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Biogeochemical indicators of environmental changes from 50 Ka to 10 Ka in a humid region of the Brazilian Amazon

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ABSTRACT

We present a geochemical record of a 113.6-cm sediment core (LPT V) from Lagoa da Pata, which is located in the forested upper Rio Negro basin. The record reveals significant changes in the environmental history of Amazonia during the late Quaternary. The results of biogeochemical analyses revealed three hydrological and climatic regimes from 50,000 to 10,000 cal yr BP. The first phase, between 50,000 and 26,300 cal yr BP, was characterized by a relatively wet climate as suggested by relatively high total organic carbon (TOC) and chlorophyll derivate concentrations, indicating high productivity linked to a high lake level. A decrease of the TOC and chlorophyll derivate accumulation rates between 43,100 cal yr BP and 26,300 cal yr BP marks a decrease in the productivity linked to a reduced lake level, indicating a decrease in moisture at the end of this phase. The second phase, between 26,300 and 15,300 cal yr BP, was characterized by a decrease in productivity, reaching a minimum at 21,950 cal yr BP, as indicated by a minima in sedimentary chlorophyll and TOC accumulation rates. Values of $\delta^{13}C$ increased by 5‰ in relation to the preceding phase, indicating an influence of the C_4 organic matter. High iron concentrations and accumulation rates, related to intense erosion of the lateritic crust in the watershed, were observed. All of the observations indicate a dry phase during this period. A third phase, from approximately 15,300 to 10,000 cal yr BP, was characterized by an increase in lacustrine productivity, as shown by an increased in TOC and chlorophyll derivate concentrations and accumulation rates. These increases likely correspond to a lake level rise due to a wetter climate.

1. Introduction

Controversies continue over the extent of dry climates in the Amazon over the past 50,000 yr. Several studies have revealed large variations in climate and vegetation throughout the Amazonia during the late Quaternary (Ab'Saber, 1977, 1982; 1992; Absy et al., 1991; Martin et al., 1993; Tricart, 1974; Van der Hammen, 1974; Van der Hammenn and Absy, 1994; Wijmstra and Van der Hammen, 1966), indicating that the high biodiversity of this region is maintained by processes other than equilibrium conditions (Haffer, 1969, 1992; Prance, 1982; Vanzolini, 1970). Analysis of the geographical distribution of different taxa characteristic of seasonally dry tropical forest indicates that the taxa may have reached their maximum extension during a dry-cool period and must be considered in relation to the climate fluctuations of the late Quaternary (Pennington et al., 2000). Turcq et al. (2002b), Behling (2002) and Anhuf et al. (2006) concluded that the extent of the Amazon rainforest decreased considerably during the last glacial maximum (LGM).

One the most convincing records of these changes was obtained in the Carajás region in a 60,000-year palynological study from a lacustrine core located at Serra Sul. The study showed four intervals of substantially reduced forest cover and its replacement by savannah, suggesting dryer climates (Absy et al., 1991). These changes in vegetation from forest to savannah were accompanied by decreases in the total organic carbon (TOC) of lake sediments (Sifeddine et al., 1994a, 1994b, 2001). Based on this study and on palynological information from Rondonia (southeastern Amazonia), Van der Hammenn and Absy (1994) concluded that a cooler climate with relatively high rainfall existed in Amazonia from ca. 62,000 cal yr BP to 31,000 cal yr BP (60,000–26,000 ^{14}C yr BP). The climate became drier between 26,400 cal yr BP and ca. 17,200 cal yr BP (22,000 ^{14}C yr BP and ca. 14,000 ^{14}C yr BP) with a reduction in precipitation of 500–1000 mm (a reduction of 25 to 40%).

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However, pollen from a marine core collected at 3334 m depth about 400 km off the Brazilian coast, representing the production of all the vegetation in the Amazon basin, shows that the Amazonian forest was not extensively replaced by savannah vegetation during the last glacial period (Haberle, 1997; Haberle and Maslin, 1999). Hooghiemstra and Van der Hammen (1998) placed three restrictions on the interpretation of this result. First, many different environments supply the graminaceous pollen characteristic of open savannah-like vegetation, for example, floating grass-rich meadows on the Amazonian rivers and in the floodplains. The second restriction is the remobilization of mixed pollen grains in sediments from different source areas and of different ages, deposited together with fresh pollen. The third restriction concerns the gallery forests that often accompany river valleys in savannah areas. In the São Gabriel da Cachoeira area, the pollen diagram of Lagoa da Pata shows that forest vegetation was dominated by arboreal elements, including cold climate elements, during the last glacial (Colinvaux et al., 1996a, 1996b). This work showed that, despite changes in the pollen composition, no substitution of the forest physiognomy for the savannah occurred as observed for Carajás during the last glaciation (Absy et al., 1991). Based on stratigraphy, algal remains and geochemical data, Bush et al. (2004) suggested a decrease in precipitation in three different watersheds in Morro dos Seis Lagos, including Lagoa da Pata. Model simulations and paleoecological data (Bush and Silman, 2004) suggest a reduction in precipitation seasonality and lowered lake level at the LGM. Geochemical data from Lagoa da Pata published by Santos et al. (2001) showed that at approximately 21,470 cal yr BP (18,000 ^{14}C yr BP), there was a sudden accumulation of ~20 cm of clastic material from ferric crust. This event is represented by a sandy layer that has the lowest carbon level in the core. This layer corresponds to an intense erosion of the watershed indicating sudden and torrential rains concentrated in a drier climate regime.

In the Andean Amazonia, a paleoclimatic interpretation based on pollen composition (Bush et al., 1990) indicated a reduction in temperature of about ~7.5 °C from 38,300 to 35,200 cal yr BP (33,000 to 30,000 ^{14}C yr BP). The distribution of the vegetation taxa in the cores collected at fourteen sites from a 2000-m elevation gradient in the Napo Refuge of the Humid Tropical Forest suggests that changes in vegetation would not have been so extensive if refuges had existed in this area. The changes in vegetation were attributed to a temperature difference and not to aridity. In opposition, palynological studies in the northern Andes at different altitudes (Van der Hammen, 1974) demonstrated that during the period between 25,200 cal yr BP and 15,300 cal yr BP (21,000 ^{14}C yr BP until 13,000 ^{14}C yr BP) the climate was considerably drier.

Thompson et al. (1998), based on isotopic and ice accumulation data from Sajama Ice cap in the Andes, concluded that cold periods were generally wet in the Andean Altiplano. Glaciers in the Cordilleras of southern Peru and Bolivia appear to have expanded before the LGM, implying that cooler global temperatures were associated with greater precipitation and/or reduced evaporation in the subtropical Andes. Thompson et al. (1998) postulated cold and wet conditions from 25,000 cal yr BP to 22,000 cal BP. Based on anion concentrations in the same ice core, Thompson et al. (1998) considered that the maximum desiccation of Altiplano lakes occurred at 21,000 cal yr BP. Notwithstanding, Baker et al. (2001a, 2001b) concluded that Lake Titicaca was deep, fresh and continuously overflowing during the last glacial stage, from 25,000 to 15,000 cal yr BP, which means that during the LGM, the Altiplanos of Bolivia and Peru were wetter than they are today.

Paleohydrological reconstructions based on geophysical studies in the floodplain lakes of central Amazonia provide evidence not only against arid and semi-arid conditions but also against the persistence of the forest cover in the Amazon lowlands during the last glaciation (Müller et al., 1995). Paleovegetation modeling simulations (Cowling et al., 2001) of the lowland Amazon basin were made to assess the relative importance of glacial climate and atmospheric CO_2 on the alteration of vegetation type and structure. Simulated reductions in LGM leaf area index are more strongly affected by low atmospheric CO_2 than by decreased precipitation. Cowling et al. (2001) concluded that the glacial cooling was probably responsible for maintaining glacial forest cover due to reduce photorespiration and evapotranspiration.

In the present work, we present a sedimentary profile of Lagoa da Pata, core LPT V. We use several geochemical markers as indicators of environmental changes to elucidate the paleohydrological changes in this lake as well as changes in watershed processes. The results will be discussed and compared to those in previous studies of the region.

2. Environmental setting

2.1. Morro dos Seis Lagos

Morro dos Seis Lagos (Hill of Six Lakes) is located at 0°17′9.68″ N and 66°40′36.18″ W (LPT V core position) in the northern Amazon State, Brazil. It is within Pico da Neblina National Park, about 100 km north of São Gabriel da Cachoeira city and northwest of Manaus. Access to the Morro is by Igarapé Iamirim, which crosses the highway between São Gabriel da Cachoeira and Cocui City, Venezuela (Fig. 1).

A thick lateritic crust rich in iron, niobium and rare earth elements characterizes the area around the Morro dos Seis Lagos. Two-thirds of the area is covered with brown to black iron hydroxides that are compacted into a hard mass (Corrêa et al., 1988). Very intense weathering caused the development of a changed cover, with a thickness exceeding 200 m (Corrêa et al., 1988). The upper course of the Rio Negro basin, where Morro dos Seis Lagos is located, is an undulating plain with an elevation of 75 m. Morro dos Seis Lagos rises about 360 m above this plain and features closed depressions occupied by the six lakes. The water levels of the six lakes vary in direct proportion to precipitation. Even though the lakes are always filled with water, there is no overflowing, suggesting a percolation system inside the lateritic crust via caves and fractures (Viégas Filho and Bonow, 1976).

The vegetation in the plain surrounding the hill is Dense Tropical Forest (Floresta Ombrofila Densa) developed on extremely poor soils. The vitality of the forests is maintained by the local hot and moist climatic conditions, which quickly recycle nutrients in the upper layers of the forest soil. These conditions allow the development of forest physiognomy in the flat areas of Morro dos Seis Lagos.

Observations during the field work indicate, from the base to the top of the hill, a transition from Dense Tropical Forest to a more open forest with low arboreal strata, lichens, and large C4 plants, such as grasses, bromeliads and orchids. The plants grow over entangled superficial roots on the lateritic crust. At the top of the hill, plant communities with trees up to 20 m high are prevelant.

The climate in the area is hot and humid, without a marked dry season and with a total annual precipitation of approximately 3000 mm. The area experiences a decrease in precipitation from July to November. The driest month is September, when precipitation levels are approximately 150 mm (IBGE, 1959).

2.2. Lagoa da Pata description

Lagoa da Pata, which is about 400 m long and 4 m deep, is surrounded by dense tropical rain forest and has never been impacted by human activities. Details on lake sediment stratigraphy and palynology have been published previously (Colinvaux et al., 1996a). The lake water is very soft (2 to 5 µS), with a pH of ~5, a color of 50 ptn (platinum units) and a temperature ranging from 28 °C to 30 °C (Justo and Souza, 1984).

Chemical analyses of the water of Lagoa da Pata show that its composition is very similar to the composition of rainwater in the area

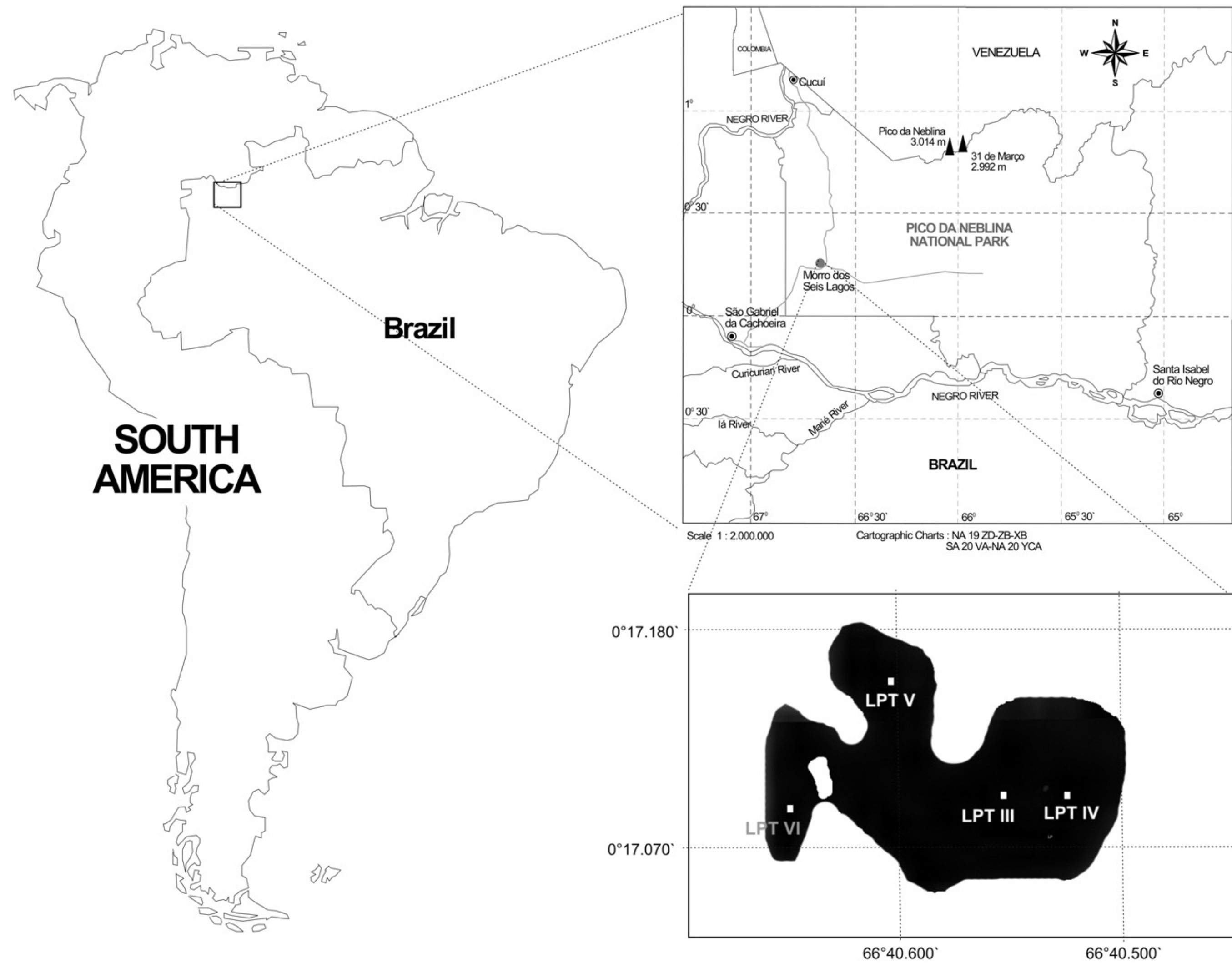

Fig. 1. Location of Morro dos Seis Lagos, Lagoa da Pata and the position of the cores collected during the 1997 expedition. The results from LPT III and LPT VI were published by Barbosa et al. (2004), and the results from LPT IV were published by Santos et al. (2001).

(Table 1). This indicates a low input of nutrients through runoff from the drainage basin. The primary productivity of the lake is probably maintained by internal cycling of nutrients.

Lagoa da Pata has a surface area of approximately 150,000 m² and subdivides into four break-up alveoli. The main pigments in the water column (chlorophyll a, b, c, carotenoids and phaeopigments) when analyzed by colorimetry show that the lake contains low concentrations of chlorophyll a (1.56 mg m^{-3}) and chlorophyll b (1.09 mg m^{-3}). The chlorophyll c concentration was relatively high (3.01 mg m^{-3}). Total carotenoids were about 2.08 mg m^{-3} (Cordeiro, 2000, Table 1).

3. Methods

The 113.6 m Lagoa da Pata core V (LPT V) was collected with a piston corer at a water depth of 5 m. The core was sliced into 1-cm layers. The bulk density of each layer was obtained by removing 8 cm³ of a wet sediment section and drying it at 60 °C to the constant weight. Seven accelerator mass spectrometry (AMS) radiocarbon dates from bulk organic matter were used to determine chronology. The ^{14}C AMS ages were transformed into calendar ages using INTCAL98 for ages less than 24,000 ^{14}C yr BP (Stuiver et al., 1998); for older ages, we used the radiocarbon curve calculated by Fairbanks et al. (2005), which is based on U/Th dating of corals. The calculations performed here were made using the CAL Pal program (Weninger, and Jöris, 2004, 2007). A continuous age scale based on interpolation of the calibrated radiocarbon ages was calculated for LPT V so that results could be presented on a time axis. These interpolations are commonly based on the age-vs.-depth curve. We used an alternative method based on the age-vs.-accumulated mass curve described by Turcq et al. (2002a).

Table 1
Physical–chemical parameters measured in rainwater, Lagoa da Pata surface water and Lagoa da Pata water at a depth of 5 m. Santos et al. (2001).

	pH	Cond (μS/cm)	Cl^- (μmol/l)	NO_2 (μmol/l)	NO_3 (μmol/l)	SO_4 (μmol/l)
Rain and Lagoa da Pata surface waters	5.05	6.81	5.20	2.91	0.54	1.32
Lagoa da Pata 5 m depth	4.99	6.72	2.54	3.05	0.37	0.99
Rainwater 16/05/1997 to 19/05/1997	5.23	4.78	8.80	1.91	0.59	0.90
Rainwater 19/05/1997 to 22/05/1997	5.35	3.48	2.47	1.45		1.27
Rainwater 22/05/1997 to 24/05/1997	5.57	3.49	5.34	2.02	0.38	0.97

The values of TOC, total organic nitrogen (TN), $\delta^{13}C$ and $\delta^{15}N$ were obtained with a mass spectrometer coupled to an automatic elemental analyzer (PDZ-Europa Tracermass-Roboprep 34 S) in the Environmental Isotope Laboratory of the University of Waterloo (Canada). Nitrogen and carbon isotope ratios are reported in the conventional-notation with respect to atmospheric N2 (AIR) and the V-PDB (Pee Dee Belemnite) carbonate standard, respectively.

Chlorophyll-derived pigments in lake sediments record the paleotrophic state of the lake (Gorham, 1960; Gorham et al., 1974; Guilizzoni et al., 1983; Lewis and Webezahn, 1981; Swain, 1985). Variations in the 667/448 ratio (chlorophyll derivates/total carotenoids) indicate changes in the oxidative environment due to greater exposure to a higher water column, promoting the preferential degradation of carotenoids. (Gorham et al., 1974; Swain, 1985). Steenbergen et al. (1994), who studied the sedimentation and degradation of pigments in a lake in the Netherlands, stated that when conditions favor the degradation of the native chlorophyll, the CD/TC ratio is high, indicating that oxidizing conditions resulted in a more pronounced degradation of carotenoids. Chlorophyll derivates were extracted with 90% acetone and measured at 667 nm. The results are expressed in arbitrary units as absorbance per gram of organic matter, where one unit (SPDU) is equal to an absorbance of 1.0 in a 10-cm cell when the derivates were dissolved in 100 ml of solvent (Swain, 1985).

Quantification of charcoal particles included a microscopy technique. One gram of wet sediment sample was subjected to an alkaline extraction with 10% NaOH. The sediment sample was then washed with distilled water and stored wet in a 100-ml water solution. From the 100-ml solution, 2 ml was taken during agitation and then filtered through a cellulose acetate filter (Millipore, HAWP 24 mm, 0.45 µm porosity). The filter was dried, weighed and then glued with ethyl acetate to a Plexiglas sheet. A minimum of twenty fields were counted to reach a minimum of 30 particles from 2 µm to 350 µm in size for each counted type under 250× magnification. Weighing the filters allowed us to quantify the particles relative to sediment dry weight and to calculate the accumulation rate. In fire history reconstructions, charcoal particles of >125 µm are often considered because studies of charcoal deposition have shown that such large particles are not transported by winds and, therefore, provided a record of fires occurring inside the lake watershed (Clark and Patterson, 1997; Millspaugh and Whitlock, 1995). In our study, the counts of smaller charcoal fragments provide an estimate of regional fires (Cordeiro et al., 2008). Counting and measuring were performed with a system consisting of a Leitz Diaplan microscope in transmitted and reflected white light connected to a camera and monitor (Cordeiro, 1995, 2000; Cordeiro et al., 1997, 2008; Elias et al., 2001).

The method used to determine black carbon was adapted from Lim and Cachier (1996) and is based on the isolation of black carbon through successive steps to eliminate the humic acid fraction (NaOH 5%), the carbonate fraction (3 M HCl), the silicate fraction (10 M HF/1 M HCl) and labile organic matter (2 M H_2SO_4/0.1 M $Cr_2O_7^-$). After these three isolation steps, the residual carbonaceous material was measured with a Carbon–Nitrogen analyzer (Perkin Elmer). Black carbon differs from unburned humin in having greater resistance to oxidation in acid solutions, with a half-life ranging from 1500 to 2000 h, in contrast to that of 5 h for humin (Kulhlbush and Crutzen, 1996).

Elemental analyses were carried out on a Jobin Yvon Ultima 2 sequential ICP-OES. All water (18 MΩ cm resistivity) used throughout the experimental work was obtained with a Simplicity Milli-Q Water System (Millipore, Milford, MA, USA). The trace metal recovery efficiency of the analyses was evaluated by simultaneous analysis of a reference material (NIST Industrial Sludge 2782) in duplicate. The results of both reference material analyses showed good recoveries (78%–97%).

For mercury determination, sediment samples were dried at 40 °C to a constant weight prior to digestion. Duplicate sub-samples of about 1.0 g were digested in 50% *aqua regia* for one hour at 70 °C in a closed system. Mercury was analyzed by CVAAS (cold vapor atomic absorption spectrometry) in a Bacharach MAS-50D mercury analyzer system. Simultaneous determination of mercury in reference standards (NIST - USA, "Buffalo River sediments"; with 60 ng g^{-1} of mercury) was performed using the same analytical procedure, and the results were 58 ± 6 ng g^{-1} ($n = 15$).

Finally, radiographs of the sediment were obtained with a SCOPIX device at EPOCH, Bordeaux I University (France).

Table 2
Stratigraphy of LPT V, Lagoa da Pata.

Depth (cm)	Description
0.0–39.7 cm	Very dark brown organic clay 10 YR 2/1
39.7–43.2 cm	Brown clay 10 YR 4/6. Discordant contact.
43.2–113.6 cm	Brown organic clay 10 YR 3/1 with lighter laminations 10 YR 3/2.

4. Results and interpretation

4.1. Lithology, chronology and sedimentation rates

Visual and petrographic observations of the sediment revealed three sedimentary units in the 113.6-cm LPT V core (Table 2): Zone 3, 113.6 to 43.2 cm, organic-rich clay (10 YR 2/1) with dark laminations; Zone 2, 43.2 to 39.7 cm, mineral rich clay (10 YR 4/6); and Zone 1, 39.7 cm to the top of the core, very organic-rich clay (10 YR 3/1).

The upper part of the core, which corresponds to ca. 9500 cal yr BP, was lost during coring. The sedimentation rate was estimated by linear extrapolation as calculated from the calibrated ages and accumulated mass values of the respective sections (Table 3, Fig. 2, Fig. 3).

Radiographs of LPT V (Fig. 3) allow the median X-ray grey level for each core slice to be compute (Fig. 4). The X-rays are absorbed more by silicate material than by organic matter. Consequently, the silica-rich horizon is shown in white. The absorption of X-rays is dependent on the radiation wavelength, on the density and width of the sample and on the atomic number of the absorbing material (Axelsson, 1983). The grey levels of the image show a good correlation ($r_2 = 0.89$, $n = 32$, $p < 0.05$) with the carbon content in a laminated core from Laguna Pallcacocha (Ecuador) (Rodbell et al., 1999). In LPT V (Fig. 4), a significant coefficient of correlation was obtained between carbon and the X-ray image ($r_2 = 0.86$, $n = 110$, $p < 0.05$).

The limits of the sedimentary facies can be defined very precisely and at a high resolution (0.215 mm) in the X-ray record. This sedimentary proxy indicates beginning of the glacial period at 26,300 cal yr BP, which is represented, as we will see, by a low lake level. The shift to a period of high water level began at 15,500 cal yr BP (Fig. 4).

^{14}C calibrated ages do not show any evidence of a hiatus in the sedimentation (Fig. 2), meaning that the apparent unconformity observed at 43 cm in the X-ray image (Fig. 3) is an artifact produced by the vibrocorer. We have previously observed such artifacts when soft sediment layers upon a harder layer.

Table 3
Radiocarbon dates from LPT V. Calibration ages until 24,000 ^{14}C BP calculated according to Stuiver et al. (1998), older ages following Fairbanks et al. (2005).

Lab number	Depth (cm)	^{14}C age (yr BP)	Age error	Cal ages (yr BP)	Age error
Beta-118630	5.0–8.0	9430	±70	10,690	±100
Beta-118631	32.0–35.0	12,420	±90	14,450	±190
AA57994	37.0–38.0	12,595	±61	14,800	±80
AA57995	40.0–41.0	16,939	±89	20,110	±120
Beta-118632	44.0–46.0	29,080	±290	33,930	±610
Beta-118633	66.0–68.0	38,790	±840	43,330	±690
Beta-118634	106.0–108.0	45,480	±1300	48,470	±1230

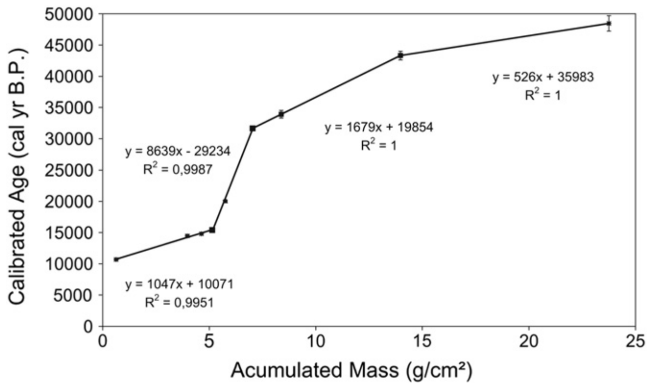

Fig. 2. ^{14}C age versus sediment depth in LPT V and the X-ray profile.

The presence of sedimentation hiatuses in Lagoa da Pata seems to depend on location at Lagoa da Pata. In LPT V and in the Colinvaux et al. (1996a, 1996b) records, no sedimentation hiatuses were observed. Ledru et al. (1998) discussed the possible presence of a hiatus in the Colinvaux et al. (1996a, 1996b) record, but new dating shows that the sedimentation is, in reality, continuous (Bush et al., 2004; Colinvaux et al., 2000). Nevertheless, Santos et al. (2001) identified a hiatus in another Pata core, LPT IV, from 29,800 cal yr BP to 19,200 cal yr BP. The considerable decrease in the sedimentation rate (Fig. 3) and carbon accumulation rate (Fig. 4) observed in LPT V between 26,300 cal yr BP and 15,300 cal yr BP was synchronous with this hiatus.

4.2. Total organic carbon, total nitrogen, C/N ratio, δ^{13}C, δ^{15}N and sedimentary pigments

The quantitative (Fig. 5) and qualitative (Fig. 6) composition of organic matter shows a clear distinction between the three major sedimentary phases.

Zone 3 (50,000–26,300 cal yr BP) is characterized by moderate concentrations of TOC (from 12.9 to 25.2%), high values of C/N ratio (from 26.2 to 34.6%) and δ^{15}N (from 1.32 to 2.19‰), and low values of chlorophyll derivates. These characteristics correspond to a predominance of allochthonous organic matter, which can also be indicated by the presence of macrodebris (mainly leaves). The low productivity evidenced by low values of sedimentary chlorophyll (average value of 0.32 SPDU) and total organic carbon is probably associated with a low water level. The δ^{13}C values range from −35.4 to −27.2‰. The highest values correspond to a period of lower TOC concentrations between 48,200 (104.6 cm) and 47,300 cal yr BP (98.4 cm). The lowest values (at approximately 87 cm) correspond to relatively high COT and chlorophyll concentrations. These low values of δ^{13}C can be explained by the input of large amounts of isotopically light, soil-derived dissolved inorganic carbon to the lake, which can lead to local production of isotopically light algal organic matter (~−32‰) (Meyers, 1997, 2003). The δ^{15}N values varied between 1.32‰ and 2.19‰, considerably higher than the values found in the two subsequent phases (Fig. 5). The δ^{15}N values in LPT V had a positive and significant correlation with the C/N ratio (Fig. 4; $r = 0.77$, $n = 112$, $p < 0.05$) and a negative and significant correlation with the sedimentary pigments (Fig. 5), suggesting that the high δ^{15}N values are not related to lacustrine primary production but that they come from the allochthonous matter from the catchment vegetation. Denitrification may be a relevant process occurring in Zone 3, where δ^{15}N has its highest value. This process is the one by which nitrate is reduced to gaseous nitrogen species (usually N_2 or N_2O) and is the dominant mechanism for removal of fixed nitrogen from the biosphere (Altabet et al., 1994). It is mediated by bacteria in suboxic environments. Denitrification produces substantial ^{15}N enrichment in subsurface nitrate (Altabet et al., 1994) and could be an important process in Lagoa da Pata in this phase.

In Zone 2 (26,300 cal yr BP to 15,500 cal yr BP), TOC decreases to its lowest values in the core, ranging from 3.07% to 5.08%. Low values of chlorophyll derivates were observed (approximately 0.094 SPDU). There was a sharp decrease of the lacustrine productivity relative to the preceding phase, probably associated with a drop of the lake level, leaving allochthonous organic matter in the sediment. δ^{13}C varied between −22.3‰ and −26.2‰ and was influenced by organic matter richer in heavy carbon (Figs. 5 and 6). The presence of isotopically heavier carbon indicates the delivery of organic matter from type C4 species (e.g., grasses from the catchment or lacustrine macrophytes). Expansions of type C4 plants are due to the ability of C4 plants to use CO_2 more efficiently than C3 plants. Thus C4 plants can achieve the same rate of photosynthesis as C3 plants with smaller stomatal openings, thereby retarding water loss (Huang et al., 2001; Mayle and Beerling, 2004.). This ability enables C4 plants to withstand drought stress, allowing them to expand in dry periods. The increase of δ^{13}C values can be attributed to increased water stress in the Lagoa da Pata vegetation. The δ^{13}C signal, therefore, seems to be more sensitive to

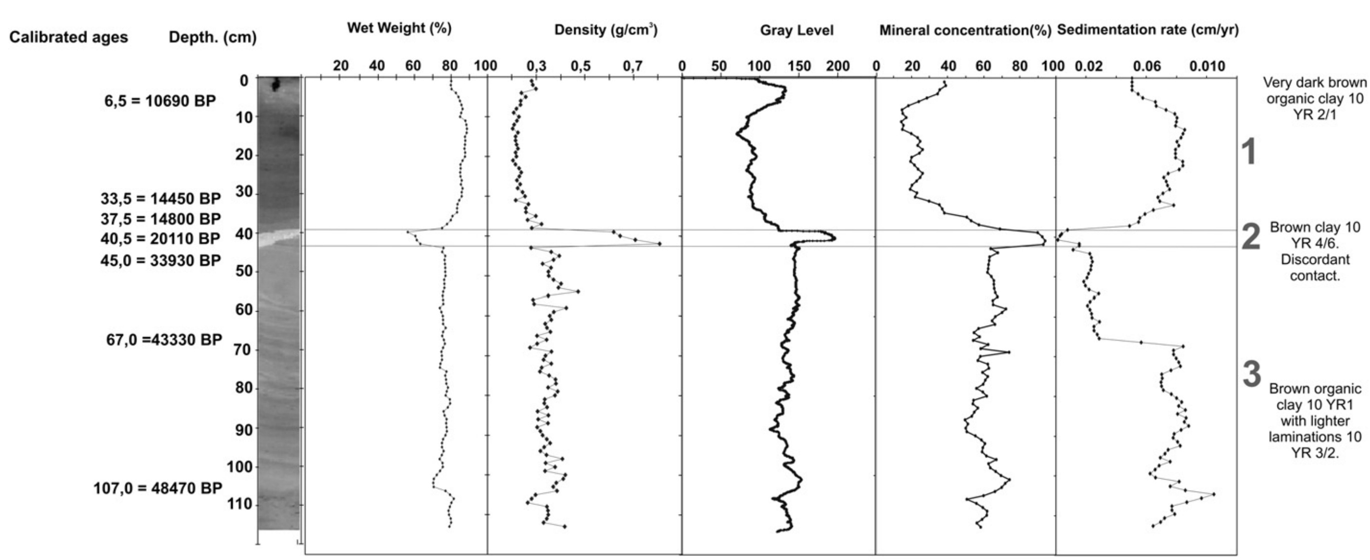

Fig. 3. Changes in sedimentary facies and wet weight, density, gray level and mineral content of the core in the first profile.

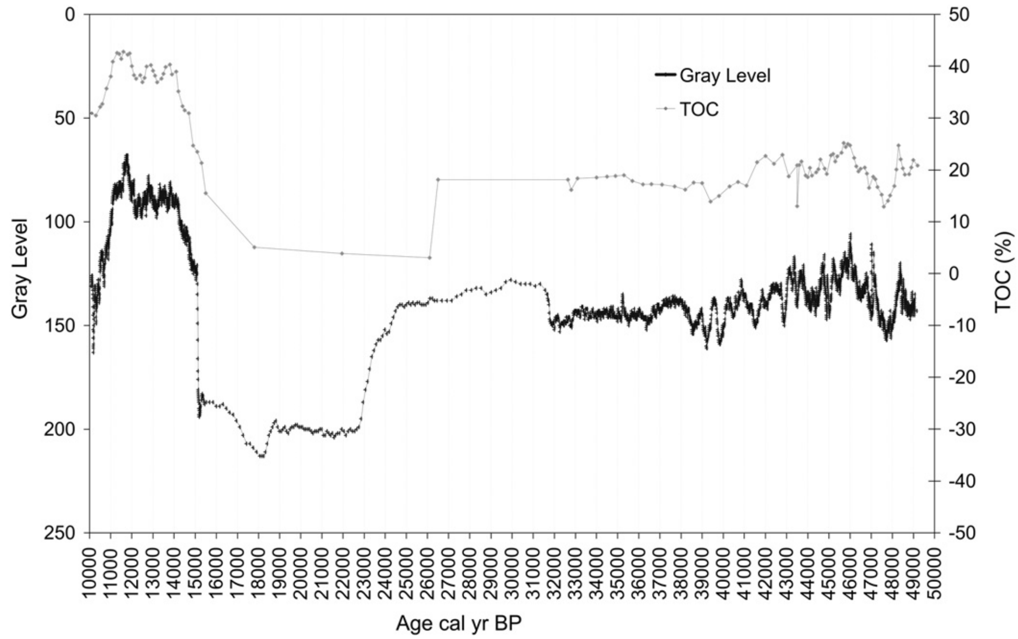

Fig. 4. Gray level depending on interpolated, calibrated ages. The age models used are shown in Fig. 2, and they were calculated as in Turcq et al. (2002a).

water stress than the pollen signal, which indicates a permanency of regional forest vegetation at that time (Colinvaux et al., 1996a, 1996b) the $\delta^{15}N$ value ranged from 2.27‰ to 1.46‰, decreasing from the end of the earlier sedimentary facies.

In Zone 1 (15,500 cal yr BP-10,000 cal yr BP (40.7 to 0 cm), TOC and TN contents increased substantially from 15.5% to 42.6% and from 0.72% to 2.02%, respectively. The C/N ratio values decreased and varied between 19.7 and 27.3, which probably represents an increase of phytoplanktonic organic matter input compared to Zones 3 and 2. Chlorophyll derivates reached their highest average values of 0.9 SPDU, with a maximum value of ca. 1.4 SPDU, indicating an increase in productivity associated with an increase of the water level in the lake. The average value at this stage is about three times higher than that of Zone 3 and about 10 times higher than that of Zone 2 (Fig. 5). The $\delta^{13}C$ values oscillated between −34.2‰ (33.2 cm, 14,350 cal yr BP) and −30.1‰ (13.0 cm, 11,750 cal BP). These values show a predominance of algal material that captures remineralized carbon from organic matter degradation, as in Zone 3. The $\delta^{15}N$ values decreased in the beginning of this phase but increased in the end and ranged from −0.75‰ to 1.63‰.

The total organic carbon accumulation rate averages 2.90 g/m²/yr for the entire record. The accumulation rate from 50,000 to 26,300 cal yr BP (Zone 3) had an average value of 2.79 g/m²/yr. In this phase, we observed a tendency for a decrease in the total organic carbon accumulation rate, principally after 43,100 cal yr BP. After 26,300 cal yr BP, the decrease in the TOC accumulation rate is more pronounced, reaching a minimum value of 0.0284 g/m²/yr at 22,000/18,000 cal yr BP. After that, an increase in TOC accumulation rate occurred, reaching 4.40 g/m²/yr in 11,600 cal yr BP.

4.3. Accumulation rates of number and area of charcoal particles and black carbon

The charcoal and black carbon concentrations and the size of the charcoal particles are presented in Fig. 7. These proxies are often expressed by their accumulation rate for further comparisons (Carcaillet et al., 2002; Cordeiro et al., 2008).

The charcoal particle accumulation rate in LPT V is high at ca. 50,000 cal yr BP (Fig. 7). A declining trend starting at approximately 43,300 cal yr BP is especially strong between 38,500 and 35,000 cal yr

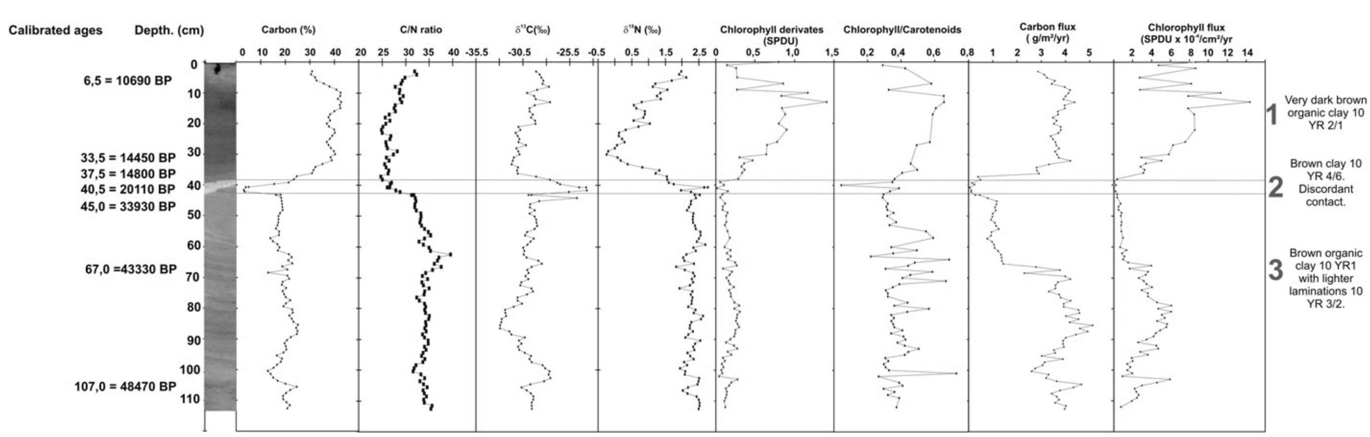

Fig. 5. Changes in sedimentary facies and organic parameters of LPT V. Carbon content, C_{org}/N_{org} molar ratio, $\delta^{13}C$, $\delta^{15}N$, chlorophyll derivate concentration, chlorophyll/carotenoids ratio, carbon accumulation rate and chlorophyll derivate accumulation rate for LPT V.

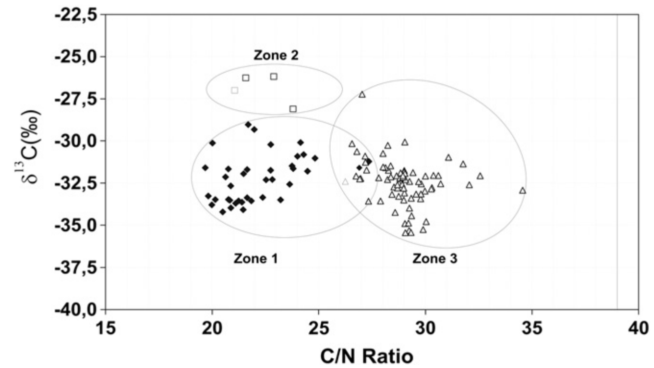

Fig. 6. Diagram showing the relationship between the C/N ratio and δ^{13}C. Three distinct phases are observed: 1) between 113.6 cm and 43.2 cm, with a significant contribution of terrestrial organic matter with low values of nitrogen in relation to carbon; 2) between 43.2 cm and 39.7 cm, the δ^{13}C increase by 5‰ representing dilution of the organic matter from C3-type plants; and 3) between 39.7 cm and 3.0 cm, the low values of C/N ratio indicating an increase in algal influence.

BP (Fig. 7). The highest value found was 12×10^3 particles/cm²/yr at 47,000 cal yr BP. The same trend is observed in the charcoal area accumulation rate since the beginning of the record at 50,000 cal yr BP. The maximum value was observed at 48,300 cal yr BP; it was 4.55×10^6 μm²/cm²/yr, showing greater occurrences of fires close to the drainage basin of the lake. The decrease of the number of particles between 43,000 cal yr BP and approximately 35,000 cal yr BP suggests a decrease of burning, probably due to a lower evaporation rate related to a decrease in temperature during this period. Increased fluxes between 35,100 cal yr BP and 20,300 cal yr BP were observed compared to the preceding phase. It should be considered that the organic indicator showed a decrease in the lake level during this period, suggesting a decrease in precipitation. After the last glacial maximum, an increase of charcoal particles was observed, reaching 5×10^3 particles/cm²/yr at 10,300 cal yr BP (Fig. 7).

The maximum accumulation rates of charcoal observed in Lagoa da Pata were 3.5 times lower than were observed during the dry climatic phase between 7600 cal yr BP and 4750 cal yr BP in the Carajás region, with an average value of ca. 42×10^3 particles/cm²/yr (52.5 cm).

The accumulation rates of black carbon are also high between 48,400 cal yr BP and 41,800 cal yr BP, reaching 0.15 mg/cm²/yr at 48,400 cal yr BP and 0.19 mg/cm²/yr at 44,300 cal yr BP. The latter value is the highest flux observed in the record. The black carbon flux shows a similar tendency as observed for charcoal particle deposition, with a decrease beginning mainly at 41,360 cal yr BP and remaining low until ca. 35,000 cal yr BP. Between ca. 35,000 cal yr BP and 16,600 cal yr BP, a considerable increase in black carbon flux was observed, reaching a value of 0.0666 mg/cm²/yr. At least from 15,100 cal yr BP to 14,400 cal yr BP, a substantial decrease in the BC flux was observed. Between 14,000 cal yr BP and 10,100 cal yr BP, large fluctuations in the BC flux were observed, with a maximum value at this stage reaching 0.0895 mg/cm²/yr at 10,100 cal yr BP. The black carbon accumulation rates recorded in LPT V were considerably lower than the ones observed in an intense land use change area at Alta Floresta (MT, South Brazilian Amazonia, 9º58′ S, 55º49′ W). In a sedimentary record representing the period from 1978 to 1996, a black carbon flux of approximately 7–8 mg/cm²/yr was observed during a period of intense land use change in this area (Cordeiro et al., 2002).

4.4. Lithogenic elements and mercury concentrations and accumulation rates

The concentration of iron along the profile has a mean value around 7.34%. At the base of the core, from c.a. 50,000 cal yr BP to 46,500 cal yr BP, high values ranging from 9.0 to 9.8% were observed, decreasing to levels ranging from 8.78 to 5.68% from 46,500 cal yr BP to 33,800 cal yr BP (Fig. 8). A gradual increase was observed starting at 33,800 cal yr BP, with maximum values between 28,000 cal yr BP and 20,000 cal yr BP (Fig. 8). From the end of the LGM, values of iron showed a gradual decrease. Aluminum has a mean concentration of 0.35% in the profile, which is considerably less than the iron concentration of 7.34%. The variability in the aluminum profile (coefficient of variation = 13%) is lower than that observed for iron (coefficient of variation = 25%).

The trend and variations of aluminum and iron profiles are almost opposite to each other (Fig. 8). Changes in temperature and moisture in different climatic regimes in the Morro dos Seis Lagos region could have acted distinctively on the lateritic crusts, causing differential weathering of iron relative to aluminum. Horbe and da Costa (2005) demonstrated that weathering under hot and humid climates in the Carajás region favored the transformation of lateric crusts into soils. This transformation caused an enrichment of aluminum minerals in the surficial soil layers. This kind of weathering of lateritic crusts probably represents a continuous source of aluminum for Lagoa da Pata sediments. Periods of increased deposition of aluminum would be related to a wet climate when rainfall was more evenly distributed, enabling the mobilization of aluminum from surficial layers of the soils that surround Lagoa da Pata. Conversely, higher iron content during the LGM is a consequence of the presence of gossan fragments

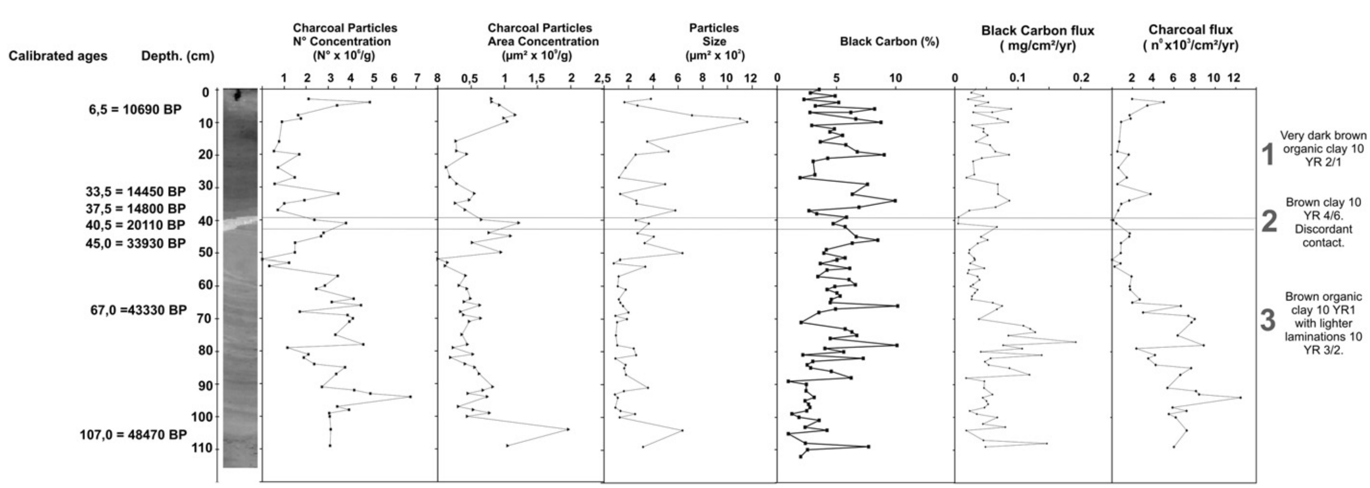

Fig. 7. Changes in sedimentary facies and concentration of charcoal particles in number and area, size of the charcoal particles, black carbon concentration, black carbon accumulation rate and charcoal particle accumulation rate.

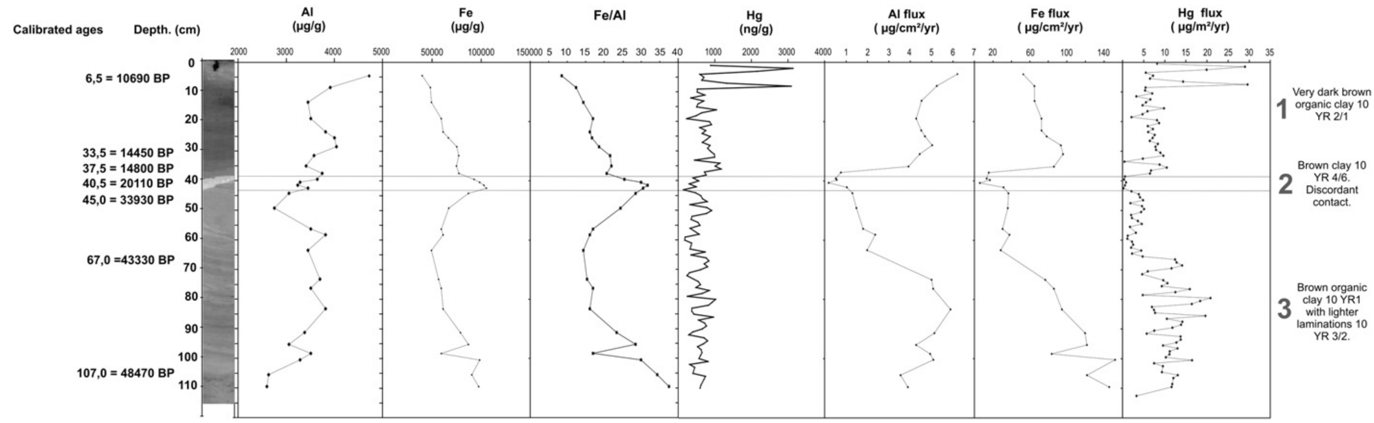

Fig. 8. Changes in sedimentary facies and concentrations of iron, aluminum, mercury and accumulation rate of iron, aluminum and mercury.

due to physical erosion and transport of these fragments to the lake. Such intense erosion of the lateritic crusts is certainly due to torrential rains. Phases of higher iron deposition in relation to the aluminum deposition occurred between 48,900 cal yr BP and 47,000 cal yr BP and from 36,000 cal yr BP to 16,000 cal yr BP. A remarkable decrease of the Fe/Al ratio beginning at 16,000 cal yr BP, when the organic indicators showed an increase in lake water level. In the Pata bay, where LPT IV (Santos et al., 2001) and LPT III (Barbosa et al., 2004) cores were collected (Fig. 1), a clastic facies with five datings around 22,400 cal yr BP (18,700 14 C yr BP) was found, corresponding to the peak of Fe/Al ratio in LPT V. It represents the occurrence of sudden and torrential rains typical of a dry climate on a very local scale and marks the end of the LGM. Turcq et al. (2002b) have also identified a phase of intense slope erosion in Amazonia at the end of the glacial period. Marine cores registered increased clastic sedimentation due to greater continental erosion after the LGM (Atz et al., 2000), and a million-year-old core off the Amazon river mouth shows that detrital peaks occurred at each shift from a glacial stage to an interglacial one (Harris and Mix, 1999).

Mercury concentrations in LPT V have a background concentration of 650 ng/g. These values are high compared to values found in gold exploration areas in the Amazon basin. The Hg concentrations in a sediment core from the gold mining area (Alta Floresta, MT) showed background concentrations of 50 to 70 ng/g in the lowest 30 cm followed by a sharp increase in the first 10 cm, with a maximum of 175 ng/g in the surface layer (Cordeiro et al., 2002; Lacerda and Solomons, 1998). The average mercury accumulation rate for the last 50,000 cal yr BP was 8.16 $\mu g/m^2/yr$ (Fig. 8), with a maximum flux of 29.6 $\mu g/m^2/yr$ and a minimum flux of 0.18 $\mu g/m^2/yr$. The mercury accumulation rates were low compared to those calculated for lakes affected by mining activities, such as those in Poconé, northwestern Brazil, where they are from 60 to 180 $\mu g/m^2/yr$ (Lacerda and Solomons, 1998), and Alta Floresta (MT, center-west Brazil), where the average flux from 1978 to 1998 was 510 $\mu g/m^2/yr$, with a maximum flux of 825 $\mu g/m^2/yr$ (Cordeiro et al., 2002). Therefore, the high Hg concentration found in LPT V is due to the low sedimentation rates that represent 500 to 1000 years of deposition in only a 1-cm slice. The results obtained for this core show the same patterns that have been observed in LPT IV (Santos et al., 2001), LPT III (Barbosa et al., 2004) and at other Amazon sites (Lacerda et al., 1999) with high accumulation during the Holocene. The distribution of mercury did not correlate with the distribution of lithogenic elements such as iron and aluminum (Fig. 8). This fact and the lack of any mercury-bearing geological formation in the lake's basin suggest that atmospheric deposition is the most significant source of mercury in Lagoa da Pata sediments. This process probably corresponds to global degassing, which at this low frequency would occur at oceanic and terrestrial sources in response to changes in the global temperature and climate. The terrestrial source could be linked to change in dynamics of vegetation change and forest fire occurrence.

5. Paleoclimatic interpretations

Changes in lake level imply fluctuations in the hydrological balance as associated to precipitation and evaporation However, the changes here described in Lagoa da Pata shown the significant changes in hydrological balance didn´t observed in palynological record shown by Colinvaux et al. (1996a, 1996b). The differences suggest that vegetation determined by pollen grain concentration from the Lagoa da Pata record was largely induced by the variables that forced the low lake level phase identified in the biogeochemical signatures mainly between 26,000 and 15,500 cal yr BP. The data presented in this work are variant with respect to the interpretations made by Colinvaux et al. (2000) of a Pleistocene climate change in Amazonia that affected only temperature and not precipitation. According to Cowling et al. (2001), the preservation of the forest can be explained by the fact that glacial cooling was probably responsible for maintaining glacial forest cover by reducing photorespiration and evapotranspiration. Another important factor was suggested by Bush and Philander (1998), who estimated that global mean specific humidity at the LGM was 10% less than at present. However, relative humidity increased by 5% because of the decrease in saturation vapor pressure induced by colder temperatures. Van der Hammen (1974) estimated in ca. 3 °C and more recently Hooghiemstra and Van der Hammen (1998) estimated in ca. 4.5°, lower temperature in the tropical lowlands during glacial times. Following Van Der Hammen and Hooghiemstra (2000) the period that lasts from approximately 60,000–32500 cal yr BP is a period with a generally cold and wet climate conditions corresponding to the high level of paleoprodutivity indicators observed in LPT V core. Between 32,500 cal BP to 15,300 cal BP (ca. 28,000–13,000 ^{14} C BP) the climatic conditions were very cold and very dry, which correspond to our interpretations about the biogeochemical indicators in Lagoa da Pata. Between 15290 cal yr BP and 11500 cal yr BP (13,000–10,000 BP) the occurrence of a sudden increase in temperature and rainfall were interpreted. It may well be that the lowland vegetation maintained a forest physiognomy over the past 40,000 years (Bush et al., 2004; Colinvaux et al., 1996a, 1996b) due to the lower glacial temperature. Bush et al. (2004) suggest that the observed cyclic reduction in lake level observed at Lake Pata was the result of a reduced wet season precipitation considering that during wet season precipitation could significantly affect the lake level without causing a change in the forest. However, the pollen composition in Lake Pata must be further investigated because in the LPT IV and LPT V cores were observed changes in the quality of organic matter (carbon isotopic composition) probably due to an influence of grass vegetation mainly between 26,000 to 22,800 cal BP.

The biogeochemical proxies in the LPT V profile indicate a decrease of the precipitation/evaporation balance culminating at 22,000 cal yr BP, coincident with the retreat of glaciers in the Andes. Based on cosmogenic ^{10}Be ages of moraines, Smith et al. (2005) proposed that glaciers in Peru and Bolivia reached their greatest extent from ~34,000 cal yr BP to 22,000/21,000 cal yr BP, after which the glaciers retreated. Smith et al. (2005) interpreted glacier expansion as related to a cold and wet climate, they determined that the deglaciation after 22,000 yr BP was due to a temperature increase. This conclusion is in agreement with previous studies in Bolivia showing high lake levels during the LGM for Titicaca Lake (Baker et al., 2001a) and Salar de Uyuni (Baker et al., 2001b). More recently, Hillyer et al. (2009), in a study of diatom assemblages in a Peruvian Andes lake, showed a short reduction in lake level at 23,500 cal yr BP but with lake levels oscillating and remaining generally high until ca. 16,000 cal yr BP. Changes in the sedimentation in Titicaca Lake and Lake Junin were determined using magnetic susceptibility as an indicator of mineral sedimentation and sedimentation rate. These proxies indicated an influence of inorganic sedimentation and decreasing terrigenous input between 30,000 and at least 19,500 cal yr BP. The deglaciation process is evidenced by inorganic and organic transitions between 22,000 and 19,500 cal yr BP, indicating glacial maximum positions at Lake Titicaca, Peru/Bolivia (16°S), and Lake Junin, Peru (11°S) (Seltzer et al, 2002). The time when the glaciers in these areas retreated (22,000/19,500 cal yr BP) partially overlaps with the lowest organic carbon accumulation rate at 21,950 cal yr BP in LPT V and the erosive phase at 22,400 cal yr BP identified by Santos et al. (2001). These sedimentological features are related to sedimentological evolution in Zone 2 of LPT V and are linked to intensely drier conditions at Morro do Seis Lagos. Paduano et al. (2003) identified very cold climatic conditions, with temperatures likely at least 5 to 8 °C cooler than those of the present, prior to ca. 21,000 cal yr BP. Increases in pollen concentration suggested initial warming began at ca. 21,000 cal yr BP, with a more significant transition towards deglaciation at ca. 17,700 cal yr BP. The analysis of Laguna La Compuerta indicated two phases of deglaciation, at ca. 34,000–32,000 cal yr BP and at 16,200 cal yr BP, separated by a period of no sediment accumulation (Weng et al., 2006). During this time, a glacial episode would have covered the landscape with ice. Deglaciation was interrupted by a dry, cold period coincident with the Younger Dryas event (Weng et al., 2006). Hillyer et al. (2009) studied diatom assemblages and found a slight reduction in lake level at 23,500 cal yr BP, with lake levels oscillating but remaining generally high until ca. 16,000 cal yr BP.

Baker et al. (2001a) pointed out that the annual cycle and interannual anomalies in the Lake Titicaca region are correlated with those in most of Amazonia (south of the equator) and, therefore, that high lake levels during the LGM in the Altiplano indicate a wet climate in Amazonia. However, the present-day pattern of such correlations may not apply to the climate of the LGM. Climate variability in the Altiplano is today controlled by anomalies in the westerly wind and show some correlation with ENSO (Garreaud et al., 2003; Vuille et al., 2000). During Southern Hemisphere summer (DJF), it is this eastward tropical jet rather than Atlantic sea surface temperature (SST) that controls the westward flow of Amazonian moisture to the central Andes (Vuille et al., 2000). Conversely, present-day rainfall and river water level anomalies in northern Amazonia are associated with distinct circulation patterns in the tropical Atlantic, particularly at the March–April peak of the rainy season. Thus, abundant rainfall in northern Amazonia, reflected in high Rio Negro water levels, is accompanied by a strong North Atlantic high, steep meridional pressure gradients on the side of the equator, accelerated northeast trades and cool surface waters in the tropical North Atlantic (Marengo, 1992). Nobre and Shukla (1996) showed that anomalous atmospheric circulation, controlled by distributions of SST over the equatorial Pacific and tropical Atlantic, affects the latitudinal position of the Intertropical Convergence Zone (ITCZ) over the Atlantic, thus influencing the distribution of precipitation over northern South America. During El Niño and La Niña events, the continental region of high convection in western Amazonia as well as the ITCZ are displaced (Poveda et al., 2001), causing rainfall anomalies in the Amazon region that generally produce negative shifts during El Niño events and positive shifts during La Niña events (Ronchail et al., 2002; Souza et al., 2000). These shifts are the cause of the indirect relation between precipitation in the central Andes and Amazonia. However, there is no correlation between present-day west Amazonia rainfall anomalies and ENSO (Garreaud et al., 2003), showing that the mechanisms controlling rainfall in each region are distinct.

Our data indicate that during glacial times as well, there was no positive relation between the interpretation of weather conditions in Altiplano and western Amazonia precipitation. In eastern Amazonia, the LGM is characterized, as in western Amazonia, by a drier climate (Absy et al., 1991; Sifeddine et al., 2001; Turcq et al., 2002b). The absence of sedimentation in Carajás region between 27,120 cal yr BP to 15,300 cal yr BP (Absy et al., 1991; Sifeddine et al., 1994a, b, 2001) were partially sincronous with decreasing productivity indicators observed between 26,300 cal yr BP to 15,500 cal yr BP and the occurrence of the sediment accumulation hiatus from 29,800 cal. B.P. to 19,200 cal yr BP as observed in the other sector of the Lagoa da Pata (LPT IV core published in Santos et al., 2001). The sedimentological interpretations in seven pollen records from South America suggest that the LGM, between ca 20,000 and 18,000 ^{14}C yr B.P., was likely represented by a hiatus of several thousand years, indicative of drier climates (Ledru et al., 1998). In Northern Andes, according to Van Der Hammen (1974) palynological studies have shown during the coldest part of the Last Glacial the tree line descended 1200–1500 m lower than where it lies today assuming a decrease of temperature between 6° and 7°. During the period between ca. 25,220 to ca. 15,300 cal yr BP (21,000 to 13,000 ^{14}C yr BP) the climate was much drier. Argollo and Mourguiart (2000) reached the same scenario based on a multi-proxy study of sediment cores from Lake Titicaca and Lake Pocoyu (Lake Poopoh, salars of Coipasa and Uyuni). They demonstrated that the LGM between 31,300 and 16,700 cal yr BP (ca. 26,000–14,000 ^{14}C BP) was marked by cooler, drier conditions, followed by a return to a wetter climate that was interrupted by short arid events between ca. 14,000 and 10,500 ^{14}C yr BP. These events were synchronous with those deduced for Lagoa da Pata.

6. Summary and conclusion

Over the past ca. 50,000 years and mainly during the last glacial maximum, as indicated by changes in the organic and inorganic geochemical contents of the LPT V core from Lagoa do Pata, there were significant variations in water level and erosional processes in the drainage basin.

Two phases of relatively high lake level, from ca. 50,000 cal yr BP until 26,300 cal yr BP and from 15,300 cal yr BP until 10,000 cal yr BP, were separated by a period of lowered lake level from 26,300 cal yr BP until 15,300 cal yr BP. In the earliest phase the productivity of the lake, which was high at the beginning of the period, decreased until the end of the period as shown by carbon accumulation rates. From ca. 26,300 cal yr BP until 15,300 cal yr BP, the paleoproductivity proxies showed the lowest values. The values of δ^{13}C increased by 5‰ in relation to the other phases, indicating a change in the quality of deposited organic matter, suggesting an influence of organic matter from C4-type plants. In this phase, the number of charcoal particles and charcoal area accumulation rates, as well as black carbon decreased showing that the decrease in precipitation did not disturb the adjacent ecosystem in low areas and areas surrounding the hill, probably because of a decrease in the evaporation. From 15,300 cal yr BP until 10,000 cal yr BP, the productivity of the lake increased significantly, as shown by paleoproductivity proxies (chlorophyll derivates and organic carbon concentrations and accumulation rates).

The more autochthonous character of the organic matter suggests that productivity and lake level were higher than during the other two phases. During this period, the lake level rose, increasing primary production. The accumulation rates of charcoal particles and black carbon were higher than in the first phase of the core. That the highest Hg accumulation rates were found in this period suggests increasing atmospheric deposition due to global temperature rise and/or forest burning (Lacerda et al., 1999), as shown in recent studies of the effect of forest fires on Hg emissions and deposition from the atmosphere (Almeida et al., 2005).

It is important to note that the charcoal accumulation rate estimated from LPT V is about 100-times lower than the values observed in an area of intensive land use change at Alta Floresta (Mato Grosso state, Brazil; Cordeiro et al., 2002) and 2- to 10-times lower than the charcoal accumulation rate observed in the Holocene at Serra Norte de Carajás (Cordeiro et al., 2008). These observations suggest that fire has only a small impact on forest ecosystems in this region.

The results discussed here showed that considerable changes in biogeochemical markers occurred without significant changes in the plant cover of the lake watershed (Bush et al., 2004; Colinvaux et al., 1996a, 1996b, 2000). Internal lake processes determined by changes in hydrobiological conditions and changes in erosion rates and forest fires, as suggested by some of the markers (e.g., Hg and charcoal particles), can result in significant changes in the lake deposition history even when large-scale vegetation changes do not occur.

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