Magnetic and geochemical characterization of Andosols developed on basalts in the Massif Central, France

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Abstract
Identification of Andosols is primarily based upon the content of their colloidal constituents—clay and metal-humus complexes—and on the determining of andic properties. This needs time and cost-consuming geochemical analyses. Our primary aim of this study is to describe the magnetic and geochemical properties of soils rich in iron oxides derived from strongly magnetic volcanic basement (in this case Andosols). Secondary aim is to explore links between magnetic and chemical parameters of andic soils with respect to genesis factors: parent material age, precipitation, and thickness of the soil profile. Six pedons of andic properties, developed on basaltic lavas, were analyzed down to parent rock by a set of magnetic and geochemical methods. Magnetic data of soil and rock samples reflect the type, concentration, and particle-size distribution of ferrimagnetic minerals. Geochemical data include soil reaction (pH in H₂O), cation exchange capacity, organic carbon, and different forms of extractable iron and aluminium content. Our results suggest the following: (1) magnetic measurements of low-field mass-specific magnetic susceptibility can be a reliable indicator for estimating andic properties, and in combination with thermomagnetic curves may be suitable for discriminating between alu-andic and sil-andic subtypes. (2) In the studied Andosols, strong relationships were found between (a) magnetic grain-size parameters, precipitation, and exchangeable bases; (b) concentration of ferrimagnetic particles and degree of crystallization of free iron; and (c) parameters reflecting changes in magneto-mineralogy and soil genesis (parent material age + soil depth).

1. Introduction
Magnetic mineral content in soils is driven by a combination of several contributions. The effect of atmospheric deposition [e.g., Flanders, 1994, 1999; Kapicka et al., 1999, 2001; Lecoanet et al., 2003] and pedogenic processes [e.g., Fassbinder et al., 1990; Han et al., 1996; Maher and Thompson, 1995; Maher et al., 2003; Geiss and Zanner, 2006] has been relatively well studied and described, whereas weathering processes of parent rocks [e.g., Maher, 1986; Dearing et al., 1996] and their influences on the enrichment of upper soil horizon are not yet sufficiently understood. Ferrimagnetic iron oxides are the key magnetic minerals responsible for enhancement of magnetic susceptibility (MS) in soils [e.g., Mullins, 1977]. Detailed and reliable knowledge on ferrimagnetic iron oxides in soils is crucial for proper interpretation of magnetic mapping of topsoils and for the studies of atmospheric pollution in surface soils [e.g., Blundell et al., 2009]. From this point of view, it is important to discriminate the three above mentioned contributions. Soils with andic properties contain large amount of iron oxides, which are presumably derived from the volcanic rock [e.g., Shoji et al., 1994]. In Europe, nonallophanic Andosols have been reported to be developed from gabbro and amphibole parent materials in Galicia, Spain [Garcia-Rodeja et al., 1987] and from granite in Austria [Delvaux et al., 2004]. Thus, these soils may be unsuitable for, e.g., the assessment of atmospherically deposited contribution using topsoil magnetic measurements due to their naturally high values of magnetic susceptibility. Therefore, detailed information on lithogenic contribution in these soils is needed. To the best of our knowledge, there has been no detailed study to characterize andic soils using rock-magnetic methods.

Generally, pedological processes are affected by several factors, such as the parent rock properties (mineralogy, structure, and texture) and environmental conditions (including climate, topography, and land use). The rapid weathering of volcanic material results in precipitation of short-range order (SRO) minerals and/or metal-humus complexes, a process commonly known as andosolization [e.g., Duchaufour, 1977]. Majority of Andosols are found under aridic or xeric moisture conditions [Wilding, 2000]. Andosols display unique morphological, physical, and chemical properties (e.g., low bulk density, large variable charge, large water...
storage, and high phosphate retention) that distinguish them from other soil types. Classification criteria for Andosols were reviewed by Parfitt and Clayden [1991] and Shoji et al. [1996]. According to the World Reference Base (WRB) for Soil Resources [IUSS Working Group WRB, 2006], identification of Andosols is primarily based upon the measure of colloidal constituents (clays and/or metal-humus complexes) and on the determination of andic properties. Diagnostic criteria of horizons having andic properties are the content of Al + 1/2 Fe dissolved in acid-oxalate must be ≥2%, phosphate retention ≥85%, bulk density (BD) <0.9 kg/dm³, and organic carbon (SOC) <25%. Additional criteria are dark color (Munsell value and chroma are 3 or less), thickness of ≥30 cm, organic carbon >8% but <25% (by mass), and the ratio of carbon to nitrogen (CN) >13. The unique properties of colloidal constituents are responsible for accumulation of organic carbon protected against its decomposition by the formation of allophanes and/or metal-humus complexes (mostly Al-organic substances). Under acidic conditions, the metal-humus complexes may cause that nonallophanic Andosols accumulate more organic matter than the allophanic ones. That is why the WRB distinguishes andic properties as exhibiting sil-andic (allophanic) or alu-andic (metal-humus complex dominated) characteristics. Their discrimination is based on determination of parameters such as content of the Alp and Alo (pyrophosphate-extractable aluminum and acid-oxalate extractable aluminum), pH, and SOC. Determination of different forms of iron (Fe) and aluminum (Al) in soils can be efficiently estimated by particular extractions [Parfitt and Childs, 1988]. Organic compounds (increased in alu-andic Andosols) can be extracted by pyrophosphate reagent at pH 7 [Bremner and Lees, 1949]. Acid-oxalate reagent [Tamm, 1922], as 0.2 M ammonium-oxalate acid at pH 3, is known to dissolve materials with SRO minerals such as allophane, imogolite, ferrihydrite, Al associated with humus, and poorly crystalline lepidocrocite, maghemite, and magnetite [e.g., Borggaard, 1982; Farmer et al., 1983]. Therefore, it can be used for estimating the allophane, imogolite, and Al-organic/silicate constituents in volcanic soils [Parfitt and Wilson, 1985]. Noncrystalline minerals are metastable and may dehydrate with time to crystalline clays, including halloysite, kaolinite, gibbsite, goethite, and hematite [Schwertmann and Taylor, 1989]. Dithionite-citrate-bicarbonate reagent has been recognized as an effective dissolvent of iron oxides, including ferrihydrite, without differentiation between various crystalline forms [Mehra and Jackson, 1958]. Many magnetic studies used this method for interpretation of paleoclimate reconstructions in different soil sequences [e.g., Han et al., 1996; Maher, 1998]. We suppose that even small concentration of all the above mentioned forms of iron oxides will be reflected by low-field mass-specific MS.

A review of volcanic soils of France, including soil distribution in the Massif Central, was given by Quantin [2004]. He summarized research published from 1960 to 2000, where soil characterization and soil genesis are described in relation to parent material, age, and environmental conditions including climate and topography. Quantin [2004] concluded that in France the permanently wet soil conditions are the key factor in Andosol genesis. Six pedons with andic properties developed on basaltic rocks in the Massif Central were studied by Soubrand-Colin et al. [2007]. The authors combined geochemical, pedological, and mineralogical approaches to identify factors influencing vertical distribution of trace elements.

Magnetic techniques were successfully used for description of properties of soils developed on basalts. For example, the mineralogy and magnetic properties of basaltic-substrate soils from the Hawaii Islands were described by Van Dam et al. [2008a]. Effect of duration and intensity of weathering in highly magnetic soils was studied by Van Dam et al. [2008b]. Tropical soils developed on basalts were studied by Igel et al. [2012] using magnetic viscosity as an aid for landmine detection. The main purpose of these studies was to understand highly magnetic soil behavior for performance of geophysical sensors used for detection of unexploded ordnance. Recently, occurrence and origin of andic soils in nonvolcanic ecosystems of the Calabria region were reported by Vingiani et al. [2014]. The authors confirmed that magnetic susceptibility may be as a low-cost proxy for the identification of volcanic constituents. In the case of the Massif Central in France, the magnetic properties of rocks and sediments were investigated by several authors for the purpose of paleomagnetic and paleoclimatic studies [e.g., Rochette et al., 1993; Williams et al., 1998; Stockhausen and Thouveny, 1999]. The detailed magnetic properties of soils in this region are nevertheless poorly described. Therefore, our primary aim is to describe the magnetic and geochemical properties of soils rich in Fe oxides derived from strongly magnetic basement (in this case Andosols developed on basaltic lavas) in a region, where climatic conditions can be considered as almost constant and atmospheric deposition of industrially derived particles is relatively insignificant and may be neglected. For the reference purposes, we determined magnetic and geochemical properties of cambisol profile from same location, but developed on granite. Our secondary aim was to examine the links between magnetic and chemical soil parameters with...
respect to soil genesis factors represented by the age of parent rock, annual precipitation, and thickness of the investigated profiles. Finally, we tested correlation between mass-specific MS of investigated andic soils and different selective dissolutions of Fe oxides.

2. Materials and Methods

2.1. Study Area

The study area was selected due to the background material (basaltic lava flows of different age) and well-developed soil profiles. The reference profile was located on granite rock. The studied sites are in the eastern part of the French Massif Central, the Veley Plateau formation, near the borders between the departments of Ardèche and La Haute-Loire. The investigated area is within three volcanic systems—the "Bas Vivarais," the "Devès," and the "Veley Oriental"—where the basaltic parent rock was formed during the Pleistocene, Pliocene, and Miocene. Basaltic lavas are composed of the alkaline basalts, hawaiites, basanites, nephelinites, and ankaramites [Defive et al., 2011]. A sketch map of volcanic systems with the locations of the sampled profiles is in Figure 1. The old surfaces of these highlands were eroded by glaciers during the Pleistocene [Hétier, 1975]. Present topsoils located at altitudes of 800–1400 m a.s.l. can be mainly considered as the result of post-Würm pedogenesis, developed either on basaltic rock, on fragments of former soils or on translocated superficial formations. The beginning of pedogenesis is thus dated at about 10,000 years ago [Quantin, 2004]. The mountainous relief is exposed to a severe temperature regime. Average summer temperature is 14°C, but a maximal temperature in July varies from 22 to 25°C. In the winter, average temperature is 0°C and the number of days with negative temperatures exceeds 90. Annual precipitation varies from 800 to 1500 mm. There are 160–180 days of precipitation, and precipitation exceeds 5 mm during 40–60 days (www.meteo-mc.fr).

Figure 1. Sketch map of investigated sites including type of volcanism.
Table 1. Summary Description of Sampling Sites

| Site Name (Location) | Age of Basement | Type of Parent Material | Altitude (m asl)/ Site Orientation, Slope Aspects | Annual Precipitation (mm) | Vegetation | Coordinates |
|----------------------|-----------------|-------------------------|-----------------------------------------------|--------------------------|------------|-------------|
| A1 Lac du Bouchet (Devès) | 1 Myr | Plio-Pleistocene basalt lava flows | 1233/N, flat | 800–1200 | Spruce, beech | 44°54’53.8" 3°47’00.7" |
| A2 Borée (Bas Vivarais) | 160 kyr | Middle and late Pleistocenebasalt lava flows | 1140/E, flat terrace | 1100–1300 | Spruce | 44°53’39.5" 4°15’10.7" |
| A3 Lac St Front (Veley Oriental) | 10 Myr | Miocene basalt lava flows | 1295/S, flat | 800–1200 | Fir, spruce | 44°56’14.8" 4°10’10.4" |
| A4 St Clement (Veley Oriental) | 8–10 Myr | Miocene trachybasalts, under basalt basement granite rock | 1200/W, gentle backslope on basaltic rift | 1100–1300 | Grass | 44°56’58.7" 4°14’20.8" |
| A6 St Victor (Devès) | 1 Myr | Plio-Pleistocene basalt lava flows | 1132/NW, flat | 800–1200 | Beech | 44°54’07.9" 3°59’45.0" |
| A8 Le Béage (Bas Vivarais) | 160 kyr | Middle and late Pleistocene basalt lava flows | 1135/SE, colluvial footslope | 1300–1500 | Beech | 44°49’08.3" 4°06’14.0" |
| Ref. A9 Issarles (Devès) | 400–300 Myr | Middle and late Paleozoic crystalline rocks: Variscan granites | 973/SW, gentle backslope | 1100–1300 | Spruce, pine | 44°50’26.1" 4°02’15.9" |

The topography of the studied sites is described in Table 1, where data on the parent rock, altitude, slope aspects, annual precipitation, vegetation, and GPS coordinates are listed. Most of the profiles are located on flat surfaces or gentle slopes, two profiles are located in footslope part. Soils exhibit an udic moisture regime and a mesic temperature regime at all sites [Soil Survey Staff, 1999].

2.2. Sampling
2.2.1. Sampling Strategy
The studied soil profiles were excavated until lava fragments became predominant. Profiles A1, A2, A3, A6, A8, and the reference granitic A9 profile were sampled in forest areas, where minimal soil erosion is supposed, and soil thickness was at least 50 cm. A4 was on basaltic-ridge with grass cover. For simplicity of this paper, the studied material from these profiles was divided into three vertical sections: top, mid, and sub. Top (T) is representing material obtained from the first 10 cm and corresponds to Ah, A/B, or B1 horizons. Mid (M) is located in the middle of the profiles, and often corresponds to B2 horizons Sub (S) is located at the profiles’ bottom, often corresponding to C horizons (see Table 4, detailed morphology of the investigated profiles is in the supporting information Table S1). Rock samples (coarse gravel > 30 mm) are denoted by R at the beginning of sample notation.

2.2.2. Magnetic Measurements In Situ
Soil surface MS was measured using a Bartington MS2D loop at each site (about 25 measurements on an area of about 150 m² per site). The position for excavation of typical profiles was found after verification of Soil surface MS was measured using a Bartington MS2D loop at each site (about 25 measurements on an area of about 150 m² per site). The position for excavation of typical profiles was found after verification of vertical distribution of MS. It was tested at least on five vertical profiles 40 cm long (diameter of 3.5 cm) by a ZHI Instruments SM400 soil susceptibility meter [Petrovsky et al., 2004]. Furthermore, MS along the walls of the dug soil pits was assessed by a Bartington MS2F stratigraphic probe. From each soil horizon about 1–2 kg of soil and rock material was sampled for further magnetic and geochemical analyses. Plastic cores 40 cm long (after MS measurements by SM400) were taken for determination of soil bulk density (BD).

2.3. Sample Preparation and Magnetic Measurements in the Laboratory
Soil and rock samples were air dried. Soil material was gently sieved through 2 mm mesh to exclude large organic fragments. The sieved material (referred to as fine earth) was used for all magnetic and geochemical analyses. Material coarser than 2 mm was carefully washed, air dried, and passed through sieves with mesh 64 and 10 mm to obtain coarse gravel (CG) 10–64 mm in size. Rock fragments > 30 mm from C horizons were considered to represent the bedrock. Magnetic characteristics of rock fragments (CG > 30 mm) from topsoils were used to evaluate possible similarities with soils (T, M, and S) and rock from C horizons. Rock fragments were crushed and visually checked that it represents parent rock before being analyzed. Soil specimens were prepared by filling plastic cylindrical pots (Bartington pots) of 10 cc volume and weighed. Measurements of volume-specific MS (μ, SI) were performed using an AGICO Kappameter MFK1-FA at the...
three frequencies 976 Hz (F1), 3904 Hz (F2), and 15,616 Hz (F3) at magnetic field of 200 A/m and mass-specific MS (μ, mT/kg) was determined. Frequency dependence of MS (νMax, %) was calculated to check for the presence of superparamagnetic (SP) pedogenic particles [e.g., Dearing, 1994]. In our case, we used the formula νMax = (F1–F2)/F1 (%) used by Dearing [1994]. It should be noted that the MFK1 instrument uses different frequencies/field than Bartington MS2B Dual Frequency meter, but offers higher sensitivity and thus more reliable and accurate νMax data. However, as shown by Hrouda [2011], the obtained data may be easily linked to those determined from measurements on Bartington MS2B.

A KLY4 kappa-bridge with CS-3 furnace and CS-L cryostat (AGICO Ltd., Czech Republic) was used for measurements of temperature dependence of the low-field MS in the temperature range between −195°C and 700°C in order to assess characteristic temperatures of iron oxides (Curie/Néel/Verwey temperatures). The detailed determination of transformation phases for determination of Fe oxides is not subject of this paper. However, we compared the shape of the heating/cooling k-T curves using MSinital, MSfinal, and maxMSheating and we calculated the A40/Amax alteration indices [Hrouda, 2003]. The A40 index characterizes the change in susceptibility after executing the entire heating/cooling cycle. The Amax index shows the maximum difference between the heating and cooling curves. In interpretation, it should be kept in mind that Amax does not reflect the intensity of alteration. MaxMSheating is the maximum mass-specific MS measured on the heating curve. Thus, we obtained numerical parameters characterizing the shape of temperature dependence of MS, which we used in principal component analyses (PCA).

The hysteresis loops and DC remagnetization curves were measured at room temperature using an EV9 Vibrating Sample Magnetometer (ADE Corporation, USA). Saturation magnetization (Ms), saturation remanence (Mrs), and coercivity (Hc) were obtained from hysteresis loops (applied field ±2 T) after the correction for the linear part, representing the paramagnetic and/or diamagnetic contributions. The remanence coercivity (Hcr) was obtained from the back-field remagnetization curve. The Ms is important for assessing the concentration of ferrimagnetic phase, while the ratios of Mrs/Ms and Hcr/Hc reflect relative trends in grain-size distribution [e.g., Day et al., 1977; Dunlop and Özdemir, 1997]. The Mrs/Ms ratio was used in PCA.

### 2.4. Geochemical Analyses

Geochemical analyses, with the exception of soil reaction, were carried out following ISO standards in a certificated laboratory of the Research Institute for Soil and Water Conservation (VUMOP). The summary of soil parameters and methods of their determination are listed in Table 2. The particle-size distribution was measured at the Institute of Geology (Prague), using a CILAS 1190 LD laser granulometer, enabling a measurement range of 0.04–2500 μm. The granulometry data were obtained for three fractions: sand, silt, and clay (2000–63 μm, 63–2 μm, and <2 μm). Particle-size analysis was performed after short
Table 3. Summary of Magnetic and Nonmagnetic Methods

| Interpretation | Method and Parameter | Comments |
|---------------|----------------------|----------|
| Soil chemical properties | Determination of soil reaction (pH2O), total cations exchange capacity (CEC), organic carbon (SOC), content of Al and Fe in different extractions (Feo, Fed, Fep, Alo, Ald, Alp) | See section 2.4 + Table 2 |
| Andic properties (WRB, 2006) | Al and Fe dissolved in acid-oxalate (Alo, Feo), bulk density (BD), organic carbon (SOC) | Alo + ½ Feo ≥ 2%, BD < 0.9 kg/dm³, SOC < 25% |
| Sil-andic characteristics | Determination of pH2O, determination of active, short-range order or amorphous Fe, Al compounds (Feo, Alp, Feo) | pH > 5, Alp/Alo < 0.3, high Alp-Alo: presence of allophane and imogolite |
| Alu-andic characteristics | Determination of pH2O, organically bound Fe and Al (Fep, Alp) | pH < 5 (allophane do not form), high Alp/Alo > 0.5; high Fep and Alp; increased content of meta-humus complexes |
| Fe oxides crystallinity | Determination of ratio (Feo/Fed) | Low ratio Feo/Fed: good crystallinity |
| Composition; mineralogy of Fe-oxides | Thermomagnetic analyses: dependence of magnetic susceptibility and temperature from −195°C to 800°C (Alp, Ald, Alp) | Numeric characterization of shape of s–T curves from all horizons; phase transition unblocking-ordering temperature (Curie, Néel, and Verwey transitions) |
| Relative grain-size distribution; magnetic domain state (SD/MD/PSD) | Remanence and hysteresis loops measurements: saturation remanence (Ms), saturation magnetization (Ms), coercivity of remanence (Hcr), coercive force (Hc) (Day plot) | High Hcr/Hc and small Ms/Ms : large MD grains |
| Magnetic mineral concentration | Magnetic susceptibility (MS) measurements; saturation magnetization from hysteresis loop measurements | High MS: dominant concentration of ferri-magnetic minerals |
| Relative significance of ultrafine SP particles (magnetite/maghemite) | Determination of frequency-dependent magnetic susceptibility (χmd (%)) | Using MFK1-FA (frequencies 976 Hz and 3904 Hz)χmd < 3%; non-SP grains dominate (it correspond Bartington χmd < 5%) |

ultrasonic dispersion (60 s) on pretreated soil samples. Pretreatment of soil samples (fine fraction) consisted of sample boiling for 10 min in KOH solution and removal of organic matter using H2O2 (boiling for 10 min).

2.5. Summary of Measured Magnetic and Nonmagnetic Parameters

In Table 3, we summarize the methods used. In the “Comments” column, we present basic values for the interpretation of the corresponding parameters.

3. Results and Discussion

3.1. Nonmagnetic Soil Characterization

The basic soil chemical properties and selective dissolutions of Fe and Al were analyzed for individual soil samples (T, M, and S) of the basaltic profiles and reference granitic A9 profile. The results are listed in Table 3. Soil properties, which we examined on the basaltic samples, are consistent with basic andic criteria: the content of Alp + ½ Feo ≥ 2%, BD < 0.9 kg/dm³, and SOC < 25% [IUSS Working Group WRB, 2006]. Sil-andic and alu-andic properties were assessed on the basis of content of the Alp and Alo (data in Table 3). The value of Alp/Alo < 0.3 was recommended by Poulenard and Herbillon [2000] to better determine the sil-andic horizon. Such values were found for all samples of the profiles A2, A6, and A8. Alu-andic properties, characterized by Alp/Alo ≥ 0.5 were found in different samples of the profiles A1 (T, S), A3 (M, S), and A4 (T, M). Soils exhibit dark color of humic A horizon with high root density. Subsurface B horizons are less dark colored, with silty texture and frequent presence of stones. At the bottom of the profiles, C horizons with stone predominance were found (except A6). The granitic A9 profile meets criteria of Dystric Cambisol [IUSS Working Group WRB, 2006] and is strongly different in chemical and physical properties from the other profiles. Main morphological features of the studied pedons are summarized in supporting information Table S1 and include soil color [Munsell ® Soil Color Charts, 2009], texture with content of CG, structure, roots density, and boundary transitions.

Grain-size distribution along profiles corresponds to silt loam with average clay content of 16.7% (Table 4). The exception is Profile A1 (silty clay loam), with high clay content (35.2% on average). Grain-size fraction of soil samples (fine earth) can be seen in supporting information Figure S1. Pretreatment by KOH with H2O2...
The chemical properties of Andosols reflect high surface area soils, rising both from clay constituents and organic material. Active soil reaction (pH$_{H_2O}$), organic carbon (SOC), and total cation exchange capacity (T(CEC)) provide general description of the chemical character of a soil. In case of Andosols, pH and content of SOC play crucial role in identification of SRO minerals (allophane and imogolite). Further, high pH is responsible for lowering the SOC content; if SOC is >10%, allophane formation progressively decreases [e.g., Arnalds, 2004]. Generally, the formation of metal-humus complexes becomes dominant at pH$_{H_2O} < 5$ when humic substances predominantly form bonds with Al and Fe. The T(CEC) reflect amount of positively charged cations, therefore highly weathered soil have low capacity to hold cations. Increasing the SOC of any soil will help to increase the CEC since it also holds cations like the clays. Accumulation of SOC in Andosols is due to the protection of organic matter from decomposition by metal-humus complexes and protection of organic C by allophane [Mizota and Van Reeuwijk, 1989].

The pH$_{H_2O}$ in investigated profiles increases with depth (from 4.4 in topsoil to 6.2 in subsoil). The soil reaction in profiles located above 1200 m a.s.l. can be classified as strongly to extremely acid [Soil Survey Division Staff, 1993]. The profiles at lower altitudes are slightly to strongly acid. The granitic A9 profile is very strongly acid along the whole depth. Sil-andic soils (dominated by allophane) often have pH$_{H_2O}$ 5.5–6.5 [Nanzyo et al., 1994]. In our case, in sil-andic profiles (A2, A6, and A8) is pH$_{H_2O}$ between 5.3 and 6.2; in alu-andic profiles (A1, A3, and A4) is pH$_{H_2O}$ between 4.4 and 5.5. In alu-andic samples, we observed significant negative correlation between pH and SOC ($R^2 = 0.87, n = 9$). Similar relationship was observed in volcanic soils of Iceland described by Arnalds [2004].

Total cation exchange capacity (T(CEC)) decreases with depth with average values 46.5, 40.0, and 37.4 mmol/100 g for T, M, and S samples, respectively. This behavior is in general similar to that of soil organic carbon (SOC) content. T(CEC) correlates well with amount of SOC ($R^2 = 0.65, n = 18$). The T(CEC) was used in PCA because it correlates well with different forms of Al. In the profiles A1, A2, A3, and A4 is average SOC 6.1%, which is similar to values for freely drained Andosols of the world reported by Shoji et al. [1994]. Average value of SOC in the profiles A6 and A8 is 11% and most probably is related to increased dissolution for investigated soils was an efficient way to disturb clay-sized aggregates [Takahashi et al., 1993].
content of allophanes. Increased SOC content even in the deep parts of these profiles can be explained by the location in colluvial footslope. Arnalds [2004] explained accumulation of organic materials in Andosol as a result of poor drainage and cold climate.

### 3.1.1. Selective Dissolutions of Fe and Al

Different selective dissolution method are commonly used in the quantification of Fe/Al fractions for soil classification purposes and to characterize some specific soil components, e.g., determining of basic andic criterion (Alo + 1/2 Feo is ≥2%), indicating the presence of amorphous and/or SRO minerals. The usefulness of these methods is limited by the existence of a continuum between very SRO to crystalline components and by weaker tendency of Al than Fe to form oxyhydroxides. Pyrophosphate should extract only organically bound Al and Fe [van Breemen and Buurman, 2002]. Acid-ammonium-oxalate dissolution is an effective way to detect amorphous, and SRO Fe constituents (organic Al, Fe, and Al silicates). Further, it dissolves large portions of allophane and imogolite, whereas pyrophosphate reagent causes little dissolution [Parfitt and Childs, 1988]. Most authors agree that hematite and goethite are not readily dissolved by acid-oxalate [e.g., Schwertmann et al., 1982]. These minerals should extract dithionite-citrate solution commonly used as dissolvent of all free Fe oxides forms, including well-crystallized Fe oxides [e.g., Cornell and Schwertmann, 2003]. The results of selective dissolution of Fe and Al compounds are shown in Table 4.

Generally, selective Fe extractions yielded the following relationship: Fed > Feo > Fep. The concentration of Fed was 2–3 times higher than that of Feo, except for in A4, where it was 4–7 times higher. This suggests that A4 is rich in well-crystallized Fe oxide minerals. The highest content of Fep and Alp suggest that A3 is the richest in metal-humus complexes.

The efficiency of Al extractions was as follows: Alo > Ald > Alp. High Alo and Feo values in A6 pointed to an increased amount of noncrystalline materials. The most typical sil-andic properties (rich in allophane), as indicated by low Alp/Alo (under 0.3) and high pH<sub>2O</sub> (5.3–6.2) were present in profiles A2, A6, and A8. These profiles also exhibit the most elevated “amorphous inorganic” parameter Alo-Alp > 20 reflecting increase content of allophane and imogolite. Similar features had been observed by Parfitt and Childs [1988]. Soil samples A1 (T, S), A3 (M, S), and A4 (T, M) exhibited high Alp/Alo values (≥0.5), thus suggesting the dominance of metal-humus (Al organic) complexes and pointing to the alu-andic subtype. Nanzyo et al., [1994] recommend Alp/Alo ratio for nonallophanic Andosols in the range 0.8–1.0. The values 0.8 reached only sample A3(S). Low concentration of allophane should reveals increased content of SOC in humus horizons [e.g., Nanzyo et al., 1994]. Complexation of Al by SOC was observed only in A4 profile. Its Ah horizon exhibits increase content of the SOC (13.1%) and low pH<sub>2O</sub> (4.4), which is in agreement with so-called antiallophanic effect, described, e.g., Shoji et al. [1994]. No relationship between Alp/Alo and SOC in profiles A1 and A3 suggests weak connection of Al-associated compounds to organic components of the soil. Further, these profiles were not analyzed in humus horizons (we tested A/B and B horizons), therefore possible interaction in humus horizons exist.

The Feo/Fed “activity ratio” suggests the crystallinity of Fe oxides in soils [Mizota and Van Reeuwijk, 1989]. Profile A4 exhibited the best FeO crystallinity with the lowest Feo/Fed ratio. In contrast, the highest activity ratio—approaching to 0.5—were exhibited in A3 (M) and A6 (T, M) samples. This is consistent with the most elevated values of Fed, Feo, and Fep in Profile A3, and the most elevated values of Feo and Alo in Profile A6. The Feo/Fed was used in PCA because positively correlates with Feo, Fed, and Fep.

### 3.2. Magnetic Characterization

#### 3.2.1. Magnetic Susceptibility Measurements

In situ topsoil MS of basaltic sites (after leaf removal) varied from 110 to 790 × 10<sup>-5</sup> SI units, while the outcropping rocks nearby reached values from 820 to 2400 × 10<sup>-5</sup> SI units. In case of the granitic A9 profile topsoil MS varied from 7 to 17 × 10<sup>-5</sup> SI units, the outcropping rocks had 8 × 10<sup>-5</sup> SI units, parent rock in the C horizon showed 16 × 10<sup>-5</sup> SI units. All investigated basaltic profiles represent typical example of lithogenically influenced soils, where MS increases with depth: in the A (Ah) horizons is between 120 and 850 × 10<sup>-5</sup> SI units, in the AB (B) horizons from 500 to 1800 × 10<sup>-5</sup> SI units, in the C horizons the values were between 2000 × 10<sup>-5</sup> SI units, and 3300 × 10<sup>-5</sup> SI units (data measured in situ by Bartington MS2F stratigraphic probe). The Profile A9 varied between 12 and 42 × 10<sup>-5</sup> SI units, with sharp peak reaching 120 × 10<sup>-5</sup> SI units in the B horizon in depth of 5 cm (Figure 2, right). This peak value is typical feature for soil profiles with well-pronounced anthropogenic contribution due to atmospheric deposition. Typical
vertical distribution of MS of basaltic profiles is represented on Profile A2 (Figure 2, left). Peak similar to that observed in the granitic A9 profile (Figure 2, right) is not visible here. Three different approaches of MS measurements are shown: in situ by the SM400, MS2F and in laboratory MFK1. Differences between the curves are most probably due to lower accuracy of Bartington MS2F. However, this probe is good enough to determine general trend. Overall agreement in observed trends justifies the selection of representative samples from different horizons. MFK1 measurements of fine earth samples (volume of 10 cc) were used to calculate mass-specific MS (m³/kg), Table 5. MS determined for frequency F1 was used in the correlations with Fe extraction parameters and in PCA. The frequency-dependent MS ($j_{fd}$) calculated for the frequencies F1 and F2 were less than 3%, F2/F3 and F1/F3 were more elevated, but never exceeded 5% and 8%, respectively. According to Hrouda [2011], $j_{fd} ≤ 5%$ is typical for samples in which non-SP grains dominate [Dearing, 1994]. This means that the contribution of SP particles as a result of pedogenic processes can be considered insignificant.

### 3.2.2. Thermomagnetic Measurements

Low and high-temperature curves ($\chi$-T) were measured in ambient atmosphere on fine earth and rock material (CG > 30 mm) from all horizons. Magnetic characteristics of rock fragments from topsoils were used to evaluate possible similarities with soils (T, M, and S) and rock from C horizons. The main aim of thermomagnetic measurements was to evaluate the influence of parent material on soil magneto-mineralogy. Thermomagnetic alteration indices enable us to characterize numerically changes in temperature dependence of MS of tested soil and rock samples. Table 5 summarizes the main characteristics of investigated $\chi$-T curves of the top and subsoil and rock samples.

All the basaltic samples show features typical for low content of paramagnetic particles, as suggested by small or even negative $A_{40}$ values. The alteration indices divide investigated samples into two main groups. The first group (A6, A8, and partly A2) includes samples where the heating curves exhibit similar or very similar shape for both soil and rock samples from both T and S horizons. This is expressed by the same signs of alteration indices of T and S samples. In case of A2, the T and S samples have opposite sign. However, low absolute values in T samples do not allow to make definite conclusion. Figures 3a and 3b show a typical example where magnetic soil mineralogy is controlled by the parent material. Cooling curves are practically reversible; magnetic minerals are very stable. Low-temperature curves confirmed the presence of multidomain magnetite in the profiles A2 and A8, where the Verwey transition is evident [Verwey, 1939]. The second group contains the alu-andic profiles (A1, A3, and A4) where the magnetic phases changed along the profiles’ depth in both soil and rock (parent material), and no obvious similarity between soil and parent material was observed. Magnetic minerals along the soil profile were less stable and topsoil samples showed signs of oxidation. Figures 3b and 3c show Profile A1 as an example of the second group. The heating curves exhibit more than two different phases and the cooling curves exhibit shapes very different from those of the heating ones. In both groups, we can observe that the cooling curve is below the heating curve.
Table 5. Main Magnetic Parameters of Top and Subsoil and Rock Samples: Mass-Specific Magnetic Susceptibility, Thermomagnetic Indices, Hysteresis, and Remanence Characteristics

| Sample                  | Mass-Specific Magnetic Susceptibility (× 10^{-9} m^3/kg) | Alteration Indices | Main Hysteresis and Remanence Characteristics |
|-------------------------|--------------------------------------------------------|--------------------|----------------------------------------------|
|                         | j^a, M_{Sinitial}, M_{Sfinal}, max{M_{Sremnant}}, A_{40}, A_{max} | Hc (A/m) | Ms (Am/kg) | Mrs/Ms | Hc/Hc |
| A1T 5–10 cm, soil A/B   | 1,095, 1,249, 1,434, 1,547                              | 0.15   | 24,334   | 1.24   | 0.19   | 2.84   |
| RA1T Rock top           | 1,223, 2,642, 3,213, 2,907                              | 0.22   | 10,888   | 3.10   | 0.11   | 2.39   |
| A1S +30 cm, soil C      | 1,230, 1,192, 1,649, 1,415                              | 0.38   | 28,196   | 0.97   | 0.19   | 2.97   |
| RA1S +30 cm, rock C     | 1,555, 2,207, 1,916, 3,972                              | −0.13  | 28,551   | 3.29   | 0.17   | 2.57   |
| A2T 2–5 cm, soil Ah     | 1,234, 1,115, 1,022, 1,307                              | −0.08  | 26,110   | 0.78   | 0.23   | 2.54   |
| RA2T Rock top           | 1,865, 1,468, 1,282, 1,634                              | −0.13  | 17,683   | 0.58   | 0.23   | 2.05   |
| A2S +40 cm, soil C      | 986, 994, 1,377, 1,207                                  | 0.39   | 30,399   | 0.72   | 0.22   | 2.63   |
| RA2S +40 cm, rock C     | 990, 1,205, 1,326, 1,916                                | 0.10   | 41,846   | 1.43   | 0.21   | 2.47   |
| A3T 2–5 cm, soil Ah     | 1,746, 1,926, 2,152, 2,023                              | 0.12   | 21,488   | 1.09   | 0.15   | 3.69   |
| RA3T Rock top           | 2,253, 3,538, 2,980, 4,246                              | −0.16  | 42,215   | 1.45   | 0.31   | 1.83   |
| A3S +30 cm, soil C      | 1,629, 1,858, 3,230, 2,124                              | 0.74   | 20,787   | 1.36   | 0.13   | 3.65   |
| RA3S +30 cm, rock C     | 1,829, 2,597, 2,056, 3,680                              | −0.21  | 13,179   | 3.25   | 0.12   | 2.53   |
| A4T 0–10 cm, soil Ah    | 548, 961, 1,041, 1,361                                  | 0.08   | 26,626   | 0.46   | 0.20   | 2.83   |
| RA4T Rock top           | 2,029, 881, 514, 1,211                                  | −0.42  | 28,036   | 1.04   | 0.19   | 2.26   |
| A4S 32–48 cm, soil B/C  | 584, 613, 1,006, 797                                   | 0.64   | 27,758   | 0.35   | 0.18   | 3.83   |
| RA4S +50 cm, C          | 2,315, 1,265, 973, 4,185                                | −0.23  | 11,379   | 1.11   | 0.15   | 2.92   |
| A6T 5–10 cm, soil A/B   | 1,981, 552, 715, 569                                   | 0.29   | 21,276   | 0.32   | 0.18   | 2.89   |
| RA6T Rock top           | 1,323, 1,253, 1,420, 1,337                              | 0.13   | 30,215   | 1.80   | 0.28   | 1.76   |
| A6S +60 cm, soil B3     | 2,037, 691, 946, 721                                   | 0.37   | 22,441   | 0.45   | 0.19   | 2.90   |
| RA6S +60 cm, rock B3    | 2,078, 924, 1,089, 1,001                                | 0.31   | 33,782   | 0.98   | 0.33   | 2.08   |
| A8T 6–13 cm, soil B1    | 444, 991, 743, 1,039                                   | −0.25  | 27,960   | 0.53   | 0.19   | 3.12   |
| RA8T Rock top           | 683, 1,094, 663, 1,137                                  | −0.39  | 31,872   | 1.10   | 0.18   | 2.60   |
| A8S +25 cm, soil CRk    | 624, 1,574, 1,193, 1,670                                | −0.24  | 20,567   | 0.84   | 0.18   | 2.89   |
| RA8S +25 cm, rock CRk   | 884, 1,460, 1,240, 1,836                                 | −0.15  | 33,447   | 0.96   | 0.29   | 2.06   |
| Ref. A9T 4–10 cm, soil Bv | 14, 67, 298, 73  | 3.42   | 22,181   | 0.015  | 0.14   | 3.73   |
| Ref. RA9T Rock top      | 4, 19, 123, 31  | 5.45   | 35,262   | 0.005  | 0.19   | 2.58   |
| Ref. A9S +25 cm, soil C | 16, 83, 247, 45 | 1.95   | 23,981   | 0.004  | 0.12   | 3.88   |
| Ref. RA9S +25 cm, rock C | 2, 41, 62, 41  | 0.50   | 28,460   | 0.008  | 0.21   | 2.38   |

^a Mass-specific susceptibility measured by MFK1.

and the final MS is lower than that initial one (expressed by the negative indices A_{max} and A_{40}, respectively). This is due to the unstable ferrimagnetic fraction, altered by heating to an antiferromagnetic fraction with lower susceptibility. Typical example may be oxidation of magnetite to hematite, or structural transformation of maghemite to hematite. However, our thermomagnetic measurements did not prove the formation of hematite with the Néel temperature of about 680°C (Néel, 1948). Granitic Profile A9 reflects very low concentration of ferrimagnetic minerals. The indices A_{max} and A_{40} in the soil and in top rock samples show only positive values, 1 order higher than in the case of basaltic ones, reflecting similar magnetic changes in soil and in rock.

3.2.3. Hysteresis and Remanence Measurements

Hysteresis and remanence experiments were performed on the same set of samples as thermomagnetic experiments. Results for the top and subsoil and rock samples (CG > 30 mm) are presented in Table 5 and shown in the Day plot in Figure 4.

The majority of soil samples exhibited similar magnetic characteristics in dependence with a depth. Obvious differences in concentration of ferrimagnetic particles between soil and rock from the same horizons suggest that lithogenic material is less preserved in the soil and its resistance to pedogenic processes may play significant role. In contrast, similar concentrations of ferrimagnetic minerals along the soil profile and rock samples from the subsoil horizons suggest higher resistance of lithologic material to weathering. However, this requires more detailed study on large set of samples.

Regarding the trends in magnetic grain-size distribution represented by Day plot, majority of rock samples show smaller magnetic grain-sizes than do their corresponding soil partners. Soil contains only relatively large magnetic grains. This supports the interpretation above. Assuming less resistant lithologic material, weathering will result in disintegration of rock into particles, which are still in the coarse MD magnetic range, but are no more included in the coarse material.
We also evaluated the slope of linear part of the hysteresis loops in order to assess the significance of paramagnetic minerals. However, there is no significant correlation with the $A_{40}$ index. This may be due to the fact that the two parameters are affected in different way by the combination of diamagnetic substances and poorly ordered Fe-bearing para and antiferro-magnetic minerals.

### 3.3. Data Analyses

#### 3.3.1. Principal Component Analysis

All the data were analyzed using STATGRAPHIC CENTURION XVI, software version 16.1.18, Statpoint Technologies, Inc., USA. The relationship between soil genesis factors: parent rock age (age), average annual precipitation (precipitation), and the thickness of soil profile (depth) on one side, and soil magnetic and chemical parameters on the other, was evaluated by principal component analysis (PCA). We analyzed all the basaltic profiles except A6, which exhibits different horizon characteristics (no rock pieces in the B horizon) and may be considered as an outlier. Chemical and magnetic parameters were chosen on the basis of multivariate correlations (23 variables) with $P$ value below 0.05 (data not shown). Andosol chemical parameters are represented by the total exchangeable bases $T_{(CEC)}$ and crystallinity ratio ($Feo/Fed$). T(CEC) positively correlates with SOC, Alo, Ald, and Alp ($R^2_{SOC} = 0.87$, $R^2_{Alo} = 0.56$, $R^2_{Ald} = 0.60$, $R^2_{Alp} = 0.57$). Ratio $Feo/Fed$ positively correlates with Feo, Fed, and Fep ($R^2_{Feo} = 0.89$, $R^2_{Fed} = 0.72$, $R^2_{Fep} = 0.69$). Selected magnetic parameters reflect concentration of iron oxides at room temperature and during heating cycle; expressed by mass-specific MS and maximum mass-specific MS ($MS_{maxMS}$heating), respectively. The other magnetic...
parameters reflect changes in magneto-mineralogy during heating-cooling treatment; expressed by thermomagnetic indices ($A_{40}, A_{\text{max}}$), and parameter reflecting magnetic grain-size distribution ($Mrs/Ms$). The PCA was done for 10 variables (described above). Figure 5 shows two components accounting for 67.71% of the

![Figure 4](image_url)

**Figure 4.** Day plot compares soil (rounds) and rock (squares) samples composed for basaltic profiles A1, A2, A3, A4, A6, A8, and granitic Profile A9 (dark colored symbols). Inset is detailed section of Day plot for all profiles composed from soil and rock samples from top and sub horizons. Magnetic-domain state is expressed as: SD (single domain), PSD (pseudo-single domain), and MD (multidomain). $Mrs/Ms$ is magnetization ratio composed from $Mrs$ (saturation remanent magnetization) and $Ms$ (saturation magnetization); $Hcr/Hc$ is coercivity ratio composed from $Hcr$ (coercivity of remanence) and $Hc$ (coercivity).

| Component | Variance | Cumulative percentage |
|-----------|----------|-----------------------|
| 1         | 41.858   | 41.858                |
| 2         | 25.850   | 67.708                |

**Table of component weights**

|                      | Component 1 | Component 2 |
|----------------------|-------------|-------------|
| depth                | 0.200466    | -0.258422   |
| age                  | 0.289655    | -0.238182   |
| precipitation        | -0.425378   | -0.0409784  |
| MS                   | 0.271624    | 0.419153    |
| $A_{40}$             | 0.392809    | -0.343583   |
| $A_{\text{max}}$     | 0.311872    | -0.421776   |
| max$MS_{\text{heating}}$ | 0.363161  | 0.379292    |
| $T(\text{CEC})$      | -0.241518   | 0.113736    |
| $Mrs/Ms$             | -0.37643    | -0.141509   |
| Feo/Fed              | 0.194321    | 0.475764    |

**Figure 5.** Principal component analysis for Andosol samples. Plot of component weights with corresponding data extracted for two components accounting together for 67.71% of the variability in the original data. The purpose of the analysis is to obtain a small number of linear combinations of the 10 variables which account for most of the variability in the data.
variability in the original data. Well-pronounced relationship was observed between Ms/Ms, precipitation, and \( T(CEC) \). The second group relates MS, \( \text{maxMS}_{\text{heating}} \), and \( \text{Feo/Fed} \), and the third group suggests a link between \( A_{40}, A_{\text{max}} \), and soil genesis factors: age and depth.

### 3.3.2. Correlations Between Magnetic Susceptibility and Fe Extraction Parameters

Correlations between mass-specific MS and Fe extraction parameters reflecting iron oxide stability (see Table 6) were determined for all soil profiles (data also shown for case when A6 was excluded). Our results suggest similar efficiency of extractions in dithionite-citrate and ammonium-oxalate solutions dissolving free, active, SRO, and amorphous Fe compounds. It is interesting that MS also reveals large amounts of Fe in organometallic complex forms, confirmed by efficient pyrophosphate dissolution, even if A6 was considered. The coefficient of determination is the highest for Fe extracted by dithionite-citrate solution, because it dissolves free Fe forms of all the iron oxides. That is why the MS and Fed-Feo reveals presence of well-crystalized iron oxides (important when A6 was not excluded). The best correlation between MS and Fed-Feo is exhibited when A6 and A8 are excluded \((R^2 = 0.77)\). The Ms and Feo-Fep reveals increased content of allophanes (amorphous FeO minerals). Significant correlation between Feo and MS is most probably caused by increased content of poorly crystalized maghemite. Well-pronounced negative correlation is between MS and Feo/Fed in sil-andic profiles \((R^2 = 0.53)\); it confirms presence of paramagnetic, amorphous Fe oxides, as ferrihydrite or lepidocrocite.

### 4. Conclusions

The aim of this study was to determine the magnetic and geochemical properties of Andosols developed on strongly magnetic parent rocks of different age. These properties were supposed to show possible links between specific magnetic and chemical soil features in relation to soil genesis. We examined six basaltic pedons, consistent with criteria for Andosols (according WRB) located in the Massif Central. Specific andic properties, as the poorly ordered minerals and the organic materials, divided investigated Andosols into two subtypes: sil-andic Andosols (rich in allophane) and alu-andic Andosols (suggesting the dominance of Al-organic complexes). Determining parameters such as Alp and Alo (pyrophosphate-extractable aluminum and acid-oxalate extractable aluminum), \( pH \) and SOC, plays the most important role in discriminating colloidal constituents. All investigated basaltic profiles represent typical example of lithogenically influenced soils, where magnetic susceptibility (MS) increases with depth. Our findings show that for andic soils thermomagnetic measurements of soil and rock samples provide a suitable tool for discrimination of the sil-andic subtype. Sil-andic Andosols showed similar magnetic phases in soil and in its bedrock. This applies to profiles located on the youngest parent material, \( pH_{12O} \) (5.3–6.2), the richest in noncrystalline phases with \( \text{Alp/Alo} \leq 0.3 \). The magnetic phases in Alu-andic soils changed along the profiles’ depth in both soil and rock (parent material), and no obvious similarity between soil and rock samples was observed. Magnetic minerals along the soil profile were less stable and topsoil samples showed signs of oxidation. In this group there are profiles developed on the oldest basement, located at the highest altitude. The Alp/Alo > 0.5 suggested increased content of organo-mineral complexes, \( pH_{12O} \) (4.4–5.3). These profiles are composed of soils showing both poorly and well-crystallized Fe oxides. Regarding the trends in magnetic grain-size distribution represented by Day plot, composed of hysteresis and remanence measurements, majority of rock samples show smaller magnetic grain-sizes than do their corresponding soil partners. Concentrations of ferri-magnetic minerals in soils were similar in samples from all the depths studied and correspond to that in the rock samples from the bottom profile. This suggests dominant lithological influence on soil magnetic properties. Assuming less resistant lithologic material, weathering will result in disintegration of rock into particles, which are still in the coarse multidomain magnetic range, but are no more included in the coarse material. PCA was used to evaluate the links among factors affecting soil development and soil magnetic
and chemical parameters. Our results agree with general conclusion that the genesis of volcanic soils is more influenced by moisture than by the parent material age. Geochemical properties reflecting composition of different forms of iron oxides correlate with mass-specific magnetic susceptibility (MS). The coefficient of determination is the highest for Fe extracted by dithionite-citrate solution, because it dissolves all forms of the iron oxides. Significant correlation between Fe extracted by acid-oxalate solution and MS is most probably caused by increased content of poorly crystallized maghemite. MS also reveals large amounts of Fe in organomagmatic complex forms, confirmed by efficient pyrophosphate dissolution.

**Notation**

**List of Abbreviations**

| Notation | Description |
|----------|-------------|
| A1       | soil samples composed from top, mid, or sub fine earth. |
| RA1      | rock samples composed from top or sub coarse gravel (only fragments >30 mm). |
| A1 (T)   | name of soil sample from topsoil (from the first 10 cm; Ah, A/B, or B horizons). |
| A1 (M, S)| name of soil samples from mid and sub part of pedon. M often corresponds to B2 horizon; S is located at the bottom, often in C horizons. |
| RA1T     | rock sample from Profile A1, from surface. |
| RA1S     | rock samples from Profile A1, from C horizon representing parent material. |
| A40, Amax| thermomagnetic alteration indices. |
| Ald      | Al (aluminum) extracted by a dithionite-citrate solution [%]. |
| Alo      | Al compounds extracted by an ammonium oxalate solution [%]. |
| Alp      | Al extracted by a pyrophosphate solution [%]. |
| BD       | bulk density [kg/dm³]. |
| CG       | coarse gravel [size of 10–64 mm]. |
| Fed, Feo, Fep | magnetic susceptibility, represented by a volume or mass-specific magnetic susceptibility [SI units; m³/kg]. |
| MS       | total cation exchange capacity [mmol/100 g]. |
| SOC [%]  | soil organic carbon [%]. |
| PCA      | principal component analyses. |

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