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Spatial and seasonal contrasts of sedimentary organic matter in floodplain lakes of the central Amazon basin

R. L. Sobrinho¹, ², M. C. Bernardes¹, G. Abril¹, ³, J.-H. Kim⁷, C. I. Zell², J.-M. Mortillaro⁴, T. Meziane⁴, P. Moreira-Turcq⁵, and J. S. Sinninghe Damsté², ⁶

¹Universidade Federal Fluminense, Department of Geochemistry, 24020-141, Niteroi, Rio de Janeiro, Brazil
²NIOZ Royal Netherlands Institute for Sea Research, Department of Marine Organic Biogeochemistry, P.O. Box 59, 1790 AB Den Burg, Texel, the Netherlands
³Laboratoire EPOC, Université Bordeaux 1, CNRS UMR5805, Avenue des Facultés, 33405 Talence, France
⁴UMR-CNRS-IRD-UPMC7208, BOREA, Département Milieux et Peuplements Aquatiques, MNHN, CP 53, 61 rue Buffon, 75231 Paris Cedex 05, France
⁵IRD (Institut de Recherche pour le Développement) GET (Géosciences Environnement Toulouse), Casilla 18-1209, Lima 18, Peru
⁶Utrecht University, Faculty of Geosciences, P.O. Box 80.021, 3508 TA Utrecht, the Netherlands
⁷Department of Marine Science and Convergence Technology, Hanyang University ERICA campus, 55 Hanyangdaehak-ro, Sangnok-gu, Ansan-si, Gyeonggi-do 426-791, South Korea
Abstract

In this study, we investigated the seasonal and spatial pattern of sedimentary organic matter (SOM) in five floodplain lakes of the central Amazon basin (Cabaliana, Janauaca, Canaçari, Miratuba, and Curuai) which have different morphologies, hydrodynamics and vegetation coverages. Surface sediments were collected in four hydrological seasons: low water (LW), rising water (RW), high water (HW) and falling water (FW) in 2009 and 2010. We investigated commonly used bulk geochemical tracers such as the C : N ratio and the stable isotopic composition of organic carbon ($\delta^{13}$C$_{org}$). These results were compared with lignin-phenol parameters as an indicator of vascular plant detritus and branched glycerol dialkyl glycerol tetraethers (brGDGTs) to trace the input of soil organic matter (OM) from land to the aquatic settings. We also applied the isoprenoid GDGT (iGDGT) crenarchaeol as an indicator of riverine suspended particulate organic matter (SPOM). Our data showed that during the RW and FW seasons, the surface sediments were enriched in lignin and brGDGTs in comparison to other seasons. Our study also indicated that floodplain lake sediments primarily consisted of allochthonous, C$_3$ plant-derived OM. However, a downstream increase in C$_4$ macrophyte derived OM contribution was observed along the gradient of increasing open waters, i.e. from upstream to downstream. Accordingly, we attribute temporal and spatial difference in SOM composition to the hydrological dynamics between the floodplain lakes and the surrounding flooded forests.

1 Introduction

Inland waters play a significant role in the global carbon budget. Lakes and rivers are active systems where the transport, transformation and storage of organic carbon (OC) affect the carbon cycle on a landscape and global scale (e.g., Cole et al., 2007; Tranvik et al., 2009; Raymond et al., 2013). In this context, the wetlands, are dynamic interfaces between the terrestrial and aquatic realms, which promote the redistribution...
of carbon sources and sinks. Thus, they must be taken into account for the carbon fluxes and storage in the continents and for climate change mitigation strategies (Bat-tin et al., 2009). Floodplain lakes are temporary or permanent water bodies formed in the wetlands of the Amazon basin. They are among the most productive ecosys-
tems in the world (Junk, 1997; Melack and Forsberg, 2001). The primary production is performed by the flooded forest, macrophytes, phytoplankton and periphyton (Junk et al., 2010). and further, the organic matter (OM) produced in the floodplain lakes fuels the outgassing CO$_2$ in the river system (Abril et al., 2014). Periodical floods inten-
sify the exchange of organic compounds, nutrients and minerals between rivers, lakes and flooded soils (Junk, 1997). Although only 10–20% of the OM produced in the water column reaches the sediment and is finally buried (Devol et al., 1984), the sediments in these lakes are important sinks of carbon (Moreira-Turcq et al., 2004). Most of the sedimentary organic matter (SOM) in freshwater systems is derived from terrestrial vascular plants (Goñi and Hedges, 1992; Moreira-Turcq et al., 2004; Mortillaro et al., 2012). In the Amazon basin, many studies have characterized the OM in the suspended particulate organic matter (SPOM) in the rivers system and in the flood-
plain lakes and concluded that the main source of OC to the aquatic system is forests and upstream Andean soils (e.g., Hedges et al., 1986; Quay et al., 1992; Victoria et al., 1992; Hedges et al., 1994; Moreira-Turcq et al., 2004; Aufdenkampe et al., 2007; Mortillaro et al., 2011; Moreira-Turcq et al., 2013; Zell et al., 2013b). However, little is
known about the molecular composition of the SOM in the floodplains in general, and in floodplain lakes in particular, and the contribution of the multiple sources of OM (up-
land soils, flooded forest, aquatic macrophytes, and phytoplankton) remain uncertain
(Mortillaro et al., 2011; Zocatelli et al., 2011; Moreira et al., 2014).

The spatiality and the seasonality of the hydrology in the Amazon basin strongly in-
fluence the dynamics and the quality of OC in the surface sediments. Most of the SOM is supposed to be transported to the floodplain lakes via river main streams during the high water season (Hedges et al., 1986; Victoria et al., 1992; Moreira-Turcq et al., 2004; Mortillaro et al., 2012; Moreira-Turcq et al., 2013). However, a significant increase in
vertical flux of OC was observed in lake Curuai during the falling water season, which is interpreted as the result of a process of concentration of periodically resuspended sediments as lakes are becoming smaller and shallower (Moreira-Turcq et al., 2004). In downstream lakes, higher values of bulk $\delta^{13}C$ were found in the sediments, when compared to upstream lakes (Victoria et al., 1992). This variability may be explained by the differences in the interfaces between the river and the lakes along the upstream-downstream transect or in aquatic primary production (mainly aquatic plants), which is more widespread in the open water lakes downstream. A previous study of bulk parameters and fatty acids in the central Amazon basin (Mortillaro et al., 2011) was not conclusive about the sources of SOM in floodplain lakes. Hence, the present work applies multiple biomarkers, namely lignin phenols, branched glycerol diacyl glycerol tetraethers (brGDGTs) and crenarchaeol, in addition to the bulk parameters, to disentangle the sources of SOM in floodplain lakes of the central Amazon basin and the role of the spatiality and seasonality in determining the composition of the SOM.

Lignin is a recalcitrant organic macromolecule composed of phenolic molecules and produced by vascular plants. The products of CuO degradation of lignin (Hedges and Ertel, 1982) have been widely applied as biomarkers to trace plant material to aquatic systems (Hedges et al., 1986; Bernardes et al., 2004; Aufdenkampe et al., 2007; Kuzyk et al., 2008). It can be an important component of fossil OC in floodplain lakes (Zocatelli et al., 2013) but also a relevant source for the outgassing of CO$_2$ in the Amazon River (Ward et al., 2013). BrGDGTs and crenarchaeol have been applied to quantify the OC proportion originating from soils (Hopmans et al., 2004; Herfort et al., 2006; Bélicka and Harvey, 2009; Smith et al., 2010) and have recently been applied to identify the terrestrial and aquatic sources of OC in rivers and floodplain lakes of the Amazon basin (Kim et al., 2012; Zell et al., 2013a; Moreira et al., 2014). A comparison between lignin phenols and GDGTs as markers for terrestrial OC has been performed before in marine and lacustrine systems (e.g., Smith et al., 2010). This comparison showed complementary information on the transport and sedimentation of terrestrial OC in aquatic systems. Finally, the combination of these two groups of biomarkers with
the bulk parameters, analyzed in superficial sediments collected in five floodplain lakes of the central Amazon basin in four hydrological seasons, provides new insights into the link between the hydrology of the Amazon basin to the sources of SOM in floodplain lakes.

2 Study area

The Amazon River is the world’s largest river with a drainage basin area of $6.1 \times 10^6$ km$^2$ covering about 40% of South America (Goulding et al., 2003). The mean annual discharge is $200 \times 10^3$ m$^3$ s$^{-1}$ at Óbidos, the most downstream gauging station in the Amazon River (Callede et al., 2010). Rivers within the Amazon drainage basin are traditionally classified according to water color, as well as physical and chemical parameters (Sioli, 1950): white water (e.g. Solimões, Madeira and Amazon), black water (e.g. Negro), and clear water (e.g. Tapajós). The total area of wetland is $350 \times 10^3$ km$^2$ (Melack and Hess, 2011). Approximately 17% of the central Amazon basin is subjected to periodical floods. This creates large temporary wetlands, i.e. seasonally flooded forests, woodlands and shrubs, which corresponds to 58% of the total flooded area during the high water season. Aquatic macrophytes, floating meadow and marsh cover 5 to 8% of the wetlands and open waters correspond to 12 and 14% in low and high water seasons, respectively (Hess et al., 2003).

Five floodplain lakes were investigated in this study: Cabaliana, Janauaca, Mirituba, Canaçari, and Curuai (Fig. 1a, Table 1). The lakes are located along the Solimões-Amazon river shoreline in a biogeographic gradient of upstream flooded forests to downstream flooded woodlands and open water lakes (Bourgoin et al., 2007; Abril et al., 2014). Cabaliana is a round shape lake surrounded by flooded forests and two sub-regions (Fig. 1b). In the northern region, the Manacapuru River discharges clear water while in the southern region, the white water brought by the Solimões River, mixes with clear water. Janauaca has a peculiar morphology with a ravine shape surrounded by flooded forests (Fig. 1b). Solimões water comes through the channel in the
north, and clear water comes through the stream system in the south. Mirituba has a round shape and receives white water from the Madeira River and the Amazon River through a complex drainage system (Fig. 1c). It can be considered as a white water lake surrounded by flooded forests and woodlands, with no significant contribution of black water streams. Canaçari has two well-defined sub-regions (Fig. 1c). In the northern region, the Urubu River discharges black water and in the southern region, the Amazon River discharges white water. It is surrounded by flooded forests and woodlands. Curuai is the largest lake in the central Amazon basin, mainly surrounded by woodlands and open waters (Fig. 1d). It receives white water from the Amazon River through small channels, apart from the main channel in the eastern side. There are small contributions of black water streams in its most Southeastern part.

3 Materials and methods

3.1 Sample collection

Surface (0–2 cm) sediment samples ($n = 57$) were collected using a grab sampler of 100 cm$^3$ in lakes Cabaliana, Janauaca, Mirituba, Canaçari and Curuai in the central Amazon basin between Manaus and Santarém (Fig. 1). The four hydrological seasons were targeted during different research cruises with a small research vessel (Fig. 2): CBM5 in June and July 2009 covered the High Water (HW) season; CBM6 in October 2009 covered the Low Water (LW) season, CBM7 in August 2010 covered the Falling Water (FW) season and CBM8 in January 2011 covered the Rising Water (RW) season. In each floodplain lake, sediment samples were collected at three stations in each season. However, sometimes only two samples were collected when stations were not accessible during a specific season.

Four riverbank sediments and three soils from well above the inundations known as “terra firme” were also collected during the LW season. In addition, four samples of C$_3$ (Eichornia sp., Pistia stratiotes) and C$_4$ (Paspalum repens) aquatic plants (macro-
phytes) were sampled during the HW season in the lakes Janauaca and Curuai. All samples were kept frozen (−20 °C) on the ship and transported frozen to the Universidade Federal Fluminense laboratory (Brazil), where they were freeze-dried.

3.2 Bulk geochemical parameters

Total carbon (TC), total nitrogen (TN), and δ\(^{13}\)C for the samples obtained during the CBM5 and CBM6 cruises were determined at the Davis Stable Isotope Facility (Department of Plant Sciences, University of California at Davis, California, USA) using a Europe Hydra 20–20 mass spectrometer equipped with a continuous flow isotope ratio monitoring device. For samples obtained during the CBM7 and CBM8 cruises were analysed using a Flash 2000 organic elemental analyser interfaced with a Delta V advantage isotope ratio mass spectrometer at Royal Netherlands Institute for Sea Research (NIOZ, The Netherlands). The average precision was ±0.1 mg C g\(^{-1}\) for TC and ±0.05 mg N g\(^{-1}\) for TN. Sixteen decarbonated sediment samples were additionally analyzed for the total organic carbon (TOC) contents at NIOZ and at Universidade Federal Fluminense (UFF) using a Carlos Erba elemental analyser EA 1110. These analyses were determined in duplicate with a precision of 0.1 mg C g\(^{-1}\) and correlated very well with TOC (wt. %) with a +0.16 intercept (\(R^2 = 0.96; \rho < 0.001; n = 16\)). This indicates that TC in floodplain lakes sediments investigated was mostly TOC. Therefore, we considered TC as TOC in this study. In order to assess contribution of inorganic nitrogen (\(\text{NH}_4^+ + \text{NO}_2^- + \text{NO}_3^-\)) to TN, TN (wt. %) and TOC (wt. %) were correlated (\(R^2 = 0.89; \rho < 0.001; n = 57\)). It showed that a contribution of mineral nitrogen present in fine-grained sediments accounted for ca. 0.06 wt. %. We thus subtracted 0.06 wt. % from the TN content and used this for calculation of the C : N ratio. The δ\(^{13}\)C values of organic carbon (δ\(^{13}\)C\(_{\text{org}}\)) are reported in the standard delta notation relative to Vienna Pee Dee Belemnite (VPDB) standard. The analytical precision (as standard deviation for repeated measurements of the internal standards) was ±0.06 ‰ for δ\(^{13}\)C\(_{\text{org}}\).
3.3 Lignin phenol analysis

Approximately 500 mg of freeze-dried sediments and macrophytes were analyzed for lignin monomers using the alkaline CuO oxidation method (Hedges and Ertel, 1982; Goni and Hedges, 1992) at the Universidade Federal Fluminense laboratory (Brazil). In brief, sediments or macrophytes were transferred to stainless steel reaction vials and digested with 300 mg CuO in 2N NaOH under N₂ in an oxygen-free atmosphere at 150 °C for 150 min. The samples were acidified to pH 1–3 and subsequently 6 mL of ethyl acetate was added. After centrifuging at 2500 rpm for 5 min the supernatant was collected, dried over sodium sulfate (Na₂SO₄), evaporated under a stream of N₂, reconstituted in pyridine, and converted to trimethylsilyl derivatives using bis-(trimethylsilyl) trifluoroacetamide (BSTFA) at 60 °C for 20 min. Oxidation products were analyzed using an HP Agilent 6890N Series gas chromatography.

The recovery factor was calculated using the internal standard ethyl vanillin added prior to analysis (values above 60% were considered). The response factor was performed using a mixture of commercial standards in four different concentrations, which were periodically injected for calibration. To confirm the identification of each lignin phenol, eight selected samples were analyzed with an Agilent 7890A gas chromatography coupled to an Agilent 5975C VL MSD mass spectrometer using a selective ion monitoring (SIM) at NIOZ (The Netherlands).

Phenol concentrations were reported as the carbon-normalized sum of eight lignin-derived reaction products (λ8 mg g⁻¹oc), including vanillyl (V-series) phenols (vanillin, acetovanillone, and vanillic acid), syringyl (S-series) phenols (syringaldehyde, acetosyringone, and syringic acid), and cinnamyl (C-series) phenols (p-coumaric and ferulic acid). Ratios S : V and C : V were calculated to identify angiosperm tissue sources. The ratio of acidic to aldehyde vanillyl phenols ((Ad : Al)ₜ) was used as an indicator of the lignin degradation state, since acidic phenols are produced from aldehyde functional groups during the lignin degradation (Hedges and Ertel, 1982).
3.4 GDGT analysis

All samples for the lipid analysis were processed at NIOZ (The Netherlands). The freeze-dried samples were extracted with a modified Bligh and Dyer technique (Bligh and Dyer, 1959; Pitcher et al., 2009). In brief, the samples were extracted three times with a mixture of methanol (MeOH):dichloromethane (DCM):phosphate buffer (8.7 g of K$_2$HPO$_4$ in 1 L bidistilled water) 10 : 5 : 4 ($\nu : \nu : \nu$) in an ultrasonic bath (10 min). Extracts and residues were separated each time by centrifugation at 2500 rpm for 2 min. DCM and phosphate buffer were added to the extracts to give a new volume ratio 1 : 1 : 0.9 ($\nu : \nu : \nu$). This mixture was centrifuged at 2500 rpm for 2 min. to obtain a good phase separation. The DCM phase was then collected in a round bottom flask. The MeOH-phosphate phase was washed twice with DCM and then discarded. The collected DCM fractions were reduced under rotary vacuum.

The total lipids extracts were fractioned into core lipids and intact polar lipids (IPLs). The separation was carried out on activated silica with $n$-hexane:ethylacetate 1 : 1 ($\nu : \nu$) for core lipids and MeOH for IPLs (Pitcher et al., 2009). To each fraction, 0.1 µg C$_{46}$ GDGT internal standard was added (Huguet et al., 2006). Two third of the IPL fraction was hydrolyzed to cleave off polar head groups. The hydrolysis was carried out by refluxing (3 h) in 2 N HCl:MeOH 1 : 1 ($\nu : \nu$). The solution was adjusted to pH 5 with 2 N KOH-MeOH. This mixture was washed three times with DCM. The DCM fractions were collected, reduced by rotary evaporation, and dried over a Na$_2$SO$_4$ column. Core lipids fractions were separated into polar (DCM:MeOH 1 : 1, $\nu : \nu$) and apolar (DCM) fraction over an activated Al$_2$O$_3$ column.

The core lipids and IPL-derived GDGTs were analyzed using high performance liquid chromatography-atmospheric pressure positive ion chemical ionization-mass spectrometry (HPLC-APCI-MS) in selected ion monitoring (SIM) mode according to Schouten et al. (2007). Quantification of the GDGTs was achieved by integrating the peak areas and using a C$_{46}$ GDGT internal standard according to Huguet et al. (2006).
3.5 Long-Chain \( n \)-Alkanes carbon isotopes

Two sediment samples collected in the LW season, one from lake Janaúca and another from lake Curuai, were used to compare the differences in the \( \delta^{13}C \) values of plant-wax derived long-chain \( n \)-alkanes in the upstream and in the downstream lakes. The extraction of \( n \)-alkanes was performed with an Accelerated Solvent Extraction method (ASE). The extracts were fractionated in apolar and polar fractions using an activated aluminum oxide (\( \text{Al}_2\text{O}_3 \)) column with hexane and MeOH:DCM (1 : 1, \( v : v \)), respectively, as the eluents. The \( n \)-alkanes in the apolar fraction were identified by a Thermo Finnigan Trace DSQ gas chromatography (GC-MS) and quantified with an HP 6890 GC system. To quantify the concentration of the \( n \)-alkanes, an internal standard was added to the apolar extracts. To further clean up the apolar fraction, the extracts were passed over a silver nitrate (\( \text{AgNO}_3 \)) column using hexane as the eluent. The \( \delta^{13}C \) values of higher \( n \)-alkanes were determined using an isotope-ratio-monitoring mass spectrometer (IRM-GC-MS) Thermo Delta V Advantage and the results were obtained using the software Isodat 3.0. Four injections were performed for each sample to calculate the analytical error.

3.6 Statistical analysis

To evaluate the differences in mean values between different groups, the non-parametric Mann-Whitney U-test was used, which does not need the normality assumption of the one-way analysis variance (ANOVA). Groups that showed significant differences (\( p < 0.05 \)) were assigned with different letters. The statistical test was performed with the software package SIGMAPLOT 11.0.
4 Results

4.1 Bulk parameters

The TOC content showed lower mean value (Table 2) in the downstream lake Curuai (2.0 ± 0.6 wt. %) and the highest mean value was found in Cabaliana (3.3 ± 0.8 wt. %; Fig. 3a). No significant seasonal variation was observed (Fig. 4a). The C : N ratio did not reveal significant spatial and seasonal variations (Figs. 3b and 4b). The lowest mean value was found in Curuai (10 ± 1) and the highest one in Mirituba (11 ± 2). The $\delta^{13}$C$_{org}$ values were significantly less negative in the downstream lakes (Fig. 3c). In Curuai the mean value was $-27 \pm 1$ ‰ and in Cabaliana $-33 \pm 2$ ‰. No significant seasonal variation was observed for the $\delta^{13}$C$_{org}$ values (Fig. 4c).

The $\delta^{13}$C$_{org}$ values in soils and riverbank sediment samples varied between $-29$ and $-19$ ‰ ($n = 7$) and the C : N ratio values varied between 6 and 16 ($n = 7$; Table 3). The C$_4$ macrophytes samples (*Paspalum repens*) showed values of $\delta^{13}$C$_{org}$ between $-14$ and $-13$ ‰ and values of the C : N ratio between 15 and 27. The C$_3$ macrophytes (*Eleocharis* sp. and *Pistia stratiotes*) had $\delta^{13}$C$_{org}$ values of $-30$ ‰ and values of the C : N ratio between 15 and 24 (Table 2).

4.2 Lignin phenols

No significant changes were observed along the upstream-downstream transect for the mean values of $\lambda_8$ (i.e. a proxy for the amount of lignin); the mean value of $\lambda_8$ for the SOC was $44 \pm 29$ mg g$^{-1}$oc. However, $\lambda_8$ values revealed significant seasonal changes. The higher values were observed in the RW (56 ± 30 mg g$^{-1}$oc) and in the FW seasons (62 ± 34 mg g$^{-1}$oc) compared to the HW (23 ± 9 mg g$^{-1}$oc) and LW (29 ± 12 mg g$^{-1}$oc) seasons (Fig. 3g). The $C : V$ ratio showed no significant seasonal and spatial variation, and the mean value for all sediment samples was $0.7 \pm 0.4$ (Figs. 3d and 4d). The values of the $S : V$ ratio did not show significant spatial differences either but higher mean values in the RW season (1.1 ± 0.1) and in the FW season (1.2 ± 0.2) were observed in
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4.3 BrGDGTs and crenarchaeol

Along the upstream-downstream transect, no significant changes were observed for the mean values of brGDGTs concentrations (Fig. 3h). The lowest value was found in Curuai (31 ± 14 µg g\textsuperscript{-1}oc) and the highest one in Canaçari (44 ± 22 µg g\textsuperscript{-1}oc). The mean concentrations of crenarchaeol were higher in Canaçari (115 ± 57 µg g\textsuperscript{-1}oc) compared to Janauaca (34 ± 33 µg g\textsuperscript{-1}oc). However, no significant difference was observed between the upstream (Cabaliana and Janauaca) lakes and the downstream lake (Curuai; Fig. 3h and i). On the other hand, brGDGTs concentrations showed significant seasonal changes. The highest mean value for brGDGTs concentrations was found in the FW season (45 ± 23 µg g\textsuperscript{-1}oc), and the lowest mean concentration was found in the HW season (24 ± 16 µg g\textsuperscript{-1}oc). The RW and LW seasons showed intermediate mean concentrations (35 ± 12 and 38 ± 16 µg g\textsuperscript{-1}oc, respectively) and no significant difference was observed if compared to the FW and HW seasons (Fig. 4h). The concentrations of crenarchaeol did not reveal significant changes over the hydrological seasons (Fig. 4i). The mean values varied between 5 ± 4 and 10 ± 6 µg g\textsuperscript{-1}oc in the HW and LW seasons, respectively. The percentage of IPL brGDGTs and IPL crenarchaeol was significantly
higher in the LW season (19 ± 7 and 23 ± 9 %, respectively). In the other three seasons, it showed values around 10 ± 2 % of IPL brGDGTs and IPL crenarchaeol with no significant variability (Table 3).

4.4 Long-chain n-alkanes

The results of n-alkane analyses are summarized in Table 6. The carbon preference indices (CPI), calculated according to Bray and Evans (1961), were high, confirming a plant wax origin of the higher n-alkanes. A somewhat lower CPI was found in the downstream lake (3.5) compared to those in the upstream lake (5.5). A significant increase in the δ¹³C values of the long-chain n-alkanes (C₂₇, C₂₉, C₃₁) was observed downstream. In the upstream lake, the mean δ¹³C for the long-chain n-alkanes was −34.1 ± 0.5 ‰ and in the downstream lake the mean value was −31.6 ± 0.6 ‰ (Table 6). This represents a difference of 2.5 ‰ from upstream to downstream.

5 Discussion

5.1 Sources of sedimentary organic matter in the floodplain lakes

To determine the origin of the SOM in the floodplain lakes, we considered five potential sources: (1) the terrestrial Andean clay-bounded and refractory SPOM, which may be transferred to the floodplain lakes via the Solimões-Amazonas and Madeira rivers (Hess et al., 2003), (2) “terra firme” soil and litter of the Amazonian lowland forest, which will be transferred to the floodplain lakes via streams, (3) the wetland soil (flooded forests) and litter (leaves, grasses, wood etc.), transferred to the floodplain lakes during the receding waters (falling water season) or in the rainy season (rising water season; Schöngart et al., 2010), (4) the wetland aquatic and semi-aquatic macrophyte vegetation of the floodplain lakes (Junk, 1997; Moreira-Turcq et al., 2004; Mortillaro et al., 2011), and (5) phytoplankton from the river or produced in the lake itself (Moreira-
The biomarkers analyzed, lignin phenols and GDGTs, enabled us to identify most of these sources of OM, except for planktonic sources. However, in this case, some information can be obtained using bulk parameters, i.e. the $\delta^{13}$C$_{\text{org}}$ and C : N ratio. Our results were compared with data reported previously (Hedges et al., 1986; Martinelli et al., 1994; Meyers, 1994; Martinelli et al., 2003; Aufdenkampe et al., 2007; Zell et al., 2013b) and with specific OM sources sampled and analyzed in this work, such as macrophytes, wetland soil and “terra firme” soil (Table 3), in order to identify the main sources of SOM in the floodplain lakes.

The average values of the various parameters of the river SPOM (Ertel et al., 1986; Hedges et al., 1986), wetland soils, “terra firme” soils and the potential biological OM sources (phytoplankton, macrophytes, grass, leaves and wood) are compared with those of the SOM of the floodplain lakes in Fig. 5 and Table 4. Data for the riverine SPOM is subdivided into fine particulate organic matter (FPOM) and coarse particulate organic matter (CPOM). For the interpretation of these data, it is important to note that the amount of CPOM in the Amazon river has been reported to be approximately eight times lower than that of the FPOM (Richey et al., 1990). The averages of important lignin parameters ($\lambda_8$, $S : V$ ratio) but also the C : N ratio of the wood samples are significantly different from those for the sediments, which clearly indicates only a minor contribution of woody material to the SOM. Furthermore, the $\lambda_8$ of riverine FPOM is substantially lower than that of the SOM of the floodplain lakes, indicating that riverine SPOM is not an important source of lignin for the SOM of the floodplain lakes either. In terms of lignin parameters, the SOM is distinguished by two clear characteristics. Firstly, the (Ad : Al)$_V$ ratio is high with an average value of 1.25 (Fig. 5). Such a high value is only noted in the wetland and “terra firme” soils. However, this ratio is affected by the oxidation state of the lignin and thus, cannot be used as a source characteristic of the lignin. Secondly, the SOM is characterized by a substantially elevated $C : V$ ratio (Fig. 6; cf. Hedges et al., 1982). Since all of the potential lignin sources, except macrophytes, have a much lower value, this indicates that macrophyte lignin and, thus accordingly, macrophyte OM (since average $\lambda_8$ values of macrophyte OM and the SOM...
do not substantially differ) largely contribute to the SOM. Since the \( S : V \) ratio of macrophyte OM is relatively lower than that of the lignin component of the SOM (Fig. 5), some contributions of lignin derived from other fresh plant OM (i.e. grasses/leaves) or wetland soils might explain the elevated \( S : V \) ratio of the SOM.

Further information with respect to sources of SOM can be obtained from the GDGT concentrations. The concentrations of both brGDGTs and crenarchaeol are higher in the riverine SPOM than in the SOM, pointing to a contribution of riverine SPOM to the SOM, in contrast to what was shown by the lignin phenols. However, the concentrations of brGDGTs in the wetland soils and river SPOM are statistically indistinguishable and, thus, it is not possible to use the brGDGTs as a specific OM source indicator. This is in line with the idea that brGDGTs can be produced in soils (e.g., Weijers et al., 2006), rivers (e.g., Zell et al., 2013a; De Jonge et al., 2015) and lake waters (e.g., Tierney et al., 2010; Buckles et al., 2014). On the other hand, riverine SPOM is the only possible OM source explain a substantially increased concentration of crenarchaeol, in the SOM of the floodplain lakes if compared to other sources (Fig. 5). Crenarchaeol is indeed produced in the Amazon river by nitrifying archaea that consume ammonium produced from degrading algal OM (Zell et al., 2015). However, it is known that crenarchaeol is also produced in lakes (Blaga et al., 2011; Tierney and Russell, 2009), indicating that it may also be produced in the floodplain lakes. Crenarchaeol is, therefore, considered as an (indirect) indicator of aquatic primary production. The enhanced concentrations of crenarchaeol in SOM thus indicate a contribution from this source.

In terms of bulk parameters, the C : N ratio in the SOM shows intermediate values between the riverine SPOM and the various OM sources but, with no distinct average values between them. Moreover, the average values of \( \delta^{13}C_{\text{org}} \) are statistically equal for sediments and most sources of OM (except for the wetland soils) and the TOC do not show any significant difference between the soils samples, riverine SPOM and lake sediments. Thus, it is not possible to discriminate any specific source of SOM based on the average values of the bulk parameters.
We have argued that the $C:V$ ratio and the crenarchaeol concentration are the only two parameters that clearly point out one specific source of SOM (i.e., macrophytes and aquatic production in the rivers or floodplain lakes, respectively). Consequently, these parameters can be applied to a two end-member model to estimate the fractions of each of these two sources in the SOM. According to this approach (Martinelli et al., 2003), the $C:V$ values of macrophytes and the average values of soil and riverine SPOM samples can be used to estimate the contribution of macrophyte OM to the SOM. Similarly, the concentration of crenarchaeol in the riverine SPOM and its concentration in soil samples can be used to estimate the contribution of aquatically produced OM to the SOM (Eq. 1–3, Table 5).

$$F_{\text{macrophyte}} = (C:V_{\text{SOM}} - C:V_{\text{other}})/(C:V_{\text{macrophyte}} - C:V_{\text{other}}) \cdot 100$$ \hspace{1cm} (1)

$$F_{\text{aquatic}} = (\text{Cren}_{\text{SOM}} - \text{Cren}_{\text{other}})/(\text{Cren}_{\text{SPOM}} - \text{Cren}_{\text{other}}) \cdot 100$$ \hspace{1cm} (2)

$$F_{\text{wetlands}} = 100 - (F_{\text{aquatic}} + F_{\text{macrophyte}})$$ \hspace{1cm} (3)

In Eqs. (1) and (2), the $F_{\text{macrophytes}}$ and $F_{\text{aquatic}}$ represent the estimated fractional abundance in SOM of macrophytes and SPOM, respectively. $C:V_{\text{SOM}}$ and $\text{Cren}_{\text{SOM}}$ are the average values of each parameter found in the sediment samples, $C:V_{\text{macrophytes}}$ and $\text{Cren}_{\text{SPOM}}$ are the values of the source of the respective parameter and $C:V_{\text{other}}$ and $\text{Cren}_{\text{other}}$ are the values of the other possible sources (Table 5). These calculations indicate that 20–30 % of the SOM is derived from macrophytes and 20–30 % from the aquatic production either in the river or in the floodplain lake itself. Consequently, the remaining 40–60 % of the SOM might be derived from other sources of OM such as the flooded forests (Eq. 3). The periodical floods link the floodplain lakes and the wetland vegetation and soil. Thus, the seasonal and spatial contrasts in the SOM should be investigated in order to better understand the connectivity between these compartments.
5.2 Spatial differences in the composition of sedimentary organic matter

Along the longitudinal transect, from upstream to downstream, most bulk geochemical parameters (i.e. TOC content and $\delta^{13}$C$_{org}$) show significant differences between the upstream and downstream lakes (Fig. 3a, c), while most of the measured biomarker parameters ($\lambda_8$, $S : V$, (Ad : Al)$_V$ and brGDGTs) do not show such a pattern (Fig. 4e, f, g, and h). On the other hand, the biomarker parameters show, in some cases, a clear seasonal contrast, which is not observed for the bulk parameters. Consequently, the bulk parameters apparently mix and homogenize the long time scale (year), while the biomarkers are more sensible to changes in short time scale (months) at the sediment surface. This observation is in agreement with previous studies about earlier diagenesis of organic molecules (Harvey, 2006). It is important to note that the results must be interpreted taking in consideration the high sedimentation rates in the floodplain lakes, typically 1–2 cm yr$^{-1}$ (Moreira-Turcq et al., 2004), and the fact that re-suspension is induced by storms during the LW and RW seasons or by currents during the receding waters (FW). These events may have a substantial effect on the material comprising the first 2 cm of sediments of floodplain lakes, which are mixed with newly arrived SOM from the water column, and are re-oxygenated favoring the degradation.

The percentage of TOC in the sediment samples shows a decrease from 3.3 (wt. %) upstream (Cabaliana) to 2.1 (wt. %) downstream (Curuai; Fig. 3a). Furthermore, over the transect of lakes the average $\delta^{13}$C$_{org}$ values increase by ca. 5 ‰ (Fig. 3c). However, the average C : N ratio does not show any significant changes over the transect (Fig. 3b). These results are in good agreement with previous studies in the central Amazon Basin (Victoria et al., 1992; Martinelli et al., 2003). The increasing trend in $\delta^{13}$C$_{org}$ from upstream to downstream lakes may be caused by an increased contribution of C$_4$ macrophytes to the SOM, whose abundance increases in open water lakes and floodplains. Alternatively, since the $\delta^{13}$C$_{org}$ values in the downstream lakes come closer to the $\delta^{13}$C$_{org}$ of the Solimões-Amazon SPOM ($\sim$ −26 to −30 ‰; Hedges et al., 1986; Moreira-Turcq et al., 2013; Mayorga et al., 2005), an increased input of riverine...
organic matter may also explain this. To disentangle whether this trend in the $\delta^{13}C_{\text{org}}$ values is caused by the contribution of $C_4$ plants or of riverine SPOM, the isotopic composition ($\delta^{13}C$) of long-chain $n$-alkanes was analysed. Sediments from the upstream lake Janauaca and the downstream lake Curuai, both collected during the LW season, were compared. The results (Table 6) show that the long-chain $n$-alkanes $\delta^{13}C$ signature is more like those of $C_3$ higher plants (Castañeda et al., 2009) for both lakes although for Curuai the values are slightly less negative. If one considers the values of $\delta^{13}C$ in the $n$-alkane $C_{29}$ in the leaf waxes of $C_3$ and $C_4$ plants, one can calculate the contribution of $C_4$ plants sedimentary $n$-alkanes according to the following equation:

$$\text{Contribution of } C_4 \text{ plants} = \frac{\delta^{13}C_{\text{org}} C_{29} (C_3 \text{ plants}) - \delta^{13}C_{\text{org}} C_{29} (\text{sediment})}{\delta^{13}C_{\text{org}} C_{29} (C_3 \text{ plants}) - \delta^{13}C_{\text{org}} C_{29} (C_4 \text{ plants})} \cdot 100 \quad (4)$$

where the end member value for $\delta^{13}C_{\text{org}} C_{29}$ (C3 plants) is $-34.7 \permil$ and for $\delta^{13}C_{\text{org}} C_{29}$ (C4 plants) is $-21.7 \permil$ (Castañeda et al., 2009). The measured values for $\delta^{13}C_{\text{org}}$ of the $C_{29}$ $n$-alkane in the sediments of Janauaca and Curuai are listed in Table 6. Accordingly, the percentage of $C_4$ plants in the upstream lake is only 3%, but for the downstream lake 22%. The difference in $\delta^{13}C_{\text{org}}$ for $C_4$ and $C_3$ higher plants is ca. 20%. A switch from almost 100% $C_3$ macrophytes to a 78% contribution would result in a change in the isotopic composition of the macrophyte “pool” of the SOM of 4–4.5‰. Since this pool is estimated to represent 20–30% of the SOM, this cannot fully explain the observed 5‰ shift (Fig. 3c). However it should be considered that the increasing fraction of $C_4$ higher plants for the SOM in the downstream lake may not solely be the consequence of changes in the contributing aquatic macrophytes. Land vegetation, mainly shrubs and grass in downstream lakes, may also affect the observed shift in $\delta^{13}C_{\text{org}}$ of SOM.
5.3 Seasonal changes in the composition of sedimentary organic matter

The $\lambda 8$ values and the $S : V$ ratio show significantly higher values in the RW and FW seasons (Figs. 4e, g, and 6a) in all lakes. The mean concentrations of brGDGTs also show higher values in the FW season (Figs. 4h and 6b). The co-occurrence of these two types of molecules indicate that litter, traced by lignin phenols, and superficial soil, traced by brGDGTs, are preferentially deposited during rising and receding waters, which increases the wetland soil runoff. Besides, the seasonal mean values of $\text{(Ad} : \text{Al)}_{v}$ show remarkably lower values in the RW and FW seasons (Fig. 4f), an inverse pattern if compared to the $S : V$, $\lambda 8$ and brGDGTs. This means that less degraded lignin is present in the surface sediments in the RW and FW seasons. Thus, the increase in the concentrations of the organic compounds is not a consequence of the re-suspension of the sediments, but to the arrival of fresher OM. In the HW and LW seasons, more degraded lignin phenols (higher values of $\text{(Ad} : \text{Al)}_{v}$) are present in the sediments concomitant with lower amounts of $\lambda 8$ and $S : V$ ratio. Since the concentration of crenarchaeol (a marker for aquatic production) and the $C : V$ ratio (mainly affected by aquatic macrophytes; see above) do not reveal significant seasonal changes, we conclude that such increase in the concentration of the lignin phenols in the RW and FW seasons and the brGDGTs in the FW season is not derived from the water column, riverine SPOM or in situ production but from the soil and leaf runoff.

Previous works postulated that Andean and low land soil material is mainly transferred to the lakes via river main stream, in particular, during the RW and HW seasons and that would be the main source of SOM of the floodplain lakes (e.g., Victoria et al., 1992; Moreira-Turcq et al., 2004; Mortillaro et al., 2011). However, according to our results, the lignin phenols increase their concentration in the RW and the FW seasons. Thus, based on the hydrodynamics of floodplain lakes and the concentration of the biomarkers applied in this study, in the RW and FW seasons, these organic molecules are mainly derived from the drainage of local wetlands soils. This is more evident for the upstream lakes, which are surrounded by flooded forests and by larger flooded area,
Se than for the downstream lakes, which are surrounded mainly by grass vegetation and shrubs. However, even in lake Curuai, where the primary production and the riverine SPOM is admittedly an important source of SOM (Moreira-Turcq et al., 2004; Zocatelli et al., 2013), the interface between the floodplain lake and the flooded soil drives the sedimentation of the organic compounds.

6 Conclusions

The vegetation coverage of the wetlands (flooded forests) are the most important source of SOM in floodplain lakes of the central Amazon basin. The macrophyte community in the floodplain lakes is also an important source of SOM whereas the river SPOM contributes to a minor fraction of it. In upstream lakes, higher TOC contents in the surface sediments is observed, if compared to the downstream large open lakes. The differences observed in the vegetation of the wetlands, affect the quality of SOM in the floodplain lakes. This pattern could only be observed in a longitudinal transect approach, with the application of molecular isotope technique apart from multiple biomarkers analysis. The sedimentation of OC in the floodplain lakes are linked to the periodical floods. The raining season (RW season), when increases the soil runoff and the receding of waters (FW season), when the organic matter is transported from the flooded soils to the floodplain lakes, are the most important hydrological factors for the sedimentation of OM in the wetlands of the central Amazon basin. Hence, together with wetland vegetation, the hydrodynamics of the floodplain seems to be the most important controlling factor on the composition of SOM in the floodplain lakes of the central Amazon basin.

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Table 1. Localization and summary of geomorphology, biogeography, and water physicochemical of the five floodplain lakes. Data of temperature, conductivity and pH represent the maximum and minimum values measured in situ for four hydrological seasons.

|                 | Cabalina | Janauaca | Mirituba | Canaçari | Curuai |
|----------------|----------|----------|----------|----------|--------|
| Latitude (S)   | 3°18'46" | 3°23'20" | 3°20'50" | 2°58'60" | 2°09'44" |
| Longitude (W)  | 60°40'11" | 60°16'26" | 58°23'60" | 58°15'40" | 55°27'53" |
| Approx. area (km²) | 300 | 85 | 360 | 290 | 1050 |
| Shape          | Ellipsoid | Ravine dendritic | Round | Ellipsoid | Triangular |
| Wetland Vegetation Type | Forests | Forests | Forests/Woodlands | Forests/Woodlands | Woodlands/Shrub |
| Water          | Black | Black | White | Black | White |
| Conductivity (µS) | 10–80 | 33–71 | 43–65 | 10–54 | 41–69 |
| Temperature (°C) | 28–34 | 29–33 | 28–34 | 29–34 | 30–36 |
| pH             | 5.0–7.5 | 6.1–8.0 | 6.2–8.5 | 5.9–9.4 | 7.3–10.1 |

Obs: All floodplain lakes receive white water from the solimões-amazon river in the flooding season.
### Table 2. Values of bulk parameters and lignin phenols in Macrophytes, Wetland soil and non floodable (terra firme) soil.

|                     | TOC (wt. %) | C : N | $\delta^{13}$C (‰) | $\lambda$ (mg g$_{OC}$$^{-1}$) | C : V | S : V | (Ad : Al)$^\nu$ |
|---------------------|-------------|-------|---------------------|-------------------------------|-------|-------|-----------------|
| **Macrophytes**     |             |       |                     |                               |       |       |                 |
| *Eleocharis* sp. (root) | 27.2        | 15    | −32.3               | 47.5                          | 3.7   | 0.6   | 0.1             |
| *Eleocharis* sp.    | 42.3        | 24.1  | −30.5               | 56.6                          | 3.1   | 0.6   | 0.8             |
| *Pistia stratiotes* | 37.1        | 15    | −29.7               | 25.9                          | 0.4   | 0.9   | 0.1             |
| *Paspalum repens*   | 41.6        | 14.9  | −12.6               | 47.9                          | 1.7   | 0.4   | 0.1             |
| *Paspalum repens* (root) | 38.5        | 27.1  | −13.6               | 93.9                          | 4     | 0.7   | 0.2             |
| **Wetland soil**    |             |       |                     |                               |       |       |                 |
| Janauaca            | 0.6         | 6.1   | −27.3               | 25.5                          | 0.2   | 0.6   | 1.2             |
| Janauaca stream     | 0.4         | 8.3   | −27.8               | 63.2                          | 0.5   | 1.1   | 1               |
| Amazon river        | 0.4         | 9.8   | −28.4               | 9                             | 0.5   | 1     | 1.3             |
| Amazon river        | 1           | 6.7   | −18.7               | 67.5                          | 0.5   | 0.9   | 0.9             |
| **Soil (Terra Firme)** |             |       |                     |                               |       |       |                 |
| Canaçari            | 2.1         | 16.3  | −27.4               | 36.6                          | 0.3   | 0.8   | 0.6             |
| Amazon river        | 4.2         | 14    | −28.7               | 9.7                           | 0.5   | 0.5   | 1.4             |
| Amazon river        | 2.3         | 11.1  | −29                 | 88.3                          | 0.4   | 0.5   | 1.5             |
Table 3. Average values for the seasonality and spatiality of bulk parameters, lignin phenols and GDGTs in sediment samples from the floodplain lakes.

| Location | n  | TOC (wt. %) | C : N | δ¹³C_{org} (‰) | L8 | C : V | S : V (Ad : Al) | brGDGTs (µg g⁻¹OC) | crenarchaeol (µg g⁻¹OC) | IPL brGDGTs (%) | IPL crenarchaeol (%) |
|----------|----|-------------|------|----------------|----|------|---------------|-------------------|----------------------|---------------|----------------------|
| Cabaliana| 10 | 3.3         | 10.9 | −33.0          | 32 | 0.6  | 1.0           | 1.6               | 33                   | 6             | 15                   | 9             |
| Janauaca | 11 | 2.7         | 10.9 | −32.2          | 50 | 0.6  | 1.1           | 1.2               | 41                   | 4             | 14                   | 15            |
| Mirituba | 11 | 2.3         | 11.3 | −29.3          | 57 | 0.7  | 1.0           | 1.4               | 33                   | 8             | 14                   | 18            |
| Canaçari | 10 | 2.0         | 10.9 | −30.0          | 42 | 0.9  | 1.1           | 1.2               | 44                   | 12            | 9                    | 11            |
| Curuai   | 15 | 2.1         | 10.0 | −27.0          | 41 | 0.9  | 1.1           | 1.0               | 31                   | 9             | 9                    | 15            |
| LW       | 12 | 2.3         | 10.2 | −30.0          | 29 | 0.7  | 0.9           | 1.5               | 38                   | 10            | 19                   | 23            |
| RW       | 15 | 2.7         | 10.6 | −30.1          | 56 | 0.8  | 1.1           | 1.0               | 35                   | 7             | 8                    | 10            |
| HW       | 12 | 2.6         | 11.1 | −29.7          | 23 | 0.8  | 1.0           | 1.7               | 24                   | 4             | 10                   | 13            |
| FW       | 18 | 2.2         | 11.0 | −30.2          | 62 | 0.6  | 1.1           | 1.1               | 45                   | 9             | 9                    | 8             |
Table 4. Average values of biomarkers and bulk parameters in the possible sources of SOM and in sediment samples. The data was obtained in the present work and in the literature (Hedges et al., 1986; Hedges and Mann, 1979; Aufdenkampe et al., 2007).

| Source            | TOC (wt. %) | C : N  | $\delta^{13}$C$_{org}$ (%) | C : V | S : V | (Ad : Al)$_V$ | $\lambda$8 $\mu g$ g$_{oc}^{-1}$ | brGDGTs $\mu g$ g$_{oc}^{-1}$ | crenarchaeol $\mu g$ g$_{oc}^{-1}$ |
|-------------------|-------------|--------|-----------------------------|-------|-------|----------------|-------------------------------|-------------------------------|-------------------------------|
| Wetland soil      | 0.9         | 8.3    | -27.0                       | 0.4   | 0.9   | 1.1            | 41.3                         | 39.6                          | 2.9                           |
| Soil (terra firme)| 1.6         | 10.5   | -27.6                       | 0.4   | 0.6   | 1.2            | 44.9                         | 21.1                          | 0.5                           |
| River (CPOM)      | 1.4         | 4.8    | -31.4                       | 0.1   | 0.7   | 0.2            | 40.0                         |                               |                               |
| River (FPOM)      | 2.2         | 7.2    | -29.9                       | 0.1   | 0.9   | 0.6            | 16.1                         | 77.4                          | 25.9                          |
| Macrophyte        | 36.6        | 28.7   | -24.7                       | 1.9   | 0.6   | 0.3            | 59.0                         |                               |                               |
| Grass/Leave       | 46.7        | 28.1   | -30.1                       | 0.4   | 1.1   | 0.2            | 37.2                         |                               |                               |
| Phytoplankton     | 13.9        | 6.7    | -31.1                       |       |       |                |                               |                               |                               |
| Wood              | 46.5        | 217.7  | -27.6                       | 0.0   | 1.5   | 0.1            | 193.3                        |                               |                               |
| Sediment          | 2.4         | 10.7   | -30.0                       | 0.7   | 1.1   | 1.3            | 43.6                         | 36.1                          | 7.8                           |
Table 5. Values applied to equations 1, 2 and 3 to estimate the fraction of OM derived from macrophytes, riverine SPOM and wetland soils to the SOM.

| Sediment Samples          | OC<sub>source</sub> | OC<sub>other</sub> | % SOM |
|---------------------------|---------------------|--------------------|-------|
| Macrophyte                | 0.7 ± 0.4           | 1.9                | 0.2   | 29.4  |
| SPOM (crenarchaeol)       | 7.8 ± 6.0           | 26.0               | 1.2   | 26.6  |
| Soil                      |                     |                    |       | 44.0  |
Table 6. Values of long-chain $n$-alkanes $\delta^{13}C$ in surface sediment samples from the upstream lake Janauaca and the downstream lake Curuai. The samples were collected in the LW season.

|          | $C_{27}$  | $C_{29}$  | $C_{31}$  |
|----------|-----------|-----------|-----------|
| Janauaca | $-33.7 \pm 0.2$ | $-33.8 \pm 0.2$ | $-34.8 \pm 0.2$ |
| Curuai   | $-31.2 \pm 0.3$ | $-31.5 \pm 0.3$ | $-32.2 \pm 0.3$ |
**Figure 1.** Study area of the central Amazon basin (a) showing five floodplain lakes (várzeas) in squares (b), (c), and (d).
Figure 2. Seasonal water level changes of the Amazon River main stem at the town Óbidos (RW = rising water, HW = high water, FW = falling water, LW = low water).
Spatial and seasonal contrasts of sedimentary organic matter

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**Figure 3.** Box plots of bulk OC parameters, lignin phenols, and GDGTs along the upstream-downstream transect. The midpoint of a boxplot is the mean. The 25 and 75 % quartiles define the hinges (end of the boxes), and the difference between the hinges is the spread. Letters indicate statistically significant groups of data ($p < 0.05$).
Figure 4. Mean values of bulk OC parameters, lignin phenols and GDGTs in the sediments of the floodplain lakes in four hydrological seasons. Error bars indicate the standard deviation.
Figure 5. Box plots of average values of multiple biomarkers and bulk parameters in sediment samples and in potential sources on SOM. Data is based on previous studies (Hedges et al., 1986; Aufdenkampe et al., 2007; Zell et al., 2013) and the present work (Table 3). Letters over the boxes indicate significant differences (p < 0.05) between the means.
Figure 6. Box plots of seasonal average values of total lignin phenol and brGDGTs. Letters indicate statistically significant groups of data ($p < 0.05$).