







The influence of elevation on soil properties and forest litter in the Siliceous Moncayo Massif, SW Europe


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Abstract: Understanding the effects of elevation and related factors (climate, vegetation) on the physical and chemical soil properties can help to predict changes in response to future climate or afforestation forcings. This work aims to contribute to the knowledge of soil evolution and the classification of forest soils in relation to elevation in the montane stage, with special attention to podzolization and humus forms. The northern flank of the Moncayo Massif (Iberian Range, SW Europe) provides a unique opportunity to study a forest soils catena within a consistent quartzitic parent material over a relatively steep elevation gradient. With increasing elevation, pH, base saturation, exchangeable potassium, and fine silt-sized particles decrease significantly, while organic matter, the C/N ratio, soil aggregate stability, water repellency and coarse sand-sized particles increase significantly. The soil profiles shared a set of

properties in all horizons: loamy-skeletal particle-size, extreme acidity (pH-H₂O<5.6) and low base saturation (<50%). The most prevalent soil forming processes in the catena include topsoil organic matter accumulation and even podzolization, which increases with elevation. From the upper to lower landscape positions of wooded montane stage of the Moncayo Massif, mull-moder-mor humus and an Umbrisol-Cambisol-Podzol soil unit sequences were found.

Keywords: Montane stage; Forest soils; Catena; Humus forms; Podzolization; Siliceous Moncayo Massif

Introduction

A catena is defined as a connected series of soils with respect to relief from the summit to the toe slope (Birkeland 1999). As described by

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Ibrahim and Lal (2014), soils within a catena may differ in properties and classification from one landscape position to another because of differences in soil forming factors such as climate (climosequence), vegetation (biosequence), relief (toposequence), parent material (lithosequence), or time (chronosequence). Catena analysis has been and is still widely used in the study of soils to achieve different objectives. For instance, mechanical properties variations were studied across a soil catena developed on Eocene marls in the Inner Depression of the Central Spanish Pyrenees (Badía et al. 2015); pyrogenic carbon content, produced by vegetation fires, were quantified across a soil catena in the Pacific Northwest (Jauss et al. 2015); soil organic carbon and nutrient contents were measured along a latitudinal gradient on the northern Tibetan Plateau (Cao et al. 2013); soil carbon pools were measured across a catena in central Ohio (Ibrahim and Lal 2014); the soil genesis on different Holocene parent materials was studied by means of a catena analysis in the Swiss Jura Mountains (Martignier and Verrecchia 2013); and the influence of two different parent materials on soil genesis and humus type was analyzed along altitudinal transects in the Eastern Pyrenees (Martí and Badía 1995).

In addition to global pedogenesis, soil humus is an effective indicator of environmental conditions. Soil humus formation depends on biotic factors, such as vegetation type, and on abiotic factors such as climate, altitude, and bedrock (Labaz et al. 2014). While changes in patterns of soil evolution can occur over millenaries, changes in the forest floor occurs within decades, being an indicator of faster environmental shifts (Jabiol et al. 2013). The monitoring of humus forms might thus help to understand the impact of land-use changes (afforestation, abandonment) or global warming on surface-accumulated organic carbon (Ponge et al. 2011). In this sense, the Moncayo Massif provides a unique opportunity to study pedogenesis and humus types in forest soils across a slope where the relief, parent material and time of formation can be considered constant. In this case, the variability of soils across the catena will be a function of the variations in climate (climosequence) and vegetation (biosequence).

Previous studies in the Moncayo Massif described its vegetation (Uribe 2002; Longares 2004), climate (Cuadrat and Pellicer 1983; Ibarra and Echeverría 2004; Ibarra et al. 2003), geomorphology (Pellicer 1984; Lemartinel 2004), geology (IGME 1980) and even soil nutrient cycles (Carceller 1995) and mineralogy (Hoyos et al. 1983). All these studies recognized the uniqueness of this mountain in the Iberian Range, which is considered Natural Site since 1927 and as Natural Park since 2007. Despite the ecological importance of the Moncayo Massif, there have not been any internationally published studies on the genesis of its soils. In the surrounding mountains, previous studies have described leached brown soils and even podzol-like soils (Guerra and Monturiol 1970; Hoyos et al. 1983; Val and Iñiguez 1981a, b).

Carceller (1995) described, using the FAO Legend (1988), a dozen soil profiles on the northern flank of Moncayo Massif, between 940 m and 2270 m elevation. He identified *Dystric* and *Humic Cambisols* at lower elevations, especially beneath oak forests and *Haplic Alisols*, interspersed with *Dystric* and *Umbric Leptosols*, beneath beech and pine forests. Even, one of the 12 profiles was classified as a *Carbic Podzol* with mor humus beneath a centennial Scots pine afforestation at 1600 m high (Carceller and Vallejo 1996). But, Hoyos et al. (1983) suggested that the prevalent humus form is moder in Moncayo montane stage on the siliceous bedrock but it changes to mull in the calcareous bedrock of the Moncayo lowlands.

The objectives of the present work are (i) to investigate the effects of elevation on soil diversity and humus forms across a catena in the siliceous Moncayo Massif, (ii) to determine statistical relationships and pedotransfer functions between soil properties and (iii) to classify humus and soil types according to the last versions of taxonomic systems, with the goal of providing information to help the future development of the universal classification systems.

1 Study Area

The Moncayo Massif (henceforth Moncayo) rises above the southern edge of the Ebro river (Figure 1), along the eastern or Aragonese sector of

the Iberian Range in NE-Spain (SW Europe). Reaching an elevation of 2313 meters, Moncayo is the highest summit in the Iberian Range and one of the most prominent peaks of the Iberian Peninsula.

This research describes in detail six forest soil profiles sampled in the montane stage from 1000 m (Monte de La Mata) to 1600 m (near San Gaudioso hermitage) above mean sea level of the northern slope of the Moncayo Massif (Table 1). The parent material is acidic and includes recent stony colluvium, which is dominated by quartzitic and micaceous sandstones, rich in mica, light gray in color and angular in shape (IGME 1980). They form solifluction mantles related to the freeze-thaw activity that characterizes periglacial environments from the Pleistocene-Holocene transition (Pellicer 1984; Lemartinel 2004). The mineralogic composition of the sandstones (Triassic Tierga Formation), sampled from the bottom of the studied catena (Monte de La Mata), consists of 67% quartz, 15% potassium feldspar, and 8% mica (Carceller 1995). Illite, in the clay fraction, and tourmaline, in the sand fraction, are the main minerals in the soils (Hoyos et al. 1983).

Total annual precipitation ranges from around 700 mm/yr in Agramonte (1060 m) to 1400 mm at the summit of the Moncayo (2313 m) and it increases at an average rate of 99.5 mm/100 elevation in oakwood stages and to 45.2 mm/100 m elevation in beechwood stages (Ibarra et al.

2003). The average annual temperature is approximately 10°C in Agramonte and it decreases with increasing elevation at a rate of 0.59°C/100 m (Cuadrat and Pellicer 1983). According to the data available for montane stage soils, we interpret the moisture regime as udic, and the temperature regime as ranging from mesic to frigid with increasing elevation. This climatic gradient creates an altitudinally zoned forest composed of deciduous oaks (*Quercus petraea* and *Quercus pyrenaica*) from 900 m to 1200 m, and beech (*Fagus sylvatica*) from 1200 m to 1600 m, with

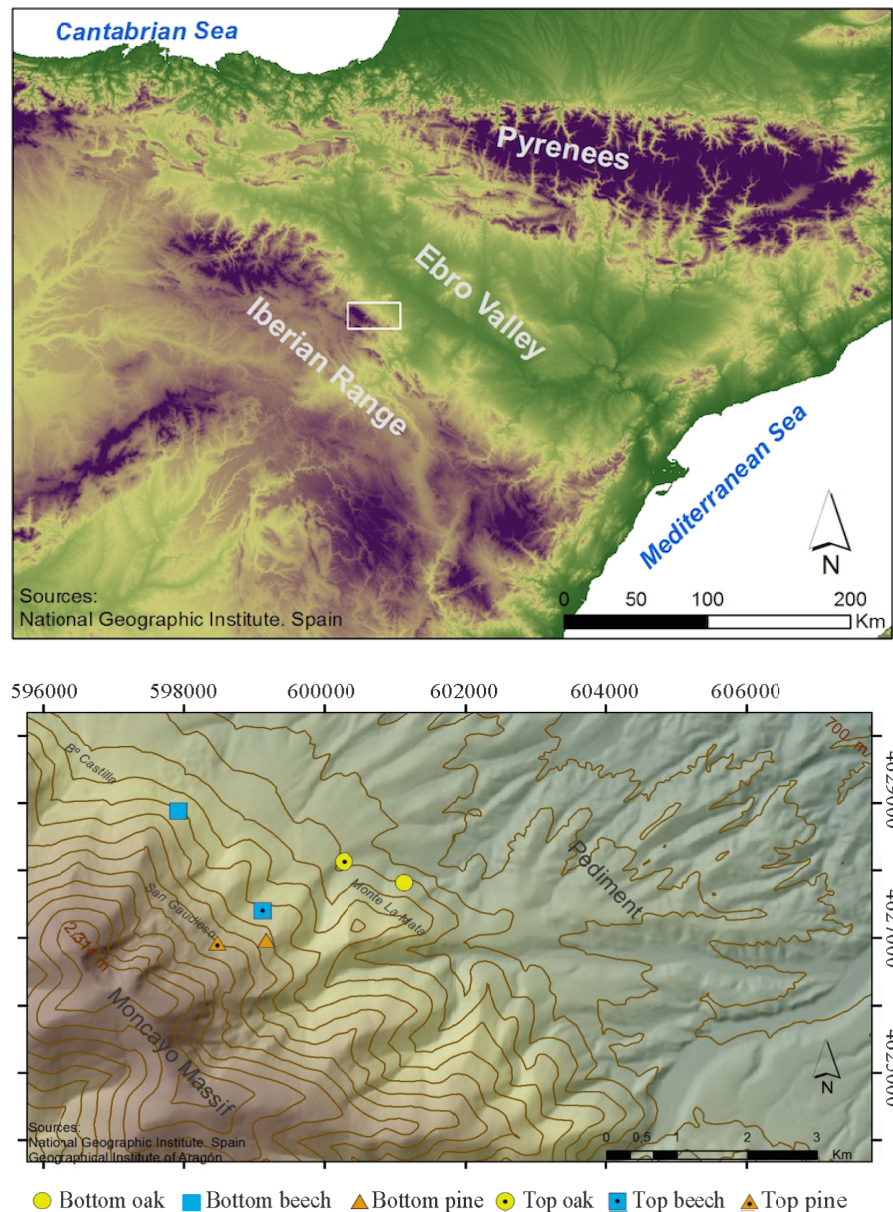


Figure 1 Location of soil profiles studied along the northeast flank of the Moncayo Massif (Iberian Range, NE-Spain).

Table 1 Formation factors of soils analyzed from the Moncayo catena

Reference Profile	UTM location (30 T)		Geomorphology Slope, Aspect	Parent material	Climate*	Vegetation	Soil sequum
	X Y	Altitude (m asl)					
Top pinewood (San Gaudioso)	0598480 4626904	1590	30%,head slope NE	Angular quartzite sandstone colluvium	1112 mm 6.3°C	<i>Pinus sylvestris</i> ; <i>Ilex aquifolium</i> ; <i>Vaccinium myrtillus</i> ; <i>Erica vagans</i> ; <i>Erica arborea</i>	O-Ah-E-Bhst-C
Bottom pinewood (Curva Herradura)	0599333 4626468	1476	35%,head slope NE	Angular quartzite sandstone colluvium	1040 mm 6.9°C	<i>Pinus sylvestris</i> ; <i>Ilex aquifolium</i> ; <i>Erica arborea</i> ; <i>Deschampsia flexuosa</i>	O-Ah-E-Bhst-BC
Top beechwood (Fuente Frailes)	0599130 4627400	1353	25%,shoulder slope NE	Subangular quartzite sandstone colluvium	983 mm 7.7°C	<i>Fagus sylvatica</i> ; <i>Ilex aquifolium</i> ; <i>Erica arborea</i> ; <i>Erica australis</i>	O-Ah-E-Bhst-BC
Bottom beechwood (Camino Bco. Castilla)	0598093 4628828	1282	40%,shoulder slope NE	Angular quartzite sandstone colluvium	912 mm 8.1°C	<i>Fagus sylvatica</i> ; <i>Vaccinium myrtillus</i> <i>Erica arborea</i> ; <i>Ilex aquifolium</i> ; <i>Abies alba</i>	O-Ah-E-Bst-BC-C
Pyrenean oakwood (Bco. Monte de la Mata)	0600243 4628086	1046	30%,back slope NE	Angular quartzite sandstone colluvium	678 mm 9.5°C	<i>Quercus pyrenaica</i> ; <i>Cistus lauri folius</i> ; <i>Erica sp. pl.</i> ; <i>Cytisus scoparius</i>	(O)-Ah-E-Bw- BCg-Cg
Sessil oakwood (Monte de la Mata)	0601146 4627798	1018	30%,back slope NE	Angular quartzite sandstone colluvium	650 mm 9.7°C	<i>Quercus petraea</i> ; <i>Cytisus scoparius</i>	(O)-Ah-C-R

* Temperature estimated according to Cuadrat and Pellicer (1983) and Rainfall estimated according to Ibarra et al. (2003); Geom.= Geomorphology.

replacement in some areas by Scots pine (*Pinus sylvestris*) due to reforestation that started around the year 1920 (García-Manrique 1960). The understory consists of heathers (*Erica vagans*, *Erica arborea*, *Erica cinerea*), hollies (*Ilex aquifolium*), blueberries (*Vaccinium myrtillus*), wavy hair-grass (*Deschampsia flexuosa*), mosses, etc. Previous reports have described other details of the vegetation (Uribe 2002; Longares 2004) and climate-plant-soil relationships (Ibarra and Echeverría 2004).

2 Materials and Methods

Two profiles were sampled beneath areas covered in oak (*Quercus petraea*, *Quercus pyrenaica*), two beneath beech (*Fagus sylvatica*), and two beneath Scots pine (*Pinus sylvestris*) forest (Table 1). Selected profiles were representative of the study area and provided reliable data for interpreting soil-forming processes in the wooded montane stage. Pedons were described according to FAO guidelines (FAO 2006); with the exception of the identification of the organic horizons and humus for which we have followed the most recent suggestions (Jabiol et al 2013; Zanella et al. 2011). We report the specific morphological characteristics of each mineral

horizon, including color (under moist and dry conditions), structure, consistency, roots and accumulations for each pedon. Soil samples were air-dried and sieved (mesh size 2 mm) to determine the percentage of gravel (> 2 mm) and fine earth (< 2 mm). Laboratory analyses were performed on the fine earth fraction. Soil pH was determined from potentiometric measurements of a 1:2.5 (w/v) suspension of soil and water (current pH or pH-H₂O) and with 1N KCl (potential pH or pH-KCl) (McLean 1982). Cation exchange capacity (CEC) and exchangeable base cations were determined by NH₄⁺ retention after leaching with a neutral solution of 1N NH₄OAc (Rhoades 1982), following the analytical procedures specified for WRB classification (IUSS 2014). Additionally, exchangeable aluminum (Al) and iron (Fe) were extracted with an unbuffered, 1M KCl solution. Al and Fe were also extracted with ammonium oxalate (Blakemore 1985) to estimate total “active” Al and Fe species. This selective extraction by ammonium oxalate (Al_{ox} and Fe_{ox}) has been used to quantify the extent of podzolization and identify Podzols (McKeague et al. 1983) based on estimates of Al_{ox}+1/2Fe_{ox} (IUSS 2014; Soil Survey Staff 2014). Al and Fe were analyzed by ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry). Total organic carbon was determined by the wet oxidation method (Nelson and Sommers 1982),

which is considered equivalent to Total C in the absence of soil carbonates. Total N was determined by the Kjeldahl method (Bremner and Mulvaney 1982).

Fine earth fraction particle size distributions were determined by the discontinuous sedimentation method after removal of organic content with H₂O₂ (30%) and clay dispersal with 5% Na-hexametaphosphate (Gee and Bauder 1986). The coarse sand fraction ranged from 2000-500 µm, fine sand from 500-50 µm, coarse silt from 50-20 µm, fine silt from 50-2 µm and clay is <2 µm in bulk diameter. Soil aggregate stability (SAS) was assayed (in aggregates 1-2 mm of diameter) using the wet-sieving method (Kemper and Koch 1966). The water content at field capacity (-33kPa) was measured volumetrically using pressure plate extractors (Richards 1947).

Water repellency was measured by the water drop penetration time (WDPT) test, placing eight drops of distilled water (20°C) on each soil sample and recording the time it takes for the water to penetrate completely into the soil. Water drops were applied to each sieved soil sample using a hypodermic syringe near the soil surface (<5 mm high). The penetration time was recorded for each drop and the average penetration time taken as representative of the WDPT for each sample. The WDPT tests gives similar results for sieved and undisturbed samples at soil water repellency class level (Badía et al. 2013a).

Soils were classified according to the WRB (IUSS 2014) and Soil Taxonomy (Soil Survey Staff 2014) systems. Both taxonomies have been endorsed by the International Union of Soil Science (IUSS) as the internationally accepted soil classification systems (Hartemink 2014). Humus identification was based on the morpho-functional classification at the group level (Jabiol et al. 2013; Zanella et al. 2011).

We calculated the Pearson correlation coefficient to evaluate the degree of linear association among variables. Correlation coefficients (*R*) presented in the text are statistically significant at the $P < 0.01$ level unless otherwise noted. Simple and multiple linear regressions among soil properties were carried out using the Statview statistical package, providing, the determination coefficient (R^2). Principal component analysis (PCA) was carried out using

XLSTAT software (version 2015), with Varimax rotation and Kaiser Normalization following the standardization of the data, as previously described (Badía et al. 2008).

3 Results and Discussion: Variations with Elevation and Soil Depth

3.1 Morphological properties

Soil profiles at lower elevations host simpler sequa, such as (O)-Ah-Bw-C or (O)-Ah-C-R. However with increasing elevation, an O-Ah-E-Bhs-C sequa indeed appears within pine and beech forest sites. The profiles analyzed contained thick horizons of litter (O) above the Ah horizons, especially beneath pinewoods with heather at the highest elevation but also beneath beech forests. The O horizons consisted of three distinct layers, including 1) OL (Oi) undecomposed litter (new or old), 2) an OF (Oe) fragmentation layer where plant remains are partially decomposed by biological activity but with plant morphology still recognizable, and 3) an OH (Oa) humus layer without recognizable plant structures and a fine granular morphology. Soils in oak forests have only the OL horizon of this sequence but at higher altitudes OF and OH horizons appear both in beech forests and especially beneath areas of Scots pine afforestations, which have replaced some beech stands. Given the O and Ah horizon characteristics (Table 2), the humus group along the toposequence can be designated as Mesomull at the base of the slope, Hemimoder at intermediate elevations and Humimor at higher elevations, following the classification system described by Jabiol et al. (2013). This humus sequence (mull-moder-mor) is the result of a progressive reduction of soil's biological activity with elevation. Climate constraints (cold), acidity and the poor nutrient content of the soil can be factors that limit biological activity with increasing elevation (Zanella et al. 2011). We must also consider the fact that the replacement of beech by pines introduces similar lignin contents but higher amounts of polyphenols (from needles and bark), which inhibit the process of organic matter decomposition and contribute to the formation of a thicker litter layer (Labaz et al. 2014). Labaz et al. (2014) have

observed, in the Stolowe Mountains of SW Poland, that the replacement of ancient European beech forests by Norway spruce stands transformed moder humus to mor humus. Moreover, litter thickness and soil organic Carbon (SOC) content increase with altitude (Labaz et al. 2014). Similarly, in a siliceous toposequence in the Eastern Pyrenees, a downslope mull humus type with OL layers was found, which evolved to OL-OF (OH) sequum at higher elevations (Martí and Badía 1995).

On the other hand, in northern Germany, the Netherlands and northern Poland, ancient Scots pine stands showed thicker O horizons than those associated with beech forests (Leuschner et al. 2013). This indicates that pine stands may have ~75% more carbon in their organic layers than ancient beech forests, although total Carbon content in beech forest soils (organic layer and mineral soil) was approximately 25% greater due to the higher Carbon concentrations within the mineral soil, mainly in 0-50 cm depth (Leuschner et al. 2013).

Below the O horizon there is an Ah horizon darkened by the incorporation of organic matter. The color of these Ah horizons ranges from 7.5YR 3/1 (very dark gray) in pine forests at high elevation to 10YR 6/2 (light brownish gray) in oak forests at low elevations. A whitish horizon (E horizon, albic) lies below the O and A horizons at highest elevations. E horizon is bleached and unstructured due to the removal or segregation of organic matter and free iron oxides (Buurman and Jongmans 2005). Bhs horizons mainly have a 7.5 YR 4/4 color (moist), suggesting iron, aluminum and/or organic matter accumulation. Similar colors characterize boreal Bhs horizons occurring in cold climates at high latitudes and elevations, such as those found in the Italian Alps (Monaci et al. 1990) and in the U.S. (Base and Brasher 1990). The structure of the Ah horizons, which exhibits a fine, granular morphology in the Ah horizons, disappears in the E horizons and becomes subangular to blocky in the Bw and Bh shorizons, if the stoniness of the horizons is not very high. Compaction of the soil matrix is soft or slightly hard at depth but it is never cemented (Appendix A).

Some horizons including O (OF and OH), Ah

Table 2 Humus characteristics ($n = 5$) of soil toposequence along the northern flank of the Moncayo, Spain

		Forest cover and elevation (m)		
		Pinewood 1600-1500	Beechwood 1400-1300	Oakwood 1100-1000
Horizon thickness (cm)	OL	1-2 cm	1-4 cm	1-2 cm
	OF	4-6 cm	3-7 cm	absent
	OH	1-6 cm	discontinuous	absent
Ah horizon	Transition Ah-O	< 3 mm	≥ 5 mm	< 3 mm
	pH water (1:2.5)	< 5	< 5	> 5
	C/N ratio	12.1-22.1	10.5-11.0	9.9-10.0
	Aggregation	micro	macro	macro
Humus Group		Humimor	Hemimoder	Mesomull

Notes: OL: undecomposed litter; OF: fragmented litter; OH: humified layer; Ah: Organo-mineral horizon.

and Bhs have dense root system of herbaceous and shrub vegetation (Appendix 1), which may take advantage of the greater availability of nutrients and water in these horizons (Buurman and Jongmans 2005).

3.2 Chemical and physical characteristics.

3.2.1 Common properties.

The profiles studied along the catena share a number of common chemical properties, including acidity (pH-H₂O <5.6; pH-KCl<4.4) and base saturation of less than 50% in all horizons (Appendix 2) similarly to Hoyos et al. (1983). The pH-KCl and the pH-H₂O values are positively correlated ($R = 0.88$). Among the exchangeable basifying cations, Ca²⁺ is the most abundant (0.8-6 cmol₊/kg), followed by Mg²⁺ (0.04-1.6 cmol₊/kg) and K⁺(0.04-0.6 cmol₊/kg). Exchangeable Al³⁺ content ranges from 0.3 to 1.1 cmol₊/kg, which greatly exceeded the range of the exchangeable Fe content (0.01-0.05 cmol₊/kg). The sum of exchangeable bases (as determined by leaching with 1 M NH₄OAc, pH 7), plus exchangeable Al³⁺ (after extraction by 1 M unbuffered KCl solution) is also less than 50% in all horizons of the profiles analyzed (Appendix 3). Exchangeable basifying cations measured in this study occurred at the same order of magnitude as that found in the nearby soils of Sierra de Urbasa (Val and Iñiguez 1981a) and Moncayo (Hoyos et al. 1983). However, the acid soils of this study show higher levels of Ca and Mg than the Haplic Podzols of the

Lehstenbach catchment in southeast Germany (extracted with 1M NH_4Cl). Moreover, the $\text{pH-H}_2\text{O}$, and the Al^{3+} and Fe^{3+} content measured from those Podzols were lower than that measured in the soils described here.

The profiles studied also show a number of shared physical properties, including high rock fragment content and a textural class, ranging from sandy loam to loam (Figure 2). Specifically, these soils have a loamy-skeletal particle-size class according to the Soil Taxonomy system (SSS 2014). This suggests the presence of a kinematic porosity, which plays an important role in accelerating the evacuation of water (Nasri et al. 2015). In contrast, soils that develop on conglomeratic colluvium on glacis in the lowlands have textures ranging from loam to clay (Hoyos et al. 1983). On the other hand, the soil horizons show a low coherence but a high soil aggregate stability (SAS) at the level of 1-2 mm sized aggregates, with maximum values in the Ah and Bhs horizons (Appendix 4).

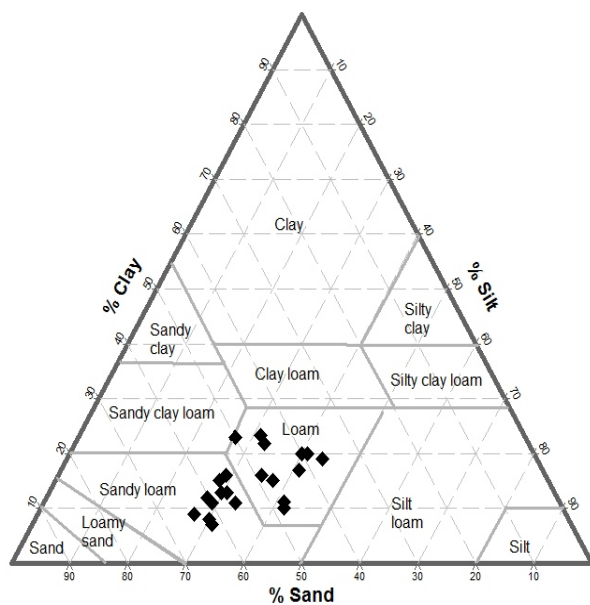


Figure 2 The distribution of 25 soil samples within the USDA-SCS soil textural triangle.

3.2.2 Variations with depth

Upslope soils show an increase in $\text{pH-H}_2\text{O}$ values with depth, which ranges from 4.0-4.7 in the A horizons to 4.9-5.3 in the lowermost horizons in profiles from both pine and beech forests. Profiles located in the downslope areas of the oak forests exhibit the opposite tendency. Increasing pH with depth is common in leached soils, as Podzols

(Bogner et al. 2012, Camps and Aizpurúa 2007; Carceller 1995).

Organic carbon content (C) shows a clear decreasing trend with depth, ranging from 2.3%–10.0% in the A horizons to 0.2%–1.5% in lowermost horizons (C or BC). The same parameter shows a relative increase in the Bhs horizons (3.1%–4.2%) where it is present (Figure 3). Total N is significantly correlated to carbon content in these soils ($r= 0.87$). The C/N ratio in oak profiles is highest within the Ah horizon (10.0-11.8) and decreases with depth. For the Ah-E-Bhs-BC sequa within pine and beech forest soils, the C/N ratio was high in the Ah horizons (11.0–22.1), decreases in E horizons (5.7–11.5) and then increases again in the Bhs horizons (7.6-18.5). The bases also have the highest concentration in the Ah horizon (3.3-7.5 cmol_+/ kg), decreasing in the E horizon (1.5-2.8 cmol_+/ kg), and increasing again in Bhs horizon, where present (2.2-3.4 cmol_+/ kg). The contents of oxalate-extracted Al (Al_{ox}) and Fe (Fe_{ox}) exhibit maximum values at certain soil depths corresponding to either the Bw, Bs or Bhs horizons (Figure 4). Al_{ox} ranges from 0.10% in the Bw horizon of oak forest soils to 0.70% in the Bhs horizon of beech forest soils and 1.0% in the Bhs horizon of pine forest soils. In addition, Fe_{ox} ranges from 0.20% in the Bw horizon of oak forest soils to 0.49% in the Bhs horizon of beech forest soils and 0.80% in the Bhs horizon of pine forest soils. The highest Al_{ox} and Fe_{ox} values occur in the Bhs horizons, while the lowest values occur in the E horizons. For example, the percentage of $\text{Al}_{\text{ox}}+1/2\text{Fe}_{\text{ox}}$ ranges from 0.53% to 1.39% in the Bhs horizons and from 0.05% to 0.11% in the E horizons. Changes in Fe and Al with soil depth are much sharper than those of organic C, but we preferred to maintain the alphabetical order of the suffixes (h, s) to name the genetic horizon as Bhs.

On the upslope areas, litter (O horizons composed of OL-OF-OH layers) overlies a dark Ah horizon. The presence of a dark and well structured Ah umbric horizon still indicates some biological activity; if the biological activity was more restricted, the Ah horizon may be lacking (O-E-Bhs-C sequum), which is typical of northern Podzols (Labaz et al. 2014). Topsoil horizons provide a permanent supply of low molecular weight organic acids (fulvic acids), which react with metal-organic complexes (Al and Fe), migrate

downwards through the E horizons (cheluviation) as soluble complexes, and then accumulate (chiluviation) in the Bhs horizons (Buurman and Jongmans 2005; Sauer et al. 2007). The accumulation of Al and Fe is interpreted as the result of the saturation at organic ligands adsorption sites (Ferro-Vázquez et al. 2014) and even from microbial degradation of some organic ligands (Lundstrom et al. 2000; Grand and Lavkulich 2011).

The CEC for each profile exhibited the highest values in the Ah and Bhs horizons and is especially related to the content of organic matter (OM), as the following pedotransfer functions show:

$$CEC(\text{cmol}_+/kg) = 1.278(\text{OM}\%) + 4.50; R^2 = 0.553; n = 25; P < 0.001$$

$$CEC(\text{cmol}_+/kg) = 0.697(\text{clay}\%) + 1.728; R^2 = 0.173; n = 25; P < 0.05$$

$$CEC(\text{cmol}_+/kg) = 1.177(\text{OM}\%) + 0.337(\text{clay}\%); n = 25; R^2 = 0.536; P < 0.001$$

The significant effect of the organic matter on the CEC can be related to a high content of aromatic and alkyl chain compounds with a high bonding capacity (Beyer 1996; Girona et al. 2015). In contrast, the clay particle size fraction in these soils has little influence on CEC, due to its scarce content and its low cation exchange capacity. In studying the mineralogy of two soil profiles in the montane stage of the Moncayo, Hoyos et al. (1983) found that soil clay minerals were primarily illite, which was particularly abundant in the surface horizons. In addition to illite, they also observed kaolinite, vermiculite, and hydromica as well as different interlayers (vermiculite-illite, vermiculite-kaolinite and vermiculite-chlorite). Kaolinite is also abundant in the clay fraction in tills of

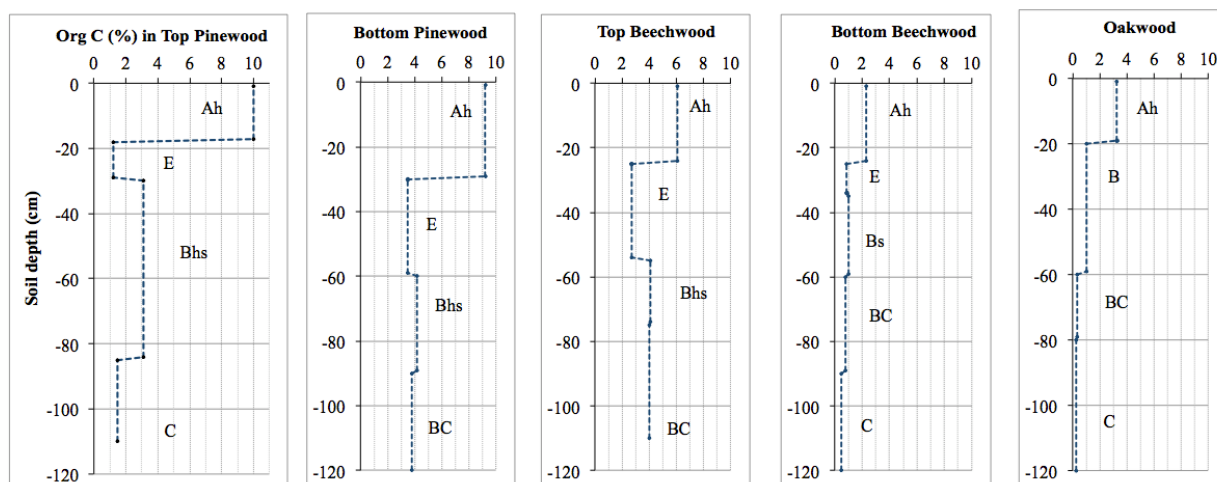


Figure 3 Soil Organic C (in %) for the catena studied along the northern flank of the Moncayo.

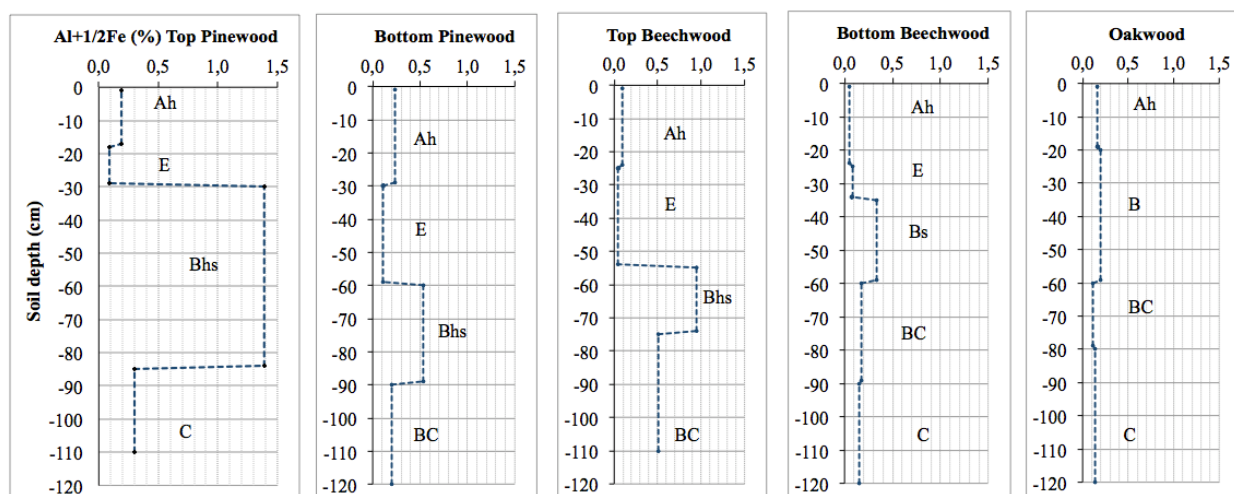


Figure 4 $Al_{ox}+1/2Fe_{ox}$ C (in %) for the catena studied along the northern flank of the Moncayo.

Moncayo Massif, with a certain proportion of illite, vermiculite and quartz (Lemartinel 2004). Val and Iñiguez (1981b) identified a similar clay mineral composition in Podzolic soils from the nearby Sierra de Urbasa, with illite and kaolinite in greater abundance than vermiculite, montmorillonite, chlorite, and various interstratified minerals. Soil acidity and strong leaching would weather illite, inherited from sandstones, to kaolinite under conditions of moderate weathering (Val and Iñiguez 1981b). Based on these previous studies and the low CEC of the soils of this study, it stands to reason that there is abundant illite and kaolinite in the scarce clay fraction of the soils of Moncayo.

The variation of certain physical properties relative to depth also followed a different pattern in the profiles beneath beech and pine forest at high elevations, than the patterns of the profiles beneath oak forests at low elevations. Soil aggregate stability (SAS) is highest in the Ah horizons (90%-96%) and decreases consistently with depth in oak forest profiles. In beech and pine forest profiles however, the highest SAS values occurred in the A and B horizons (80%-94%), while the lowest values occurred in the E horizons (28%-83%). SAS is significantly ($P < 0.01$) correlated with organic matter ($R = 0.61$), Mg^{2+} ($R = 0.64$), and Ca^{2+} ($R = 0.41$) content and with lesser degree ($P < 0.05$) with Al_{ox} ($R = 0.38$) and Fe_{ox} ($R = 0.32$) content but not with clay-sized particle ($R = 0.04$) content. It is well known that cations and organo-metallic compounds form bridges between particles and the SOC enhances aggregation through the bonding of

primary soil particles (Bronick and Lal 2005).

The relative clay content increase in some B horizons (Figure 5) may relate to the illuviation of crystalline clays as shown by the occasional presence of coatings of oriented clay on the surfaces of pores and pedes (clay films) within the Bs or Bhs horizons. It may be also related to the dispersion of illuviated Al and Fe in the particle-size separation process, thereby joining these to the measured clay fraction. The increase of illuvial clay content in the genetic Bhs horizon may justify the addition of the "t" suffix to this horizon (Bhst), as do Camps and Aizpurúa (2007) for Albic Podzols in Iturrieta heath lands. This process of clay illuviation should be identified in future research based on thin sections of undisturbed soil monoliths.

As with previous parameters, water content at field capacity (FC) also exhibited maximum values within the Ah and Bhs horizons due to its relation with organic matter and, especially in this case, with clay content, as described below:

$$FC(\%) = 0.62 (\text{clay}\%) + 10.70; R^2 = 0.474; n = 25; P < 0.001$$

$$FC(\%) = 0.518 (\text{OM}\%) + 16.60; R^2 = 0.336; n = 25; P < 0.001$$

$$FC(\%) = 0.30 (\text{OM}\%) + 0.485 (\text{clay}\%) + 10.998; R^2 = 0.558; n = 25; P < 0.001$$

The water-holding capacity of each profile ranges from moderate to very low due to the high percentage of stoniness (sandstones) typical of all the soils analyzed. This low soil water retention capacity and high permeability can make forests growing on it vulnerable to drought, as the ability

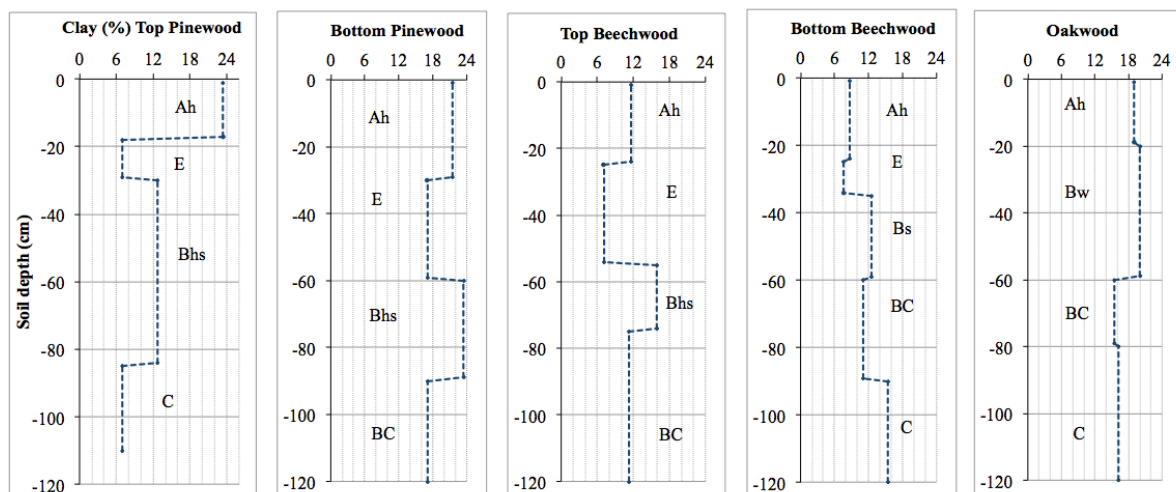


Figure 5 Clay-sized particles (in %) for the catena studied along the northern flank of the Moncayo.

to first store water and then supply it is limited. However, they fulfill other ecological functions, such as enabling the replacement of groundwater (Sauer et al. 2007). The relatively high field moisture capacity together with the increased availability of nutrients in the Ah and Bhs horizons can explain the abundance of fine roots in both horizons (Buurman and Jongman 2005).

High water repellency (WR) is observed in surface horizons (Ah) and sometimes in subsurface (Bhs) horizons beneath pine forests (WDPT > 3600 s). WR in this study correlates positively with OM content ($R = 0.71$) and to a lesser degree ($P < 0.05$), with coarse sand particles ($R = 0.42$) similarly to the findings of previous studies (Badía et al. 2013a and references therein). A higher WR in topsoils beneath coniferous forests (spruce, pine) relative to beech forests (Butzen et al. 2015), evergreen oaks (Badía et al. 2013a), or scrublands (Zavala et al. 2009) has usually been found. This may be due to the contribution of resins, waxes and aromatic oils from coniferous litter (González-Pérez et al. 2004). As a result of higher WR, an increase of overland flow is expected, which may have a hydrogeomorphological influence (Butzen et al. 2015).

3.2.3 Variations with elevation

The significance of elevation on soil properties and processes is confirmed in this study. Thus, value (or lightness in the Munsell color system), base saturation, soil reaction, potassium and fine silt content significantly decrease with increasing elevation. In contrast, coarse sand, stoniness and organic matter content and related properties (SAS, CEC, WR, C/N) significantly increase, to lesser or greater extents, with elevation (Table 3). PCA revealed, graphically, these trends (Figure 6) by identifying two principal components that account for 29.3% and 21.5% of the overall variation. Elevation parameters are clustered relative to the axes representing each component. The lower right quadrant shows positive scores for the first principal component and negative scores

for the second one, and this space represents soil properties that are enhanced with elevation. The upper left quadrant represents soil properties that are diminished with elevation (Figure 6).

Both OM and the C/N ratio increase with elevation, which is related to: 1) the greater rainfall and net primary production and litter input to the soils (Ibarra and Echeverría 2004) and 2) the temperature decrease, which reduces biological activity and the humification degree of organic matter (Carceller 1995; Girona et al. 2015; Zanella et al. 2011). A positive correlation between elevation and organic matter content and C/N ratios has been well documented in the literature. For instance, forest soils at high elevations in the German Alps have particularly large OM stocks due to the low air temperature and high precipitation amount (Prietz and Christophel 2014). Similar results are found in loess-derived soils of the USA Central Great Plains by Klopfenstein et al. (2015). Organic matter positively correlates with total nitrogen, CEC, Mg, structural stability, and water repellency. The abundance of SOM generates a dark color, and for this reason value and chroma (color purity) are negatively correlated with SOM. Base saturation (BS) correlated positively with soil reaction (pH-H₂O and pH-KCl) and negatively with Al and Fe (Figure 6). A negative correlation of elevation with pH and base saturation has also been documented previously (Martí and Badía 1995; Klopfenstein et al. 2015).

Soils beneath oak forests in Moncayo Massif from the lowlands do not show signs of Al and Fe leaching and accumulation (podsolization). But at the highest elevation considered in this study (approximately 1600 m), beneath pine forest vegetation, amorphous Al and Fe content is 16 times higher in the Bhs horizon than in the E horizon (1.39% and 0.09% Al_{ox}+1/2Fe_{ox}, respectively). This pattern is also found in Podzols from the subalpine stage of the Pyrenees (Boixadera et al. 2008).

Table 3 Pearson correlation coefficients showing the degree of linear association (negative and positive) between soil properties and elevation. * $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$

Negative	pH (H ₂ O)	pH (KCl)	K ⁺	BS	Value	Fine silt	Coarse silt	Clay
Elevation	-0.402*	-0.234	-0.603***	-0.443*	-0.615***	-0.588***	-0.361	-0.159
Positive	OM	C/N	Al _{ox}	CEC	SAS	WR	Stones	Coarse sand
Elevation	0.440*	0.498*	0.374	0.358	0.567**	0.463*	0.476*	0.413*

Notes: BS: Base saturation; OM: Organic matter; Al_{ox}: Aluminum extracted with Oxalate; CEC: Cation Exchange Capacity; SAS: Soil Aggregate Stability; WR: Water Repellency.

3.3 Processes and soil classification

Soil forming processes in the Moncayo include weathering, accumulation of organic matter, and podzolization, which results in different sequa and diagnostic horizons. Downslope, beneath deciduous *Quercus* forests in Monte La Mata, soils exhibit relatively simple OL-Ah-C sequum, with dark, moderate acidic surface horizons that are poor in bases and rich in organic matter (Ah, umbric horizon) on a stony C layer. This profile is classified as *Skeletal Umbrisol, Loamic* (i.e., beneath sessile oak vegetation). The profile sometimes includes a cambic subsurface horizon, with a base saturation of less than 50%, leading to its WRB classification as a *Dystric Cambisol, Humic, Loamic* (i.e., beneath Pyrenean oak vegetation). With increasing elevation, at approximately 1300 m elevation and beneath beech forest, podzolization processes become evident but the B-horizon does not meet all the requirements for a spodic horizon, such as color, classifying the soil profile as intergrade of *Cambisols*, specifically a *Dystric Skeletal Cambisol, Loamic, Protospodic*. Therefore soils in the upper half of the catena can have an O-Ah-E-Bhs-C sequa, both in beech and

pine forests. In these soils, the Ah horizon meets the requirements for an umbric horizon, the E horizon meets the albic material conditions, and Bhs horizon satisfies the requirements of a spodic horizon. This combination leads to soil classification as Podzol (IUSS 2014) and Spodosol according to WRB and Soil Taxonomy System, respectively; spodic criteria is only different in terms of organic C content (0.6% in Soil Taxonomy system, and 0.5% in WRB system). Specifically, upslope soils are classified as *Skeletal Umbric Albic Podzol, Loamic*. In summary, Umbrisol and Cambisol soil WRB units (*Dystrudepts* according to STS) evolved to Podzols (*Haplorthods* according to STS) with elevation (Figure 7). Several different processes of mobilization and immobilization of SOM, Fe and Al may lead to *Podzol* development, and the specific combination of soil-forming factors at each location determines which of the possible processes take place and to what degree, as has been previously reviewed (Lundström et al. 2000; Buurman and Jongmans 2005; Sauer et al. 2007).

The presence of *Podzols* at the Moncayo Massif is geographically significant. Podzolization is considered part of a natural progression of soil

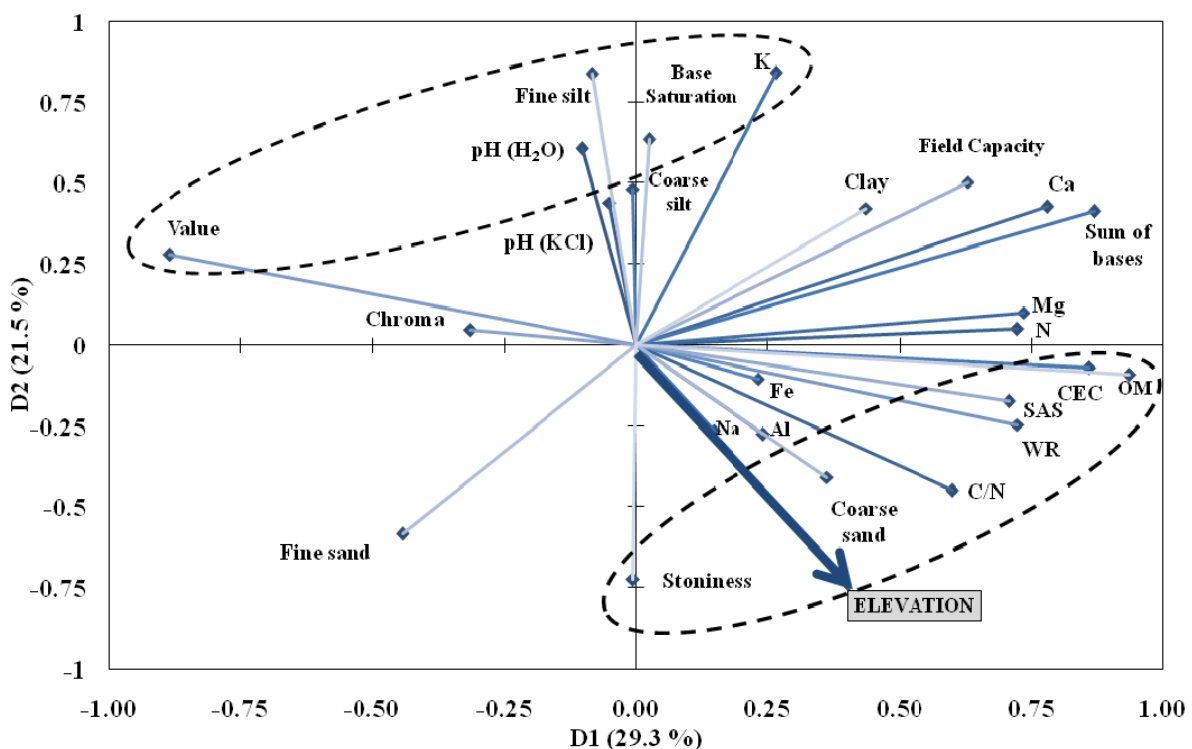
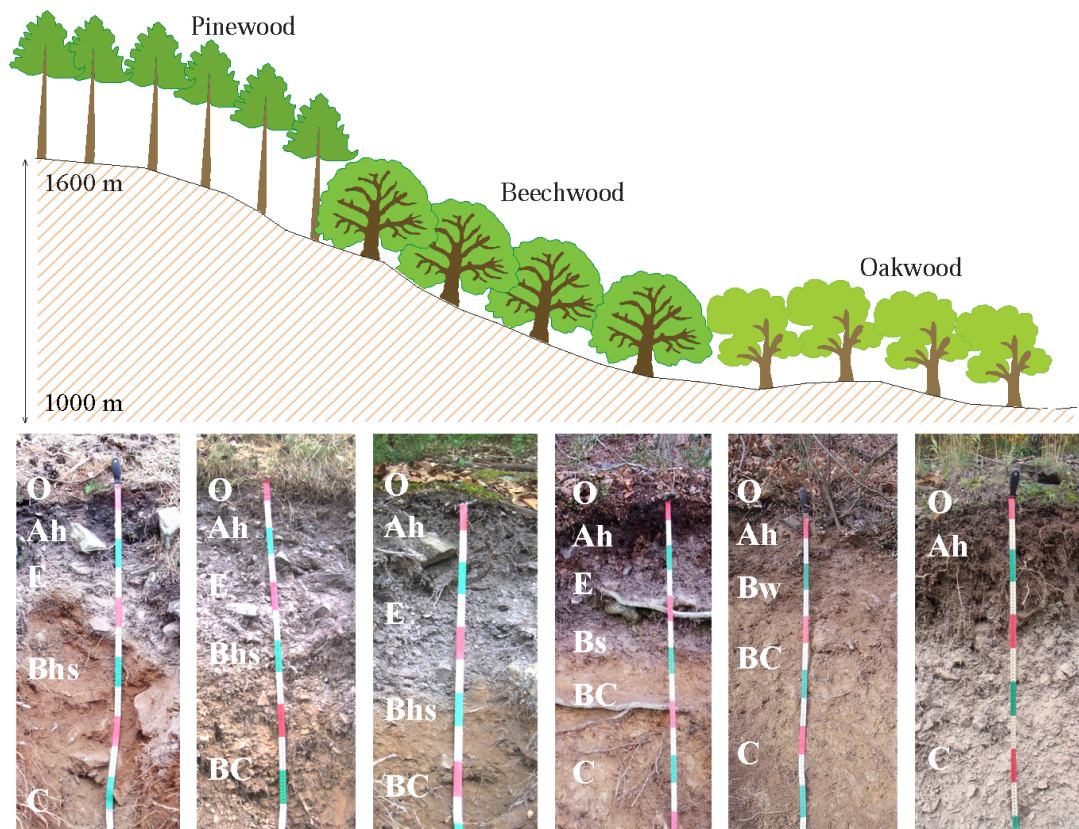


Figure 6 Principal components analysis (PCA) of soil properties from the Moncayo catena. Two distinct clusters highlight the respective positive (lower cluster) and negative (upper cluster) effects of elevation on soil properties.

development from glacial retreat starting 9000-13,000 years ago, to the colonization of till or scoured rock surfaces, and the subsequent ecological succession to boreal forest (Lundstrom 2000; Waroszewski et al. 2015). The development of an incipient Podzol morphology usually becomes visible after hundreds of years and mature podzolization develops in 1000–6000 years (Sauer et al. 2007). Podzolization occur on a widespread basis throughout the northern hemisphere where cover 485 million ha, mainly in Scandinavia, the northwest of Russia and in eastern Canada (Bridges et al. 1998). Nearly 20% of soil on the European continent consists of Podzols (Toth et al. 2008) but this soil type becomes rare in Spain, where it covers only a 0.1% of the country (Gómez-Miguel and Badía 2016). Podzols in Spain have

been described only in small and scattered areas primarily in NW Spain (Galicia) where they arise from quartz-rich parent materials developing beneath coniferous forest vegetation in a cold and very humid climate (Macías and Calvo de Anta 2001; Carballas et al. 2016). Similar formation factors appear in the mountains of NE-Spain and in the Catalan Pyrenees (Bech et al. 1981; Boixadera et al. 2008) at elevations of approximately 2000 meters on granitic till, with acidophilous vegetation (*Pinus uncinata*), high rainfall (udic moisture regime) and low temperatures (cryic temperature regime). Podzols have also been described in the Basque Country (Camps and Aizpurúa 2007) at elevations of approximately 1000 m on stable sandy colluvium, with acidophilous shrubs (heather), high rainfall



Reference Profile	Top	Bottom	Top	Bottom	Top	Bottom
	Pinewood		Beechwood		Oakwood	
WRB (IUSS 2014)	Skeletal Umbric Albic Podzol (Loamic)	Skeletal Umbric Albic Podzol (Loamic)	Skeletal Umbric Albic Podzol (Loamic)	Dystric Skeletic Cambisol (Loamic, Protospodic)	Dystric Cambisol (Humic, Loamic)	Skeletal Umbrisol (Loamic)
STS (2014)	Typic Haplorthod	Typic Haplorthod	Typic Haplorthod	Spodic Dystrudept	Typic Dystrudept	Humic Dystrudept

Figure 7 Soil classification for the catena studied along the northern flank of the Moncayo.

(udic moisture regime) and moderate temperatures (mesic-frigid temperature regimes). Under similar environmental conditions, Podzol-like profiles have been described in the Sierra de Urbasa, Navarra (Val Legaz and Iñiguez 1981a); these soils were associated with heath and beech vegetation, exhibiting udic-mesic regimes, and developing on Oligocene sandstones. Val Legaz and Iñiguez (1981b) concluded that these soils have macro- and micro-morphologic podzolic characteristics but that their B-horizons do not always meet the analytical diagnostic criteria for a spodic horizon. Podzols described in the Moncayo Massif may represent the most southern examples of Podzols in Europe with the particularity of being located at the southern edge of the semiarid Ebro Basin, beside saline, gypseous and calcareous soils (Badía et al. 2011; Badía et al. 2013b; Badía and Del Moral 2016). This highlights the soil pedodiversity of the Moncayo and the didactic potential of the region (Badía et al. 2013c). The presence of Podzols at the Moncayo Massif is a consequence of the coincidence of favorable soil forming factors in this part of the Iberian Range (NE Spain), which has been previously predicted by some pioneering works (Hoyos et al. 1983; Carceller 1995; Carceller and Vallejo 1996). This formation occurs on highly permeable parent material that is poor in base cations and under vegetation producing slowly degradable and nutrient-poor litter, such as coniferous forests and heather. In Moncayo Massif, the replacement of oaks and beech stands by Scots pine afforestations could promote soil acidification and the development of Podzols with mor-type humus, although more detailed studies should be conducted in the future that compare different forest stands at the same altitude (i.e., beech versus pine stands along the montane stage).

4 Conclusions

This study, conducted across a catena in the northern Moncayo Massif, confirmed the significance of elevation in soil properties, classification and humus forms. Soils of the Moncayo Massif exhibit a significant increase in coarse sand, stoniness, organic matter, C/N ratio,

SAS and WR with increasing elevation. In contrast, fine silt, lightness, pH, base saturation and potassium, significantly decrease with increasing elevation across soil catena. The soil profiles described in the wooded montane stage show a number of common properties, including a loamy-skeletal particle-size class, extreme acidity (pH $H_2O < 5.6$) and a very low base saturation (<50%).

The soils in the wooded montane stage of the siliceous Moncayo Massif are experiencing the accumulation of organic matter and podzolization processes that intensify with increasing elevation. For that reason, the mull humus in the downslope oak forest evolves into moder in beech forests and mor in the pine forests at the highest elevation. Upslope humus provides organic acids to form metal-organic complexes (Al and Fe), which migrate and accumulate in an illuvial Bhs-spodic horizon. As a result of podzolization, various properties (organic C, C/N, Fe, Al, field capacity, cations, clay-sized particle) exhibit irregular variations with depth, resulting in minimum contents within E and C horizons and maximum values in the Ah and Bhs horizons. As a result of this, Umbrisol and Cambisol soil WRB units (Dystrudepts according to STS) evolved to Podzols (Haplorthods by STS) with increasing elevation, highlighting the environmental uniqueness of the Moncayo Massif.

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