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The roles of parent material and toposequence on geochemical characteristics and pedogenic iron oxides of soils

T Tunçay[*,a,†] & O Dengiz[b,$]

[a]Soil Fertilizer and Water Resources Central Research Institute-Ankara-06110, Turkey
[b]Ondokuz Mayis University Agricultural Faculty Department of Soil Science and Plant Nutrition-Samsun-55105, Turkey

[E-mail: [†]tulaytuncay@gmail.com; [$]odengiz@omu.edu.tr]

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Soil formation is highly associated with topographic position and parent material, both of which play roles in the morphological, mineralogical and weathering processes of soils, particularly on the local level. Landscape topography conducts soil formation through affecting biogeochemical process and regulating soil hydrological process in the surface part of the earth, while parent material has a considerable effect on the types and concentrations of elements found in soil. This study aimed to determine how pedogenic and other factors affect soil classification by identifying the geochemical characteristics of soils classified as vertisols, inceptisols and entisols located on different topographies and possessing different parent material. Following macro-morphological identification of six typical soil pedons, samples were taken from different soil layer and their geochemical, mineralogical and other characteristics were analyzed. These characteristics were also evaluated for possible use in identifying soil maturity stages and periods of late-quaternary soil formation. The pedogenic evolution of soils was also examined using genetic ratios, which combine major oxides and selective dissolution analysis (Fe_o-Fe_d) values into a single metric. All pedons had Si/Al ratios above 2, indicating arid, sub-arid, sub-humid or high precipitation with cold areas. In addition, Fe_d (dithionite extractable iron) values were higher than Fe_o (oxalate extractable iron) and lower Fe_t (total Fe oxides) values, ranging between 0.007 % and 0.031 %. Therefore, the results clearly showed that local soil geochemical, mineralogical and morphological characteristics in the research area were strongly influenced by topographic conditions and parent material either directly or indirectly.

[Keywords: Chemical weathering, Geochemical evolution, Selective dissolution analysis, Soil formation]

Introduction

There are strong links between soil composition and biochemical and geochemical processes such as weathering and storage of major, minor and trace elements. Understanding the rate at which these processes occur is fundamental to understand the soil function and its interaction with the surrounding environment. During early pedogenesis, a soil's chemical composition is largely determined by the constitution of its geological material. Soil constitution has diverged gradually from that of the parent material under the impress of genetic procedures governed by land shape, climate and vegetation[1,2] with time. Thus, the chemical compositions of mature soil more strongly result in the effects of the weathering environment. Weathering involves the physical micro division, chemical dissolution and transformation of soil minerals by precipitation and ion exchange.

Chemical weathering means chemical alteration or decomposition of rocks and minerals, operating the geochemical cycles of elements and altering the earth's surface. Elemental constituents of soil conducted by various factors, comprising climate, relief, organisms, time and parent material, developed by way of numerous physical and biochemical processes which include weathering with associated geomorphical and pedogenical process such as erosion and transport. To understand the evolutionary history of the earth, the weathering of rocks and the formation of sediments, was regarded as geochemical behavior of elements[3]. In addition, Tunçay and Dengiz[4] reported in their study carried out in Bafra Plain that topographic conditions strongly affect soil pedogenic process in the regional scale. This outcome was promoted by chemical weathering indices such as Chemical weathering indices (CIW)[6], Chemical Index of Alteration (CIA)[5], Base/R_2O_3 (Al_2O_3 + Fe_2O_3)[7] sesquioxide or R_2O_3 and Weathering Index of Parker (PIA)[8] as well. Slope position, or relief, plays a key role in soil development and in how water and energy are combined to and are removed from soil.

Some researchers stressed that it is significantly important to understand how a landscape unit such as a catchment or watershed functions requires an understanding of the lateral transfer of water and energy on, in and through the soil[9]. Soil systems are defined as either open or closed based on the flow of water and energy. Numerous researchers[9-11] have reported the significant effects of slope gradient, length and aspect on the mineralogical, chemical and physical characteristics of soil. Particularly in upslope positions, the main factor in soil erosion is a high slope gradient, which leads to a subsequent loss of upper horizons and land degradation[12]. It has been stressed by the down slope redistribution of elements released by weathering[13]. Most of the studies mentioned changes in the balance between erosion developed on fresh kolluvial material or on disclosed erosional surfaces and weathering[14,15].

Despite its generally dynamic nature, a slope contains stability zones where the ratio of pedogenic process is greater than the rate of denudation or accumulation, allowing from young to mature soils to form. Since the timing of soil development is particularly dependent upon slope, aspect and vegetation, soils in mountainous areas tend to be arranged in a kind of mosaic generated by a combination of slope processes and pedogenesis[16].

Using geochemical data, this study carried out a pedological assessment aimed to identify individual geochemical characteristics of Vertisols, Inceptisols and Entisols. In addition to that, as these soils are formed on distinct parent materials and are located on different topographies studies were also undertaken to understand the relationship between particular soils and the land shapes-landscapes and ecosystems in which they function. Geo-chemical, mineralogical and other analytical properties are described here to evaluate their use in quantifying the developing stages and durations of late quaternary soil formation.

Materials and methods

The location and climate

This research was conducted in the southern part of the Samsun-Bafra Plain located in the Kızılırmak Delta in the central Black Sea Region of Turkey (Fig. 1). The site is found approximately 200 km west to the Samsun provincial center (4598500 - 4597500 N, 749250 - 750 000 E, UTM/WGS 84 m).

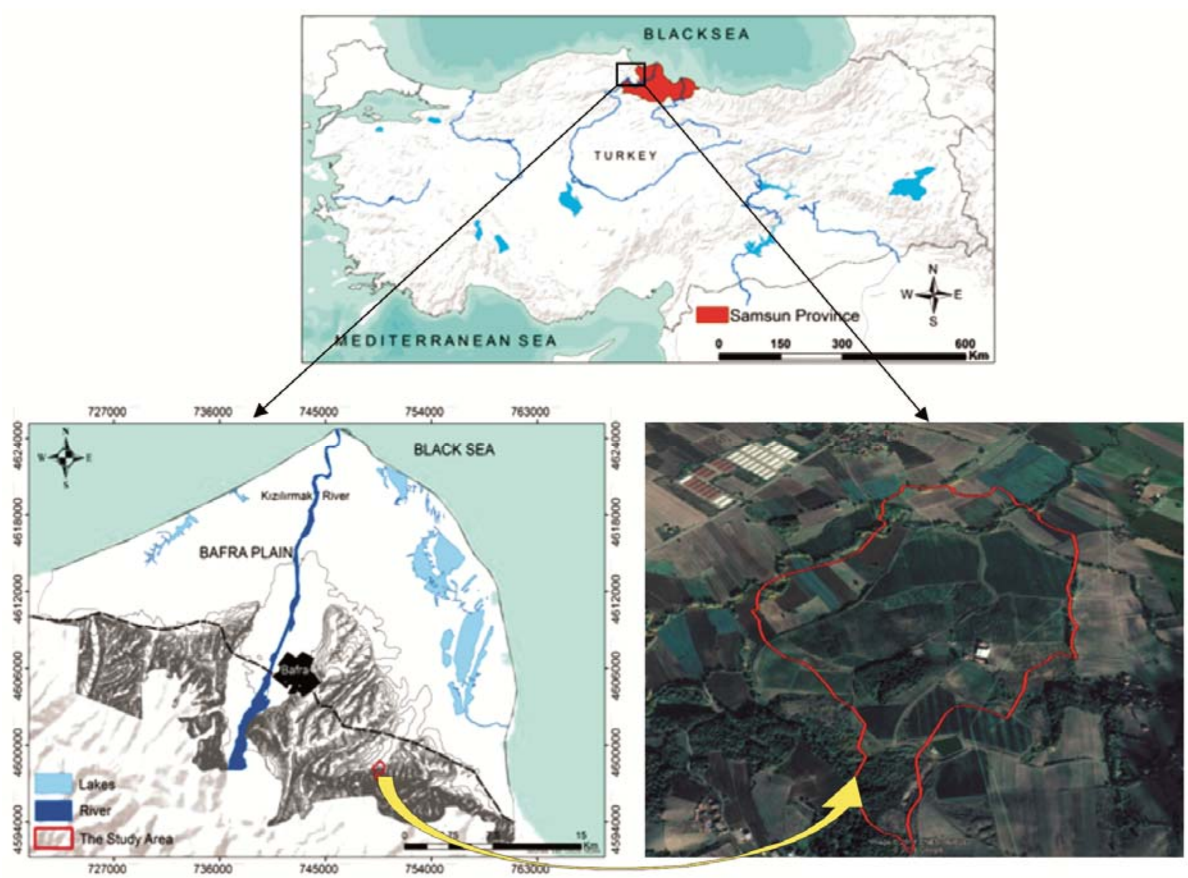

Fig. 1 — Rainfall stations in Vaigai river basin

The climate type in the region is classified as semi-humid[4]. Summer periods are warmer than winter periods (Avg. temperatures: July, 22.2 °C; January, 6.9 °C). The region exhibits an average annual temperature of 13.6 ºC, average annual rainfall of 764.3 mm and mean annual evaporation of 726.7 mm. The research area has a mesic soil temperature regime and us tic soil moisture regime based on the Soil Survey Staff[17]. The area is covered mainly by pasture and fruit orchards (e.g. apple, peach, pear and cherry).

Physiographic setting

Physiographically, the area is comprised of four main units (footslope, backslope, shoulder and summit). The majority of the site has a slightly sloped (0.0 - 2.0 %) alluvial plain and other units are hilly and moderately to severe sloped (3 - 20 %). The research field changes from 20 m to 130 m in relief and includes four landscape positions (floodplain, backslope, shoulder and summit) delineating variations in physiographic, topographic gradient, geological material and soil features. The underlying bedrock comprises mainly of i) Alluvial and colluvial deposits belonging to Quaternary-age on the footslope and low backslope and, ii) Basalt and marl-limestone belonging to Mesozoic-age on the summit, shoulder and high backslope.

Soil sampling and analysis

A definition of the research area and six typical soil pedons studied along a North-South transect are presented in Table 1 and Figure 2. Pedons I and II are located on flat land and gentle slopes, Pedons III and VI on moderate slope, and Pedons IV and V on steep slope. Six profiles were identified based on morphological characteristics of the collected soil samples according to genetic horizons, and were classified based on Soil Survey Division Staff[17,18].

A total of 19 undisturbed and disturbed soil samples were taken from top sequence on transect. The disturbed soil samples were air-dried and passed through a 2 mm sieve to make them ready for the determination of chemical, physical and mineralogical properties. Physical, chemical and mineralogical

Table 1 — Selected site characteristics of pedons

Pedon	Coordinates (WGS 84-UTMm)		Parent Material	Elevation (m)	Slope Position	Slope (%)	Land cover/Land Use
	East	North					
I	749718	4598608	Alluvial deposit	20	Flat	0-2	Fruit (apple) cultivation
II	749666	4598375	Kolluvial deposit	22	Foot slope	4-6	Fruit (peach) cultivation
III	749529	4598263	Marl	63	Back slope	6-12	Fruit (peach) cultivation
IV	749284	4598109	Sand stone-Lime stone, Marl	83	Back slope	12-20	Pasture
V	749484	4597741	Basalt, Sand stone-Marl	120	Shoulder	20-30	Fruit (apple) cultivation
VI	749634	4597893	Basalt	130	Summit	6-12	Fruit (apple) cultivation-Pasture

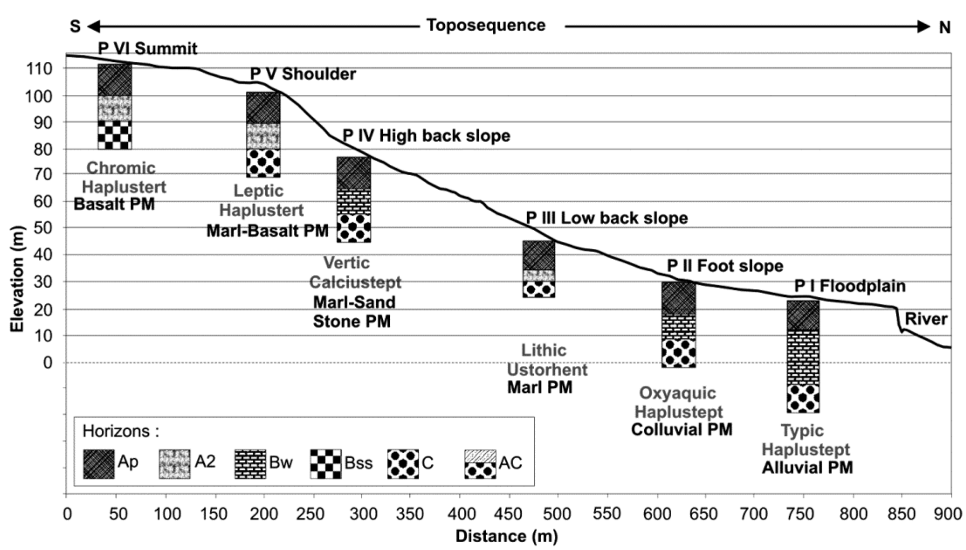

Fig. 2 — Transect of the six different soil pedons on different parent material and topographic positions

analysis included evaluations of pH, EC (electrical conductivity, dS cm^{-1}), lime content ($CaCO_3$, %), organic matter (OM, %), exchangeable cations (Na, K, Mg and Ca, cmolc kg^{-1}), cation exchange capacity (CEC, cmolc kg^{-1}), bulk density (BD, gr cm^{-3}) and total element analysis of soil pedons (SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O, K_2O, TiO_2, P_2O_5, %).

Samples were agitated in 10 ml 40 % sodium hexametaphosphate to achieve dispersion[19], and the distribution of particle size was measured using a hydrometer[20]. Bulk density was measured from undisturbed samples[21]. Wet digestion was used to measure organic matter and total nitrogen in air-dried samples according to Walkley-Black[22]. The pH and EC (dS.cm^{-1}) were measured with a pH electrode in accord with Soil Survey Laboratory[23], the lime content (CaCO3, %) with a Scheibler calcimeter[18], exchangeable cations and cation exchange capacities[19,23] using 1 N NH4OAC (pH 7).

The clay fraction (< 2 µm) was obtained from soil samples after the removal of OM, by dispersion with Calgon and sedimentation in water. The samples were positioned on glass slides and X-ray diffraction was done to determine Mg saturation, ethylene glycol solvation (EG) and K saturation, followed by heating for 2 h at 550 ^{0}C. Mineral ratios and types were identified using both relative peak intensities and XRD spacing[24].

Total elemental analysis of all samples was conducted by Chao and Sanzolone[25] as following. Solutions were obtained using 0.25 g soil powder and 0.75 g lithium tetra metaborate ($LiBO_2$) flux diluted in a HNO_3-HF solution to 1:1000. Aliquots were analyzed for trace and rare earth elements using a combination of simultaneous and sequential inductively coupled plasma mass spectrometry (ICP-MS) which was also calibrated using certified standard reference materials (SO-18/CSC) before sample was measured. It was used 0.002 to 0.01 ppm for all major elements and 0.1 to 1 ppm for all trace elements. Cations were designated by subscripts 'o' and 'd' for the respective methods. Ammonium oxalate and dithionite-citrate bicarbonate (DCB) extraction were used to determine selective dissolution of Fe, and their amounts were carried out by ASS[23].

Results and discussion

Morphological properties and classification

Soils in the research area exhibit variations with respect to particle size distribution, colour and top soil horizon thickness. These variations reflects the obvious effect of soil erosion, through top soils have been transported from the high slope (shoulder) to the low slope (foot), their accumulation leading to progressively darker, deeper and finer-textured soils with decrease in elevation. Colour of soil is closely reflective of the parent material, marl stone, with a hue of 2.5Y on the shoulder surface position, blackening progressively to make a maximum hue value of 10YR on the position of foot slope. The colour of the surface soil in Pedon VI, located on the summit, was also dark, reflecting its parent material, basalt. The accumulation of calcium carbonate in Pedon IV and the redoximorphic features in Pedon II were decisive of genetical developments showed in the changes in texture, color, and top horizon depth. Highly mottled areas observed at the foot slope were indicative of poor drainage locally, reflecting the influence of topography on micro-climate[26]. The subsurface horizon (below 88 cm) of the foot slope was predominately a hue of grey (5/5B), suggesting soils comprised of fine-textured colluvial and alluvial material. For all pedons, soil pedons involved a strongly or moderately improved surface (A) horizon with a granular and angular blocky structure; a strongly or moderately developed pedologic B horizon with an angular blocky structure (except for Pedon III that has no developed subsurface layer); and a C horizon with a massive or graded structure.

In the present study the classification systems used were Soil Taxonomy[17] and FAO/ISRIC[27]. According to these two classification systems, Pedon I is located on a floodplain and developed on alluvial sediment and was classified as Typic Haplustept and Vertic Cambisol, respectively. The main genetic horizon in Pedon I was the subsurface cambic horizon, resulted from structural development, observed especially at depths between 30 - 98 cm.

Pedon II was classified as Oxyaquic Haplustept and Oxyaquic Cambisol. In addition to the subsurface cambic diagnostic horizon found in Pedon I, Pedon II, it also showed redoximorphic features such as grayish mottles.

Pedon III was classified as Lithic Ustorhent and Lithic Leptosol. Slope and topographic shape has been indicated as one of the most important parameters controlling the pedological procedures in this profile, which is found on a high backslope position. In addition, slope promotes to more runoff, as well as to greater translocation of surface fine earth materials downslope by means of surface soil erosion and movement of soil. Genetic horizons in Pedon III were described as surface soil emblematized as A, AC (transition) and Cr (parent material), with no developed genetic subsurface horizons and low pedological development, reflecting it to be a young soil. On the other hand, the presence of secondary $CaCO_3$ nodules, mycelia, carbonate leaching and accumulation at greater depths, Pedon IV was classified as Vertic Calciustept[17] and Calcaric Cambisol[27].

Pedon V was classified as Lithic Haplustert and as Haplic Vertisol. Soils in this pedon, were located on shoulder and summit, and were developed from a basalt rock containing an excessive amount of clay, as designated by surface cracks varying between 1 and 5 cm in width and shiny pressure faces (intersecting slickensides) in the subsurface genetic horizon symbolized as B, which also reflect a swelling and shrinking of the soil. The sub-horizons in this pedon include a layer more than 25 cm thick associated with slickensides and lithic contact layer at a depth of 50 cm.

Pedon VI was classified as Chromic Haplustert and Chromic Vertisol. Similar to Pedon V, this pedon was formed on basalt parent material located on the shoulder and summit, showed cracking in arid periods along with shiny pressure faces (intersecting slickensides) and excessive clay in the sub-surface horizon.

Physical and chemical characteristics

The basic physico-chemical features of the soils in each pedon in the research area are described in Table 2. Properties of soil in the different pedons varied due to a dynamic interaction among environmental parameters involving land cover/land use, climate, parent material and topography[2,11]. Solum depth ranged from 20 - 102 cm, depending upon topographic position. All pedons had a moderately alkaline soil pH (pH 7.55 - 8.26) and a slightly soluble salt content, with no significant differences among pedons. The dominant soil texture class for all pedons was clay or clayey loam, with the highest clay content in Chromic Haplustert and the highest sand content in Typic Haplustept. Soil CEC varied between 26.4 to 44.9 cmolc kg^{-1}, with the highest CEC in Chromic Haplustert, in which smectite was the common clay type, indicating the presence of stratified aluminosilicates with a high load intensity. The lowest CEC value was found in the soil classified as Oxyaquic Haplustept. Ca+Mg were the dominant exchangeable cation for all pedons, with a base saturation value of 100 %. For all pedons, the organic matter content was highest in the top soil horizon (0.2 % - 2.7 %) and the lowest in the subsurface horizons, with a sharp decrease between the two. The low levels of organic matter in the subsoil can be referred to the quick decomposition and mineralization. Soil bulk density values varied from 1.32 to 1.61 g cm^{-3}, with values generally higher

Table 2 — Some physical and chemical properties of soils

Hori-zon	Depth (cm)	pH (1/2,5)	EC (dS.cm^{-1})	$CaCO_3$ (%)	O.M (%)	Exchangeable Cations (cmolc·kg^{-1})				CEC (cmolc·kg^{-1})	B.D (g.cm^{-3})	P.S.D (%)			
						Na	K	Ca	Mg			C	Si	S	Class
P I Pedon I (*Typic Haplustept / Vertic Cambisol*)															
Ap	0-30	7.85	0.26	3.2	1.9	7.8	6.9	19.0	2.6	39.3	1.43	38.8	25.2	35.9	CL
Bw1	30-85	7.78	0.26	1.1	1.8	8.3	3.9	18.3	2.9	33.8	1.50	38.2	29.3	32.4	CL
Bw2	85-98	7.55	0.24	1.3	1.1	8.2	2.8	22.3	4.5	28.5	1.45	38.5	27.6	33.7	CL
C	98+	8.20	0.23	2.2	0.8	9.0	2.7	22.1	2.7	39.7	-	41.0	26.8	32.0	C
P II Pedon II (*Oxyaquic Haplustept / Oxyaquic Cambisol*)															
Ap	0-23	8.01	0.45	2.4	1.9	7.5	4.5	27.8	0.9	39.1	1.50	42.9	23.8	33.2	C
Bw	23-64	7.97	0.48	3.5	1.8	3,8	3.8	24.8	4.9	26.4	1.40	47.5	23.3	29.1	C
C1g	64-88	7.64	0.83	0.4	1.1	6,8	4.9	25.1	2.7	36.4	1.36	41.4	28.1	30.3	C
C2g	88+	7.56	0.73	0.6	0.5	5,7	4.7	23.6	4.8	36.2	-	49.2	28.5	22.2	CL
P III Pedon III (*Lithic Ustorhent / Lithic Leptosol*)															
Ap	0-10	8.24	0.26	6.9	0.7	5.6	5.1	19.8	5.4	33.8	1.60	44.8	24.1	31.0	C
AC	10-30	8.09	0.29	22.3	0.5	4.2	4.0	21.1	5.0	31.5	1.48	48.5	29.3	22.1	C
P IV Pedon IV (*Vertic Calciustept / Calcaric Cambisol*)															
Ap	0-22	7.92	0.24	3.4	1.1	4.2	1.8	24.5	2.2	31.1	1.61	38.5	20.8	40.6	CL
Bw	22-43	8.01	0.19	11.8	0.7	8.6	1.7	24.0	3.1	34.6	1.23	43.3	32.1	24.5	C

in surface horizons (especially Ap horizons) than subsurface horizons as a result of relatively intensive field traffic associated with agricultural activities. $CaCO_3$ content was close to the detection limit in Pedon I and Pedon II located on alluvial and colluvial parent material, especially in surface horizons, and was ranged from 2.4 to 3.2 %. In addition, Lithic Ustorhent and Vertic Calciustept were developed on marl parent material, which induced to higher $CaCO_3$ content in the pedons. Moreover, the lime content was even much higher in the subsurface horizons with secondary carbonate accumulation (i.e. calcic horizons) (Table 3). Chromic Haplustert developed on basaltic parent material had calcium carbonate between 2.0 % - 7.1 %. Lime in basaltic primary material is known to have four resources. These are i) basaltic lava's is contaminating some part of limy material while flowing ii) minerals in basalt which include Ca ion form $CaCO_3$ in the appropriate environment iii) crystallization of hydrothermal water which is rich in lime and found in pores after the flow of basaltic lava and iv) re-calcification process with wind materials including lime[28]. Similar to our results, Aksoy[29] determined $CaCO_3$ content of 2 % - 26 % in profiles on the Kayacik plains in Gaziantep province, even though the major material in the area of their research was basalt parent material.

Geochemical properties and genetic ratios

The results of total element analysis and genetic ratios for Pedons I - VI are given in Table 4 and Table 5, respectively. The findings for Pedons III, IV, V and VI are in line with their parent material (marl, limestone-marl and basalt). Soils in all pedons contained large amounts of SiO_2, Al_2O and Fe_2O_3. On the other hand, in Pedons III and IV which are located in line with their parent material (marl and limestone) lacks Fe_2O_3. The highest SiO_2 concentration was found as 59.89 %. In addition, Al_2O_3 values changed between 12.94 % and 17.21 % and this case tends to increase with depth as well as soil maturity (i.e. in Chromic Haplustert and Lithic Haplustert soils) and showed a direct relationship to clay distribution in profile. These values are close to those for parent rock

Table 3 — Morphological properties and classification (FAO/ISRIC (2006) - Soil Taxonomy (Soil Survey Staff)) of pedons

Horizon	Depth (cm)	Color (dry)	Color (moisture)	Structure	Boundary	Special features
			P I Pedon I *(Typic Haplustept / Vertic Cambisol*)			
Ap	0-30	10YR 4/4	2.5Y 3/3	2fmgr	as	-
Bw1	30-85	10YR 4/4	2.5Y 3/3	2mgr	cw	structure development
Bw2	85-98	10YR 5/4	2.5 Y 4/4	2msbk	gw	structure development
C	98+	10YR 4/2	2.5Y 4/3	mas	-	-
			P II Pedon II (*Oxyaquic Haplustept / Oxyaquic Cambisol)*			
Ap	0-23	2,5 Y 4/4	2,5 Y 4/3	2fgr	as	cracks
Bw	23-64	2,5 Y 5/3	2,5 Y 4/3	2msbk	cw	structure development
C1g	64-88	2,5 YR 5/6	2,5 YR 4/6	mas	gw	seldom mottles
C2g	88+	Gley 6/5B	Gley 5/5B	mas	-	common mottles
			P III Pedon III (*Lithic Ustorhent / Lithic Leptosol*)			
Ap	0-10	2,5 Y 7/4	2,5 Y 6/6	2mgr	as	-
AC	10-30	2,5 Y 7/4	2,5 Y 6/6	3mgr/2fsbk	cw	-
			P IV Pedon IV (*Vertic Calciustept / Calcaric Cambisol)*			
Ap	0-22	2,5 Y 6/4	2,5 Y 5/4	2mgr	as	-
Bw	22-43	2,5 Y 5/6	2,5 Y 5/4	2msbk	gw	structure development
Ck	43-95	2,5 Y 8/3	2,5 Y 7/6	mas	-	common carbonate nodules and micelles
			P V Pedon V (*Lithic Haplustert / Haplic Vertisol)*			
A	0-19	10 YR4/3	10 YR 4/4	3mgr	aw	cracks
Bss	19-50	10 YR 5/3	10 YR 5/4	2mabk	cw	-
2C	50+	2,5 Y 7/2	2,5 Y 6/3	mas and sg	-	-
			P VI Pedon VI (*Chromic Haplustert / Chromic Vertisol)*			
A1	0-18	10 YR 5/3	10 YR 5/3	2mgr	cw	cracks
A2	18-48	10 YR 5/4	10 YR 5/3	3cgr and 2mabk	gw	-
Bss	48+	10 YR 6/3	10 YR 6/4	3cabk	-	slickenside

Abbreviations: Boundary: a = abrupt; c = clear; g = gradual; d = diffuse; s = smooth; w = wavy; i = irregular. Structure: 1 = weak; 2 = moderate; 3= strong; sg = single grain; mas = massive; vf = very fine; f = fine; m =medium; c = coarse; gr = granular; pr = prismatic; abk = angular blocky; sbk = subangular blocky.

Table 4 — The results of total element analysis of studied pedons (%)

Horizon	Depth (cm)	SiO_2	Al_2O_3	Fe_2O	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	LOI
P I Pedon I (*Typic Haplustept / Vertic Cambisol*)											
Ap	0-30	58.53	13.31	7.93	1.68	2.49	0.54	2.43	0.86	0.13	12.34
Bw1	30-85	58.42	13.67	6.93	1.64	1.91	0.71	2.59	0.86	0.14	12.34
Bw2	85-98	57.49	13.27	7.18	1.67	4.19	0.36	2.36	0.88	0.10	12.24
C	98+	56.65	13.34	7.09	1.45	3.17	0.43	2.23	0.90	0.06	13.85
P II Pedon II (*Oxyaquic Haplustept / Oxyaquic Cambisol*)											
Ap	0-23	55.48	13.02	7.67	1.63	2.50	0.16	2.21	0.92	0.10	15.46
Bw	23-64	52.12	13.76	7.52	2.17	7.45	0.09	2.05	0.89	0.09	13.24
C1g	64-88	58.80	13.05	7.47	1.63	1.98	0.57	2.64	0.90	0.21	11.67
C2g	88+	59.89	13.60	7.85	1.64	2.57	0.89	2.76	0.92	0.25	9.21
P III Pedon III (*Lithic Ustorhent / Lithic Leptosol*)											
Ap	0-10	44.47	13.06	7.02	2.15	18.59	0.08	2.13	0.80	0.10	9.97
AC	10-30	48.72	13.41	7.21	2.20	14.77	0.08	2.39	0.78	0.11	13.44
P IV Pedon IV (*Vertic Calciustept / Calcaric Cambisol*)											
Ap	0-22	50.92	13.29	7.43	1.69	10.25	0.09	2.03	0.81	0.10	18.88
Bw	22-43	47.73	12.94	7.95	1.76	13.15	0.09	2.48	0.80	0.11	12.24
Ck	43-95	45.85	13.79	7.92	1.72	21.31	0.09	2.45	0.87	0.12	12.36
P V Pedon V (*Lithic Haplustert / Haplic Vertisol*)											
A	0-19	53.48	15.94	9.46	1.74	2.24	0.34	3.45	0.93	0.14	11.75
Bss	19-50	53.53	14.44	8.03	1.48	2.40	0.22	2.29	0.79	0.24	19.25
2C	50+	31.55	10.57	6.18	1.67	5.01	0.08	1.82	0.44	0.11	22.25
P VI Pedon V (*Chromic Haplustert / Chromic Vertisol*)											
A1	0-18	47.98	15.81	9.71	1.60	6.43	0.09	2.00	0.95	0.08	18.25
A2	18-48	46.52	15.06	7.82	1.56	8.74	0.09	1.89	0.92	0.07	19.04
Bss	48+	42.39	17.21	8.65	1.85	8.71	0.09	1.83	0.86	0.08	19.24

LOI: Loss on Ignition

Table 5 — Some genetic ratio of pedons

Horizon	SiO_2 / Al_2O_3	SiO_2 / Fe_2O_3	Al_2O_3 / Fe_2O_3	CaO / MgO	K_2O+Na_2O+CaO / Al_2O_3	K_2O+Na_2O / Al_2O_3	CaO+MgO / Al_2O_3	K_2O / Na_2O
P I Pedon I (*Typic Haplustept / Vertic Cambisol*)								
Ap	4.40	7.38	1.68	1.48	0.41	0.22	0.31	4.51
Bw1	4.27	8.43	1.97	1.16	0.38	0.24	0.26	3.64
Bw2	4.33	8.01	1.85	2.51	0.52	0.21	0.44	6.55
C	4.25	7.99	1.88	2.18	0.44	0.20	0.35	5.24
P II Pedon II (*Oxyaquic Haplustept / Oxyaquic Cambisol*)								
Ap	4.26	7.23	1.70	1.53	0.37	0.18	0.32	13.58
Bw	3.79	6.93	1.83	3.44	0.70	0.16	0.70	23.15
C1g	4.51	7.87	1.75	1.22	0.40	0.25	0.28	4.62
C2g	4.40	7.63	1.73	1.56	0.46	0.27	0.31	3.09
P III Pedon III (*Lithic Ustorhent / Lithic Leptosol*)								
Ap	3.41	6.33	1.86	7.25	1.36	0.17	1.36	25.53
AC	3.63	6.76	1.86	5.34	1.06	0.18	1.04	28.36
P IV Pedon IV (*Vertic Calciustept / Calcaric Cambisol*)								
Ap	3.83	6.85	1.79	2.52	0.48	0.16	0.45	23.44
Bw	3.69	6.00	1.63	7.47	1.21	0.20	1.15	27.61
Ck	3.32	5.79	1.74	6.00	0.93	0.18	0.87	28.38
P V Pedon V (*Lithic Haplustert / Haplic Vertisol*)								
A	3.36	5.65	1.68	1.29	0.38	0.24	0.25	10.07
Bss	3.71	7.61	2.05	1.62	0.39	0.20	0.31	10.45
2C	2.98	5.11	1.71	14.94	2.55	0.18	2.52	21.75
P VI Pedon V (*Chromic Haplustert / Chromic Vertisol*)								
A1	3.03	5.84	1.93	4.03	0.66	0.16	0.63	22.94
A2	3.09	5.95	1.93	5.59	0.89	0.16	0.85	21.99
Bss	2.46	5.54	2.25	4.71	0.95	0.17	0.94	20.87

and primary material and reflect a low level of weathering. However, Al_2O_3 values for other pedons were found like in solum and parent material as a consequence of the low weathering ratio. Considering these criteria, it is seen that weathering and soil formation is slow process and there are not many processes such as joining, losses, leavings or changes in the soil. Pedon VI had the highest Fe_2O_3 value in the study area (9.712 %), which is attributable to its basaltic parent material. In line with the total amount of Fe_2O_3 found in the study area, amounts of dithionite-citrate extractable Fe (Fe_d) were also quite low, indicating a slow rate of weathering. Pedons III and IV had the highest CaO values (10.25 % - 21.31 %). MgO values were ranged from 1.45 % to 2.17 % indicating no significant differences among the horizons. K_2O and Na_2O values ranged from 1.82 % to 3.45 % and from 0.09 % to 0.89 %, respectively.

For weathering pedon the genetic ratios were estimated institutionally by using the essential element oxides' molecular dimensions. Stoichio-metrical variations are shown in the index ratio that takes place during alteration and weathering process. The molecular ratio of each oxide is easily estimated from the percentage of the oxide based on weight. Low Si/Al ratio (less than 2) can be obtained in tropic condition due to lateritic process. On the other hand, all pedons in the study area had Si/Al ratios above 2, indicating arid, sub-arid, sub-humid or high precipitation with cold areas, which prevents Si from dissolving and leaching from the soil profile, leading to a relative increase in Si concentrations. Basic oxides of K/Na determined significant differences among pedons. This ratio related to clay types (illite and smectite) was determined in high level in all pedons. On the other hand, when compared to each other, Pedon I showed the lowest ratio values. Moreover, the highest Ca/Mg ratio was found in parent materials of Pedon V formed on commonly marl rock.

Selective dissolution analysis and mineralogical properties

Various analytical procedures have been used to analyze soil components, including selective chemical dissolution analysis, such as dithionite-citrate and ammonium oxalate extraction, as well as X-ray diffraction analysis. In line with these procedures, quantitative and semi-quantitative operational definitions were used to identify broad groupings of soil constituents, e.g., crystalline phyllosilicate, amorphous, poorly crystalline, paracrystalline, noncrystalline, allophane, imogolite and short-range-order minerals[30].

The iron values identified using selective dissolution analysis can be considered significant information about variations in the mineralogical compound and weathering of soils in connection to their basic and ultra-basic magmatic parent material. Originally, dithionite-citrate extraction was aimed to identify free iron oxides and to remove their amorphous coatings and crystals, which acts as cementing agents, prior the conduct of physico-chemical analysis of soil, sediment and clay minerals[30-32]. Fe_d is identified as a measure of 'free iron' in soils. This case is genetically important in terms of soil formation and classification and it was given the relation between Fe_d concentrations and weathering as well as the effect of Fe_d on soil color[33].

Ammonium oxalate has been used in the selective dissolution of non-crystalline material to measure quantities of poor crystalline material in soil[34-38]. The procedure removes most of the non-crystalline and para-crystalline material (allophane and imogolite) as well as short-range-ordered oxides and hydroxides of Al, Fe and Mn[36,39].

Table 6 presents index values for iron obtained from selective dissolution analysis. Fe_o values varied between 0.0009 % and 0.0126 %. These, rather low values indicate that Fe_o appears mainly in crystalline form, with non-crystalline material absent or appearing only in trace amounts. Fe_d values were higher than Fe_o and were lower than Fe_t values, ranging between 0.007 % and 0.031 %. Moreover, both Fe_o and Fe_d values decrease with increases in soil depth.

The Fe_o/Fe_d ratio is considered to provide an approach of the relative proportion of ferrihydrite, or degree of crystallization and weathering in soils[40]. In the present study, Fe_o/Fe_d values were quite low in all pedons, varying between 0.071 - 0.962 %. When compared between parent materials to solum which includes high pedological process, this ratio is higher in solum than parent material's ratio. Fe_d/Fe_t is another important indicator of the degree of weathering in soils. Fe_t or total iron, refers to the percentage of Fe_2O_3 and is given in Table 4. It was observed that the Fe_t values for all pedons varied between 6.18 % and 9.46 %. The Fe_d/Fe_t ratios decreased with depth, with the higher Fe_d/Fe_t ratios in surface soils which indicating the greater amount of weathering. There are no significant differences in

Table 6 — Index values of selective dissolution analysis of the studied pedons

Horizon	Depth (cm)	Fe_d (%)	Fe_o (%)	Fe_o/Fe_d	$(Fe_d- Fe_o)$ *10 Fe_d	Fe_d/Fe_t
PI Pedon I (*Typic Haplustept / Vertic Cambisol*)						
Ap	0-30	0.009	0.0074	0.822	17.48	0.0013
Bw1	30-85	0.011	0.0085	0.757	24.29	0.0016
Bw2	85-98	0.012	0.0064	0.538	46.18	0.0016
C	98+	0.009	0.0067	0.751	24.95	0.0013
PII Pedon II (*Oxyaquic Haplustept / Oxyaquic Cambisol*)						
Ap	0-23	0.013	0.0082	0.624	37.64	0.0017
Bw	23-64	0.011	0.0051	0.453	54.73	0.0015
C1g	64-88	0.013	0.0126	0.962	3.84	0.0017
C2g	88+	0.007	0.0009	0.138	86.22	0.0008
PIII Pedon III (*Lithic Ustorhent / Lithic Leptosol*)						
Ap	0-10	0.017	0.0024	0.142	85.78	0.0023
AC	10-30	0.016	0.0023	0.143	85.73	0.0023
PIV Pedon IV (*Vertic Calciustept / Calcaric Cambisol*)						
Ap	0-22	0.031	0.0042	0.134	86.63	0.0042
Bw	22-43	0.013	0.0023	0.175	82.54	0.0016
Ck	43-95	0.016	0.0011	0.071	92.92	0.0020
PV Pedon V (*Lithic Haplustert / Haplic Vertisol*)						
A	0-19	0.017	0.0139	0.816	18.41	0.0018
Bss	19-50	0.008	0.0069	0.889	11.12	0.0011
2C	50+	0.001	0.0009	0.738	26.20	0.0002
PVI Pedon V (*Chromic Haplustert / Chromic Vertisol*)						
A1	0-18	0.035	0.0069	0.669	33.12	0.0036
A2	18-48	0.028	0.0058	0.533	46.71	0.0035
Bss	48+	0.018	0.0052	0.661	33.90	0.0020

Fed : dithionite extractable iron, Feo: oxalate extractable iron, Fet: total Fe oxides

terms of this ratio in Typic Haplustept (Pedon I) soil formed on fine alluvial deposit carried by Horror River. On the other hand, the highest weathering ratios were found in Chromic Haplustert formed on basaltic parent material. The proportion (Fe_d-Fe_o) x $100/Fe_d$ shows the degree of crystallization of iron oxides in soil[37]. This ratio was found to be high in Lithic Ustorhent and Vertic Calciustept soils, indicating that the majority of Fe was released through the weathering process and was found as crystallized iron. This was generally located in the solum (about 50 cm), in the form of iron at greater depths appearing as amorphous or poorly crystalline material.

X-ray diffractograms of selected soil samples are presented in Figure 3. Phyllosilicates of varying amounts and degrees of crystallization were found in all six pedons including kaolinite at 1:1 and various 2:1 minerals. Smectite in various 2:1 clay types was common, whereas vermiculite and zeolite were found only in trace amounts. Peaks for most clay minerals were strong and indicated good crystallization (Table 7). Mg-saturated clay displayed three intensity peaks at 1.44 - 1.40 nm, 0.95 - 1.00 nm and 0.71 - 0.72 nm. The reflection at 0.72 nm vanished at 550 °C. The 1.4 - 1.5 nm peak was partly expanded to 1.6 - 1.5 nm by glycolation and contracted to 1.43 - 1.20 nm following K saturated at 20 °C. An illite characterize diffraction band was observed between 1.0 and 1.1 nm at 550 °C, signifying the presence of smectite (Sm), illite (I), kaolinite (K), vermiculite (Vm) and zeolite (Ze). Illite was the most plentiful clay mineral in Pedons I, II and III, whereas smectite was the most plentiful clay mineral in Pedons IV, V and VI. Some researchers[1] have also reported in their studies related to soils developed on a calcic and marl toposequences that the most abundant clay minerals were detected as smectite, followed by kaolinite and illite.

Table 7 — The relative ratios of the clay minerals in the surface horizons of the pedons

Pedon/ Horizon/ Topographic positions	Depth (cm)	Clay Minerals				
		Vermiculite	Zeolite	Illite	Kaolinite	Smectite
P I-A/ Floodplain	0-30	+	+	+++++	+++	++++
P II-A/ Footslope	0-23	++	+	+++++	+++	++++
P III- Ap/ Low backslope	0-10	-	+	+++++	++	++++
P IV- Ap/ High backslope	0-22	-	++	++++	+++	+++++
P V-A/ Shoulder	0-19	-	++	+	+++	+++++
P VI- A/ Summit	0-18	-	+	+++	++	+++++

'+++++': Dominate, '++++': Plenty, '+++': Moderate, '++': Poor, '+': Very poor, '-': non crystallization

XRD findings indicated distribution of clay mineral type in surface horizons to vary somewhat by pedon, as follows: Pedon I: illite> smectite> kaolinite> vermiculite = zeolite; Pedon II: illite> smectite> kaolinite> vermiculite> zeolite; Pedon III: illite> smectite> kaolinite >zeolite; Pedon IV: smectite> illite> kaolinite> zeolite; Pedon V: smectite> kaolinite> zeolite> illite; Pedon VI: smectite> illite> kaolinite> zeolite. Moreover, quartz, as a primer mineral, was determined in X-ray diffractograms of chosen samples.

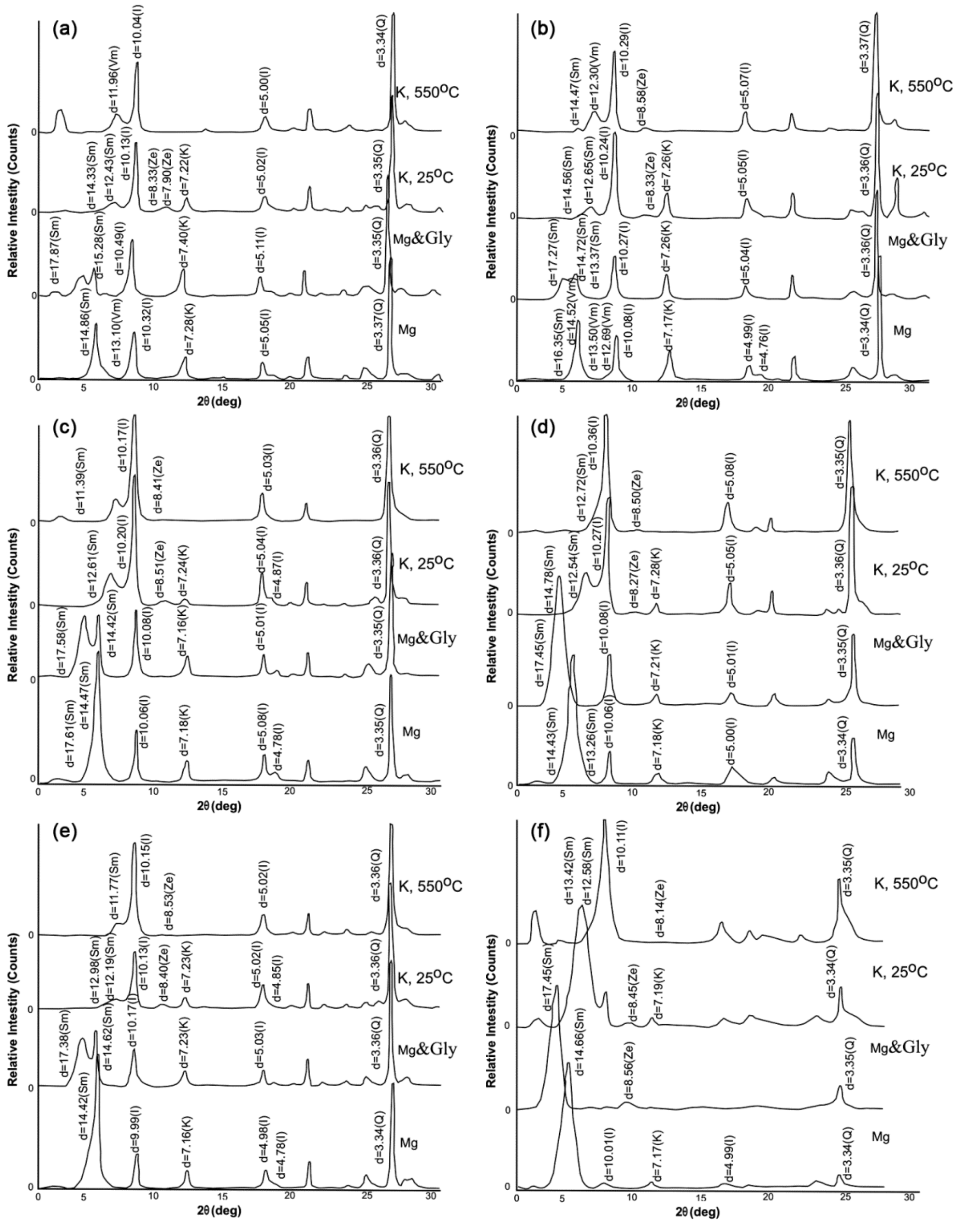

Fig. 3 — X-ray diffractograms of selected samples A: PI-Ap (0-30 cm), B: PII-Ap (0-23 cm), C: PIII-Ap (0-10 cm), D: PIV-Ap (0-22 cm), E: PV-A (0-19cm), F: PVI-A (0-18 cm). d-values in nm

Conclusion

The six pedons in the research area were assessed by taking into consideration of their genetical development and were classified based on Soil Taxonomy[17] and FAO/ISRIC[27]. Significant variations in soil properties among pedons may be attributed to significant differences in pedogenic processes related to landscape position, climate and parent material, which have a key role in soil-formation processes, especially at the local level. Identifying variations in soil features is not only important for soil classification and survey-mapping, but also for soil management, which requires detailed data on the spatial distribution of soil characteristics.

Erosion was determined to be the major negative parameter in soil development on hillside positions (shoulder and back slope) in the research area. Especially in mountainous terrain, the most significant geomorphic process is soil erosion and mass movement.

The process of soil formation progresses on all parts of the regolith-covered landscape, and can be interrupted at any stage by runoff or mass movement event – an interruption that is relatively common where the slope degree is high; as a result, such areas are often characterized by having Lithic Ustorhent soils, which are defined as young soils and is the case in the present study.

In comparison, soils in lower slope positions were classified as Chromic Haplustert (summit), Oxyaquic Haplustept (foot slope) and Typic Haplustept (flood plain). Soil development in these areas had not experienced interruption and thus had more developed sub-surface profiles, with cambic, slicken side and calcic horizons comprising majority of the subsurface.

The findings of this study showed a strong relationship among land shape, parent material and certain morphological, physico-chemical and mineralogical features of soil. The results clearly showed that the physiographical conditions strongly affect soil physico-chemical, mineralogical and morphological features either directly or indirectly in the small area or local region. Also, parent material was found to have a strong effect on soil properties and soil development, as made clear by the findings of various commonly used genetic ratios that characterize weathering pedons by incorporating bulk major element oxide chemistry and selective dissolution analysis values for iron into a single metric.

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Conflict of interest

Authors should declare no competing or conflict of interest.

Author contributions

TT: Field work, laboratory analysis, data assessment, writing-original draft; OD: Conceptualization, field work, data assessment, writing-original draft and editing.

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