



Cite this: *Environ. Sci.: Processes Impacts*, 2021, 23, 1542

## Insights into the factors influencing mercury concentrations in tropical reservoir sediments†

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Thousands of dams are currently under construction or planned worldwide to meet the growing need for electricity. The creation of reservoirs could, however, lead to conditions that promote the accumulation of mercury (Hg) in surface sediments and the subsequent production of methylmercury (MeHg). Once produced, MeHg can bioaccumulate to harmful levels in organisms. It is unclear to what extent variations in physical features and biogeochemical factors of the reservoir impact Hg accumulation. The objective of this study was to identify key drivers of the accumulation of total Hg (THg) in tropical reservoir sediments. The concentration of THg in all analyzed depth intervals of 22 sediment cores from the five contrasting reservoirs investigated ranged from 16 to 310 ng g<sup>-1</sup> ( $n = 212$ , in the different sediment cores, the maximum depth varied from 18 to 96 cm). Our study suggests reservoir size to be an important parameter determining the concentration of THg accumulating in tropical reservoir sediments, with THg ranging up to 50 ng g<sup>-1</sup> in reservoirs with an area exceeding 400 km<sup>2</sup> and from 100 to 200 ng g<sup>-1</sup> in reservoirs with an area less than 80 km<sup>2</sup>. In addition to the reservoir size, the role of land use, nutrient loading, biome and sediment properties (e.g., organic carbon content) was tested as potential drivers of THg levels. The principal component analysis conducted suggested THg to be related to the properties of the watershed (high degree of forest cover and low degree of agricultural land use), size and age of the reservoir, water residence time and the levels of nutrients in the reservoir. A direct correlation between THg and tested variables was, however, only observed with the area of the reservoir.

Received 19th April 2021  
Accepted 17th August 2021

DOI: 10.1039/d1em00156f

rsc.li/epsi

### Environmental significance

The creation of hydroelectric reservoirs is well known to alter the biogeochemical cycle of mercury (Hg) and to potentially enhance the accumulation of Hg within the reservoirs. Although many of the currently constructed and planned reservoirs are located in South America, few studies have focused on the accumulation of Hg in tropical reservoirs. In this study we show the size of the reservoir to be a critical driver of the concentrations of total Hg in tropical reservoir sediments. In addition to the reservoir size, our study suggests that factors such as the nutrients levels in the reservoirs and the degree of forest cover around the reservoir could play a role in the levels of total Hg accumulating in the sediments.

## 1. Introduction

Hydroelectricity is the oldest renewable energy source and today accounts for around 80% of the renewable energy produced worldwide.<sup>1–3</sup> With the global need for energy growing, extensive hydroelectricity expansion is currently underway.<sup>4</sup> Construction of reservoirs and dams is, however, associated with substantial environmental costs, such as biodiversity loss,<sup>5,6</sup> fish migration,<sup>5</sup> increased emissions of greenhouse gases,<sup>7,8</sup> and the

potential for increased contaminant exposure, including exposure to mercury (Hg).<sup>9–11</sup>

The accumulation of Hg in aquatic systems poses a threat to biota and to human health, particularly when it is transformed to methylmercury (MeHg), a highly toxic form of Hg that bioaccumulates and biomagnifies in aquatic food webs.<sup>12,13</sup> Several studies have demonstrated elevated concentrations of Hg in fish from constructed reservoirs in comparison to the concentrations found in unperturbed rivers and natural lakes.<sup>14</sup> The effects observed, however, vary greatly between systems and with time. In recently impounded reservoirs, flooding of the landscape typically results in a greater flux of Hg and organic matter (OM) to the reservoir water column.<sup>15,16</sup> In combination with decreased flow rates, increased inputs of OM lead to a greater accumulation of material, including OM and Hg, in reservoir sediments. Increased deposition of OM tends to result in oxygen depletion towards bottom waters and conditions

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/d1em00156f



favorable for the microbial methylation of Hg to MeHg.<sup>14,17,18</sup> During the operation of the reservoir, water level fluctuations may continue to promote Hg methylation due to changing redox conditions.<sup>16,18,19</sup> Such redox shifts result in, *e.g.*, the oxidation of sulfur, which enhances the activity of sulfate-reducing bacteria, including Hg methylators.<sup>20,21</sup>

Although many of the planned and newly constructed reservoirs are located in Brazil and other parts of South America,<sup>4</sup> there is a lack of studies on the accumulation of Hg in tropical reservoirs. Thus, the cycling of Hg and reservoir features explaining differences in the accumulation between systems are poorly understood. Here, we have studied sediment cores from five Brazilian reservoirs with contrasting features in order to identify and discuss potential key drivers for the THg levels in tropical reservoir surface sediments. Using generated data from these five reservoirs and previously published data from other tropical reservoirs, THg in the surface sediments of the different reservoirs was then tested as a function of physical reservoir features (*e.g.*, reservoir size, trophic status and catchment land use and biome) and ancillary parameters, such as: total organic carbon content (TOC), total nitrogen (TN), the TOC/TN ratio and the  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  isotopic signatures.

## 2. Material and methods

### 2.1 Study area and sample collection

In total, 22 sediment cores were collected from the five reservoirs, Curuá-Una (CUN,  $n = 4$ ), Monte Serrat, Bonfante and Santa Fé (MBS,  $n = 3$ ), Chapéu D'Uvas (CDU,  $n = 5$ ), Furnas (FNS,  $n = 3$ ) and Funil (FUN,  $n = 7$ ; Fig. 1 and Table S1†). The MBS reservoirs consist of a cascade system with three dams located in the Paraíba river.<sup>22</sup> The physical and hydrological features of the reservoirs are presented in Table 1. Details of the sampling have been described elsewhere.<sup>8,22</sup> Briefly, the sediment cores were collected during the dry season in 2015 (July, September and October) and 2017 (July and October) at accumulation bottoms in transects (for CUN, CDU, FNS and FUN) from the inflow of the main river to the dam. Sediment cores were obtained using a gravity corer equipped with a hammer (6 cm internal diameter, UWITEC, Mondsee, Austria) and then sliced in intervals of three or six cm (information of the depth intervals used in this study are presented in Table S1†).<sup>23</sup> The resulting samples ( $n = 212$ ) were dried at 40 °C, homogenized using a mortar and pestle, sieved through 72  $\mu\text{m}$ , and placed in airtight plastic bags until analysis. This drying procedure has

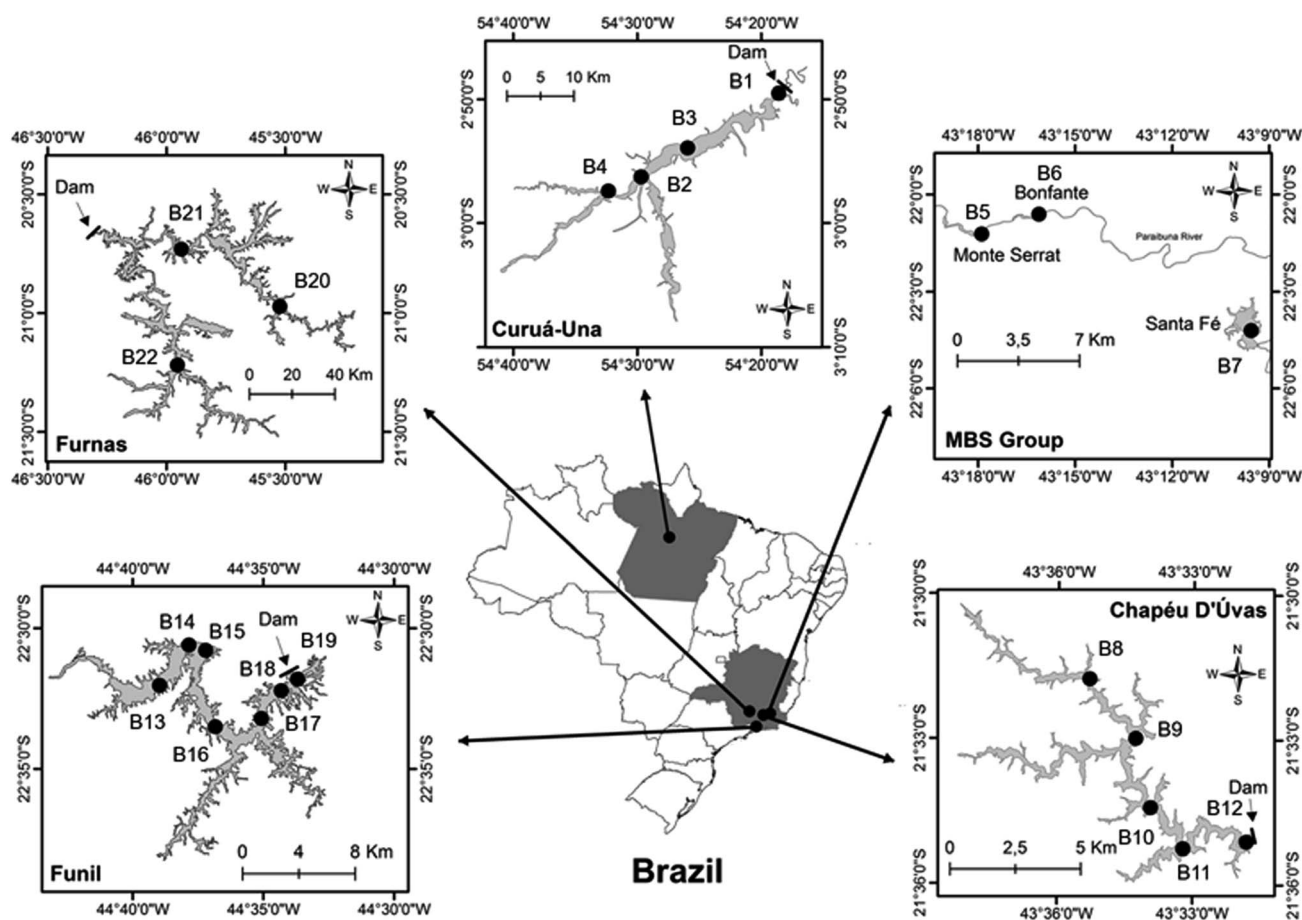


Fig. 1 Location of the reservoirs Curuá-Una (CUN), Monte Serrat, Bonfante and Santa Fé (MBS), Chapéu D'Uvas (CDU), Furnas (FNS), and Funil (FUN). The gray areas indicate the state of Pará (north Brazil), and the state of Minas de Gerais and Rio de Janeiro (southeast Brazil). The cores were labelled as B and numbered from 1 to 22 in each reservoir.



**Table 1** Description of the reservoirs including their location, physical and hydrological features (area, water residence time, maximum depth and annual precipitation), reservoir age and use, nutrient status (trophic state) and information of the surrounding area (type of surrounding, biome of the region and anthropogenic influences)

Features	CDU <sup>22,25,26</sup>	CUN <sup>8,22,27</sup>	FUN <sup>22,28,29</sup>	FNS <sup>30–32</sup>	MBS <sup>22,33</sup>
Location (state in Brazil)	Minas Gerais	Pará	Rio de Janeiro	Minas Gerais	Minas Gerais bordering Rio de Janeiro
Surrounding area	Urban	Forest	Urban	Urban	Urban
Main river	Paraibuna	Curuá Una	Paraíba do Sul	Grande	Paraibuna
Year of damming	1994	1977	1969	1963	2008 and 2009
Reservoir age (time between damming and sampling)	21	40	46	52	8 and 7
Mean area (km <sup>2</sup> )	12	72	35	1342	0.3, 0.2 and 2
Water residence time (days)	716	30	20	511	Unknown
Maximum depth (m)	41	19.5	60	127	15, 10 and 25
Annual precipitation (mm per year)	1443	1750	1337	1126	1600
Biome	Atlantic forest	Amazon	Atlantic forest	Savanna	Atlantic forest
Trophic state	Oligotrophic	Oligotrophic	Eutrophic	Mesotrophic, and eutrophic	Mesotrophic
Activities and anthropogenic influence	Domestic effluents, deforestation	Artisanal gold mining, vegetation burning, other mining, deforestation	Industrial, agriculture and domestic effluents, deforestation, fish farming	Agricultural (coffee, potatoes, corn), sewage discharge, fish farming	Domestic, industrial effluents (textile, tannery)
Reservoir use(s)	Water supply	Electricity	Electricity, aquaculture, water supply	Electricity, irrigation, industry supply	Electricity

previously been shown to not alter the THg concentrations, but to be problematic for the determination of MeHg.<sup>24</sup>

## 2.2 Sample analysis

**2.2.1 Determination of THg concentration.** The concentration of THg in sediments was analyzed through thermal decomposition followed by pre-concentration of Hg on a gold trap and cold vapor and Hg detection by atomic absorption spectrophotometry (CV-AAS) using a Milestone Direct Mercury Analyzer (DMA-80).<sup>34</sup> The concentration of THg was determined for all the sediment depth intervals collected ( $n = 212$ , Table S1†), as well as for a subset of samples where the fine-grained fractions ( $<72 \mu\text{m}$ ) were extracted ( $n = 43$ ). For the quality control, an in-house sediment reference material with a previously determined THg concentration of  $210 \pm 10 \text{ ng g}^{-1}$  was used. The observed mean and standard deviation (SD) concentration of this in-house reference sediment material was  $213 \pm 8.2 \text{ ng g}^{-1}$  (relative standard deviation (RSD) of 3.8%, relative error of 1.6%,  $n = 21$ ). In a separate study, in which the THg concentration of the in-house reference sediment material measured was  $212 \pm 6.4 \text{ ng g}^{-1}$ , the accuracy of the analysis was also validated with a commercially available reference sediment material (NIST2702, measured THg:  $432 \pm 10 \text{ ng g}^{-1}$ , certified THg:  $447.4 \pm 6.9 \text{ ng g}^{-1}$ ). Randomly selected samples ( $n = 12$ ) were analyzed in triplicate (RSD ranged from 1.2 to 3.7%). Blanks were measured ( $n = 30$ ) and limit of detection ( $3 \times \text{SD}$ ) was calculated to  $0.2 \text{ ng}$ . In comparison, the amount of THg detected in samples ranged from 1.1 to 36 ng.

**2.2.2 Ancillary parameters.** Surface sediment samples ( $<12 \text{ cm}$ ) were analyzed for TOC, TN and for their  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  isotopic signatures (Table S2†). In addition, TOC/TN ratios were calculated. TOC and TN content and their isotopic composition ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ) were analyzed at the UC Davis Stable Isotope Facility using an elemental analyzer interfaced to a continuous flow isotope ratio mass spectrometer. Approximately 10 to 15 mg of prepared sample material were weighed in silver capsules, then 50  $\mu\text{l}$  Milli-Q water and 100  $\mu\text{l}$  of HCl 12 M were added. The samples were left overnight in a desiccator to remove the carbonates and then dried in an oven at  $60 \text{ }^\circ\text{C}$  before being sent out for analysis. In addition, loss on ignition (LOI) was carried out on sediments from the CUN reservoir to assess the organic matter content in the deeper sediment layers by combusting the samples at  $550 \text{ }^\circ\text{C}$  for 4 h.<sup>35</sup>

## 2.3 Statistical analysis

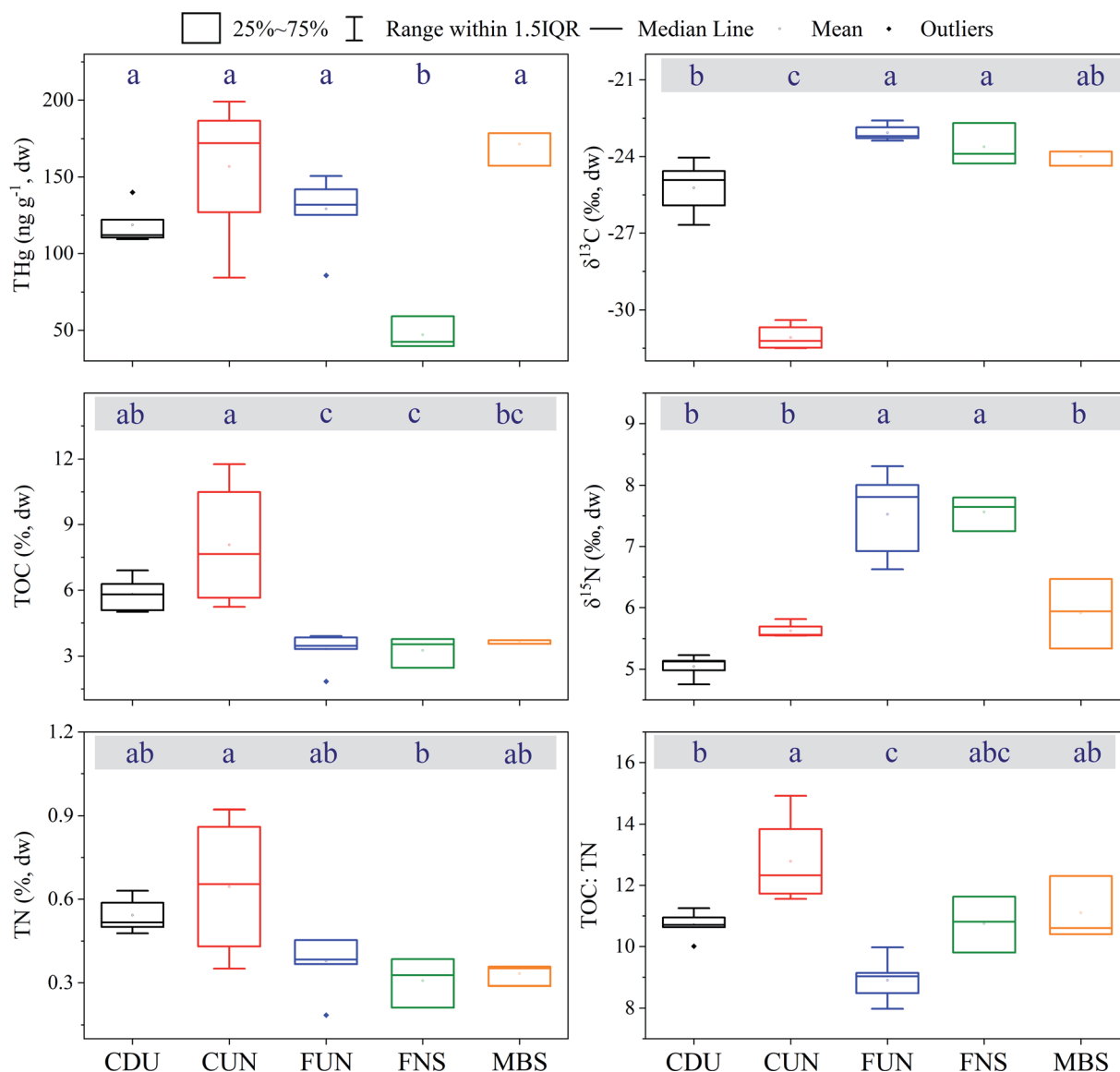
All statistical analyses and plots were done using JMP Pro 15 and Origin 2020, respectively. The distribution of the data was tested using the Anders–Darling test (with normal distribution rejected when  $p < 0.05$ ). When testing the entire dataset of THg ( $n = 212$ ) normal distribution was rejected. Depth-weighted concentration of HgT, TOC:TN ratio,  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  ( $n = 22$ ) was deemed to be normally distributed while TOC and TN were deemed to have a lognormal distribution. One-way ANOVA tests were carried out to test for statistically significant differences of HgT, TOC:TN ratio,  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , TOC and TN between the five reservoirs (using depth-weighted data and log transformed



depth-weighted data for TOC and TN). Pairwise post-hoc tests were then done using the Tukey–Kramer HSD test. All further statistical data analyses were conducted using non-parametric methods (no log transformation of the data was done for these tests). Correlation between variables was tested using the Spearman ranked correlation ( $\rho$ ) test (Tables S2 and S4†). All reported concentrations of THg and the ancillary parameters are presented as median  $\pm$  IQR (interquartile range).

A principle component analysis (PCA) was performed by combining the chemical and physical data of the five reservoirs in this study (Table 1) with those of the five reservoirs (Tucuruí, Samuel, Manso, Itaipú, and Ribeirão das Lajes, Table S5†) included in the review by Pestana *et al.*<sup>36</sup> to identify drivers between reservoirs and variables and to explore their

correlations and influence on THg concentrations. The number of variables included in the analysis was limited to 9 ( $n - 1$ ,  $n$  being the number of reservoirs). Mean concentrations of THg and content of TOC were calculated in each reservoir. The trophic state (nutrient levels) was converted to a trophic state index variable ranging from 1 to 5, where 1 is considered to be oligotrophic, 3 is mesotrophic and 5 is eutrophic. Visual inspection of satellite images was performed to identify major land use patterns around each reservoir. From this inspection, the density of agriculture and forest was assessed and scored from 0 (minor land use), 0.5 (*ca.* 50% of the land use) to 1 (dominant land use). Tropical status and the density of agriculture and forest were treated as continuous variables in the PCA. The PCA was performed using data from 10 reservoirs and



**Fig. 2** Boxplots of depth-weighted concentrations in surface sediments (<12 cm) of THg, content of total organic carbon (TOC) and total nitrogen (TN), isotopic compositions of  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$ , and TOC:TN ratios in the reservoirs Curuá-Una (CUN), Monte Serrat, Bonfante and Santa Fé (MBS), Chapéu D'Uvas (CDU), Furnas (FNS), and Funil (FUN). All concentrations or isotopic compositions are presented as per dry weight (dw) of the sediments. Letters represent the results of pairwise comparisons using Tukey–Kramer HSD and indicate significant differences in concentrations and content among the reservoirs. Reservoirs with different letters are significantly different at the 0.05 significance threshold.



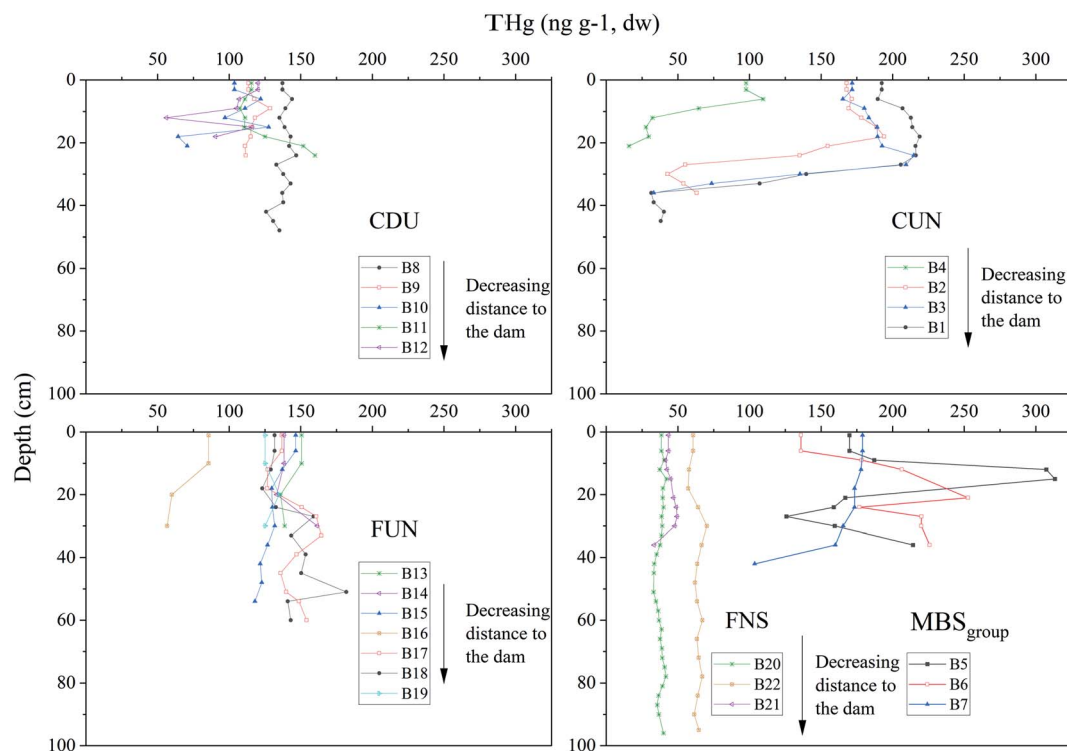


Fig. 3 Vertical profiles of THg concentrations (dry weight, dw) in sediment cores from the reservoirs: Curuá-Una (CUN), Monte Serrat, Bonfante and Santa Fé (MBS), Chapéu D'Uvas (CDU), Furnas (FNS), and Funil (FUN).

the following 9 variables: THg, TOC, age and area of reservoir, maximum depth, trophic state index, water residence time, agriculture cover, and forest cover. A separate PCA was performed that also included biome as a variable (Fig. S4†). To avoid scaling effects, the data was standardized by subtracting the mean and dividing by the standard deviation for each value of each feature (*Z*-score). To maximize the loadings of the variables, a varimax rotation was applied, and the selection of the number of components was based on eigenvalues <1. Two-dimensional charts, *i.e.*, biplots, were constructed (Fig. 4 and S4†) and the relationship between variables was evaluated. Correlation between variables in this data set was tested using the Spearman ranked correlation ( $\rho$ ) test (Table S6†). To test the potential of THg concentration to overfit the model, another PCA was performed excluding THg concentrations.

## 3. Results

### 3.1 Ancillary parameters

The content of TOC and TN in the analyzed surface sediments ranged from 1.84 to 11.8% ( $4.9 \pm 3.1\%$ ,  $n = 49$ ), and from 0.18 to 0.92% ( $0.45 \pm 0.23\%$ ,  $n = 49$ ), respectively (Tables S2 and S3† and Fig. 2). When comparing depth-weighted TOC and TN, differences were observed between the reservoirs (TOC: CUN > FUN, FNS and MBS, CDU > FUN and FNS, TN: CUN > FUN). Calculated TOC/TN ratios ranged from 8.0 to 15.1 ( $11 \pm 1.6$ ,  $n = 49$ ). The isotopic composition of  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  in the analyzed depth sections ranged from  $-31.5$  to  $-22.6\text{‰}$  and from 4.8 to 8.3‰, respectively, with a more depleted signature of  $\delta^{13}\text{C}$

found in CUN ( $-31.2 \pm 0.8\text{‰}$ ,  $n = 4$ , for CUN, in comparison to  $-23.2 \pm 0.4\text{‰}$  to  $-24.9 \pm 1.3\text{‰}$  in the other reservoirs). For the  $\delta^{15}\text{N}$  signature, more enriched signals were found in FUN ( $7.8 \pm 1.1\text{‰}$ ,  $n = 7$ ) and FNS ( $7.6 \pm 0.5\text{‰}$ ,  $n = 3$ ) in comparison to the other three reservoirs (CDU:  $5.1 \pm 0.2\text{‰}$ ,  $n = 5$ , CUN:  $5.6 \pm 0.1\text{‰}$ ,  $n = 4$ , MBS:  $5.9 \pm 1.1\text{‰}$ ,  $n = 3$ ). There are significant correlations among the proxies  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , TOC, TN and the TOC/TN ratios (Table S4†).

### 3.2 Distribution of THg in reservoir sediments

The concentrations of THg in sediments (Fig. 2) ranged from 40 to 199  $\text{ng g}^{-1}$  ( $126 \pm 44$ ,  $n = 22$ ) in the upper 12 cm of the sediment cores, and from 16 to 310  $\text{ng g}^{-1}$  ( $130 \pm 96$ ,  $n = 212$ ) in all analyzed depth intervals (in the different sediment cores, the maximum depth varied from 18 to 96 cm). In most of the cores, the concentration of THg remained fairly constant with depth (relative percentage range of <50%) compared to the variability observed between cores (relative percentage range of 120%, Fig. 3 and S1†). In some of the cores (from MBS and CDU), however, concentrations of THg peaked at sediment depths of 10 to 18 cm. For the cores collected at CUN, lower concentrations of THg were also observed in the deeper layers of the cores (>24 cm). For the top 12 cm, lower concentrations of THg were observed in FNS compared to the other reservoirs (Fig. 2). For a subset of the samples, where the fine-grained (<72  $\mu\text{m}$ ) fraction of the sediments was also analyzed, a close to 1 : 1 relationship was observed between the THg concentrations in bulk and the fine-grained fraction ( $R^2 = 0.97$ ,  $n = 43$ , Fig. S2†).



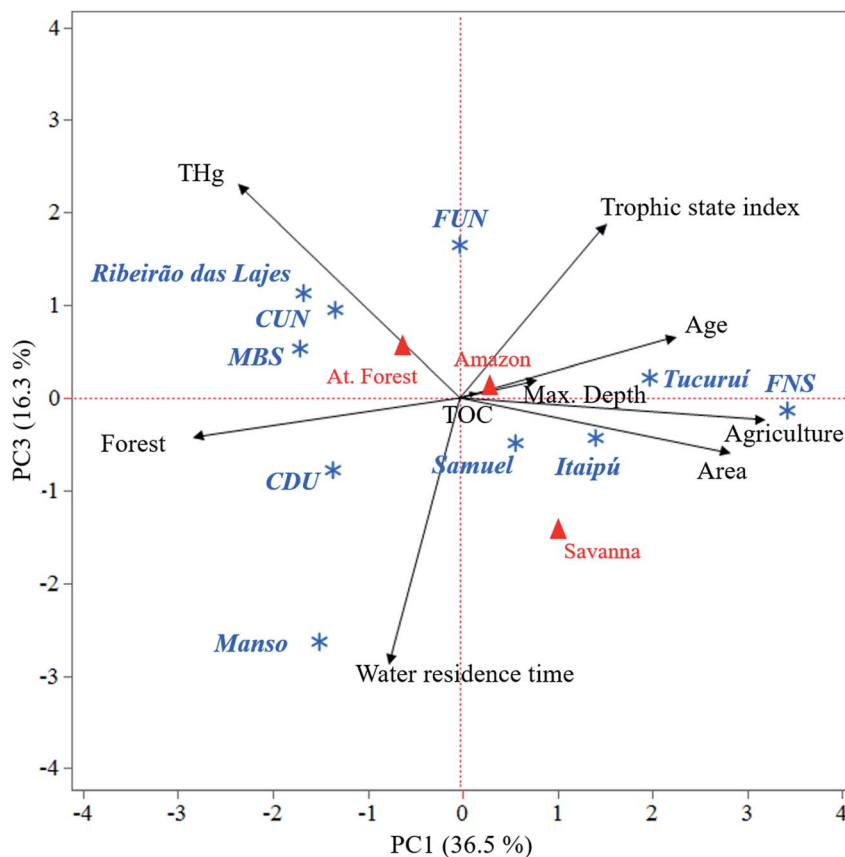


Fig. 4 Principal component biplot showing PC scores of the reservoirs (blue asterisks), type of biome (red triangles), and loading of the variables (black arrows) for component 1 (PC1) and component 3 (PC3). Max. depth: maximum depth; age: reservoir age; area: reservoir area; agriculture: cover of agriculture as land use; forest: cover of forest as land use; TOC: total organic carbon; water residence time; THg; At. forest: Atlantic forest biome; Amazon: Amazon biome; Savanna: Savanna biome; reservoirs: FNS – Furnas, FUN – Funil, CUN – Curuá Uná, CDU – Chapeú D'Uvas, and MBS – Monte Serrat, Bonfante, and Santa Fé. Information from the reservoirs Tucuruí, Itaipú, Samuel, Manso and Ribeirão das Lajes were collected from Pestana *et al.*<sup>36</sup> and other earlier studies (Table S5†).

The concentration of THg increased with increasing concentrations of TOC and TN (including the top 12 cm of the sediment, Table S4†). There was no clear trend (*i.e.* change in concentration) when visually inspecting the depth-weighted concentration of THg (for the upper 20 cm of the sediments) within each reservoir as a function of the distance from the constructed dams (Fig. S3†).

### 3.3. Grouping according to PCA

The PCA resulted in three significant components (eigenvalues > 1) accounting for 76.3% of the total variance of the data set. The first component (PC1, physical features, Fig. 4) explained 36.5% of the variance and was positively influenced by the degree of agricultural cover and reservoir area and age and negatively influenced by THg and degree of forest cover. The second component (PC2) explained 23.5% of the variance and was positively influenced by maximum water depth and water residence time, negatively influenced by TOC but was not influenced by THg (Fig. S4†). The third component (PC3, biological productivity, Fig. 4) explained 16.3% of the variance, and was positively influenced by THg and negatively influenced by water residence time and trophic index. When excluding THg

concentrations in the PCA, the number of significant components, the variance explained, and the variables accounting for each component did not change. Furthermore, the eigenvalues were comparable when running the PCA with and without THg. These results show that THg can be considered an independent variable.

## 4. Discussion

### 4.1 THg concentrations

The concentrations of THg observed in the five reservoirs are in the same range as the THg concentrations previously reported from tropic reservoirs<sup>36</sup> and other reservoirs worldwide.<sup>44</sup> The lack of information on the local THg background levels from these environments hinders us in evaluating whether or not these sediments' THg concentrations are influenced by local point sources. Based on the observed concentration ranges, however, we assume these THg pools to, first and foremost, reflect THg originating from natural and secondary anthropogenic sources rather than local anthropogenic point sources such as small-scale gold mining. This assumption is supported by the fact that the observed THg ranges in the reservoirs are orders of magnitude



lower than many of the observations made elsewhere (THg concentrations ranging up to 10 000–100 000 ng g<sup>-1</sup>) at sites known to be heavily impacted by mining activities.<sup>14</sup> Furthermore, no clear THg hotspots were observed within the reservoirs when exploring the spatial distribution of THg as a function of the distance from constructed dams. We cannot, however, rule out the fact that local point sources may still have contributed to observed THg concentrations. Mining activities have, for instance, been reported from the Tapajós National Forest, where the CUN reservoir is located.<sup>37–40</sup>

Bulk concentrations of TOC have been shown in many systems to explain the variability of THg concentrations observed in sediments.<sup>41</sup> In our study, we also observed a positive correlation between TOC and THg in the surface sediments among the collected cores (top 12 cm,  $n = 49$ , Spearman ranked correlation test:  $\rho = 0.306$ ,  $p$ -value = 0.033, Table S4†). TOC was, however, not a variable that was related to THg in the PCA analysis of the extended dataset (PCA analysis including mean THg and TOC from 10 reservoirs).

The sediment analyzed here is assumed to consist of material accumulated after the reservoirs were constructed. This assumes that the visually observed transition between the mineral and the organic-rich layer in each core also represents the transition between material accumulated before and after the flooding, respectively.<sup>22</sup> At CUN, lower concentrations of THg were found in the lower parts of the cores (Fig. 3), likely due to lower OM content in these sections as indicated by the lower LOI<sub>550</sub> values observed (Table S7†). If these more minerogenic layers represent material accumulated before the reservoir impoundment, these results would also suggest a greater accumulation of THg in the sediment as a result of the flooding. Higher concentrations of THg in sediment layers accumulated after flooding have also been shown previously in, e.g., the Urrá reservoir, Sinú River, Colombia.<sup>42,43</sup>

## 4.2 Factors influencing THg concentrations

Several processes, such as dilution and reduction of THg exported to the reservoirs, may alter the final concentration of THg in reservoir surface sediments. These processes may, in turn, be influenced by various reservoir features such as watershed land use, reservoir age and surface area. Here, we evaluated reservoir size, trophic state index and catchment land use and biome as potential drivers of THg in the surface sediments of 10 tropical reservoirs (data from this study and data compiled by Pestana *et al.*<sup>36</sup>).

Terrestrial runoff is the primary source of THg in most freshwater systems.<sup>14</sup> The loading of THg to downstream systems (and reservoirs) may, however, depend on the properties of the catchment. Foliar uptake is recognized to be of importance for the flux of Hg from the atmosphere to the watershed, as well as for the export of Hg to downstream systems.<sup>44,45</sup> In our PCA analysis, the degree of forest cover surrounding the reservoirs was also related to THg for PC1 (Fig. 4). Furthermore, the amounts of Hg exported to downstream systems may depend on the type of vegetation present, as vegetation type may lead to large differences in the amount of

THg accumulated, retained in, and export from, the watershed.<sup>46,47</sup> The reservoirs included in this study are located in regions with three different biomes: Savanna, Atlantic forest and Amazon. The amount of THg exported from the watershed is typically coupled with the amount of OM exported.<sup>13,48</sup> Regions with the savanna biome are less productive and have less OM-rich soils<sup>49</sup> compared to the Amazon and Atlantic forest biomes.<sup>50</sup> These regions are thus less likely to accumulate high amounts of Hg and also less likely to export high amounts of Hg to downstream systems. From the PCA that also included biomes (Fig. S4†), however, none of the three components suggested that the type of biome was related to THg. Furthermore, the PCA did not suggest that TOC accumulating in the sediments was related to THg. These results suggest that features other than the biome control THg in the reservoir surface sediments. It should however be noted that the biome only describes the vegetation in the region, and not the actual coverage of forests around the reservoir investigated.

In the PCA, PC1 was positively influenced by the degree of agricultural cover and negatively influenced by the THg. Similarly, THg positively influenced PC3 while trophic state index (with a higher index for eutrophic systems) negatively influenced the same PC. These observations suggest low THg to be related with a high degree of agricultural land use and more eutrophic conditions within the reservoir. Earlier studies have suggested that catchments with substantial agricultural cover result in lower concentrations of THg in the runoff compared to catchments dominated by urban and forested areas.<sup>51–53</sup> The excess of nutrients from areas with intensive agricultural land use can also result in lower THg concentrations in downstream systems due to the increased production of biomass within the aquatic system<sup>54,55</sup> and the subsequent dilution of Hg.<sup>56,57</sup> Among the reservoirs included in this analysis, no correlation was found between the agricultural land use and the nutrient status in the reservoirs ( $p = 0.575$ , Table S6†). The agricultural land use, however, correlated positively with the reservoir area ( $\rho = 0.675$ ,  $p = 0.032$ ). The fact that THg correlated with the area of the reservoir ( $\rho = -0.721$ ,  $p = 0.019$ ), suggests that the results of the PCA that low THg was related with a high degree of agricultural land use could be a spurious relationship, rather than to demonstrate a true causality.

For the set of reservoirs sampled in this study, we analyzed ancillary parameters related to land use and reservoir productivity (TOC/TN ratios and  $\delta^{15}\text{N}$ ). The TOC/TN ratios observed in all reservoirs, except for FUN, were greater than 10 and suggest significant contributions of allochthonous organic carbon in most of the surface sediments.<sup>58</sup> The variation in TOC/TN ratios is strongly linked to plant–microbial–soil OM transformations (litter decomposition and build-up of soil OM),<sup>59</sup> and to the contribution of different OM pools (from vegetation, leaf litter, roots, and soil microbes). In the same way as these OM pools differ in TOC and TN content, THg concentrations vary among different environmental compartments.<sup>60–62</sup> In the studied reservoirs, however, lower TOC/TN ratios were not consistent with lower THg concentrations (Fig. 2), suggesting either TOC/TN ratios do not reflect differences in the dilution of terrestrially derived material between sites, that dilution of the



terrestrial material does not play a major role, or that differences in TOC/TN ratios do not reflect differences in THg loading from different OM sources.

In comparison to CDU, MBS and CUN, the catchments of FUN and FNS (where low THg concentrations were observed) have a high percentage of agricultural land cover (Table 1).<sup>8,31,33,63</sup> For both reservoir systems, enriched  $\delta^{15}\text{N}$  signals were observed, indicating these sediments are influenced by the input of agricultural and/or wastewater runoff.<sup>64,65</sup> As mentioned above, high agricultural land use can result in lower Hg loading to downstream systems and dilution of the Hg within the reservoir due to eutrophication. Lower concentrations of THg were, however, only observed in FNS and not in FUN. As can be seen in the Fig. 4, these two sites were also not close to each other in the PC1–PC3 biplot. As discussed further below, other features of the reservoirs were likely more important in controlling the accumulation of Hg than the agricultural land use. It would however, still be of interest to further explore the correlation between these proxies ( $\delta^{15}\text{N}$  and TOC/TN) and THg in future studies as the PCA indicated that nutrient loadings could play a role in THg concentrations in the reservoir sediments.

The age of the reservoir was another variable influencing THg concentrations in sediments for PC1. A correlation between the reservoir age and THg in sediments was also suggested by Pestana *et al.*<sup>36</sup> and was observed in a study comparing reservoirs of different ages in China.<sup>66</sup> It should, however, be noted that our data fit poorly with the modelled relationship between sediment THg and reservoir age put forth in Pestana *et al.*<sup>36</sup> Furthermore, Khopkar suggests catchment features (*e.g.*, hydrology, land use, organic matter input) to be more important for THg in surface sediments than the reservoir age.<sup>67</sup> We also note that most studies examining the short- and long-term effects of the Hg biogeochemical cycle in reservoirs focus on the timing of enhanced methylation of Hg<sup>68,69</sup> or peaks of Hg concentrations in fish (which is driven by Hg methylation and the subsequent bioaccumulation and biomagnification of MeHg).<sup>70,71</sup> The same processes are, however, unlikely to drive the concentration of THg in surface sediments. Age-related shifts in THg concentrations in surface sediments are thus not necessarily expected.

Among the five reservoirs investigated in this study, we observed higher concentrations of THg in the four smaller reservoirs in comparison to the larger FNS reservoir. This observation is in line with the meta-analysis from Pestana *et al.*<sup>36</sup> which included data from four smaller and one larger reservoir (Fig. 5 and Table S5†). The relationship between THg concentration and the area of the reservoir is also represented in PC1 (Fig. 4), which is, in addition, influenced by land use (represented here as agriculture/forest cover) and reservoir age. Together, the data currently available from reservoirs in South America (this study and the data synthesized by Pestana *et al.*<sup>36</sup>) suggest sediment concentrations of THg of up to  $50 \text{ ng g}^{-1}$  in reservoirs with an area exceeding  $400 \text{ km}^2$  and concentrations ranging from  $100$  to  $200 \text{ ng g}^{-1}$  in reservoirs with an area less than  $80 \text{ km}^2$  (Fig. 5). There are several processes that may contribute to lower THg concentrations in the sediments of the larger reservoirs. First of all, the distribution of terrestrial

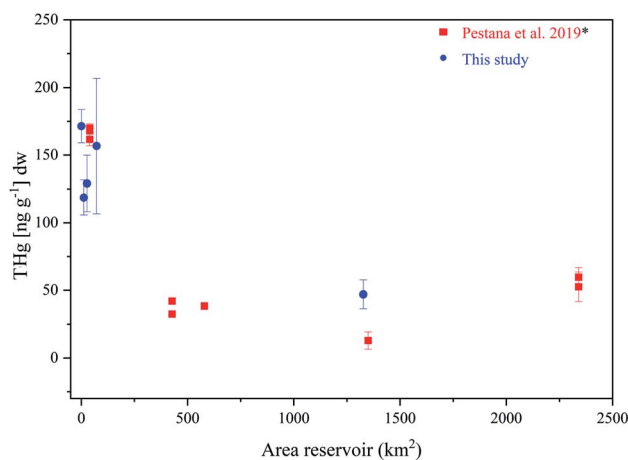


Fig. 5 Relationship between THg concentration (ng per g dry weight) and the reservoir area of tropic reservoirs in surface sediments in this study (blue circle) and from other reservoirs in South America (red square),  $n = 9$  from \*Pestana *et al.*<sup>36</sup>

material over greater areas in the largest reservoirs can result in a higher fraction of the THg derived from the terrestrial compartment being reduced through, *e.g.*, photochemical pathways<sup>72</sup> and subsequently evading out of the aquatic system as elemental Hg ( $\text{Hg}^0$ ). Secondly, the distribution of THg over larger areas can result in a greater dilution of the terrestrial material with autochthonous carbon. Given the similar direction of both size and agricultural landcover in the biplot, we cannot separate the contribution of the two. A significant direct correlation was, however, only observed between THg and reservoir size (Table S6†) and not between THg and agricultural cover, suggesting reservoir size to be the primary reservoir feature influencing THg in surface sediments.

## 5. Conclusions

Given the extensive hydroelectricity expansion currently underway in South America,<sup>4</sup> understanding drivers of Hg accumulation across systems is needed in order to mitigate the risks of Hg upon the construction of the reservoirs. Here, we explored the potential role of physical reservoir features (*e.g.*, reservoir size, nutrient levels, and catchment land use and biome) and ancillary parameters, such as: TOC, TN, TOC/TN, and the  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  isotopic signatures for the accumulated concentrations of THg in tropical reservoirs. Out of the tested variables, the size of the reservoirs was the feature that best predicted THg concentrations, with greater concentrations of THg found in the smaller reservoirs (area  $< 100 \text{ km}^2$ ). Although the concentrations of Hg accumulating in the reservoir sediments not necessarily reflects the amounts of Hg accumulating in the fish,<sup>73</sup> these results indicate higher concentrations of Hg to accumulate in the abiotic compartment of the smaller reservoirs. The risks associated with the Hg in these reservoirs are thus likely to be greater. We further note that higher concentrations of Hg also have been previously noted elsewhere in the biota from smaller freshwater systems in comparison to larger reservoirs.<sup>73</sup>



In addition to the size of the reservoir, the PCA suggested that the type of watershed (high degree of forest cover and low degree of agricultural land use), age of the reservoir, water residence time and the levels of nutrients in the reservoir may influence THg concentrations in surface sediments in tropical reservoirs. Although we in this study cannot tease the influence of these parameters apart, or eliminate the possibility that some of these relationships are spurious, the results presented points to potential drivers that warrants further investigation. Our data also shows that both in-reservoir and watershed drivers need to be considered. In addition to the forest coverage and other properties of the natural environment that influence the cycling of Hg, perturbations of the watershed may alter the capacity of the landscape to retain the Hg deposited.<sup>14</sup> Forestry, for instance, increases both the re-emission of Hg back to the atmosphere as well as the export of Hg to downstream systems. Our study suggest that the smaller reservoirs may be more vulnerable for such perturbation as these systems already accumulate higher concentrations of Hg in the abiotic compartment.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

We are grateful for the study area map provided by José Reinaldo Paranaíba. This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior—Brasil (CAPES)—Finance Code 001. The fieldwork was funded partially by the European Research Council under the European Union's Seventh Framework Programme (FP7/2007–2013)/ERC grant agreement n° 336642.

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