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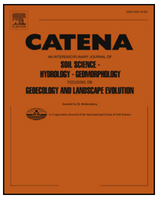

Lignin phenols in the paleoenvironmental reconstruction of high mountain peatlands from Atlantic Rainforest, SE - Brazil

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ABSTRACT

Tropical peatlands are very different from boreal and temperate regions, because they have particular climatic characteristics and different vegetation types. Similarly, high mountain peatlands differ significantly from those found at low altitudes. Lignin components were investigated as phyto-physiological proxies of landscape evolution in two big national environmental conservation parks of Southeastern Brazil. Lignin phenols showed a high degree of humification and indicated the same land-use for both forest parks, suggesting minimal anthropic intervention over the last 150 years, predominating native grasslands. However, total organic carbon (TOC) and total nitrogen (TN) parameters evidenced the influence of indirect effects of human activities, mainly from atmospheric deposition since 1950s, associated to the early Brazilian industrial development. This study reinforces the importance of protection and conservation to those pristine areas.

1. Introduction

A small portion of the earth's surface (2.84%) is covered by peatlands, approximately 400 million ha (Xu et al., 2018). Only 12% of the remaining area is located in tropical regions, that hold over 20% of the global peatland carbon stocks (Page et al., 2004; Page and Banks, 2007). However, these environments have undergone devastation and degradation mainly by anthropogenic pressure from agricultural production, environmental pollution and climate change (Dohong et al., 2017). Peatlands are important service providers to terrestrial ecosystems, which besides being responsible for hydrological function and biological resources, have an invaluable contribution in global carbon storage as a sink for carbon dioxide (Sorensen, 1993; Martini et al., 2006; Byg et al., 2017). In addition, peatlands are mainly formed by accumulation of plant debris under anaerobic conditions (Campos et al., 2012; Silva et al., 2013). They store approximately 455 billion tons of carbon, which correspond to 28.4% of all the stocked carbon in soils (Gorham, 1991; Hayes and Clapp, 2001). Furthermore, in tropical areas, peatlands store about 83 million tons of carbon (Rieley et al., 2008), have a singular role in the hydrological flow control (Bispo et al., 2016) and are a biodiversity hotspot (Posa et al., 2011).

Organic matter peat degradation (humification) is intrinsically associated with its physical, chemical, and biological properties. It is a very complex process including many environmental variables of degradation and synthesis reactions, which depend on different geographic conditions and climatic characteristics (Klavins et al., 2013). The degradation of these environments can play a significant role in climate change (Fatoyinbo, 2017). The formation of tropical peat is different from boreal and temperate peatlands, mainly with respect to the specific climatic conditions (e.g., high temperature and high humidity) and vegetation cover composition. Boreal and temperate peatlands are located in cooler climates, where the peat matter is primarily generated by *Sphagnum* moss and covered by herbaceous vegetation (Rydin and Jeglum, 2013).

It is estimated that peatland have three to four times more lignin, than found into the soil (Crawford, 1981; Kögel-Knabner, 2000; Gleixner et al., 2018). Lignin is more refractory than lipids, like sterols and n-alkanes, being also a more specific compound because some of its phenols are only found in vascular plants (Lallier-Vergès, 2008). In higher plants, the lignin compounds are chemically connected to cellulose and hemicellulose, and represent fiber walls, providing strength and hardness to the plant structures as well as resistance to the biodegradation of carbohydrates (e.g., enzymatic hydrolysis) and to environmental stresses (Brown, 1961; Kirk and Farrell, 1987; Argyropoulos and Menachem, 1997). The lignin degradation can be accelerated in aerobic conditions whereas in anaerobic this process is more slow, especially in flooded environments, thus allowing greater lignin accumulation e.g., in tropical peatlands (Benner et al., 1984; Kirk

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and Farrell, 1987). This plant component tends to be an efficient database to record plant debris in peatlands, due to slow decomposition rates under anoxic conditions (Kirk and Farrell, 1987; Williams and Yavitt, 2003).

Some recent studies have shown a link between soil lipid biomarker imprints in peatland and plant diversity in terrestrial ecosystems in which they are applied (Trendel et al., 2010; González-Pérez et al., 2011; Ronkainen et al., 2013; Zocatelli et al., 2014). However, few studies in tropical regions have addressed the use of lignin compounds as a recorder biomarker of vegetation cover, distinguishing different land-uses (Zocatelli et al., 2012; Lavrieux et al., 2012). This technique can be a good alternative for the reconstruction of peat vegetation, especially when the peat is very degraded to identify the botanical composition using vegetal macrofossils.

Lignin composition in peatlands is an available record of the original sources of plants and its degradation degree that may provide useful information about past environmental conditions (Bourdon et al., 2000; Disnar et al., 2008; Kuder and Kruge, 1998; Zaccone et al., 2008). Lignin phenols molecules can be shortened by side chain oxidation during decay (Kögel-Knabner, 2002) and its structure can be oxidized and thus broken in smaller phenols, such as cinnamyl (C), syringyl (S) and vanillyl (V), where C is more degradation susceptible and V is less degradation susceptible (Hedges and Mann, 1979; Hedges and Ertel, 1982). For example, lignin phenolic groups such as syringyl/vanillyl (S/V) ratio can be an important proxy to distinguish angiosperm from gymnosperm plants while cinnamyl/vanillyl (C/V) ratio can be used to differentiate woody from non-woody plant tissues (Hedges and Mann, 1979). The highest values of C/V ratio compared to S/V ratio are an indicative of the higher non-woody angiosperm contribution to the sedimentary OM. On the other hand, the S/V higher values compared to C/V ratio indicate a larger contribution of woody angiosperm tissue (Hedges and Mann, 1979; Kuzyk et al., 2008). When values of both ratios are close to zero, it indicates a contribution of vascular plants from gymnosperm group (Dittmar and Lara, 2001). Despite the importance of peatlands, there is still a great scarcity of scientific information related to these ecosystems in tropical regions. The main goals of this study were to assess the degree of humification and to characterize different types of vegetation through lignin compounds as a proxy of vegetation cover in two high mountain peatlands from the two oldest National Parks of Brazil.

2. Material and methods

Peat cores were collected from two Conservation Units of the Rio de Janeiro State. The first one is Itatiaia National Park – INP (22° 17′ 57″ S, 44° 37′ 15″ W, at 1888 m a.s.l.) being the oldest Brazilian National Park. The second one is Serra dos Órgãos National Park - SONP (22° 27′ 32″ S, 43° 1′ 37″ W, at 2117 m a.s.l.) (Fig. 1). Both sites are situated in highland forest environments, marked by low annual average temperatures (10 to 15 °C) and high level of humidity (annual rainfall of 2500 mm in INP and 3600 mm in SONP) (Nimer, 1979).

Peat cores (up to 0.50 m length and internal diameter of 10 cm) were collected from the soil surface into the basal substrate in each park. On average, the INP core had 41 cm depth and SONP had 30 cm. Each core was then sectioned with 1.5 cm resolution. The peatland soils of both sampling sites were classified as Typic Haplosaprists (Histosols order), as described by Embrapa (2013). Vegetation composition samples of both parks were identified in the following taxonomic families: Myrtaceae, Asteraceae, Euphorbiaceae, Rubiaceae, Leguminosae, Cyperaceae, Bromeliaceae, Fabaceae and with great predominance of Poaceae (ICMBio, 2013a, b).

Total organic carbon (TOC) and total nitrogen (TN) were analyzed in a Perkin Elmer Elemental Analyzer using approximately 10 mg of dry sample with a detection analysis limit of 0.05% and 0.03% for TOC and TN, respectively.

Analysis of lignin phenols in peat samples were performed according to Hedges and Ertel (1982) methodology. Approximately 200 mg of sample were transferred to a stainless steel vial and hydrolyzed with CuO in 8% NaOH under N_2 in an oxygen-free atmosphere at 155 °C for 3 h. The alkaline solution was acidified with pH values from 1 to 3 and the lignin phenols were extracted with ethyl acetate. After centrifuging, the supernatant was collected, dried with sodium sulfate (Na_2SO_4), evaporated under a steam of N_2, reconstituted in pyridine and converted to trimethylsilyl derivatives using bis-(trimethylsilyl) trifluoroacetamide (BSTFA) at 60 °C for 20 min. Ethyl vanillin was used as internal standard.

The extracts were analyzed on an Agilent gas chromatograph, model HP 6890 equipped with an ionizing flame detector (FID) in split mode (1:10), using a DB5 capillary column (J&W Scientific, 30 m long and internal diameter of 0.25 mm), programmed from 100 °C to 320 °C at 3 $°C·min^{-1}$ rate with hydrogen as carrier gas. The response factor was performed using a mixture of commercial standards in four different concentrations, which were periodically injected for calibration.

Phenol concentrations were reported as the carbon-normalized sum of eight lignin-derived reaction products ($\lambda 8$ mg 100 mg TOC^{-1}), including vanillyl (V - vanillin, acetovanillone, and vanillic acid), syringyl (S - syringealdehyde, acetosyringone, and syringic acid), cinnamyl (C - cumaric acid and ferulic acid) and 3.5-dihydroxybenozic acid (3.5 Bd). Ratios S:V and C:V were calculated to identify angiosperm tissue sources. The ratio of acidic to aldehyde vanillyl phenols ((Ad:Al)v) and 3.5-dihydroxybenzoic acid to vanillyl phenols (3.5 Bd/V) was used to indicate the level of diagenetic alteration and sources of terrestrial organic matter (OM) (Hedges and Ertel, 1982 and Kuzyk et al., 2008, respectively).

^{210}Pb activity was used to determine the sedimentation rates and the chronology. Gamma spectrometric measurements were conducted using a high-purity germanium detector (Canberra) housed in a lead shield, coupled to a multichannel analyzer. Activities of ^{210}Pb were determined following the method of Cutshall et al. (1983). Details of the cores' dating are provided by Lourençato et al. (2017).

3. Results and discussion

In accordance with Lourençato et al. (2017) the chronology of INP core showed an age of 1896 with a peat accumulation rate (PAR) of 0.18 $g\,m^{-2}\,yr^{-1}$ before the 1950s, while since 1950s it has had a PAR of 0.08 $g\,m^{-2}\,yr^{-1}$ (calculated by: $PAR = SR \cdot BD$; in which BD is the bulk density and SR is sedimentation rate). At SONP, the core reached an age of 1934 with a homogeneous PAR, around 10 $g\,m^{-2}\,yr^{-1}$.

Carbon accumulated in peat is important in mitigating the greenhouse effect, since OM is formed from the material carbon-rich material having been accumulated over past geological periods (Bispo et al., 2016). At INP, the mean of carbon content was 12%, and it was observed an increase since the 1950s (Fig. 2) with a coincident reduction in nitrogen contents (mean 0.43%) and historically reflect the intensive industrial development of this period in Brazil. Furthermore, an increase in C/N ratio from 38 prior to 1950 to 71 afterwards can be observed (Fig. 2). Drake et al. (1997) and Idso and Idso (1994) observed that plants growing under high CO_2 concentrations tend to fix more carbon through photosynthesis, showing greater biomass. Thus, the increase from industrialization can lead to increase atmospheric carbon and consequently, the increase in deposition of this element on litter and soil (Oertel et al., 2016). In this study, such evidence can be observed from 1950s in peatland surface (until a 15 cm depth). In the top of peatlands, have been frequent to find high C/N values, which can be associated to the litterfall that occurs from plants and trees, since they take up the nitrogen from their leaves during the wilting process (Cabral, 2012). Lower C/N ratios from periods preceding 1950s may be due to polysaccharide degradation (Ertel and Hedges, 1983; Müller and Mathesius, 1999; Bourdon et al., 2000). Furthermore, deeper peat tends to be older, suggesting that the lower C/N ratio may be associated with a more advanced state of decomposition. Kuhry and Vitt (1996) also