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Sequential Micronutrients Extraction from Toposequences of Pasture Soils

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The objective of this study was to determine changes in soil properties and micronutrient content (Fe, Cu, Mn and Zn) development along a slope in pasture soils. The study area is located in Kocadag, Samsun, Turkey. Three landscape positions *i.e.*, summit, backslope and footslope, were selected. Soil samples for all genetic horizons were taken from all landscape positions of pasture. Some physico-chemical properties such as organic matter content, pH, $CaCO_3$, exchangeable cations and sequential micronutrient fractions (exchangeable, organically complexed, manganese oxide bounded, amorphous and crystalline iron oxide bounded and residual) were determined. All micronutrient pools, horizons were affected by slope position. The micronutrient fractions and particularly the exchangeable (EX-), organically complexed (OM-) fractions tended to decline with soil dept. The residual fraction (R-) was proportionally the largest fraction and EX- and OM- fraction were the smallest fractions at all horizon and landscape position. In footslope position, the soils had generally the higher total micronutrient contents and their R- fractions than the other positions at all genetic horizons. In all positions, except for R- fraction, micronutrient fractions in soils decreased from the surface downward indicating that the major part of the location is existed to the A horizon.

Key Words: Pasture soil, Landscape positions, Micronutrient, Fractions.

INTRODUCTION

Parent material, climate and geological history are major important factors to affect soil properties on regional and continental scale[1-3]. However, landscape position may be the dominant factors of soil properties under a hillslope and small catchment scale. Landscape positions influence runoff, drainage, soil temperature and soil erosion and consequently soil formation[4,5]. Differences in soil formation along a hillslope result in differences in soil properties[6], which can affect pattern of plant production[7], litter production and decomposition[2,3].

As far as physico-chemical soil properties are concerned, numerous studies[2,3,8-11] have focused on the landscape position and its impact soil physico-chemical properties of the soil. The physical properties of the soil such as clay content distributions with depth, sand content and pH have been shown correlated with landscape position[8]. While the organic matter has been shown to vary by slope position[9,11]. Furthermore, Pierson and Mulla[10] found that soils on foot slope and toeslope positions had a higher organic carbon contents and lower clay contents than those on summit positions. Relationships between landscape position and soil physical properties, pH, N, P, K have already been described[2,3,10,11]. On the contrary, little information on the relationships between landscape position and soil sequential micronutrient fractions is available.

The effects (*e.g.*, mobility, bioavailability, toxicity) of micronutrients in soils depend on the physico-chemical forms in which the particular metal exists in soils[12,13]. Micronutriens in soil may be (i) in soil solution as ionic or organically complexed species (ii) on exchange sites of relative soil components (iii) complexed with organic matter (iv) included in oxides and hydroxides of Al, Fe and Mn and (v) entrapped in primary and secondary minerals[14,15]. Micronutriens present in these categories have different remobilization behaviours under changing environmental conditions. In the last few decades a number of sequential extraction (fractionation, portioning) techniques have been developed and widely used to study these forms. Although the operational details of the commonly applied techniques differ, the main principle, to select the physico-chemical forms that influence element activity, stays the same. However, the integrity and reliability of sequential extraction techniques remain controversial[16-18], as some of the assumptions behind the methods are difficult to validate. Nevertheless the methods can be useful in helping to understand micronutrient mobility and bioavailability in soils[19,20].

We hypothesized that a wide array of soil micronutrients may vary among landscape positions. In this work, micronutrient (Fe, Mn, Cu and Zn) fractions in soils were quantified using the Shuman[16,21-23] sequential extraction procedure. The soils represent one important semi-humid climate regime in the whole Turkey northern semi-humid area. The objectives of this study were (1) to assess the effects of three landscape position (summit, footslope and backslope) on soil micronutrients including total concentrations and their sequential fractions (exchangeable, organically complexed, manganese oxide bounded, amorphous iron oxide bounded, crystalline iron oxide bounded and residual) and (2) to explore vertical distribution micronutrients in soils.

EXPERIMENTAL

The study area is located in the Black Sea Region, Northern Turkey Latitude, 41º 19' N; longitude, 36º 02' W). The climate is semi humid, (R_f = 52.5) with temperatures ranging from 6.6ºC in February to 23ºC in August. The annual mean temperature is 14ºC and annual mean precipitation is 735 mm.

The study area was defined as pasture of Kocadag, Samsun that has relatively homogeneous vegetation in traditional form and had similar grazing history. Native vegetation in the pasture of Kocadag was dominated by grasses *Plantago lanceolata* L., *Bellardia* sp., *Bellis perennis* L., *Circium arvense* L., *Bromus squarrosus* L., *Taraxacum* sp., *Stellaria* sp., *Trifolium resupinatum*, *Medicago hirpida Gaertn.*, *Medicago arabica* L., *Medicago scutellata* L. and *Poa* sp. No fertilizer use was recorded for all soils studied.

Soil sampling: In May 2002, nine soil samples were taken from three soil profiles at summit, backslope and footslope positions were described (Fig. 1). The profile I was located on more stable summit landscape position and classified as Lithic Udifolist. The profile II was classified as Typic Hapludols on backslope position and profile on the footslope position was described as Vertic Calciudols[24]. Samples from all the genetic horizons in the summit, backslope and footslope profile from each toposequence were collected, air dried, crushed and passed through a polyethylene sieve with 2 mm opening in preparations for characterization and fractionation analysis.

Soil physico-chemical properties: Selected soil physico-chemical properties were determined by means of appropriate methods, particle size distribution by hydrometer method, pH and electrical conductivity (EC) in 1:1 (w/v) in soil, water suspension by pH-meter and EC-meter, lime content by Scheibler Calsimeter, exchangeable cations (Na, K, Ca, Mg) by ammonia acetate extraction, cation exchange capacity (CEC) by Bower method. Whole soil samples were sieved through a 150 μm mesh to determine total organic carbon by the wet oxidation method (Walkley-Black) with $K_2Cr_2O_7$.

Micronutrients in soils: The procedure by Shuman[16,21-23], selected for this study, is designed to separate micronutrients in to six operationally defined fractions *viz.*, exchangeable (EX-), organically complexed (OM-), manganese oxide bounded (MnO-), amorphous iron oxide bounded (AFeO-), crystalline iron oxide bounded fractions (CFeO-) and residual (R-) fractions. A summary of the procedures are given in Table-1. The soil samples sieved from 2 mm openings for EX- and OM- heavy metal fractions and from 0.5 mm openings for the other micronutrient fractionations. After each successive extraction, separation was done by centrifuging

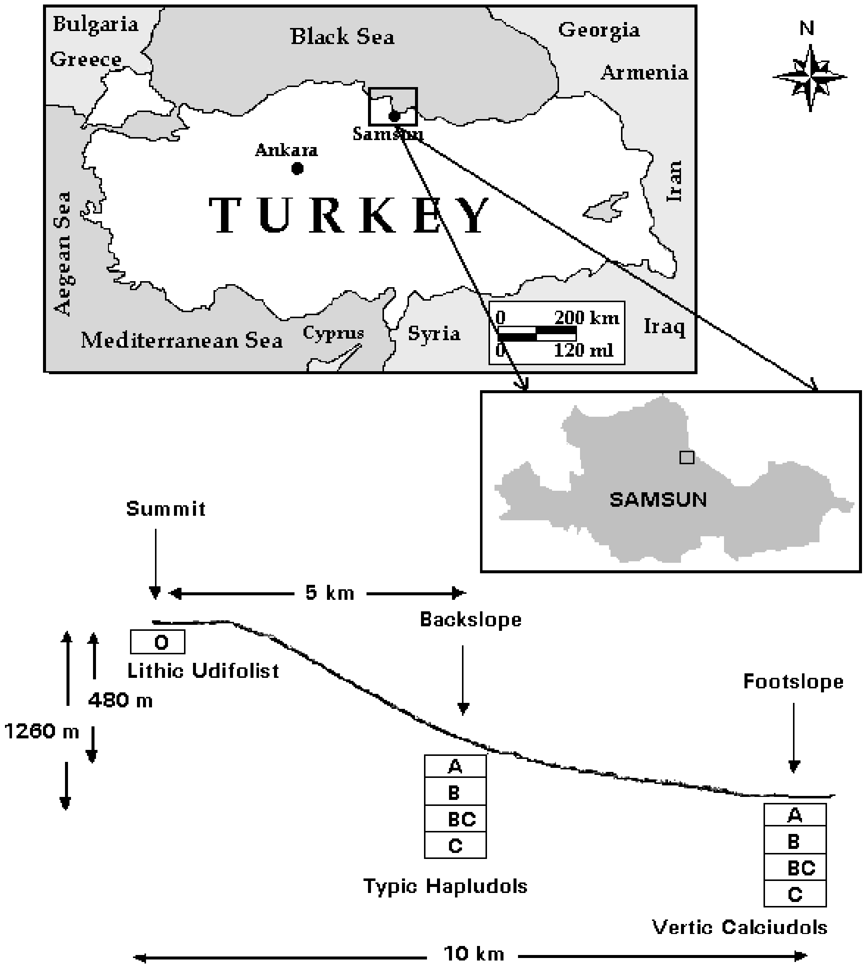


Fig. 1. Location map of the Kocadag, Samsun and study area

at 5000 rpm for 10 min and filtered with Whatman 42 filter paper. Total soil micronutrients were determined using aqua regia - HF - HNO_3 and HCl solutions. Micronutrient (Fe, Mn, Cu and Zn) contents were determined using atomic absorption spectrophotometer (Perkin Elmer 2280) with flame. Residual fraction (R-) was calculated as follow; R- = total - (EX- + OM- + MnO- + AFeO- + CFeO-). Results were expressed as mg kg^{-1}.

Statistical analysis: The means and standard deviation of triplicates were found. All the figures presented include standard deviations of the data. The analysis of variance (Anova) was mainly carried out using randomized complete plot design with $\alpha = 0.05$ by using SPSS 10.0 programs.

TABLE-1
MICRONUTRIENT FRACTIONATION PROCEDURE

Fraction	Solution	Soil (g)	Solution (mL)	Conditions
Exchangeable (EX-)	1 M $Mg(NO_3)_2$ (pH 7.0)	10	40	Shake 2 h
Organically complexed (OM-)	0.7 M NaOCl (pH 8.5)	10	20	0.5 h in boiling water bath. Stir occasionally. Repeat extraction
Manganese oxide bound (MnO-)	0.1 M $NH_2OH.HCl$ (pH 2)	1	50	Shake 0.5 h
Amorphous iron oxide bound (AFeO-)	0.2 M $(NH_4)_2C_2O_4$ in 0.2 M $H_2C_2O_2$ (pH 3)	1	50	Shake 4 h in the dark
Crystalline iron oxide bound (CFeO-)	0.1 M ascorbic acid in the above oxalate solution	1	50	0.5 h boiling water bath. Stir occasionally.

RESULTS AND DISCUSSION

Soil physico-chemical properties: Clay contents of soils was the lowest at backslope position, while was the highest at footslope position. This result was expected because backslope positions encourage soil erosion more than the other landscape positions (Table-2). Organic matter contents was highest at summit position which may be directly related to higher surface cover rates. $CaCO_3$ contents of the soils was quite different from each other. $CaCO_3$ contents of the soils was the highest at footslope position. These indicate that footslope position get excess water from the upper positions which leached $CaCO_3$ from surface layer. Similar to the variation of exchangeable Na and CEC was the lowest at backslope positions (Table-2).

Total micronutrient concentration: Total micronutrient contents in the studied profiles were different (Fig. 2). On the other hand, except for Fe, Mn, Cu and Zn in backslope position profiles were considerably lower than in other landscape position profiles under both natural vegetation. Similarity in the deeper horizons indicates differences of parent material in each toposequence and difference soil development under the same climatic condition. With the exception of Fe, it was expected that, B horizon of the footslope position and A horizon of the backslope position would have higher Mn, Cu and Zn contents than the other horizons. The highest levels in total Fe occured on the footslope position. Total concentrations of

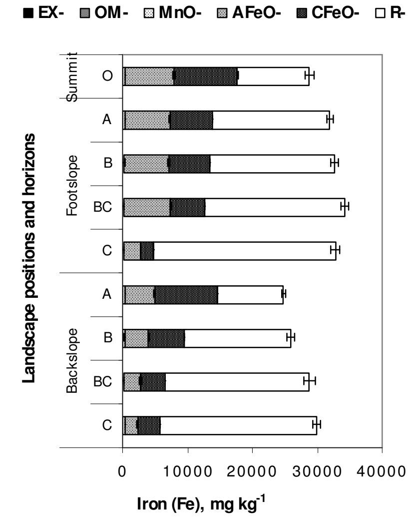
TABLE-2
PHYSICO-CHEMICAL PROPERTIES OF SOILS STUDIED

Landcape position	Hr	Dept (cm)	Texture (%)			%		(1:1)		me 100 g^{-1}			
			S	Si	C	OM	$CaCO_3$	pH	EC	CEC	Na	K	Ca + Mg
Summit	O	0-20	29.0	42.2	28.8	30.2	-	6.50	0.29	49.4	0.61	0.26	13.6
Backslope	A	0-12	53.8	23.0	23.2	5.34	-	6.50	.024	23.3	0.32	0.58	19.4
	B	12-23	53.8	21.8	24.4	4.65	-	6.60	0.36	22.3	0.16	0.67	17.7
	BC	23-40	60.9	13.4	25.7	2.75	-	6.80	0.13	26.3	0.11	0.74	22.3
	C	40+	67.4	7.7	24.9	1.32	-	6.90	0.67	24.9	0.11	0.71	20.5
Footslope	A	0-7	6.9	22.2	70.9	4.26	17.58	7.70	0.54	32.0	0.92	0.38	29.5
	B	7-22	17.3	19.6	63.1	4.46	17.26	7.90	0.49	38.2	0.59	0.58	29.9
	BC	22-41	11.5	23.3	65.2	1.93	29.98	8.00	0.52	28.5	0.17	0.61	28.4
	C	41-60	10.0	31.9	58.1	1.76	40.04	8.10	0.35	25.3	0.07	0.24	25.6

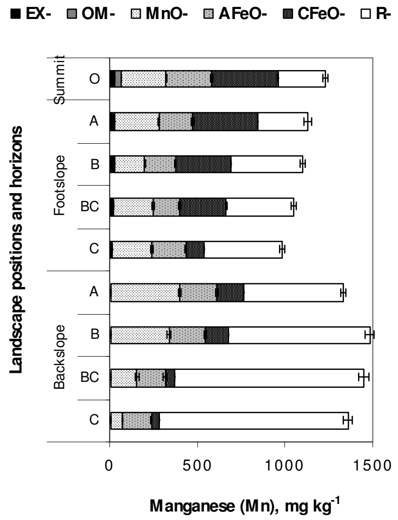
Hr : Horizon, S: Sand, Si : Silt, C:Clay; CEC : Cation exchange capacity.

micronutrients in the studied profiles reflect both natural differences in soil genesis and properties and toposequence of soils. With the exception of residual fractions (R-) it was expected that the top horizon of the backslope position would have a higher Fe, Cu, Zn and Mn fraction contents than the top horizons of the footslope position because of the accumulation of enriched micronutrients soil eroded these later position. The absence of this effect indicates that there was erosion or that gains and loses were equivalent in all positions. Similar results were obtained for the superficial horizons of a Nigerian toposequence[25,26].

Micronutrient fractions: There were significant differences in micronutrient fractions contents among landscape positions (Figs. 2 and 3). Close observation suggests that there is a tendency for greater values in micronutrient fractions at the footslope position. In all landscape positions, except for R- fraction, Fe, Cu, Zn and Mn fractions in soils decreased from the downwards surface (Fig. 2) indicating that the major part of the location is existed to the A horizon. On the contrary, the majority of the R-fraction of all micronutrient has generally remained in the B, BC and C horizon of the profiles (Figs. 2 and 3). Moreover, all total contents of micronutrients and their fractions on footslope position were significantly higher than the other positions. Additionally, all micronutrient contents except for Mn fractions exhibited similar pattern on all profiles. Comparisons of Fe, Cu and Zn fractions by landscape positions revealed that EX-, OM-, MnO-, AFeO-, CFeO and R- contents on footslope were significantly higher than those on summit and backslope positions (Fig. 2). The lowest levels in Fe, Cu and Zn fractions occurred on the backslope position. In contrast, the highest levels in total Fe occured on the footslope position



(A)



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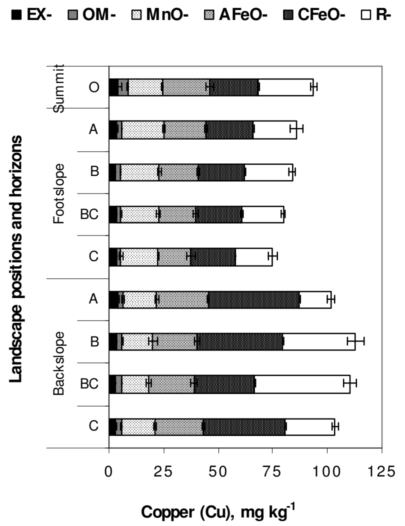

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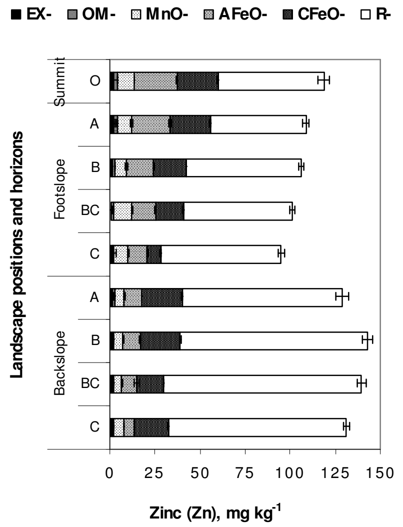

(D)

***F*-value**	**Summit**	**Backslope**	**Footslope**
Micronutrients (MN)	5344.424***	20738.949***	33900.996***
Micronutrient fractions (MF)	1158.148***	9514.949***	14050.306***
Horizons (HR)	-	40.840***	7.287***
MN x MF	1082.323***	8354.250***	13434.178***
MN x HR	-	40.711***	7.935***
MF x HR	-	451.175***	283.646***
MN x MF x HR	-	409.930***	271.145***
LSD (1%)	300.554	282.517	267.999

(E)

Fig. 2. Micronutrient fractions in soil horizons of toposequences of pasture soils in northern Turkey (a) Fe, (b) Mn, (c) Cu, (d) Zn and (e) Results of Anova

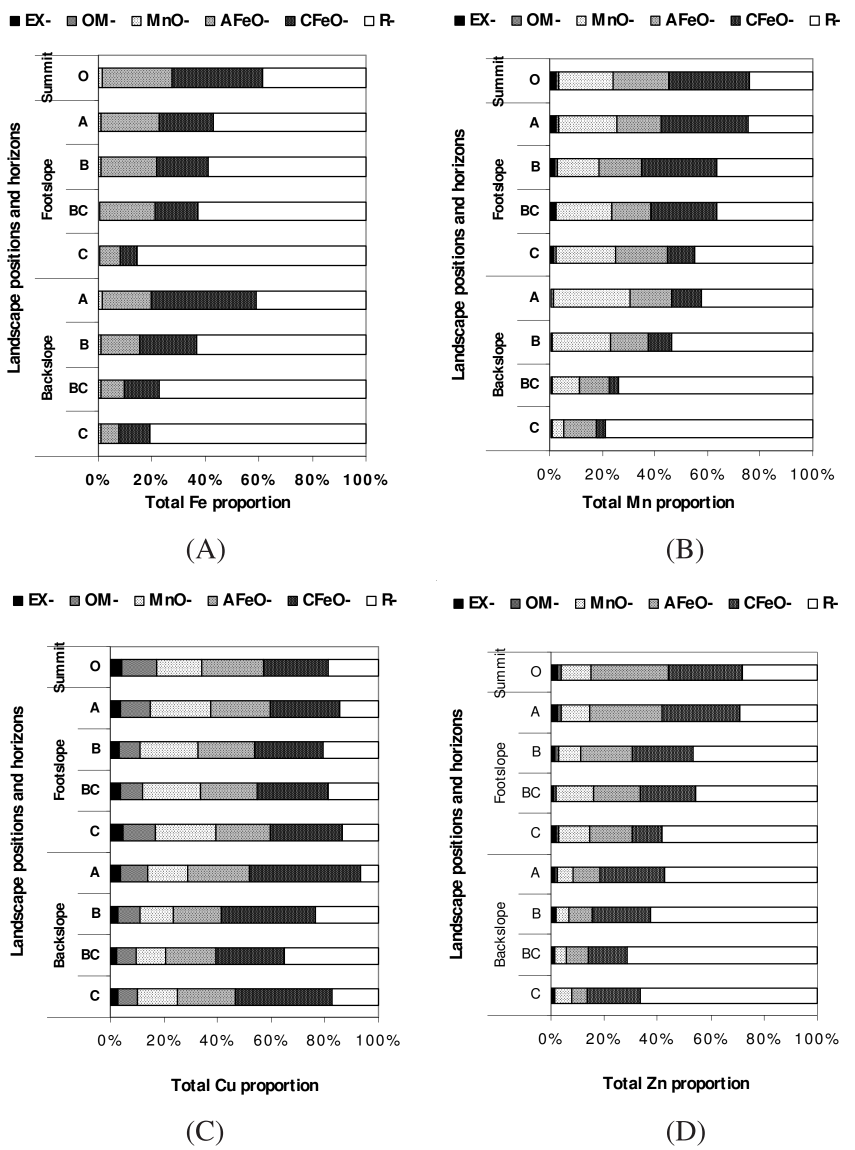

Fig. 3. Mean proportions of exchangeable (EX-), organically complexed (OM-), manganese oxide bound (MnO-), amorphous iron oxide bound (AFeO-), crystaline iron oxide bound (CFeO-) and residual (R-) micronutrient (Fe, Mn Cu and Zn) in relation to total contents at three slope positions in toposequences of pasture soils in northern Turkey

and some Mn fractions (CFeO-, EX- and OM-) occured on the backslope position. Generally, most micronutrient (Fe, Mn, Zn and Cu) were found in the R- and low amounts of micronutrients were in the EX- and OM- fractions at all landscape position and all profiles, which was agreement with previous workers[26-28]. The greater percentage of micronutrients in the R- probably reflects the greater tendency for micronutrients to become unavailable once these were in soils along the slope. Among the nonresidual fractions, the Fe-Mn oxide fraction (AFeO-, CFeO and MnO-) contained the greatest amount of micronutrients in all landscape position and all profiles. This may be partially due to high stability constants of oxides forms. Several other workers[27,28] have also found micronutrients to be associated with Fe-Mn oxides.

Anova results indicated that significant differences in micronutrient fractions for aspects and micronutrient fractions for the interaction of landscape positions and horizons were found.

Conclusion

The results of this study indicated that soil physico-chemical properties and micronutrient fractions along a hillslope had great differences among the rangelands with similar grazing histories. Total micronutrient contents and their fractions were generally higher at footslope positions as compared to the other positions. This means that clay particles, organic matter and micronutrient fractions were lost at more severe rates on the summit and backslope landscapes. On the other hand, some micronutrient fractions of upper soils were lowest at footslope position, which was attributed to leaching effect. Micronutrient distribution in various chemical fractions depend on the total micronutrient content of the soils (Figs. 2 and 3). As the total micronutrient concentration in the soils increased, the per cent of the total contents in the R- fractions increased and micronutrient in the OM-, EX-, CFeO-, AFeO- and MnO fractions decreased along the slope and deeper horizons. The R- fraction was the most abundant pool for all the micronutrients in the soils studied. However, in most of the soils, a significant percentage of the total Cu was associated with the nonresidual fractions.

Land use conversion and landscape position associated with erosion resulted in high variability of nutrients. It is, therefore, a special and interesting area for the performance of an integrated analysis of soil micronutrients in relation to landscape position. Such a local analysis is necessary to estimate micronutrient storage in semi humid and cultivated ecosystems and potential changes in nutrient contents due to land use change in regional scale. Consequently, the results of this study clearly indicated that the rangelands around Samsun province are under water erosion problems. Furthermore, soil erosion must be controlled, as in all around Turkey and degradated rangelands must be taken into rehabilitation program.

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