop yield and the quality of agricultural products (20). However, the excessive accumulation of heavy metals through agriculture activities can cause pollution to the soil and also to the quality and safety of the food.

There are previous studies relating to the contamination of heavy metals in soils across the world (21; 22), but mainly on the surface soil, which do not provide complete information of the soil because the soil functions are influenced by the pedogenic processes, while studies that assess the whole soil profile are still lacking. While, studies from peninsular Malaysia showed that most agricultural soils contain high volume of cadmium (Cd) and zinc (Zn), and may lead to high values of Cu in the plants grown on such soil (23). In addition, (24) reported increasing volume of As, Cu and Zn in agricultural soil resulting from the addition of phosphatic fertilizers.

Since peat soils are acidic and are deficient in some soil nutrients, lime and agrochemicals such as pesticides and fertilizers are widely used to increase the soil pH, control pests and enhance the growth of crops for better yields. These activities may be seen as conducive to the accumulation of heavy metals in agricultural soils which need to be monitored regularly, because crops grown on such soil may adsorb heavy metals from the growth medium and consequently may cause harm to the human health. Therefore, this study determined the concentration status, sources of some selected heavy metals (Cu, Zn, Pb, Mn, Fe, As and Cd), its effect on crop yield and compared with the acceptable limit (Soil) by WHO in a farm located in Sepang district in the southern part of the State of Selangor, Malaysia.

II. MATERIALS AND METHODS

The study was conducted at a cassava farm located in Sepang district in the southern part of the state of Selangor, Malaysia (latitude $02^{\circ}45'N$ and longitude $101^{\circ}40'E$) with an elevation of 4m above water level. The soil type in the study site comprises of both the peat (60 cm in depth) and an admixture of peat and mineral soil underlying the peat (60-100 cm depth). The study site covers 12 hectares. Soil samples were collected using systematic grid method (3m by 3m). A total number of 30 grids (sample points) was made and soil samples were collected at 5 different depths (0-20 cm, 20-40 cm, 40-60 cm, 60-80 cm and 80-100 cm) at each sample points (150 soil samples) using a hand auger. The soil samples were air-dried, ground with mortar and pestle, sieved to pass a 2 mm mesh sieve and stored for further laboratory analysis. The soil pH (H_2O) was determined according to the method prescribed by (25). Soil organic carbon was determined by wet oxidation potassium dichromate method as proposed by (26).

The Total content of heavy metals (Fe, Cu, Zn, Mn, Pb, As, Cd) was determined by wet digestion in Aqua Regia method, using Nitric acid and Conc. Hydrochloric acid for extraction (27). Available contents of these elements (Fe, Cu, Zn, Mn) were extracted using double acid method (0.05M of hydrochloric acid (HCl) and 0.025M of sulphuric acid (H_2SO_4), and analyzed using Atomic Absorption Spectrophotometer (AAS).

Data analysis

Data were analyzed using Statistical Analysis System (SAS Ver. 9.4). Analysis of variance (One-way ANOVA) was determined. The least significant difference (LSD) was used for mean separation at $P \leq 0.05$. Pearson correlation was done to investigate the relationships among the chemical properties and the heavy metals (28).

III. RESULTS AND DISCUSSIONS

The soils in Sepang was extensively investigated for chemical properties (soil pH and soil organic carbon), Total heavy metals (Fe, Cu, Zn, Mn, Pb, As, Cd) and Available heavy metals (Fe, Cu, Zn, Mn) to assess the concentration and distribution status, sources and the possible effect on the crops and the human consuming the crops grown on the soil in the study area. The results from this study revealed that sampling of soil in the study area produced the heavy metal concentration status which is significantly different with varying depth. Table 1 below shows the descriptive statistics of the soil pH, soil organic carbon and total heavy metals assessed in the study area.

The values of soil pH across the study area ranged from 2.71-5.30 with mean values down the depth ranges from 3.03-4.46 with the highest value (4.46) recorded at the top soil 0-20 cm, while the lowest mean value of soil pH was recorded at depth 60-80 cm (3.03) which is the last layer of peat in the study area. The mean values from 80-100 cm tend to rise which indicates that the soil at this depth is a mineral soil (Fig 7). It can be concluded that the soil in the study area is very strongly acidic to a strong acidic. The acidity of the soil in the study area was a result of organic acids that contains fulvic and humic acid (29). The result also showed decreasing value with increasing depth and it is similar to the report by (30). (31) also reported that typical Malaysian peat contains soluble aluminum in the soil solution could cause the decrease in the pH value down the depth of the soil profile. There were significant differences with varying depth down the soil profile at $p \leq 0.05$.

Soil Organic Carbon (SOC): The content of soil organic carbon in this study was found to range from 7.0-19.78 %, with the mean values in all depth also at 9.30 % to 17.64 %. The highest mean value (17.64 %) was found at the top soil (0-20 cm) and tends to be decreasing down the depth to the lowest value (9.30 %) recorded at 80-100 cm, which is classified as a mineral soil ($<12\%$). The result of this study is similar to previous studies (32, 33, 34) which showed that when the depth is getting to the mineral soil layer, the value tends to decrease up to less than 12 %. The high content of carbon at the top soil as a result of plant cycling and carbon inputs from plant roots as well as plant residues (which

contains high nitrogen and carbon contents) in the topsoil (35). There were no significant differences ($p \leq 0.05$) with varying depth (Table 2).

Total heavy metals (micronutrients): The total Iron (Fe) concentration was found ranging from 1775 to 48920 mg/kg in the soil across the study area with mean values ranging from 3584 mg/kg as the lowest value at the top soil (0-20 cm) to 20487 mg/kg as the highest value at the sub soil layer (80-100 cm). The result obtained showed that the depths are significantly different (Table 2) at $p \leq 0.05$. The high concentration of Fe recorded was due to Fe forming a complex with organic materials like humic and fulvic acid as the soil is high in organic matter and low in pH. The values recorded across the field suggest a natural source mostly from the parent material which could be sedimentary rock rich in Fe with an approximate of 47200 mg/kg (36). The result is similar to the report by (37) that an organic soil at pH 3 has a high concentration of Fe. The result suggests that Fe might not be readily available for plant uptake due to the type of soil in the study area (peat) which has a higher ability to retain and hold heavy metals (38) due to the high content of organic matter. The values obtained at all depth were within the range of the permissible limit for total Fe (40000 mg/kg) in soils for agricultural purpose (39).

The concentration of total Copper (Cu) in the study area ranges from 0.5-58.9 mg/kg with the mean values across the depths ranging from 8.24-20.21 mg/kg with the highest concentration at the top soil (20.21 mg/kg) and the lowest at the last depth (80-100 cm). The total Cu concentration tends to decrease with increasing depth (Fig 2). There was no significant difference with varying depth (Table 2). The higher concentration was found at the peat layer compare to the mineral layer of the study site and this could be due to the high content of organic matter (also from animal manure) and it suggest anthropogenic input. The high content of heavy metal present in the livestock feed as additive to the animal diet which is consumed by the animals are thereby passed out as excrete, and such excrete will be added to the soil and it may lead to a high concentration of Cu in such soil (40). Although the values obtained at all depths in this study for total Cu were below the WHO permissible limit (36 mg/kg) and also it is within range for organic soils as reported by (41).

Total Zinc (Zn) concentration in this study showed that the mineral layer had a higher concentration than that of the peat layer. The total Zn concentration across the study area varied from 17.5-131.8 mg/kg. The mean values across all the depths also ranged from 30.69-53.59 mg/kg with the highest value found at 80-100 cm (53.59 mg/kg) while the lowest value (30.69 mg/kg) was recorded at 40-60 cm (Table 1). The result also showed that there was no significant different with varying depth in the study area as shown in table 2. The high concentration of Zn at the mineral layers suggests a natural source while the high concentration at the peat layers indicates anthropogenic input (agrochemicals). Previous studies report that, these activities (fertilizer and pesticides application) contributed to the accumulation of heavy metal in the soil especially Cu, Zn, Pb, Cd and As (40). The concentration of total Zn obtained in this study were within the permissible limit for agricultural soils except at (80-100 cm) which is above the permissible limit of 50 mg/kg of total

Zn in soils meant for agriculture purpose (Table 3). High concentration at the subsurface was a result of the high mobility of Zn (42).

The values recorded for total Lead (Pb) across the study area ranged from 6.3-36.8 mg/kg with the mean values across depths ranging from 12.30-16.37 mg/kg. The highest value was at 80-100 cm while the lowest mean value was in the top soil (0-20 cm). The result showed an increasing value with increasing depth down the soil profile as shown in fig 5. There was no significant different with varying depth (Table 2). The mean values obtained in all depths were below the permissible limit of WHO for soils (85 mg/kg). The high concentration of total Pb at the mineral layer was associated with the parent material, and similar to previous studies (43; 44) that sedimentary rocks have an average of 23 mg/kg content of Pb and the concentration in the peat layer could be as result of high organic matter contents and applications of agrochemicals. Although Pb is not essential for plant growth but it is taken up by the plant and accumulate by plant toxic form (45).

Total Manganese (Mn) concentration in the entire soil samples analyzed from the study area varied from 16.9-131.6 mg/kg, with the mean values across all depths ranging from 29.21- 52.66 mg/kg. The highest value was at 80-100 cm and the lowest value was recorded at 40-60 cm. The mean value trend was decreasing with increasing depth from the top soil until the last depth of the peat layer (60 cm), thereafter, showing an increasing value from the first depth of the mineral layer to the last depth (Fig3). The concentration of total Mn was in all the depth. The high concentration of total Mn at both layer (peat and mineral) was seen to have been influenced by the acid state (strongly acidic) of the soil and the high content of organic matter. This result is similar to a report by (46). There was no significant difference ($p \leq 0.05$) with varying depth (Table 2). The values at the peat layer were found to be lower than the permissible limit while the mineral layer of the study site already exceeded the permissible limit by WHO (48 mg/kg) as shown in table 3.

The cadmium concentration in the study area ranged from <DL- 1.7 mg/kg, with the mean values for all depth ranged from 0.2-0.7 mg/kg. The highest value (0.7 mg/kg) was recorded at the top soil (0-20 cm) while the lowest mean value of 0.2 mg/kg was at 20-40 cm and 60-80 cm. the concentration of cadmium across the study site was below the permissible limit by WHO (0.8). this shows that activities of the farmers on the farm were not sufficient enough to increase the concentration of Cd. The result obtained for Arsenic as shown in samples collected was <DL, which means the concentration of arsenic on the farm is very low and the soil in the study area is safe from As contamination and pollution.

Available Micronutrients (Zn, Cu, Mn, Fe): There is a need to assess the soil available micronutrients in the study area to ascertain the adequate supply of the selected micronutrients (Zn, Cu, Mn, Fe), as they are essential for the plant growth. The descriptive statistics of the selected available micronutrients are shown in table 4 at two different depths (0-20 and 20-40 cm) each at every sample point, while fig 7 shows the concentration of each selected micronutrients in the study area.

The concentration of available Cu across the study area varied from 0.11-0.50 mg/kg and 0.16-0.56 mg/kg, with a mean value of 0.26 and 0.28 mg/kg for 0-20 and 20-40 cm respectively (table 4). The value obtained for the available Cu in this study showed a decreasing value with increasing depth, and the result is per (47). The values obtained across the study area and depths (2) were all above the critical limit (0.2 mg/kg) as proposed by (48). The bioavailability of available Cu in the study area at both depths suggest anthropogenic input such as application of fertilizer, fungicides and livestock manure, as they contain an appreciable amount of copper in them. There were no significant differences with varying depth (Table 4). The high concentration of Cu in this study does not indicate fertility problems to the crops grown.

The available Mn values recorded for this study ranged from 4.0-32.06 mg/kg and 3.31-24.46 mg/kg, with a mean value of 14.94mg/kg and 10.55 mg/kg at 0-20 cm and 20-40 cm respectively. The result showed a decreasing value with increasing depth (Table 4). All values obtained for the available Mn were above the critical limit (2 mg/kg) by (48), and 1-4 mg/kg by (49). The high concentration of Mn at both depth was influenced by the acid state of the soil and the content of organic matter as reported by (46). The source of high Mn in this study shows there is an affinity of Mn with organic matter since the top soil is rich in organic matter, and could also be through the application of agrochemicals rich in Mn (anthropogenic input).

The values recorded for the available Fe across the study area and depths ranged from 7.90-99.08 mg/kg and 13.45-199.33 mg/kg, with a mean of 52.05 mg/kg and 83.98 mg/kg for 0-20 cm and 20-40 cm respectively (Table 4). The result revealed that all samples analyzed with depths showed values above the critical limit of 4.5 mg/kg (48) and 2.5-5.8 mg/kg (50) for available Fe in soils meant for agricultural purposes. The high available Fe in the study area is similar to a report by (52), that tropical peat soils usually have high content of Fe. The values obtained for available Fe tended to increase with increasing depth down the soil profile and the result is similar to previous studies (53; 54). The high concentrations of available Fe are also due to the acid condition of the soil in the study area, and also could be a result of the concretion of Fe and Mn. The high values surely pose no problem of fertility in the soil.

3.3 Correlation Analysis:table 5 below shows the relationships between the selected heavy metals assessed in this study. The result showed that Cu had a high correlation with Zn ($r=0.873$, $p<0.01$), Mn ($r=0.7428$, $p<0.01$). The relationship could be as a result of the competition between

the elements for the same carrier site in the soil, and they can also induce the deficiency of each other. SOC had a high correlation with Cu ($r=0.4074$, $p<0.01$) which shows that the concentration of Cu was influenced by the organic material (anthropogenic source). pH shows a high correlation with all the element except for Fe that had a negative correlation ($r=-0.7903$, $p<0.01$). This relationship could be related to the elements been pH dependent. Fe had a negative correlation with most of the heavy metals assessed in this study. The correlation between all the elements in this study could be related to their respective sources i.e the heavy metals concentration is most likely to be from the same source either natural or anthropogenic or a combination of the two.

IV. CONCLUSION

Soils of a selected farm in Sepang were extensively investigated in terms of heavy metals (Fe, Cu, Zn, Mn, Pb, As, Cd) with the aim of assessing the concentration and distribution status of the total and available heavy metals, sources and possible effect on the crops and human consuming the crops grown on the soil in the study area. All the soil sample analyzed for this study were acidic and have high organic carbon content. The result showed that the soil in the study area produced the heavy metal concentration status which is significantly different with varying depth using T-test. From the result, it is revealed that the concentration of the total heavy metals analyzed was all below the permissible limit (WHO) except for Zn and Mn which are above the limit at the mineral layer, while the available heavy metals in all depths were above the critical limit. The high available heavy metals in this study do not signify any fertility implications. Also, the findings revealed that the sources of the heavy metals are from natural and anthropogenic inputs, with Fe as the dominant element and perhaps related to the parent material. The study showed that the soils in the study area do not indicate serious heavy metal contamination or pollution including Aresnic and Cadmium which are below the detection limit, although they are not essential for plant growth, but when they accumulate in a plant they become toxic to the animals and human consuming such plant. Therefore, it is recommended that further analysis for heavy metals concentration in the plants grown in the study area be carried out to ascertain the transfer effect of the elements from the soil to the plants.

Table 1: Mean Concentration of Total Heavy Metals at all depths in the Study Area.

Depth (Cm)	N	Fe	Cu	Zn	Mn	Pb	As	Cd	p H	S.O. C (%)
	 (mg/kg)								
0-20	30	3584	21	39.69	38.35	12.3	BDL	0.7	4.	17.6
20- 40	30	5644	3	34.33	32.67	2	BDL	0.2	4.	13.6
40-60	30	9471	32	30.69	29.21	4	BDL	0.2	3.	11.1

60-80	30	15172	8.5	38.3	37.31	7	16.2	BDL	0.2	3	9.98
80-100	30	20487	8.2	53.59	52.66	7	16.3	BDL	0.3	41	9.30

N-number of samples analyzed per depth, Fe-Iron, Cu-Copper, Zn-Zinc, Mn-Manganese, Pb-Lead, As-Arsenic, Cd-Cadmium, S.O.C-Soil Organic Carbon, BDL-Below Determination Limit.

Table 2: Statistical Description Total heavy metals assessed in the study area.

Depth (Cm)	Fe mg/kg	Cu	Zn	Mn	Pb	pH	S.O.C %
0-20	3584 ^d	20.21 ^a	39.69 ^b	38.35 ^b	12.30 ^c	4.64 ^a	17.64 ^a
20- 40	5644 ^d	16.30 ^{ab}	34.33 ^b	32.67 ^{bc}	13.82 ^{bc}	4.18 ^b	13.67 ^b
40-60	9471 ^c	11.32 ^{bc}	30.69 ^b	29.21 ^c	16.04 ^b	3.66 ^c	11.10 ^c
60-80	15172 ^b	8.50 ^c	38.30 ^b	37.31 ^b	16.27 ^a	3.3 ^c	9.98 ^c
80-100	20487 ^a	8.24 ^c	53.59 ^a	52.66 ^a	16.37 ^a	3.41 ^c	9.31 ^{cd}
P-value	<0.0001	<0.0001	<0.0001	<0.0001	0.0006	<0.0001	<0.0001

abcd- mean values with different subscript are significantly different at p=0.05 level of LSD test while means with the same subscript are not significantly different.

Table 3: Comparison between the Mean Concentration of Heavy Metals in the Study Area and WHO Permissible Limit.

	WHO	Peat layermg/kg.....	Mineral layer
Fe	40,000	9471	20487
Cu	36	20.21	8.5
Zn	50	39.69	53.59*
Mn	48	38.35	52.66*
Pb	85	16.04	16.37
As	29	BDL	BDL
Cd	1	0.7	0.3

*- above permissible limit, WHO-World Health Organization, BDL-Below Detection Limit.

Table 4: Descriptive statistics showing the available micronutrients values across the study area and depths.

Depth (cm)	Cu mg/kg		Mn		Zn		Fe	
	0-20	20-40	0-20	20-40	0-20	20-40	0-20	20-40
Mean	0.26 ^a	0.28 ^a	14.94 ^a	10.55 ^b	11.11 ^a	8.51 ^b	52.05 ^b	83.98 ^a
Stdev	0.09	0.10	8.89	6.79	6.52	5.23	26.39	56.54

CV (%)	35.05	35.06	59.51	64.37	58.66	61.45	50.69	67.32
Min	0.11	0.16	4.01	3.31	4.49	3.41	7.90	13.45
Max	0.50	0.56	32.06	24.46	26.35	20.67	99.08	199.33

abcd- mean values with different subscript are significantly different at p=0.05 level of LSD test while means with the same subscript are not significantly different.

Table 5: Pearson Correlation Coefficient of Selected Heavy Metals with pH and S.O.C in the Study Area.

	pH	SOC(%)	Cu(mg/kg)	Zn(mg/kg)	Mn(mg/kg)	Pb(mg/kg)	Fe(mg/kg)
pH	1						
SOC(%)	0.5248*	1					
Cu(mg/kg)	0.35**	0.407	1				
Zn(mg/kg)	0.3497*	0.179	0.873*	1			
Mn(mg/kg)	0.4788*	0.258	0.7428*	0.8545*	1		
Pb(mg/kg)	0.4044*	-0.457	0.0593	0.1825	0.1243	1	
Fe(mg/kg)	-0.7903*	-0.644	-0.3**	-0.1234	-0.3484**	0.4476*	1

*-significant at 0.01, **-significant at 0.05

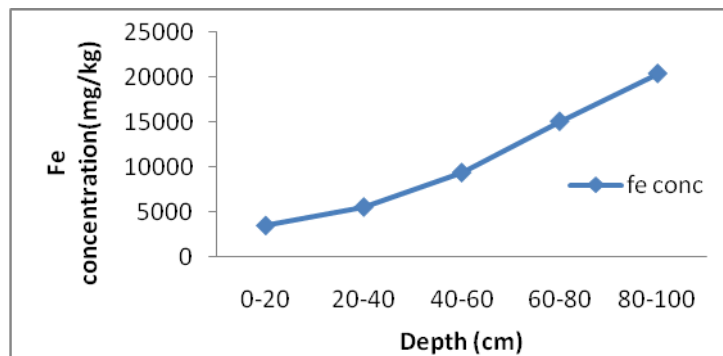


Fig 1: concentration of Fe within the depth

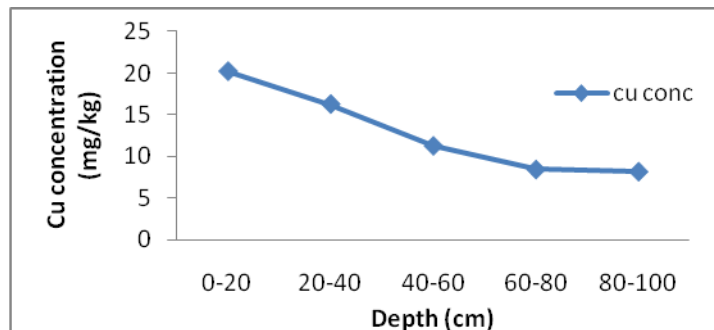


Fig 2: concentration of Cu across all depth.

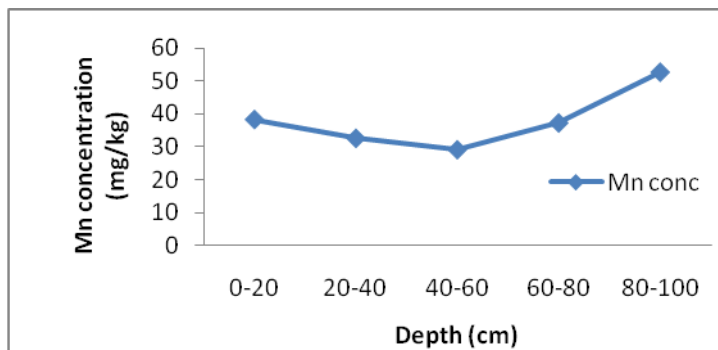


Fig 3: concentration of Mn across all depth.

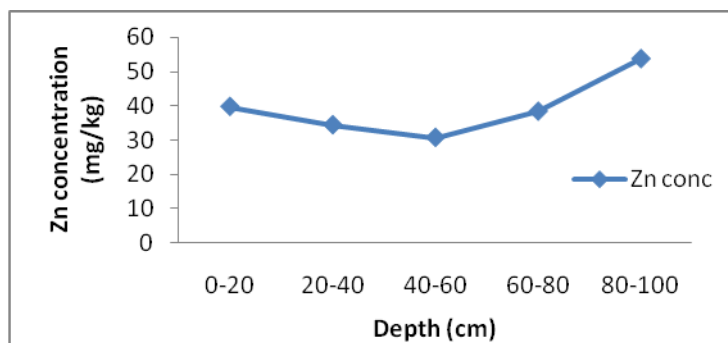


Fig 4: concentration of Zn across depth.

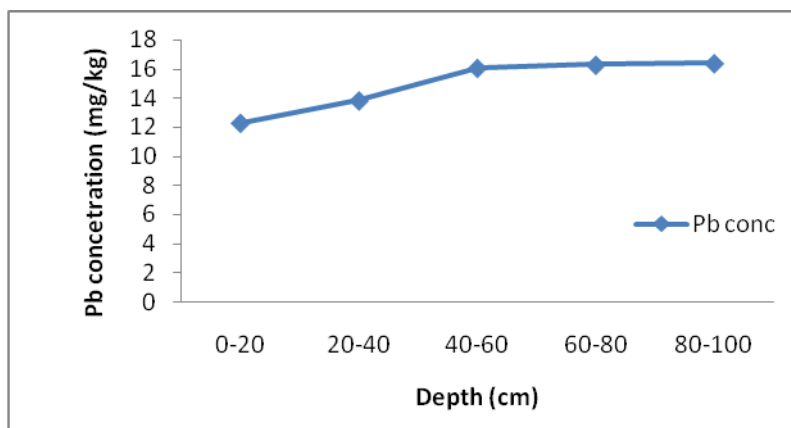


Fig 5: concentration of Pb across all depth.

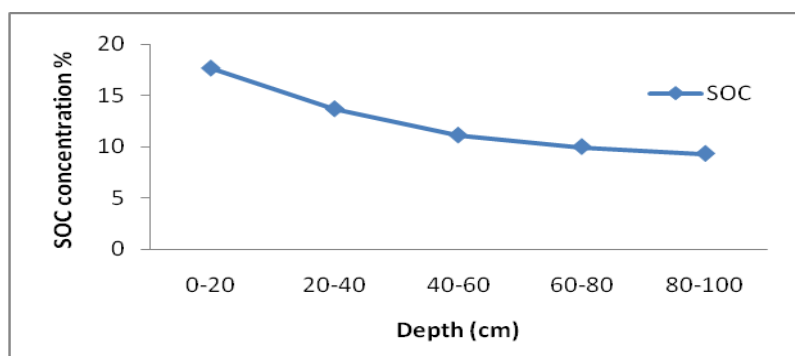


Fig 6: concentration of soil organic carbon across all depth.

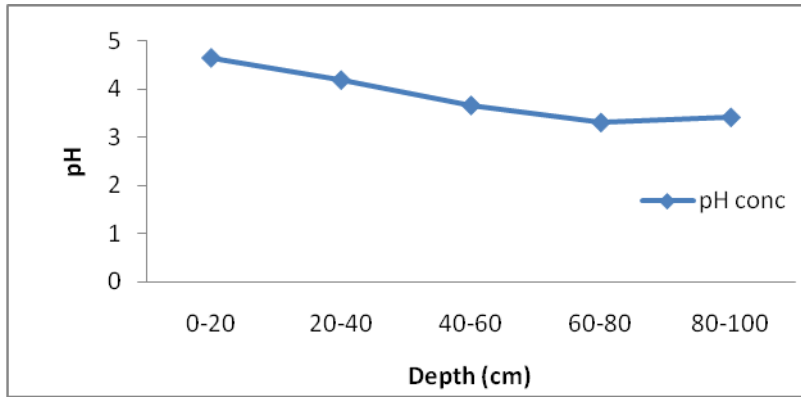


Fig 7: Soil pH across all depth.

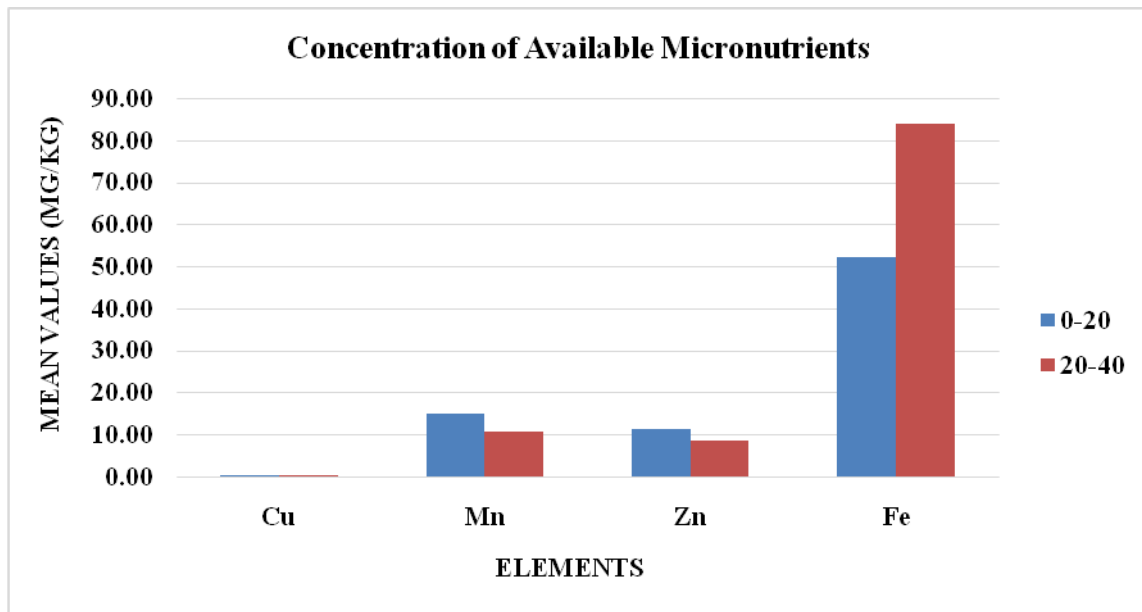


Fig 8: Graphical representation of the concentration of some soil available micronutrient in the Study Area.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

Thanks to all the co-authors for their respective contribution to the success of this research and the coordinator of the study area (TKPM Ulu Chucoh).

Funding

This research did not receive any specific funding

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