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Formation of black carbon rich 'sombric' horizons in the subsoil – A case study from subtropical Brazil

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ABSTRACT

The formation of sombric horizons (dark horizons in the subsoil) is still not understood. In order to improve our understanding of the formation of sombric horizons we studied these soils in southern Brazil from various perspectives. The lateral configuration and grain size distribution excluded the possibility that the sombric horizon is a paleosol covered by an eolian deposit or colluvium. Micromorphology showed intense biological activity, indicating strong bioturbation. The absence of clay and OM coatings indicates that the sombric horizon in the study area was not formed by illuviation. Considering changes with depth, phytoliths and δ^{13}C isotopes clearly showed that the OM from the sombric horizon had a larger contribution from grasses, while a larger contribution from black carbon (BC) was evidenced by the molecular composition. A larger contribution from grasses and BC both correspond to drier climatic conditions. However, similar depth trends for δ^{13}C and PAHs were found in the reference profile (without sombric horizon), in agreement with climatic change but not explaining the different morphology. The molecular composition and C/N ratio showed that the profiles differed in degree of decomposition, with the OM in the soils that contained a sombric horizon being more decomposed than that in the reference profile. The sombric horizon is thus a remnant of an earlier phase of soil formation under a drier climate, which is made visible by differences in decomposition of OM related to subsequent more humid conditions. Stronger decomposition in the profiles with a sombric horizon may be related to better drainage, explaining their occurrence in the highest positions within the landscape and suggesting a topographic control.

1. Introduction

Organic matter (OM) in soils is generally associated with surface horizons, but in southern Brazil, non-podzol OM-rich horizons are also common in the subsoil (Almeida et al., 2015). The formation of these dark horizons in the subsoil is not yet understood, but they show a similar morphology as sombric horizons that are described from high-altitude areas of tropical and subtropical regions (Caner et al., 2003; Frankart, 1983). According to Soil Taxonomy (Soil Survey Staff, 1999) and World Reference Base for Soil Resources (IUSS Working Group WRB, 2015) the sombric horizon is a horizon with illuvial humus that is not associated with aluminum as in Podzols or with sodium as in Natric horizons. Several theories for the genesis of the sombric horizon have been proposed. According to Sys et al. (1961) the sombric horizon is formed by illuviation of OM. Studying Andean soils of Colombia, Faivre (1990) proposed migration and precipitation of clay-humic complexes as a cause, while Caner et al. (2003) concluded that the genesis of these horizons in India is related to a different OM source caused by climate induced changes in vegetation composition.

Our purpose is to improve the understanding of the formation of the sombric horizon. Knowledge on the formation of the sombric horizon may improve our understanding of (1) soil OM stability, and (2) the function of soil as paleoenvironmental archive. We hypothesized that the formation of the sombric horizon is related to: a) changes in the

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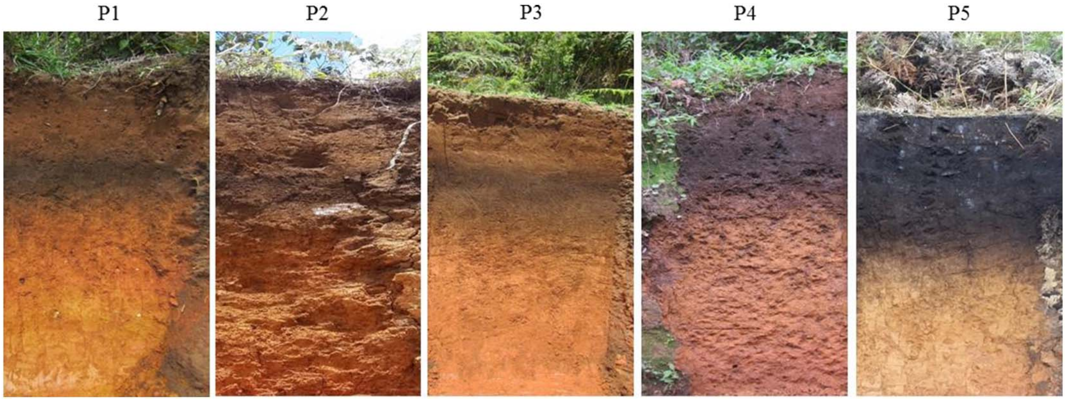

Fig. 1. Photographs of the five studied soil profiles (P1–P5; the photographs roughly show the first 2 m for all profiles, but scales may slightly differ).

nature of the OM from the surface horizon induced by environmental changes with persistence of more stable OM in the subsurface, or b) OM has been transported and accumulated in these horizons in combination with clay or in the form of OM-metal complexes similar to the podzolization process.

In order to test these hypotheses, we selected four soils with a sombric horizon and a reference soil from southern Brazil and studied these soils from different perspectives. To judge whether the sombric horizon has been covered by eolian deposits or colluvia, we used depth records of Zr/Ti, silt/clay, and the uniformity value (UV) to identify possible lithologic discontinuities (LDs; Schaetzl, 1998). Micromorphology was used to test the presence of illuviation coatings (hypothesis b; Bullock et al., 1985). In order to elucidate changes in past environmental conditions (hypothesis a), the soils were studied for phytoliths and δ^{13}C isotopic composition, both of which are well-known proxies to reconstruct vegetation composition in combination with ^{14}C dating (Pessenda, 1996; Velasco-Molina et al., 2013). To examine the contribution from OM to the sombric horizon and to provide an indication for its degree of decomposition, total carbon (C) and total nitrogen (N) were determined. The molecular composition of soil OM was studied by pyrolysis-gas chromatography–mass spectrometry (pyrolysis-GC/MS) to connect and support the data obtained by other methods. The relative contribution from plant, microbial, and burnt materials can be obtained by the relative contribution from lignin phenols, microbial N-containing compounds, and polycyclic aromatic hydrocarbons (PAHs), respectively (Carr et al., 2013; Derenne and Quénéa, 2015; González-Pérez et al., 2014). A sequential extraction was applied to the soil samples to separate OM fractions with different binding affinity, including the (1) NaOH extractable OM, which is comparable with the operationally defined humic plus fulvic acid fractions (Leinweber and Schulten, 1999) and extracts the major part of soil OM (Von Lützow et al., 2007), (2) the $Na_4P_2O_7$ extractable OM, that may represent the OM in metal-organic complexes (Nierop et al., 2005), and (3) the residue after both extractions, which is comparable with the humin fraction (Lichtfouse et al., 1998) and may contain OM that is strongly bound to the mineral phase, litter, and hydrophobic condensed polyaromatic structures (Knicker et al., 2005; Schellekens et al., 2017).

2. Materials and methods

2.1. Study area and sampling

Our study area is located on an elevated plateau under Precambrian rocks in Tijucas do Sul (Paraná State, Brazil; 25°55′41″S, 49°11′56″W; 950 m a.s.l.). The geomorphology is characterized by hills belonging to the Curitiba plateau (ITCG, 2006). The parent material is derived from migmatites with local influence of other metamorphic rocks (Santos et al., 2006). The native vegetation is a mosaic of mixed ombrophilous forest (with a considerable contribution from *Araucaria* trees) and grassland. The climate is temperate and humid (Cfb, Köppen classification) subtropical with a mean annual precipitation of 2000 mm/yr and a mean annual temperature of 22 °C (Behling et al., 2001).

The sampled profiles included three profiles with a dark subsurface horizon which was classified in the field as sombric horizon followed by a nitic horizon (Umbric Nitisol humic; IUSS Working Group WRB, 2015; profiles P1–P3). These profiles were situated in a toposequence, with P1 at the summit of a hill, P2 on the upper backslope at a distance of 58 m from P1, and P3 on the lower backslope at a distance of 30 m from P2. A reference soil without a sombric horizon, classified as an Abruptic Acrisol humic (IUSS Working Group WRB, 2015), was located at a distance of 2 km from the toposequence, on the footslope of another hill (profile P5). At the very summit of the hill from profile P5, an Umbric Nitisol humic (profile P4) (IUSS Working Group WRB, 2015) was sampled; based on morphology of the dark subsurface horizon, profile P4 seemed an intermediate between the sombric and reference soils. The occurrence of both sombric horizons and umbric horizons is common in this region (Almeida et al., 2009, 2015; Velasco-Molina et al., 2013). Photographs of all five profiles and their horizons are given in Fig. 1. The five profiles were sampled according to pedogenic horizons as determined in the field, resulting in a total of 54 samples. Most analyses were done using these samples. In addition, profiles P1, P4 and P5 were sampled at regular depths for δ^{13}C (5 cm intervals) and phytolith (10 cm intervals) analysis. The samples were air-dried and sieved through 2 mm for laboratory analysis.

2.2. General chemical and physical soil characteristics

Chemical analysis included pH (H_2O), Ca^{2+}, Mg^{2+} and Al^{3+} exchangeable by KCl 1 M, H and Al by calcium acetate at pH 7, and P, K^+ and Na^+ by Mehlich. Cation exchange capacity (CEC) was calculated by the sum of the exchangeable cations at pH 7 (Ca^{2+}, Mg^{2+}, K^+, H^+, Al).

The clay fraction (%) was determined by the hydrometer method after removing OM with hydrogen peroxide and dispersion with 1 M NaOH (Donagema et al., 2011). The sand fraction was sieved into five size fractions: very coarse (2–1 mm), coarse (1–0.5 mm), medium (0.5–0.25 mm), fine (0.25–0.10 mm) and very fine (0.10–0.05 mm) sand. The silt fraction was calculated by subtraction.

Ti and Zr of bulk samples were determined by X-ray fluorescence spectroscopy at the University of Santa Catarina - Lages Campus (Brazil), using an Epsilon 3 equipment of Panalytical.

2.3. Phytoliths

Phytolith extraction was performed according to Calegari et al. (2013). Organic matter and iron oxides were removed using 30% hydrogen peroxide and dithionite-citrate-bicarbonate, respectively. Thereafter, the separation of phytoliths was carried out with sodium