

Organic carbon burial efficiency in a sub-tropical hydroelectric reservoir

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Abstract

Hydroelectric reservoirs bury significant amounts of organic carbon (OC) in their sediments. Many reservoirs are characterized by high sedimentation rates, low oxygen concentrations in bottom water, and a high share of terrestrially derived OC, and all of these factors have been linked to a high efficiency of OC burial. However, investigations of OC burial efficiency (OCBE, i.e. the ratio between OC buried and deposited) in reservoirs is limited to a few studies, none of which include spatially resolved analyses. In this study we determined the spatial variation in OCBE in a large sub-tropical reservoir and related it to sediment characteristics. Our results show that the sediment accumulation rate explains up to 92% of the spatial variability in OCBE, outweighing the effect of other variables, such as OC source and oxygen exposure time. OCBE at the pelagic sites varied from 48 to 86% (mean 67%) and decreased towards the dam. At the margins, OCBE was lower (9 to 17%) due to the low sediment accumulation in shallow areas. Our data show that the variability in OCBE both along the rivers-dam and the margin-pelagic axes must be considered in whole-reservoir

1 assessments. Combining these results with a spatially resolved assessment of sediment
2 accumulation and OC burial in the studied reservoir, we estimated a whole-basin OC burial
3 efficiency of 57%. Being the first whole-basin assessment of OCBE in a reservoir, these
4 results suggest that reservoirs may bury OC more efficiently than natural lakes.

5

6 **1 Introduction**

7 The sediments of freshwater systems are important sinks of atmospheric CO₂ assimilated
8 through photosynthesis both in the aquatic and in the terrestrial environments (Stallard, 1998).
9 This carbon sink corresponds to the fraction of the organic carbon (OC) that reaches the
10 sediments and escapes mineralization by heterotrophic organisms and (photo)chemical
11 reactions, remaining buried (accumulated). The percentage of the total OC reaching the
12 sediments that is actually buried corresponds to the OC burial efficiency (OCBE) of a system
13 (Betts and Holland, 1991; Hartnett et al., 1998). OCBE, thus, depends on the processes and
14 factors affecting burial and mineralization. OCBE is closely negatively linked to
15 mineralization: processes favoring mineralization tend to decrease burial and vice versa.

16 While the mechanisms controlling the carbon fluxes in marine sediments have received
17 considerable attention (see Burdige (2007) for a review), freshwater sediments have only
18 recently become focus of study (Sobek et al., 2009; Gudasz et al., 2012; Gudasz et al., 2010).
19 What is known about freshwater sediments is that OCBE tends to be strongly positively
20 correlated with sedimentation rates, especially of terrestrially-derived OC (Sobek et al., 2009;
21 Gudasz et al., 2012). This explains, for instance, why hydroelectric reservoirs tend to be more
22 important sites for OC accumulation, compared to lakes, as reservoirs receive relatively high
23 inputs of fluvial sediments. OC burial in reservoirs is about one order of magnitude higher
24 than in natural lakes (Mulholland and Elwood, 1982). In spite of the increasing importance of
25 reservoirs as OC burial sites (Mendonca et al., 2012) due to the rising demand for
26 hydroelectricity, assessments of the OC burial efficiency in hydroelectric reservoirs are, to our
27 knowledge, so far limited to two studies on tropical and sub-tropical systems (Kunz et al.,
28 2011; Sikar et al., 2012) and one in a temperate system (Sobek et al., 2012). None of these
29 assessments are based on integrative (whole-system) data.

30 Organic carbon in hydroelectric reservoirs can originate from several sources (De Junet et al.,
31 2009). First, carbon derived from flooded soil and vegetation may fuel the system's
32 metabolism for long periods, leading to elevated green house gases (GHG) emissions,

1 especially during the initial ~10 years after damming (Abril et al., 2005; Tremblay et al.,
2 2004; Barros et al., 2011). Second, variable amounts of terrestrial organic matter are
3 continuously flushed into reservoirs through tributary rivers and erosion of the margins.
4 Terrestrial inputs are, thus, important during the entire reservoir lifetime. Finally, the
5 combination of the usually long water residence time, the high transparency due to the settling
6 of suspended sediment and the high nutrient availability favors planktonic primary production
7 in reservoirs (Bayne et al., 1983; Rangel et al., 2012). Terrestrial- and aquatic-derived OC
8 occur in different proportions along reservoirs length and may be mineralized/buried at
9 different rates (Gudasz et al., 2012; Cardoso et al., 2014). Moreover, the hydrology of
10 hydroelectric reservoirs, marked by the transition between high stream velocities at the river
11 inflow and low velocities near the dam, often leads to remarkable limnological gradients, e.g.
12 water physical and chemical properties, sedimentation and productivity (Thornton, 1990;
13 Armengol et al., 1999).

14 Reservoir heterogeneity may cause a strong variation in carbon fluxes (Roland et al., 2010;
15 Cardoso et al., 2013). While spatial variation in CO₂ emissions from reservoir's surface to the
16 atmosphere have been described (Roland et al., 2010), the effect of heterogeneity on the
17 sediment-carbon flows is unknown, even though reservoir heterogeneity is clearly reflected in
18 sediment characteristics (De Junet et al., 2009). The main purpose of this study was to
19 determine the OCBE in a sub-tropical hydroelectric reservoir, and to evaluate the importance
20 of variable factors driving it. OCBE was obtained from direct measurements of OC burial and
21 estimations of OC mineralization rates along the length of a hydropower reservoir in Brazil,
22 including the margins and the pelagic zone. Subsequently, these site-specific measurements
23 were extrapolated to the whole reservoir based on spatially resolved measurements of
24 sediment accumulation and OC burial rates (Mendonça et al., 2014). This approach resulted in
25 the first a whole-system OCBE estimate for a reservoir.

26

27 **2 Methods**

28 **2.1 Reservoir description**

29 This study was conducted in Mascarenhas de Moraes, a large (272 km²) and deep (maximum
30 depth 60 m) hydroelectric reservoir located in southeastern Brazil (20°17' 1.52" S,
31 47°3'46.53" W; **Fig. 1**), in the Cerrado (savannah-type) biome, in a region characterized by

1 sub-tropical climate. The reservoir was formed by damming the Rio Grande in 1957. Its
2 watershed is currently dominated by agriculture (mainly coffee, corn, and soybean), with
3 some remnants of original Cerrado forests. Water residence time in the Mascarenhas de
4 Moraes reservoir is relatively short (approximately 51 days, Rangel et al. (2012)). Total
5 phosphorus concentrations range from 15 to 168 $\mu\text{g P l}^{-1}$ and chlorophyll a concentrations are
6 low (ranging from 2.6 to 3.9 $\mu\text{g l}^{-1}$; Rangel et al. (2012)). Water transparency is high (Secchi
7 disk depth of 4–8 m near the dam; Rangel et al. (2012)) and the bottom water is oxygenated
8 year-round, even though the water column is often stratified near the dam (Huszar personal
9 communication, 2012).

10

11 **2.2 Sampling**

12 Sediment cores (6 cm internal diameter) were sampled at 16 sites of which 12 were
13 located in the pelagic zone, i.e. in the area of highest sediment accumulation within
14 transversal transects (from margin to margin), and 4 sites were located close to the margins,
15 i.e. in the area of low sediment accumulation (**Fig. 1**). In one of the margin sites (site 11) the
16 sediment was fully composed of compact pre-flooding soil, i.e. OC burial was zero. From
17 each of the remaining 15 sites, two sediment cores were retrieved using a gravity corer
18 equipped with a hammer device (UWITEC, Mondsee, Austria). The core was hammered into
19 the sediment as deep as possible resulting in cores containing the entire sediment layer at the
20 sampling site and preferentially pre-flooding sediment/soil as well. After retrieval the cores
21 were sealed with plastic caps and transported to the field station for slicing. The first set of
22 cores was used for determination of sediment accumulation rate, OC burial (or OC
23 accumulation) rates (Mendonça et al., 2014) and physical and chemical analysis. The second
24 set of cores was used for measurements of O_2 and CH_4 concentrations in pore water depth
25 profiles.

26

27 **2.3 Sediment characteristics**

28 One sediment core from each sampling site (including pre-flooding material, when
29 present) was sub-sampled in 2 cm thick slices which were stored in air tight plastic containers
30 at -5°C until further lab analysis. At the lab, water and organic matter contents (%) of each

1 slice were measured gravimetrically, based on the difference between wet and dry weights
2 and loss on ignition at 550°C for four hours, respectively. Sediment porosity (\emptyset) was
3 calculated from water content (WC) and dry bulk density (ρ), as follows:

$$4 \quad \emptyset = WC / (WC + (1-WC) * \rho)$$

5 Dry bulk density (ρ) was calculated assuming that sediment is formed by a mixture of
6 minerals (approximate density of 2.65 g cm⁻³) and organic matter (approximate density of 1 g
7 cm⁻³):

$$8 \quad \rho = OM * 1 + IM * 2.65, \text{ where}$$

9 OM is the fraction of organic matter, and IM the fraction of inorganic matter in the sediment
10 (OM + IM = 1). OC content, nitrogen content and carbon isotopic composition ($\delta^{13}\text{C}$) were
11 determined using a CN analyzer (ANCA-GSL, PDZ Europa, Ltd., Sandbach, UK) coupled to
12 a mass spectrometer (Sercon Ltd., Cheshire, UK). These analyses were performed in the two
13 top slices, in the two bottom post-flooding sediment slices, in the two top pre-flooding slices,
14 and in one slice every 10 cm along the entire cores (except for site 01 where we analyzed all
15 slices). OC content in the non-analyzed slices was estimated by linear interpolation.
16 Particulate inorganic carbon was not present in the sediment since sediment samples did not
17 react when exposed to acid (HCl), in accordance with water pH in the Mascarenhas de
18 Moraes reservoir varying between 6.6 and 7.8 (Rangel et al., 2012).

19

20 **2.4 Gas concentrations in pore water**

21 At the field station, profiles of oxygen concentration and samples for CH₄ analysis were
22 immediately acquired. Oxygen concentrations in sediment pore water were measured using a
23 microsonde (model PA 2000, UNISENSE, Aarhus, Denmark) equipped with a microelectrode
24 (Clark type). Calibration was performed using air-saturated and oxygen-free solutions,
25 prepared by bubbling air (air-saturated solution) and pure nitrogen gas (oxygen-free solution)
26 into distilled water for approximately 30 minutes. Analytical precision was 0.1 $\mu\text{mol l}^{-1}$. The
27 microelectrode was moved vertically in steps of 1 mm from the sediment-water interface
28 down to the anoxic layer. Oxygen exposure time (yr) for each core was calculated as the ratio
29 between oxygen penetration depth (cm) and sediment accumulation rate (cm yr⁻¹).

1 Samples for the analysis of CH₄ dissolved in pore water were taken after carefully
2 transferring the sediment from the sampling tube into a tube with the same dimensions but
3 equipped with sampling ports of 2 cm diameter positioned spiral-wise every 2 cm along the
4 length of the tube. Approximately 10 mL of sediment was retrieved using a plastic syringe
5 through each sampling port (starting from the top layers). The sediment was then transferred
6 to glass vials which were immediately sealed with a silicon septa and an aluminum crimp
7 seal. After taking 4 mL of air out through the silicon septa, using a syringe and a needle, 4 mL
8 of 2.5% NaOH was injected into the vials in order to have all dissolved CH₄ transferred to the
9 headspace; vials were shaken and stored upside-down until analysis.

10 Concentrations of CH₄ in pore water were determined by injecting 1 mL of equilibrated
11 headspace air into a gas chromatograph (Shimadzu GC-2010) equipped with a flame
12 ionization detector (FID). Ultra pure nitrogen, hydrogen and synthetic air were used as carrier
13 gases. Injection, detection and column temperatures were 120, 200 and 85°C, respectively.
14 Headspace CH₄ concentrations were expressed as mmol/L, in relation to a known
15 concentration standard. From the headspace concentrations ([CH₄]_h), pore-water CH₄
16 concentrations ([CH₄]_{pw}) were determined as follows:

17
$$[\text{CH}_4]_{\text{pw}} = ([\text{CH}_4]_{\text{h}} * V_{\text{h}}) / (V_{\text{s}} * \text{WC}), \text{ where}$$

18 V_{h} is the headspace volume (determined from the weight of water necessary to fill the
19 headspace, considering water density = 1g.cm⁻³), V_{s} is the sediment volume (determined by
20 subtracting the headspace and the NaOH volumes from the total vial volume) and WC is the
21 water content (%).

22

23 **2.5 Gas flux estimates**

24 OC mineralization (gC m⁻² yr⁻¹) was estimated as the sum of CO₂ and CH₄ fluxes from
25 sediment to the water calculated using Fick's first law of diffusion. Details on the calculations
26 are as follows.

27 Sediment-water fluxes of CO₂ were calculated based on changes in oxygen concentrations
28 with sediment depth, using the software PROFILE (Berg et al. 1998). The calculations
29 considered sediment porosity and the CO₂ molecular diffusion coefficient which varies as a

1 function of temperature (Broeker & Peg 1974). Depth-integrated oxygen consumption rates
2 were converted to CO₂ production by using the respiratory coefficient of 0.9 (Granéli, 1979).
3 CH₄ concentrations decreased quasi-linearly from a depth of 6 to 10 cm to the top of the
4 sediment, likely caused by CH₄ oxidation at the oxic-anoxic boundary and by diffusive loss at
5 the sediment-water interface. Diffusive fluxes of CH₄ were calculated based on this gradient,
6 assuming that it extends across the diffusive boundary layer, and thus including CH₄
7 oxidation (e.g. Sobek et al. (2009)).

8

9 **2.6 OC burial and burial efficiency**

10 Sediment accumulation rates (cm yr⁻¹) were calculated as the ratio between total accumulated
11 sediment depth (cm) in each sampling site and the reservoir age (54 years in 2011). OC burial
12 rate (gC m⁻² yr⁻¹) was calculated from total OC mass (gC, i.e. the sum of OC mass in all post-
13 flooding sediment slices) in each sampling site, core surface area (2.8 x 10⁻³ m²) and the total
14 reservoir age (see details in Mendonça et al. (2014)). OCBE (%), defined as the percentage of
15 the total OC reaching the sediments that is present in the sediment, was calculated as the ratio
16 between OC burial rate and OC gross sedimentation rate (gC m⁻² yr⁻¹). The gross OC
17 sedimentation rate was calculated as the sum of OC burial and OC mineralization, which was
18 estimated by the sum of CO₂ and CH₄ diffusive fluxes.

19 Extrapolation of the site measurements (i.e. the data we obtained from the cores) to the whole
20 reservoir was done following two different approaches. In the first approach, we combined
21 the relationship between OCBE and sediment accumulation rate (this relationship is strong,
22 see results section) with spatially explicit integrative (whole-reservoir) sediment accumulation
23 rate data (obtained through a seismic approach; Mendonça et al. (2014)) to calculate the mean
24 reservoir-wide OCBE. In the second approach, we calculated the integrative OCBE for the
25 Mascarenhas de Moraes reservoir from the integrative OC burial rate (Mendonça et al., 2014)
26 and the mean mineralization rates estimated from the cores.

27

1 **2.7 Data analysis**

2 We used the Shapiro-Wilk test to check variables' distribution for normality, and the two-
3 tailed Spearman rank-order correlation (as some of the distributions were not normal) to
4 assess associations between variables. Distance to the dam along the rivers-dam axis was
5 defined as the shortest distance from each sampling site to the dam, following the
6 river/reservoir shape; because of the many tributary rivers to the reservoir, the term "rivers-
7 dam gradient" may be more appropriate. The three sites sampled close to the margins (03, 07
8 and 10) were excluded from the analysis that included the rivers-dam gradient (i.e. distance to
9 the dam) because margin sediments were very different from pelagic sediments (see
10 discussion). We used one-way ANOVA to test for difference of sediment characteristics and
11 carbon fluxes between margin and pelagic sites.

12

13 **3 Results**

14 Sediment accumulation rates and OC burial rates at the sampling sites varied from 0.04 to 1.8
15 cm yr^{-1} and from 3.1 to 210 $\text{gC m}^{-2} \text{yr}^{-1}$, respectively (**Table 1**), and significantly decreased
16 towards the dam ($r=0.74$ and $r=0.82$, respectively; $p<0.001$). The OC burial rates were on
17 average 13 times higher at the pelagic sites than at the sites close to the margins (**Table 1**).
18 OC mineralization rates, on the other hand, varied within a narrow range (17 to 48 $\text{gC m}^{-2} \text{yr}^{-1}$;
19 **Table 1**) and did not show a specific spatial pattern. Fluxes of CO_2 represented, on average,
20 65% of the total carbon flux from the sediment to the water in the sampling points.

21 Site-specific OCBE values varied from 9% to 86% (mean 56% for all sites, or 67% if only the
22 pelagic sites were included, **Table 1**) and were strongly positively correlated to sediment
23 accumulation rates (**Fig. 2**) but only weakly correlated to sediment composition (OC content
24 and isotopic composition) and oxygen exposure time (**Fig. 3**).

25 The mean OC content in the sampled cores in Mascarenhas de Moraes varied from 1.2 to
26 3.1% for the pelagic sites and from 1.8 to 2.5% for the margin sites. Mean $\delta^{13}\text{C}$ and mean C:N
27 ratio in the sampled cores varied from -23.3 to -19.8 and from 9.6 to 12.1, respectively
28 (**Table A1**). Sediment became more OC-enriched and ^{13}C -depleted towards the dam (pelagic
29 sites only) and from the margins to the pelagic zone (**Fig. 4**). Oxygen penetration depth varied
30 from 0.3 to 1.2 cm and did not vary significantly between margin and pelagic sites. Oxygen
31 exposure time did not show a steady increase nor decrease along the rivers-dam axis, but was

1 significantly lower in the pelagic sediments (0.4 to 1.2 years) than in the sites close to the
2 margins (8.1 to 14.9 years); **Table A1**).

3 The first integrative estimate, based on the strong relationship between sediment
4 accumulation rate and OCBE and on the integrative sediment accumulation rate from a
5 previous study (Mendonça et al., 2014), resulted in OCBE of 57% on the entire Mascarenhas
6 de Moraes reservoir. The second estimate, based on average mineralization rate (34.3 gC m^{-2}
7 yr^{-1} ; **Table 1**) and the whole-reservoir OC burial rate ($42.2 \text{ gC m}^{-2} \text{ yr}^{-1}$; Mendonça et al.
8 (2014)), resulted in an integrative OCBE of 55%.

9

10 **4 Discussion**

11 **4.1 Organic carbon burial efficiency in reservoirs**

12 Sediment OC burial was higher than, or similar to OC mineralization in all pelagic sites in the
13 Mascarenhas de Moraes reservoir, leading to site-specific OC burial efficiencies varying from
14 48 to 86% in pelagic sites (mean 67%; **Table 1**). These values are close to the upper end of
15 OCBE of natural lakes. An evaluation of OCBE in lakes mostly situated at latitude $>30^{\circ}\text{N}$
16 (with one exception at 2°S) resulted in efficiencies varying from 3% to 93% (median and
17 mean 48%; Sobek et al. (2009)). Due to the positive effect of temperature on OC
18 mineralization (Gudasz et al., 2010; Cardoso et al., 2014) OCBE may be expected to be lower
19 in sub-tropical and tropical lakes (Alin and Johnson, 2007). A recent assessment on arctic
20 lakes with low OCBE (mean 22%, ranging from 11 to 32%), however, indicated that the
21 strong effect of environmental conditions may overrule the effect of latitude on OCBE (Sobek
22 et al., 2014). Measurements of OCBE in man-made reservoirs are scarce, and to the best of
23 our knowledge limited to three studies. The first is in the tropical Lake Kariba, where OCBE
24 at a single coring site close to the dam was estimated to be 41% (Kunz et al., 2011). As our
25 study suggests that OCBE tends to be higher at sites far from the dam, 41% is probably at the
26 lower end of the in-reservoir variation in Lake Kariba. The second is in the temperate Lake
27 Wohlen, where OCBE at six coring sites ranged from 83% to 94% (mean 87%; Sobek et al.
28 (2012)). The third study is in 8 tropical and sub-tropical Brazilian systems, including the
29 Mascarenhas de Moraes reservoir, and OCBE varied roughly from 6 to 16% (Sikar et al.,
30 2012). These low OCBE values may be related to the sampling strategy adopted: the (one to
31 three) sites sampled in the Brazilian reservoirs were mostly located in small arms and close to

1 the shore. Sediment accumulation is typically low in these areas as compared to the deeper
2 areas (e.g. Mendonça et al. 2014). Additionally, the OCBE calculations are based on current
3 silicate settling rates, whereas historical rates were likely higher (Sikar et al. 2012) which may
4 lead to an underestimation of OCBE. The first two examples, in combination with this study,
5 reinforce that OC is buried efficiently in the sediment of man-made reservoirs and points
6 towards reservoirs as burial-prone environments. In marine systems, areas with extremely
7 high sedimentation rates, low oxygen concentrations at the bottom and a high share of
8 terrestrially-derived OC have been identified as sites of exceptionally high and efficient OC
9 burial (Hartnett et al., 1998; Burdige, 2007; Galy et al., 2007). The fact that these
10 characteristics are typical for many reservoirs (Dean and Gorham, 1998; Sobek et al., 2012)
11 likely explains why OCBE in reservoirs appears to be higher than in natural lakes.

12 The OC mineralization in the Mascarenhas de Moraes sediments (17 to 48 gC m⁻² yr⁻¹) was
13 low when compared to other freshwater systems (e.g. 15 to 198 gC m⁻² yr⁻¹ in temperate
14 lakes; (Sobek et al., 2009), especially due to the low CO₂ fluxes. The range of CO₂ fluxes (4
15 to 32 gC m⁻² yr⁻¹) corresponded to the lower end in the ranges of values reported for
16 sediments of boreal and temperate (5 to 269 gC m⁻² yr⁻¹, Gudasz et al. 2010) and of sub-
17 tropical and tropical freshwater systems (18 to 2412 gC m⁻² yr⁻¹, Cardoso et al. 2014). CO₂
18 fluxes in Mascaranhas de Moraes were similar to the rates reported for three other reservoirs
19 in the Brazilian Cerrado (mean 66 gC m⁻² yr⁻¹; (Cardoso et al., 2014)). The range of CH₄
20 fluxes from the Mascarenhas de Moraes sediments (3 to 23 gC m⁻² yr⁻¹) was low when
21 compared to a set of temperate lakes (0.2 to 46 gC m⁻² yr⁻¹, (Sobek et al., 2009). Terrestrially
22 derived sediments have been shown to be less labile and degrade more slowly than aquatic
23 derived sediments (Gudasz et al., 2012), especially under low oxygen concentrations (Sobek
24 et al., 2009). Low mineralization rates in the Mascarenhas de Moraes reservoir may, thus,
25 result from the deposition of OC-poor (mean 2.3% OC, **Table A1**) and mainly terrestrially-
26 derived sediment (see *Rivers-dam gradients*) and from short oxygen exposure times (**Table**
27 **A1**). However, we might have underestimated mineralization rates as we only included
28 diffusive CO₂ and CH₄ fluxes from the sediment and lacked an estimate of the CH₄ flux
29 through ebullition (bubbling), which is usually an important process in tropical reservoirs
30 (Bastviken et al., 2004). CH₄ bubbling mostly occurs when the OC supply to deeper sediment
31 layers is high (Sobek et al., 2012). In the case of the Mascarenhas de Moraes reservoir,
32 supersaturated CH₄ concentrations in sediment pore water were observed in 6 of 16 sites
33 (example in **Fig. A1**). This indicates that, although we have no data to reliably quantify the

1 ebullitive flux from the sites we samples, the occurrence of ebullition is likely, especially at
2 the 6 sites where CH₄ supersaturation in sediment porewater was observed. A previous study
3 in the Mascarenhas de Moraes reservoir, however, reports CH₄ emission through ebullition
4 from the water to the atmosphere to be close to zero (data from 2005 and 2006; (Ometto et al.,
5 2011). Moreover ebullition affects the sedimentary carbon budget only marginally even in
6 reservoirs with extreme ebullition (Sobek et al., 2012). We are, therefore, confident that not
7 including ebullition data does not affect the magnitude of our OCBE estimates for the
8 Mascarenhas de Moraes reservoir to any large degree, especially when considering the OCBE
9 in the whole reservoir area.

10 **4.2 OCBE driven by sediment accumulation rates**

11 According to the statistical analysis (Spearman correlation) sediment accumulation rate was
12 the most important variable, explaining 76% (only pelagic sites; $p < 0.0001$; $r = 0.76$) and 92%
13 (all sites; $p < 0.0001$; $r = 0.92$) of the OCBE variability (**Fig. 2**). Considering that OC
14 mineralization is usually most intense in the uppermost oxygenated sediment layers (e.g.
15 Hartnett et al. (1998)), it is reasonable to conclude that rapid sedimentation directly affects
16 OC burial (Burdige, 2007; Sobek et al., 2009). Sediment deposition creates a physical barrier
17 to oxygen penetration, reducing the length of time sediment particles are exposed to oxygen
18 dissolved in the pore water. Because OC mineralization is less efficient under anoxic
19 conditions (especially so for terrestrial OC; Sobek et al. (2009)), increasing sediment
20 accumulation rates implies, then, a higher increase in OC burial than in OC mineralization.

21 Our statistical analysis also focused on other factors often reported to determine OCBE in
22 aquatic systems: oxygen exposure time (Ferland et al., 2014; Sobek et al., 2009; Fenner and
23 Freeman, 2013) and OC source (for which we used $\delta^{13}\text{C}$ as a proxy; (Sobek et al., 2009;
24 Gudasz et al., 2012). Another variables potentially affecting OCBE (e.g. distance to the dam,
25 OC content and OC mineralization rates) were included as well. Temperature, which is also
26 clearly important (Gudasz et al., 2010; Cardoso et al., 2014) was not included in these
27 analysis, since variation in bottom temperatures among samplings sites was small (23 to
28 25°C) and related to daily conditions (samplings were performed within 10 days) rather than
29 to site-specific conditions.

30 Despite the documented effect of oxygen availability on OC mineralization, our analysis
31 suggests a low importance of oxygen exposure time (given by the ratio between oxygen

1 penetration depth and sediment accumulation rate) to OCBE in our data set. Probably due to
2 the narrow range of oxygen exposure times in pelagic sites, it only explained the variability in
3 OCBE when combining pelagic with marginal sites in one analyses (**Fig. 3a**). The same was
4 observed for the effect of OC sources (see “*Rivers-dam gradients*”) and OC content on OCBE
5 (**Fig. 3b, 3c**). It is likely that the large variability of sediment accumulation rate (coefficient of
6 variation of 0.7) and its strong effect on OCBE in the Mascarenhas de Moraes reservoir
7 outweighed the effect of other important variables.

8 **4.3 Rivers-dam gradients**

9 The usually high nutrient availability of fluvial inflow and the gradual decrease in turbulence
10 towards the dam lead to rivers-dam gradients of, for example, sediment accumulation rates
11 and sedimentary OC sources in reservoirs (De Junet et al., 2009). The combined effect of an
12 increase in the relative contribution of more labile autochthonous-derived OC (further
13 discussed below) and a decreasing sediment accumulation rate result in a decrease in OCBE
14 towards the dam ($p=0.01$; $r=0.69$). Thus, estimating OCBE from reservoirs based on sampling
15 of the lacustrine zone alone and neglecting the higher sedimentation in more upstream zones
16 may lead to significant underestimation of the total amount of buried OC.

17 The characterization of the OC source can be facilitated by the use of OC quality tracers (e.g.
18 C:N ratio and stable isotopic composition, which indicate the relative contribution of
19 terrestrial and autochthonous OC sources; (Meyers and Ishiwatari, 1993). There was no clear
20 trend of variation in C:N ratios along the rivers-dam axis in the Mascarenhas de Moraes
21 reservoir, possibly due to the narrow range of values found in the top sediment samples (8.7
22 to 10.8). The $\delta^{13}\text{C}$ values showed a decreasing trend, albeit only marginally significant
23 ($p=0.07$; $r=-0.53$), implying an increasing share of autochthonous OC towards the dam. The
24 non-significant correlation was obviously caused by a single outlier – low $\delta^{13}\text{C}$ (-24.4‰)
25 indicating an atypical share of autochthonous OC in an upstream site (**Fig. 4a**). This is
26 possibly caused by the occurrence of aquatic macrophytes, registered in some upstream areas
27 of the Mascarenhas de Moraes reservoir. Furthermore, there was a strong negative correlation
28 between the $\delta^{13}\text{C}$ values and the OC content of top sediment samples (**Fig. 4b**), suggesting
29 that OC increase in the Mascarenhas de Moraes sediments was indeed caused by
30 autochthonous primary production, although the higher OC concentrations near the dam may
31 also be due to a lower dilution with inorganic particles that have already settled near the river
32 inlet.

1 In spite of the important contribution of autochthonous primary production to sediment OC,
2 our data suggest that terrestrial material dominates the sedimentation in the Mascarenhas de
3 Moraes reservoir. The isotopic composition of the top sediment in all sites (-24.6 to -20.0‰)
4 is similar to that of pre-flooding terrestrial material (-23.2 to -19.8‰) and chlorophyll *a*
5 concentrations in the water are low (Rangel et al., 2012).

6 **4.4 Margin-pelagic gradients**

7 The spatial heterogeneity in sediment accumulation rates caused OCBE to vary significantly
8 between margin and pelagic zones in the Mascarenhas de Moraes reservoir ($p < 0.0001$). The
9 sites close to the margins (03, 07 and 10) had the lowest sediment accumulation rates (and,
10 thus, OC burial rates) due to the intense wind and water current driven resuspension causing
11 sediment focusing (see Mendonça et al. (2014)). Mineralization rates in these sites, though,
12 did not differ from the pelagic area ($p = 0.36$), resulting in much lower site-specific OCBE
13 (**Table 1**). Because of focusing, sediment deposited at the margins is usually considered
14 transient storage (Blais and Kalff, 1995; Davis and Ford, 1982), and in this case, the
15 calculated OCBE may not reflect the efficiency of long-term OC burial at those sites. It has
16 been shown, though, that neglecting the characteristics of marginal sediment may lead to
17 large errors on whole-lake carbon fluxes estimations, even when integrative methods for total
18 sediment accumulation rates (e.g. bathymetry surveys) are used (Rippey et al., 2008; Mackay
19 et al., 2012).

20 The sediment in the three sites close to the Mascarenhas de Moraes margins had lower OC
21 and organic matter contents, lower porosity and higher $\delta^{13}\text{C}$ when compared to the three
22 adjacent pelagic sites ($p < 0.05$ for all variables, **Table A1**). Even though the marginal sites are
23 located within the downstream half of the reservoir (**Fig. 1**), their sediment characteristics
24 were only similar to those of the furthest upstream site (i.e. under higher influence of the
25 terrestrial fluvial inputs; site 16; **Table A1**). This may be explained by the fact that marginal
26 sediments receive more soil material from bank erosion, but possibly also by the fact that a
27 higher fraction of deposited autochthonous organic matter in the marginal sediments is
28 mineralized (probably due to higher oxygen exposure, **Table A1**), leading to more OC-
29 depleted and ^{13}C -enriched sediments. It suggests that even though the sediment deposits close
30 to the margins are small and transient, marginal OC is probably highly resistant to
31 mineralization (Gudasz et al., 2012). Indeed, mineralization rates in the margins of the
32 Mascarenhas de Moraes reservoir were not higher than those in pelagic sites even though the

1 marginal environment is more favourable to mineralization (e.g. higher exposure to oxygen).
2 Thus, if marginal sediment is transported to pelagic regions (where oxygen exposure time is
3 much smaller), it tends to be efficiently buried at those sites. Then, regardless of the final
4 accumulation site (marginal or pelagic zone), the sediment at the margins should not be
5 disregarded.

6 **4.5 Integrative analysis of OCBE**

7 Our data show that the variability in sediment accumulation rates both along the rivers-dam
8 axes (due to gradual decrease in water sediment transport capacity) and the margin-pelagic
9 axes (due to sediment focusing) ultimately determine the spatial heterogeneity of OCBE.
10 Thus, neglecting the higher sedimentation in deltaic zones and the lower sedimentation in
11 marginal zones may lead to significant underestimation of the fraction of OC buried in
12 reservoirs. The strong predictability of OCBE based on sediment accumulation rate (**Fig. 2**),
13 permits the use of whole-reservoir sediment accumulation rate (0.51 cm yr^{-1} , from a seismic
14 survey; see Mendonça et al. (2014) to estimate the integrative OCBE in Mascarenhas de
15 Moraes. This analysis shows that 57% of the total OC deposited into the Mascarenhas de
16 Moraes sediments are buried while the remaining 43% are mineralized. The estimate based on
17 the whole-reservoir OC burial rate (Mendonça et al., 2014) and the average mineralization
18 rate resulted in a similar integrative OCBE in the Mascarenhas de Moraes reservoir – 55%.
19 The extrapolation based on the OCBE at the pelagic sites, i.e. not applying any whole-basin
20 integrative analysis, would result in an overestimation of 15 to 18% (mean OCBE of 67% in
21 pelagic sites).

22 The 43% of the deposited OC that is mineralized in the MSM sediments may contribute to the
23 CO_2 and CH_4 emissions to the atmosphere. Particularly, the share emitted as CH_4 represents a
24 potential impact of dams on global warming when compared to the previous fluvial
25 environment. Importantly, this impact cannot be estimated based on our data, which only refer
26 to the carbon balance of the sediment, since a considerable portion of the CH_4 produced in the
27 sediment may be oxidized before reaching the atmosphere (Guerin and Abril, 2007).
28 However, as part of the OC burial may alleviate emissions, our robust account of OCBE adds
29 important information to the current knowledge about the net GHG emissions from
30 hydroelectric reservoirs.

1 This is the first reservoir-wide OCBE assessment that we know of. A similar approach has
2 been used in natural boreal lakes, most of which showed integrative OCBE of 5% to ~40%
3 (only one lake had OCBE of 62%; Ferland et al. (2014)). The high sedimentation rates in
4 some areas of the sub-tropical Mascarenhas de Moraes reservoir resulted in a higher
5 integrative OCBE than in the boreal lakes, despite the negative effect of temperature on OC
6 burial (Gudasz et al., 2010; Cardoso et al., 2014). The boreal lakes' assessment suggested that
7 integrative OCBE can be predicted based on lake area and shape, with small lakes acting as
8 more efficient carbon sinks than large ones (Ferland et al., 2014). Lake models for OC burial,
9 however, are not applicable to large reservoirs (Stallard, 1998; Clow et al., 2015) due to their
10 distinct characteristics (for example, reservoirs have higher share of terrestrial OC but lower
11 sediment OC concentrations and higher and more heterogeneous sedimentation rates).
12 Therefore, the actual effect of damming rivers on the fate of terrestrial OC, which depends on
13 the OC burial efficiency of reservoirs as compared to downstream environments, is currently
14 largely unknown, even though our data suggest that reservoirs tend to bury OC more
15 efficiently than natural lakes.

16

17

1 **Appendix A: Table A1**

2 Table A1. Water column depth (WCD) and characteristics of post-flooding sediment (top 2
 3 cm and mean) and oxygen exposure time in sediment (OET). Note that at site 11 sediment
 4 accumulation was zero. Sites close to the margin (M) and in the pelagic zone (P) in the same
 5 transects perpendicular to the river-dam transect are boldfaced. Numbering started at the dam
 6 (i.e. site 16 is furthest away from the dam; see Fig. 1).

7

Site number (type)	WCD (m)	OC (%)		$\delta^{13}\text{C}$ (‰)		C/N		Porosity \emptyset		OET (yr)
		2cm	Mean	2cm	Mean	2cm	Mean	2cm	Mean	
01 (P)	40	3.1	2.6	-24.0	-22.7	8.7	9.6	0.74	0.61	0.5
02 (P)	38	3.1	2.7	-24.4	-22.4	9.5	11.2	0.61	0.48	0.7
03 (M)	13	1.8	1.8	-21.9	-21.9	10.8	10.8	0.26	0.26	8.1
04 (P)	30	3.4	2.6	-24.6	-21.3	9.7	9.9	0.80	0.61	0.7
05 (P)	22	3.3	2.9	-24.4	-23.3	9.1	9.7	0.72	0.60	1.2
06 (P)	39	3.1	3.1	-24.2	-21.0	8.9	11.2	0.77	0.60	0.7
07 (M)	8	2.5	2.5	-20.9	-20.9	9.6	9.6	0.48	0.48	13.5
08 (P)	26	2.8	2.1	-23.2	-19.8	9.6	10.9	0.75	0.48	1.0
09 (P)	30	2.7	2.4	-23.1	-22.1	9.6	10.0	0.71	0.52	0.7
10 (M)	10	2.0	1.9	-21.9	-21.7	9.9	10.6	0.41	0.36	14.9
11 (P)	5									
12 (P)	10	3.0	2.7	-23.9	-22.0	8.8	9.7	0.52	0.31	0.4
13 (P)	20	2.7	2.2	-22.9	-20.1	10.1	12.1	0.68	0.45	0.5
14 (P)	24	2.8	2.1	-23.4	-20.6	9.6	11.2	0.57	0.33	0.5
15 (P)	10	2.8	2.1	-24.4	-21.8	9.9	11.8	0.55	0.28	0.5
16 (P)	2	1.4	1.2	-21.9	-20.2	9.1	11.3	0.23	0.15	0.8

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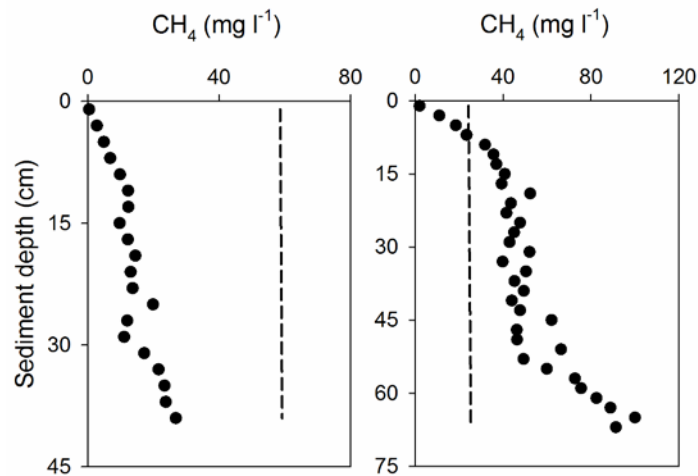
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2 Appendix B: Figure A1



3

4 Figure A1. Example of CH₄ profiles from two coring sites showing the absence (site 01) and
5 the presence (site 12) of CH₄ supersaturation in the sediment pore water. The dots represent
6 measurements of CH₄ concentration in pore water and the dashed lines represent the
7 calculated CH₄ saturation concentration. Saturation concentration (i.e. the maximum
8 concentration that dissolves in water, above which bubbles are formed) was calculated based
9 on pressure and temperature along the sediment profile.

10

11 Authors Contributions

12 R. Mendonça, S. Kosten and F.Roland planned the manuscript and designed the sampling
13 strategy. R. Mendonça, C.H.D. Estrada, S. Kosten and S.J. Cardoso did the field work. R.
14 Mendonça and M.P.F. Barros carried out laboratory analysis. R. Mendonça, S. Sobek, S.
15 Kosten and S.J. Cardoso carried out data analysis. All authors contributed to writing the
16 manuscript.

17

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4

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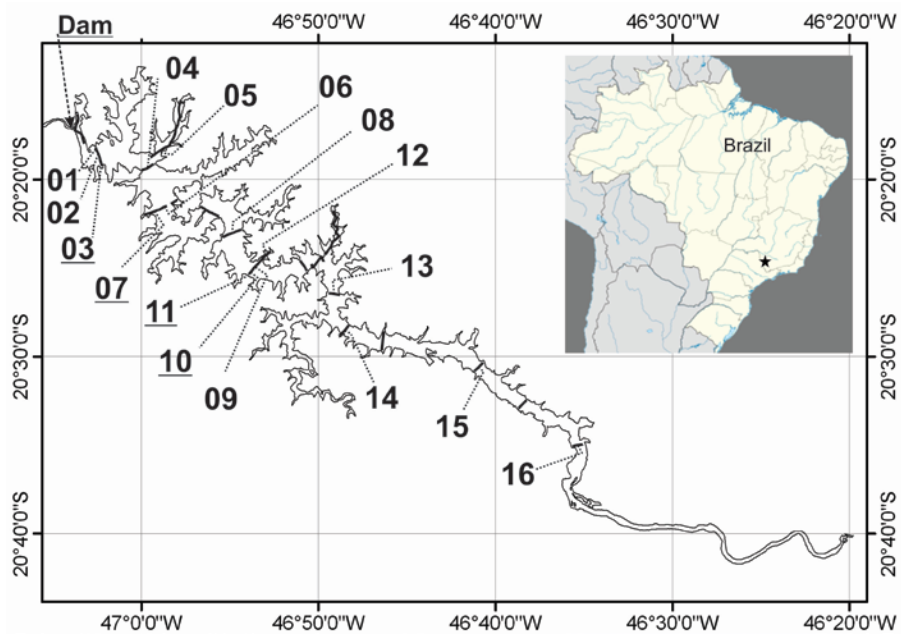
1 Table 1. Sediment accumulation rate (SAR), OC burial, OC mineralization, OC gross
 2 sedimentation (OCS) and OC burial efficiency (OCBE) at each of the sampling sites in
 3 Mascarenhas de Moraes. Sites close to the margin (M) and in the pelagic zone (P) in the same
 4 transects perpendicular to the river-dam transect are boldfaced. Numbering started at the dam
 5 (i.e. site 16 is furthest away from the dam; see Fig. 1).

Site number (type)	SAR (cm yr ⁻¹)	OC burial (gC m ⁻² yr ⁻¹)	OC Mineralization (gC m ⁻² yr ⁻¹)			OCS (gC m ⁻² yr ⁻¹)	OCBE (%)
			CO ₂ flux	CH ₄ flux	Total		
01 (P)	0.56	34.4	30.4*	7.0	37.4	71.8	47.9
02 (P)	0.81	56.0	30.4	15.8	46.2	102.2	54.8
03 (M)	0.04	3.1	4.1	16.9	21.0	24.1	12.9
04 (P)	0.41	37.7	21.4	16.2	37.6	75.3	50.0
05 (P)	0.41	31.9	26.7	5.6	32.3	64.2	49.7
06 (P)	0.74	58.2	11.4	5.3	16.7	75.0	77.7
07 (M)	0.04	3.3	27.2	4.7	31.9	35.1	9.3
08 (P)	1.15	92.9	18.0	4.2	22.1	115.0	80.8
09 (P)	0.85	60.3	31.9	8.3	40.2	100.5	60.0
10 (M)	0.07	7.4	29.9	5.6	35.5	42.9	17.3
11 (P)	0.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
12 (P)	1.81	209.4	22.3	23.3	45.6	255.0	82.1
13 (P)	0.85	69.8	29.9	13.1	43.0	112.8	61.9
14 (P)	1.56	141.1	18.8	3.3	22.1	163.2	86.5
15 (P)	1.37	140.2	22.3	13.0	35.3	175.5	79.9
16 (P)	1.00	102.5	23.1	25.2	48.2	150.8	68.0

6 *CO₂ flux was not measured at site 01; it was considered as the same as at the closest site, 02.

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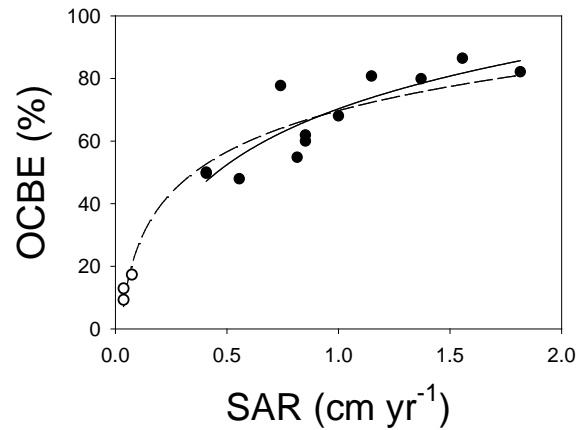
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Figure 1. Location of the Mascarenhas de Moraes reservoir (black star in the map of Brazil), its dam and the sampling sites. Underlined numbers correspond to sites located on the margins; other numbers correspond to pelagic sites.

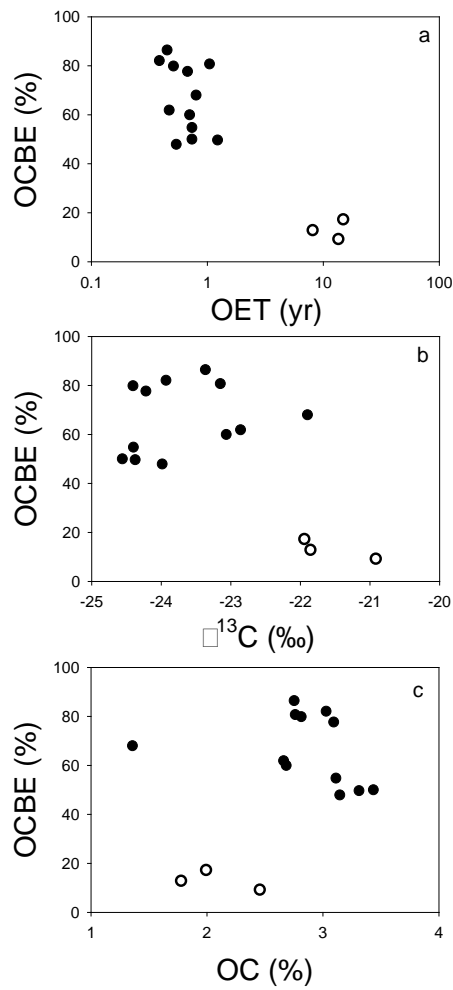
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2

3 Figure 2. Relationship between OC burial efficiency (OCBE) and sediment accumulation rate
4 (SAR) in Mascarenhas de Moraes. Open circles correspond to sites close to the margins and
5 closed circles correspond to pelagic sites. The dashed line represents the logarithmic
6 regression for all sites: $OCBE = 19.0\ln(SAR) + 69.7$; $R^2=0.92$; $p<0.0001$; $n=15$. The solid line
7 represents the logarithmic regression for pelagic sites only: $OCBE = 25.8\ln(SAR) + 70.3$;
8 $R^2=0.76$; $p<0.0001$; $n=12$.

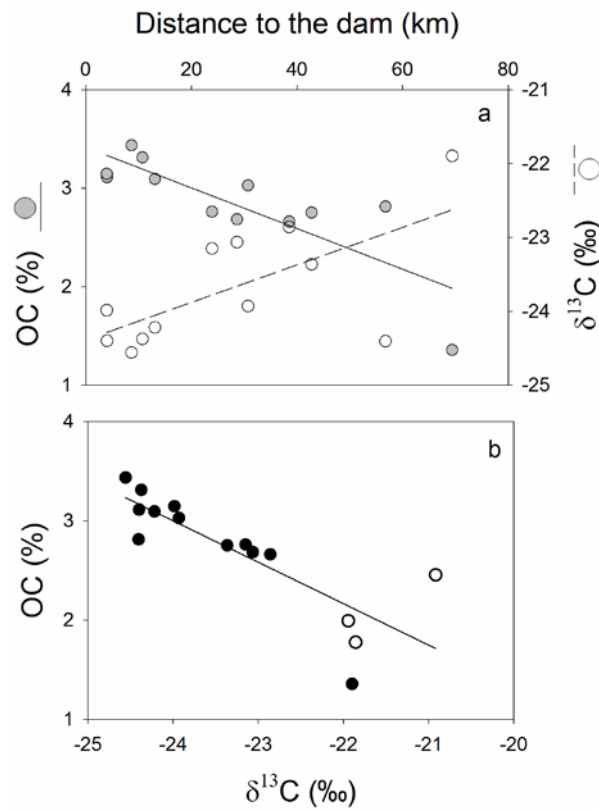
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2 Figure 3. Relationships between OC burial efficiency (OCBE) and a) oxygen exposure time
 3 (OET), b) OC isotopic composition of top sediment ($\delta^{13}\text{C}$) and c) OC content in the top
 4 sediment. In all cases, the analysis of pelagic sites alone (closed circles) resulted in non-
 5 significant correlations (Spearman; OET: $r=-0.47$, $p=0.12$; $\delta^{13}\text{C}$: $r=-0.30$, $p=0.33$; OC: $r=-$
 6 0.53 , $p=0.07$). If margin sites (open circles) are included, the correlation between OCBE and
 7 OET becomes significant ($r=-0.72$, $p=0.002$).

8



1

2 Figure 4. a) Variation in OC content (%) and OC isotopic composition ($\delta^{13}\text{C}$, ‰) of top
 3 sediment of pelagic sites related to the distance to the dam. The lines represent the linear trend
 4 of variation for OC (solid line, gray circles) and for $\delta^{13}\text{C}$ (hashed line, white circles).
 5 Spearman correlation coefficient for OC was $r = 0.81$ ($p < 0.001$) and for $\delta^{13}\text{C}$ was $r = -0.53$
 6 ($p = 0.07$). b) Relationship between OC content and OC isotopic composition ($\delta^{13}\text{C}$) of top
 7 sediment in all sampling sites. Open circles correspond to sites by the margins and closed
 8 circles correspond to pelagic sites. The solid line represents the linear trend of variation for all
 9 sites. Correlation between these variables was strong ($r = -0.90$, $p < 0.0001$).

10