American Journal of Agriculture and Forestry
2022; 10(6): 210-219
http://www.sciencepublishinggroup.com/j/ajaf
doi: 10.11648/j.ajaf.20221006.11
ISSN: 2330-8583 (Print); ISSN: 2330-8591 (Online)

Science PG
Science Publishing Group

Profile Distribution of Micronutrients and Their Interrelationships with Related Soil Properties in Typical Cultivated Lands

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To cite this article:
Assefa Menna. Profile Distribution of Micronutrients and Their Interrelationships with Related Soil Properties in Typical Cultivated Lands. *American Journal of Agriculture and Forestry*. Vol. 10, No. 6, 2022, pp. 210-219. doi: 10.11648/j.ajaf.20221006.11

Received: August 31, 2022; **Accepted**: September 21, 2022; **Published**: November 4, 2022

Abstract: Profile distribution of micronutrients: cupper, manganese, iron, zinc, boron and molybdenum and related properties were investigated in soils developed in central Ethiopian cultivated lands at a depth of 0–150 cm in five different intervals from six profiles. Results showed that the micronutrient contents under instigations were much differentiated across soil profiles and sites. Though, the pattern of changes differ, the pH, clay content, bulk density, Mn, B and Mo were found to increase irregularly from topsoil to subsoil, whereas the organic carbon, Cu, Fe and Zn showed decreasing trends of change with depth. The results of investigation also revealed a relative larger accumulation of clay in the underlying horizon than topsoil. Correlation among the micronutrients and related soil properties also varied significantly with depth. The observed higher percentage of OC, Cu, Fe and Zn in the topsoil than the underlying layer may indicate the roles biomass recycling and rates may have played in their vertical distribution. More generally, among the analyzed soil properties, soil pH was found to be the most important factor influencing the micronutrients concentration in soils. Therefore, from annual crops production point of view, for those nutrients that are fairly abundant in subsoil, deep-tillage operations like sub-soiling are expected to bring their available forms to top-layers for plants uptake or recycling. Deep capture of nutrients by tree-roots like that in the agroforestry system can also recycle nutrients leached to deeper layers, thus improving nutrient use efficiency, thereby reducing potential environmental impacts. In general, the results of such vertical patterns of nutrient elements variability can yield insights into the patterns and processes of nutrient cycling over time: at small, medium or large-scales.

Keywords: Soil Profile, Micronutrients, Depth Distribution, Pedogenesis, Illuviation, Nutrient Cycles, Leaching

1. Introduction

Micronutrients are mineral elements that belong to the transition metals in the Periodic Table. They are among the 17 essential elements in plant nutrition that are critically important in completing the lifecycle of plants or in performing a range of physiological functions [1, 2]. They also play critical roles in animal nutrition and human dietary conditions. In recent years, the degradation of soil fertility notably, the micronutrients status is becoming a serious problem negatively affecting the sustainability of agriculture.

However, as their name implies these trace elements are needed in small quantities by plants; and as such their deficiency symptoms are not easily recognizable [3]. Furthermore, according to the author, the lack of responses to soil-applied micronutrients in cereals, and the very narrow gaps that exist between their levels that are considered deficient, sufficient or toxic to plants are recognized to pose major challenges in assessing their sufficiency status in farm-fields. As a result, even with minor deficiency symptoms crop yields or quality can be affected significantly. The low levels of micronutrient availability in soils, however, can't only be due to their inherent low levels in soils, but also be due to either chemical or biological fixation, spatial or temporal unavailability among others [4]. As a matter of fact, in such instances, micronutrient efficient genotypes will have greater yield in comparison with in-efficient ones, even when fertilized with very smaller amounts or less frequently.

More generally, almost all soil properties exhibited variability as a result of the dynamic interactions among the intrinsic (soil-forming processes) and extrinsic factors like soil fertilization and cultivation practices [5]. Among the natural environmental factors (climate, parent material, vegetation and topography) play important roles. Overall, soil chemical properties and plant growth are significantly controlled by the variation in landscape, including slope gradient, slope aspect, and elevation. These in turn influence the distribution of energy, plant nutrients and vegetation or organic matter, runoff or run-on processes, natural drainage conditions, and exposure of the soil to wind and precipitation. Sharma et al., studied the distribution of micronutrients in soil profiles and reported that they are increased with an increase in organic carbon and cation exchanged capacity, whereas they decreased with increasing soil pH, sand and the contents in the calcium carbonate [6]. In other similar studies made by [7], the distributions of micronutrients correlate to the make-up of the parent materials. Soil forming processes might also significantly influence the distribution of trace elements within the profile [8]. In this regard, knowing the profile distribution of soil micronutrients in agricultural fields and their interrelationships with other soil properties is critically important to improve management practices. This will enable one to correct the problems and/or at least to maintain productivity and sustainability of soils, thereby increasing precision of the farming practices. In view of the above background, the present study was aimed at evaluating the vertical distribution of micronutrients and related soil properties in selected profiles, and their interrelationships in typical cultivated lands.

2. Materials and Methods

2.1. Soil Sampling, Preparation and Analysis

Six sites were selected randomly in three representative locations on lands cultivated for wheat and/or faba bean in central Ethiopia during 2015-16 cropping seasons. The sites were geo-referenced using global positioning system (GPS)–GARMIN-model #GPS-60. The sites were selected based on the variations in vegetation, altitude, land-use and soil heterogeneity. In the selected sites, six soil profiles (P1, P2, P3, P4, P5 & P6) were exposed accordingly and studied for depth-wise distribution of micronutrients. With respect to soil reaction two profiles had medium; two had alkaline; and two had strongly acidic topsoil pH conditions. Furthermore, the selected soils represent areas ranging from valley-bottom in the rift-valley system to high altitude zones. Then, before planting wheat soil samples were taken from five depth categories: 0–20, 20–40, 40–60, 60–90 and 90–120 cm. A total of 30 composite surface and sub-surface samples were taken. This form of sampling allowed the assessment of spatial variability of soil properties at different scales. Soil samples then were, air-dried and ground to pass 1-mm stainless steel sieve, and analyzed for pH, organic carbon (OC), the micronutrients, particle size distributions and other related soil properties like bulk density (BD) in laboratory (Lab) using the following procedures. The pH was analyzed in water at 1:2.5 soil (water ratio) solutions using a combined glass electrode, pH meter as described by [9]. The OC was analyzed by hydrometer method, wet-oxidation [10] method. Plant available fractions of the micronutrients cupper (Cu), manganese (Mn), iron (Fe), and zinc (Zn) were analyzed by using 20 ml of diethylene-triamine-penta-acetic acid (DTPA)-extraction (0.005 M DTPA + 0.01 M $CaCl_2$ + 0.1 M 2 tri-ethanol-amine, adjusted to pH: 7.3) as developed by [11], and the contents were read by using atomic absorption spectrometer (AAS). Boron (B) was determined by hot-water method as developed by [12], whereas molybdenum (Mo) was determined using Acid-NH_4-Oxalate, pH: 3.3-extractable, a method developed by [13]. Particle size distribution of the soil samples was determined by International Pipette method [14]. For BD determination the undisturbed blocks of soils in each depth category were sampled using stainless steel ring in 0–40 cm depth, and 5 soil-cores of 7.5 cm diameter from each depth. The volume and weight of the soils were determined on a dry-weight basis, after oven-dried at 105°C. Exact volume of the soil was determined by measuring the volume of the cylinder (core-sampler). Volume of the cylinder = $\pi r^2 h$, where: π = 3.14; r = radius of the cylinder; and h = height of the cylinder. Then, BD was calculated as the quotient of oven-dry weight of soils by the volume of the cylindrical core.

2.2. Statistical Data Analysis

Analysis of variance (ANOVA) was performed to test the significance of variations in micronutrients distribution and soil properties in different sites using PROC MIXED of generalized linear model (GLM) of SAS system [15] to evaluate differences between the variables. When the differences were significant, least significant difference (LSD) was used to separate the means with a significant level at (p= 0.05, 0.01 & 0.001). Soil variables were also evaluated by correlation and slopes were compared through parallelism and coincidence test using PROC REG-corr procedure. Finally, the fertility status of soils of the study areas were evaluated based on the concentrations of the respective parameters (physico-chemical) obtained from Labs. Results of soil analysis were compared with established ratings or critical limits (CLs) for different classes of the respective micronutrient and related variables using descriptive statistics.

3. Results and Discussion

Results of soil profiles data of different sites are presented in (Tables 1 & 2), while the graphical representations of the micronutrients are depicted in figures 1–6. The results of investigations showed important variations in micronutrients concentrations and associated soil properties across profiles and sites. The upcoming sections discuss the trends of change on the variables considered.

3.1. Soil Texture

Results of particle size analysis showed significant variations in the distributions of soil texture corresponding from sandy, clay to clay-loam brought about by the variation in parent material, slope and degrees of weathering. In general, the clay percentage (%) of soils was found to increase steadily with depth (from topsoil to subsoil) (figures 1–6). Such tendency of increasing fineness of soils was also observed on the landscapes descending from highlands to low-lying rift-valley system as a result of clay-eluviation. Gradual increase of clay % with depth at valley-bottoms might also be due to the relative higher rate of down ward erosion or destruction of clay particles. Indeed, this is in accordance with the findings reported by other workers [7, 16, 17]. For Vertisols, the % of clay fraction was the highest ranging from 60–80% in the subsoil to about 25–35% in the topsoil compared with other soils types. For example, sandiness was highest (35%) at Bekejo site topsoil in the rift-valley system compared with other soil or land forms.

Table 1. *Contents of micronutrients' related soil properties: Arsi, East Shewa and West Shewa zones, before planting wheat or faba bean.*

Zone/Location	FA/Site	Lat. (N)		Long. (E)		Alt (m)	Soil Type	Depth (cm)	pH (H_2O)	Clay (%)	BD (Mg/m^3)	OC (%)	$CaCO_3$ Nodules	Soil Tex.
		X°	Y'. Z"	X°	Y'. Z"									
Arsi (Ar)	WG1(Do2)	7	59.944	39	8.876	2418.32	PV	(0-20)$_a$	5.36	45.8	1.22	2.71	no	C
Arsi (Ar)	WG1(Do2)	-	-	-	-	2418.32	PV	(20-40)$_b$	5.66	46.1	1.12	2.41	no	C
Arsi (Ar)	WG1(Do2)	-	-	-	-	2418.32	PV	(40-60)$_c$	5.76	55.4	1.23	2.06	no	C
Arsi (Ar)	WG1(Do2)	-	-	-	-	2418.32	PV	(60-90)$_d$	6.25	53.2	1.33	1.35	no	C
Arsi (Ar)	WG1(Do2)	-	-	-	-	2418.32	PV	(90-120)$_e$	6.76	65.0	1.41	0.71	no	C
Percent change						-	-	-	26.12	41.92	15.57	-73.80	-	-
Arsi (Ar)	GS2	8	0.833	39	8.444	2151.10	niti	(0-20)$_a$	6.24	22.6	1.12	2.18	No	CL
Arsi (Ar)	GS2	-	-	-	-	2151.10	niti	(20-40)$_b$	6.40	21.1	1.23	1.97	No	CL
Arsi (Ar)	GS2	-	-	-	-	2151.10	niti	(40-60)$_c$	6.55	24.5	1.42	1.67	no	C
Arsi (Ar)	GS2	-	-	-	-	2151.10	niti	(60-90)$_d$	6.75	26.2	1.53	1.00	no	C
Arsi (Ar)	GS2	-	-	-	-	2151.10	niti	(90-120)$_e$	6.75	27.2	1.61	0.50	no	C
Percent change						-	-	-	8.17	20.35	43.75	-77.06	-	-
East Shewa (ES)	Ke2	8	52.814	39	2.344	2224.37	PV	(0-20)$_a$	8.00	35.0	1.12	1.15	yes	C
East Shewa (ES)	Ke2	-	-	-	-	2224.37	PV	(20-40)$_b$	8.10	35.6	1.24	0.80	yes	C
East Shewa (ES)	Ke2	-	-	-	-	2224.37	PV	(40-60)$_c$	8.40	40.2	1.32	0.81	yes	C
East Shewa (ES)	Ke2	-	-	-	-	2224.37	PV	(60-90)$_d$	8.76	45.7	1.41	0.40	yes	C
East Shewa (ES)	Ke2	-	-	-	-	2224.37	PV	(90-120)$_e$	8.99	47.4	1.42	0.40	yes	C
Percent change						-	-	-	12.38	35.43	26.79	-65.22	-	-
East Shewa (ES)	Bk2	8	37.378	38	55.796	1874.16	CV	(0-20)$_a$	7.15	25.5	1.12	1.17	yes	SC
East Shewa (ES)	Bk2	-	-	-	-	1874.16	CV	(20-40)$_b$	7.53	25.6	1.22	0.88	yes	SC
East Shewa (ES)	Bk2	-	-	-	-	1874.16	CV	(40-60)$_c$	7.46	30.8	1.42	0.79	yes	C
East Shewa (ES)	Bk2	-	-	-	-	1874.16	CV	(60-90)$_d$	7.64	34.3	1.45	0.70	yes	C
East Shewa (ES)	Bk2	-	-	-	-	1874.16	CV	(90-120)$_e$	7.78	40.1	1.54	0.30	yes	C
Percent change						-	-	-	8.81	57.25	37.50	-74.36	-	-
West Shewa (WS)	N/S2	8	57.249	38	29.989	2229.54	Nit	(0-20)$_a$	5.85	22.0	1.22	0.96	no	C
West Shewa (WS)	N/S2	-	-	-	-	2229.54	Nit	(20-40)$_b$	5.93	21.0	1.43	0.64	no	C
West Shewa (WS)	N/S2	-	-	-	-	2229.54	Nit	(40-60)$_c$	5.89	22.3	1.52	0.61	no	C
West Shewa (WS)	N/S2	-	-	-	-	2229.54	Nit	(60-90)$_d$	5.9	26.1	1.53	0.55	no	C
West Shewa (WS)	N/S2	-	-	-	-	2229.54	Nit	(90-120)$_e$	5.91	27.5	1.61	0.35	no	C
Percent change						-	-	-	1.03	25.00	31.97	-63.54	-	-
West Shewa (WS)	BT2	9	0.227	38	30.826	2252.64	PV	(0-20)$_a$	4.85	36.9	1.22	2.03	no	C
West Shewa (WS)	BT2	-	-	-	-	2252.64	PV	(20-40)$_b$	4.94	41.5	1.43	1.70	no	C
West Shewa (WS)	BT3	-	-	-	-	2252.64	PV	(40-60)$_c$	4.91	45.6	1.52	1.63	no	C
West Shewa (WS)	BT2	-	-	-	-	2252.64	PV	(60-90)$_d$	4.93	52.9	1.43	1.00	no	C
West Shewa (WS)	BT2	-	-	-	-	2252.64	PV	(90-120)$_e$	4.95	60.5	1.61	0.51	no	C
Percent change						-	-	-	2.06	63.96	31.97	-74.88	-	-

Key: Wherever it appears: Nit = Red Nitisol, PV = Pellic Vertisol, and CV = chromic Vertisols); and Soil Texture (SCL = Sandy clay loam, C = Clay, SC = Sandy Clay, and CL = Clay loam). Study areas [(Ar = Arsi, ES = East Shewa (E/Shewa), WS = West Shewa (W/Shewa); WG1(Do2) = Wonji Gora1 (Dosha2); GS2 = Gora Silingo2; Ke2 = Keteba2; Bk2 = Bekejo2; N/S2(NS2) = Nano Suba2; BT2 = Berfeta Tokofa2. The numbers 1 or 2 in the site names like WG1/Do2, GS-2, Ke-2 and N/S2, BT2 etc. indicate the season in which the samplings were made. FA = farmer field/site/village.

3.2. Bulk Density

Bulk density (BD) of the soils varied consistently with depth ranging from 1.17 Mg/m^3 at the surface to 1.53 Mg/m^3 at the sub-surface, with mean value 1.368 and standard deviation (STDEVA), 0.1429 (Tables 1 & 2). These values are in close range to the average BD values for mineral soils, 1.30–1.40 Mg/m^3 as reported by [18]. The BD of soils in the top-layers and mean value of composite samples for the six profiles (P1–P6) were found to be lower than the underlying horizons. The relatively lower BD values observed on topsoil could be due to the relative high OM contents (Tables 1 & 2) which resulted in high total porosity (> 52%). On the other hand, the relative high BD at subsoil could be due to reduced root penetration and compaction caused by the weight of the overlying soil materials.

Table 2. *Persian-correlation coefficients of the mean values of the soil the micronutrients and related soil properties across profiles.*

	Depth	pH	Clay	BD	OC	Cu	Mn	Fe	Zn	B	Mo
Depth	1.00000	0.99221	0.97763	0.98476	-0.98768	-0.89040	0.85703	-0.88986	-0.90845	0.98372	0.50175
		0.0008	0.0040	0.0023	0.0016	0.0428	0.0635	0.0431	0.0328	0.0025	0.3891
pH	0.99221	1.00000	0.96270	0.96193	-0.99627	-0.91941	0.87894	-0.91707	-0.93544	0.95811	0.47055
	0.0008		0.0086	0.0089	0.0003	0.0271	0.0496	0.0283	0.0195	0.0102	0.4238
Clay	0.97763	0.96270	1.00000	0.94568	-0.97504	-0.90778	0.91581	-0.92515	-0.92751	0.95343	0.40041
	0.0040	0.0086		0.0151	0.0047	0.0332	0.0290	0.0243	0.0232	0.0120	0.5041
BD	0.98476	0.96193	0.94568	1.00000	-0.94701	-0.80217	0.76460	-0.79765	-0.82335	0.99843	0.60328
	0.0023	0.0089	0.0151		0.0145	0.1024	0.1322	0.1059	0.0867	<.0001	0.2814
OC	-0.98768	-0.99627	-0.97504	-0.94701	1.00000	0.93664	-0.91615	0.94334	0.95402	-0.94671	-0.43328
	0.0016	0.0003	0.0047	0.0145		0.0190	0.0288	0.0161	0.0118	0.0147	0.4661
Cu	-0.89040	-0.91941	-0.90778	-0.80217	0.93664	1.00000	-0.93078	0.98709	0.99720	-0.79656	-0.09559
	0.0428	0.0271	0.0332	0.1024	0.0190		0.0216	0.0018	0.0002	0.1067	0.8785
Mn	0.85703	0.87894	0.91581	0.76460	-0.91615	-0.93078	1.00000	-0.97727	-0.95176	0.77844	0.20762
	0.0635	0.0496	0.0290	0.1322	0.0288	0.0216		0.0041	0.0126	0.1209	0.7376
Fe	-0.88986	-0.91707	-0.92515	-0.79765	0.94334	0.98709	-0.97727	1.00000	0.99463	-0.80034	-0.14565
	0.0431	0.0283	0.0243	0.1059	0.0161	0.0018	0.0041		0.0005	0.1038	0.8152
Zn	-0.90845	-0.93544	-0.92751	-0.82335	0.95402	0.99720	-0.95176	0.99463	1.00000	-0.82081	-0.15194
	0.0328	0.0195	0.0232	0.0867	0.0118	0.0002	0.0126	0.0005		0.0886	0.8073
B	0.98372	0.95811	0.95343	0.99843	-0.94671	-0.79656	0.77844	-0.80034	-0.82081	1.00000	0.61258
	0.0025	0.0102	0.0120	<.0001	0.0147	0.1067	0.1209	0.1038	0.0886		0.2720
Mo	0.50175	0.47055	0.40041	0.60328	-0.43328	-0.09559	0.20762	-0.14565	-0.15194	0.61258	1.00000
	0.3891	0.4238	0.5041	0.2814	0.4661	0.8785	0.7376	0.8152	0.8073	0.2720	

Wherever it appears: $p \leq 0.05$; $p \leq 0.01$; $p \leq 0.001$; and $p \geq 0.05$, $p \geq 0.01$, $p \geq 0.001$; *, **, *** respectively; + = increasing with depth; - = decreasing with depth.

3.3. Soil pH

Soil pH ranged from strongly acidic in WS zone; near neutral (in Arsi); to slightly alkaline in ES zone (Tables 1 & 2). The soils, particularly in ES zone are rich in $CaCO_3$ (calcareous). When considering only the topsoil, strongly acidic soils came from the highlands, while they are alkaline in valley bottoms or the rift-valley system and its peripheries. Most importantly, the pH of soils within the soil profile were found to increase linearly with depth (Figures 1–6) which might be ascribed to the accumulation of base-cations in subsurface due to their leaching or low levels of OM whose decomposition that releases organic acids. Similar findings were reported by different workers [19–21]. In general, the increased levels of basic-cations in the underlying horizons in turn, may suggest the existence of downward movement of these constituents within the profile.

3.4. Organic Carbon

Organic carbon (OC) content of all soil profiles decreased consistently with depth ranging from 1.70% (topsoil, 0–20 cm); to 0.46% (subsoil) with mean value 1.130 and STDEVA, 0.4883 (Tables 1 & 2; and figures 1–6) as indicated by the decreasing trends of percentage changes. On the other hand, the composite surface soil samples collected from the respective six sites topsoil ranged from 0.96% to 2.71%. Only in one site, the OC content was falling reasonably above the suggested critical levels (CLs). Reasons for the low levels of OC observed in topsoil in the studied areas could be intensive cultivation of the lands which enhances the oxidation and/or total removal of crop residues for alternative uses. Furthermore, the practice of adding organic fertilizers, such as farmyard manure and green manure that could contribute to SOM pool in the study areas was very low. This is indeed in accordance with that reported by [22, 23] in cultivated lands. The decreased levels of SOC with depth might also be attributed to the fact that surface layers are the most biologically active of soil profile and/or the physical restriction of the movements of OM to deeper layers.

In the whole, the relative high content of OC in topsoil (the active rooting depth), is the result of regular biomass addition and its subsequent mineralization in tropical climatic conditions. Tillage operations, however, can physically combine soil layers and result in rapid decomposition of OM transiently reducing the contribution of OM and microbial processes to nutrient cycling. The overall results of this investigation indicate that plants play a major role in the vertical distribution of SOC.

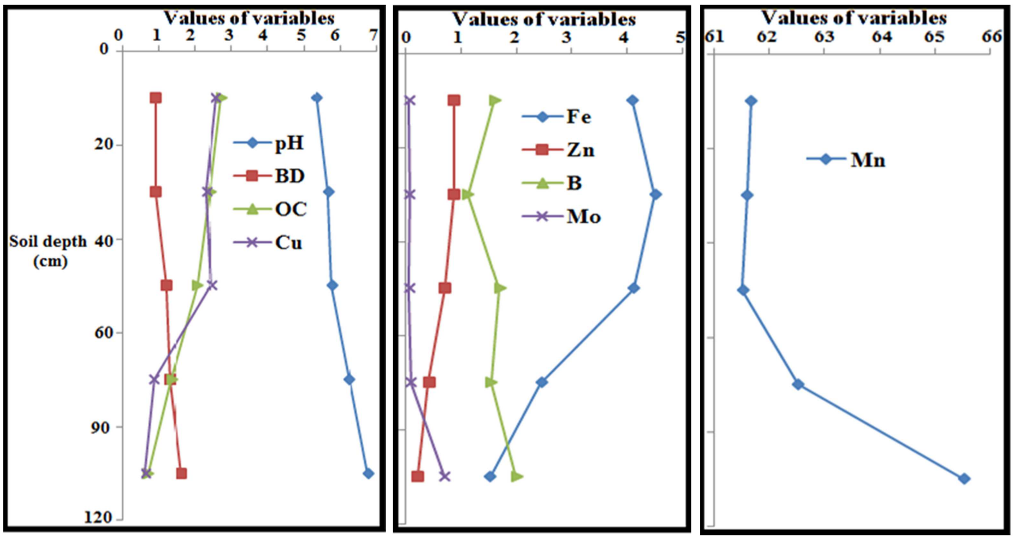

Figure 1. *Profile distribution of micronutrients & related soil properties in the first five depth intervals (0–120 cm) at Arsi zone, Wonji Gora site (P1).*

3.5. Copper

Average concentration of Cu in the earth's crust was reported to be 28 mg/kg [24]. The DTPA extractable Cu in the studied topsoil (0–20 cm depth) (Tables 1 & 2; and figures 1–6) varied from 1.47 to 3.20 mg/kg, with mean value 2.532 and a STDEVA, 0.622. Considering, < 0.2 as CL for DTPA-extractable Cu for normal growth of plants as reported by [11], none of the studied soils were deficient in plant available Cu. In accordance with this [25] reported a normal range with no excess levels of Cu in Arsi and Shewa provinces in Ethiopia.

But, for the soil samples collected from different profile or pedons, the contents of Cu showed nearly constant trend of changes within (0–60 cm depth); but for the depth range below 60 cm, the contents of Cu generally showed a declining trend of changes. The relative higher level of Cu in topsoil compared with subsoil might be ascribed to the contribution of OC in topsoil. This can also be affirmed by a significant positive correlation between Cu and OC ($r = 0.937$ at $p < 0.05$) (Table 2). However, the copper's positive correlation with OC may suggest its complex formation with OM and/or its strong affinity to SOM as a divalent cation. According to [26], the observed significant correlation of Cu with OC suggests its greater extractability from soils with higher levels of OC. But, Cu was significantly and negatively correlated with pH, clay-content and BD vis-à-vis their depth distributions.

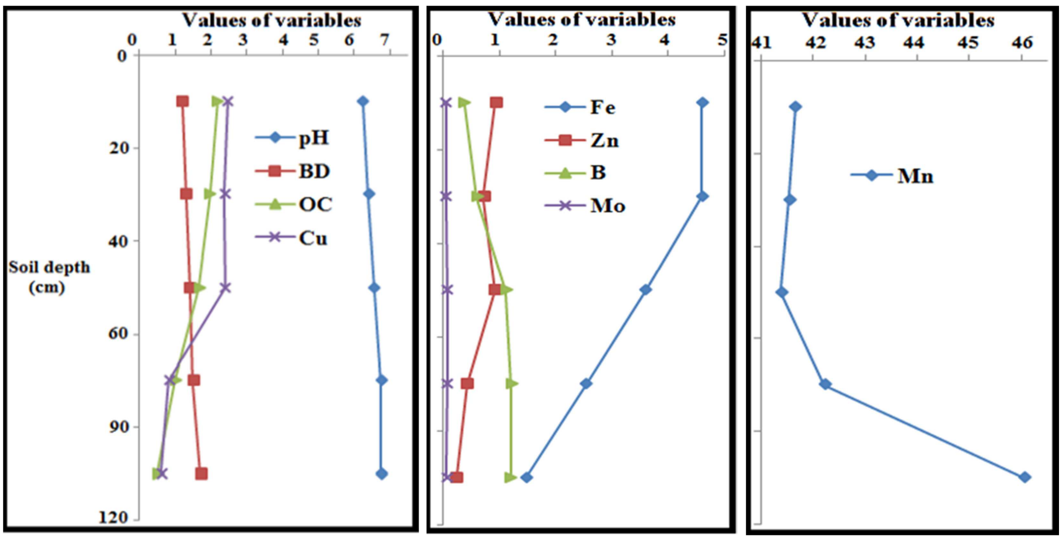

Figure 2. *Profile distribution of micronutrients & related soil properties in the first five depth intervals (0–120 cm) at Arsi zone, Gora Silingo2 site (P2).*

3.6. Manganese

Manganese concentration in the earth's crust is reported to be 1000 mg/kg [24]. The contents of DTPA-extractable Mn in topsoil (Tables 1 & 2; and figures 1–6) are much differentiated, ranging between 5.50–65.0 mg/kg with a mean value, 39.26 and a STDEVA of 26.901. Lindsay and Norvell, reported < 2.5 mg/kg as CLs for Mn-deficiency in soils [11]. Based on this rating, all soils under investigations were adequate in Mn for sustaining annual crop production. But, [27] suggested the CL for Mn deficiency to be 5.7 mg/kg. Based on this rating, however, only 10% of the soils fall within a marginal range. More generally, according to [2], a substantial percentage of Ethiopian soils form Sidamo, Arsi and Shewa provinces were categorized in high Mn zone. But, in few of the soils from sites like WG and BT are strongly acidic Vertisols, which are waterlogged. In such soils, the Mn-toxicity is more likely. Indeed, [3] made a similar observation.

With regard to the vertical distribution, Mn contents showed significant increases with depth which might be related to its high mobility in soils system. Such increasingly high concentrations of Mn in subsoil might become toxic to some plants, when taking, 55 mg/kg as a CLs for Mn-toxicity as suggested by [27]. Based on this rating, the sites like WG2; and BT2 were already surpassed the toxic level for Mn. In fact, in soils with considerably high levels of Mn, liming might be necessary.

A significantly positive correlation (Table 2) was observed between Mn with pH, clay content and BD (r= 0.879, 0.916 and 0.765; at p = 0.05 respectively). But it had a strong negative correlation with OC in relation to its depth distribution. Manganese was positively and significantly correlated also with clay, suggesting that fine textured soils had ample Mn compared to coarse textured soils, which might be due to higher adsorption and retention of Mn by finer fractions. When only the surface soils are considered, however, Mn showed negative correlation with pH. According to [28], the reason for this is the conversion of Mn to its water-insoluble oxide forms. Sharma et al., also reported a negative correlation between Mn and pH [29]. In line with this, [30] reported lower DTPA-extractable Mn from soils having high pH. Particularly, this finding may suggest the role the pH would play in Mn availability.

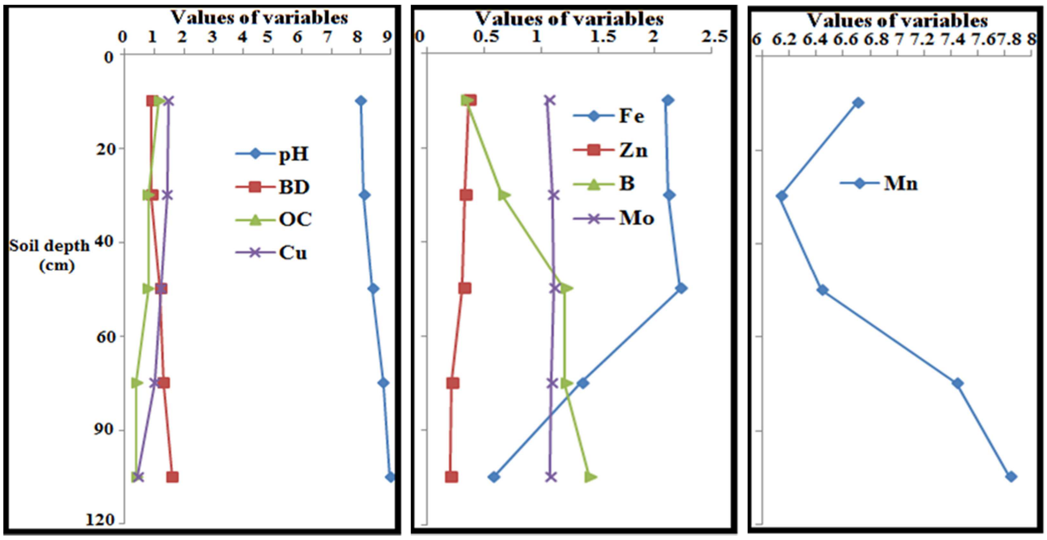

Figure 3. *Profile distribution of micronutrients & related soil properties in the first five depth intervals (0–120 cm) at ES zone, Keteba2 site (P3).*

3.7. Iron

Iron comprises about 5% of the earth's crust and it is the 4th most abundant metal in the lithosphere after oxygen, silicon and aluminum [24]. According to the authors, most of the soil Fe is found in primary minerals, clays, oxides and hydroxides.

Plant available Fe in the present investigation for topsoil varied between 2.10–8.20 mg/kg with mean value 4.68 and a STDEVA, 2.469 (Tables 1 & 2; and figures 1–6). Considering < 4.5 mg/kg as CL for DTPA-Fe for normal plant growth as suggested by [11], it can be deduced that 66.7% of the samples were low in Fe; and some 20% were marginal falling within a range 4.60–6.90 mg/kg. Only about 13.3% of the soils were adequate in plant available Fe. The results are in according with that report by [2]. In general, the present study showed that, relatively high-pH and sandy soils were found to be more deficient in Fe, but the reverse is true for soils with low pH. Previous studies by [31, 32], reported much similar findings. The reason might be that, high levels of bicarbonate and phosphate lower Fe-availability due to its precipitation reactions.

With regard to profile distribution, Fe content of the investigated soils generally showed significant decline particularly within the profile ranging particularly from 60 to 120 cm depth. This is indeed in accordance with that reported by [33]. Depth wise, relatively higher content of available Fe was observed in surface horizons compared with the subsurface. This variability could be due to its low mobility in soils, which is possibly governed by it redox potential and various soil properties like pH, OM and moisture regimes. Generally, the contents of Fe are low in most studied topsoil which is perceived to affect the normal growth of certain kinds of deep-rooted plants.

Considering the correlation coefficients, available Fe showed significant negative relationships (Table 2) with pH, clay content and BD (r= -0.917, -0.925, -0.798; at p ≤ 0.05). Particularly, a strong negative relationship of Fe with pH might be due to its conversion from Fe^{2+} to Fe^{3+} or may be its precipitation as insoluble $Fe(OH)_2$. In the calcareous soils like that of ES zone, the presence of excess phosphates may be responsible for the formation of Fe phosphates thereby decreasing its solubility. But, the correlation between Fe and OC was strongly positive (r= 0.943, at $p < 0.05$) suggesting a strong bonding effect between Fe and OM that may be ascribed to the formation of chelates called, side-rophores that enhance its solubility. Najafi-Ghiri et al., attributed this relationship to the exchange capacity of OM for Fe, the chelating ability of organic compounds and the acidifying property of OM [34]. Positive correlation between Fe and OC may signify that, OC would be an exclusive source of this nutrient in cultivated lands/soils. But, the negative correlation between Fe and clay might suggest that the increase in clay content leads to decrease in DTPA extractable Fe.

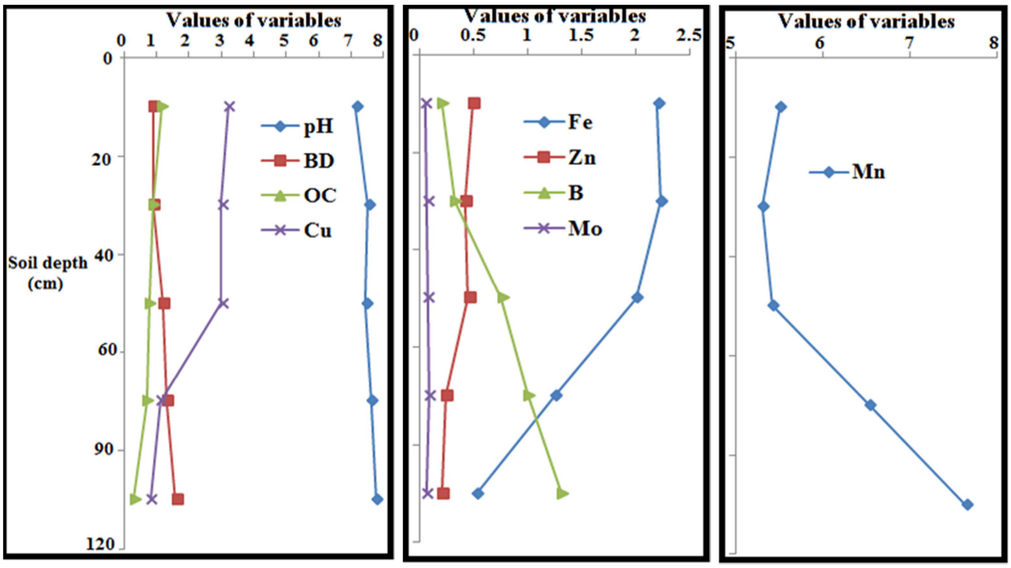

Figure 4. *Profile distribution of micronutrients & related soil properties in the first five depth intervals (0–120 cm) at ES zone, Bekejo2 site (P4).*

3.8. Zinc

On average, the contents of Zn in the lithosphere were reported to be 67 mg/kg [24]. It was further stated that, Zn has a strong tendency to combine with sulfide bearing mineral ores and occurs most frequently as sphalerite. In the present investigation, plant available Zn in topsoil (Tables 1 & 2; and figures 1–6) ranged from 0.36 to 1.21 mg/kg with mean value 0.81 and STDEVA, 0.320. Taking 1.0 mg/kg as a CL for Zn deficiency and/or for the normal plant growth [11], 90% of the soils were deficient in Zn. Some 10% were marginally above the CL with no adequate levels. The present result is also in accordance with the finding reported by [31].

With regard to its vertical distribution, the contents of Zn showed an irregular trend of change with increasing depth. For example, it generally showed steadily decreasing trend with depth in all sites. This may show Zn element's low mobility in soils and its tendency to be adsorbed on clay sized particles. The relative higher level of Zn in surface horizons could result from bio-mining and turnover by plant residues. A study made on some Alfisols, [29] reported similar results.

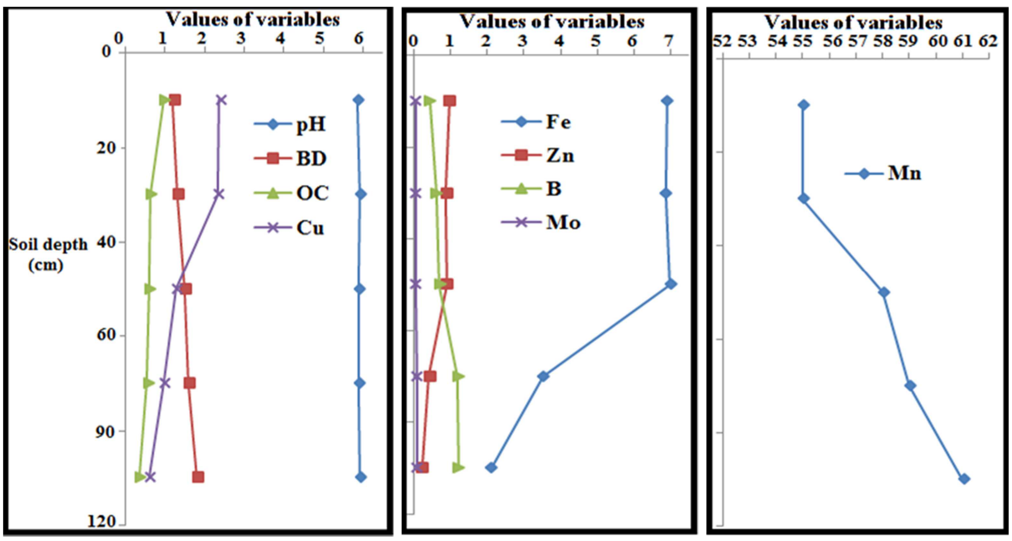

Figure 5. *Profile distribution of micronutrients & related soil properties in the first five depth intervals (0–120 cm) at WS zone, N. Suba2 site (P5).*

With regard to Persian correlation coefficients, plant available Zn showed significantly negative correlation (Table 2) with pH, clay and BD (r= -0.935, -0.928, -0.823, at $p < 0.05$). But, the correlation of Zn with OC was significantly positive, which may suggest that pH and OC are the most influential soil properties that predict Zn availability.

3.9. Boron

Boron concentrations in soils reported to range between 20–200 mg/kg [35]. Plant available B content in the studied topsoil (Tables 1 & 2; and figures 1–6) ranged from 0.21 to 1.60 mg/kg with a mean value 0.56 and a STDEVA, 0.514. Based on the CLs for B-deficiency reported by [36], only 20% of the soils were deficient in B. Some 13.3% were found to be either in equilibrium or marginally above the suggested CL. The rest, about 66.7% of the soils were regarded as adequate in plant available B. Sillanpää M., made a similar, but more general report [25]. According to the author, the average B-contents of Ethiopian soils and pot-grown wheat were lower than the respective international averages.

But, for soil samples collected from different profiles, the contents of B were found to increase irregularly with depth owing probably to its solubility and subsequent leaching down to the subsoil. From this it is learnt that, increasing levels of B in subsoil may suggest that it is highly mobile in the soils system. Its relative low content in the topsoil might be due to severe B-deficiency; its uptake by plants; or its leaching down to the profile owing to its mobility.

Available B showed significantly positive correlation (Table 2) with pH, clay and BD (r= 0.958, 0.953, 0.998, at $p \leq 0.001$). This may suggest that, among the analyzed parameters, soil pH and clay content are the most important factors that influenced B concentration in soils. But, B showed an inverse relationship with OC vis-à-vis its depth distribution, indicating that these variables follow an opposite trends of change with depth. Ayan Kumar Das & Aloke Purkait, made a similar observation [37]. Overall, the plant available B, not only varied across soil profiles, but also it varied from soil to soils. Overall, adequate knowledge about its sources, factors affecting its availability, different B fractions in soils, and its kinetics are needed to understand the dynamics of B in soils.

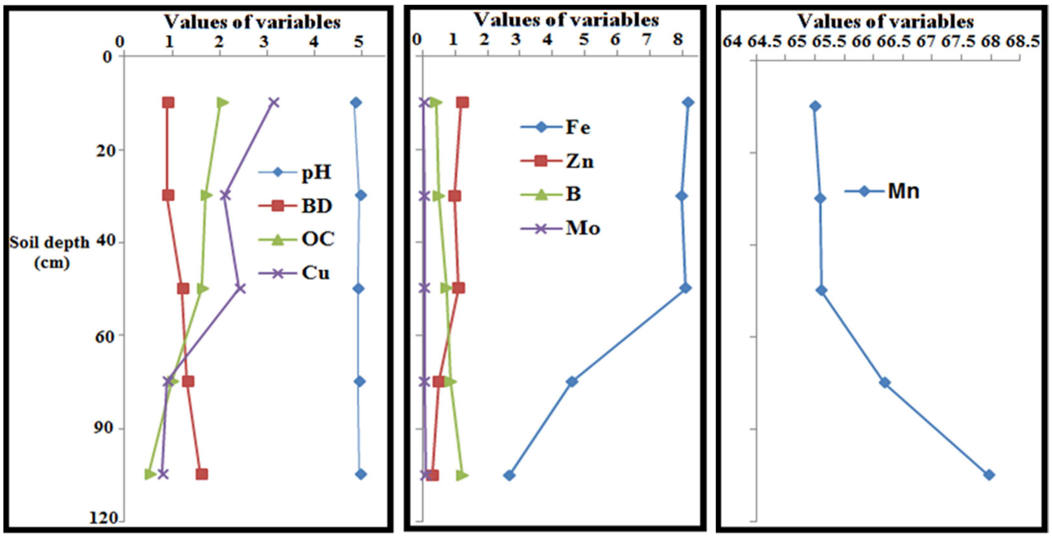

Figure 6. *Profile distribution of micronutrients & related soil properties in the first five depth intervals (0–120 cm) at WS zone, B. Tokofa2 site (P6).*

3.10. Molybdenum

Molybdenum (Mo) is a transition metal element that has variable oxidation states as $Mo^{(+2-6)}$ with the Mo^{+6} considered to be the most stable state. In soils, Mo usually occurs in extremely small quantities, < 1 mg/kg [24].

In the present investigation plant available Mo in topsoil (Tables 1 & 2; and figures 1–6) varied from 0.04 to 1.06 mg/kg with mean value 0.22 and a STDEVA of 0.412. Considering 0.1 mg/kg as a CL for Mo-deficiency [28], about 73.3% of the soils were found to be below this level, and therefore, deficient in Mo. The results of the investigation clearly elucidate that, low Mo soils, were acidic soils with a relative coarser texture.

With regard to its profile distribution, the concentrations of Mo were generally constant until the depth of 90 cm. But, within the depths ≥ 90 cm it had showed a steadily increasing trends of change with depth in all profiles. This may also indicate its relative better mobility in soils system. Such increasing levels of Mo with depth were particularly pronounced in alkaline soils that came from the ES zone. Generally, in most profiles the concentrations of Mo in topsoil was lower compared with subsoil, particularly in strongly acidic soils that came from WS zone. Considering its extremely low level in the lithosphere, however, making comprehensive conclusions may need more detailed studies.

Coefficient correlation result showed that the available Mo showed significantly positive correlation (Table 2) with pH, clay % and BD (r= 0.471, 0.400, 0.603; at $p \geq 0.10$) further affirming its low availability in acidic soils. This is in accordance with that reported by [3]. But, the correlation of

Mo with OC was negative in relation to its profile distribution. This means that, among the analyzed soil parameters, soil pH and clay content might be the most important factors influencing Mo concentration in soils. Indeed, this is in accordance with that reported by [38]. In general, the overall increasing trends of change of Mo with depth may be due to its leaching loss to deeper profiles due to its relative better mobility. But, according to, [39] high levels of Mo seldom retard plant growth, but levels of more than 10 mg/kg in feed, reported to be toxic to ruminants. Hence, in acidic soils, similar to Mn, liming may be recommended to enhance its availability.

4. Conclusion

Micronutrient contents in soils were much differentiated within and among soil profile and across sites owing to multitude of factors: the parent material, topography, climate, biochemical and geochemical processes in the soil. Though, the pattern of changes differs, the contents of Mn, B, Mo, soil pH, the clay % and BD were found to increase irregularly with depth owing to leaching; and weathering dissolution; whereas Cu, Fe, Zn and OC followed reverse trends of changes. Increase in clay % with depth is principally due to its clay-illuviation or pedoturbation in Vertisols. Correlations among soil properties also varied significantly with depth. Higher content of the micronutrient elements like Cu, Fe and Zn in the topsoil may clearly elucidate the role biomass cycling and rates have played in the vertical distribution. On the whole, for those micronutrients that are reasonably abundant in the subsoil, deep-tillage operations like sub-soiling are recommended to bring their available forms to the top-layers for shallow-rooted plants uptake and recycling. Deep capture of nutrients by tree roots (e.g., like that in the agroforestry system) can also recycle nutrients leached, thus improving nutrient use efficiency and reducing potential negative environmental consequences. Overall, the control that biomass cycling exert on the vertical distribution of plant nutrients can produce a strong positive feedback for soil nutrients availability and hence crop productivity.

Competing Interests

The author declares that they have no competing interests.

Acknowledgements

EIAR and Pawe research centers allowed and supported the study. Kulumsa, Debre Zeit and Holeta research centers under the EIAR hosted the overall field study and provided all needed supports.

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