# Depth-partitioning of particulate organic carbon composition in the rising and falling stages of the Amazon River

Sarah Rosengard<sup>1</sup>, Jose Mauro S. Moura<sup>2</sup>, Robert Spencer<sup>3</sup>, Carl G Johnson<sup>4</sup>, Ann P. McNichol<sup>4</sup>, Andrew D. Steen<sup>5</sup>, and Valier Galy<sup>6</sup>

<sup>1</sup>The School of the Art Institute of Chicago <sup>2</sup>Universidade Federal do Oeste do Pará <sup>3</sup>Florida State University <sup>4</sup>Woods Hole Oceanographic Institution <sup>5</sup>University of Tennessee at Knoxville <sup>6</sup>woods hole oceanographic institution

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#### Abstract

The Amazon River mobilizes organic carbon across one of the world's largest terrestrial carbon reservoirs. Quantifying the sources of particulate organic carbon (POC) to this flux is typically challenging in large systems like the Amazon River due to hydrodynamic sorting of sediments. Here, we analyze the composition of POC collected from multiple total suspended sediment (TSS) profiles in the mainstem at Óbidos, and surface samples from the Madeira, Solimões and Tapajós Rivers. As hypothesized, TSS and POC concentrations in the mainstem increased with depth and fit well to Rouse models for sediment sorting by grain size. Coupling these profiles to Acoustic Doppler Current Profiler discharge data, we estimate a large decrease in POC flux (from 540 to 370 kilograms per second) between the rising and falling stages of Amazon River mainstem. The C/N ratio, stable and radiocarbon signatures of bulk POC are less variable within the cross-section at Óbidos, and suggest that riverine POC in the Amazon River is predominantly soil-derived. However, smaller shifts in these compositional metrics with depth, including leaf wax n-alkanes and fatty acids, are consistent with the perspective that deeper and larger particles carry fresher, less degraded organic matter sources (i.e., vegetation debris) through the mainstem. Overall, our cross-sectional surveys at Óbidos highlight the importance of depth-specific sampling for estimating riverine export fluxes. At the same time, they imply that this approach to sampling is perhaps less essential with respect to characterizing the composition of POC sources exported by the river.

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# Depth-partitioning of particulate organic carbon composition in the rising and falling stages of the Amazon River

Sarah Z. Rosengard<sup>1,2,3\*</sup>, Jose Mauro S. Moura<sup>4</sup>, Robert G.M. Spencer<sup>5</sup>, Carl Johnson<sup>1</sup>, Ann
McNichol<sup>6</sup>, Andrew D. Steen<sup>7</sup>, and Valier Galy<sup>1</sup>

- 1. Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA, USA
- 2. Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA, USA
- Department of Liberal Arts, The School of the Art Institute of Chicago, Chicago, IL, USA\*
- Programa de Pós-Graduação em Recursos Naturais da Amazônia, Universidade Federal do Oeste do Pará, Santarém, Pará, Brazil
- Department of Earth, Ocean & Atmospheric Science, Florida State University, Tallahassee, FL, USA
- Department of Marine Geology and Geophysics, Woods Hole Oceanographic Institution,
   Woods Hole, MA, USA
- Departments of Microbiology and Earth and Planetary Sciences, University of Tennessee,
   Knoxville, TN, USA
- 20 \*Corresponding author's current affiliation

# 21 Key points

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- Amazon River suspended sediments show little variation in organic carbon composition
   with depth, despite hydrodynamic sorting.
- Estimated particulate organic carbon fluxes range from 370 to 540 kilograms per second
   between rising and falling stages.
  - The majority of Amazon River particulate organic carbon exported from the mainstem at Óbidos is soil-derived.

# 28 Abstract

29 The Amazon River mobilizes organic carbon across one of the world's largest terrestrial 30 carbon reservoirs. Quantifying the sources of particulate organic carbon (POC) to this flux is 31 typically challenging in large systems like the Amazon River due to hydrodynamic sorting of 32 sediments. Here, we analyze the composition of POC collected from multiple total suspended 33 sediment (TSS) profiles in the mainstem at Óbidos, and surface samples from the Madeira, 34 Solimões and Tapajós Rivers. As hypothesized, TSS and POC concentrations in the mainstem 35 increased with depth and fit well to Rouse models for sediment sorting by grain size. Coupling 36 these profiles to Acoustic Doppler Current Profiler discharge data, we estimate a large decrease 37 in POC flux (from 540 to 370 kilograms per second) between the rising and falling stages of 38 Amazon River mainstem. The C/N ratio, stable and radiocarbon signatures of bulk POC are less variable within the cross-section at Óbidos, and suggest that riverine POC in the Amazon River 39 40 is predominantly soil-derived. However, smaller shifts in these compositional metrics with depth, 41 including leaf wax *n*-alkanes and fatty acids, are consistent with the perspective that deeper and 42 larger particles carry fresher, less degraded organic matter sources (i.e., vegetation debris) 43 through the mainstem. Overall, our cross-sectional surveys at Óbidos highlight the importance of 44 depth-specific sampling for estimating riverine export fluxes. At the same time, they imply that 45 this approach to sampling is perhaps less essential with respect to characterizing the composition 46 of POC sources exported by the river.

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#### 48 **Plain language summary**

49 The Amazon River transports one of the largest quantities of freshwater organic carbon into the 50 Atlantic Ocean. In this study, we collected suspended particles at different depths within a cross-51 section of the Amazon River mainstem, during the rising and falling stages of the river's 52 hydrological cycle. We analyzed the organic carbon, nitrogen, grain size, and leaf-derived 53 compounds in these particles, and integrated water velocity measurements to calculate the 54 quantity of carbon in particle form moving through the river at these two stages. The analyses 55 showed that large, dense particles concentrate with depth in the Amazon River mainstem. The 56 composition of these particles is relatively homogenous, but slight variations in metrics like 57 carbon-to-nitrogen ratio, age derived from carbon-dating, and leaf waxes imply that less 58 degraded sources of organic carbon are found in the deeper and coarser grained particles.

59 Overall, the data suggest that the majority of Amazon River particulate organic carbon comes

60 from a mixture of soil organic carbon washing in from different landscapes and soil depth

- 61 horizons. A small but globally significant quantity of this carbon will get buried in the deep
- 62 Atlantic Ocean, forming a long-term carbon sink.







Figure 1. Top row (a): the Amazon River Basin and all field sites from June 2005, April 2014 and July

65 2014. Image credit: Paul Lefebvre and Greg Fiske (Woods Hole Research Center). Second row from top:

66 monthly mainstem discharge time-series in 2014, compiled by the Brazilian Agência Nacional de Águas 67 (https://www.snirh.gov.br/hidroweb/serieshistoricas). Each number represents the average flow measured 68 on the first day of each month of the year (month #1 is January; month #12 is December). The vertical 69 solid lines represent the two sampling months, April and July. Third row from top: Acoustic Doppler 70 Current Profiler (ADCP) transects in latitude/longitude across the Amazon River at Óbidos in April and 71 July 2014, with color indicating river depth. Transects started at the right bank across from Obidos, and 72 ended at the left bank near Obidos. The markers indicate approximate locations of each TSS sample. Note 73 that exact GPS coordinates of each individual sample were not recorded during the April transect. Bottom 74 row: measured and extrapolated water velocities within the cross-section at Obidos in April 2014 and July 75 2014, with the colorbar representing water velocity.

76 77

# 78 1 Introduction

79 The Amazon River Basin, a global biodiversity hotspot, is one of the largest reservoirs of 80 biospheric organic carbon on the planet. The river network includes eight major tributaries that 81 extend across a six million square kilometer drainage basin. Torrential seasonal rains mobilize 82 massive quantities of suspended sediments across flooded and upland rainforests, drier savannah, 83 high-elevation Andean landscapes, as well as cropland and pasture, into the tributaries and 84 mainstem. As a result, the Amazon River sustains the highest freshwater discharge (Dai & 85 Trenberth, 2002) and one of the largest export fluxes of suspended sediments and particulate 86 organic carbon (POC) to the ocean globally (see compilation by Galy et al., 2015). The Amazon 87 River Basin's role as a major conduit for POC transport from land to sea has motivated decades 88 of research into its influence on the global carbon cycle and long-term climate (Hedges et al., 89 1986; Richey et al., 1990, 2002; Mayorga et al., 2005; Bouchez et al., 2010, 2014; Ward et al., 90 2013, 2015; Sun et al., 2017)

In large river basins, spatial heterogeneity is a significant challenge to quantifying annual, basin-wide POC fluxes (Bouchez et al., 2011b; Galy et al., 2008; Lupker et al., 2011). The majority of knowledge on riverine particulate geochemistry and POC transport through the Amazon River mainstem has accrued through years of field measurements collected near the municipality of Óbidos in the State of Pará (Fig. 1a), the most downstream gaging station unaffected by seawater intrusion from the Atlantic Ocean (Kosuth et al., 2009; Moreira-Turcq et al., 2003; Richey et al., 1986). In the mainstem near Óbidos, which is about two kilometers wide

98 and over 60 meters deep during some seasons of the year, hydrodynamic sorting might cause 99 larger grain-size sediments to settle faster and concentrate at deeper depths (Bouchez et al., 100 2011b; Curtis et al., 1979; Rouse, 1950) leading to compositional differences between deeper, 101 coarser sediments and shallower, finer sediments (Bouchez et al., 2014; Bouchez et al., 2011a). 102 In particular, depth-specific differences in total suspended sediment (TSS) concentrations in the 103 mainstem cross-section can change five-fold (Bouchez et al., 2011a), implying that 104 measurements traditionally based on surface TSS concentrations alone are susceptible to 105 considerable error. For this reason, more recent Amazon POC export flux measurements have 106 integrated across depths with sub-surface measurements (e.g., Bouchez et al. 2011b; Bouchez et 107 al. 2014).

108 Potential depth-dependent differences in organic matter composition in the Amazon 109 River have been explored less, but have implications for our understanding of the sources of 110 POC that are eventually exported to the Atlantic Ocean. Here, we analyze particulate organic 111 matter (POM) from two cross-sectional surveys at Óbidos during two stages of the river's 112 hydrological cycle (i.e., rising and falling water levels), integrating measurements of the bulk 113 POM pool with compound-specific lipid abundances and carbon stable isotope composition. 114 While bulk metrics shed light on the predominant origins of organic matter in the river (Kim et 115 al., 2012; Martinelli et al., 1994; Powell et al., 2012), lipid-specific measurements provide a 116 nuanced understanding of specific carbon sources in the bulk pool, such as terrestrial vegetation 117 and *in situ* primary production (e.g., Saliot et al. 2001; Häggi et al. 2016; Feakins et al. 2018). 118 Our results expand understanding of the variability of POC composition in the narrow and deep 119 mainstem of the Amazon River. To our knowledge, these data represent the highest resolution 120 survey of POC within an Amazon mainstem cross-section.

121 Our study further compiles analyses of surface riverine POC samples collected from 122 tributaries both upstream and downstream of our main study location (Obidos). At this location 123 on the mainstem, the Amazon River's particle composition integrates suspended sediments from 124 most of the major tributaries of the drainage basin, particularly the Solimões and Madeira rivers, 125 which join to form the Amazon upstream of Óbidos. Importantly, particle input from the 126 Tapajós, Xingu, and Tocantins Rivers downstream can still alter the composition of POC that is 127 ultimately exported to the Atlantic Ocean (Ward et al., 2015). Following prior studies that have 128 attempted to sample river suspended sediments along transects, and understand the loss and

replacement of POC from the floodplain to the mouth (e.g., Hedges et al. 1986; Guyot et al.

130 1996; Kim et al. 2012; Ward et al. 2015; Häggi et al. 2016; Sun et al. 2017), our study endeavors

131 to contextualize the cross-sectional distribution of POC composition at Óbidos within a range of

132 new and previously published observations of POC both upstream and downstream.

133

#### 134 2 Methods

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# 2.1 Overview of sampling expeditions

136 The suspended sediments we discuss in this study were sampled during three expeditions 137 to the Amazon River Basin in June 2005, April 2014 and July 2014 (Table 1, Fig. 1a). The 2005 samples were collected from the mainstem at Óbidos, and at two upstream locations near the 138 139 Madeira River mouth to the Amazon River (~Foz Madeira) and near the Solimões River 140 connection to the mainstem (~Manacapuru). The reader may refer to Bouchez et al. (2011b) for 141 more description on the field collection and archival of these samples. The 2014 samples were 142 collected primarily at Óbidos. Sampling occurred once in the rainy season in March/April, and 143 once in the dry season, July 2014. In July 2014, suspended sediments were also retrieved from 144 the Tapajós River downstream from Óbidos.

In 2014, mainstem discharge at Óbidos varied by a factor of two between a minimum during the dry season and a maximum during the rainy season (Fig. 1b). Continuous gauge measurements near Óbidos (https://www.snirh.gov.br/hidroweb/serieshistoricas), conducted by the Brazilian Agência Nacional de Águas, showed that in 2014, discharge peaked in May and June at ~250,000 m<sup>3</sup>/s (Fig. 1b). Thus, the two sampling months in 2014 reflect different river stages, rising in April and falling in July, prior to and after peak discharge, respectively.

Each expedition served a unique purpose in this study. The two 2014 expeditions to Óbidos provided the majority of samples we analyze in this study, as well as an opportunity to quantify TSS and POC fluxes during two hydrological stages of the river, using a depthintegrated method complementary to the prior expeditions (Bouchez et al., 2011b). The other samples collected in 2005 and the one Tapajós River sample collected in 2014 allowed for an extended comparison between Amazon River POC at Óbidos and POC from its most immediate upstream and downstream tributaries.

# 58 Table 1. *Sample Locations and Times*.

River	Location	Latitude	Longitude	Date	Channel position	Sample depth	Temperature	Volume	Discharge	zR	TSS flux	POC flux
		°S	°W		km	т	°C	-	m3/s	unitless	kg/s	kg/s
mainstem	Óbidos	1.937*	55.503*	8 June 2005	-	0	no data	>100 L	128,000	0.39	61,300	604
Madeira	Foz Madeira	3.456*	58.808*	6 June 2005	-	0	no data	>100 L	21,800	0.10	1,300	14
Solimões	Manacapuru	3.314*	60.554*	4 June 2005	-	0	no data	>100 L	124,700	0.09	17,400	168
mainstem	Óbidos	1.946	55.510	2 April 2014	0.32	35.49	25.9	~10 L	270,000	0.26	53,000	544
mainstem	Óbidos	1.946	55.510	2 April 2014	0.32	15.3	27.3	~10 L	270,000	0.26	53,000	544
mainstem	Óbidos	1.946	55.510	2 April 2014	0.32	2.1	no data	~10 L	270,000	0.26	53,000	544
mainstem	Óbidos	1.942	55.503	2 April 2014	1.1	49.1	no data	~10 L	270,000	0.26	53,000	544
mainstem	Óbidos	1.942	55.503	2 April 2014	1.1	30.15	27.5	~10 L	270,000	0.26	53,000	544
mainstem	Óbidos	1.942	55.503	2 April 2014	1.1	13.33	26.8	~10 L	270,000	0.26	53,000	544
mainstem	Óbidos	1.942	55.503	2 April 2014	1.1	2.7	26.4	~10 L	270,000	0.26	53,000	544
mainstem	Óbidos	1.938	55.496	2 April 2014	2.00	27.8	27.5	~10 L	270,000	0.26	53,000	544
mainstem	Óbidos	1.938	55.496	2 April 2014	2.00	10.4	26.1	~10 L	270,000	0.26	53,000	544
mainstem	Óbidos	1.938	55.496	2 April 2014	2.00	2.8	26.1	~10 L	270,000	0.26	53,000	544
mainstem	Óbidos	1.940	55.501	1 April 2014	-	0	28.0	>100 L	270,000	N/A	53,000	544
Tapajós	Tapajós	no data	no data	27 July 2014	-	0	no data	>100 L	no data	N/A	no data	no data
Tapajós	Tapajós	no data	no data	27 July 2014	-	bed	no data	N/A	no data	N/A	no data	no data
mainstem	Óbidos	1.946	55.509	28 July 2014	0.34	42.8	28.9	~10 L	249,000	0.34	48,000	369
mainstem	Óbidos	1.945	55.510	28 July 2014	0.34	20.6	no data	~10 L	249,000	0.34	48,000	369
mainstem	Óbidos	1.945	55.509	28 July 2014	0.34	3.5	no data	~10 L	249,000	0.34	48,000	369
mainstem	Óbidos	1.944	55.494	28 July 2014	1.6	54	28.9	~10 L	249,000	0.34	48,000	369
mainstem	Óbidos	1.942	55.497	28 July 2014	1.6	39.83	29	~10 L	249,000	0.34	48,000	369
mainstem	Óbidos	1.941	55.499	28 July 2014	1.6	30.4	28.9	~10 L	249,000	0.34	48,000	369
mainstem	Óbidos	1.941	55.499	28 July 2014	1.6	14.95	no data	~10 L	249,000	0.34	48,000	369

mainstem	Óbidos	1.939	55.501	28 July 2014	1.6	3.14	no data	~10 L	249,000	0.34	48,000	369
mainstem	Óbidos	1.933	55.497	28 July 2014	2.2	53.06	29	~10 L	249,000	0.34	48,000	369
mainstem	Óbidos	1.931	55.499	28 July 2014	2.2	29.83	no data	~10 L	249,000	0.34	48,000	369
mainstem	Óbidos	1.933	55.498	28 July 2014	2.2	3.33	no data	~10 L	249,000	0.34	48,000	369
mainstem	Óbidos	1.942	55.496	28 July 2014	-	0	29.2	>100 L	249,000	0.34	48,000	369
mainstem	Óbidos	no data	no data	28 July 2014	-	bed	no data	N/A	249,000	N/A	48,000	369
mainstem	Óbidos	no data	no data	28 July 2014	-	bed	no data	N/A	249,000	N/A	48,000	369
mainstem	Óbidos	no data	no data	28 July 2014	1	flood	no data	N/A	249,000	N/A	48,000	369

161 Note: Depth-specific samples at Óbidos were collected in three positions across the mainstem channel, referenced to the right bank across from

162 Óbidos (Fig. 1). The 2005 data are taken from Bouchez et al. (2011b) and Bouchez et al. (2014). Discharge, total suspended solid (TSS) and

163 particulate organic carbon (POC) fluxes, and water temperatures are provided when available. In the sample depth column, "bed"=bedload and

164 "flood"=floodplain deposit.

165 \* Latitude & longitude reflects one GPS coordinate for this sampling station and date

# 166 2.2 Particle collection

167 All suspended sediments were collected by filtering several large-volume (100-200 L) 168 samples of surface river water and a number of small-volume (~10 L) samples at specified 169 depths below surface. The exact volumes were calculated by weighing the water samples after 170 collection and converting mass to volume using the density of fresh water, ~1 kg/L. With the 171 exception of the 2005 samples, all water samples were filtered in pressurized Teflon-coated units 172 through 0.22 µm diameter pore size Millipore PES membrane filters within two days after 173 collection. Between collection and filtration, samples were either covered in a dark tarp or stored 174 in the shade to minimize exposure to sunlight. After filtration, the particles on the filters were 175 immediately frozen on board the ship. Although previous studies have highlighted the 176 compositional differences across particle size fractions in the Amazon River (Aufdenkampe et 177 al., 2007; Hedges et al., 1986, 1994), we have chosen to pool all particles above 0.22 µm in 178 diameter for analysis of the total riverine particle pool, following Bouchez et al. (2011b).

179 The large-volume samples were acquired at Óbidos (April 2014, July 2014 and June 180 2005), and each upstream/downstream tributary site using a bucket submerged a few tens of 181 centimeters below the surface. Each sampling location was roughly in the center of each river 182 channel. The 10 L samples were collected within three depth profiles at Óbidos in April and July 183 2014, using a depth-specific horizontal isokinetic sampler. Each profile, consisting of three to 184 five depths from 2-3 m to ~50 m, was located at a different position in the channel of the 185 mainstem between the right bank and the left bank closer to Obidos (Fig. 1c, d, Table 1). The 186 depth-specific water sampler was equipped with a depth sensor to accurately record the 187 collection depths.

In July 2014, additional bedload samples from the Tapajós River and mainstem at Óbidos were taken using a dredge sampler. One flood deposit sample from the right bank of the mainstem, across from Óbidos, was also collected during this same expedition. Similar to the water-column particle samples, these bedload and flood deposit samples were immediately frozen following collection until analysis.

In the laboratory, each suspended sediment sample was re-suspended from the filters in milli-Q water and freeze-dried, while bed samples and the floodplain deposit were directly freeze-dried. All dried samples were sieved through a 2 mm mesh to remove any coarse impurities such as rock fragments and leaf debris, and homogenized before subsequent analyses. 197 The homogenized quantities of suspended sediments were weighed to calculate suspended198 sediment concentrations (mg/L).

199

#### 200 2.3 Flux calculations

201 During both sampling trips, on 3 April and 29 July 2014, water velocity profiles were 202 measured across the mainstem channel using a Sontek RiverSurveyor® M9 Acoustic Doppler 203 Current Profiler (ADCP). The ADCP operated on a 1 MHz frequency, and was equipped with a 204 0.5 MHz vertical beam sensor for river depth measurements and an external GPS for compass 205 heading, latitude and longitude tracking. The external GPS did not function over most of the 206 transect in April, so an average offset from the external GPS was applied to correct the internal 207 Sontek compass, which did provide continuous heading measurements. The RiverSurveyor® 208 software integrated velocities measured through the instrument's transect and modeled within the 209 "edge" regions between each end of the instrument transect and the nearest river bank to 210 calculate a water discharge value through the river's cross-section.

211 The velocity cross-sections guided our choice of sample depths and locations for each 212 depth profile (Fig. 1c, d, Table 1, Sect. 2.2) and enabled us to calculate suspended sediment 213 fluxes across the mainstem. The ADCP measured three velocity components (E, N, U) down to 214 40 m depth. Horizontal velocities,  $V_{mag}$ , were calculated as the vector combination of the E (east) 215 and N (north) components. Because 40 m was often shallower than the river bed and a further 216 10% of each velocity profile data was discarded prior to data export, the deepest measured 217 velocities had to be extrapolated to the river bed, using the following relationship between 218 horizontal velocity, V<sub>mag</sub>, and vertical distance above river bed, z (Chen, 1989; Mueller et al., 219 2009):

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$$V_{mag} = a_v z^{1/6} \tag{1}$$

The  $a_v$  values for each ADCP transect position were first extracted by fitting the measured  $V_{mag}$ profiles to Equation 1. Then, the extrapolated  $V_{mag}$  values for all depths between the deepest measured  $V_{mag}$  and the river bed were calculated using the fitted  $a_v$  values.

226 Suspended sediment concentration profiles  $(C_z)$  were modeled based on the assumption 227 that the Amazon River mainstem was deep enough in April and July 2014 to allow for separation of sediment grain size and density by depth. Following Bouchez et al. (2011b), who also reported
hydrodynamic sorting in the Amazon mainstem, all depth-specific suspended sediment
concentrations from each sampling month were fitted to a Rouse equation, which relates
sediment concentration to river depth (Rouse, 1950):

232

- 233  $\frac{C_z}{C_a} = \left(\frac{H-z}{z}\frac{a}{H-a}\right)^{z_R}$ (2)
- 234

In this relationship,  $C_z$  is suspended sediment concentration at *z*, the vertical distance above the river bed, which has a depth of *H*. The constant *a* is the depth of the shallowest point measurement in the depth profile,  $C_a$  is the suspended sediment concentration at a, and  $z_R$  is the Rouse number. We used a nonlinear least-squares fit to calculate the Rouse number for April and July. The Rouse fits allowed us to model  $C_z$  across the entire mainstem cross-section by varying *H* from the ADCP data, but using constant  $C_a$  values, averaged across the surface-most measurement of the three channel positions in each sampling month.

We calculated suspended sediment fluxes at Óbidos during each sampling month by integrating the product of suspended sediment concentration ( $C_z$ , modeled by Equation 2) and water velocity (both measured and extrapolated  $V_{mag}$  values, according to Equation 1) across channel position and over river depth (Bouchez et al., 2011b):

- 246
- 247

TSS flux =  $\iint V_{mag}C_z dx dz$  (3)

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In Equation 3, *dx* values were calculated by projecting the distance of the boat track using ADCP
transect coordinates (Fig. 1) against the azimuth of the mainstem at Óbidos.

251

252 2.4 Enzyme activity assays

Enzyme assays were conducted on suspended particles from the July 2014 Óbidos depth profiles to probe variations in heterotrophic activity in the Óbidos cross-section. Samples were analyzed using –AMC (7-amino-4-methylcoumarin) and –MUB (4-methylumbelliferone)-based fluorogenic substrate proxies (Mullen et al., 2018) (Table 2) and buffered with 100 mM carbonate buffer (pH=6.85). Assays were performed in triplicate for all samples and for one control, boiled to denature all enzymes, which served as a blank correction. Fluorescence was

- 259 measured three to four times during 4-hour sample and control incubations in 1 mL cuvettes at
- ambient temperature. Enzyme activities in each sample were inferred by the blank-subtracted
- substrate hydrolysis rates calculated from these four time points.
- 262
- 263
  - 3 Table 2. Substrates for Measuring Enzyme Activities in the Amazon River Mainstem, July 2014.
- 264

Substrate	Abbreviation	Enzyme	Element
leucine-AMC	Leu-AMC	leucyl aminopeptidase	Ν
Phenylalanine-AMC	Phe-AMC	phenyalanyl aminopeptidase	Ν
Ala-Ala-Phe-AMC MUB-beta-N-acetyl	AAF-AMC	chymotrypsin	Ν
glucosamine	MUB-NAG	N-acetylglucosaminidase	Ν
MUB-cellobiose	MUB-cello	cellulase	С
MUB-beta glucose	MUB-beta-glu	beta-glucosidase	С
MUB-beta xylose	MUB-xyl	xylanase	С
MUB-PO4	MUB-PO4	phosphomonoesterase	Р

Note: AMC is -amino-4-methylcoumarin and MUB is 4-methylumbelliferone.

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265

268 2.5 Bulk particle composition

The distribution of grain sizes in the homogenized particle samples (Sect. 2.2) was analyzed using a Beckman Coulter Laser Diffraction Particle Size Analyzer (LS 13 320). Samples were sonicated for 10 seconds in tap water before loading into the detector. The LS 13 320 detects particles in the 0.4  $\mu$ m to 2 mm size range, and reports mean and median grain size for each sample. The software additionally calculates the volumetric contribution of particle sizes throughout the distribution, as well as the d10, d50, and d90 diameters, which delineate the 10<sup>th</sup>, 50<sup>th</sup> and 90<sup>th</sup> percentiles of the size distribution, respectively.

Bulk weight % organic carbon (%OC), weight % total nitrogen (%N),  $\delta^{13}$ C, and  $\delta^{15}$ N in the homogenized suspended and bed sediments were analyzed using a *Fisons Instruments Carlo Erba 1108* elemental analyzer interfaced via a *Finnigan MAT Conflo II* to a *Delta-Plus* Stable

279 Light isotope ratio mass spectrometer (IRMS). Prior to measuring % OC and  $\delta^{13}$ C, sub-samples

280 were weighed, loaded in silver boats, fumigated in concentrated hydrochloric acid (12 N HCl)

vapors for 72 hours at 60°C, and then dried in a desiccator at 60°C for 72 hours to remove the

- inorganic carbon in the sediment (Whiteside et al., 2011). One bedload sediment from Óbidos
- 283 was analyzed after just 12-16 hours of acid fumigation. Weighed sub-samples were not

fumigated prior to measuring %N and  $\delta^{15}$ N. All analyses were conducted in triplicate. The results only report the average and standard deviation of the triplicate measurements.

286 For bulk radiocarbon composition, sub-fractions of selected sediment samples were 287 similarly decarbonated via acid fumigation for 72 hours. After drying, the fumigated sample was 288 sealed in an evacuated quartz tube with 2 g copper oxide, and baked at 850°C for 6 hours, which 289 converted all the sample organic carbon to CO<sub>2</sub> gas (McNichol et al., 1995). The evolved CO<sub>2</sub> 290 was then cryogenically purified under vacuum, graphitized by iron catalysis in pure H<sub>2</sub> gas at 291 450°C, and analyzed for its radiocarbon composition at the National Ocean Sciences Accelerator 292 Mass Spectrometry (NOSAMS) facility at Woods Hole Oceanographic Institution (McNichol et 293 al., 1992).

294

# 295 2.6 Compound-specific lipid analysis

296 Abundances of specific biomolecules provide higher-resolution details of organic matter 297 composition. Straight-chain *n*-alkanes and fatty acids were quantified in each large-volume 298 sample collected in 2005 and 2014, and in four depth-specific samples collected in 2014 (Table 299 1). Total lipids were extracted from sediment into 15-20 mL of 9:1 dichloromethane 300 (DCM)/methanol at 100°C for 20 minutes using a Microwave Accelerated Reaction System 301 (MARS, CEMS Corp.). The total lipid extracts were then saponified in 15 mL of 0.5 M 302 potassium hydroxide (KOH) in wet methanol at 70°C for two hours. After adding 20 mL milli-Q 303 water and 0.5 g of sodium chloride to the KOH solution, the basic lipids were extracted from the 304 aqueous phase via five hexane rinses. The remaining KOH solution was acidified to pH~2 using 305 12 N HCl to isolate the acidic lipids in five rinses with 4:1 hexane/DCM.

306 Each basic and acidic lipid fraction was separated into five biomolecular classes on the 307 basis of polarity. The concentrated lipid fractions were loaded onto aminopropyl silica gel 308 columns and sequentially flushed with hexane (for *n*-alkanes), 4:1 hexane/DCM (for ketones), 309 9:1 DCM/acetone (for sterols, alcohols and other polar compounds), 2.6% oxalic acid in 310 methanol (for fatty acids), and 1:1 DCM/methanol (for residual compounds). Both acidic and 311 basic fraction-derived fatty acids were re-combined and methylated in 95:5 methanol:HCl with a known  $\delta^{13}$ C value and  $^{14}$ C composition for 12-16 hours at 70°C. The fatty acid methyl esters 312 313 (FAMES) were isolated on an additional aminopropyl silica gel column after methylation. Prior 314 to compound-specific isotope analysis, large-volume FAMES and *n*-alkanes were urea-adducted

in 40 mg/mL methanol urea solution as an additional purification step to separate the branched
 compounds from straight-chain compounds. There was no need to further purify the four depth specific FAMES and *n*-alkane fractions that were selected for compound-specific isotope
 analysis.

319 All compound abundances were measured using a flame ionization detector coupled to a 320 Hewlett Packard 5890 Series II Gas Chromatograph (GC-FID). Urea-adducted, combined acid 321 and base fractions of *n*-alkanes and FAMES were injected in high purity hexane. In addition, the 322 non-adducted fractions of FAMES and *n*-alkanes, as well as the other fractions of the post-323 methylation FAMES columns were analyzed in the GC-FID. Any "residual" FAMES and n-324 alkane quantities in these other fractions were added to the FAMES and *n*-alkane quantities from 325 the purified fractions, and are reported as such in Sections 3 and 4, all supplementary Tables and 326 Figures 4-6.

327 All GC-FID analyses were accompanied by a suite of standard *n*-alkanes and FAMES to 328 cross-reference sample peak retention times and quantify compound abundances by peak areas. 329 Some analyses were accompanied by just one standard injection at one known concentration, 330 while others were accompanied by injection of three different standard concentrations. When 331 three standard concentration chromatograms were available, standard curves were applied to 332 sample peak areas to estimate analyte mass (in nanograms). When analyses included just one 333 standard concentration, a response factor, equivalent to the average peak area/ng compound 334 across standard compounds, was used to convert sample peak area to mass.

The  $\delta^{13}$ C values of specific FAMES and *n*-alkanes were measured using a *HP6890* gas chromatograph fitted with a *Gerstel PTV* and interfaced via a *Finnigan MAT Conflo II* to a *Delta-Plus* IRMS. When compound abundances were sufficient,  $\delta^{13}$ C values were measured in duplicate or triplicate, with only average and standard deviation values reported.

339

340 2.7 Error analysis

We equate the error of the average %OC, %N, bulk  $\delta^{13}$ C and  $\delta^{15}$ N, and compoundspecific  $\delta^{13}$ C to the standard deviation of triplicate analyses of each sample. Because the relative errors in bulk F<sub>m</sub> values were small, ranging from ~0.2%-0.5%, they are not reported in the following sections. A conservative relative error of ±10% was used for lipid masses per extraction, based on the relative standard deviation of standard compound peaks across GC-FIDanalyses. Errors were propagated for any metrics calculated from these values.

347 **3** 

348

349 3.1 Mainstem discharge in 2014

Data

350 Maximum river depth of the Amazon River mainstem at Obidos was 67-68 m in both 351 April and July 2014, varying more by channel position than by season (Fig. 1). The M9 352 *RiverSurveyor*® ADCP logged >1400 velocity profiles from surface to riverbed in April and 353 >1300 profiles in July. The average water velocity across the transect was  $2.0 \pm 0.6$  m/s in April 354 and  $1.7 \text{ m/s} \pm 0.6 \text{ m/s}$  in July. In both seasons, velocities tended to be highest (3-4 m/s) in the 355 middle of the cross-section, where depths exceeded 40 m. Velocities near the river bed were 356 generally slower, less than 1.5 m/s. Total calculated discharge (Sect. 2.3) at Óbidos decreased slightly between sampling months, ranging from 270,000 m<sup>3</sup>/s in April and 249,000 m<sup>3</sup>/s in 357 358 July (Table 1). While our July value was consistent with measurements from the Brazilian 359 Agencia Nacional de Aguas (Fig. 1b), our instantaneous April value overestimated discharge at 360 Óbidos by ~18%.

361

362

# *3.2 TSS concentrations and fluxes in 2014*

363 Total suspended sediment concentrations ([TSS]) throughout the main-stem cross-section 364 at Obidos varied from 55.5 to 318.5 mg/L in April 2014 (Fig. 2, Table 3), within the range of all 365 suspended sediment concentrations analyzed at Óbidos in 2005 (Bouchez et al., 2011a). July 366 values were broader, ranging from 16.4 to 741.4 mg/L. Concentrations were highest in the 367 deepest samples near the right bank (i.e., across from the municipality of Óbidos) in both April 368 and July 2014. Positioned inside of a bend in the Amazon mainstem, a greater abundance of 369 particles accumulates in river waters here, leading to significantly higher TSS concentrations 370 (i.e., greater than mean + 1 S.D. of all other depth-specific [TSS] values). In July, this deep 371 sample has the highest C/N value of all depth-specific samples from the same sampling period, 372 potentially bearing the signature of re-suspended organic matter deposits from the adjacent river 373 bank, which has a higher C/N value compared to the other April/July suspended sediments.



Figure 2. Profiles of TSS concentration, organic matter composition, and median grain size (d50) at Óbidos in April (blue) and July (black) 2014. Data from profiles near the right bank (triangles), left bank (circles) and river center (crosses) are separate. All y-axes are normalized to the river depth at the channel position of each profile. The errors in %POC, %PN and fraction modern are relatively small and therefore not plotted.  $\delta^{13}$ C values are expressed in units of ‰.

- 380
- 381

382 Table 3. Total Suspended Sediment Concentration, Organic Matter Composition and Grain Size of 2005 and 2014 Samples.

Location	Depth	Channel position	[TSS]	%POC	NG%	C/N	δ <sup>13</sup> C	Fraction modern	Grain- mean	Grain-d50	Grain-d10	Grain-d90
	т	km	mg/L	mg/mg	%	µmol/ µmol	%0	unitless	μт	μт	μm	μm
mainstem*	0	-	data no	$0.85\pm0.01$	$0.14\pm0.005$	$7.3\pm 0.5$	$\textbf{-28.5}\pm0.05$	0.71	no data	no data	no data	no data
Solimões*	0	-	data no	$1.12\pm0.06$	$0.17\pm0.003$	$7.9\pm1.8$	$-27.0 \pm 0.05$	0.72	no data	no data	no data	no data
Madeira*	0	-	data	$0.49\pm0.01$	$0.08\pm0.0004$	$7.2\pm1.9$	$\textbf{-27.7}\pm0.3$	0.67	no data	no data	no data	no data
mainstem	0	-	55	$1.37\pm0.01$	$0.19\pm0.004$	$8.5\pm0.2$	$\textbf{-28.1}\pm0.06$	0.72	no data	no data	no data	no data
mainstem	35.49	0.32	319	$0.98\pm0.02$	$0.12\pm0.001$	$9.6\pm0.2$	$\textbf{-28.3}\pm0.07$	no data	44	29	4	109
mainstem	15.3	0.32	150	$1.01\pm0.02$	$0.12\pm0.001$	$9.5\pm0.2$	$\textbf{-28.3}\pm0.2$	no data	48	31	5	121
mainstem	2.1	0.32	79	$1.32\pm0.02$	$0.20\pm0.001$	$7.8\pm 0.1$	$\textbf{-28.4} \pm 0.09$	no data	50	29	4	131
mainstem	49.1	1.1	208	$0.96\pm0.01$	$0.13\pm0.001$	$8.8\pm 0.1$	$\textbf{-28.2}\pm0.05$	0.77	63	44	6	153
mainstem	30.15	1.1	233	$0.93\pm0.01$	$0.11\pm0.001$	$10\pm0.1$	$\textbf{-28.2}\pm0.03$	0.78	48	30	5	119
mainstem	13.33	1.1	111	$1.35\pm0.01$	$0.19\pm0.002$	$8.4\pm 0.1$	$\textbf{-28.0}\pm0.08$	0.78	43	27	4	106
mainstem	2.7	1.1	72	$1.52\pm0.01$	$0.24\pm0.004$	$7.4\pm0.1$	$\textbf{-28.1}\pm0.03$	0.77	70	49	4	171
mainstem	27.8	2.00	149	$1.09\pm0.01$	$0.15\pm0.001$	$8.5\pm0.1$	$\textbf{-28.2}\pm0.1$	no data	61	39	5	154
mainstem	10.4	2.00	126	$1.19\pm0.05$	$0.16\pm0.003$	$8.7\pm 0.4$	$\textbf{-28.1}\pm0.02$	no data	60	43	6	142
mainstem	2.8	2.00	107	$1.22\pm0.03$	$0.17\pm0.002$	$8.2\pm 0.3$	$\textbf{-28.1}\pm0.1$	no data	44	28	4	110
Tapajós	bed	-	N/A	$0.14\pm0.002$	$0.017\pm0.0003$	$10\pm0.3$	$\textbf{-29.4} \pm 0.2$	1.02	no data	no data	no data	no data
Tapajós	0	-	0.52	$15.71\pm0.13$	$2.69\pm0.005$	$6.8\pm 0.1$	$\textbf{-31.0}\pm0.1$	0.89	no data	no data	no data	no data
mainstem	0	-	16	$1.80\pm0.02$	$0.23\pm0.003$	$9.0\pm0.1$	$\textbf{-29.1}\pm0.06$	0.77	no data	no data	no data	no data
mainstem	42.8	0.34	741	$0.79\pm0.04$	$0.07\pm0.002$	$14\pm0.9$	$\textbf{-28.5}\pm0.1$	no data	80	69	11	165
mainstem	20.6	0.34	135	$1.01\pm0.003$	$0.11\pm0.002$	$11\pm0.2$	$\textbf{-28.8} \pm 0.03$	no data	71	52	9	163
mainstem	3.5	0.34	103	$0.85\pm0.02$	$0.10\pm0.001$	$10\pm0.3$	$\textbf{-28.8} \pm 0.03$	no data	66	51	8	146
mainstem	54	1.6	305	$0.51\pm0.02$	$0.054\pm0.001$	$11\pm0.5$	$-28.4\pm0.2$	0.80	106	96	15	212
mainstem	39.83	1.6	182	$0.54\pm0.01$	$0.064\pm0.002$	$9.8\pm0.3$	$\textbf{-28.6} \pm 0.1$	0.78	80	66	9	176

mainstem	30.4	1.6	169	$0.77\pm0.02$	$0.086\pm0.001$	$11\pm0.3$	$\textbf{-28.9}\pm0.05$	0.78	77	65	9	168
mainstem	14.95	1.6	53	$1.06\pm0.02$	$0.12\pm0.004$	$10\pm0.4$	$\textbf{-29.1} \pm 0.05$	0.77	60	45	7	139
mainstem	3.14	1.6	44	$1.31\pm0.02$	$0.16\pm0.002$	$9.5\pm0.2$	$\textbf{-28.9} \pm 0.06$	0.74	55	38	6	133
mainstem	53.06	2.2	286	$0.61\pm0.01$	$0.066\pm0.001$	$11\pm0.3$	$\textbf{-28.6} \pm 0.1$	no data	93	80	13	194
mainstem	29.83	2.2	108	$1.00\pm0.01$	$0.11\pm0.001$	$11\pm0.2$	$\textbf{-28.8} \pm 0.07$	no data	71	50	8	171
mainstem	3.33	2.2	56	$1.28\pm0.02$	$0.14\pm0.0003$	$11\pm0.2$	$\textbf{-28.9} \pm 0.07$	no data	62	42	7	153
mainstem	flood	0	N/A	$0.50\pm0.03$	$0.048{\pm}\ 0.001$	$12\pm0.9$	$\textbf{-28.1}\pm0.08$	no data				
mainstem	bed	0	N/A	$0.064{\pm}\ 0.002$	$0.0093 {\pm} 0.0004$	$}8.0\pm 0.5$	$\textbf{-26.6} \pm 0.09$	0.60	no data	no data	no data	no data
mainstem	bed	0	N/A	$0.022{\pm}\:0.001$	BDL	no data	$\textbf{-26.9} \pm 0.02$	0.87	no data	no data	no data	no data

385 Note: Channel position for depth-specific samples at Óbidos are referenced to the right bank across from Óbidos (Fig. 1). Errors for C/N and  $\delta^{13}$ C

386 are reported. Relative errors of depth-specific  $F_m$  values are < 1%, and are not reported.

387 \* 2005 sample (refer to Table 1 for specific sampling dates).

388 BDL= below detection limit.

389 "bed"=bedload.; "flood"=floodplain deposit.

390 Total suspended sediment concentrations increased with depth in all profiles at Óbidos 391 (Fig. 2, Table 3). Other than in the right bank profiles in April, mean, median/d50, d10, and d90 392 grain size diameters generally increased with depth and [TSS], providing clear evidence for 393 hydrodynamic sorting of sediment in the cross-section (Bouchez et al., 2011b; Rouse, 1950). All 394 10 L [TSS] values were fitted to the Rouse equation (C<sub>z</sub> in Equation 2). We chose to combine 395 profiles within each sampling month rather than calculate one Rouse number per channel 396 position profile per month, following the reasoning that the errors from fitting individual, 397 instantaneous profiles in a given depth profile could be offset by the spatial heterogeneity of 398 three depth profiles spanning the cross-section (Bouchez et al., 2011b). The reference height 399 above the river bed,  $z_a$ , varied from 36.9 m to 56.2 m in April and from 41.5 to 58.9 m in July. 400 The suspended sediment concentration at  $z_a$ ,  $C_a$ , varied from 71.6 to 106.8 mg/L in April and 401 from 43.9 to 102.7 mg/L in July. These TSS concentration fits yielded a Rouse numbers of 0.26 402 and 0.34, respectively, in April and July (Table 1). The modeled concentration profiles fit the 403 data well, suggesting that the Rousean description of hydrodynamic sorting adequately explains 404 our observations (Fig. 3).

The integrated product of [TSS] and water velocity within each cross-section yielded instantaneous suspended sediment fluxes of ~53,000 kg/s in April and ~48,000 kg/s in July (Equation 3). We note that while these values do not incorporate water discharge and sediment concentrations within the cross-sectional area between each river bank and the ends of the ADCP transects (i.e., the "edge" discharge values calculated by the RiverSurveyor® software, as described in Sect. 2.3), discharge in these "edge" sections of the transect represents less than 1% of total discharge at the mainstem.

412

# 413 3.3 Bulk POC composition

The weight % organic carbon (%OC) within depth-specific sediments at Óbidos ranged from 0.51 - 1.52% and decreased with depth in all profiles across channel positions and seasons (Fig. 2, Table 3). At the same time, particulate organic carbon concentrations ([POC]), which ranged from 0.6 - 5.9 mg/L, increased with depth, as TSS concentrations increased. Weight % nitrogen (%N) values in suspended sediments ranged from 0.05 - 0.24% and also decreased with depth. Molar C/N ratios exhibited a large range from 7.4 to 14.1, and tended to increase with depth in all profiles. Even though [TSS], %OC, and [POC] varied within profiles at Óbidos, the



Figure 3. Fits of all depth-specific TSS concentration ( $C_z$ ) profiles measured at Óbidos in 2014 to the Rouse Equation (Equation 2; Bouchez et al., 2011; Rouse 1950). Variable *z* is the height above the river bed *H* of each profile, and  $C_a$  is the surface-most measured  $C_z$  value of each profile. The vertical lines corresponding to  $C_z \sim 196$  mg/L and 193 mg/L are the sediment concentrations needed to compute equivalent sediment fluxes based on sampling at a single (50%) depth.

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429 isotopic composition of organic carbon in the sediments did not vary significantly with depth. 430  $\delta^{13}$ C values ranged from -29.1‰ to -28.0‰ across all profiles and seasons, while  $\delta^{15}$ N values 431 ranged from 3.1‰ to 4.3‰. The range in fraction modern (F<sub>m</sub>) values was also relatively small 432 (0.74 - 0.80), corresponding to a radiocarbon age span of 680 years (1790 to 2470 years). 433 The composition of POC and particulate nitrogen in all mainstem surface samples 434 collected in 2005 and 2014 was similar to the POC composition of the depth-specific samples 435 from 2014. The only difference was that the POC in these surface samples was consistently

436 older, with  $F_m$  values as low as 0.71 (2,760 years before present), than the POC analyzed at

- 437 specific depths. Surface suspended sediment concentrations in the Solimões and Madeira rivers,
- 438 collected in 2005, were also similar to the range observed at Óbidos (Bouchez et al., 2011b). The
- 439 % OC in these sediments ranged from 0.49% in the Madeira River to 1.12% in the Solimões
- 440 River (Table 3). Weight %N ranged from 0.08% in the Madeira River to 0.17% in the Solimões
- 441 River. Stable and radiocarbon measurements of POC in the Solimões and Madeira River
- 442 sediments were slightly more <sup>13</sup>C-enriched and older than the Óbidos depth-specific samples.
- 443 The Tapajós River had the most compositionally distinct suspended sediments of the data set.

444 Surface suspended sediment concentrations in July 2014 were much lower than observed at any

other river, only 0.52 mg/L. But, % OC in these sediments was the highest measured, 15.7%.

- 446 Weight %N was also high, 2.69%. The F<sub>m</sub> value was 0.89 (955 years before present),
- 447 corresponding to a younger  ${}^{14}$ C age than any of the values measured at Óbidos.

448 The weight %OC and %N in the three bed sediment samples from near the left bank of 449 Óbidos, the right bank of Óbidos, and the Tapajós River were lower than corresponding values in 450 all suspended sediment samples, ranging from 0.022% to 0.14% organic carbon and from 451 0.0027% to 0.017% nitrogen, consistent with other bedload observations in the basin (Bouchez et al., 2014) (Table 3). The  $\delta^{13}$ C composition of bed samples at Óbidos and in the Tapajós River 452 were consistently more  ${}^{13}$ C-enriched (by ~1-2 ‰) than POC in suspended sediments in their 453 454 respective rivers. While radiocarbon ages in the Óbidos bed samples ranged from F<sub>m</sub> 0.60 (4,090 455 years before present) to 0.87 (1,100 years before present), we neglect the higher  $F_m$  value (0.87) 456 on the basis of specimen contamination (e.g., fresher plant litter debris), as bed samples with 457 such low %OC are typically older across the Amazon River Basin (Bouchez et al., 2010). The 458 Tapajós bed sample was modern (F<sub>m</sub>>1.0), younger than POC in the Tapajós suspended 459 sediment. Values of %OC and %N of right bank flood deposit near the Óbidos cross-section 460 were more similar to the range in depth-specific sediments, 0.50% and 0.048%, respectively. The 461 stable isotope composition of the flood deposit was closer to the range observed across depth-462 specific suspended sediment samples, as well.

463

464 3.4 Lipid abundances and isotope composition

Measurements of leaf wax compounds provide a useful tool for tracing POC sources in complex mixtures like riverine sediments. Alongside our other analyses, these lipid abundances and carbon stable isotopes enable a more nuanced understanding of the organic matter pools that 468 contribute to bulk POC among different sampling seasons and tributary locations. Total lipids

- 469 were extracted from all large-volume suspended sediment samples from the surface of the
- 470 Amazon River mainstem (June 2005, April 2014 and July 2014), the Tapajós River (July 2014),
- 471 the Solimões River (June 2005) and the Madeira River (June 2005), as well as from four depth-
- 472 specific samples from the two 2014 Óbidos center profiles (Table 1). Compound-specific  $\delta^{13}$ C
- 473 values were not resolved for the April 2.7 m sample because the total lipid extract was too small.
- 474 Compound-specific  $\delta^{13}$ C values were also not measured in *n*-alkanes in the tributary samples.
- 475 Abundances of straight-chain *n*-alkanes in Óbidos samples were quantified for sixteen 476 carbon chain lengths from 19 ( $C_{19}$ ) to 35 ( $C_{35}$ ), and ranged from 0.001 to 0.4 ng/µg of total POC (Table S1, Fig. 4a, 5c, e). Generally, POC-normalized compound abundances at Óbidos were 477 478 greater at the surface than abundances measured deeper in the water column. The distribution of 479 abundances above chain lengths C<sub>23</sub> displayed an odd-over-even carbon chain length 480 predominance in all samples, characteristic of terrestrial vegetation (Eglinton & Hamilton, 481 1963) (Fig. 5c, e). Average chain lengths (ACL) for *n*-alkanes (Equation 4a, Fig. 4c) spanned a 482 small range from 29.6 to 30.1, decreasing slightly with depth.
- 483

484 
$$ACL_{n-alkane} = \frac{25[C_{25}] + 27[C_{27}] + 29[C_{29}] + 31[C_{31}] + 33[C_{33}] + 35[C_{35}]}{[C_{25}] + [C_{27}] + [C_{29}] + [C_{31}] + [C_{33}] + [C_{35}]}$$
(4a)

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486

$$ACL_{fatty acid} = \frac{24[C_{24}] + 26[C_{26}] + 28[C_{28}] + 30[C_{30}] + 32[C_{32}] + 34[C_{34}]}{[C_{24}] + [C_{26}] + [C_{28}] + [C_{30}] + [C_{32}] + [C_{34}]}$$
(4b)

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By comparison, stable isotope values of odd chain-length *n*-alkanes spanned a larger range across months and depths than all  $\delta^{13}$ C values measured in bulk POC from the Óbidos depth profiles, ranging from -37.3‰ to -28.3‰ (Fig. 4b, Table S1). Generally, lipids at the surface were more <sup>13</sup>C-enriched than lipids at deeper depths.

Relative abundances of straight chain *n*-alkanes in surface suspended sediments of the
Solimões River were similar to relative abundances observed in the Óbidos samples (Fig. 5a),
while Madeira River *n*-alkanes abundances were higher than both Óbidos and Solimões River
samples, particularly for chain lengths 28-33. While *n*-alkanes from the Solimões River exhibited



Figure 4. Depth profiles of *n*-alkane (a) abundances (ng/µg total particulate organic carbon), (b)  $\delta^{13}$ C values (‰) and (c) average chain lengths (ACL) measured in Óbidos center profiles in April 2014 (blue) and July 2014 (black). Additional ACL values for surface samples at Óbidos in 2005 and different river tributaries are plotted, as well. Different lines in (a)-(b) plot values for a different chain length between 19 and 35. The thicker width lines in (a) plot chain lengths 29 and 31 only, highlighting the highest abundance *n*-alkanes.



Figure 5. Abundances of (a, c, e) straight chain *n*-alkanes and (b, d, f) fatty acids measured in the Amazon
River mainstem and tributaries over a range of longer chain lengths. Each line in the Óbidos April and
July panels plots data from a different depth of the center profile, with the boldest line indicating data
from the surface large-volume sample.





511 Figure 6. Profiles of fatty acid (a)  $\delta^{13}$ C values (‰) and (b) average chain lengths (ACL) measured in 512 mainstem samples collected at Óbidos in April (blue) and July (black) 2014. Each line in (a) plots values 513 for a different chain length from 14 to 34, all showing little trends with depth. Additional ACL values are 514 plotted for the surface samples taken from the Tapajós, Solimões and Madeira Rivers, and from the 515 mainstem in 2005. Panel (c) plots fatty acid  $\delta^{13}$ C values in these tributary and mainstem samples over a 516 range of chain lengths.

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odd-over-even predominance, as observed in the mainstem, the odd-over-even predominance in
the *n*-alkanes from the Madeira River was weaker. Surprisingly, average chain lengths in all

521 Óbidos and Madeira River samples were similar, while ACL values for the Solimões River

522 sample were lower, 29.3 (Fig. 4c).

523 Abundances of saturated straight-chain fatty acids  $(C_{14}-C_{34})$  measured at Óbidos ranged 524 from 0.008 to 4.0 ng/µg POC (Fig. 5d, f, Table S2). In most samples, the most abundant 525 compounds were  $C_{16}$  and  $C_{18}$  (0.18 – 4.0 ng/µg POC). At chain lengths above 22, the abundances 526 exhibited even-over-odd predominance in all samples, reflecting an important contribution from 527 terrestrial vegetation. Differences in relative fatty acid abundances at different sampling months

- and across depths were negligible, though notable spillage of the large-volume surface sample collected in July could have depressed abundances quantified by the FID. Average chain lengths of fatty acids (Equation 4b, Fig. 6b) did increase with depth from 27.6 near the surface to 28.6 at 49 m in April 2014, and to a lesser extent from 28.2 near the surface to 28.6 at 54 m in July 2014. The stable carbon isotope composition of even chain-length fatty acids across the depthspecific samples spanned a greater range than bulk  $\delta^{13}$ C values in the same samples, from -37.5‰ to -27.7‰ (Fig. 6a).
- 535 Straight-chain fatty acids were also quantified in surface suspended sediment samples 536 from the Tapajós, Solimões and Madeira rivers. The upstream tributary samples displayed strong 537 even-over-odd predominance among the higher chain-length fatty acids (Fig. 5b). Fatty acid 538 abundances and ACL values generally exhibited a similar range to the Óbidos samples (Table 539 S2, Figs. 5, 6b). Only the Tapajós River sample showed very elevated concentrations of C<sub>14</sub>, C<sub>16</sub> 540 and  $C_{18}$  that were up to ~100 times higher than the abundances of these fatty acids across all 541 other 2014 and 2005 samples, and the lowest ACL calculated in the data set (25.8). Compound 542 abundances from chain lengths 24 to 28 in the Tapajós River were also significantly elevated relative to Óbidos, and Solimões and Madeira River samples. By contrast, differences in  $\delta^{13}C$ 543 544 values among Tapajos and other river samples were smaller. Even though the bulk POC from the Tapaiós River is relatively <sup>13</sup>C-depleted, only  $\delta^{13}$ C values of fatty acid chain length 22 were 545 lower (e,g,  $\delta^{13}C_{C22} = -39.4\%$ ) than values at Óbidos and other tributaries (Fig. 6c). 546
- 547

# 548 3.5 Enzyme activities

549Activities of eight extracellular enzymes measured at various depths within the Óbidos550cross-section in July 2014 ranged from 0 to 0.09 μmol/L-hr (Table S3, Fig. 7). Values generally551did not vary with depth or channel position. Activities of the N- and P-yielding enzymes (i.e.,552leucyl aminopeptidase, phenylalanyl aminopeptidase, and phosphomonoesterase) (Table 2),553exceeded activities of the C-yielding enzymes (i.e., cellulase, beta-glucosidase and xylanase)554throughout profiles.

555



569 4.1 TSS and POC flux at Óbidos

570 Increasing TSS concentrations with depth in all profiles compiled at Óbidos in April and 571 July 2014 are indicative of hydrodynamic sorting (Rouse, 1950), and consistent with prior depth profiles of the same size-fraction of sediments compiled by (Bouchez et al., 2011b) across the central Amazon River Basin (Figs. 2, 3). This is supported by even lower TSS concentrations in the surface large-volume samples (<1 m depth) (Table 3). Despite the lack of change in river discharge between April and July 2014,  $z_R$  values increased significantly, by 0.08 units from 0.26 to 0.34. The Rouse numbers that we report are similar in magnitude and temporal variation to the numbers estimated from profiles at Óbidos in March 2006 ( $z_R = 0.24$ ) and June 2005 ( $z_R = 0.39$ ) (Bouchez et al., 2011b).

579 Consistent increases in grain sizes with depth in July 2014 sediment profiles relative to 580 April 2014 profiles (Student's t-test, p<0.05) could have enhanced the depth gradient in July 581 sediment concentrations, leading to higher  $z_R$  values. This is consistent with a Ganga River study 582 (Lupker et al. 2011), which partitioned and modeled Rouse profiles of suspended sediment 583 concentrations by grain size, reporting higher  $z_R$  values for larger grain size profiles. Of the three 584 major tributaries upstream of Obidos, variations in the sediment-rich Solimões and Madeira 585 Rivers contribute disproportionately to seasonal variations in sediment grain size in the 586 mainstem, relative to the sediment-deplete Negro River (Kim et al., 2012). Although we do not 587 have 2014 grain size data from these upstream tributaries, Bouchez et al. (2011) reported higher 588 median grain diameters in the Solimões River relative to the Madeira River. Therefore, a higher 589 relative discharge from the sediment-rich Solimões River in July, as was recorded by the 590 Agência Nacional de Águas, would result in a larger gradient in [TSS] between river surface and 591 river bed in July.

592 Overall, our TSS flux estimates (53,000 kg/s in April and 48,000 kg/s in July) are similar 593 in magnitude, though less variable, to fluxes estimated by Bouchez et al. (2011b) in June 2005 594 and March 2006 (61,300 kg/s and 39,700 kg/s, respectively) (Table 1). They generally diverge 595 from studies that estimate flux by multiplying discharge by TSS concentration at a single depth. 596 For example, our fluxes are more than five times greater than surface-based fluxes calculated by 597 Kim et al. (2012) during two expeditions to Óbidos in 2005 and 2009 (4-8 tons/second or 3600-598 7300 kg/s). Computing sediment fluxes equivalent to ours as the product discharge  $\times$  [TSS] 599 from a single depth requires TSS concentrations of 196 mg/L in April and 193 mg/L in July, 600 much greater than surface values reported in Kim et al. (2012). Interestingly, other studies at 601 Óbidos have focused on sampling TSS at the midpoint depth rather than at the river surface 602 (Ward et al., 2015). As Fig. 3 illustrates, these target concentrations are greater than our modeled 603 Rousean TSS values at their midpoint depths, though some of our discrete midpoint samples are

- 604 close to 196 mg/L and 193 mg/L. Importantly, these juxtapositions are incomplete in that both
- 605 Kim et al. and Ward et al. sampled particles in different years and within different pore size
- 606 intervals,  $>0.7 \mu m$  and 0.45- 297  $\mu m$ , respectively, compared to  $>0.2 \mu m$  in this study.
- 607 Nonetheless, they highlight the necessity and impact of accounting for cross-sectional variation
- 608 in [TSS] when calculating TSS fluxes out of the river cross-section.

609 Particulate organic carbon concentrations increased with depth alongside TSS. We 610 calculated POC fluxes during each sampling month by linearly regressing [POC] against [TSS] 611 (Equation 5), using a Type II regression function in Matlab. This yielded a slope (mg [TSS]/mg 612 [POC]) and intercept (mg/L [POC]) which can then be substituted into the Rouse-modeled  $C_z$  in 613 Equation 2:

614

$$[POC] = m[TSS] + b \tag{5}$$

615

616 In this equation, m is the slope of the linear relationship (0.0079 mg POC/mg TSS in April and)617 0.0072 mg POC/mg TSS in July while b is the intercept (0.46 mg POC in April and 0.075 mg 618 POC in July). The integrated POC flux in April 2014 was 544 kg/s, while the integrated POC 619 flux in July 2014 was 369 kg/s (Table 1). This difference can be explained by a significant 620 decrease in the average %OC in depth-specific suspended sediments from  $1.16 \pm 0.2\%$  (mean  $\pm$ 621 1 S.D.) in April to  $0.88 \pm 0.27\%$  in July (Student's t-test, p<0.05). Again, these fluxes are similar 622 to those reported in (Bouchez et al., 2014), and ~35-240% higher than those reported by Kim et 623 al. (2012) during high water. Scaling 544 kg/s or 369 kg/s to one year results in a flux of ~12-17 624 Tg/year, which is similar to earlier flux estimates of 14 Tg/year by (Richey et al., 1990), 625 who deployed a depth-integrated sampler to measure POC concentrations in fine (<63 µm) and 626 coarse (>63 µm) particles (Richey et al., 1986). Likely, our flux range overestimates the annual 627 POC flux because our April and July 2014 values represent the high discharge period only. 628 Moreira-Turcq et al. (2003) showed that fluxes could be much lower at lower discharge periods, 629 and reported annual average POC fluxes of 5.8 Tg/year. 630

631 4.2 Vertical distributions in POM composition

632 While TSS and POC concentrations increased with depth, the %OC and %N per unit 633 sediment weight decreased in all April and July 2014 profiles at Obidos (Table 3, Fig. 2).

634 Bouchez et al. (2014) argued that greater associations between POC and mineral surfaces and/or 635 greater concentration of fine carbon-rich particles from buoyant organic debris drive enrichment 636 of POC in the surface and decreased POC loading with coarser sediments at depth. Despite the 637 clear hydrodynamic sorting of sediment and POC concentrations in the mainstem, POC 638 composition is less variable throughout both cross-sectional surveys in April and July 2014, and changes in C/N and carbon isotope composition ( $\delta^{13}$ C and F<sub>m</sub>) are smaller. Thus, even while 639 640 depth-specific sampling may be necessary to accurately calculate POC fluxes across the 641 mainstem, single measurements may be sufficient to understand POC composition. This also 642 means that when comparing compositional measurements across studies, differences in sampling 643 depth are less important than differences in sampling methodologies like pore size or, 644 potentially, time of year.

645 The lack of large depth-specific variations in bulk POC composition is one likely reason 646 that enzyme activities were homogenous throughout the cross-section at Obidos, supporting an 647 argument that the homogenous organic matter composition throughout the mainstem controls 648 enzyme activities to a greater extent than do changes in particle surface area/grain size and TSS 649 concentrations. Surprisingly, incubation studies have reported a relationship between microbial 650 respiration rates and water velocity in Amazon River water samples (Ward et al., 2018, 2019), 651 which do span a large range with depth (Fig. 1). However, if these enzyme activities are free-652 living, detached from bacterial cells in the aquatic environment, they are not likely to correlate 653 with changes in microbial respiration in the water column (Baltar, 2018). These invariable 654 activities do not negate the importance of particle-microbe interactions in the metabolism of 655 organic matter in mainstem waters (Satinsky et al., 2014). Given that our results comprise the 656 first measurement of enzyme activities in the Amazon River mainstem, we suggest further 657 exploration of enzyme activities to understand in situ microbial dynamics in relation to sediment 658 sorting and POC composition in the mainstem and tributaries.

There are, however, a few notable differences in POC composition across sample depths that follow the hydrodynamic models discussed in Sect. 4.1, particularly in July. We observed lower fraction modern values measured in surface POC samples and higher values measured in deeper samples at Óbidos in July 2014 (Fig. 2), which indicate a greater input of younger organic matter near the river bed compared to shallower sediments. Although the bed load sample at Óbidos still exhibits the oldest bulk carbon signature (lowest  $F_m$ ) value, consistent with  $F_m$  profiles in Bouchez et al. (2010), these profile data suggest an accumulation of fresher (i.e., less degraded) vegetation debris just above the river bed. This is further supported by a small increase ( $\sim$ 16%) in center profile C/N ratios with depth, and an even larger increase ( $\sim$ 40%) within profiles near the right bank, implying a shift towards fresher organic matter degradation states (Hedges et al., 1986).

670 Our data suggest that coarser size fractions of organic matter export fresher organic 671 matter pools, which sort vertically and are associated with higher z<sub>R</sub> values, as observed in our 672 July 2014 Rouse fits (Sect. 4.1) (Feakins et al., 2018). By contrast, finer particle size fractions 673 carry old and/or more degraded organic matter, remaining homogenous throughout the water 674 column and yielding low z<sub>R</sub> values in TSS profiles (Bouchez et al., 2010; Lupker et al., 2011), 675 which is especially apparent in the less variable  $F_m$  and grain size profiles in April (Fig. 2). This 676 understanding is consistent with earlier Amazon River Basin studies that typically divided 677 riverine POC between an older <63 µm "fine" fraction and a fresher >63 µm "coarse" fraction 678 (Aufdenkampe et al., 2007; Hedges et al., 1986, 1994, 2000; Richey et al., 1990). But, notably, 679 we are able to report complementary results by pooling all suspended sediment data into one 680 size-fraction (>0.2 µm), rather than into discrete size classes, assuming that organic matter 681 degradation stages are more likely to partition along a continuum of grain sizes.

682 The terrestrial leaf wax *n*-alkane data from the mainstem further supplement this argument (Fig. 4). POC-normalized abundances and  $\delta^{13}$ C values of chain lengths 29 and 31 683 decreased between the surface (i.e., large-volume) and deepest samples. This differentiation of n-684 alkane  $\delta^{13}$ C with depth fits the perspective of fresher C3 vegetation accumulating near the river 685 bed, leaving more <sup>13</sup>C-enriched leaf wax compounds at the surface from a more degraded 686 687 organic matter origin relative to deeper samples (Feakins et al., 2018; Häggi et al., 2016). The 688 following section elaborates on the potential sources of this degraded organic matter pool that 689 dominates the finer, well-mixed particles in the Amazon River mainstem.

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- 691

# *4.3 Differentiating soil organic matter sources to riverine POC*

This section endeavors to identify the POC pools that explain the small variations in POC
composition observed in depth profiles of the Amazon River mainstem. Importantly, the
abundances of *n*-alkanes and fatty acids measured in suspended sediment samples from various
depths at Óbidos underscore the influence of terrestrial vegetation in riverine POC within the

- 696 mainstem. Odd-over-even predominance of the higher chain length n-alkanes (C<sub>25</sub>-C<sub>35</sub>), even-
- 697 over-odd predominance of the higher chain length fatty acids ( $C_{24}$ - $C_{34}$ ), and high ACL values of
- 698 each compound class reflect input from land plants (Figs. 4c, 5, 6b) (Cranwell, 1982). Stable
- 699 carbon isotope values for the long-chain *n*-alkanes and fatty acids are within range of previous
- 700 long-chain *n*-alkanes and fatty acids measured across the Amazon River Basin (Feakins et al.,
- 2018; Häggi et al., 2016) (Tables S1, S2, Figs. 4b, 6a, b). These isotope values are similar to the
- bulk leaf  $\delta^{13}$ C composition of woody C3 plants from *terra firme* forests (average = -32.3 %), and
- roughly 4‰ more depleted than C3 leaf samples from the savannah region (average = -29.0 ‰)
- 704 (Ometto et al., 2006; Powell et al., 2012; Sanaiotti et al., 2002). Notably, these offsets are smaller
- than previously published offsets (e.g.,  $\sim$ 5.9 ‰ difference between *n*-alkanes and bulk C<sub>3</sub> leaves)
- 706 (Collister et al., 1994), suggesting additional sources of  $^{13}$ C-enriched *n*-alkanes.
- Even the small presence of high elevation plants from the Andes and C4 plants from southern
- regions of the Amazon River floodplain could contribute  ${}^{13}$ C-enriched *n*-alkanes in the mainstem
- 709 (Feakins et al., 2018; Feng et al., 2016; Martinelli et al., 1994; Powell et al., 2012; Wu et al.,
- 710 2017). Another reason that compound-specific  $\delta^{13}$ C values are more  $^{13}$ C-enriched than expected
- for fresh vegetation is that the majority of vegetation-derived POC in the Amazon River Basin
- enters the river via the soil organic matter reservoir, which bears a strong degraded vegetation
- signature (Feakins et al., 2018; Hedges et al., 1986). Indeed, long-chain ( $C_{24-32}$ ) fatty acids from
- 714 Óbidos in 2005 exhibited a fraction modern value of 0.83, corresponding to 1,530 radiocarbon
- years (Eglinton et al. 2021), implying that a significant fraction of the organic matter derived
- from vegetation in the mainstem POC is likely pre-aged. Feakins et al. (2018) found that the  $\delta^{13}$ C
- values of *n*-alkanes in soils from the Madre de Dios River catchment area in the Andes were
- 718 more <sup>13</sup>C-enriched due to flushing from deeper, older soil layers. If these n-alkanes came from
- atmospheric  $CO_2$  that was fixed centuries ago, they also suggested that the Suess Effect
- 720 (Ehleringer et al., 2000) could have a compound effect in raising the  $\delta^{13}$ C value of older *n*-
- alkanes relative to modern vegetation.
- 722



Figure 8. Bulk N/C ratios as a function of (a)  $\delta^{13}C_P$  (‰) and (b) fraction modern (F<sub>m</sub>) in samples collected in June 2005, April 2014 and July 2014. In the legend, colors are specific to location and/or time, while the symbols refer to sample type (circles for depth-specific samples, triangles for surface samples, and diamonds for bed/floodplain samples).

723

729

730 Adding to the argument that riverine POC is largely soil derived and pre-aged, the bulk C/N and  $\delta^{13}$ C values measured for POC throughout the mainstem at Óbidos are within the range 731 732 of values observed for soils across the drainage basin (Table 3, Fig. 2) (Ometto et al., 2006; 733 Quesada et al., 2010; Sanaiotti et al., 2002). Figure 8a illustrates a weak but positive correlation between bulk N/C and  $\delta^{13}$ C values measured in suspended sediments at Óbidos, highlighting a 734 mixing relationship between a fresher, low N/C, and <sup>13</sup>C-depleted end-member and a more 735 degraded, high N/C and <sup>13</sup>C-enriched end-member ( $r^2 = 0.23$ ). This mixing relationship is slightly 736 stronger in July samples only ( $r^2=0.34$ ), and when including bedload, floodplain deposit and 737 upstream tributary samples ( $r^2 = 0.26$ ). Figure 8b illustrates a complementary negative 738 739 relationship between bulk N/C and  $F_m$  values in the same samples ( $r^2 = 0.36 - 0.39$ ), supporting 740 the perspective that these low N/C samples are indeed younger in age (higher F<sub>m</sub>), while the high 741 N/C samples are older (lower F<sub>m</sub>). Two non-mutually exclusive hypotheses could account for these distinct soil-derived end-members exported by the Amazon River mainstem: (1) the mixing 742 of several soil sources from different landscapes that bear distinct  $\delta^{13}$ C signatures and 743 744 degradation histories, and (2) the mixing of soils from different depth horizons throughout the 745 drainage basin.

The first hypothesis makes sense considering that, while the majority of the surface area 746 covering Amazônia is dominated by <sup>13</sup>C-depleted C3 landscapes in the low-lying floodplain, 747 there are sources of more <sup>13</sup>C-enriched POC from C4 grassland ecosystems and higher altitude 748 749 Andean landscapes. The soil POC exported by higher elevation landscapes into the Madeira and 750 Solimões Rivers are <sup>13</sup>C-enriched relative to floodplain POC because of altitude effects 751 (Aufdenkampe et al., 2007; Feakins et al., 2018; Wu et al., 2017) and the flushing of petrogenic 752 organic carbon (Bouchez et al., 2014). To return to seasonality, this mixing of geographically 753 and isotopically diverse landscapes, both soil-derived and petrogenic, would provide one 754 explanation for the slight differences in the bulk POC composition observed at Óbidos between 755 sampling months. Lower average molar C/N ratios of  $8.7 \pm 0.89$  in April compared to  $10.8 \pm 1.2$ 756 in July (p<0.05, Student's t-test) in depth-specific samples, as well as significantly more <sup>13</sup>Cenriched bulk  $\delta^{13}$ C values in April (-28.2 ± 0.1‰) than in July (-28.8 ± 0.2‰), suggest a small 757 758 shift in soil source between river stages.

759 The bulk values in July (Table 3) are consistent with increased drainage of the adjacent 760 floodplain during receding water levels, as the floodplain and várzea lakes are dominated by 761 soils replete with the residual organic carbon from C<sub>3</sub> plants (Quay et al. 1992; Moreira-Turcq et 762 al. 2013; Feakins et al. 2018). This enhanced exchange between the river bed and riverine POC 763 explains how the C/N ratio of suspended POC in July is closer in composition to that of the N-764 depleted floodplain deposit sample. By contrast, the distribution of data from April 2014 imply 765 that the mainstem during rising waters is influenced by a greater proportion of POC from the upstream tributaries, and is compositionally more similar to their <sup>13</sup>C-enriched and N-enriched 766 767 signature (Table 3, Fig. 8a). Further, the lower C/N of POC in this sampling month is consistent with lower bulk F<sub>m</sub> values and older radiocarbon ages observed for the Solimões and Madeira 768 river samples. Indeed, data from the Agência Nacional de Águas show that Solimões River 769 770 discharge rose from April to May 2014, while Madeira River discharge peaked in March to April 771 2014, decreasing thereafter. Increased incidence of landslides in the Andes during the months leading up to April would increase the input of high altitude <sup>13</sup>C-enriched POC from these 772 773 tributaries to Óbidos (Clark et al., 2013), as well as the supply of old petrogenic organic carbon 774 (Bouchez et al., 2014). Thus, the preferential transport of the more degraded pools of this Andean soil source to Óbidos would explain both the more degraded and <sup>13</sup>C-enriched signatures 775 776 of POC observed in April.

777 The second hypothesis could also explain the partitioning of POC in mainstem because soil organic matter across the Amazon River Basin typically gets more <sup>13</sup>C-enriched with depth 778 779 within the first ~2 meters below surface, a result of microbial degradation and the Suess Effect 780 (Ehleringer et al., 2000; Ometto et al., 2006; Sanaiotti et al., 2002). In the Amazon headwaters in the Andes, *n*-alkanes from vegetation preserved in soils were  ${}^{13}$ C-enriched in deeper soil 781 782 horizons (Feakins et al., 2018). This second hypothesis does not exclude the importance of 783 riverine POC sources from different landscapes (i.e., our first mechanism, described above). But, similarly, it does explain the temporal shifts in bulk  $\delta^{13}$ C and C/N values of POC at Óbidos, 784 particularly the greater input of <sup>13</sup>C-depleted, higher C/N soil POC in July, as falling river waters 785 786 draw more carbon from the superficial layers of the floodplain (Bouchez et al., 2014). Again, 787 input of this fresher organic matter to the river in July is consistent with accumulation of higher 788  $F_m$  POC, possibly from coarser and less degraded vegetation debris, in the deeper sections of the 789 river (Fig. 2).

790

791 4.4. Small influence of autochthonous organic matter in the mainstem

792 While floodplain lakes surrounding the mainstem have been observed to be sites of high 793 phytoplankton and macrophyte growth, in situ primary production is not a significant component 794 of riverine organic matter at Óbidos (Saliot et al. 2001; Moreira-Turcq et al. 2013). This is 795 particularly clear when comparing to the composition of Tapajós POC, which clearly falls off the mixing line in Fig. 8a, with its high N/C and low  $\delta^{13}$ C value. This observation is consistent with 796 797 prior observations of Tapajós River POC composition and chlorophyll-a concentrations that 798 imply a dominant input of *in situ* primary production (Martinelli et al., 1994; Mortillaro et al., 799 2011; Ward et al., 2015). The combination of a relatively deep euphotic zone depth (from low 800 TSS concentrations) and slower water velocities in the Tapajós River, especially during the low 801 water season, encourages greater growth of phytoplankton and cyanobacteria compared to the 802 sediment-rich Amazon River (Mortillaro et al., 2011).

803 Interestingly, even-over-odd predominance of fatty acids in this sample indicates that 804 vegetation still comprises a source of POC in the Tapajós River. A shifting balance between 805 terrestrial POC inputs and primary production could explain observations of more <sup>13</sup>C-enriched 806 POC collected during other months of the year (e.g., Mortillaro et al. 2011; Ward et al. 2015). 807 But, far greater  $C_{16}$  and  $C_{18}$  abundances (23.2 ng/µg POC and 11.4 ng/µg POC, respectively)

808 relative to higher chain length fatty acids highlight the dominance of phytoplankton-derived

809 organic matter in July 2014 (Mortillaro et al., 2011) (Table S2). A low fatty acid-based ACL

810 value at the tributary surface (Fig. 6b) indicates that lower chain length lipids produced by

aquatic phytoplankton contribute much more to POC in this tributary, while they are

812 comparatively absent in POC from the mainstem and both the Solimões and Madeira Rivers

813 upstream (Cranwell, 1982).

814 The radiocarbon ages measured in the Tapajós River samples are more perplexing. The 815 Tapajós River bed sample exhibited a modern-aged F<sub>m</sub> value of 1.02 (Table 3, Fig. 8b), 816 supporting the perspective that fresh organic matter is indeed a source of organic material deposited on the river bed, though its  $\delta^{13}$ C and C/N signature implies a terrestrial, rather than 817 818 phytoplankton-derived, source (Martinelli et al., 1994; Quesada et al., 2010) (Fig. 8a). Possibly, 819 backwashing of the Amazon River mainstem into the Tapajós River slows the river flow down 820 enough to promote settling of coarse and fresh POC flushed in from the floodplain, complicating 821 the inputs of river carbon to the Tapajós bedload (Fricke et al., 2017). Preferential respiration of 822 autochthonous organic matter and burial of terrestrial POC may also contribute to the terrestrial 823 signature of the Tapajós river bed (Bertassoli Jr et al., 2017). More importantly, suspended POC in the Tapajós River is not modern, exhibiting a surprisingly low  $F_m < 0.9$  (Table 3, Fig. 8b). 824 825 Assuming *in situ* fixation of DIC with a modern radiocarbon age, an age which is empirically 826 unknown for the Tapajós River but observed elsewhere across the floodplain (Mayorga et al., 827 2005b), one would have expected a Tapajós POC  $F_m$  value >1, similar to the bed sample. Further 828 analyses of the radiocarbon age distribution of bulk POC using temperature-controlled ramped 829 pyrolysis/oxidation analysis (Hage et al., 2020; Rosenheim & Galy, 2012) could provide further 830 insight towards the isotopically distinct POC exported by the Tapajós River.

831 **5** Conclusions

As the world's largest river by discharge and drainage basin, the Amazon River mainstem transports over 10 Tg of particulate organic carbon (POC) per year, representing the fraction of organic carbon export with the highest likelihood of sequestration in Atlantic Ocean sediments. This quantity alone comprises 1% of the magnitude of increase in global riverine organic carbon export to the ocean during the Industrial Revolution from soil mobilization,  $1 \pm 0.5$  Gt carbon per year (Friedlingstein et al., 2019; Regnier et al., 2013). Building upon decades of prior research, our bulk and compound-specific analyses of POC from two Óbidos surveys (2005 and 2014) highlight that the majority of these particles are soil-derived, though input of POC from riverine
algae from tributaries like the Tapajós River may be important downstream. Our approach to
sampling suspended sediments from several profiles of the Amazon River cross-section show
that depth-related differences in total POC concentration follow trends expected from vertical
hydrodynamic sorting, supporting application of the depth-specific sampling approach to
calculate export fluxes in large rivers in the Amazon River Basin.

845 Meanwhile, compositional differences in bulk POC and lipid isotope composition are 846 considerably smaller, and support a perspective developed over multiple earlier studies that 847 larger grain sizes in the river, which tend to accumulate deeper, are associated with less degraded 848 vegetation debris, while finer grain sizes, well mixed throughout the water column, are 849 associated with more degraded soil organic matter sources. Overall, because these vertical 850 differences in organic matter composition are relatively small, we suggest that the depth-specific 851 sampling approach is perhaps not essential to tracing the sources of POC exported by the 852 Amazon River. Given the large seasonal variations in Amazon River discharge, it is possible that 853 this conclusion is not applicable for suspended sediments from other stages of the hydrological 854 cycle before and after the high/peak flow months, which we did not sample.

855

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866

# 867 **Open Research Statement**

All discrete sample data for this research are included and tabulated in the current paper and its supplementary information files, as well as in Bouchez et al. (2011b) and Bouchez et al. (2014).

- 870 These sample data, including raw water velocity data sets obtained from the Acoustic Doppler
- 871 Current Profiler, are further located in an open access (Creative Commons Attribution 4.0
- 872 International) repository on Zenodo (Rosengard, 2023). Readers may access this repository by
- 873 navigating to the following DOI address their Internet browser:
- 874 https://doi.org/10.5281/zenodo.8392815.

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### Geochemistry, Geophysics, Geosystems

### Supporting Information for

# Depth-partitioning of particulate organic carbon composition in the rising and falling stages of the Amazon River

Sarah Z. Rosengard<sup>1,2,3\*</sup>, Jose Mauro S. Moura<sup>4</sup>, Robert G.M. Spencer<sup>5</sup>, Carl Johnson<sup>1</sup>, Ann McNichol<sup>6</sup>, Andrew D. Steen<sup>7</sup>, and Valier Galy<sup>1</sup>

- Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA, USA
  - Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA, USA
- Department of Liberal Arts, The School of the Art Institute of Chicago, Chicago, IL, USA\*
- Programa de Pós-Graduação em Recursos Naturais da Amazônia, Universidade Federal do Oeste do Pará, Santarém, Pará, Brazil
- Department of Earth, Ocean & Atmospheric Science, Florida State University, Tallahassee, FL, USA
- Department of Marine Geology and Geophysics, Woods Hole Oceanographic Institution, Woods Hole, MA, USA
- Departments of Microbiology and Earth and Planetary Sciences, University of Tennessee, Knoxville, TN, USA

\*Corresponding author's current affiliation

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### Introduction

The following supplementary tables elaborate on the compound-specific lipid and enzyme data discussed in the main text. Tables S1 and S2 provide the abundances and stable carbon isotope ratios of a number of compound-specific *n*-alkanes (carbon chain lengths 19-41) and fatty acids (carbon chain lengths 14-34) quantified in particulate organic carbon from the Amazon River mainstem, Tapajós River, Madeira River and Solimões River in 2005 and 2014. The lipids were extracted and purified using a number of methods described in Section 2.6 of the main text. Table S3 provides depth-specific activities of eight different enzymes analyzed in the Amazon River mainstem in July 2014 only. These enzyme activities were analyzed using –AMC (7-amino-4methylcoumarin) and –MUB (4-methylumbelliferone)-based fluorogenic substrate proxies (Mullen et al. 2018).

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**Table S1**. Abundances and  $\delta^{13}$ C values of straight-chain *n*-alkanes (C<sub>19</sub>-C<sub>41</sub>) in large-volume (>100 L) and depth-specific (10 L) samples collected in June 2005, April 2014 and July 2014.

			Chain		Abundance		δ <sup>13</sup> C
Location	Date	Depth	length	Abundance	error	δ <sup>13</sup> C	error
			#	ng/µg POC	ng/µg POC	‰	‰
Mainstem	28 July 2014	0	19	2.87E-03	2.88E-04	-32.5	0.1
Mainstem		0	20	4.12E-03	4.14E-04	no data	no data
Mainstem		0	21	5.16E-03	5.18E-04	-31.2	0.8
Mainstem		0	22	4.86E-03	4.87E-04	no data	no data
Mainstem		0	23	6.74E-03	6.76E-04	no data	0.6
Mainstem		0	24	4.71E-03	4.72E-04	no data	no data
Mainstem		0	25	9.36E-03	9.40E-04	-31.4	0.4
Mainstem		0	26	7.33E-03	7.36E-04	no data	no data
Mainstem		0	27	1.53E-02	1.53E-03	-31.1	0.1
Mainstem		0	28	9.55E-03	9.59E-04	no data	no data
Mainstem		0	29	3.70E-02	3.72E-03	-33.1	0.0
Mainstem		0	30	1.15E-02	1.15E-03	no data	no data
Mainstem		0	31	3.97E-02	3.99E-03	-33.4	0.1
Mainstem		0	32	1.12E-02	1.13E-03	no data	no data
Mainstem		0	33	2.00E-02	2.01E-03	-32.6	0.2
Mainstem		0	34	7.02E-03	7.05E-04	no data	no data
Mainstem		0	35	6.09E-03	6.11E-04	-31.0	0.3
Mainstem		0	36	3.00E-03	3.01E-04	no data	no data
Mainstem		0	37	3.69E-03	3.71E-04	-30.1	2.0
Mainstem		0	38	2.39E-03	2.40E-04	no data	no data
Mainstem		0	39	1.97E-03	1.98E-04	-31.6	1.8
Mainstem		0	40	1.39E-03	1.39E-04	no data	no data
Mainstem		0	41	1.01E-03	1.01E-04	no data	no data
Mainstem	1 April 2014	0	19	1.09E-02	1.09E-03	-28.3	0.2
Mainstem		0	20	1.53E-02	1.53E-03	no data	no data
Mainstem		0	21	1.16E-02	1.16E-03	-28.9	0.1
Mainstem		0	22	1.14E-02	1.15E-03	no data	no data
Mainstem		0	23	1.28E-02	1.28E-03	-29.6	0.2
Mainstem		0	24	9.95E-03	9.97E-04	no data	no data
Mainstem		0	25	1.21E-02	1.21E-03	-29.8	0.1
Mainstem		0	26	9.98E-03	1.00E-03	no data	no data
Mainstem		0	27	1.58E-02	1.59E-03	-30.3	0.4
Mainstem		0	28	1.04E-02	1.04E-03	no data	no data
Mainstem		0	29	3.26E-02	3.27E-03	-33.1	0.3

Mainstem		0	30	1.07E-02	1.07E-03	no data	no data
Mainstem		0	31	3.38E-02	3.39E-03	-33.7	0.2
Mainstem		0	32	9.28E-03	9.29E-04	no data	no data
Mainstem		0	33	1.67E-02	1.67E-03	-32.4	0.3
Mainstem		0	34	4.97E-03	4.98E-04	no data	no data
Mainstem		0	35	6.05E-03	6.06E-04	-31.2	0.4
Mainstem		0	36	3.25E-03	3.26E-04	no data	no data
Mainstem		0	37	3.37E-03	3.38E-04	-31.0	0.3
Mainstem		0	38	2.50E-03	2.50E-04	no data	no data
Mainstem		0	39	2.14E-03	2.14E-04	-31.3	0.7
Mainstem		0	40	1.71E-03	1.72E-04	no data	no data
Mainstem		0	41	1.33E-03	1.34E-04	-34.1	0.7
Mainstem	8 June 2005	0	19	2.09E-02	2.09E-03	no data	no data
Mainstem		0	20	1.21E-02	1.21E-03	no data	no data
Mainstem		0	21	1.10E-02	1.10E-03	no data	no data
Mainstem		0	22	1.40E-02	1.40E-03	no data	no data
Mainstem		0	23	1.71E-02	1.71E-03	no data	no data
Mainstem		0	24	1.10E-02	1.11E-03	no data	no data
Mainstem		0	25	1.59E-02	1.59E-03	no data	no data
Mainstem		0	26	1.01E-02	1.01E-03	no data	no data
Mainstem		0	27	1.95E-02	1.95E-03	no data	no data
Mainstem		0	28	1.78E-02	1.79E-03	no data	no data
Mainstem		0	29	4.07E-02	4.08E-03	no data	no data
Mainstem		0	30	2.45E-02	2.46E-03	no data	no data
Mainstem		0	31	4.15E-02	4.16E-03	no data	no data
Mainstem		0	32	1.61E-02	1.62E-03	no data	no data
Mainstem		0	33	2.14E-02	2.14E-03	no data	no data
Mainstem		0	34	7.28E-03	7.30E-04	no data	no data
Mainstem		0	35	9.55E-03	9.57E-04	no data	no data
Mainstem		0	36	2.00E-03	2.00E-04	no data	no data
Mainstem		0	37	3.28E-03	3.29E-04	no data	no data
Mainstem		0	38	1.55E-03	1.56E-04	no data	no data
Mainstem		0	39	2.74E-03	2.74E-04	no data	no data
Mainstem		0	40	2.00E-03	2.00E-04	no data	no data
Mainstem		0	41	1.65E-03	1.65E-04	no data	no data
Solimões	4 June 2005	0	19	8.29E-03	9.40E-04	no data	no data
Solimões		0	20	5.56E-03	6.31E-04	no data	no data
Solimões		0	21	5.76E-03	6.53E-04	no data	no data
Solimões		0	22	7.86E-03	8.91E-04	no data	no data
Solimões		0	23	1.12E-02	1.27E-03	no data	no data
Solimões		0	24	8.57E-03	9.72E-04	no data	no data
Solimões		0	25	1.81E-02	2.05E-03	no data	no data
Solimões		0	26	1.86E-02	2.11E-03	no data	no data

Solimões		0	27	2.95E-02	3.35E-03	no data	no data
Solimões		0	28	2.59E-02	2.94E-03	no data	no data
Solimões		0	29	4.58E-02	5.19E-03	no data	no data
Solimões		0	30	2.09E-02	2.37E-03	no data	no data
Solimões		0	31	3.80E-02	4.31E-03	no data	no data
Solimões		0	32	1.11E-02	1.26E-03	no data	no data
Solimões		0	33	1.67E-02	1.89E-03	no data	no data
Solimões		0	34	3.20E-03	3.63E-04	no data	no data
Solimões		0	35	5.25E-03	5.95E-04	no data	no data
Solimões		0	36	1.35E-03	1.53E-04	no data	no data
Solimões		0	37	1.81E-03	2.05E-04	no data	no data
Solimões		0	38	7.15E-04	8.11E-05	no data	no data
Solimões		0	39	1.05E-03	1.19E-04	no data	no data
Solimões		0	40	6.93E-04	7.85E-05	no data	no data
Solimões		0	41	6.80E-04	7.71E-05	no data	no data
Madeira	6 June 2005	0	19	2.13E-02	2.16E-03	no data	no data
Madeira		0	20	1.73E-02	1.76E-03	no data	no data
Madeira		0	21	1.78E-02	1.80E-03	no data	no data
Madeira		0	22	1.87E-02	1.90E-03	no data	no data
Madeira		0	23	2.25E-02	2.29E-03	no data	no data
Madeira		0	24	1.65E-02	1.67E-03	no data	no data
Madeira		0	25	2.25E-02	2.29E-03	no data	no data
Madeira		0	26	1.94E-02	1.97E-03	no data	no data
Madeira		0	27	3.19E-02	3.24E-03	no data	no data
Madeira		0	28	4.18E-02	4.25E-03	no data	no data
Madeira		0	29	7.80E-02	7.92E-03	no data	no data
Madeira		0	30	6.65E-02	6.75E-03	no data	no data
Madeira		0	31	7.74E-02	7.86E-03	no data	no data
Madeira		0	32	4.47E-02	4.54E-03	no data	no data
Madeira		0	33	3.43E-02	3.48E-03	no data	no data
Madeira		0	34	1.38E-02	1.41E-03	no data	no data
Madeira		0	35	9.87E-03	1.00E-03	no data	no data
Madeira		0	36	3.91E-03	3.97E-04	no data	no data
Madeira		0	37	3.89E-03	3.96E-04	no data	no data
Madeira		0	38	2.38E-03	2.42E-04	no data	no data
Madeira		0	39	2.75E-03	2.79E-04	no data	no data
Madeira		0	40	2.36E-03	2.40E-04	no data	no data
Madeira		0	41	1.16E-03	1.18E-04	no data	no data
Mainstem	28 July 2014	54	19	1.15E-03	1.27E-04	no data	NaN
Mainstem		54	20	1.57E-03	1.73E-04	no data	NaN
Mainstem		54	21	2.68E-03	2.95E-04	-30.9	0.2
Mainstem		54	22	2.33E-03	2.56E-04	-29.6	0.4
Mainstem		54	23	2.75E-03	3.02E-04	-30.9	0.5

Mainstem		54	24	2.72E-03	2.99E-04	-29.9	0.5
Mainstem		54	25	4.67E-03	5.14E-04	no data	NaN
Mainstem		54	26	4.42E-03	4.86E-04	-29.6	0.6
Mainstem		54	27	6.18E-03	6.80E-04	-34.1	0.2
Mainstem		54	28	3.07E-03	3.38E-04	-28.5	3.7
Mainstem		54	29	1.62E-02	1.78E-03	-34.0	0.5
Mainstem		54	30	3.26E-03	3.59E-04	-37.3	0.5
Mainstem		54	31	1.57E-02	1.73E-03	-34.6	0.3
Mainstem		54	32	2.79E-03	3.07E-04	no data	NaN
Mainstem		54	33	6.95E-03	7.64E-04	-34.6	1.2
Mainstem	2 April 2014	30.15	19	1.67E-03	1.69E-04	no data	NaN
Mainstem		30.15	20	2.22E-03	2.24E-04	no data	NaN
Mainstem		30.15	21	3.07E-03	3.09E-04	-29.6	0.4
Mainstem		30.15	22	3.02E-03	3.05E-04	-29.4	0.1
Mainstem		30.15	23	3.62E-03	3.65E-04	-31.1	0.1
Mainstem		30.15	24	2.61E-03	2.63E-04	-30.0	0.5
Mainstem		30.15	25	3.84E-03	3.87E-04	-30.3	0.3
Mainstem		30.15	26	3.50E-03	3.53E-04	-30.1	0.4
Mainstem		30.15	27	6.71E-03	6.77E-04	-32.3	0.2
Mainstem		30.15	28	3.07E-03	3.09E-04	-31.8	0.4
Mainstem		30.15	29	1.86E-02	1.88E-03	-34.5	0.1
Mainstem		30.15	30	3.47E-03	3.49E-04	-33.6	0.4
Mainstem		30.15	31	1.86E-02	1.88E-03	-34.9	0.0
Mainstem		30.15	32	2.81E-03	2.83E-04	-34.2	0.2
Mainstem		30.15	33	8.04E-03	8.11E-04	-34.7	0.3
Mainstem	2 April 2014	2.7	19	0.00E+00	0.00E+00	no data	NaN
Mainstem		2.7	20	0.00E+00	0.00E+00	no data	NaN
Mainstem		2.7	21	3.59E-03	3.61E-04	no data	NaN
Mainstem		2.7	22	2.85E-03	2.86E-04	no data	NaN
Mainstem		2.7	23	0.00E+00	0.00E+00	no data	NaN
Mainstem		2.7	24	0.00E+00	0.00E+00	no data	NaN
Mainstem		2.7	25	0.00E+00	0.00E+00	no data	NaN
Mainstem		2.7	26	9.37E-03	9.41E-04	no data	NaN
Mainstem		2.7	27	0.00E+00	0.00E+00	no data	NaN
Mainstem		2.7	28	0.00E+00	0.00E+00	no data	NaN
Mainstem		2.7	29	5.26E-03	5.28E-04	no data	NaN
Mainstem		2.7	30	0.00E+00	0.00E+00	no data	NaN
Mainstem		2.7	31	6.35E-03	6.37E-04	no data	NaN
Mainstem		2.7	32	0.00E+00	0.00E+00	no data	NaN
Mainstem		2.7	33	0.00E+00	0.00E+00	no data	NaN
Mainstem	2 April 2014	49.1	19	1.58E-03	1.58E-04	no data	NaN
Mainstem		49.1	20	2.36E-03	2.37E-04	no data	NaN
Mainstem		49.1	21	2.85E-03	2.86E-04	-30.4	0.7

Mainstem	49.1	22	2.92E-03	2.93E-04	-30.0	0.0
Mainstem	49.1	23	3.48E-03	3.49E-04	-31.0	0.2
Mainstem	49.1	24	2.45E-03	2.46E-04	-29.8	0.1
Mainstem	49.1	25	4.22E-03	4.23E-04	-31.2	0.1
Mainstem	49.1	26	4.74E-03	4.75E-04	-30.5	0.3
Mainstem	49.1	27	6.24E-03	6.25E-04	-34.4	0.5
Mainstem	49.1	28	2.68E-03	2.68E-04	-31.8	0.4
Mainstem	49.1	29	1.60E-02	1.60E-03	-34.2	0.1
Mainstem	49.1	30	2.88E-03	2.88E-04	no data	NaN
Mainstem	49.1	31	1.69E-02	1.69E-03	-35.9	0.1
Mainstem	49.1	32	2.05E-03	2.06E-04	-34.3	0.7
Mainstem	49.1	33	6.70E-03	6.71E-04	-34.2	0.1

			Chain		Abundance		δ <sup>13</sup> C
Location	Date	Depth	length	Abundance	error	δ <sup>13</sup> C	error
			#	ng/µg POC	ng/µg POC	%0	%0
Mainstem	1 April 2014	0	14	0.31171	0.031	-27.7	0.1
Mainstem		0	16	2.4949	0.250	-29.2	0.2
Mainstem		0	18	3.3937	0.340	-28.6	0.3
Mainstem		0	20	0.097067	0.010	-29.2	0.2
Mainstem		0	22	0.20945	0.021	-31.6	0.5
Mainstem		0	24	0.14455	0.014	-28.8	0.4
Mainstem		0	25	0.037764	0.004	no data	no data
Mainstem		0	26	0.10798	0.011	-30.2	0.5
Mainstem		0	27	0.024168	0.002	no data	no data
Mainstem		0	28	0.091665	0.009	-32.0	0.5
Mainstem		0	29	0.026517	0.003	no data	no data
Mainstem		0	30	0.081735	0.008	-33.2	0.2
Mainstem		0	31	0.021069	0.002	no data	no data
Mainstem		0	32	0.061277	0.006	-33.5	2.3
Mainstem		0	33	0.012159	0.001	no data	no data
Mainstem		0	34	0.031169	0.003	-33.1	0.1
Mainstem	28 July 2014	0	14	0.1952	0.020	-33.0	0.0
Mainstem		0	16	3.4245	0.344	-30.8	0.4
Mainstem		0	18	3.9505	0.397	-29.2	0.2
Mainstem		0	20	0.096981	0.010	-30.9	0.0
Mainstem		0	22	2.3583	0.237	-34.2	0.5
Mainstem		0	24	0.15264	0.015	-32.5	0.6
Mainstem		0	25	0.037073	0.004	no data	no data
Mainstem		0	26	0.13925	0.014	-33.0	0.4
Mainstem		0	27	0.029239	0.003	no data	no data
Mainstem		0	28	0.13231	0.013	-32.9	0.6
Mainstem		0	29	0.037333	0.004	no data	no data
Mainstem		0	30	0.13233	0.013	-33.0	0.2
Mainstem		0	31	0.034962	0.004	no data	no data
Mainstem		0	32	0.10498	0.011	-33.3	0.3
Mainstem		0	33	0.021529	0.002	no data	no data
Mainstem		0	34	0.054067	0.005	-32.8	0.2
Tapajós	27 July 2014	0	14	2.2663	0.227	-36.7	0.1
Tapajós		0	16	23.249	2.333	-33.6	0.3
Tapajós		0	18	11.378	1.142	-29.7	0.3
Tapajós		0	20	0.33744	0.034	-34.1	0.6

**Table S2.** Abundances and  $\delta^{13}$ C values of fatty acids (C<sub>14</sub>-C<sub>34</sub>) from large-volume (>100 L) and depth-specific (10 L) samples collected in June 2005, April 2014 and July 2014.

Tapajós		0	22	0	0.000	-39.4	0.2
Tapajós		0	24	0.93488	0.094	-36.2	0.6
Tapajós		0	25	0.18406	0.018	no data	no data
Tapajós		0	26	0.62779	0.063	-35.5	0.7
Tapajós		0	27	0.069807	0.007	no data	no data
Tapajós		0	28	0.4066	0.041	-36.6	1.2
Tapajós		0	29	0.031529	0.003	no data	no data
Tapajós		0	30	0.095123	0.010	-35.5	0.2
Tapajós		0	31	0.040663	0.004	no data	no data
Tapajós		0	32	0.031174	0.003	-34.9	0.1
Tapajós		0	33	0.0079396	0.001	no data	no data
Tapajós		0	34	0.012265	0.001	no data	no data
Mainstem	8 June 2005	0	14	0.19	0.019	-35.9	1.6
Mainstem		0	15	0.063	0.006	no data	no data
Mainstem		0	16	0.871	0.087	-34.3	7.4
Mainstem		0	17	0.018	0.002	no data	no data
Mainstem		0	18	0.18	0.018	-31.0	1.5
Mainstem		0	19	0.05	0.005	no data	no data
Mainstem		0	20	0.049	0.005	-33.0	0.4
Mainstem		0	21	0.047	0.005	no data	no data
Mainstem		0	22	0.097	0.010	-37.5	0.8
Mainstem		0	23	0.028	0.003	no data	no data
Mainstem		0	24	0.175	0.018	-37.0	1.5
Mainstem		0	25	0.035	0.004	no data	no data
Mainstem		0	26	0.194	0.019	-36.5	1.6
Mainstem		0	27	0.04	0.004	no data	no data
Mainstem		0	28	0.223	0.022	-37.2	1.9
Mainstem		0	29	0.049	0.005	no data	no data
Mainstem		0	30	0.166	0.017	-35.3	1.4
Mainstem		0	31	0.038	0.004	no data	no data
Mainstem		0	32	0.099	0.010	-34.3	0.8
Mainstem		0	33	0.023	0.002	no data	no data
Mainstem		0	34	0.048	0.005	-34.2	0.4
Mainstem		0	35	0.066	0.007	no data	no data
Solimões	4 June 2005	0	14	0.187	0.021	-34.9	2.1
Solimões		0	15	0.046	0.005	no data	no data
Solimões		0	16	0.885	0.100	-34.7	9.9
Solimões		0	17	0.017	0.002	no data	no data
Solimões		0	18	0.169	0.019	-30.3	1.9
Solimões		0	19	0.012	0.001	no data	no data
Solimões		0	20	0.049	0.006	-30.9	0.5
Solimões		0	21	0.018	0.002	no data	no data
Solimões		0	22	0.087	0.010	-34.5	1.0

Solimões		0	23	0.031	0.004	no data	no data
Solimões		0	24	0.19	0.022	-34.1	2.1
Solimões		0	25	0.044	0.005	no data	no data
Solimões		0	26	0.316	0.036	-34.2	3.5
Solimões		0	27	0.046	0.005	no data	no data
Solimões		0	28	0.27	0.031	-35.4	3.0
Solimões		0	29	0.059	0.007	no data	no data
Solimões		0	30	0.203	0.023	-34.6	2.3
Solimões		0	31	0.05	0.006	no data	no data
Solimões		0	32	0.141	0.016	-34.4	1.6
Solimões		0	33	0.032	0.004	no data	no data
Solimões		0	34	0.064	0.007	-34.5	0.7
Solimões		0	35	0.102	0.012	no data	no data
Madeira	6 June 2005	0	14	0.089	0.009	-37.7	0.4
Madeira		0	15	0.024	0.002	no data	no data
Madeira		0	16	0.508	0.052	-37.6	2.5
Madeira		0	17	0.013	0.001	no data	no data
Madeira		0	18	0.099	0.010	-31.0	0.5
Madeira		0	19	0.006	0.001	no data	no data
Madeira		0	20	0.032	0.003	-31.2	0.2
Madeira		0	21	0.01	0.001	no data	no data
Madeira		0	22	0.05	0.005	-34.1	0.2
Madeira		0	23	0.018	0.002	no data	no data
Madeira		0	24	0.09	0.009	-35.5	0.4
Madeira		0	25	0.021	0.002	no data	no data
Madeira		0	26	0.085	0.009	-35.0	0.4
Madeira		0	27	0.018	0.002	no data	no data
Madeira		0	28	0.087	0.009	-35.0	0.4
Madeira		0	29	0.023	0.002	no data	no data
Madeira		0	30	0.075	0.008	-34.5	0.4
Madeira		0	31	0.018	0.002	no data	no data
Madeira		0	32	0.053	0.005	-33.7	0.3
Madeira		0	33	0.012	0.001	no data	no data
Madeira		0	34	0.027	0.003	-33.5	0.1
Madeira		0	35	0.034	0.003	no data	no data
Mainstem	28 July 2014	54	14	0.054832	0.006	-32.4	0.4
Mainstem		54	16	0.63583	0.070	-30.4	0.2
Mainstem		54	18	0.39584	0.044	-29.2	0.1
Mainstem		54	20	0.036354	0.004	-30.6	1.1
Mainstem		54	22	0.74563	0.082	-32.4	0.4
Mainstem		54	24	0.086899	0.010	-31.5	0.3
Mainstem		54	25	0.022954	0.003	no data	no data
Mainstem		54	26	0.10196	0.011	-31.1	0.8

Mainstem		54	27	0.023842	0.003	no data	no data
Mainstem		54	28	0.12934	0.014	-31.5	0.1
Mainstem		54	29	0.031932	0.004	no data	no data
Mainstem		54	30	0.13955	0.015	-32.2	0.2
Mainstem		54	31	0.028885	0.003	no data	no data
Mainstem		54	32	0.094013	0.010	-32.8	0.3
Mainstem		54	33	0.019822	0.002	no data	no data
Mainstem		54	34	0.045886	0.005	-32.6	0.8
Mainstem	2 April 2014	30.15	14	0.070165	0.007	-29.9	1.3
Mainstem		30.15	16	1.7788	0.179	-29.2	0.4
Mainstem		30.15	18	1.7946	0.181	-28.8	0.3
Mainstem		30.15	20	0.053737	0.005	-30.1	0.3
Mainstem		30.15	22	0.2279	0.023	-31.5	0.6
Mainstem		30.15	24	0.097517	0.010	-32.0	0.3
Mainstem		30.15	25	0.023434	0.002	no data	no data
Mainstem		30.15	26	0.097554	0.010	-32.0	0.3
Mainstem		30.15	27	0.023332	0.002	no data	no data
Mainstem		30.15	28	0.11045	0.011	-32.7	0.2
Mainstem		30.15	29	0.029705	0.003	no data	no data
Mainstem		30.15	30	0.11388	0.011	-33.3	0.2
Mainstem		30.15	31	0.027346	0.003	no data	no data
Mainstem		30.15	32	0.083013	0.008	-33.3	0.3
Mainstem		30.15	33	0.015861	0.002	no data	no data
Mainstem		30.15	34	0.038895	0.004	-33.4	0.9
Mainstem	2 April 2014	2.7	14	0.21517	0.022	no data	no data
Mainstem		2.7	16	3.6379	0.365	no data	NaN
Mainstem		2.7	18	3.4641	0.348	no data	NaN
Mainstem		2.7	20	0.0699	0.007	no data	no data
Mainstem		2.7	22	0.55703	0.056	no data	NaN
Mainstem		2.7	24	0.078868	0.008	no data	NaN
Mainstem		2.7	25	0.018353	0.002	no data	no data
Mainstem		2.7	26	0.056486	0.006	no data	NaN
Mainstem		2.7	27	0.022969	0.002	no data	no data
Mainstem		2.7	28	0.050916	0.005	no data	NaN
Mainstem		2.7	29	0.012918	0.001	no data	no data
Mainstem		2.7	30	0.05081	0.005	no data	NaN
Mainstem		2.7	31	0.011095	0.001	no data	no data
Mainstem		2.7	32	0.034628	0.003	no data	NaN
Mainstem		2.7	33	0.0078758	0.001	no data	no data
Mainstem		2.7	34	0.016382	0.002	no data	NaN
Mainstem	2 April 2014	49.1	14	0.10537	0.011	-28.7	1.3
Mainstem		49.1	16	3.1154	0.312	-29.4	0.3
Mainstem		49.1	18	3.0324	0.304	-28.9	0.2

Mainstem         49.1         22         0.25316         0.025         -32.8         0.9	
Mainstem 49.1 24 0.090366 0.009 -32.1 0.3	
Mainstem         49.1         25         0.022487         0.002         no data         no data	
Mainstem         49.1         26         0.092227         0.009         -32.1         0.1	
Mainstem         49.1         27         0.024705         0.002         no data         no data	
Mainstem         49.1         28         0.10805         0.011         -32.7         0.2	
Mainstem         49.1         29         0.031813         0.003         no data         no data	
Mainstem         49.1         30         0.11688         0.012         -33.2         0.2	
Mainstem         49.1         31         0.031116         0.003         no data         no data	
Mainstem         49.1         32         0.08853         0.009         -33.7         0.2	
Mainstem         49.1         33         0.020959         0.002         no data         no data	
Mainstem         49.1         34         0.045168         0.005         -33.2         0.3	

Channel position	Depth	Substrate	Avg. activity	S.D. activity
km	т		µmol/L/hr	µmol/L/hr
0.34	42.8	Leu	0.077	0.0091
0.34	42.8	Phe	0.049	0.0042
0.34	42.8	AAF	0.021	0.0033
0.34	42.8	NAG	0.008	0.0039
0.34	42.8	Cello	0.000	0.0002
0.34	42.8	b-glu	0.001	0.0005
0.34	42.8	xyl	0.000	0.0000
1.6	54	Leu	0.040	0.0065
1.6	54	Phe	0.031	0.0019
1.6	54	AAF	0.013	0.0006
1.6	54	NAG	0.003	0.0005
1.6	54	Cello	0.001	0.0000
1.6	54	b-glu	0.003	0.0001
1.6	54	xyl	0.001	0.0001
1.6	54	PO4	0.028	0.0008
1.6	39.83	Leu	0.056	0.0037
1.6	39.83	Phe	0.045	0.0020
1.6	39.83	AAF	0.020	0.0101
1.6	39.83	NAG	0.005	0.0006
1.6	39.83	Cello	-0.001	0.0003
1.6	39.83	b-glu	0.004	0.0002
1.6	39.83	xyl	0.000	0.0002
1.6	39.83	PO4	0.030	0.0035
1.6	30.4	Leu	0.053	0.0034
1.6	30.4	Phe	0.040	0.0045
1.6	30.4	AAF	0.012	0.0023
1.6	30.4	NAG	0.005	0.0002
1.6	30.4	Cello	0.001	0.0001
1.6	30.4	b-glu	0.003	0.0003
1.6	30.4	PO4	0.007	0.0032
1.6	14.95	Leu	0.040	0.0029
1.6	14.95	Phe	0.031	0.0014
1.6	14.95	Cello	0.006	0.0088
1.6	14.95	b-glu	0.002	0.0006
1.6	14.95	xyl	-0.001	0.0033
1.6	14.95	PO4	0.018	0.0021
1.6	0.15	Leu	0.090	0.0042

**Table S3.** Activities of eight enzymes within particles throughout the Óbidos cross 

 section in July 2014.

1.6	0.15	Phe	0.065	0.0028
1.6	0.15	AAF	0.014	0.0022
1.6	0.15	NAG	0.006	0.0002
1.6	0.15	Cello	0.001	0.0004
1.6	0.15	b-glu	0.005	0.0003
1.6	0.15	xyl	0.001	0.0002
1.6	0.15	PO4	0.036	0.0150
2.2	53.06	Leu	0.063	0.0047
2.2	53.06	Phe	0.028	0.0214
2.2	53.06	AAF	0.003	0.0025
2.2	53.06	NAG	0.005	0.0004
2.2	53.06	Cello	0.001	0.0001
2.2	53.06	b-glu	0.003	0.0001
2.2	53.06	xyl	0.001	0.0001
2.2	53.06	PO4	0.023	0.0019
2.2	29.83	Leu	0.064	0.0035
2.2	29.83	Phe	0.044	0.0115
2.2	29.83	AAF	0.010	0.0029
2.2	29.83	NAG	0.004	0.0009
2.2	29.83	Cello	0.002	0.0016
2.2	29.83	b-glu	0.002	0.0002
2.2	29.83	xyl	0.000	0.0001
2.2	29.83	PO4	0.015	0.0028
2.2	3.33	Leu	0.071	0.0288
2.2	3.33	Phe	0.040	0.0050
2.2	3.33	AAF	0.020	0.0186
2.2	3.33	NAG	0.003	0.0001
2.2	3.33	Cello	0.001	0.0004
2.2	3.33	b-glu	0.003	0.0012
2.2	3.33	xyl	0.001	0.0003
2.2	3.33	PO4	0.018	0.0010