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Impact of drainage and soil hydrology on sources and degradation of organic matter in tropical coastal podzols

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ABSTRACT

In podzols important environmental issues converge, including dissolved organic matter (DOM) transport, DOM-metal binding, and carbon storage in the subsoil. Therefore, it is important to understand the formation and degradation of podzols in relation to (changes in) environmental conditions. For this purpose a Holocene barrier island with coastal sand dunes (Ilha Comprida, SE Brazil) was chosen as study area. The island is build-up of five geomorphic units that have different age (from > 5000 to 325 y BP), vegetation (*restinga* ecosystems), soil hydrology (flat units or units with ridges and swales) and drainage (poorly drained, well-drained, and improved drainage). Representative profiles were studied for each geomorphic unit, resulting in 100 samples from A, E, B, and C horizons, from which soil organic matter (SOM) was isolated by alkaline extraction. To better understand carbon sources and dynamics, we additionally sampled litter from different vegetation types and DOM from various sources. The molecular composition of SOM, DOM and litter was analyzed with pyrolysis gas chromatography mass spectrometry (pyrolysis-GC/MS). Comparing the pyrolysates of all samples (DOM, SOM and litter) factor analysis demonstrated that the major difference in molecular composition (factor 1) was related to the contribution from DOM (phenol, acetic acid, benzofurans, pyridine, benzene and naphthalene) or in-situ root material (straight chain aliphatics and methoxyphenols from the biomacromolecules suberan and lignin, respectively). The contribution from DOM or roots was characteristic for a profile i.e. without much change with depth. Factor 2 reflected decomposition processes, and showed that the predominantly DOM-derived B horizons were relatively enriched in aromatics compared to DOM, indicating selective decay and/or selective precipitation. In geomorphic units with swales and ridges that received DOM via groundwater flow from the catchment area, the B horizon was predominantly DOM-derived; these profiles showed large differences in the contribution from black carbon (BC; (poly)aromatics), with the younger profiles showing a larger contribution from BC in precipitated DOM. B horizons with a relatively large contribution from in-situ root materials were found in well-drained soils and in some of the poorly drained soils without lateral groundwater flow from the catchment area, i.e., the flat geomorphic unit without ridges and swales. Microbial material (N-containing compounds and sugars) was associated with relatively recent SOM and with well-drained conditions at present. i.e., well-drained profiles, and profiles with improved drainage.

1. Introduction

Natural organic matter in soil and water plays a key role in environmental biogeochemical processes. The stability of soil organic matter (SOM) is important in the global carbon cycle and its relation to climate change (Schlesinger and Andrews, 2000). Dissolved organic matter (DOM) is responsible for binding and transport of nutrients and contaminants in the environment (Jones and Brian, 1998; Kaiser and Kalbitz, 2012). The interaction of (dissolved) organic matter with metals and minerals is important to understand the mechanisms that control SOM stability (Lehman and Kleber, 2015). In podzols, the complexation and transport of DOM with Fe and Al plays an essential role in the formation of distinctive horizons. The morphology of podzols primarily reflects the processes of transport and accumulation of organic matter (OM) and Al and Fe compounds, i.e., podzols are typically composed of a shallow dark surface A horizon, followed by a grayish white eluvial E horizon from which OM, Al and Fe are removed, and a black to reddish brown illuvial B horizon enriched in OM and Al and sometimes also Fe (Anderson et al., 1982; Buurman and Jongmans, 2005; De Coninck, 1980; Lundstrom et al., 2000; Petersen, 1976; Sauer

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et al., 2007). Thus important environmental issues such as DOM transport, OM-metal binding, and carbon storage in the subsoil converge in podzols. Podzols may thus provide a natural laboratory to study carbon stability and OM-metal interactions, which may contribute to our understanding of the processes involved in the stability of SOM.

Organic matter dynamics in podzols are closely associated with soil hydrology and drainage conditions during their formation. In poorly drained podzols the B horizon is water-saturated during large part of the year, and the organic matter is predominantly DOM derived. In well-drained podzols, the B horizon may have a contribution from in-situ root materials and the DOM has a very local source due to vertical movement of percolating water (Buurman and Jongmans, 2005; Kaiser and Guggenberger, 2000; Kalbitz and Kaiser, 2008; Nierop and Buurman, 1999). Other terms that are frequently used include groundwater podzols and hydromorphic podzols (poorly drained), and xeromorphic podzols (well-drained), classified as carbic podzols and haplic podzols, respectively (IUSS Working Group WRB, 2015). Soil hydrology and drainage conditions are not static but may change with time, and B horizons from poorly drained podzols are degraded due to improved drainage (Buurman et al., 2005, 2013; Reuter, 1999). In addition, drainage conditions are closely related to topography and may therefore show vertical and lateral variation within short distance (Jankowski, 2014; Lopes-Mazzetto et al., 2018). This demonstrates the relevance of studying transects of related profiles, so that the chemical composition can be interpreted in the context of the landscape and its dynamics.

Our purpose was to study the effects of time and variation in drainage conditions on the formation and degradation of podzols. To this end we studied the molecular composition of SOM for podzol profiles at Ilha Comprida, a Holocene barrier island on the SE Brazilian coast. The podzols on Ilha Comprida have been studied by our group in relation to topography (Martinez et al., 2018) and soil morphology and micromorphology (Lopes-Mazzetto et al., 2018). Five geomorphic units with estimated ages between > 5000 and 325 years BP were distinguished by studying two cross sections perpendicular to the coastline. In the youngest surfaces, morphological differences of the predominantly poorly drained podzols were related to actual soil hydrology and topography of ridges and swales, while in the older geomorphic units landscape development in combination with converging groundwater flow caused hyper-developed B horizons. The 1800 m long cliff with its exposed profiles was used by Lopes-Mazzetto et al. (2018) to systematically study decay features in relation to hydrology. These studies thus provide a unique context to interpret the composition of SOM.

The role of DOM is crucial in podzols, and SOM stability in the B horizon is associated to the sorption or co-precipitation of DOM with Fe and Al (De Coninck, 1980; Hagedorn et al., 2015; Kaiser and Kalbitz, 2012; Jansen et al., 2003; Petersen, 1976). DOM that accumulates in the B horizon may originate from root exudates, decaying roots or surface litter, desorption of OM from B horizons, and microbial detritus (Hagedorn et al., 2015; Kaiser and Kalbitz, 2012), which may be representative for the ecosystem in the case of lateral groundwater flow from the catchment area, or have a very local source (produced in-situ and from vertical percolation). To identify differences and similarities in molecular structure between DOM and SOM, we additionally sampled DOM from various sources, including surface pools, streams and boreholes.

Pyrolysis gas chromatography/mass spectrometry (pyrolysis-GC/MS) was chosen to analyse the molecular composition of SOM, DOM and litter. Analytical pyrolysis techniques provide detailed molecular information, which has been valuable in understanding sources and degradation of SOM and DOM (Derenne and Quénéa, 2015; Schulten, 1999). The objective of this study was to link variations in SOM composition to sources and decay processes.

2. Materials and methods

2.1. Study area

Ilha Comprida consists predominantly of sandy sediments in the form of ridges, which are geomorphic expression of a prograding barrier. Its south coast runs perpendicular to the Atlantic coast, and thus exposes a sequence of ridges that can be divided in five geomorphic units (Units I–V; Martinez et al., 2018). The climate at Ilha Comprida (southern São Paulo state, Brazil) is humid tropical (Af according to the Köppen classification), with a mean annual temperature of 23 °C, and mean annual precipitation of 2130 mm (Alvares et al., 2013). Rainfall is well distributed throughout the year. The *restinga* vegetation is typical for sandy coastal plains (Suguio and Martin, 1990).

2.2. Soil profiles and sampling

Sixteen soil profiles were selected along the 1800 m long south coast and the west coast of the southern end of Ilha Comprida, including profiles from the cliffs and at locations 50–100 m inland (Fig. 1). This selection of profiles was representative for the different geomorphic units and field morphology of the profiles (Fig. 1; Lopes-Mazzetto et al., 2018). The same profiles have been studied for general physicochemical properties, soil morphology and micromorphology (Lopes-Mazzetto et al., 2018). The profiles were sampled in detail according to pedogenic horizons, resulting in a total of 100 samples, and included samples from A, E, B, and C horizons, and transition horizons (Table 1). In some profiles, horizontal OM-bands within E horizons (P2) and B horizons (P2, P37) were sampled separately. Some profiles contained an additional buried podzol, which is indicated by a number before the horizon (3 EB and 3Bh in P41, 2Bhm in P10, Table 1). From five profiles litter has been sampled as well. Litters were finely crushed and homogenised before analysis, without further treatment. In addition, water with DOM was collected during the wet season (February 2014) from streams, small pools, and boreholes (4 m) that were left open, resulting in 12 samples (SI_Fig. 1); the samples were filtered over 0.45 μm, freeze-dried and homogenised.

2.3. Soil organic matter extraction

After sieving (< 2 mm), 5 g of air-dried soil were shaken with 25 mL 0.1 M NaOH for 24 h. The suspension was centrifuged (1 h, 10,000*g*) and the extract was decanted. The extract was then acidified to pH 1–2 with concentrated HCl to protonate the OM, after which 1 mL of concentrated HF was added to remove minerals. The acid mixture was shaken for 48 h. To remove excess salt, the extract was dialysed in cellulose dialysis membranes (pore size 10 kD) against ultrapure demineralised water and freeze-dried. Because the E horizons contained insufficient OM for analysis, E horizons were represented by their transition horizons (AE, EB and BE; Table 1).

2.4. Pyrolysis-GC/MS

Pyrolysis was performed at the Department of Soil Science from ESALQ/USP (Piracicaba, Brazil) using a single shot PY-3030S pyrolyser (Frontier Laboratories, Fukushima, Japan) coupled to a GCMS-QP2010 (Shimadzu, Kyoto, Japan). The pyrolysis temperature was set at 600 °C (± 0.1 °C); Helium was used as carrier gas at a constant flow of 34.5 mL min^{-1}. The injection temperature of the GC (split 1:20) and the GC/MS interface were set at 320 °C. The GC oven was heated from 50 to 320 °C (held 10 min) at 15 °C min^{-1}. The GC instrument was equipped with an UltraAlloy-5 column (Frontier Laboratories LTD.), length 30 m, thickness 0.25 mm, diameter 0.25 μm. The MS was scanning in the range of *m/z* 45–600. Pyrolysis products were identified using the NIST ‘14 mass spectral library.