Dear referees and editor,

We thank you for the time and effort in reviewing our manuscript. We are pleased to hear that you have found our work interesting, and we are also grateful for the issues you pointed out to help us improve the quality of our work.

Motivated by your comments, we have restructured our manuscript and tried to address all the issues you mentioned. The responses to your comments and the corresponding changes in the manuscript are listed in the following:

Comments from X. Feng:

Abstract Line 19:

Results from this study somehow contrasts with those from some other marine environments. For instance, lignin phenols in the Washington continental shelf and slope (affected by the Columbia River) are concentrated in the sand-size sediments due to the export of plant debris (e.g., Keil et al. 1998 GCA 62, 1347-1364). Tesi et al. (2016 JGR) has also found that lignin distribution in the Siberian Shelf coincides with the distribution of coarse particles enriched in plant debris. This study, however, reports that lignin is preferentially preserved in fine particles. What characteristics of the Amazon basin make lignin distribution in particles different from that in the Washington and Siberian Shelves? Does it have anything to do with the narrow range of Al/Si ratios, indicating relatively coarse particle sizes of the studied sediments? This should be discussed in the paper.

Response:

We have noticed that our conclusion that the lignin is preferentially preserved in fine particles is in contrast to some previous studies. We do not think this is due to the narrow range of Al/Si ratios. Our Al/Si ratios are between 0.11 and 0.56, which represent grain size (reported as D90) from 10 μm to 330 μm, according to Bouchez et al. (2011, GGG, 12). Even the narrow Al/Si ranges in the Solimões and Madeira rivers represent mean grain sizes varying from 41 μm to 191μm. This range furthermore includes both of the size fractions investigated in earlier studies (i.e., the coarse fraction> 63 μm, the fine fraction<63 μm) (Hedges et al. 1986 Limnol Oceanogr. 31).

In our opinion, the discrepancy likely derives from the different methods of characterizing the grain size distribution of lignin on one hand, and on the other hand might be the result of differences in climatic settings which influences the sediment composition.

In the studies of Keil et al. (1998 GCA 62, 1347-1364) and Tesi et al. (2016 JGR), the sediments were separated into different fractions based on grain size and density. Our samples, in contrast, were not separated in this way. Our sediments were directly ground with the plant debris and mineral particles homogenized. The sediments were thus characterized and discussed as a whole. If we compare our results to those previous studies that like us used mean grain size to explore the effect of grain size distribution on lignin preservation, our results are not in contrast to them. For instance, in the study of Wu et al. (2013 JGR) on the organic matter in surficial sediments of the East China Sea, lignin is enriched in fine-grained sediments, suggesting important contributions form soils. Schmidt et al. (2010 Mar. Chem.) have observed that lignin phenols are preferentially associated with the silt fraction on the Iberian margin.

Alternatively, the discrepancy pointed out by Y. Feng could arise from the distinct climatic settings of the study areas. Our study area in the tropics may be characterized by very efficient degradation

of large plant debris, which is typically enriched in the low density fractions reported to contain high amounts of lignin in the studies by Keil et al. and Tesi et al. Those studies were carried out in higher latitude settings (Washington margin and Laptev Sea), where degradation on land is likely less efficient than in the tropical areas drained by the Amazon River. The particulate organic matter in the riverbed sediments of the lower Amazon basin derives most likely from soils, and plant debris contributes very insignificantly to the sedimentary organic matter. Therefore, it is conceivable that in their studies, a different overall trend in lignin concentrations versus bulk grain size exists. These are the reasons why our results are different from those of Keil et al. (1998 GCA 62, 1347-1364) and Tesi et al. (2016 JGR).

Changes in manuscript:
This point is now discussed in the manuscript in the third paragraph in section 5.1.3.

Comments from X. Feng:
Page 7, Line 9: why is Xingu different from the other tributaries and mainstem?

Response:
Unlike the other tributaries and the Amazon mainstream, the $\Sigma 8$ and $\Lambda 8$ of the Xingu River are not correlated (r^2=0.0239). The Xingu River is a clear water river and has higher levels of in situ primary production relative to the turbid Amazon River. The phytoplankton-derived organic matter will settle out of the water column and dilute the lignin derived compounds. This will decrease the carbon-normalized lignin yields ($\Lambda 8$) but does not influence the sediment-normalized parameter $\Sigma 8$.

Changes in manuscript:
The (r^2=0.0239) of the relation between $\Lambda 8$ and $\Sigma 8$ of the Xingu River is added and the environmental explanation is provided at the second line in section 5.1.2.

Comments from X. Feng:
Page 8, Line 9: lignin increases with distance from the river mouth. This is interesting. Is it statistically significant? If so, why?

Response:
The slight increasing $\Lambda 8$ with distance from the Amazon river mouth was observed only in the SE sector. It is commonly thought that the lignin content should decrease with the distance from the river mouth, because the terrestrial organic matter is diluted by the marine organic matter during the transport. However, in the SE sector we observe the opposite trend. So, we conclude that the lignin in the SE sector derived from the small rivers in the southeast area. This inference is consistent with the evidence that the distribution of the Amazon River plume and the associated sedimentation are affected by the North Brazil Current, which flows northwestward. Because our focus is on the organic carbon derived from the Amazon River, so we did not emphasize details about the SE sector.

Changes in manuscript:

The explanation outlined above is now included in the second paragraph in section 5.2.1.

Comments from X. Feng:

Page 11, Line 1: here and the discussion below mentions that the processing of terrestrial OC is minimal in the Amazon. This contradicts with the findings by Ward et al. (2013 Nature Geoscience) that lignin is being fast degraded within the Amazon River. How do you reconcile the discrepancy? This should also be discussed in the paper.

Response:

In the study of Ward et al. (2013 Nature), dissolved and particulate lignin and phenolic concentrations from Amazon waters were measured before and after incubation experiments. Their conclusion of a rapid degradation is based on the finding of a post-incubation decrease in concentrations of phenolic compounds. The lignin measured in the study of Ward et al. (2013) exists in water column as free particulate and dissolved phase, which is exposed to favourable conditions for degradation. However, our study focuses on the lignin associated with mineral particles，which are deposited and protected from degradation. That is the reason for the contradiction.

Changes in manuscript:

The point is discussed at the end in section 5.1.2.

Comments from X. Feng:

Page 11, Line 32: it is commonly thought that OC in fine particles are more degraded. Your observation is different. Feng et al. (2015 JGR) has found that lignin phenols in the forest O horizons of the upper Amazon basin exhibit very high Ad/Al values. Does this have a play in your observation? This may also explain the constant ratios of C/V and S/V (unaffected by degradation) versus increasing Ad/Al ratios?

Response:

The apparent discrepancy between our finding and the common expectation about the correlation between Ad/Al values and grain size that is pointed out here has a similar origin as the issue discussed above, i.e. the explanation for why lignin is enriched in fine-grained particles in our study but more abundant in coarser fraction in some other studies. It probably depends on whether the sediments are studied as different grain size fractions or as bulk sample. In the study of Schmidt et al. (2010 Mar. Chem.), who like us studied bulk sediments, the Ad/Al values are positively related to mean grain size, which indicates the lignin is less degraded in finer grained particles. This is consistent with our observation.

Moreover, the distribution of Ad/Al ratios within grain size classes is related to the content of plant debris. If plant debris accounts for a large proportion in the sediment, the coarse fraction will show very low Ad/Al values, because of the existence of fresh plant tissue. If the contribution of plant debris is poor, the Ad/Al values will follow a trend as we observed with better preserved lignin in finer grained particles.

The finding of Feng et al. (2016 JGR) provides another possible explanation that the lignin associated with fine particles is more likely from the surface mineral soils (lower Ad/Al values)

and the lignin associated with coarse particles derives from the forest O horizons (higher Ad/Al values). However, their setting in high altitude in Andean area is different from the lowland basin. The Andean signal might not dominate the lowland tributaries. So we refrained from including a speculation based on the observation of Feng et al. (2016 JGR) in the revised manuscript.

In our study, we have observed that the C/V ratios in the the Madeira River, the Solimões River and the Negro River decrease with decreasing grain size. Our C/V ratios and $(Ad/Al)_V$ ratios are positively related, while it is commonly thought that C/V ratios decrease with increasing Ad/Al ratios, because cinnamyl phenols are more easily degraded compared to vanillyl phenols. The S/V ratios are basically constant versus Ad/Al ratios. This unexpected correlation between lignin composition and the Ad/Al ratios probably means S/V and C/V ratios are not influenced by degradation as indicated by Feng et al. (2016 JGR).

Changes in manuscript:
The explanation is added in the fourth paragraph in section 5.1.3.

Comments from X. Feng:
Page 13, Line 10: "Spatial variation" of the degradation state of lignin…
References: -Feng et al. 2016 JGR has recently investigated and compiled lignin phenol distributions in the soil-river (POM & DOM) –marine sediment continuum of the Madre de DOIS-Amazon system. This paper may be a good comparison to your data.

Response:
The sampling locations of marine samples in Feng et al. (2016 JGR) are further away from our samples in the Amazon Fan sector with water depth deeper than 4000 m. It is interesting that some of the Ad/Al ratios in the study of Feng et al. (2016 JGR) are only 0.04 or 0.1, which correspond to values found in fresh plant tissues. The $\Lambda 8$ values in the marine samples in Feng et al. (2016 JGR) are much lower than our results in the NW and Fan sectors. This means there is increasing loss of lignin as the terrestrial organic material is transported to the deep sea region.

Changes in manuscript:
We refer to Feng et al. (2016) in the second and fourth paragraph in section 5.2.1 of the revised manuscript.

Comments from R. Sparkes:
Page 9 Line 10:
The phrase "reflects the characteristics of the tributaries (Fig 2A)" was a bit confusing. After reading through the following section it seems that dilution of carbon by mineral sediment is the main reason for changes in TOC. Authors could consider being more explicit about this at the start of the section.

Response:
Usually the tributaries of the Amazon River are classified by their water colors. Our intention was to say that the TOC contents reflect the features of tributaries with different colors. The color of a tributary is influenced be the predominance of either dissolved organic matter or suspended

sediment.

Changes in manuscript:
Rephrased. The new sentence reads "The distribution of TOC contents basically reflects the characteristics of the tributaries, which are mainly influenced by the content of dissolved organic matter and suspended sediment (Fig. 2A)" (page 9, line 9-11of the revised paper).

Comments from R. Sparkes:
Page 9, Line 28:
A good relation is claimed between $\Lambda 8$ and $\Sigma 8$. Authors could consider referring to a figure or providing the p value?

Response:
The $\Lambda 8$ and $\Sigma 8$ values for individual tributaries (except for the Xingu River) are correlated. We do not think that an additional figure is necessary here, as the relationship is rather straightforward and also to be expected for most settings. Therefore we only report the average r^2=value (average r2=0.76, p<0.05, n=39). The p-values for these correlations are 0.02 for the Negro River, 0.03 for the Solimoes River, 7.0×10^{-4} for the Madeira River and 6.8×10^{-6} for the Amazon mainstream. All p-values are all smaller than 0.05, which is given with the average r2 value.
Probably we should not show the size of the sample (n=39) here, because it is not the size for individual tributaries. We will delete it in the modified version. We will also show the r^2 value of Xingu River (r^2=0.02, p=0.71) to compare.

Changes in manuscript:
R2 value of the Xingu River is provided in the first sentence in section 5.1.2.

Comments from R. Sparkes:
Page 12, Line 15: Authors could use a simple mixing model to estimate the proportion of marine and terrestrial carbon in their offshore sediments.

Response:
This is indeed a good way to estimate the contribution of marine and terrestrial organic carbon in the offshore sediments. However, the focus of this manuscript is on investigating the distribution of terrigenous OC represented by lignin in the lowland Amazon basin and offshore and the effect of grain size on the distribution. Estimating the proportion of marine and terrestrial contributions in the marine sediments is beyond the scope of this study and would only add another side aspect.

Changes in manuscript:
No changes conducted.

Comments from R. Sparkes:
Page 12, Line 25:
$\Lambda 8$ and d13C are positively correlated. Authors could show this using p values or a figure.

Response:

Figure 6 shows the positive relation between $\Lambda 8$ and d13C of all samples, the r^2 and p-value have been added.

Changes in manuscript:

r2 and p values for all samples (r^2=0.53, p<0.05, n=27) and for samples from Fan and NW sectors (r^2=0.58, p<0.05, n=21) are added in section 5.2.1.

Comments from R. Sparkes:

Page 13, Line 28:

Sample GeoB16225-2 is 30 km offshore, 30 km from a small local river, and in only 34 m water depth with a fine sand sedimentology. Can the authors be confident that this sample reflects material from the Amazon and not local input?

Response:

The sample GeoB16225-2 is located about 30 km away from the Sinnamary River mouth and located far away from the Amazon River mouth. Although the Brazil-Guianas coastal mud belt is about 1800 km long and the mudbanks on the inner shelf extend seaward to the limit of the coastal mud wedge (20-25 m water depth) (Allison and Lee, 2004, Mar. Geol. 163), which reaches the location of GeoB16225-2, we can not exclude a contribution from a local river. Nevertheless, given the basically constant lignin content over the lowland Amazon basin, the organic matter from the small local river likely has similar characteristics as the Amazon River system, which makes a distinction from Amazon-derived material virtually impossible.

Changes in manuscript:

This problem is pointed out and discussed in the second paragraph of section 5.2.2.

Typographical changes:

Page 6 Line 13. "were". The rest of this paragraph is in the present tense

Page 7 Line 15. "varied" The rest of this paragraph is in the present tense

Page 9 Line 19. "‰)". There is an extra space

Page 9 Line 20. "Bouchez et al. , 2014". There is a space in the wrong location

Page 12 Line 24. "reaching very low $\Lambda 8$ value". It is unclear whether the authors mean to use the singular or plural form "reaching a very low $\Lambda 8$ value"/"reaching very low $\Lambda 8$ values"

Response:

Thanks for pointing out these typos.

Changes in manuscript:

These mistakes are corrected accordingly.

Origin and processing of terrestrial organic carbon in the Amazon system: lignin phenols in river, shelf and fan sediments

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Abstract. The Amazon River transports large amounts of terrestrial organic carbon (OC_{terr}) from the Andean and Amazon
15 neotropical forests to the Atlantic Ocean. In order to compare the biogeochemical characteristics of OC_{terr} in the fluvial sediments from the Amazon drainage basin and in the adjacent marine sediments, we analysed riverbed sediments from the Amazon mainstream and its main tributaries as well as marine surface sediments from the Amazon shelf and fan for total organic carbon (TOC) content, organic carbon isotopic composition ($\delta^{13}C_{TOC}$), and lignin phenol compositions. TOC and lignin content exhibit positive correlations with Al/Si ratios (indicative of the sediment grain size) implying that the grain
20 size of sediment discharged by the Amazon River plays an important role in the preservation of TOC and leads to preferential preservation of lignin phenols in fine particles. Depleted $\delta^{13}C_{TOC}$ values (-26.1 ‰ to -29.9 ‰) in the main tributaries consistently correspond with the dominance of C3 vegetation. Ratios of syringyl to vanillyl (S/V) and cinnamyl to vanillyl (C/V) lignin phenols suggest that non-woody angiosperm tissues are the dominant source of lignin in the Amazon basin. Although the Amazon basin hosts a rich diversity of vascular plant types, distinct regional lignin compositions are not
25 observed. In the marine sediments, the distribution of $\delta^{13}C_{TOC}$ and Λ8 (sum of eight lignin phenols in organic carbon (OC), expressed as mg/100mg OC) values implies that OC_{terr} discharged by the Amazon River is transported north-westward by the North Brazil Current and mostly deposited on the inner shelf. The lignin compositions in offshore sediments under the influence of the Amazon plume are consistent with the riverbed samples suggesting that processing of OC_{terr} during offshore transport does not change the encoded source information. Therefore, the lignin compositions preserved in these offshore
30 sediments can reliably reflect the vegetation in the Amazon River catchment. In sediments from the Amazon Fan, low lignin content, relatively depleted $\delta^{13}C_{TOC}$ values and high $(Ad/Al)_V$ ratios indicating highly degraded lignin imply that a significant fraction of the deposited OC_{terr} is derived from petrogenic (sourced from ancient rocks) sources.

1 Introduction

Rivers deliver annually about 200 Tg of particulate organic carbon (POC) to the oceans (Galy et al., 2007; Ludwig et al., 1996; Schlünz and Schneider, 2000; Galy et al., 2015), which is predominantly deposited on continental shelves and slopes (Hedges and Keil, 1995). Terrestrial organic carbon (OC_{terr}) buried in marine sediments has been intensely studied in order to reconstruct climate and environmental conditions on land (Bendle et al., 2010; Collins et al., 2014; Vogts et al., 2012) with rivers playing a role not only as conduits between terrestrial and marine reservoirs but also as efficient reactors of the OC_{terr} (Aufdenkampe et al., 2011; Battin et al., 2009). During transport in fluvial systems, OC_{terr} is subject to various natural processes, such as selective preservation within the watershed and microbial degradation, as well as anthropogenic processes associated to land-use change (Jung et al., 2014; Wang et al., 2015; Wu et al., 2007). In marine environments, OC_{terr} mixes with marine organic carbon and experiences further diagenetic alteration (Aller and Blair, 2006). The refractory fractions of OC_{terr}, which survive these processes, are preserved at sites of sediment deposition. As a result of this extensive processing, the climatic and environmental information recorded by OC_{terr} in marine sediments may be subject to temporal and spatial offsets. Hence, a comparison between the characteristics of OC_{terr} in drainage basins and adjacent continental margins is helpful to decipher which depositional sites can provide reliable marine sedimentary archives and to what extent they reflect climatic and environmental changes within the catchment.

The Amazon River is of special interest due to its large drainage basin size and discharge of OC_{terr} to the ocean. Previous studies that assessed the fate of OC_{terr} transported and discharged by the Amazon mainly relied on bulk organic parameters, isotope compositions of total organic carbon ($\delta^{13}C_{TOC}$ and $\Delta^{14}C_{TOC}$) (Bouchez et al., 2014) as well as on analyses of various biomarkers (e.g., lignin, plant-waxes and tetraether lipids) (Zell et al., 2014). Based on the correlation between TOC contents and Al/Si ratios, the latter being indicative of grain-size variations, Bouchez et al. (2014) showed a distinct mineral and size class association of particulate organic matter (POM), which in turn affects its transport in the fluvial system. Moreover, the $\delta^{13}C_{TOC}$ and $\Delta^{14}C_{TOC}$ of POM indicated that rock-derived POM accounts for a significant proportion of riverbed sediments. Hedges et al. (1986) reported lignin compositions of typical plant tissues in the Amazon basin and found that POM has distinct lignin compositions in different grain size fractions.

Offshore the Amazon River mouth, the predominant depo-center of terrestrial organic matter has been shown to change between glacial and interglacial periods (Schlünz et al., 1999). During glacials (i.e., low sea-level), most of the Amazon derived OC_{terr} is deposited on the Amazon Fan, while during interglacials (i.e., high sea-level), along-shore currents result in deposition of OC_{terr} on the continental shelf northwest of the Amazon River mouth. Terrestrial climate and vegetation from the last glacial period has thus been reconstructed by analysing molecular biomarkers, such as lignin, plant-wax lipids, and branched glycerol dialkyl glycerol tetraethers (GDGTs) in sediment cores recovered from the Amazon Fan (Bendle et al., 2010; Boot et al., 2006; Goñi et al., 1997; Kastner and Goñi, 2003)

Lignin is a useful tracer for OC_{terr} because it is exclusively produced by vascular plants and accounts for about 20-30 % of dry biomass in woody plants (Zhu and Pan, 2010) and 15-20 % in grasses (Perez-Pimienta et al., 2013). It is relatively

resistant to microbial degradation (Killops and Killops, 2005) and abundant in many environments (e.g. Kuzyk et al., 2008; Loh et al., 2012; Winterfeld et al., 2015). To date, little is known about the factors influencing lignin composition in the Amazon basin and adjacent marine sediments, its transport pathways in the Amazon continental margin, and the potential of lignin in offshore sedimentary archives to constrain sources and compositions of OC_{terr}.

5   Here we determined lignin contents and composition in riverbed sediments of the Amazon River and its lowland tributaries as well as in surface sediments of the Amazon shelf and slope. By doing so, we provide evidence on the spatial distribution of OC_{terr}, its plant sources, its origin within the catchment, and its dispersal patterns on the Amazon continental margin.

2 Study area

The Amazon River originates from the confluence of the Ucayali and Marañon Rivers in the Andean region in southwestern
10 Peru and receives numerous tributaries that form the largest hydrographic basin in the world (Goulding et al., 2003). It covers an area of about $6.1 \times 10^6\,km^2$ extending from the Guiana Highlands in the north to the Central Brazil Highlands in the south, and is bordered by the Andes mountain range in the west (Guyot et al., 2007). The Peruvian and Bolivian Andean tributaries Solimões (upper stretch of the Amazon River from its confluence with the Negro River) and Madeira are typical white water rivers. Because they drain the steep slope and rapidly weathering Andean region, they are characterized by high
15 concentrations of suspended sediments and dissolved nutrients (Gibbs, 1967). The other major tributaries in the Amazon basin drain lowland regions and are classified as either black or clear water rivers. The black water rivers, such as the Negro River, are rich in dissolved humic substances derived from podzols and depleted in suspended sediments (Mounier et al., 1999). The clear water rivers (e.g., the Xingu River) have low concentrations of suspended sediments and dissolved organic matter compared to the white and black water rivers, and their clarity allows high phytoplankton productivity (Junk, 1997;
20 Richey et al., 1990). Although the deforested area of the Amazon basin is increasing significantly in the eastern and south-eastern portions, the remainder of the lowland Amazon basin is largely forested except for some small areas dominated by savannah (Houghton et al., 2001). Elsewhere, some grasses grow along the shoreline regions of white water rivers (Guyot et al., 2007; Hedges et al., 1986).

The Amazon basin annually receives an average of about 2500 mm rainfall and has the world's largest water discharge of
25 about $2 \times 10^5\,m^3 s^{-1}$ (Callede et al., 2000; Guyot et al., 2007). Up to 40 Tg of carbon are discharged along with $8\text{-}12 \times 10^{11}\,kg$ suspended sediment load each year by the Amazon River into the Atlantic Ocean, which makes the Amazon the largest fluvial source of OC_{terr} to the ocean (Dunne et al., 1998; Moreira-Turcq et al., 2003). The Amazon-derived plume of water and suspended sediment is advected northwestward along the northern South American coastline by the North Brazil Current, eventually forming the Amazon subaqueous delta-Guianas mud belt extending 1600 km along the northeastern coast of
30 South America (Geyer et al., 1996; Nittrouer and DeMaster, 1996). The Amazon Fan is located off the northern coast of Brazil centered around 4 °N, extending 700 km from the shelf break seaward reaching a maximum width of about 650 km. The Amazon Fan is largely inactive today, but during past periods of low sea level such as the Last Glacial Maximum, large

amount of suspended sediment and bed load were transported via submarine canyons and deposited on the Fan (Schlünz et al., 1999).

3 Materials and methods

3.1 Sample collection

5   Riverbed sediments were collected from the Amazon River mainstream and its main tributaries during two sampling campaigns in November 2011 and May 2012, corresponding respectively to the dry and wet seasons. Sediment samples were retrieved from sites with different channel depths to reflect their range of grain size variability. A Van Veen grab sampler was used for sampling, and the station locations are shown in Table 1 and Fig. 1A.

Marine surface sediments from the Amazon shelf and fan were collected during two cruises (Table 2, Fig. 1B). The GeoB

10   samples were recovered with a multicorer in February/March 2012 during the R/V Maria S. Merian cruise MSM 20/3, while the other marine surface sediments were taken in February/March 2010 with a box corer deployed from R/V Knorr during cruise KNR197-4. All samples were kept frozen at -20 ℃ before analysis and were subsampled into 1-cm intervals. The uppermost 2 cm of GeoB multicore samples and slices of 1 cm from intervals between 5 and 8 cm sediment depth of cores taken during cruise KNR197-4 were used in this study.

15   The GeoB surface sediments were oven dried at 50 ℃, while the riverbed and the other marine surface sediments were freeze dried in a Christ Alpha 1-4 LD plus freeze dryer. After drying, all samples were homogenized for further analysis.

3.2 Grain size analysis

Grain size analysis was only conducted for marine sediments, because the riverbed sediment samples had already been ground before sub-sampling. For grain size measurement of the terrigenous fraction, bulk marine sediments were pre-treated

20   as follows. Samples of about 0.5 g were successively boiled with H_2O_2 (35 %), HCl (10 %) and NaOH to remove respectively organic matter, carbonate and biogenic silica. To prevent potential aggregation, 10 ml of dissolved sodium pyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$) was added immediately prior to grain size analysis. Samples were measured using a Laser Diffraction Particle Size Analyser (Beckman Coulter laser particle sizer LS-13320) in 116 size classes ranging from 0.04 to 2000 μm. All measurements were performed in demineralized and degassed water to avoid interference of gas bubbles.

25   ### 3.3 Elemental and bulk isotopic analysis

About 4 g dry sediment was used to measure the Al and Si elemental concentrations by energy dispersive polarization X-ray fluorescence (EDP-XRF) spectroscopy. The device was operated with the software Spectro X-Lab Pro (Version 2.4) using the Turboquant method. Analytical quality of measurements was assessed by repeated analyses of the certified standard reference material MAG-1, and the standard deviation of replicate measurement of sediment samples was better than 0.5%.

4

After removal of carbonates with 12.5 % HCl and drying, the total organic carbon content (TOC) of all samples was determined by a LECO CS 200 CS-Analyzing System. The relative standard deviation of duplicate analyses was better than 1%.

Stable carbon isotopic ratios of TOC ($\delta^{13}C_{TOC}$) were analyzed on a Finnigan MAT Delta plus coupled with a CE elemental
5   analyzer and a Con-Flo II interface. Samples were pre-treated by the same method as used for the TOC measurement. $\delta^{13}C_{TOC}$ values are reported using the standard notation relative to the Vienna Pee Dee Belemnite (VPDB) standard. The uncertainty was less than ±0.1‰, as calculated by long-term repeated analyses of the internal reference sediment (WST2).

3.4 Lignin-phenol analysis

Alkaline CuO oxidation was used to obtain eight lignin-derived phenols (vanillyl phenols, syringyl phenols and cinnamyl
10   phenols) and three para-hydroxybenzenes. A CEM MARS5 microwave accelerated reaction system was used to perform alkaline CuO oxidation of lignin based on the approach described by Goñi and Montgomery (2000). Dried sediment samples (containing about 2-5 mg of TOC) were oxidized with CuO (500 mg) and ferrous ammonium sulfate (50 mg) in de-aerated 2 N NaOH at 150 ℃ for 90 min under a nitrogen atmosphere. After the oxidation, known amounts of recovery standards (ethyl vanillin and *trans*-cinnamic acid) were added to each reaction tube. The alkaline supernatant was transferred and acidified to
15   pH 1 by addition of concentrated HCl. Reaction products were extracted twice with ethyl acetate and water in the ethyl acetate solution was removed by addition of Na_2SO_4. Ethyl acetate was evaporated under a continuous nitrogen flow. Once dry, 400 μl of pyridine was added immediately to re-dissolve the reaction products. Lignin phenols were analyzed by gas chromatography-mass spectrometry (GC-MS). Prior to the injection to the GC-MS, compounds in pyridine were derivatized with bis-trimethylsilyl-trifluoroacetamide (BSTFA) +1 % trimethylchlorosilane (TMCS) to silylate exchangeable hydrogen.
20   Chromatographic separation was achieved by a 30 m×0.25 mm (i.d.) DB-1MS (0.25 μm film thickness) capillary GC column. The temperature program was 100 ℃ initial temperature, 4 ℃min⁻¹ ramp and 300 ℃ final temperature with a hold of 10 minutes.

The eight lignin-derived phenols obtained by alkaline CuO oxidation are subdivided into the following groups: the vanillyl (V) phenols include vanillin (Vl), ancetovanillone (Vn), and vanillic acid (Vd); syringyl (S) phenols are syringaldehyde (Sl),
25   acetosyringone (Sn) and syringic acid (Sd); and cinnamyl (C) phenols consist of *p*-coumaric acid (*p*-Cd) and ferulic acid (Fd). The para-hydroxybenzenes include *p*-hydroxybenzaldehyde (Pl), *p*-hydroxybenzophenone (Pn) and *p*-hydroxybenzoic acid (Pd). The C phenols are only present in non-woody tissues of vascular plants while the S phenols are unique to angiosperms and V phenols exist in all vascular plants. Therefore, the ratios of S/V and C/V divide the plant sources of lignin into four types, non-woody and woody tissues of gymnosperms and angiosperms (Hedges and Mann., 1979a). $(Ad/Al)_V$ and $(Ad/Al)_S$
30   refers to the acid to aldehyde ratios of V and S phenols, which indicate the degradation of lignin (Ertel and Hedges, 1985). The lignin phenols and identified compounds were quantified by individual response factors calculated from mixtures of commercially available standards analyzed periodically. The yields of Pl, Vl and Sl were calculated by the recovery rate of

ethyl vanillin and the recovery rate of trans-cinnamic acid was applied for the yield estimation of other lignin-derived compounds (Kuzyk et al., 2008).

Carbon-and sediment-normalized lignin yields are respectively reported as Λ8 (mg/100mg OC) and Σ8 (mg/10g dry sediment). These measures indicate respectively the relative contributions of vascular plant material to the TOC, and to the

5   total samples, and were respectively calculated as the sum of S, V and C phenols in 100 mg organic carbon and 10 g dried sample (Hedges and Mann, 1979b).

4 Results

4.1 Riverbed sediments

4.1.1 TOC and stable carbon isotopic composition

10   Part of the TOC，stable carbon isotopic composition and Al/Si data were previously published in Häggi et al. (2016). Riverbed sediments contain between 0.13 % and 3.99 % dry weight (wt) TOC (Table 1, Fig. 2A). Negro River and Xingu River sediments have similar TOC contents (0.53 % -3.99 %, mean=2.08±1.15 %, n=7 and 0.52 % -3.82 %, mean=2.44±1.37 %, n=8, respectively), which are higher than the TOC contents in other main tributaries. Consistently low TOC contents ~~were~~ are observed in the Madeira River varying from 0.14 % to 0.52 % (mean=0.36±0.17 %, n=6). Solimões

15   River sediments display TOC contents ranging from 0.28 % to 0.90 % with an average of 0.62±0.20 % (n=7). Amazon River mainstream sediments have intermediate TOC contents ranging from 0.13 % to 1.44 % (mean=0.73±0.36 %, n=19).

The range of $\delta^{13}C_{TOC}$ values of all riverbed samples is from -26.1 ‰ to -29.9 ‰ (Table 1, Fig. 2B). The most enriched (-26.1 ‰) and depleted (-29.9 ‰) $\delta^{13}C_{TOC}$ values are both observed in Solimões River sediments, which have an average value of -28.2±1.2 ‰ (n=6). A similar scatter of $\delta^{13}C_{TOC}$ values is obtained from sediments of the Negro River varying

20   between -26.5 ‰ and -29.8 ‰ (mean=-28.7±1.3 ‰, n=7). In comparison, narrower ranges are found in the other tributaries and the Amazon River mainstream, with values ranging from -27.8 ‰ to -28.4 ‰ (mean=-28.0±0.3 ‰, n=3) for the Madeira River, from -27.9 ‰ to -29.8 ‰ (mean=-29.2±0.8 ‰, n=8) for the Xingu River, and from -27.5 ‰ to -29.4 ‰ (mean=-28.2±0.5 ‰, n=15) for the Amazon River mainstream.

4.1.2 Lignin phenols

25   The Λ8 values in riverbed sediments vary from 0.73 mg/100mg OC in the Madeira River to 9.27 mg/100mg OC in the northern channel of the Amazon River mouth (Table 1, Fig. 2C). The highest average Λ8 of 4.92±1.44 mg/100mg OC (n=8) is observed in the Xingu River with values ranging between 3.30 and 6.91 mg/100mg OC. In contrast, Madeira River sediments display the lowest average Λ8 value of 2.61±1.30 mg/100mg OC (n=6; 0.73 to 4.42 mg/100mg OC). The Λ8 values of samples in the Negro River and the Solimões River vary respectively between 3.55 and 4.89 mg/100mg OC

30   (mean=4.38±0.51 mg/100mg OC, n=7) and 3.49 and 6.44 mg/100mg OC (mean=4.59±0.96 mg/100mg OC, n=7). The Λ8

values of the mainstream sediments have the largest variability, from 0.75 to 9.27 mg/100mg OC (mean=4.88±1.93 mg/100mg OC, n=19).

Negro River and Xingu River sediments have higher $\Sigma8$ values and greater variability, ranging respectively from 1.89 to 19.52 mg/10g dry sediment (mean=9.50±5.90 mg/10g dry sediment, n=7) and from 2.73 to 17.97 mg/10g dry sediment (mean=11.18±5.93 mg/10g dry sediment, n=8). In contrast, the samples from the other tributaries and the Amazon mainstream display lower $\Sigma8$ values, 0.99-4.94 mg/10g dry sediment (mean=2.91±1.22 mg/10g dry sediment, n=7) for the Solimões River, 0.10-2.30 mg/10g dry sediment (mean=1.11±0.85 mg/10g dry sediment, n=6) for the Madeira River and 0.10-11.05 mg/10g dry sediment (mean=3.96±2.93 mg/10g dry sediment, n=19) for the Amazon River mainstream. Apart from the Xingu River, the $\Sigma8$ values and $\Lambda8$ values in individual tributaries are well correlated (r^2 from 0.64 to 0.96, p<0.05). S/V and C/V of all riverbed samples range respectively from 0.70 to 1.51 and 0.08 to 0.47 (Table 1, Fig. 3). Negro River and Xingu River sediments show slightly lower average S/V ratios (0.88 and 1.00) than samples from the Solimões River, the Madeira River and the Amazon mainstream (1.08, 1.10, and 1.09, respectively). The range of average C/V ratios of all tributaries is from 0.16 to 0.24 and the highest mean C/V ratio was observed in the Madeira River. Except for the highest P/V ratio in the Madeira River (0.38), the P/V ratios in the other tributaries ~~varied~~ vary only slightly (0.24-0.27). $(Ad/Al)_V$ values in all riverbed samples (Table 1, Fig. 2D) vary from 0.26 to 0.71 with an average of 0.42, and $(Ad/Al)_S$ values range from 0.15 to 0.57 with an average of 0.28. The $(Ad/Al)_V$ and $(Ad/Al)_S$ are correlated ($r2$=0.76, p<0.05, n=47), but all $(Ad/Al)_S$ values are lower than the respective $(Ad/Al)_V$ values.

4.1.3 Al/Si

In riverbed sediments, the Al/Si varies from 0.11 to 0.56 (Fig. 4A), which is larger than the Al/Si range of riverbed sediments reported by Bouchez et al. (2011). Solimões River sediments have a narrow Al/Si range (0.27-0.37) with an average of 0.33±0.04. The samples in the Madeira River and the Amazon River mainstream display lower Al/Si values (0.17-0.37, mean=0.26±0.08, n=6 and 0.11-0.38, mean=0.29±0.07, n=19, respectively). On the contrary, Negro River and Xingu River sediments have larger variations and higher average Al/Si ratios (0.17-0.51, mean=0.37±0.15, n=7 and 0.14-0.56, mean=0.40±0.15, n=8, respectively).

4.2 Marine sediments

4.2.1 TOC and stable carbon isotopic composition

TOC content in the marine surface sediments on the Amazon shelf varies from 0.11 % to 0.98 % (Table 2, Fig. 5A). Three samples near the Amazon River mouth exhibit low TOC contents of less than 0.2 % (0.13±0.04 %, GeoB16209-2, GeoB16210-2 and GeoB16211-2). The highest TOC content is obtained for BC61C, the southernmost sample from the Amazon Fan. The $\delta^{13}C_{TOC}$ values for marine surface sediments range from -18.6 ‰ at station GeoB16202-1, which is located southeast of the river mouth (SE sector), to -26.7 ‰ at station MC33A (near the river mouth) (Table 1 and Fig. 5B).

The samples from the SE sector reveal the most enriched $\delta^{13}C_{TOC}$ values between -18.6‰ and -21.6‰ (-19.6±1.1‰, $n=6$). The samples collected off the Amazon River mouth exhibit the most depleted $\delta^{13}C_{TOC}$ values (-24.8±1.4‰, $n=5$). $\delta^{13}C_{TOC}$ values increase along the shelf towards the northwest from the Amazon River mouth to around -20.4‰ at the north-westernmost stations deeper than 2000m. Apart from the relatively depleted $\delta^{13}C_{TOC}$ value of -24.5‰ at station BC61C, the
5   $\delta^{13}C_{TOC}$ values on the Amazon Fan range between -21.4‰ and -23.0‰.

4.2.2 Lignin phenols

The $\Lambda 8$ values in marine surface sediments vary from 0.04 to 2.01 mg/100 mg OC (Table 2, Fig. 5C). The samples in the SE sector display very low $\Lambda 8$ values (0.04-0.17 mg/100mg OC), which increase slightly with distance from the Amazon River mouth. Apart from the higher lignin content at station BC61C (0.57 mg/100mg OC), the samples in the Amazon Fan (Fan
10 sector) also have low $\Lambda 8$ values ranging from 0.05 to 0.22 mg/100mg OC with a decreasing trend with distance from the Amazon River mouth. The distribution pattern of lignin content in the northwest area (NW sector) is similar to that shown by $\delta^{13}C$ values. In the NW sector, $\Lambda 8$ values increase first from 0.19 to 2.01 mg/100mg OC at stations closest to the Amazon River mouth, decrease north-westward and reach rather constant low values of 0.18 mg/100mg OC on the offshore slope of the NW sector. The $\Sigma 8$ values in marine surface sediments vary from 0.01 to 1.49 mg/10g dry sediment and are highly
15 correlated with $\Lambda 8$ values ($r^2=0.85$, $p<0.05$, $n=30$).

Ranges of S/V and C/V ratios in marine sediments are similar to those observed in riverbed sediments. S/V and C/V ratios vary respectively from 0.59 to 1.62 and from 0.10 to 0.43 (Table 2, Fig. 3). Sediments in the SE sector have higher C/V ratios (mean=0.30±0.11, $n=9$). The $(Ad/Al)_V$ and $(Ad/Al)_S$ values in marine samples vary respectively from 0.37 to 1.16 (Table 2, Fig. 5D) and from 0.32 to 0.97 (Table 2). However, our marine samples show no correlation between $(Ad/Al)_V$ and
20 $(Ad/Al)_S$ values. Samples from the Amazon Fan exhibit the highest average $(Ad/Al)_{V,S}$ values of 0.81 and 0.71. Samples in the SE and NW sectors have similar average $(Ad/Al)_V$ values (0.62 and 0.61, respectively), but samples from the NW region exhibit larger variation.

4.2.3 Al/Si and grain size

In marine sediments, the Al/Si varies from 0.14 to 0.47. The SE and Fan sectors have narrow Al/Si ranges, which are
25 respectively 0.37-0.41 with an average of 0.39±0.01 and 0.40-0.46 with an average of 0.43±0.02 (Table 2.). In contrast, the samples in the NW sector display large Al/Si variance (0.14-0.47, mean=0.32±0.14).

Grain size of marine sediments is reported as mean grain size and varies between 3.23-92.90 µm (Table 2). Coincident with the Al/Si ratio distribution, samples in the SE and Fan sectors respectively have narrow grain size ranges, which are 4.44-11.79 µm with an average of 8.07±2.75 µm and 3.23-14.50 µm with an average of 5.84±3.38 µm. On the contrary, sediments
30 in the NW sector display wide range grain sizes (4.74-92.90 µm, mean=31.23±35.19 µm). The correlation between grain size and Al/Si ratio ($r^2=0.85$, $p<0.05$, $n=28$) indicates that the Al/Si ratio is a reliable proxy for the grain size of terrestrial sediments.

5 Discussion

5.1 Lowland Amazon River system

5.1.1 Spatial distribution and isotopic composition of OC_{terr}

The TOC contents of our riverbed sediments in individual tributaries are larger than values of bedload sediments reported by Bouchez et al. (2014) (mean=0.23±0.42 % in the Solimões and Madeira rivers and the Amazon mainstream), but lower than the values of suspended materials (e.g. mean=1.14±0.33 % in the Solimões and Madeira rivers and the Amazon mainstream) in the Amazon lowland basin (Hedges et al., 1986; Moreira-Turcq et al., 2003; Bouchez et al., 2014). The distribution of TOC contents basically reflects the characteristics of the tributaries, which are mainly influenced by the content of dissolved organic matter and suspended sediment (Fig. 2A). The relatively high TOC contents in the Negro River are due to the low suspended sediment content and high content of humic substances (Ertel et al., 1986). The Xingu river is characterized by low suspended sediment content and high phytoplankton production, which lead to the high TOC contents in riverbed sediments (Moreira-Turcq et al., 2003). In contrast, the Solimões River and the Madeira River being the primary contributors of the suspended sediment to the Amazon River mainstream, have large suspended sediment load (Moreira-Turcq et al., 2003). Consequently, the low TOC contents in the riverbed sediments in these tributaries are due to dilution by lithogenic material. The lower-intermediate TOC contents for the Amazon River mainstream results from the mixing of different signals from these tributaries with a greater influence from the Solimões and the Madeira Rivers.

The $\delta^{13}C_{TOC}$ values of our riverbed sediments (i.e., from -26.1 ‰ to -29.9 ‰) (Fig. 2B) are similar to the values reported for riverbed sediments (e.g. from -27.6 ‰ to -28.8 ‰) and suspended particulate matter (e.g. -28.3±1.1 ‰) in the Amazon River system in previous studies (Hedges et al., 1986; Cai et al., 1988; Kim et al., 2012; Bouchez et al., 2014). Hedges et al. (1986) studied $\delta^{13}C_{TOC}$ values of different organic carbon sources in samples from the Amazon River and found the respective average $\delta^{13}C_{TOC}$ values of C3 tree leaves, woods, macrophyte tissues and C4 grasses to be -30.1±0.9 ‰, -27.6±1.0 ‰, -21.4±8.4 ‰ and -12.2 ‰. The total average $\delta^{13}C_{TOC}$ value of riverbed sediments in this study (-28.5±0.9 ‰) confirms the dominant contribution from terrestrial C3 plants. There is no significant difference in the distribution of $\delta^{13}C_{TOC}$ values among the sampled tributaries.

5.1.2 Characteristics of lignin phenols

With the exception of the samples from the Xingu River (r^2=0.02, p=0.71), all riverbed sediments exhibit a good relation between Λ8 values and Σ8 values (average r^2=0.76, p<0.05, n=39). In the Xingu River, the high level of in situ primary production and low-turbidity conditions favour the settling of phytoplankton-derived organic matter from the water column (Moreira-Turcq et al., 2003). The deposited phytoplankton-derived organic matter dilutes the abundance of lignin in TOC (Λ8) but has only a small influence on sediment mass and, as a result, Σ8, resulting in divergence of Λ8 and Σ8 (Rezende et al., 2010). Based on previous studies, the Λ8 values of different organic matter fractions range from 0.45 to 2.40 mg/100 mg OC for fine particulate organic matter (FPOM, silt and clay fraction, <63 µm), and from 1.21 to 10.46 mg/100 mg OC for

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coarse particulate organic matter (CPOM, sand-size fraction, >63 µm) (Aufdenkampe et al., 2007; Hedges et al., 1986; Hedges et al., 2000). In this study, riverbed sediments (Fig. 2C), except for three samples with lignin contents lower than 2.0 mg/100 mg OC, had $\Lambda 8$ values (2.42-9.27 mg/100 mg OC) similar to those of CPOM. Most of the $\Lambda 8$ values of our samples are smaller than the average $\Lambda 8$ values of tree wood tissues (19.3 mg/100 mg OC) and C4 grasses (9.1 mg/100 mg OC), and closer to the range of tree leaves and macrophytes (3.7 mg/100mg OC and 6.4 mg/100mg OC, respectively) (Hedges et al., 1986). This finding is also supported by the distribution of C/V and S/V ratios. The plot of S/V vs. C/V (Fig. 3) indicates that angiosperm leaves are the major origin of lignin in the lower Amazon basin. It is noteworthy that the range of typical C/V values for angiosperm leaf material in the Amazon basin is larger (i.e., including C/V values as low as 0.07) than in other regions (with lowest C/V values around 0.20) (Bianchi et al., 2011; Cathalot et al., 2013; Tesi et al., 2014). The resulting small difference between C/V ratios of non-woody and woody tissues of angiosperms in the Amazon region results in a larger uncertainty in inferring the plant sources of lignin. C/V values around 0.1 could be interpreted either as signals exclusively from leaves or as signals from a mixture of woody tissues and leaves. To circumvent this uncertainty, the P/V values are also used to identify the lignin sources. P phenols in our samples are derived from lignin, as supported from the significant correlation of the content of P phenols and lignin content (r^2=0.50, p<0.05, n=47). All P/V values of our samples (0.17-0.64) are higher than the average P/V ratio of woods (0.05) and similar to the range observed for leaves (0.16-6.9) (Hedges et al., 1986). Considering all parameters, non-woody angiosperms are the most likely major source of lignin in the lowland Amazon basin. The slightly higher C/V ratios in the Solimões River (0.20) and the Madeira River (0.24) suggest a small contribution of grass-derived material (C/V>1) probably from the Andean highlands (Aufdenkampe et al., 2007; Hedges et al., 2000).

The degradation extent of OC_{terr} can be assessed by $(Ad/Al)_V$ and $(Ad/Al)_S$ ratios as more degraded lignin yields elevated $(Ad/Al)_V$ and $(Ad/Al)_S$ values (Hedges et al., 1988; Opsahl and Benner, 1995). In the case of the Amazon basin, the $(Ad/Al)_V$ and $(Ad/Al)_S$ ratios of typical fresh woods and tree leaves both range from 0.11 to 0.24 (Hedges et al., 1986). All of our samples exhibiting values between 0.26 and 0.71 for $(Ad/Al)_V$ (Fig. 2D) and between 0.15 and 0.57 for $(Ad/Al)_S$ are outside of the range of fresh plant materials, suggesting degraded OC_{terr} in all samples. Instead, the $(Ad/Al)_{V,S}$ ratios observed in our samples are within the ranges of suspended particulate solids obtained in the lower Amazon basin and Bolivian headwaters ($(Ad/Al)_{V,S}$ of 0.21-0.39 and 0.13-0.22 for CPOM and $(Ad/Al)_{V,S}$ of 0.38-0.79 and 0.22-0.41 for FPOM (Hedges et al., 1986; Hedges et al., 2000)). The Negro River displayed the highest average $(Ad/Al)_V$ ratio (0.55), reflecting a greater degree of degradation. This might be indicative of more efficient degradation in the podzols of the lateritic landscapes in the Negro River watershed (Bardy et al., 2011). The $(Ad/Al)_V$ ratios in the Solimões and the Madeira Rivers increase with increasing C/V values (r^2=0.50, p<0.05, n=13), which implies that the plant tissues with higher C/V values (higher grass contributions) are more degraded. This further supports the inference that the Solimões and the Madeira Rivers receive POC from grass sources from high-altitude watersheds, where deeper soil erosion of more degraded OC_{terr} could occur. The degradation status of lignin in riverbed sediments does not display a downstream increasing trend and is similar to previous studies on suspended POC of different size fractions. This leads to the conclusion that OC_{terr} processing during transport through the

Amazon river system probably has limited influence on the composition of lignin recorded in the riverbed sediments and the degradation information likely reflects source characteristics of OC_{terr} prior to fluvial transport (Hedges et al., 1986; Hedges et al., 1994). This finding contradicts the conclusion of Ward et al. (2013) that lignin is rapidly degraded within the Amazon River. Ward et al. (2013) studied particulate and dissolved lignin in the water column, which is exposed to degradative environments. In contrast, our study focuses on the lignin associated with mineral particles, which are deposited and protected from degradation. This discrepancy highlights the important role of matrix association effects in the preservation of organic matter.

5.1.3 Sedimentological control on OC_{terr} characteristics

As grain size data could not be obtained directly on the riverbed sediment samples, we inferred grain size information based on the relationship between the Al/Si ratio and grain size of riverbed sediments observed by Bouchez et al. (2011) in samples from the Amazon basin. High Al/Si indicates aluminium-rich fine-grained sediment, whereas low Al/Si suggests silicon-rich particles of larger grain size (Bouchez et al., 2011; Galy et al., 2008).

As expected, the TOC contents increase with Al/Si (Fig. 4A), indicating that fine particles, associated with larger specific surface areas and likely rich in clay, carry more TOC than coarser particles. The Negro and the Xingu Rivers have larger Al/Si and TOC variations, and for a given Al/Si ratio, the Negro and the Xingu Rivers show higher TOC contents compared to the other tributaries. As these rivers have distinct chemical characteristics and clay mineral composition (e.g., lower pH in the waters of the Negro River and higher kaolinite content in the sediments of the Negro and the Xingu Rivers than in other tributaries; Guyot et al., 2007), the adsorption affinities of OC_{terr} on different clay minerals or under different chemical conditions may be distinct.

Different grain size classes may not only have different TOC content but also the composition of their OC_{terr} might vary. For example, previous studies on POM in the Amazon basin found that CPOM has a higher content of lignin phenols than FPOM and that CPOM is composed of fresher lignin with lower C/V ratios (Hedges et al., 1986). Nevertheless, contradictory results were observed in our riverbed sediments. The Λ8 values in the Madeira River, the Solimões River and the mainstream Amazon River show a remarkable increase with decreasing grain size (indicated by increasing Al/Si ratios) (Fig. 4B). This rise in lignin content in organic matter associated with finer minerals implies preferential preservation of lignin on finer particles compared with other components. A similar trend has been observed in other environments, such as in surficial sediments of the East China Sea (Wu et al., 2013) and the Iberian margin (Schmidt et al., 2010). However, opposite distribution patterns with lignin enriched in coarser size-classes and low density fractions have been found in sediments from the Washington margin (Keil et al., 1998) and the Laptev Sea (Tesi et al., 2016). This is likely because codeposited plant debris preferentially accumulates within coarser and low density fractions. Thus the apparent discrepancy between these studies may derive from the different methods employed, i.e. partitioning sediments into discrete size and density fractions (Keil et al., 1998, Tesi et al., 2016) versus characterizing the mean grain size of bulk sediments, respectively (Wu et al., 2013, Schmidt et al., 2010, and our study). On the other hand, the distinct environmental settings in

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which these studies were conducted, may influence the grain size distribution of lignin. The Amazon River drains tropical lowlands where degradation on land is efficient, and the turbid waters of the Amazon River might limit the settling of plant fragments. Consequently, in our riverbed samples sedimentary organic matter likely contains only a small contribution of plant debris, whereas less efficient degradation on land in the colder climates of the higher latitudes will result in deposition of more coarse plant debris. In the Negro River, there is only a slight increase in Λ8 values as mineral particles become finer, probably as a result of the large amount of sediment-associated chemically stable humic substances (Hedges et al., 1986), in which the lignin content is relatively constant. However, Xingu River sediments exhibit decreasing Λ8 values with decreasing grain size probably because the lignin content in finer particles from the Xingu River is diluted by other non-lignin organic components. With respect to the indicator of plant sources (Fig. 4C), the C/V ratios for samples from the Madeira River, the Solimões River and the Negro River decrease with decreasing grain size, which implies that lignin with higher C/V ratios is typically enriched in coarser particles. This suggests that the non-woody tissues with higher proportions of cinnamyl phenols are enriched in coarse-grained sediments. Xingu River and Amazon River mainstream sediments present no pronounced trend between C/V ratios and Al/Si values.

$(Ad/Al)_V$ values for all riverbed sediments do not show any obvious relationship with Al/Si (Fig. 4D). Only Madeira River and Solimões River sediments exhibit decreasing $(Ad/Al)_V$ values with increasing Al/Si, which suggests that lignin associated to larger mineral particles is more degraded. This observation implies preferential preservation of lignin in finer-grained sediments due to better protection against oxidative degradation (Killops and Killops, 2005). Like the correlation between Λ8 values and Al/Si, our observation on $(Ad/Al)_V$ values is different to the trends found by Keil et al. (1998) and Tesi et al. (2016), where lower $(Ad/Al)_V$ values have been found in coarser fractions. Again, this is likely due to the fact that these studies investigated individual grain size and density fractions, and that they were conducted in higher latitudes with less efficient processing of plant remains prior to deposition. As a result, fresh plant tissue would be found in the coarse fractions leading to low $(Ad/Al)_V$ values (see discussion above). Because our sediments likely contain limited amounts of plant debris, the $(Ad/Al)_V$ are lower in finer sediments implying that lignin is better preserved in finer grained particles. In previous studies on suspended sediments, lignin in the coarse fractions is more abundant and less degraded compared to the counterpart in fine fractions (e.g. Hedges et al., 1986). In contrast, our results for riverbed sediments suggest that lignin is preferentially preserved and better protected against degradation on fine-grained material. The different grain size effects on OC_{terr} composition between suspended and riverbed sediments suggest that there are other processes working on OC_{terr} in suspended sediments and riverbed sediments which cause post-depositional changes in the OC_{terr} characteristics.

In summary, our data indicate that lignin derives mainly from non-woody tissues of angiosperms in the lowland Amazon basin, and there is little evidence for contribution from C4 plants to riverbed sediments. Grain size plays an important role in OC_{terr} preservation and lignin composition in the Amazon River. Fine inorganic particles have high adsorption affinity for OC_{terr}, especially for lignin compared to other OC_{terr} components and efficiently protect lignin from degradation.

5.2 Amazon shelf and fan

5.2.1 Spatial distribution and characteristics of OC_{terr} and lignin phenols

Because of the depleted average $\delta^{13}C_{TOC}$ values of the riverbed sediments (-28.5±0.9 ‰), contribution of C4 plants is not expected in the offshore sediments affected by the Amazon outflow. Therefore, enriched $^{13}C_{TOC}$ values in the SE sector (-
18.6 ‰ to -21.6 ‰) likely indicate organic matter predominantly of marine origin. $\delta^{13}C_{TOC}$ values in the Amazon Fan sector ranging from -21.4 ‰ to -24.5 ‰, (Fig. 5B) also reflect dominantly marine organic matter. These values are within the range of published values for high sea-level periods (Schlünz et al., 1999), when most terrestrial POM discharged from the Amazon River is transported to the north-western shelf. In the NW sector, increasing $\delta^{13}C_{TOC}$ values with distance from the Amazon River mouth indicate that the terrestrial POM input from the Amazon River transported to the NW by the North
Brazil Current is increasingly diluted by marine organic matter. OC_{terr} is dominant on the continental shelf, corroborating previous results (e.g., Schlünz et al., 1999).

Sediments in the SE sector exhibit much lower Λ8 values than observed in the Fan and NW sectors. Here, slightly increasing Λ8 values with distance from the Amazon River mouth suggest that this terrestrial material is predominantly supplied by rivers to the southeast of the Amazon mouth and not by the Amazon River itself. The Λ8 values in sediments near the
Amazon River mouth are highly variable and decrease with distance from the river mouth to the Fan and NW sectors, reaching very low Λ8 values in the slope of the NW sector. Lower lignin contents (0.05-0.32 mg/mg OC) have been observed in the deep sea fan sediments measured in the study of Feng et al. (2016), which means there is increasing loss of lignin during the transport seawards to the Fan and NW sectors. Λ8 and $\delta^{13}C_{TOC}$ values show similar spatial distribution and are positively correlated (r^2=0.53, p<0.05, n=27) (Fig. 6). The agreement in the spatial patterns of lignin content and isotope
composition of organic matter suggest that lignin is a reliable tracer of OC_{terr} in the Amazon shelf and fan, and that the SE sector receives little OC_{terr} contribution from the Amazon River. The intercept of the correlation between Λ8 and $\delta^{13}C_{TOC}$ of NW and Fan sediments (r^2=0.58, p<0.05, n=21) is at -20.8 ‰, which corresponds to conditions with minimal OC_{terr} input to the marine sediments. It should be noted that the samples from the Amazon Fan have the same low lignin contents as in the SE sector, which indicates low contribution of OC_{terr} from terrestrial vascular plants under modern conditions. However, the
Fan sediments show more depleted $\delta^{13}C_{TOC}$ than sediments from the SE sector, which implies that a small terrestrial fraction is contained in the organic matter of the modern Fan sediments. Potentially, the OC_{terr} from vascular plants deposited in the Amazon Fan is readily degraded as indicated, e.g., by the high $(Ad/Al)_{V,S}$ ratios, while the relict OC_{terr} is predominantly rock-derived (with estimated $\delta^{13}C_{TOC}$ between -24.3 ‰ and -25.7 ‰) (Bouchez et al., 2014) and responsible for the depleted $\delta^{13}C_{TOC}$. Petrogenic organic matter is thus likely a significant component in the offshore sediments because of its refractory
nature and resulting high preservation potential.

C/V and S/V ratios (0.08-0.47 and 0.70-1.57, respectively; Fig. 3) in the entire Amazon shelf and fan are comparable to those in the riverbed sediments of the lowland Amazon basin, which indicates the same predominant source of non-woody angiosperm tissues. This also implies no further alteration of Amazon-derived lignin after it is discharged into the ocean and

deposited in marine sediments. Lignin in offshore marine sediments thus can provide reliable evidence for the reconstruction of the vegetation cover in the Amazon basin.

The distribution of the degradation state of lignin based on $(Ad/Al)_V$ is shown in Fig. 5D. The strikingly elevated $(Ad/Al)_V$ values in the Amazon Fan are probably caused by longer exposure to oxygen (Blair and Aller, 2012) at the sediment-water interface under low sedimentation rates, corroborating our previous interpretation of the low $\Lambda 8$ values but intermediate $\delta^{13}C_{TOC}$ values in the Fan sediments (Fig. 6). In the NW sector, there is no obvious decreasing trend of the $(Ad/Al)_V$ values with the distance from the river mouth. Low $(Ad/Al)_V$ values found at shallow nearshore sites far from the Amazon River mouth (e.g., GeoB16218-3 and GeoB16225-2) may be due to rapid transport and deposition of the material discharged from the Amazon River (Nittrouer et al., 1995) or contributions from local small rivers which may carry an indistinguishable lignin signature from the Amazon River. In the study of Feng et al. (2016), the sampling locations in the Amazon deep sea fan are in deeper water depths than our samples (>4000 m). Despite, very low $(Ad/Al)_{V,S}$ (0.04-1.3 and 0.03-0.8 for V and S phenols, respectively) were observed. Neither S/V nor C/V ratios decrease with $(Ad/Al)_{V,S}$ in the marine sediments, which would be expected because cinammyl and syringyl pheonls are preferentially degraded compared to vanillyl phenols (Benner et al., 1990; Opsahl and Benner, 1995). Despite the fact that the degradation of lignin preserved in marine sediments is slightly higher than that preserved in riverbed sediments, degradation has no major impact on the lignin composition.

5.2.2 Influence of grain size on OC_{terr} deposition in marine sediments

The grain size and Al/Si in the Amazon Fan and SE sectors vary within a rather small range. The grain size and Al/Si relationship in the NW sector is in accordance with the results obtained by Bouchez et al. (2011). The sediments in the NW sector have similar Al/Si ratios as our riverbed sediments (Table 2) which are correlated with grain size. We use grain size data for the following discussion of the sedimentological control on the distribution pattern of OC_{terr} in the NW sector and refer to the relationship between TOC and Al/Si as observed in the riverbed sediments.

Fine sand sediments were observed at the position closest to the Amazon River mouth (GeoB16209-2) and at site GeoB16225-2, which is far from the Amazon River mouth (about 700 km) but near the coast in a water depth of 34 m. The sample GeoB16225-2 probably receives additional input from local smaller rivers, from which coarser sediments are discharged. Considering that the characteristics of organic matter in the lowland Amazon basin are almost uniform, the local contributions deposited in GeoB16225-2 cannot reliably be distinguished from the material from the Amazon River system. The trend of increasing TOC contents with decreasing grain size (Fig. 7A) parallels the one demonstrated for the riverbed sediments (Fig. 4A) and in other marine sediments (Keil et al, 1997; Mayer 1994). The lignin content in organic matter ($\Lambda 8$) and grain size are not significantly related likely because the OC_{terr} is mixed with marine-derived organic matter in marine environments (Fig. 7B). For example, according to the enriched $\delta^{13}C_{TOC}$ values (mean=-20.4±0.1 ‰), sites GeoB16216-2, GeoB16217-1 and GeoB16223-1, which are the sites located farthest offshore, contain the largest fractions of marine organic matter, which reduces their $\Lambda 8$ values to about 0.18 despite their small mean grain size (<14 µm). Except for these three

locations, the Λ8 values are higher in finer grained sediments than in sandy sediments. This suggests that in marine sediments, as in the riverbed sediments, sorption of lignin on finer sediment is the dominant control on its distribution.

C/V and (Ad/Al)$_V$ values are not related to the grain size in the NW sector (Fig. 7C, D), which suggests that the influence of grain size on lignin composition and degradation is not as important as in the riverbed sediments. The control on the degradation of lignin on the inner Brazil-French Guiana shelf and slope is probably complex and influenced by many factors, including oxygen exposure time, contribution of material by coastal rivers, and sedimentation rate. Compared with riverbed sediments, offshore sediments also exhibit better preservation of organic matter and selective preservation of lignin in finer grain size particles, but grain size has limited impact on the lignin composition and degradation status.

In summary, the spatial patterns of lignin content and isotope compositions of organic matter corroborates earlier findings (Geyer et al., 1996; Nittrouer and DeMaster, 1996; Schlünz et al., 1999) that material discharged by the Amazon River is transported north-westward by the North Brazil Current. The modern Amazon Fan area receives more marine organic matter, and petrogenic organic matter is a significant component of OC$_{terr}$ in the Amazon Fan sediments. The similarity of lignin composition (C/V and S/V) of marine and riverbed sediments suggests that lignin is a reliable tracer reflecting the plant source of terrestrial organic matter in the Amazon basin and can be applied to reconstruct vegetation changes and paleoclimate conditions. Organic matter and lignin content furthermore vary with sediment grain size in the Amazon shelf and slope area and show the same preservation trend, better preservation in finer grained sediments, as in riverbed sediments. However, lignin composition is rather uniform in sediments of different grain sizes.

6 Conclusions

In this study, we use TOC content, stable carbon isotopic composition of organic matter, lignin phenol concentrations, sediment grain size and Al/Si ratios (as indicator of grain size) to investigate the characteristics of OC$_{terr}$ in the lowland Amazon basin and its fate on the adjacent continental margin. Depleted $\delta^{13}C_{TOC}$ of all riverbed sediments prove that there are limited contributions from C4 plants to the OC$_{terr}$ in the lowland Amazon basin. As evidenced by lignin compositions and stable carbon isotopes of organic matter, the most important plant sources of organic matter in the lowland Amazon basin are non-woody angiosperm C3 plants. There are no distinct regional lignin compositional signatures in the lowland Amazon basin, although the Amazon River receives contributions from tributaries draining different watersheds. Both the bulk organic matter parameters and the lignin compositions were observed to be related to the grain size of the riverbed sediments. Fine inorganic particles in the Amazon River carry more organic matter, preferentially preserving lignin against degradation. Lignin with higher C/V ratio is inclined to be adsorbed to coarse inorganic particles.

In marine surface sediments, the bulk parameters and lignin compositions indicate that the continental shelf southeast of the Amazon River mouth receives little OC$_{terr}$ from the Amazon River. Most of the OC$_{terr}$ discharged from the Amazon River is transported by the North Brazil Current to the northwest and deposited on the continental shelf close to the coast. Modern organic matter in the Amazon Fan is composed predominantly of marine-derived organic matter and the terrestrial organic

matter undergoes extensive diagenetic alteration before deposition. On the Amazon shelf, the OC_{terr} and lignin are both associated preferentially with fine-grained sediments. Despite long-distance transport in the marine environment, the lignin composition found in the marine sediments retains its plant source information in accordance with riverbed sediments. Lignin can thus be used to reliably provide assessments on the integrated vegetation cover in the Amazon basin.

References

Aller, R. C. and Blair, N. E.: Carbon remineralization in the Amazon–Guianas tropical mobile mudbelt: A sedimentary
15 incinerator, Cont. Shelf Res., 26(17–18), 2241–2259, doi:10.1016/j.csr.2006.07.016, 2006.

Aufdenkampe, A. K., Mayorga, E., Hedges, J. I., Llerena, C., Quay, P. D., Gudeman, J., Krusche, A. V. and Richey, J. E.: Organic matter in the Peruvian headwaters of the Amazon: Compositional evolution from the Andes to the lowland Amazon mainstem, Org. Geochem., 38, 337–364, doi:10.1016/j.orggeochem.2006.06.003, 2007.

Aufdenkampe, A. K., Mayorga, E., Raymond, P. a., Melack, J. M., Doney, S. C., Alin, S. R., Aalto, R. E. and Yoo, K.:
20 Riverine coupling of biogeochemical cycles between land, oceans, and atmosphere, Front. Ecol. Environ., 9(1), 53–60, doi:10.1890/100014, 2011.

Bardy, M., Derenne, S., Allard, T., Benedetti, M. F. and Fritsch, E.: Podzolisation and exportation of organic matter in black waters of the Rio Negro (upper Amazon basin, Brazil), Biogeochemistry, 106(1), 71–88, doi:10.1007/s10533-010-9564-9, 2011.

25 Battin, T. J., Luyssaert, S., Kaplan, L. a., Aufdenkampe, A. K., Richter, A. and Tranvik, L. J.: The boundless carbon cycle, Nat. Geosci., 2(9), 598–600, doi:10.1038/ngeo618, 2009.

Bendle, J. a., Weijers, J. W. H., Maslin, M. a., Sinninghe Damsté, J. S., Schouten, S., Hopmans, E. C., Boot, C. S. and Pancost, R. D.: Major changes in glacial and Holocene terrestrial temperatures and sources of organic carbon recorded in the Amazon fan by tetraether lipids, Geochemistry, Geophys. Geosystems, 11(12), Q12007, doi:10.1029/2010GC003308, 2010.

30 Benner, R., Hatcher, P. G. and Hedges, J. I.: Early diagenesis of mangrove leaves in a tropical estuary: Bulk chemical

characterization using solid-state 13C NMR and elemental analyses, Geochim. Cosmochim. Acta, 54(7), 2003–2013, doi:10.1016/0016-7037(90)90268-P, 1990.

Bianchi, T. S., Wysocki, L. A., Schreiner, K. M., Filley, T. R., Corbett, D. R. and Kolker, A. S.: Sources of Terrestrial Organic Carbon in the Mississippi Plume Region: Evidence for the Importance of Coastal Marsh Inputs, Aquat. Geochemistry, 17, 431–456, doi:10.1007/s10498-010-9110-3, 2011.

Blair, N. E. and Aller, R. C.: The Fate of Terrestrial Organic Carbon in the Marine Environment, Ann. Rev. Mar. Sci., 4(1), 401–423, doi:10.1146/annurev-marine-120709-142717, 2012.

Boot, C. S., Ettwein, V. J., Maslin, M. a., Weyhenmeyer, C. E. and Pancost, R. D.: A 35,000 year record of terrigenous and marine lipids in Amazon Fan sediments, Org. Geochem., 37(2), 208–219, doi:10.1016/j.orggeochem.2005.09.002, 2006.

Bouchez, J., Gaillardet, J., France-Lanord, C., Maurice, L. and Dutra-Maia, P.: Grain size control of river suspended sediment geochemistry: Clues from Amazon River depth profiles, Geochemistry, Geophys. Geosystems, 12(3), n/a-n/a, doi:10.1029/2010GC003380, 2011.

Bouchez, J., Galy, V., Hilton, R. G., Gaillardet, J., Moreira-Turcq, P., Pérez, M. A., France-Lanord, C. and Maurice, L.: Source, transport and fluxes of Amazon River particulate organic carbon: Insights from river sediment depth-profiles, Geochim. Cosmochim. Acta, 133, 280–298, doi:10.1016/j.gca.2014.02.032, 2014.

Cai, D.-L., Tan, F. C. and Edmond, J. M.: Sources and Transport of Particulate Organic Carbon in the Amazon River and Estuary, Estuar. Coast. Shelf Sci., 26, 1–14, 1988.

Callede, J., Kosuth, P., Loup, J.-L. and Guimarães, V. S.: Discharge determination by Acoustic Doppler Current Profilers (ADCP): a moving bottom error correction method and its application on the River Amazon at Óbidos, Hydrol. Sci. J., 45(6), 911–924, doi:10.1080/02626660009492392, 2000.

Cathalot, C., Rabouille, C., Tisnérat-Laborde, N., Toussaint, F., Kerhervé, P., Buscail, R., Loftis, K., Sun, M.-Y., Tronczynski, J., Azoury, S., Lansard, B., Treignier, C., Pastor, L. and Tesi, T.: The fate of river organic carbon in coastal areas: A study in the Rhône River delta using multiple isotopic (δ13C, Δ14C) and organic tracers, Geochim. Cosmochim. Acta, 118, 33–55, doi:10.1016/j.gca.2013.05.001, 2013.

Collins, J. a., Schefuß, E., Govin, A., Mulitza, S. and Tiedemann, R.: Insolation and glacial–interglacial control on southwestern African hydroclimate over the past 140 000 years, Earth Planet. Sci. Lett., 398, 1–10, doi:10.1016/j.epsl.2014.04.034, 2014.

Dunne, T., Mertes, L. a K., Meade, R. H., Richey, J. E. and Forsberg, B. R.: Exchanges of sediment between the flood plain and channel of the Amazon River in Brazil, Bull. Geol. Soc. Am., 110(4), 450–467, doi:10.1130/0016-7606(1998)110<0450:EOSBTF>2.3.CO;2, 1998.

Dunne Thomas, Mertes Leal A.K., Meade Robert H., R. J. E. an. F. B. R.: Exchanges of sediment between the flood plain and channel of the Amazon River in Brazil, Geol. Soc. Am. Bull., 110, 450–467, 1998.

Ertel, J. R. and Hedges, J. I.: Sources of sedimentary humic substances: vascular plant debris, Geochim. Cosmochim. Acta, 49(10), 2097–2107, doi:10.1016/0016-7037(85)90067-5, 1985.

Ertel, J. R., Hedges, J. I., Devol, A. H., Richey, J. E. and Ribeiro, M. de N. G.: Dissolved humic substances of the Amazon river system, Limnol. Oceanogr., 31(4), 739–754, 1986.

Feng, X., Feakins, S. J., Liu, Z., Ponton, C., Wang, R. Z., Karkabi, E., Galy, V., Berelson, W. M., Nottingham, A. T. and West, A. J.: Source to sink : Evolution of lignin composition in the Madre de Dios River system with connection to the Amazon basin and offshore, , 1–23, doi:10.1002/2016JG003323, 2016.

Galy, V., France-Lanord, C., Beyssac, O., Faure, P., Kudrass, H. and Palhol, F.: Efficient organic carbon burial in the Bengal fan sustained by the Himalayan erosional system., Nature, 450(November), 407–410, doi:10.1038/nature06273, 2007.

Galy, V., France-Lanord, C. and Lartiges, B.: Loading and fate of particulate organic carbon from the Himalaya to the Ganga-Brahmaputra delta, Geochim. Cosmochim. Acta, 72, 1767–1787, doi:10.1016/j.gca.2008.01.027, 2008.

Galy, V., Peucker-ehrenbrink, B. and Eglinton, T.: Global carbon export from the terrestrial biosphere controlled by erosion, , doi:10.1038/nature14400, 2015.

Gon, M. A. and Montgomery, S.: Alkaline CuO Oxidation with a Microwave Digestion System : Lignin Analyses of Geochemical Samples, anal. chem., 72(14), 3116–3121, 2000.

Goñi, M.: Record of terrestrial organic matter composition in Amazon Fan sediments, Proc. Ocean Drill. Program. Sci. …, 155, 519–530 [online] Available from: http://cat.inist.fr/?aModele=afficheN&cpsidt=2169715, 1997.

Guyot, J. L., Jouanneau, J. M., Soares, L., Boaventura, G. R., Maillet, N. and Lagane, C.: Clay mineral composition of river sediments in the Amazon Basin, Catena, 71(2), 340–356, doi:10.1016/j.catena.2007.02.002, 2007.

Häggi, C., Sawakuchi, A. O., Chiessi, C. M., Mulitza, S., Mollenhauer, G., Sawakuchi, H. O., Baker, P. A., Zabel, M. and Schefuß, E.: Origin, transport and deposition of leaf-wax biomarkers in the Amazon Basin and the adjacent Atlantic, Geochim. Cosmochim. Acta, 192, 149–165, doi:10.1016/j.gca.2016.07.002, 2016.

Hedges, J. I. and Keil, R. G.: Sedimentary organic matter preservation : an assessment and speculative synthesis, Mar. Chem., 49, 81–115, 1995.

Hedges, J. I. and Mann, D. C.: The characterization of plant tissues by their lignin oxidation products, Geochim. Cosmochim. Acta, 43, 1803–1807, doi:10.1016/0016-7037(79)90028-0, 1979a.

Hedges, J. I. and Mann, D. C.: The lignin geochemistry of marine sediments from the southern Washington coast, Geochim. Cosmochim. Acta, 43(11), 1809–1818, doi:10.1016/0016-7037(79)90029-2, 1979b.

Hedges, J. I., Clark, W. A., Quay, P. D., Richey, J. E., Devol, A. H. and Santos, U. de M.: Compositions and fluxes of particlate organic material in the Amazon River, Limnol. Oceanogr., 31, 717–738, 1986.

Hedges, J. I., Blanchette, R. a., Weliky, K. and Devol, A. H.: Effects of fungal degradation on the CuO oxidation products of lignin: A controlled laboratory study, Geochim. Cosmochim. Acta, 52, 2717–2726, doi:10.1016/0016-7037(88)90040-3, 1988.

Hedges, J. I., L, C. G., Richey, J. E., Quay, P. D., Benner, R., Mike, S. and Forsberg, B. R.: Origins and processing of organic matter in the Amazon River as indicated by carbohydrates and amino acids, Limnol. Oceanogr., 39(4), 743–761, 1994.

Hedges, J. I., Mayorga, E., Tsamakis, E., McClain, M. E., Aufdenkampe, A., Quay, P. and Richey, J. E.: Organic matter in Bolivian tributaries of the Amazon River: A comparison to the lower mainstream, Limnol. Oceanogr., 45(7), 1449–1466, doi:10.4319/lo.2000.45.7.1449, 2000.

Houghton, R. a, Lawrence, K. T., Hackler, J. L. and Brown, S.: The spatial distribution of forest biomass in the Brazilian Amazon: a comparison of estimates, Glob. Chang. Biol., 7(7), 731–746, doi:DOI 10.1046/j.1365-2486.2001.00426.x, 2001.

Jung, B.-J., Jeanneau, L., Alewell, C., Kim, B. and Park, J.-H.: Downstream alteration of the composition and biodegradability of particulate organic carbon in a mountainous, mixed land-use watershed, Biogeochemistry, 122(1), 79–99, doi:10.1007/s10533-014-0032-9, 2014.

Junk, W. J.: The Central Amazon Floodplain: Ecology of a Pulsing System., Springer, Berlin., 1997.

Kastner, T. P. and Goñi, M. a: Constancy in the vegetation of the Amazon Basin during the late Pleistocene: evidence from the organic matter composition of Amazon fan deep sea sediments, Geology, 31, 291–294, doi:10.1130/0091-7613(2003)031<0291, 2003.

Keil, R. G., Mayer, L. M., Quay, P. D., Richey, J. E. and Hedges, J. I.: Loss of organic matter from riverine particles in deltas, Geochim. Cosmochim. Acta, 61(7), 1507–1511, doi:10.1016/S0016-7037(97)00044-6, 1997.

Keil, R. G., Tsamakis, E., Giddings, J. C. and Hedges, J. I.: Biochemical distributions (amino acids, neutral sugars, and lignin phenols) among size-classes of modern marine sediments from the Washington coast, Geochim. Cosmochim. Acta, 62(8), 1347–1364, doi:10.1016/S0016-7037(98)00080-5, 1998.

Killops, S. and Killops, V.: Introduction to Organic Geochemistry Second Edition., 2005.

Kim, J. H., Zell, C., Moreira-Turcq, P., Pérez, M. a P., Abril, G., Mortillaro, J. M., Weijers, J. W. H., Meziane, T. and Sinninghe Damsté, J. S.: Tracing soil organic carbon in the lower Amazon River and its tributaries using GDGT distributions and bulk organic matter properties, Geochim. Cosmochim. Acta, 90, 163–180, doi:10.1016/j.gca.2012.05.014, 2012.

Kuzyk, Z. Z. a, Goñi, M. a., Stern, G. a. and Macdonald, R. W.: Sources, pathways and sinks of particulate organic matter in Hudson Bay: Evidence from lignin distributions, Mar. Chem., 112(3–4), 215–229, doi:10.1016/j.marchem.2008.08.001, 2008.

Loh, P. S., Chen, C. T. A., Anshari, G. Z., Wang, J. T., Lou, J. Y. and Wang, S. L.: A comprehensive survey of lignin geochemistry in the sedimentary organic matter along the Kapuas River (West Kalimantan, Indonesia), J. Asian Earth Sci., 43, 118–129, doi:10.1016/j.jseaes.2011.09.005, 2012.

Ludwig, W., Probst, J.-L. and Kempe, S.: Predicting the oceanic input of organic carbon by continental erosion, Global Biogeochem. Cycles, 10(1), 23, doi:10.1029/95GB02925, 1996.

Mayer, L. M.: Relationships between mineral surfaces and organic carbon concentrations in soils and sediments, Chem. Geol., 114(3–4), 347–363, doi:10.1016/0009-2541(94)90063-9, 1994.

Michael Goulding, Ronaldo Barthem, E. J. G. F.: The Smithsonian Atlas of the Amazon, Washington, DC., 2003.

Moreira-Turcq, P., Seyler, P., Guyot, J. L. and Etcheber, H.: Exportation of organic carbon from the Amazon River and its main tributaries, Hydrol. Process., 17(July 2002), 1329–1344, doi:10.1002/hyp.1287, 2003.

Mounier, S., Braucher, R. and Benaïm, J. Y.: Differentiation of organic matter's properties of the Rio Negro basin by crossflow ultra-filtration and UV-spectrofluorescence, Water Res., 33(10), 2363–2373, doi:10.1016/S0043-1354(98)00456-4, 1999.

Nittrouer, C. a. and DeMaster, D. J.: The Amazon shelf setting: tropical, energetic, and influenced by a large river, Cont. Shelf Res., 16(5), 553–573, doi:10.1016/0278-4343(95)00069-0, 1996.

Nittrouer, C. A., Kuehl, S. A., Sternberg, R. W., Figueiredo, A. G. and Faria, L. E. C.: An introduction to the geological significance of sediment transport and accumulation on the Amazon continental shelf, Mar. Geol., 125(3–4), 177–192, doi:10.1016/0025-3227(95)00075-A, 1995.

Opsahl, S. and Benner, R.: Early diagenesis of vascular plant tissues: Lignin and cutin decomposition and biogeochemical implications, Geochim. Cosmochim. Acta, 59(23), 4889–4904, doi:10.1016/0016-7037(95)00348-7, 1995.

Perez-Pimienta, J. a., Lopez-Ortega, M. G., Varanasi, P., Stavila, V., Cheng, G., Singh, S. and Simmons, B. a.: Comparison of the impact of ionic liquid pretreatment on recalcitrance of agave bagasse and switchgrass, Bioresour. Technol., 127, 18–24, doi:10.1016/j.biortech.2012.09.124, 2013.

R.J., G.: Amazon River system: Environmental factors that control its dissolved and suspended load, Science (80-.)., 156, 1734–1737, 1967.

Rezende, C. E., Pfeiffer, W. C., Martinelli, L. a., Tsamakis, E., Hedges, J. I. and Keil, R. G.: Lignin phenols used to infer organic matter sources to Sepetiba Bay - RJ, Brasil, Estuar. Coast. Shelf Sci., 87(3), 479–486, doi:10.1016/j.ecss.2010.02.008, 2010.

Richey, J.E., Hedges, J.I., Devol, A.H., Quay, P.D., Victoria, R., Martinelli, L., Forsberg, B. R.: Biogeochemistry of carbon in the amazon river, Limnol. Oceanogr., 35(2), 352–371, 1990.

Rockwell Geyer, W., Beardsley, R. C., Lentz, S. J., Candela, J., Limeburner, R., Johns, W. E., Castro, B. M. and Dias Soares, I.: Physical oceanography of the Amazon shelf, Cont. Shelf Res., 16(5–6), 575–616, doi:10.1016/0278-4343(95)00051-8, 1996.

Schlunz, B., Showers, W. J. and Wefer, G.: Terrestrial organic carbon accumulation on the Amazon deep sea fan during the last glacial sea level low stand, 1999.

Schlünz, B. and Schneider, R. R.: Transport of terrestrial organic carbon to the oceans by rivers: re-estimating flux and burial rates, Int. J. Earth Sci., 88, 599–606, doi:10.1007/s005310050290, 2000.

Schmidt, F., Hinrichs, K. and Elvert, M.: Sources, transport, and partitioning of organic matter at a highly dynamic continental margin, Mar. Chem., 118(1–2), 37–55, doi:10.1016/j.marchem.2009.10.003, 2010.

Tesi, T., Semiletov, I., Hugelius, G., Dudarev, O., Kuhry, P. and Gustafsson, Ö.: Composition and fate of terrigenous organic matter along the Arctic land–ocean continuum in East Siberia: Insights from biomarkers and carbon isotopes, Geochim. Cosmochim. Acta, 133, 235–256, doi:10.1016/j.gca.2014.02.045, 2014.

Tesi, T., Semiletov, I., Dudarev, O., Andersson, A. and Gustafsson, Ö.: Matrix association effects on hydrodynamic sorting and degradation of terrestrial organic matter during cross-shelf transport in the Laptev and East Siberian shelf seas, , 731–

752, doi:10.1002/2015JG003067.Received, 2016.

Vogts, A., Schefuß, E., Badewien, T. and Rullkötter, J.: n-Alkane parameters from a deep sea sediment transect off southwest Africa reflect continental vegetation and climate conditions, Org. Geochem., 47, 109–119, doi:10.1016/j.orggeochem.2012.03.011, 2012.

5   Ward, N. D., Keil, R. G., Medeiros, P. M., Brito, D. C., Cunha, A. C., Dittmar, T., Yager, P. L., Krusche, A. V. and Richey, J. E.: Degradation of terrestrially derived macromolecules in the Amazon River, Nat. Geosci., 6(7), 530–533, doi:10.1038/ngeo1817, 2013.

Winterfeld, M., Goñi, M. A., Just, J., Hefter, J. and Mollenhauer, G.: Characterization of particulate organic matter in the Lena River delta and adjacent nearshore zone, NE Siberia - Part 2: Lignin-derived phenol compositions, Biogeosciences,

10   12(7), 2261–2283, doi:10.5194/bg-12-2261-2015, 2015.

Wu, Y., Dittmar, T., Ludwichowski, K.-U., Kattner, G., Zhang, J., Zhu, Z. Y. and Koch, B. P.: Tracing suspended organic nitrogen from the Yangtze River catchment into the East China Sea, Mar. Chem., 107(3), 367–377, doi:10.1016/j.marchem.2007.01.022, 2007.

Wu, Y., Eglinton, T., Yang, L., Deng, B. and Montluçon, D.: Spatial variability in the abundance , composition , and age of

15   organic matter in surficial sediments of the East China Sea, , 118, 1495–1507, doi:10.1002/2013JG002286, 2013.

Zell, C., Kim, J.-H., Hollander, D., Lorenzoni, L., Baker, P., Silva, C. G., Nittrouer, C. and Sinninghe Damsté, J. S.: Sources and distributions of branched and isoprenoid tetraether lipids on the Amazon shelf and fan: Implications for the use of GDGT-based proxies in marine sediments, Geochim. Cosmochim. Acta, 139, 293–312, doi:10.1016/j.gca.2014.04.038, 2014.

Zhu, J. Y. and Pan, X. J.: Woody biomass pretreatment for cellulosic ethanol production: Technology and energy

20   consumption evaluation, Bioresour. Technol., 101(13), 4992–5002, doi:10.1016/j.biortech.2009.11.007, 2010.

Table 1. Sample information, results of bulk OC and lignin analyses of riverbed sediment samples from the Amazon basin presented in this study.

Sample code	River	Long	Lat	TOC (%)	$\delta^{13}C_{TOC}$ (‰)	$\Lambda 8$ (mg/100mgOC)	C/V	S/V	P/V	(Ad/Al)v	(Ad/Al)s	$\Sigma 8$ (mg/10g dry sediment)	Al/Si (weight ratio)
MAO02d	Negro	-60.36	-3.07	1.44	-29.5	3.79	0.26	0.82	0.34	0.59	0.44	5.44	0.19
MAO02e	Negro	-60.35	-3.06	2.93	-29.3	4.62	0.13	0.85	0.24	0.43	0.30	13.53	0.51
MAO02f	Negro	-60.35	-3.05	1.22	-27.3	4.46	0.13	0.97	0.25	0.59	0.32	5.44	0.43
MAO1	Negro	-60.30	-3.06	3.99	-29.3	4.89	0.14	1.09	0.23	0.61	0.30	19.52	0.50
MAO03a	Negro	-60.20	-3.05	2.13	-26.5	4.73	0.10	0.70	0.25	0.56	0.26	10.08	0.49
MAO03h	Negro	-60.20	-3.05	0.53	-29.6	3.55	0.18	0.91	0.31	0.71	0.36	1.89	0.17
MAO4	Negro	-60.15	-3.11	2.31	-29.8	4.59	0.18	0.81	0.28	0.35	0.24	10.59	0.31
MAO11c	Solimões	-60.38	-3.30	0.90	-29.9	3.86	0.20	1.12	0.24	0.32	0.20	3.48	0.37
MAO09b	Solimões	-60.29	-3.27	0.28	n.a.	3.49	0.17	1.19	0.30	0.28	0.15	0.99	0.30
MAO08b	Solimões	-60.21	-3.30	0.59	-27.9	4.97	0.21	0.99	0.25	0.33	0.28	2.93	0.37
MAO08a	Solimões	-60.20	-3.29	0.74	-28.4	4.34	0.24	1.13	0.22	0.32	0.23	3.19	0.34
MAO05a	Solimões	-60.03	-3.27	0.50	-26.1	4.30	0.28	1.10	0.23	0.52	0.34	2.13	0.27
MAO05d	Solimões	-60.02	-3.29	0.57	-28.4	4.71	0.1	0.94	0.17	0.35	0.26	2.69	0.33
MAO13c	Solimões	-59.88	-3.20	0.77	-28.4	6.44	0.17	1.06	0.24	0.28	0.19	4.94	0.37
MAO23a	Madeira	-59.08	-3.68	0.52	-28.4	4.42	0.14	0.96	0.21	0.29	0.23	2.30	0.37
MAO25e	Madeira	-58.91	-3.52	0.47	-27.8	3.29	0.21	1.21	0.26	0.35	0.22	1.55	0.31
MAO28d	Madeira	-58.80	-3.44	0.52	-27.9	3.10	0.24	1.17	0.25	0.39	0.25	1.61	0.23
MAO23c	Madeira	-59.08	-3.67	0.16	n.a.	1.69	0.29	1.04	0.44	0.49	0.40	0.28	0.17
MAO25d	Madeira	-58.91	-3.53	0.14	n.a.	0.73	0.36	1.07	0.63	0.67	0.57	0.10	0.17
MAO25b	Madeira	-58.91	-3.53	0.35	n.a.	2.42	0.23	1.16	0.48	0.71	0.38	0.84	0.31
MAO15e	Amazon	-59.38	-3.19	0.25	n.a.	2.84	0.20	1.14	0.18	0.31	0.21	0.70	0.24
MAO15a	Amazon	-59.38	-3.15	0.80	-27.9	4.01	0.1	0.91	0.20	0.40	0.24	3.21	0.36
MAO17	Amazon	-59.29	-3.15	0.59	-28.9	3.51	0.14	1.16	0.34	0.37	0.20	2.06	0.26
MAO19	Amazon	59.13	-3.18	1.00	-29.4	4.22	0.14	0.92	0.23	0.48	0.32	4.22	0.37
MAO21f	Amazon	-59.03	-3.23	0.99	-28.7	5.04	0.12	0.96	0.26	0.29	0.21	5.01	0.38
MAO36	Amazon	-58.62	-3.25	1.44	-28.1	4.76	0.21	0.84	0.24	0.45	0.26	6.85	0.31
OB1	Amazon	-55.56	-1.89	0.61	-28.4	3.79	0.21	1.10	0.30	0.48	0.28	2.33	0.32
MC11	Amazon	-51.09	-0.06	0.13	n.a.	0.75	0.47	1.01	0.64	0.61	0.56	0.10	0.11
MC12-2	Amazon	-51.05	-0.08	1.19	-28.3	9.27	0.11	0.88	0.17	0.28	0.25	11.05	0.37

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MC12-1	Amazon	-51.05	-0.08	1.01	-28.1	7.20	0.13	1.05	0.19	0.42	0.29	7.29	0.36
MC8	Amazon	-50.66	-0.13	0.62	-27.5	5.30	0.13	1.20	0.37	0.30	0.19	3.27	0.31
MC1	Amazon	-50.65	-0.12	0.60	-28.0	3.83	0.16	1.51	0.35	0.35	0.15	2.29	0.30
MC2	Amazon	-50.64	-0.13	0.40	-28.0	3.82	0.15	1.14	0.20	0.36	0.22	1.53	0.26
MC3	Amazon	-50.62	-0.15	0.26	n.a.	6.36	0.15	1.17	0.19	0.26	0.22	1.67	0.18
MC4	Amazon	-50.61	-0.17	0.72	-28.0	5.06	0.16	1.14	0.20	0.27	0.19	3.64	0.30
MC7	Amazon	-50.59	-0.21	0.37	n.a.	3.51	0.13	1.08	0.29	0.38	0.22	1.29	0.27
MC5	Amazon	-50.58	-0.20	1.29	-28.0	7.11	0.11	1.01	0.18	0.30	0.31	9.18	0.23
MC6	Amazon	-50.56	-0.19	0.80	-27.8	5.13	0.21	1.31	0.33	0.57	0.25	4.10	0.29
MC10	Amazon	-50.09	-0.05	0.76	-28.4	7.18	0.11	1.22	0.35	0.30	0.23	5.49	0.26
XA14L	Xingu	-52.69	-3.88	3.37	-29.7	5.33	0.16	0.98	0.20	0.55	0.36	17.97	0.29
XA30	Xingu	-52.24	-1.69	0.83	-27.9	3.30	0.16	1.23	0.28	0.31	0.18	2.73	0.33
XA36	Xingu	-52.13	-2.22	3.24	-29.8	3.33	0.08	0.90	0.24	0.43	0.26	10.81	0.55
XA25	Xingu	-51.97	-2.64	3.82	-29.4	3.90	0.19	1.12	0.25	0.42	0.27	14.90	0.54
XA38	Xingu	-52.02	-2.47	3.52	-29.6	4.47	0.15	1.05	0.25	0.55	0.28	15.73	0.49
XA31	Xingu	-52.25	-1.79	1.11	-28.4	6.91	0.19	0.91	0.19	0.34	0.26	7.70	0.30
XA34	Xingu	-52.26	-1.79	0.52	-28.3	6.88	0.19	0.75	0.40	0.38	0.27	3.55	0.14
XA35	Xingu	-52.19	-2.04	3.07	-29.8	5.22	0.16	1.03	0.36	0.53	0.37	16.04	0.56

n.a.: not available

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Table 2. Sample information, results of bulk OC and lignin analyses of marine surface sediment samples from the Amazon continental margin presented in this study.

Sample code	Long	Lat	TOC (%)	$\delta^{13}C_{TOC}$ (‰)	Λ8 (mg/100mg OC)	S/V	C/V	(Ad/Al)v	(Ad/Al)s	Σ8 (mg/10g sediment)	Al/Si (weigt ratio)	Mean grain size (μm)
The Amazon Fan sector (Fan)												
BC14B	-48.35	4.04	0.46	-23.0	0.09	0.81	0.15	0.91	0.81	0.04	0.42	5.2
BC17B	-48.54	3.96	0.44	-21.8	0.14	1.33	0.13	0.99	0.65	0.06	0.42	6.2
BC24B	-48.89	3.80	0.49	-22.2	0.22	1.62	0.18	0.88	0.49	0.11	0.40	14.5
BC3C	-48.61	4.46	0.60	-21.9	0.19	1.33	0.35	0.65	0.71	0.11	0.45	3.9
BC44C	-48.17	3.78	0.44	-21.8	0.10	0.59	0.11	0.75	0.70	0.04	0.41	4.7
BC50C	-47.31	3.65	0.57	-22.3	0.09	0.78	0.22	0.87	0.80	0.05	0.45	3.8
BC55C	-47.64	3.07	0.46	-21.7	0.13	0.76	0.14	0.81	0.70	0.06	0.40	8.2
BC61C	-47.74	2.85	0.98	-24.5	0.57	1.28	0.24	0.92	0.61	0.37	0.46	3.2
BC71C	-46.25	3.39	0.50	-21.4	0.06	1.28	0.35	0.70	0.77	0.03	0.46	n.a.
MC12A	-48.34	4.04	0.67	-22.6	0.13	1.61	0.27	0.56	0.78	0.09	0.43	5.1
MC6A	-48.62	4.46	0.77	-22.2	0.06	1.04	0.26	0.92	0.76	0.05	0.45	3.5
The southeast sector (SE)												
BC75C	-45.35	1.68	0.31	n.a.	0.04	0.81	0.25	0.86	0.92	0.01	0.40	n.a.
BC80C	-44.35	0.66	0.21	n.a.	0.10	0.80	0.11	0.49	0.42	0.02	0.38	4.8
BC82C	-44.21	0.34	0.35	-21.6	0.05	0.91	0.31	0.80	0.77	0.02	0.40	4.4
BC90B	-42.74	-1.03	0.43	n.a.	0.08	1.25	0.20	0.76	0.48	0.04	0.40	6.0
GeoB16202-1	-41.59	-1.91	0.47	-18.6	0.06	0.86	0.27	0.50	0.64	0.05	0.37	9.3
GeoB16203-2	-41.72	-2.04	0.75	-19.1	0.08	0.98	0.43	0.51	0.67	0.07	0.41	8.3
GeoB16204-1	-42.34	-2.00	0.91	-19.6	0.09	1.05	0.43	0.52	0.68	0.10	0.39	11.8
GeoB16205-3	-43.10	-1.35	0.50	-19.7	0.17	0.70	0.23	0.54	0.53	0.12	0.40	10.9
GeoB16206-2	-43.02	-1.58	0.55	-18.9	0.07	0.87	0.43	0.59	0.85	0.05	0.39	9.1
The northwest sector (NW)												
MC33A	-49.79	3.23	0.70	-26.7	2.01	1.23	0.16	0.73	0.54	1.49	0.46	5.0
GeoB16209-2	-49.37	2.83	0.11	-23.2	0.19	0.83	0.20	0.64	0.97	0.03	0.15	88.4
GeoB16210-2	-49.36	2.87	0.11	-24.1	0.39	1.06	0.29	0.50	0.48	0.04	0.17	48.7

GeoB16211-2	-49.35	2.88	0.18	-24.1	1.08	0.84	0.12	0.46	0.35	0.22	0.22	41.9
GeoB16212-2	-49.39	3.10	0.73	-25.7	1.55	1.01	0.16	0.51	0.35	1.05	0.46	5.7
GeoB16216-2	-51.26	6.24	0.79	-20.4	0.18	1.17	0.31	0.66	0.90	0.17	0.41	5.7
GeoB16217-1	-51.29	6.07	0.50	-20.3	0.18	1.10	0.25	1.16	0.76	0.10	0.30	13.1
GeoB16218-3	-51.52	4.77	0.76	-23.7	1.18	0.99	0.16	0.47	0.32	0.95	0.47	4.7
GeoB16223-1	-52.12	6.63	0.79	-20.5	0.19	1.11	0.29	0.65	0.86	0.17	0.38	6.1
GeoB16225-2	-52.86	5.67	0.27	-21.7	1.05	0.63	0.10	0.37	0.32	0.33	0.14	92.9

n.a.: not available

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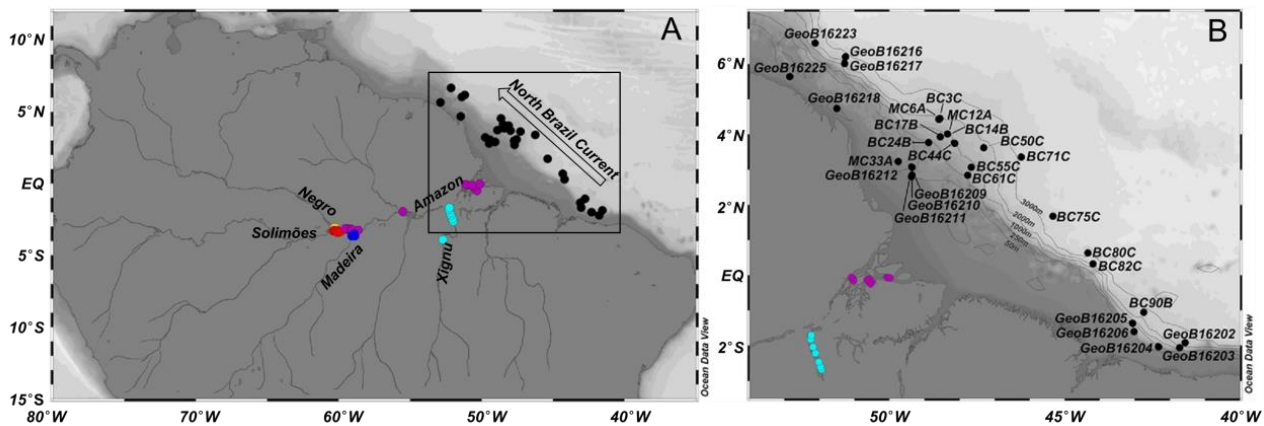
Figure 1: A) Map of the Amazon basin with the sample locations in individual tributaries and offshore area indicated by colored dots (red dots=Solimões, yellow dots=Negro, blue dots=Madeira, aqua dots=Xingu, violet dots=Amazon mainstream, black dots=offshore), the black rectangle indicates the area of map B and B) Map of the Amazon continental margin with the sample locations indicated by black dots. Maps were created using Ocean Data View 4.7.8 (Schlitzer, 2016).
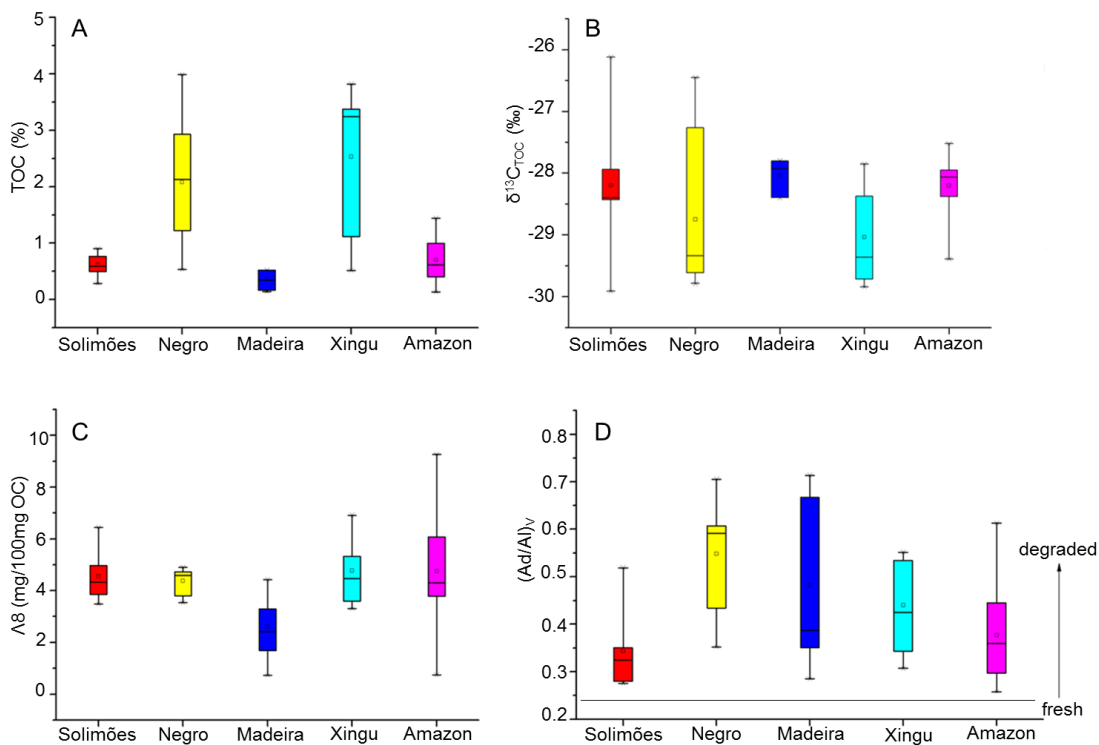

Figure 2: A) Total organic carbon (TOC) content, B) stable carbon isotopic composition of total organic carbon ($\delta^{13}C_{TOC}$), C) carbon-normalized lignin content ($\Lambda 8$) and D) degradation index of lignin $(Ad/Al)_V$ in different tributaries and in the Amazon mainstream. In D, $(Ad/Al)_V \leq 0.24$ suggests fresh vascular plant tissues, whereas $(Ad/Al)_V > 0.24$ reveals degraded plant material. See Table 1 and Fig. 1 for the location of the samples.

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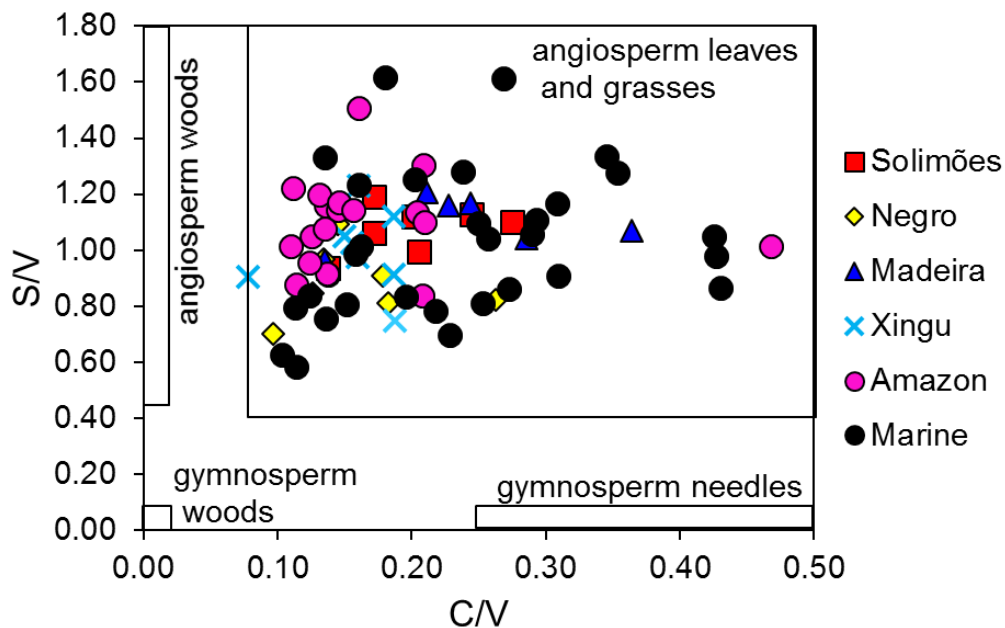
Figure 3: Syringyl:vanillyl (S/V) vs. cinnamyl:vanillyl (C/V) ratios of lignin from Amazon basin river bed sediments and marine surface sediments from the adjacent continental margin. The black boxes show typical ranges for different vascular plant tissues from the Amazon basin (Hedges et al.,1986, Goñi et al.,1998). See Tables 1 and 2, and Fig. 1 for the location of the samples.
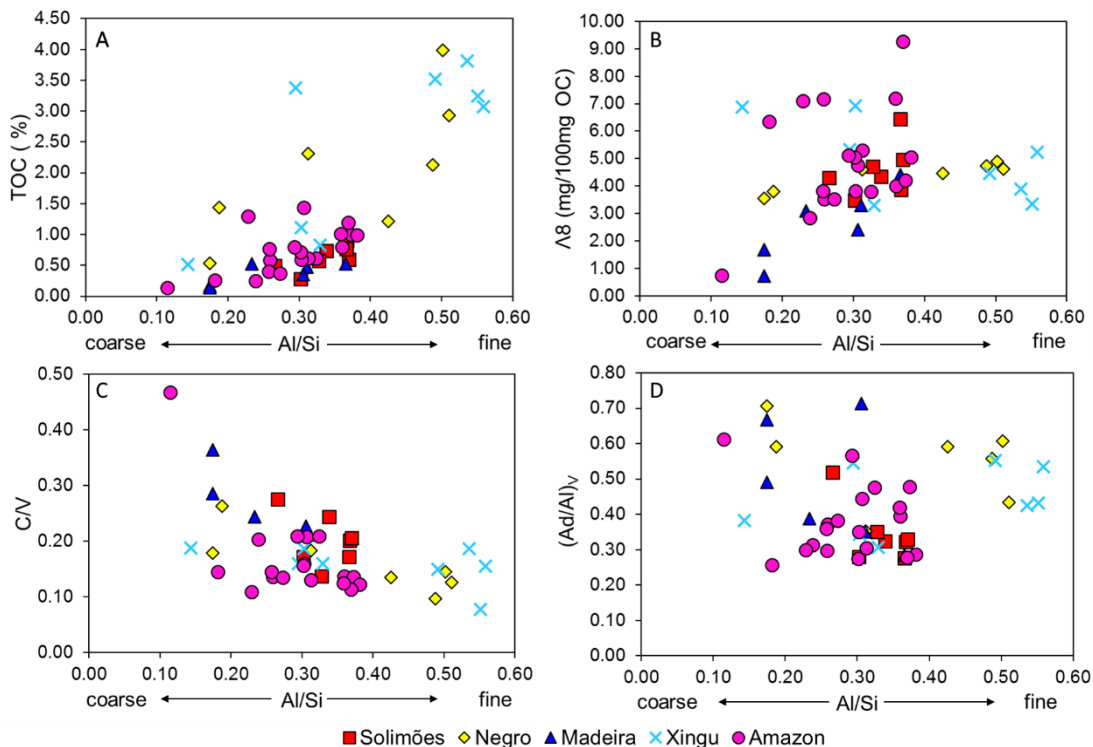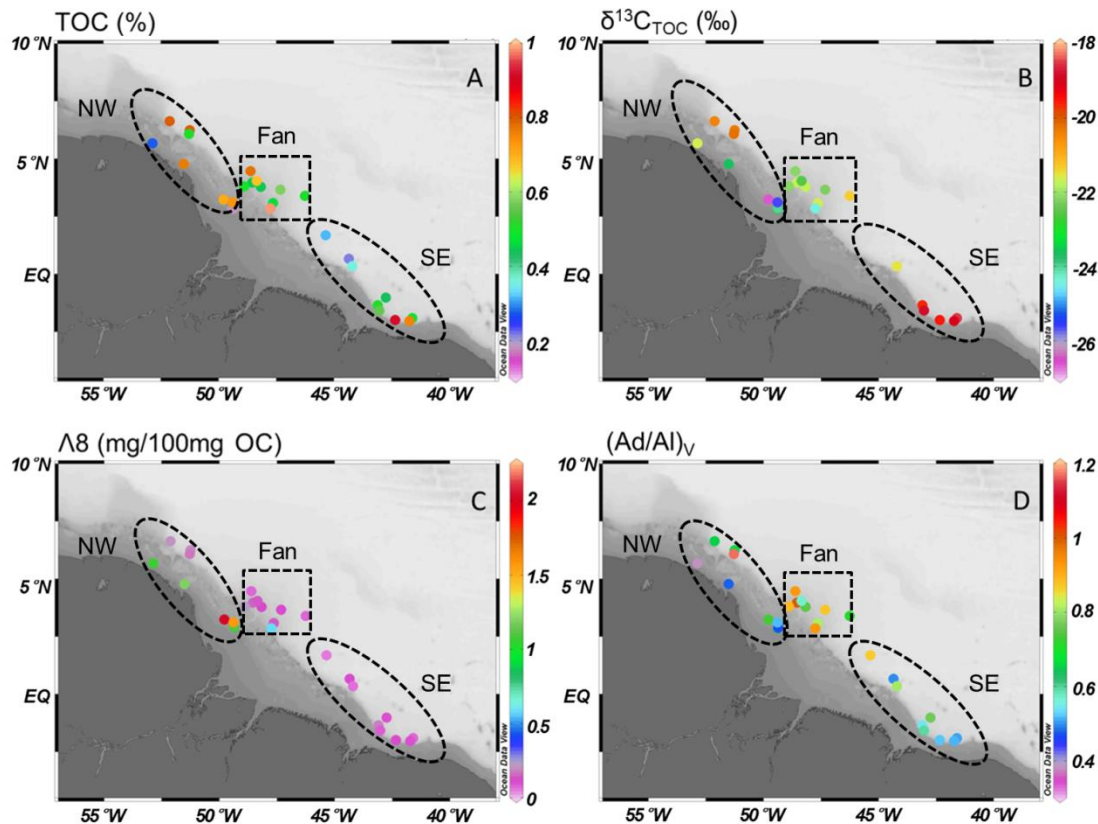

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Figure 4: A) Total organic carbon (TOC) content vs. Al/Si, **B)** carbon-normalized lignin content (Λ8) vs. Al/Si, **C)** cinnamyl:vanillyl (C/V) ratio vs. Al/Si, and **D)** degradation index of lignin ((Ad/Al)$_V$) vs. Al/Si from Amazon basin riverbed sediments. See Table 1 and Fig. 1 for the location of the samples.

5   **Figure 5:** Spatial distribution of **A)** total organic carbon (TOC) content, **B)** stable carbon isotopic composition of total organic carbon (δ^{13}C$_{TOC}$), **C)** carbon-normalized lignin content (Λ8), and **D)** degradation index of lignin ((Ad/Al)$_V$) in marine surface sediment samples from the Amazon continental margin. The dashed ellipses and the rectangle represent the northwest sector (NW), the Amazon Fan sector (Fan) and southeast sector (SE).
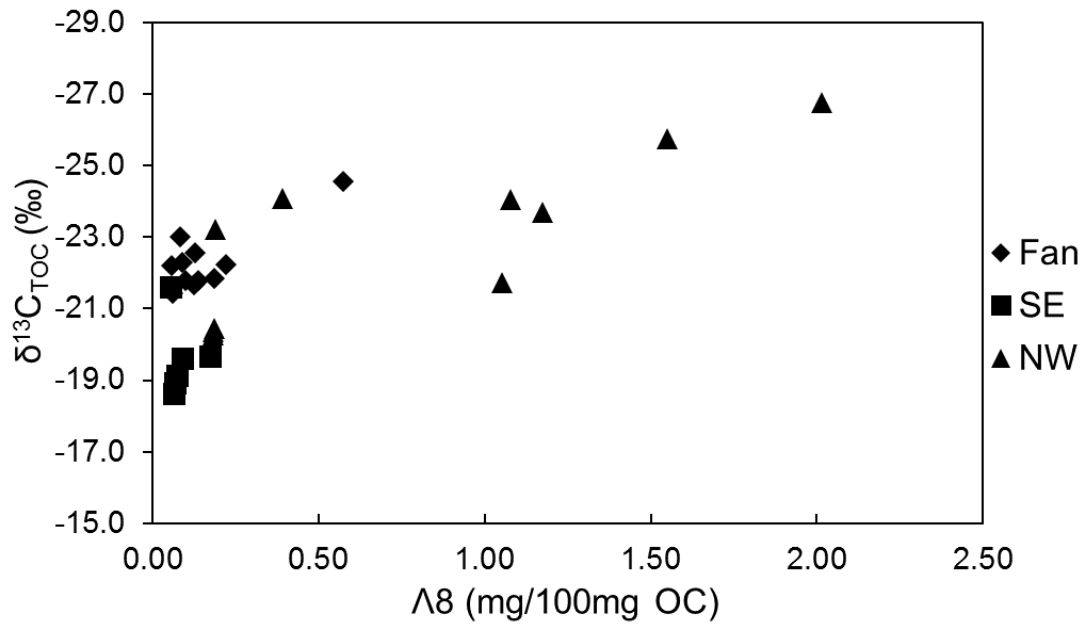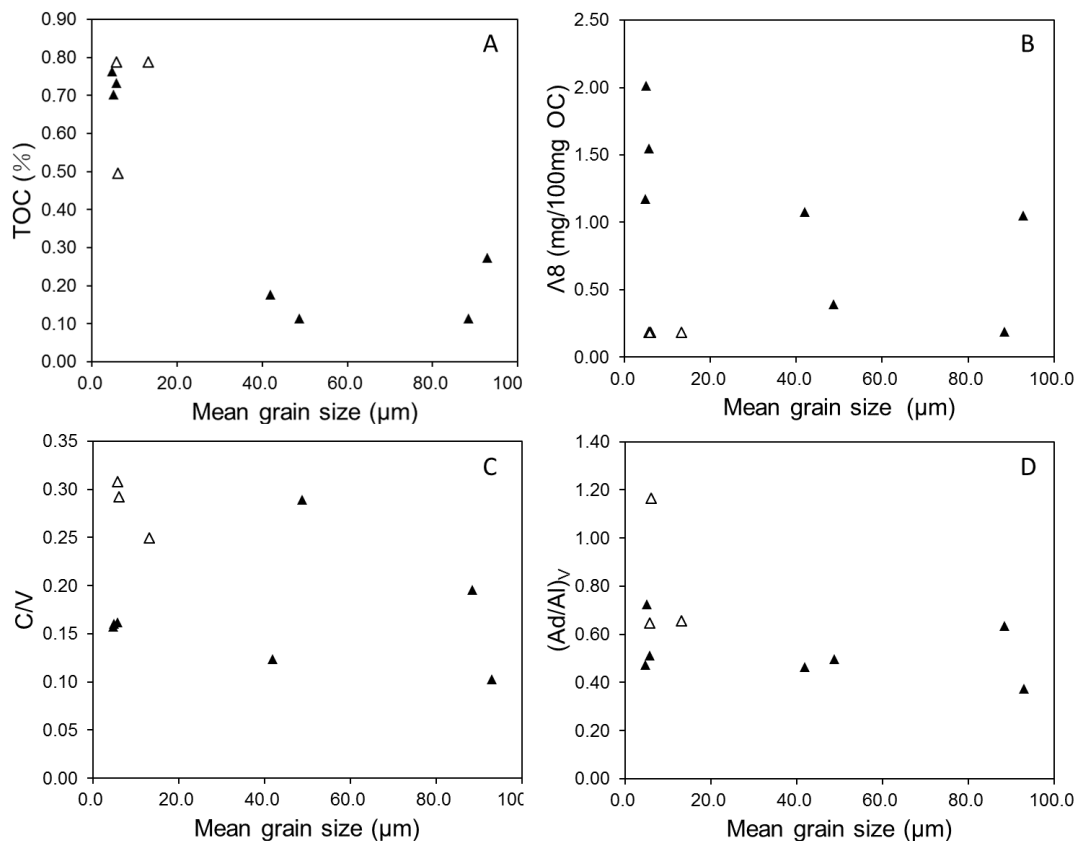
Figure 6: Stable carbon isotopic composition of total organic carbon ($\delta^{13}C_{TOC}$) vs. carbon-normalized lignin content ($\Lambda 8$) for marine surface sediment samples from the Amazon continental margin.

Figure 7: A), B), C) and D) indicate total organic carbon (TOC) content, carbon-normalized lignin content (Λ8), cinnamyl:vanillyl (C/V) ratio and lignin degradation index ((Ad/Al)$_V$) for marine surface sediment samples from the NW sector vs. mean grain size, respectively. Empty triangles represent the three deepest sites (>2000 m) far from the coast, and filled triangles represent the other sites in the NW sector with water depth shallower than 100 m. See Table 2 and Fig. 5 for the location of the NW sector.