

Delivery and deposition of organic matter in surface sediments of Lagoa do Caçó (Brazil)

Abdelfettah Sifeddine · Philip A. Meyers · Renato Campello Cordeiro · Ana Luiza S. Albuquerque · Marcelo Bernardes · Bruno Turcq · Jorge João Abrão

Received: 17 February 2010 / Accepted: 31 January 2011 / Published online: 18 February 2011
© Springer Science+Business Media B.V. 2011

Abstract Elemental and isotopic compositions of organic matter in surficial sediments from five transects across Lagoa do Caçó (Brazil) were analyzed to identify the depth-related processes that affect the production and deposition of sedimentary organic matter in this shallow tropical lake. Each of four transverse transects began at a margin dominated by aquatic macrophytes (*Eleocharis*), crossed the central deep part of the lake, and terminated in the opposite, macrophyte-dominated margin. In each transect, TOC concentrations, C/N ratios, and $\delta^{13}\text{C}$ values decreased between 0 and 4 m, whereas $\delta^{15}\text{N}$ values increased.

A. Sifeddine · B. Turcq
Institut de Recherche pour le Développement, France
(IRD), LOCEAN, UMR 7159 CNRS-IRD-Univ. P. & M.
Curie-MNHN), 32, Avenue Henri Varagnat, 93 143
Bondy cedex, France

A. Sifeddine · R. C. Cordeiro · A. L. S. Albuquerque ·
M. Bernardes · J. J. Abrão
Departamento de Geoquímica, Universidade Federal
Fluminense, Niterói, Brazil

A. Sifeddine · R. C. Cordeiro · A. L. S. Albuquerque ·
M. Bernardes · B. Turcq · J. J. Abrão
LMI Paleoclimatologie tropicale: Traceurs et Variabilités
“PALEOTRACES”, Institut de Recherche pour le
Développement, Bondy cedex, France

A. Sifeddine · R. C. Cordeiro · A. L. S. Albuquerque ·
M. Bernardes · B. Turcq · J. J. Abrão
LMI Paleoclimatologie tropicale: Traceurs et Variabilités
“PALEOTRACES”, Universidade Federal Fluminense,
Niterói, Brazil

The variables remained stable in sediment from 4 m water depth to the center of the lake at 10 m. The depth-related patterns reflect differences in both the delivery and the deposition of organic matter in the lake. Organic matter is produced in abundance in the marginal area by emerged and submerged macrophyte vegetation that diminishes with depth and disappears at 4 meters. After the disappearance of macrophytes, organic matter is produced at low rates principally by open-lake phytoplankton. Drawdown of dissolved oxygen is high in the lake margins, but it is low in the oligotrophic open waters of the lake.

A. Sifeddine · R. C. Cordeiro · A. L. S. Albuquerque ·
M. Bernardes · B. Turcq · J. J. Abrão
LMI Paleoclimatologie tropicale: Traceurs et Variabilités
“PALEOTRACES”, Universidad de Antofagasta,
Antofagasta, Chile

P. A. Meyers (✉)
Department of Geological Sciences, The University
of Michigan, 1100 North University Avenue, Ann Arbor,
MI 48109-1005, USA
e-mail: pameyers@umich.edu

Preservation of organic matter is consequently better in sediments of the lake margins than in deep waters. The depth-related pattern of organic matter delivery and deposition in the sediments of Lagoa do Caçó, in which water levels are sensitive to groundwater fluctuations, shows that the elemental and isotopic compositions of sediment organic matter can provide a record of changes in the paleohydrology of this and other similar shallow lake systems.

Keywords Sediment organic carbon concentration · C_{org}/N_{total} values · $\delta^{13}C_{org}$ · $\delta^{15}N_{total}$ · Lacustrine sedimentation · Lacustrine organic matter sources

Introduction

Lake sediments contain a variety of organic geochemical paleoenvironmental proxies that can be used to reconstruct local, and often regional, continental climate histories. In particular, the bulk organic matter properties of C_{org}/N_{tot} ratios and carbon and nitrogen isotopic compositions have been widely used as paleoenvironmental proxies (Krishnamurthy et al. 1986; Talbot and Livingstone 1989; Hassan et al. 1997; Brenner et al. 1999; Kaushal and Binford 1999; Talbot and Laerdal 2000; Sifeddine et al. 2004; Jacob et al. 2004a; Routh et al. 2009). Their utility is based on differences between the compositions of algal and vascular plant organic matter, which can be used to reconstruct changes in relative delivery from these sources. Protein-rich algal organic matter has molar C/N values that are usually between 4 and 8, whereas vascular land plants, which are cellulose-rich and protein-poor, commonly create organic matter that has C/N ratios of 20 and more (Meyers 1994; Meyers and Teranes 2001). Organic matter produced by algae (C_3 plants) using dissolved CO_2 in isotopic equilibrium with the atmosphere is usually isotopically indistinguishable from organic matter produced by C_3 plants on land and the lake margins. Algal $\delta^{13}C$ values are, however, sensitive to changes in lake primary productivity and are also distinctly more negative than organic matter produced by C_4 land plants. Application of $\delta^{15}N$ values to identify organic matter sources is based primarily on the larger $\delta^{15}N$ values of the dissolved

NO_3^- that is used by most algae, relative to the atmospheric N_2 that is used by nitrogen-fixing bacteria in soil and made available to land plants and aquatic plants at lake edges. The isotopic difference between these two sources of nitrogen to lake plants is generally preserved in the $\delta^{15}N$ values of organic matter from algae and epiphytes (+4 to +9‰) and from emergent and submerged C_3 macrophytes (−3 to +4‰; Boon and Bunn 1994), although this distinction can be blurred in some lakes by cyanobacterial nitrogen fixation.

The proportion of land-plant components in the organic matter of lake sediment typically decreases with greater distance from shore (Talbot and Laerdal 2000). This simple principle has been combined with the bulk organic geochemical indicators of organic matter sources to reconstruct climate-induced changes in water levels of tropical lakes during the last ~20 kyr (Talbot and Laerdal 2000; Jacob et al. 2004a). However, studies that describe the organic geochemical content of potential plant sources and that identify changes in the delivery of this material to different parts of a lake are rare. Here, we report the results of our systematic study of the organic matter elemental and isotopic compositions of lake-margin plants and of surficial sediments from different depths in Lagoa do Caçó, Brazil, a tropical lake in which changes in organic matter accumulation over the past 20 kyr have been related to climate-induced changes in water depth (Sifeddine et al. 2003; Jacob et al. 2004a, b).

Study site

Lagoa do Caçó (2°58'S, 43°25'W, 120 m a.s.l.) is located in Maranhão state, northeast Brazil, on the eastern border of the Amazon basin, about 80 km from the Atlantic coast (Fig. 1). The lake occupies a former river valley in a Pleistocene dune field that is presently covered by *cerrado* (shrub savannah) vegetation. The weather in the region is tropical, semi-humid, with an annual dry season extending for 4–5 months. Average annual temperature is 26°C, with daily averages that range between 36°C in the austral summer and 16°C in the winter. Annual rainfall ranges from 1,500 to 1,750 mm and is essentially controlled by seasonal shifts in the position of the Inter-Tropical Convergence Zone. The polymictic lake is about 5 km long and

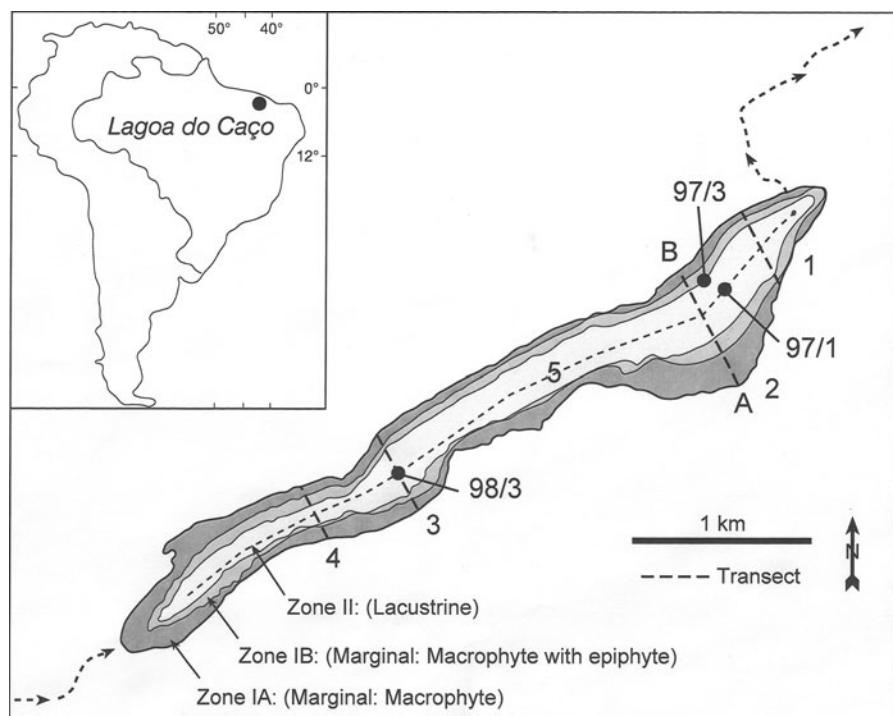


Fig. 1 General bathymetry of Lagoa do Caçó, showing the depth-dependent floral biozones and surficial-sediment transects that were sampled in January 2001. The positions that yielded sediment cores studied by Sifeddine et al. (2003) are labeled as 97-1 and 97-3, and the position of the core studied

by Jacob et al. (2004a, b, 2007a, b) is marked as 98-3. The combined inlet of the São José and Manioc rivers is shown at the southwest end of the lake, and the lake outlet is at its northeast end. Inset shows the location of the lake in tropical northeastern Brazil

0.2–0.5 km wide, and it has a surface area of about 2.5 km². Its maximum water depth is 10 m in the summer-fall wet season and 9 m in the winter-spring dry season. Lake level is largely maintained by groundwater, but two small streams flow into the lake during the wet season from the southwest, and seasonal discharge occurs at the northeast end of the lake. Lagoa do Caçó is oligotrophic to mesotrophic, although it has high phytoplanktonic diversity (Dellamano-Oliveira et al. 2003). Most of the organic matter in this lake originates from emergent vascular plants dominated by *Eleocharis* sp. and submerged plants growing in the shallow waters of the lake margins (Jacob et al. 2004a). These plants also act as filters that prevent significant wash-in of land-derived organic matter to the deeper parts of the lake.

Various paleoclimate proxies in sediment cores collected in 1997 and 1998 from Lagoa do Caçó were used to reconstruct the postglacial paleoclimate history of northeast Brazil. The glacial climate of northeast Brazil evidently was arid until about 19 ka,

when subaqueous sediments first started to accumulate in the Lagoa do Caçó basin (Ledru et al. 2006). Changes in pollen assemblages indicate that a moist, but cool climate allowed development during the late Pleistocene of rainforest that first replaced, and then at the end of the Pleistocene, was succeeded by savannah. An abrupt drop in leaf-wax D/H ratios at ~17 ka records the start of a period of wetter late Pleistocene climate (Jacob et al. 2007a). By comparison to vegetation inhabiting modern climate zones, a shift in moisture delivery from the southeast to the northwest evidently accompanied the vegetative and paleohydrologic changes (Ledru et al. 2001). The change in moisture origin was likely associated with a repositioning of the Inter-Tropical Convergence Zone that also affected the amount of moisture that was delivered (Ledru et al. 2002; Sifeddine et al. 2003). Biomarker molecular contents of the lake sediments provide evidence of plants adapted to dry conditions during the Last Glacial Maximum and the Younger Dryas (Jacob et al. 2004b) and of the

abundance of a ring of *Eleocharis* on the lake margins during periods of wetter climate in the late Pleistocene and the late Holocene (Jacob et al. 2007b). Finally, changes in the amount and composition of bulk organic matter in the Lagoa do Caçó sediment cores reflect variations in delivery and preservation of the organic matter that suggest the local climate fluctuated over the past 20 kyr, between being drier and wetter than its present state. Although changes in lake water levels are implicit in these paleoclimate reconstructions, a systematic description of how the amount and kind of organic matter might actually vary in sediments at different depths in this lake had not been described before our study.

Materials and methods

Surficial sediments and vegetation sampling

The 59 samples of surficial sediment were collected from four transverse and one longitudinal transect during the austral summer of 2001 (Fig. 1). Each transverse transect originated from a margin populated by emerged macrophytes, crossed the central part of the lake and terminated in the opposite margin of the lake. A diver used a short PVC coring tube to collect ten cm of sediment, and we then collected the topmost slice (0–1 cm), corresponding to the nepheloïd sediment layer. We also collected samples of modern vegetation that represent the dominant plants in and around the lake. All samples were immediately packaged and transported to the laboratory at Universidade Federal Fluminense in Niteroi, Rio de Janeiro State.

C and N elemental and isotopic compositions

Total organic carbon (TOC) and nitrogen (TN) concentrations and isotopic compositions were measured on dried whole sediment samples by combustion with a Shimatzu CHN analyzer coupled to a Prism mass spectrometer at the University of Waterloo, Canada. Because sediments of Lagoa do Caçó contain no CaCO_3 (Sifeddine et al. 2003; Jacob et al. 2004b), the whole-sediment results correspond to bulk organic matter elemental and isotopic compositions. The vegetation samples were analyzed at the Laboratory of Isotope Geochemistry at the University

of Arizona using a Costech elemental analyzer interfaced directly with a Finnigan Delta Plus XL mass spectrometer. $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values are expressed relative to PDB and atmospheric dinitrogen, respectively. Precision is better than $\pm 0.06\text{\textperthousand}$ for carbon and $\pm 0.2\text{\textperthousand}$ for nitrogen.

Statistical analyses

To detect structure in the relations between the multiple geochemical variables measured in the surficial sediments, analytical results were subjected to Principal Component Analysis (PCA), which is the simplest multivariate analysis involving a mathematical procedure that transforms a number of possibly correlated variables into a smaller number of groups of closely related variables (Jolliffe 2002). We also applied an analysis of variance (ANOVA) to test whether the geochemical characteristics of multiple surficial samples collected in different biozones of Lake Caçó are statistically comparable. In all cases we use the statistical program STATISTICA 6.0.

Results

Water depth controls the different kinds of plant life that sharply define two major biozones in Lagoa do Caçó (Fig. 1). The first of these (Biozone 1) is the lake margin, which is divided into subzone 1a (0–2 m water depth) that is inhabited by the emerged macrophyte *Eleocharis* and subzone 1b (2–4 m water depth) that is inhabited by submerged macrophytes with abundant epiphytic algae that are dominated by diatoms (Nascimento et al. 2010). The second major biozone (Biozone 2) is an open lacustrine system (>4 m water depth), dominated principally by phytoplankton and having minor amounts of submerged macrophytes. Dissolved O_2 concentrations vary dramatically in the three depth-related lake zones (Cardoso 2004). They are low in Biozone 1b, and the water becomes anoxic at 1.5 meters during the summer high lake level (Fig. 2). Oxygen concentrations are higher in deeper parts of the lake and remain close to saturation in Biozone 2 during both the wet and dry seasons (Dellamano-Oliveira et al. 2003). Concentrations of NO_3^- and NH_4^+ (Table 1) are highest in the shallow zones of the lake, especially in the entrance, margin and exit, where *cerrado*,

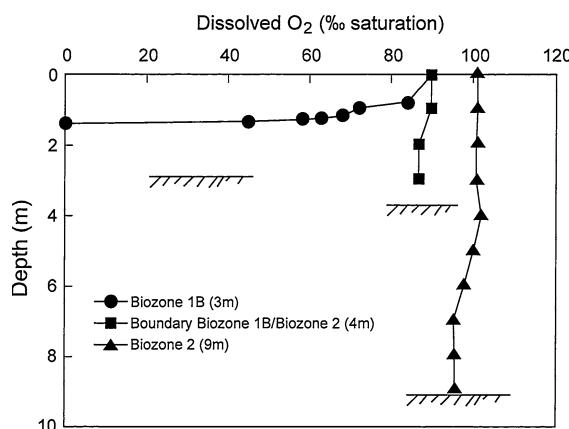


Fig. 2 Profiles of dissolved oxygen in water depths of 3 m (lake margin subzone 1b), 4 m (boundary between subzone 1b and Biozone 2), and 9 m (open lake Biozone 2). From Gustavo (2004)

Table 1 Concentrations of dissolved nitrate and ammonium in input and output waters and at different locations and depths in Lagoa do Caçó

Origin	NO_3^- (μM)	NH_4^+ (μM)
Inflow		
São José River	6.1	0.9
Manioc River	3.9	0.8
Rain		
Storm	3.5	3.3
Normal	6.7	4.0
Lake		
Surface water from 0 m water depth	8.4	0.9
Surface water from 2.5 m water depth	8.3	0.9
Bottom water from 2.5 m water depth	7.9	0.5
Bottom water from 5.4 m water depth	8.0	0.0
Surface water from 9 m water depth	0.4	0.4
Outflow		
	7.4	0.1

From Gustavo (2004)

macrophytes, and Gramineae are the respective dominant forms of vegetation. In subzone 1b, NO_3^- and NH_4^+ concentrations are higher in the surface than in the bottom. In contrast, concentrations of these bioavailable forms of nitrogen are essentially constant with water depth in Biozone 2. Sediment in the marginal zone consists of gyttja that is rich in

plant debris; it is fine-grained gyttja in the deep-lake zone.

Results of the elemental and isotopic analyses of the modern plant samples reveal important differences in C/N ratios and $\delta^{15}\text{N}$ values of these potential organic matter sources (Table 2). Samples of land plants: (tree leaves, *capim* [lemon grass], *serrapilheira* [litter]) and emerged macrophytes (*Eleocharis*) have high C/N ratios and low $\delta^{15}\text{N}$ values, whereas floating and submerged macrophytes (*Nymphaea* and *Cabomba*) and diatoms have lower C/N ratios. Higher $\delta^{15}\text{N}$ values of some samples (diatoms, Gramineae) suggest that these plants utilize NO_3^- dissolved in the lake waters. In contrast to the C/N ratios and $\delta^{15}\text{N}$ values, little difference is evident in the $\delta^{13}\text{C}$ values of most of the vegetation samples (Table 2). A notable exception to this generalization is the mixture of emerged macrophyte biomass and epiphytic diatoms, which has a markedly less negative $\delta^{13}\text{C}$ value ($-22.4\text{\textperthousand}$) than the other eight samples.

The elemental and isotopic properties of the bulk organic matter of surficial sediments differ among the Lagoa do Caçó biozones. Mean TOC concentrations are greatest in subzone 1a (17.4%), decrease to 12.4% in subzone 1b, and drop to 9.4% in Biozone 2 (Table 3). Mean molar $\text{C}_{\text{org}}/\text{N}_{\text{tot}}$ ratios in these biozones are 12.6, 11.0, and 12.6, respectively. Like TOC concentrations, the isotopic values change with distance from the lake shoreline. Organic $\delta^{13}\text{C}$ values

Table 2 Elemental and isotopic compositions of potential plant sources of organic matter to the sediments of Lagoa do Caçó

Organic matter source	C_{org} (%)	C/N (atomic)	$\delta^{13}\text{C}$ (‰)	$\delta^{15}\text{N}$ (‰)
Land plants				
Tree leaves	46.9	50.2	-30.5	-1.4
Grass	41.3	67.7	-29.0	1.4
Litter	43.9	43.1	-29.2	-1.5
Biozone 1a (0–2 m)				
Spikerush (<i>Eleocharis</i>)	41.8	72.3	-26.2	-1.7
Water grass (Gramineae)	46.1	23.7	-29.6	3.2
Biozone 1b (2–4 m)				
Water lily (<i>Nymphaea</i>)	30.4	16.3	-27.1	0.1
Fanwort (<i>Cabomba</i>)	39.6	26.6	-25.0	-4.7
Epiphyton (diatoms)	27.7	15.2	-27.2	2.6
Macrophyte-epiphyte mix	44.8	33.1	-22.4	-1.0

Table 3 Ranges, average values, and standard deviations (SD) of water depths and sediment organic matter elemental and isotopic compositions in the three biozones of Lagoa do Caçó

Variable	Biozone 1A Valid N = 14	Biozone 1B Valid N = 18	Biozone 2 Valid N = 27
Depth (m)			
Min	0.5	2.3	5.0
Max	2.0	4.0	10.0
Mean ± SD	1.3 ± 0.5	3.4 ± 0.6	7.2 ± 1.7
TOC (%)			
Min	6.89	3.35	3.19
Max	22.89	16.35	14.20
Mean ± SD	17.45 ± 4.45	12.43 ± 3.06	9.38 ± 2.53
$C_{org} : N_{tot}$			
Min	9.7	9.2	8.7
Max	20.2	13.0	16.8
Mean ± SD	12.6 ± 3.0	11.0 ± 1.1	12.6 ± 1.3
$\delta^{13}C$ (‰)			
Min	-30.1	-29.8	-30.1
Max	-24.9	-26.7	-27.0
Mean ± SD	-26.7 ± 1.3	-27.1 ± 0.8	-28.3 ± 0.5
$\delta^{15}N$ (‰)			
Min	0.1	0.7	0.6
Max	3.4	6.3	6.1
Mean ± SD	1.8 ± 1.1	4.0 ± 1.9	4.8 ± 1.0

average -26.7‰ in subzone 1a, -27.1‰ in subzone 1b, and -28.3‰ in Biozone 2, and mean $\delta^{15}N$ values increase from 1.8‰ to 4.0‰ to 4.8‰ with greater distance from land.

The sediment organic geochemical variables change within these transects as water depth changes. TOC concentrations, C/N ratios, and $\delta^{13}C$ values generally decrease and $\delta^{15}N$ values increase in the transverse transects as water depth increases from 0 to 4 m (Fig. 3). The respective variables start at 1 m with values around 20%, 14 and -26‰ and 0-3‰ and reach 12%, 11, -28‰ and 5‰ at 4 m water depth. All four variables change little between 4 and 10 m. The sediment samples from water depths less than 1 m in Transect 2 deviate from this general pattern in having lower TOC concentrations and larger C/N values than somewhat deeper samples (Fig. 3). Within the longitudinal transect, the pattern of organic matter variations with depth is slightly different from that in the transverse transects, although these samples were collected from a somewhat narrower depth range (3–10 m) than the transverse samples. TOC concentrations and $\delta^{13}C$ values decrease, whereas C/N

ratios and $\delta^{15}N$ values increase. Their respective values are ~15%, -28‰, 10, and ~3‰ at 3 m, and they reach values ~10%, -29‰, 12, and 4–5‰ at 10 m (Fig. 3).

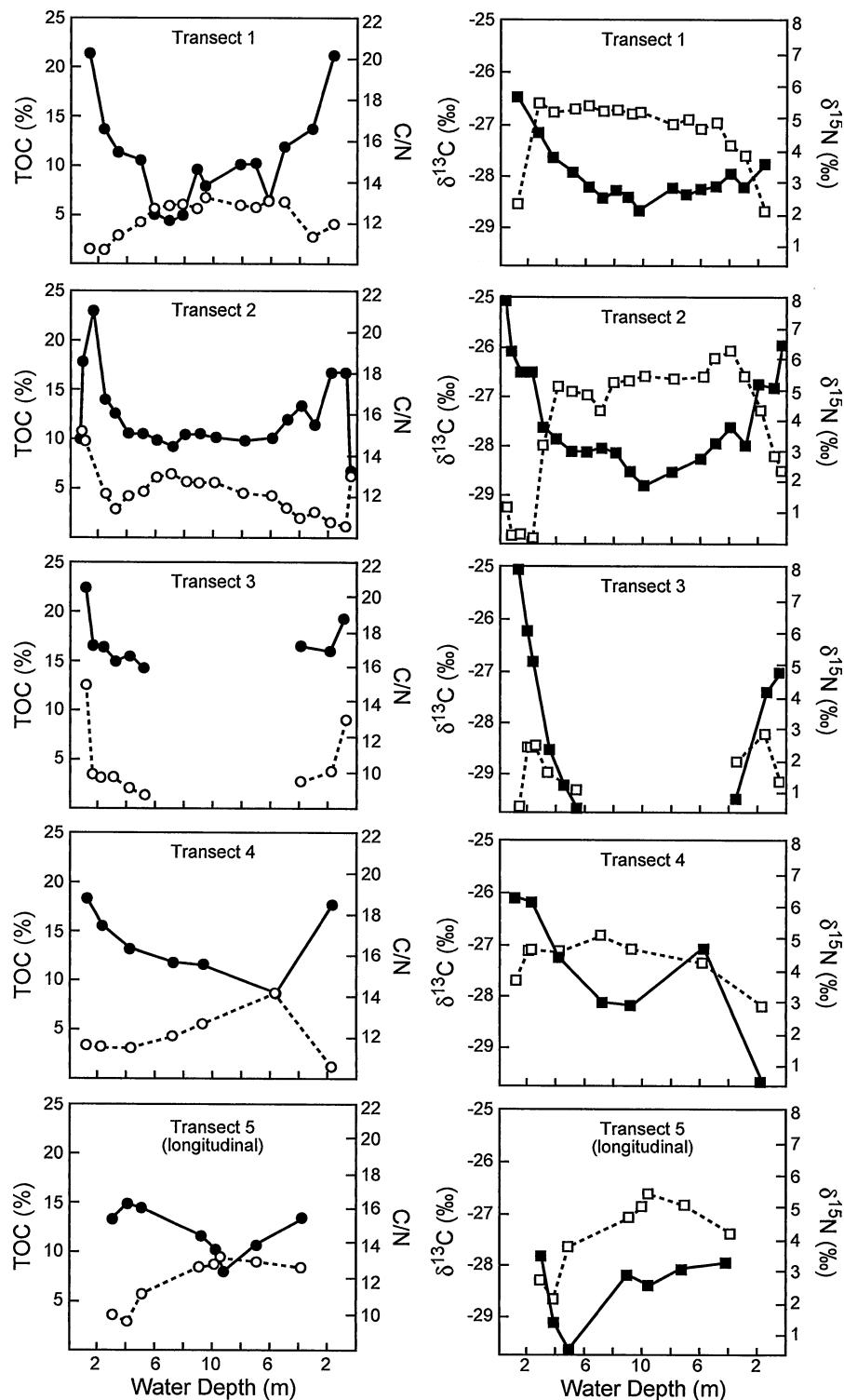
ANOVA test results show that TOC concentrations, $\delta^{13}C_{org}$ values, and $\delta^{15}N_{tot}$ values yield probabilities (*p* values) of less than 0.001 (Table 4), which indicates that the values of these parameters are statistically different and provides evidence of spatial differences between the biozones, although the C/N ratios (*p* = 0.294) are not statistically different. The ANOVA results suggest that Biozones 1a and 1b and Biozone 2 could each be considered different with respect to the origins of their organic matter. Because the geochemical signature of each biozone might be explained by how much organic matter each received from plants in the marginal biozone, we assessed the organic matter source relations by principal component analysis (PCA). The PCA results show that more than 82% of variance in the surficial sediment samples is explained by two factors (Fig. 4). The first PCA factor, which represents 52% of the variance (Fig. 4), is dominated by $\delta^{15}N_{tot}$, which reflects the nitrogen assimilation processes of the plants in the respective biozones. The second factor is dominated by the $\delta^{13}C_{org}$ and C/N values (Fig. 4), which likely represent the influence of vascular plant organic matter (Table 2).

Discussion

Delivery of organic matter to different parts of Lagoa do Caçó

TOC concentrations range widely from 3.2 to 22.9% in the four transverse transects (Table 3; Fig. 3) and reveal that some of the sediments of Lagoa do Caçó are very rich in organic matter and that large differences in organic matter abundance exist in different sectors of the lake. Decreasing mean TOC concentrations in subzone 1a (17.4%), subzone 1b (13.1%), and Biozone 2 (10.3%) indicate that organic matter accumulation on the lake bottom decreases as distance from shore and water depth increase. This accumulation pattern is similar to that on the margin of Lake Victoria, Africa, where Talbot and Laerdal (2000) showed that TOC concentrations progressively decrease from 40% at the swampy lake edge to

Fig. 3 Total organic carbon (TOC) concentrations (solid circles), molar C_{organic}/N_{total} ratios (open circles), δ¹³C_{org} values (solid squares) and δ¹⁵N_{tot} values (open squares) versus water depth for the four transverse (1–4) and one longitudinal (5) transects of Lagoa do Caçó surficial sediments



12% 400 m offshore. The patterns of decreasing TOC concentrations in both Lagoa do Caçó and the Lake Victoria margin imply that the vegetation that is more

abundant on the shores and in the shallower parts of these lakes is a major source of the organic matter to the lake sediments.

Table 4 Results of the one-way ANOVA test of variations in the organic matter elemental and isotopic compositions of 59 samples of Lagoa do Caçó surface sediments obtained from five cross-lake transects

	TOC (%)	TN (%)	C/N	$\delta^{13}\text{C}$ (‰)	$\delta^{15}\text{N}$ (‰)
F	36.34	17.88	1.12	71.60	31.54
P	0.000	0.000	0.294	0.000	0.000

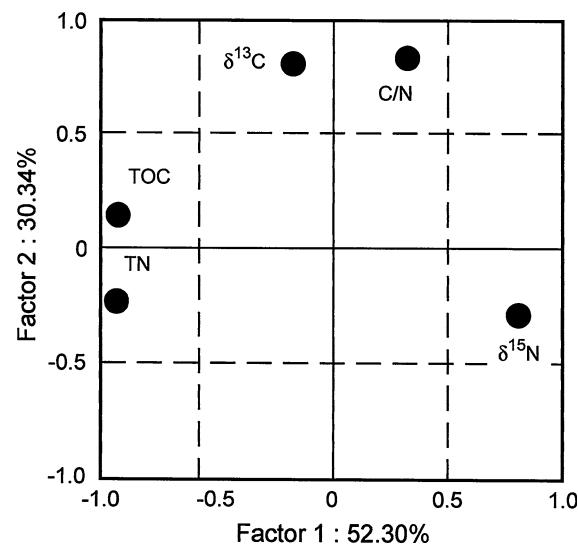


Fig. 4 Principal component analysis factor analysis plot, showing that more than 82% of the variance in organic matter composition is explained by two principal component factors

A notable exception to the general pattern of decreasing TOC concentrations with increasing water depth exists in Transect 2, which includes sediment samples that were collected from water depths <1 m during the summer wet season. Their TOC concentrations are less than half those of sediment samples from between 1 and 2 m deep (Fig. 3). Because lake water level fluctuates ~1 m between the wet season and the winter dry season, sediments under less than 1 m of water in the summer experience sub-aerial exposure during the winter. The lower TOC concentrations and larger C/N values in the samples from <1 m are consistent with oxidation of their organic matter while they are exposed to air (Fellerhoff et al. 2003). Interestingly, neither the organic $\delta^{13}\text{C}$ nor the total $\delta^{15}\text{N}$ values appear to be affected by the subaerial oxidation of organic matter in the Transect 2 shallow samples (Fig. 3).

In contrast to the wide ranges of TOC on the four transverse transects, the TOC concentrations in the longitudinal transect vary relatively little, between 2.4 and 9.5% (Fig. 3). The smaller TOC concentrations in these deeper sediments reflect both their isolation from the principal lake-margin sources of organic matter and partial oxidation of the organic matter owing to the high levels of dissolved oxygen in the open-water parts of the lake (Fig. 2). Relatively small variations in the C/N, $\delta^{13}\text{C}$, and $\delta^{15}\text{N}$ values in sediment from this transect (Fig. 3) indicate some

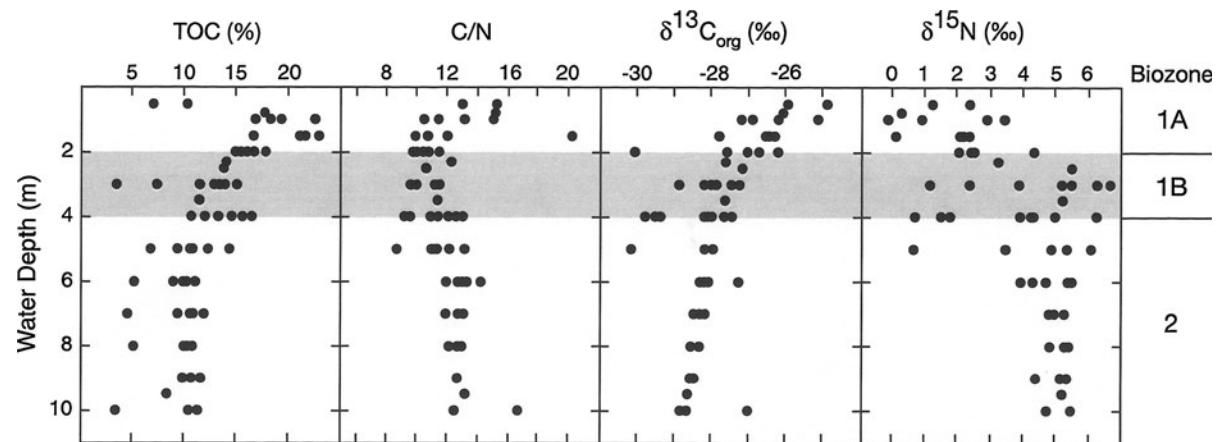


Fig. 5 Summarized depth-related patterns of TOC concentrations, $\text{C}_{\text{organic}}/\text{N}_{\text{total}}$ ratios, and $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}_{\text{tot}}$ values of surficial sediment from the five transects in Lagoa do Caçó. The relations of these organic matter variables to the depth-

dependent floral biozones within this lake are shown: *Biozone 1A* lake margin with emergent plants; *Biozone 1B* lake margin with floating and submerged plants; *Biozone 2* open lake waters

degree of homogenization of organic matter during delivery to the more central parts of the lake.

Deposition of organic matter in different parts of Lagoa do Caçó

We combined the elemental and isotopic results from all five surficial sediment transects to explore depth-related patterns in organic matter deposition (Fig. 5). Actually, the carbon isotope values are highest in Biozone 1a, generally -27 to -25 per mil (Fig. 5). These geochemical features indicate the predominance of C₃ vascular plants as the main source of organic matter in this subzone. It is very probable that the *Eleocharis* that dominates the shallow margins of Lagoa do Caçó is the principal origin of this organic matter. This source interpretation is supported by the $\delta^{15}\text{N}$ values that vary between 0 and 1‰ and that are characteristic of atmospheric nitrogen fixation, the process that is the dominant subaerial plant nitrogen source (Meyers and Teranes 2001). In addition, during the dry season from May to November, the lake level drops around 1 m, and sediments exposed during this time exhibit sub-aerial exposure effects, including seasonal colonization by nitrogen-fixing land plants.

The carbon isotope values in Biozone 1b are lower (i.e. more negative) than those in Biozone 1a. See Fig. 5. The transition from subzone 1a to subzone 1b is marked by decreases of C/N and $\delta^{13}\text{C}$ values from 14 to 10 and $-25\text{\textperthousand}$ to $-29\text{\textperthousand}$, respectively. These changes in organic geochemical properties imply an increased algal contribution to the sediment organic matter inasmuch as these biota are rich in nitrogenous components and poor in cellulosic material. This source change is probably linked to the predominant presence of epiphytic diatoms that are attached to macrophyte stalks and that dilute the organic signal of the submerged macrophytes that occupy Biozone 1b. This interpretation is supported by an important shift to higher $\delta^{15}\text{N}$ values, indicating that this different kind of organic matter contains nitrate-nitrogen that has experienced denitrification. As evident from the higher $\delta^{15}\text{N}$ values of organisms that are fully submerged in Lagoa do Caçó (Table 2), the producers of the organic matter in subzone 1b have assimilated much of their nitrogen from the lake water, likely as dissolved nitrate.

The shift from subzone 1a to subzone 1b is linked to the depth-related transition in marginal vegetation that begins first with marginal emergent macrophytes and then with submerged macrophytes that host epiphytes in deeper water. Slightly deeper in subzone 1a, the organic matter still originates mostly from vascular plants, but with an increasing algal influence. At the beginning of subzone 1b the predominance of the algal signal over land plant organic matter becomes evident. This shift increases and reaches a maximum at 4 m in subzone 1b, where organic matter origin is predominately algal. These observations indicate that from 0 to 1 m, organic matter deposition is controlled largely by macrophyte vegetation. The epiphyte influence in the sediment begins at 1 m and intensifies between 3 and 4 m, where it overprints the macrophyte signal.

The organic geochemical properties of the samples of open-lake Biozone 2 are marked by a decrease of $\delta^{13}\text{C}$ to more negative values that reflect the influence of algal organic matter. The $\delta^{15}\text{N}$ values increase to between 5 and 7‰, a change that is probably linked to recycling and loss of the organic matter from subzone 1b and that implies that the sedimentary organic matter deposited in this zone is mostly phytoplanktonic in origin (Meyers and Teranes 2001). The shift to slightly larger C/N values may represent contributions of organic matter from down-slope transfer of detrital ligno-cellulosic material from the marginal zone, or it may reflect partial degradation of the organic matter and preferential removal of its nitrogenous components (Fellerhoff et al. 2003).

The processes that are involved with the production and delivery of sedimentary organic matter in Lagoa do Caçó, as inferred from our elemental and isotopic organic geochemical source proxies, are schematically illustrated in Fig. 6. Primary production by the emergent and submerged macrophytes that fringe the lake dominates organic matter production in this lake, although epiphytic diatoms are an important additional source of organic matter to sediments in water 2–4 m deep (subzone 1b). The presence of macrophytes limits wind-induced mixing of waters of the lake margin with the dual results that organic matter produced there remains to a large degree on the margin, and that its degradation is slowed in the low-oxygen conditions prevalent in this sector of the lake. Organic carbon concentrations are

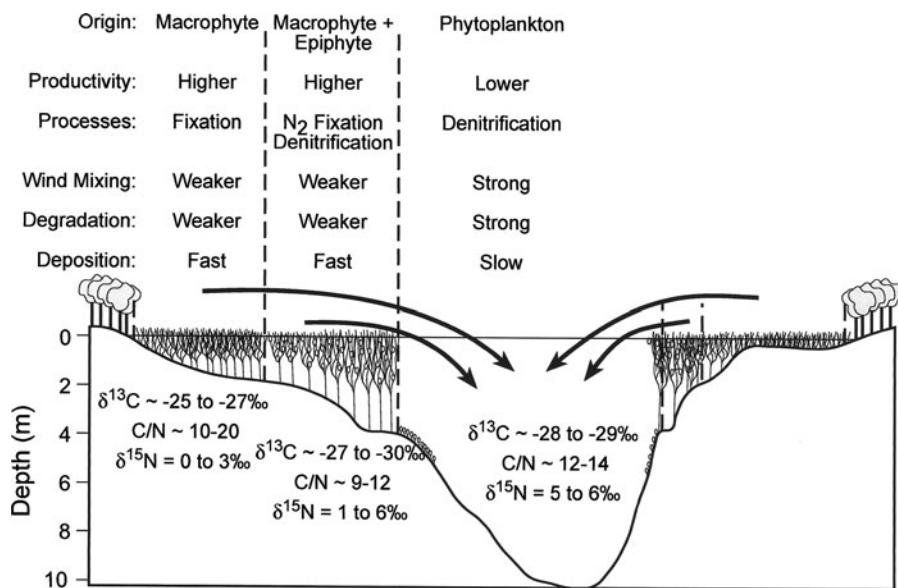


Fig. 6 Schematic interpretation of organic matter origins and delivery processes as inferred from $C_{\text{organic}}/N_{\text{total}}$ ratios, and $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}_{\text{tot}}$ values of Lagoa do Caçó surficial sediments. The major source of organic matter is macrophytes and their associated epiphytes that live in the shallow waters of

the lake margins. A portion of this organic matter is transferred to the deeper waters of the open lake, where it is subject to partial oxidative degradation. These zones of organic matter production and deposition are sensitive to changes in water level

therefore highest in sediments along parts of the lake margins that remain submerged throughout the annual cycle of lake level change. Some of the lake-margin organic matter is nonetheless transported to the deeper parts of the lake, where algae also contribute organic matter to the bottom sediments. Despite the increased water depth of this part of the lake, the absence of macrophytes allows wind mixing to ventilate the hypolimnion and to increase organic matter degradation. Organic carbon concentrations are consequently lower in the deeper parts of the lake than in sediments on the lake margin.

Conclusions

The results of our organic matter elemental and isotopic analyses of 59 surficial sediments collected from four transverse and one longitudinal transect in Lagoa do Caçó reveal depth-related patterns in delivery and deposition of organic matter. Our organic geochemical proxy approach allowed assessment and reconstruction of the relative contributions of the multiple origins of the organic matter delivered to the lacustrine sediments. A clear distinction

between shallow-water and open-lake environments is illustrated in each transverse transect, which individually show a gradient of the organic matter sources and also in the delivery and depositional processes linked to depth-related floral zonation across the lake. In each transect, the geochemical variables show a predominance of organic matter from C_3 vascular plants that corresponds to the development of emergent macrophyte vegetation in marginal subzone 1a. The transition to the deeper subzone 1b is marked by the appearance of organic matter that is richer in protein and lower in cellulosic material and reflects the importance of epiphytes attached to the stalks of submerged macrophytes, diluting their vascular plant organic signal. Finally, a predominantly phytoplanktonic source of organic matter in Biozone 2 overprints deliveries of macrophyte debris from the margin system.

Our study of the elemental and isotopic characteristics of surface sediments in Lagoa do Caçó also identified an unusual depth-related pattern in organic matter preservation. It is greatest in sediments from the shallow waters of the lake margins where macrophyte populations simultaneously produce an abundance of organic matter and restrict water

mixing, which together lead to depletion of dissolved oxygen in the littoral region. Organic matter preservation is poor in the well-mixed open waters of the lake, and it is poorest in the very shallow parts of the lake margin that are subaerially exposed during the winter dry season.

Differences in surface sediment organic matter elemental and isotopic compositions among the depth-related zones in Lagoa do Caçó suggest that changes in lake level have the potential to leave an imprint on the sediment record of this lake. Therefore, these characteristics and other components of the sediment record can help reconstruct the history of lake level changes in this and other lakes in which shallow-water macrophytes are important contributors to sediment organic matter. Because the macrophyte populations in Lagoa do Caçó are best developed in water less than 4 m deep, it is the repositioning of this biozone due to changes in water level that will leave the strongest paleolimnologic signal in the sediment record. Studies of sediment records for paleohydrologic reconstructions should therefore contain multiple cores that capture the repositioning history of the marginal biozone as well as the history of the deeper parts of the lake that are likely to have remained under water.

Acknowledgments We thank T. C. Moore for his helpful comments on our statistical analyses. This study was supported by the “PALEOTRACES” International Mixed Laboratory between Institut de Recherche pour le développement, Universidade Federal Fluminense and Universidad de Antofagasta, as well as by the CLIMPAST project (CNPq-IRD), which corresponds to the international cooperation project between the Brazilian CNPq and the IRD (Processo CNPq n°: 490735/2006-1). The authors sincerely thank the ESCARSEL ANR for financial support. Finally, we deeply appreciate the constructive comments from the reviewers and editors that helped us to improve this contribution.

References

- Boon PI, Bunn SE (1994) Variations in the stable isotope composition of aquatic plants and their implications for food web analysis. *Aquat Bot* 48:99–108
- Brenner M, Whitmore TJ, Curtis JH, Hodell DA, Schelske CL (1999) Stable isotope ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) signatures of sedimented organic matter as indicators of historic lake trophic state. *J Paleolimnol* 22:205–221
- Cardoso AGA (2004) Reconstrução paleoambiental na Lagoa do Caço (Maranhão–Brasil) durante os últimos 21.000 anos A.P. por marcadores e processos inorgânicos sedimentares. PhD dissertation, Department of Geochemistry, Fluminense Federal University, 127 pp, unpublished PhD dissertation
- Dellamano-Oliveira MJ, Senna PAC, Taniguchi GM (2003) Limnological characteristics and seasonal changes in density and diversity of the phytoplanktonic community at the Caçó Pond, Maranhão State, Brazil. *Braz Arch Biol Tech* 46:641–651
- Fellerhoff C, Voss M, Wantzen KM (2003) Stable carbon and nitrogen isotope signatures of decomposing tropical macrophytes. *Aquat Ecol* 37:361–375
- Hassan KM, Swinehart JB, Spalding RF (1997) Evidence for holocene environmental change from C/N ratios and $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values in Swan Lake sediments, western Sand Hills, Nebraska. *J Paleolimnol* 18:121–130
- Jacob J, Disnar J-R, Boussafir M, Ledru M-P, Albuquerque ALS, Sifeddine A, Turcq B (2004a) Onocerane attests to dry climatic events during the quaternary in the tropics. *Org Geochem* 35:289–297
- Jacob J, Disnar J-R, Boussafir M, Ledru M-P, Sifeddine A, Turcq B, Albuquerque ALS (2004b) Major environmental changes recorded by lacustrine sedimentary organic matter since the last glacial maximum near the equator (Lagoa do Caçó, NE Brazil). *Palaeogeogr Palaeoclimatol Palaeoecol* 205:183–197
- Jacob J, Disnar J-R, Boussafir M, Ledru M-P, Albuquerque ALS, Sifeddine A, Turcq B (2007a) Contrasted distributions of triterpenes derivatives in the sediments of Lake Caçó reflect paleoenvironmental changes during the last 20,000 yrs in NE Brazil. *Org Geochem* 38:180–197
- Jacob J, Huang Y, Disnar J-R, Sifeddine A, Boussafir M, Albuquerque ALS, Turcq B (2007b) Paleohydrological changes during the last deglaciation in Northern Brazil. *Quat Sci Rev* 26:1004–1015
- Jolliffe IT (2002) Principal component analysis, 2nd edn. Springer, NY
- Kaushal S, Binford MW (1999) Relationship between C: N ratios of lake sediments, organic matter sources, and historical deforestation of Lake Pleasant, Massachusetts, USA. *J Paleolimnol* 22:439–442
- Krishnamurthy RV, Bhattacharya SK, Kusumgar S (1986) Palaeoclimatic changes deduced from $^{13}\text{C}/^{12}\text{C}$ and C/N ratios of Karewa lake sediments. *Nature* 323:150–152
- Ledru M-P, Cordeiro RC, Dominguez JML, Martin L, Mourguia P, Sifeddine A, Turcq B (2001) Late-glacial cooling in Amazonia inferred from pollen at Lagoa do Caçó, northern Brazil. *Quat Res* 55:47–56
- Ledru M-P, Mourguia P, Ceccantini G, Turcq B, Sifeddine A (2002) Tropical climates in the game of two hemispheres revealed by abrupt climate change. *Geology* 30: 275–278
- Ledru M-P, Ceccantini G, Gouveia SEM, Lopez-Sáez JA, Pessenda LCR, Ribeiro AS (2006) Millennial-scale climate and vegetation changes in a northern Cerrado (Northeast Brazil) since the Last Glacial Maximum. *Quat Sc Rev* 25:1110–1126
- Meyers PA (1994) Preservation of elemental and isotopic source identification of sedimentary organic matter. *Chem Geol* 114:289–302
- Meyers PA, Teranes JL (2001) Sediment organic matter. In: Last WM, Smol JP (eds) *Tracking environmental changes*

- using lake sediments—volume II: physical and chemical techniques. Kluwer, Dordrecht, pp 239–269
- Nascimento LR, Sifeddine A, Torgan LC, Albuquerque ALS (2010) Diatom assemblage in a tropical lake of north-eastern Brazil. *Braz Arch Biol Tech* 53:241–248
- Routh J, Choudhary P, Meyers PA, Kumar B (2009) A sediment record of recent nutrient loading and trophic state change in Lake Norrviken, Sweden. *J Paleolimnol* 42:325–341
- Sifeddine A, Albuquerque ALS, Ledru M-P, Turcq B, Knoppers BA, Martin L, Mello WZD, Passenau H, Dominquez JML, Cordeiro RC, Abrão JJ, Bittencourt ACSP (2003) A 21,000 cal years paleoclimate change in Caçó Lake, northern Brazil: evidence from sedimentary and pollen records. *Palaeogeogr Palaeoclimatol Palaeoecol* 189:25–34
- Sifeddine A, Wirrmann D, Albuquerque ALS, Turcq B, Cordeiro RC, Gurgel MHC, Abrão JJ (2004) Bulk composition of sedimentary organic matter palaeoenvironmental reconstructions: examples from the tropical belt of South America and Africa. *Palaeogeogr Palaeoclimatol Palaeoecol* 214:41–53
- Talbot MR, Laerdal T (2000) The late pleistocene-holocene palaeolimnology of Lake Victoria, East Africa, based upon elemental and isotopic analyses of sedimentary organic matter. *J Paleolimnol* 23:141–164
- Talbot MR, Livingstone DA (1989) Hydrogen index and carbon isotopes of lacustrine organic matter as lake level indicators. *Palaeogeogr Palaeoclimatol Palaeoecol* 70:121–137