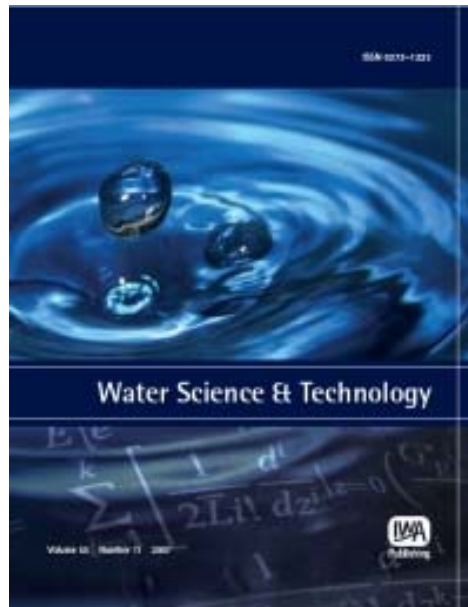


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## Role of the sediments of two tropical dam reservoirs in the flux of metallic elements to the water column

Rita Fonseca, Carla Patinha, Fernando Barriga and Manuela Morais

### ABSTRACT

In tropical climates, the high rainfall and temperature, throughout the annual cycle, allow high leaching rates of metallic elements from the basin upstream, which accumulate in the reservoirs. However, the concentration of these elements in natural waters is usually lower than expected, due to the ease of adsorption and co-precipitation in solid phases. We have studied two tropical dam reservoirs in Brazil, Três Marias (Minas Gerais) and Tucuruí (Pará), with the aim of understanding the correlation between physical–chemical parameters of the water column, chemical and mineralogical characteristics of the accumulated material and the solubility, mobilization and precipitation of metals in reservoirs. Metals speciation performed in selected samples determined that metallic micronutrients are preferentially adsorbed or retained through precipitation/co-precipitation onto fine-size charged crystalline/amorphous Fe-oxides. Under the prevailing reducing and low pH conditions of the bottom reservoirs, some adsorbed metals (particularly Fe and Mn) are easily released from their metal bearing-phases and mobilized to the aqueous phase of sediments, which show high levels of soluble forms of these elements. However, the solubilization process and the release to the water column are not very extensive, as abundances of metals such as Fe, Mn, Zn and Cu in water are low, although increasing with depth.

**Key words** | aquatic systems management, metals speciation, reservoir sediments, water quality

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### INTRODUCTION

In natural and artificial lakes, sediments represent one of the last receptacles for heavy metals discharged into the drainage network. Their contents and distribution in these systems, as well as the various forms found in the sediments, are determined by the chemical conditions of the environment and by the geochemical characteristics of the weathered materials in their source (soils and layers of rock alteration) which, in turn, were inherited from the parent rocks (Fonseca *et al.* 2003). Due to the toxicity and ability of the heavy metals to accumulate in the biota, these elements represent a serious problem in the environment.

In lacustrine systems, concentrations of metals in the water result from: (1) entry into the basin through point and diffuse sources, (2) transport as dissolved and particulate forms resulting from erosion processes in the basin, and (3) transformations and immobilization by bottom sediments through adsorption, fixation or sedimentation. Watersheds provide the vast majority of metals through

streams and rivers (Giblin 2009) and a large proportion of the total load that enters a lake is transported in particulate form in association with bottom or suspended sediments (Chapman *et al.* 1998). These elements are present in the environment in various inorganic and organic forms, including different oxidation states (Gilmour & Riedel 2009). Considering the metals with higher concentrations in the freshwaters ecosystems, 90–99% of the total Fe and more than 80% of the total Mn are found in particulate form. Only minor amounts are transported in dissolved forms as they quickly precipitate upon reaching oxic water, except under acidic conditions (Giblin 2009). In a tropical setting, the organic matter transported by rivers represents a major link in the global cycles of bioactive elements, such as metals. Different processes (advective transport, degradation, complexation, sorption) involving organic matter, take place in mixing zones such as river confluence (Moreira-Turcq *et al.* 2004).

These metallic elements undergo extensive cycling within lake sediments and within the water column. Because of this extensive recycling, many lakes are extremely retentive to metals and often the majority of elements entering a lake is lost to the sediments. Sediments have been recognized as the most important trace metals reservoir in the ecosystem (Marcovecchio *et al.* 2004). However, the retention rate depends on the chemical and mineralogical composition of the sediments and on the mixing, trophic status and chemistry of the lake (Giblin 2009). Even considering that sediments are the main sink for these elements, when environmental conditions change (pH, redox potential, etc.), sediments can act as a source of metals (Zoumis *et al.* 2001).

In tropical climates, the high rainfall and temperature throughout the annual cycle allow for high leaching rates of metallic elements from the basin upstream, which accumulate in the reservoirs. However, the concentration of these elements in natural waters is usually lower than expected from the inputs of these elements into the hydrological system, due to the tendencies of metals for adsorption and/or co-precipitation in solid phases (Chapman *et al.* 1998). In tropical lakes, unlike lakes in temperate regions, there are no convective currents (thermally driven), which may annually oxygenate the water column. In these weakly stratified lakes with relatively warm and uniform temperatures and low physical stability, there are significant flows of allochthonous oxides/hydroxides, resulting from the intense weathering of the basins (Crowe *et al.* 2008).

A study conducted in two tropical dam reservoirs in the San Francisco River (Três Marias, MG) and Tocantins River (Tucuruí, PA), Brazil, showed high levels of metals in the soluble phase from the sediment with an extraction medium (solution of ammonium acetate at pH 4.65, acetic acid and EDTA), much higher than the corresponding levels in the parent soils (Fonseca *et al.* 2007, 2009), having however, much lower concentrations in the water column (Morais *et al.* 2009). With the purpose of explaining the reason why the water column of these tropical lakes is relatively poor in dissolved metals (e.g. Fe, Mn, Cu, Zn), despite the high values in the soluble phase of the bottom sediments, the lithologies and soils in the hinterland rich in metallic elements and the high annual rainfall which allow high leaching rates from the basin to these systems, we have analysed *in situ* redox and pH on the sediment-water interface and in the water column, and the contents and forms of the most abundant metals in the sediments (Fe, Mn, Cu and Zn) in the total, soluble fractions (with an extraction medium) and by sequential extraction

methods. This study also aims to elucidate the role that the chemical conditions of the environment and the sediments may play in the solubility and flux of these elements to the water column.

## CHARACTERIZATION OF THE RESERVOIRS AND DRAINAGE AREA

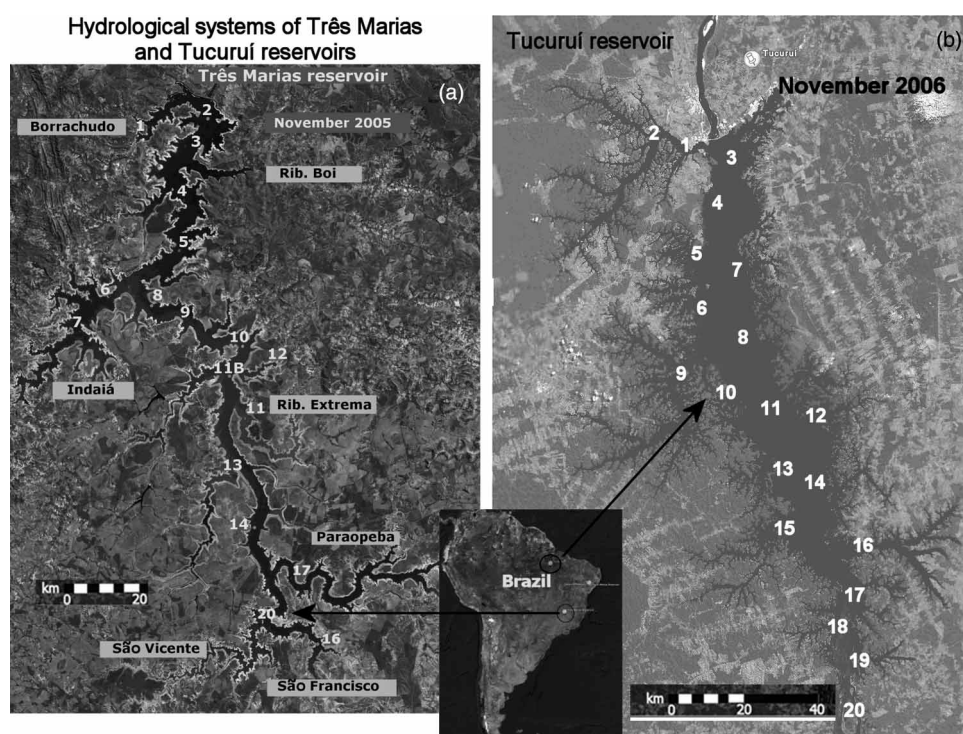
The Três Marias reservoir (latitude: 18°–21° S, longitude: 43°30'–46°40' W), in the São Francisco River (Figure 1(a)) is a large lake, with 1,050 km<sup>2</sup> of inundated area, a volume of 17.8 km<sup>3</sup>, and maximum length of 150 km, and an average depth of 16.8 m. It is located in a tropical savanna climate, characterized by very dry winters and rainy summers, with an average annual precipitation near 1,200–1,300 mm. The region has an annual average temperature of 22.5 °C, ranging from the maximum of about 28.8 °C (in January) and the minimum of 16.5° (in July).

It is fed by a large variety of waterways, tributaries of the main watercourse.

The geology of the drainage area is dominated by the Três Marias Formation, which belongs to the 'Série Bambuí' group; it is mainly composed of detrital sedimentary rocks consisting of micaceous and clayey siltstones with a calcareous matrix, arkoses, ferruginous shales and metamorphosed limestones. In the West sector of the reservoir catchment, alluvium is abundant. This sector is also under the influence of the Mata da Corda Formation, which is responsible for the input of a large variety of nutrients, due to its kamafugitic composition. These are intrusive and extrusive ultramafic, potassic rocks, mainly lavas, volcanic breccias, tuffs and ash (Fonseca *et al.* 2007).

The Tucuruí reservoir (latitude: 3°43'–5°15' S, longitude: 49°12'–50°00' W) is located in the Tocantins River (Figure 1(b)), in the Amazon basin and has a wet tropical climate. With annual average temperatures ranging from 24° to 28 °C, the maximum (38 °C) occurs in August and September, and the minimum (22 °C) in June. It is the second largest reservoir in Brazil, with a watershed of 758,000 km<sup>2</sup> area, 2,850 km<sup>2</sup> of inundated area, 45.5 km<sup>3</sup> maximum volume and an average depth of 19 m. The air temperature and the rain are higher throughout the annual cycle (precipitation up to 2,400 mm/year), leading to high erosion rates of the finer particles and the soluble elements from the soils, which concentrate in the bottom of the reservoir and in the water column.

The sources of the sediments of the Tucuruí reservoir have a higher diversity compared with the Três Marias



**Figure 1** | Geographical location and sampling sites of the Três Marias (a) and Tucuruí (b) reservoirs.

reservoir and belong to three large geological unities: Cráton Amazônico, Araguaia Belt and Sedimentary Basin of Parnaíba (Tassinari & Macambira 1999). Bedrock and surficial deposits consist of: (1) Sedimentary rocks (Cretaceous-Quaternary) – Fe-sandstones, Fe-siltstones, shales, lateritic cover, alluvium; (2) Igneous rocks (lower Precambrian) – granites, basalts; and (3) Metamorphic rocks (Precambrian) – schists, quartzites, phyllites, amphibolites, gneisses, orthogneisses. Strongly acidic latosols containing gibbsite and/or iron oxide which varies in concentration depending on depth, and sandy to clayey kaolinitic podzolic soils are the sole soil classes in the area (Fonseca *et al.* 2009).

## METHODS

In both reservoirs, the studies were performed in two periods, after the rainy season (Três Marias: April 2005; Tucuruí: March–April 2006) and after the dry season (Três Marias: November 2005; Tucuruí: November 2006). To have a broad knowledge of the structure and behaviour of these reservoirs, in both periods, we have collected samples of bottom sediments and water. The surface layer (approximately 40 cm thick) of sediments was sampled, using a modified Shipeck dredge, in places subjected to different

conditions of sedimentation and fed by different tributaries: (Três Marias: 18, Tucuruí: 20 sampling stations). This sediment sampling method was the only possible one to use in Tucuruí, which was not deforested before filling the dam, having a dense rain forest submerged by its deep waters. Due to the high hydrodynamics of these tropical systems, the water column has a high spatial homogeneity and thus water samples were only collected at 12 stations, at the same locations of sediment samples, at two depth levels (surface and bottom). Bottom samples were collected with a Van Dorn bottle. Simultaneously, at each sampling site, vertical water profiles were performed, with *in situ* measurements every 2 m of pH, dissolved O<sub>2</sub> concentration, O<sub>2</sub> saturation and Eh, using a multiparameter probe TURO T611.

## Water analysis

The concentrations of Fe, Mn, Cu and Zn were determined by atomic absorption spectrophotometry (AAS)-GF in acidified (with HNO<sub>3</sub>) and filtered samples (through a 0.45 µm cellulose nitrate membrane). These metals were chosen because they are present in relatively high concentrations in freshwaters ecosystems and they can be viewed as ‘master metals’ owing to their ability to strongly influence



the cycles of other biologically important elements. The metals quantification in water was carried with three replicates for quality control purposes.

### Sediment analysis

In both reservoirs and in each sampling period, in preserved samples (cooling at  $4 \pm 2^\circ\text{C}$ ), we have performed analysis of total contents of major elements, grain-size, pH ( $\text{H}_2\text{O}$ ), organic carbon and soluble contents (with an extraction medium) of the major metallic elements: Fe, Mn, Cu and Zn. However, information on total concentrations of metals alone is not sufficient to assess the solubility and flux of these elements and the environmental impact of sediments in the water column because heavy metals are present in different chemical forms in sediments, which determine their mobilization capacity and bioavailability (Lopez-Sanchez *et al.* 1996; Yu *et al.* 2001). In order to study metals speciation, selected samples (based on total and soluble metals contents and textural characteristics), five from Tr s Marias and five from Tucuru , were submitted to a sequential extraction procedure using six reagents, each reagent or mixture being able to dissolve selectively specific mineralogical constituent (a potential carrier of trace elements in the sample). These samples belong to the period in which the redox conditions are lowest, and less stable, influencing the release of metals from sediments (after the drought, in November).

**Major elements:** total contents of a range of major metals ( $\text{Fe}_2\text{O}_3$ , MnO, Cu, Zn) were determined by ICP-MS after lithium metaborate/tetraborate fusion at ActLabs laboratories. All major element concentrations are expressed in percent dry weight of oxide/element.

**Grain-size analysis:** was performed in three steps: separation of grain size classes by wet sieving (gravel-sand-silt-clay), dry sieving (grain-size sand distribution) and measurement of clay and silt distribution by a laser sedimentometer. The clay, silt and sand proportions were represented in a Shepard (1954) triangular diagram, followed by subsequent classification.

**pH:** pH ( $\text{H}_2\text{O}$ ) was measured by a potentiometer in a water-sediment (2.5:1) suspension.

**Organic carbon:** was determined using an elemental analyser for CHNS-O (Eurovector, EA3000) based on the principle of dynamic flush combustion coupled with gas chromatography (Pansu & Gauthierou 2006).

**Soluble contents of Fe, Mn, Cu and Zn:** were based on extraction of Fe, Cu, Mn and Zn with a solution of ammonium acetate at pH 4.65, acetic acid and EDTA,

followed by determination by AAS: Lakanen and Ervio method (Cottenie 1980).

**Sequential chemical extraction:** the procedure of sequential chemical extraction was begun as soon as the cooled samples arrived at the laboratory. This procedure, consisting of a series of six fractions followed by AAS analysis, has been discussed by Cardoso Fonseca & Ferreira da Silva (1998). The chemical fractions dissolved by a selected mixture of reagents are as follows: F1–ammonium acetate (1 mol/L  $\text{NH}_4\text{Ac}$ , pH 4.5, 640 min continuous agitation, room temperature): water soluble metals and dissolved exchangeable ions, specifically adsorbed and bound to carbonates; F2–hydroxylamine hydrochloride (0.1 mol/L  $\text{NH}_4\text{OHCl}$ , pH 2.0, 600 min continuous agitation, room temperature): metals bound to Mn oxyhydroxides; F3–ammonium oxalate (0.175 mol/L  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  – 0.1 mol/L  $\text{H}_2\text{C}_2\text{O}_4$ , pH 3.3, 600 min continuous agitation, room temperature, in darkness): metals bound to amorphous Fe oxides; F4– $\text{H}_2\text{O}_2$  35%: metals bound to organic matter (shaking at  $60^\circ\text{C}$  until reaction stopped reaction: sulfide (primary sulfide minerals could not be totally leached out in this step); F5–ammonium oxalate (0.175 mol/L  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  – 0.1 mol/L  $\text{H}_2\text{C}_2\text{O}_4$ , pH 3.3, 600 min continuous agitation under UV radiation): metals bound to crystalline Fe oxides; F6–mixed acid ( $\text{HCl} + \text{HNO}_3 + \text{HF}$ ) attack: residual metals – matrix bound in lattice positions, in resistant oxides and sulfides.

For quality control of total contents of metals in sediments, analysis of a Certificate Reference Material (MESS-3, NRC, Canada) using the same procedure, yielded 95–105% recovery from the certified concentrations. For the chemical analyses for which there are no certified reference material, samples were repeated to ensure that consistent results were obtained.

The accuracy and analytical precision of the sequential analysis have been checked by the analysis of reference materials (Certified reference materials: soil samples 979 and 1218 from the United States Department of the Interior) and duplicate samples in each analytical set. The precision was expressed by the coefficient of variation (CV%). The CV showed by the various elements was the following: Cu–4%, Zn–3%, Mn–5% and Fe–3%. The accuracy of the sequential treatment considered as a whole may be estimated by comparison of the total sum of the amounts obtained after each step with the well-defined amount obtained after hot mixed-acid attack of the same sample. The overall recovery rates (the sum of six fractions/the independent total concentration) ranged from 80 to 115%.

Although admitting there might be some overlap in the extractions of Mn-Oxides, amorphous Fe oxyhydroxides

and crystalline Fe oxides, or even partial oxidation of sulfides, in all the steps, the identification of the extracted material was checked through analysis of RX diffraction and RX fluorescence.

## RESULTS AND DISCUSSION

In both systems, the grain-size distribution of the bottom sediments, nearly homogeneous between the two main seasons (Figure 2), clearly evidences the selective erosion of the fine-grained soil particles of the drainage basins, showing a slight increase of the clay fraction in the post-drought season, especially in Tucuruí (average values for Tucuruí: April – sand: 8.35%; silt: 59.66%; clay: 31.99%; November – sand: 3.0%; silt: 39.30%; clay: 57.70%). The wide-ranging sediments are composed of a mixture of several grain-size sub-populations, which define distinct sources or distinct hydrodynamic environments. Most sediments are characterized by the major contribution of fine-grained material and their textural classification falls in the silty clay and clayey silt classes. Unlike the grain-size distribution observed in similar Mediterranean artificial lakes (e.g. Fonseca *et al.* 2003), high amounts of rainfall with a regular distribution over the year, typical of the tropical climate of the studied systems, determine a uniform input and distribution of granulometric populations and a higher and regular hydraulic flow inside the lakes, giving a higher textural homogeneity. Only in the margins and at the entrance of the main water-courses in the reservoirs do sediments have a more sandy component.

Earlier studies achieved by XRD on the mineralogy of the clay fraction of sediments of both reservoirs (Fonseca *et al.* 2011), identified a small variety of clay minerals,

characterized by simple clay assemblages, detrital or formed under the high leached weathering conditions, denoting a high mineralogical evolution in both reservoirs. Minerals are mainly represented by illite and kaolinite in Três Marias (average values: April – illite: 36.3%; kaolinite: 57.4%; November – illite: 43.85%; kaolinite: 50.9%) and in Tucuruí (average values: April – illite: 31.8%; kaolinite: 62.2%; November – illite: 42.6; kaolinite: 50.0%). Degraded chlorite, with unstable interlayers, does not occur in all the sediments, but when present, it is <10%. In the southern part of Tucuruí, smectite occurs (ranging between 2 and 10%), probably derived from the basalts of the Tucuruí Formation, which crop out in the southern region of the drainage basin. In agreement with the main soil group in the watershed of both reservoirs, acidic red latosols rich in Fe and Al, illites are commonly Fe-rich in the octahedral sheet and amorphous and crystalline Fe and Al oxides/hydroxides are abundant in the clay fraction, associated with clay minerals.

Regarding the geochemical analyses of sediments, iron is present in high concentrations in these depositional systems when compared with medium values for mineral soils and for Mediterranean reservoirs (Fonseca 2002), while Mn has approximately identical contents (Table 1). The redox cycling of both elements may play important roles in determining the forms and cycling of trace metals and other biologically important elements, through microbially mediated and abiotic chemical reactions, (Thamdrup 2000; Giblin 2009), being especially important in regulating the chemical composition of the water column. Both elements are also abundant in the soils of the catchment area of each reservoir, dominated by strongly acidic latosols containing gibbsite and/or iron oxide (Fonseca *et al.* 2007).

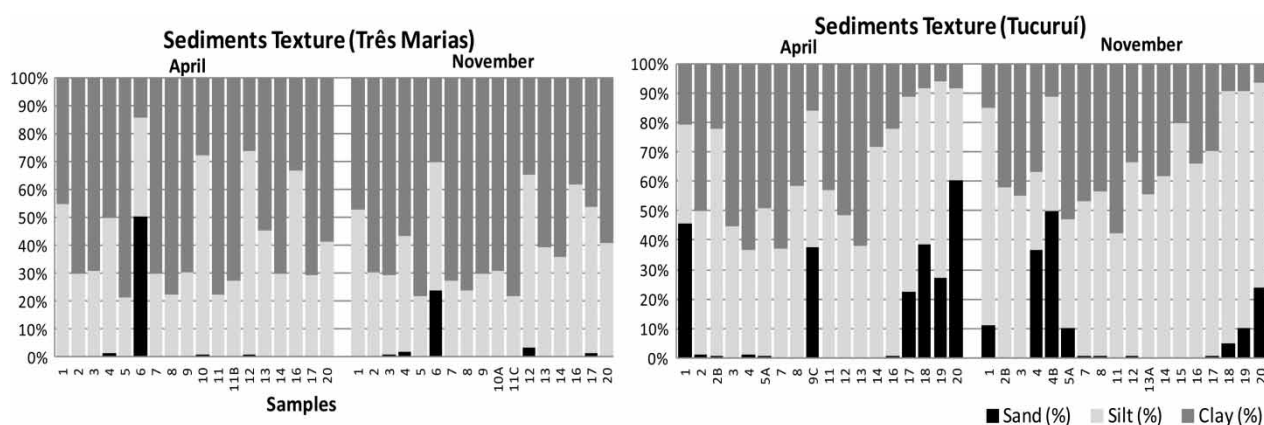


Figure 2 | Graphical representation of grain-size distribution of the bottom sediments from Três Marias and Tucuruí reservoirs, in both sampling periods.

Três Marias (November 2005)

**Tucuruí (November 2006)**

Contrary to previously studied Mediterranean systems (e.g. Fonseca 2002; Fonseca *et al.* 2003), the total fractions of iron, manganese, copper and zinc, have some notable differences in the distribution patterns, in each reservoir; for example, in Três Marias, TM1 is comparably poor in Fe and Cu, but rich in Zn, while TM12 has intermediate Fe contents, high Mn, but low Cu and Zn; in Tucuruí, TUC18 has comparably low Fe, Cu and Zn, and medium Mn; TUC2B, with intermediate Fe and Mn, has extremely high Cu and Zn. In both reservoirs the ratio between the contents of these elements is in accordance with their abundance on the Earth's surface (Fe→Mn→Zn→Cu) indicating their lithogenic inheritance.

The higher values of the total contents of these metallic elements (especially Fe, Cu and Zn) in the sediments when compared with data achieved in similar systems under a Mediterranean climate (e.g. Fonseca 2002; Fonseca *et al.* 2003) and the pattern soils, can be a consequence of: (1) higher values of temperature and precipitation throughout the annual cycle, which leads to a higher intensity of rock and soil weathering, followed by extreme leaching rates of metallic elements from the basin, (2) predominance of latosols rich in Fe-oxides (Fonseca *et al.* 2007) which can easily scavenge trace elements from the environment, and (3) predominance of kaolinite in the clay fraction of sediments (Fonseca *et al.* 2007, 2009); although it is the clay mineral having lower cationic exchange capacity, it strongly adsorbs metallic elements through its siliceous tetrahedral surfaces.

Some heavy metals derived from weathered rocks and soils are mobilized and dispersed downstream, and may be frequently immobilized by adsorption onto mineral and organic particles when these particles are leached into the reservoirs as suspended load or adsorbed and concentrated by algal or other forms at the lower trophic. The sorption of dissolved organic matter on mineral particulate surfaces containing metals and forming organometallic complexes, represents one of the most important geochemical processes and seems to be responsible for the transport of a few metallic species and for the preservation of organic matter (Moreira-Turcq *et al.* 2004). In fact, the contents of organic C, slightly higher after the rainy season and far higher than in the soils of the drainage basins (average values: Três Marias – April: 1.34%; November: 1.41%; Soils: 0.80%; Tucuruí – April: 2.47%; November: 2.55%; Soils: 1.18%), show that the sediments accumulated in the bottom of these reservoirs represent an efficient sink for organic nutrients deriving from the over-erosion of soils in the catchment area and for autochthonous sources from

settling phytoplankton and seston particles, studied by Morais *et al.* (2009). One of the reasons for the higher levels of organic C in Tucuruí could be an effect of the non-deforestation before filling up. In the water column, the highest values of dissolved organic matter concentrate at the bottom, where there are the highest levels of metals such as Fe and Mn (see Table 2). Although metals and organic matter could be associated forming organometallic complexes, the higher levels of metals in the deeper layers of water, are probably a consequence of the chemical conditions of the bottom. Under the acidic conditions of sediments of both reservoirs (average pH(H<sub>2</sub>O) values: Três Marias – 5.1; Tucuruí – 5.2) and the prevailing reducing conditions of the bottom, most of the adsorbed metals can be easily released from their solid hosts to the interstitial water of sediments or directly to the water column. Whereas most of the samples in both reservoirs and in both periods have pH values below 5, two samples of Tucuruí (TUC 4: April – 4.6, November – 8.0; TUC 20: April – 5.5, November – 7.1) have an alkaline level in the dry season, much higher than the level observed after the rain period. After drought, the water level in the reservoir falls between 12 and 15 m, leaving some sampling points, such as TUC 4 and TUC 20, out of water with a high degree of salts that precipitate due to evaporation, the surface layer of sediments becoming much more alkaline.

The processes that lead to low oxygen conditions in the deeper water masses could be: (1) the degradation of organic matter (either produced in the lake itself or delivered by rivers), and (2) the weak but nevertheless existing stratification that effectively isolates the oxygen-depleted deep water. This solubilization process, induced by the use of microorganisms during the degradation of organic matter that use particularly the Fe and Mn (oxyhydr) oxides as electron acceptors, can probably explain the high solubility of these elements found in the studied sediments (see Table 1). Although there is an obvious increase of metal solubility with decreased pH, this pH-solubility relationship is not linear because the solubility is also highly affected by the redox potential (Eh). Under reducing conditions, the ionic soluble forms of elements such as Fe and Mn, are the most stable and, conversely, Zn and Cu ions may be mobile in oxidizing environments but as Eh becomes more reducing, their solubility decreases and they precipitate as sulfide constituents. It should be noted that the upper 40 cm thickness layer of sediments does not correspond to the most appropriate samples to study the redox characteristics of the bottom sediments because they represent a mixture of different redox zones that usually



**Table 2** | Chemical parameters of the water column of both reservoirs in both sampling periods

<b>Três Marias Reservoir</b>								
<b>Parameters</b>	<b>May 2005</b>				<b>November 2005</b>			
	<b>Surface</b>		<b>Bottom</b>		<b>Surface</b>		<b>Bottom</b>	
	<b>Average</b>	<b>Std. Dev.</b>	<b>Average</b>	<b>Std. Dev.</b>	<b>Average</b>	<b>Std. Dev.</b>	<b>Average</b>	<b>Std. Dev.</b>
Oxygen saturation (%)	92.6	11.1	44.2	22.1	78.2	2.6	21.5	25.5
Dissol. oxygen (mg/l)	7.0	0.8	3.4	1.7	6.2	0.2	1.8	2.1
pH	7.5	0.2	7.0	0.4	7.2	0.3	6.4	0.3
Redox potential (mV)	226	28	195	63	186	38	62	168
Nitrates (mg/l NO <sub>3</sub> -N)	0.119	0.122	1.027	1.711	0.048	0.035	0.128	0.122
Organic matter (mg/l)	2.45	0.72	25.23	37.25	3.82	0.95	6.29	4.70
Iron (mg/l Fe)	0.04	0.005	0.05	0.004	0.02	0.003	0.068	0.166
Manganese (mg/l Mn)	0.010	0.004	0.107	0.004	0.006	0.002	0.175	0.005
Zinc (mg/l Zn)	0.004	0.001	0.003	0.002	0.005	0.001	<0.0003	0.0001
Copper (mg/l Cu)	0.003	0.001	0.001	0.001	0.005	0.002	<0.0003	0.0001
<b>Tucuruí Reservoir</b>								
<b>Parameters</b>	<b>April 2006</b>				<b>November 2006</b>			
	<b>Surface</b>		<b>Bottom</b>		<b>Surface</b>		<b>Bottom</b>	
	<b>Average</b>	<b>Std. Dev.</b>	<b>Average</b>	<b>Std. Dev.</b>	<b>Average</b>	<b>Std. Dev.</b>	<b>Average</b>	<b>Std. Dev.</b>
Oxygen saturation (%)	72.83	7.81	25.41	23.73	70.56	10.53	29.29	30.98
Dissol. oxygen (mg/l)	5.42	0.52	1.93	1.83	4.36	0.62	2.03	2.32
pH	6.72	0.47	6.26	0.18	7.54	0.21	7.13	0.31
Redox potential (mV)	258	65	118	184	160	65	13	154
Nitrates (mg/l NO <sub>3</sub> -N)	0.253	0.178	0.158	0.096	0.042	0.027	0.044	0.007
Organic matter (mg/l)	4.00	0.98	4.70	2.11	5.96	7.95	20.10	18.33
Iron (mg/l Fe)	0.054	0.044	0.058	0.039	0.020	0.018	0.085	0.119
Manganese (mg/l Mn)	0.037	0.034	0.082	0.082	0.049	0.049	0.145	0.161
Zinc (mg/l Zn)	0.006	0.002	<0.0003	0.0001	0.008	0.002	<0.0003	0.0001
Copper (mg/l Cu)	0.004	0.002	<0.0003	0.0001	0.005	0.001	<0.0003	0.0001

occur within the uppermost layers of a sediment column (i.e. oxic zone with oxygen utilization, zone of nitrate reduction, zone of Mn and Fe (oxyhydr)oxide reduction, potentially zone of sulfate reduction). However, this sampling method was the only one able to achieve the first studies performed on the sediments of the second largest artificial lake in Brazil, given the coverage of its bottom by a dense vegetation typical of the Amazon rainforest.

Considering the relatively high metal content, both in the total and in the soluble fractions of sediments (especially Fe and Mn), their concentrations in natural waters are lower than expected (Table 2).

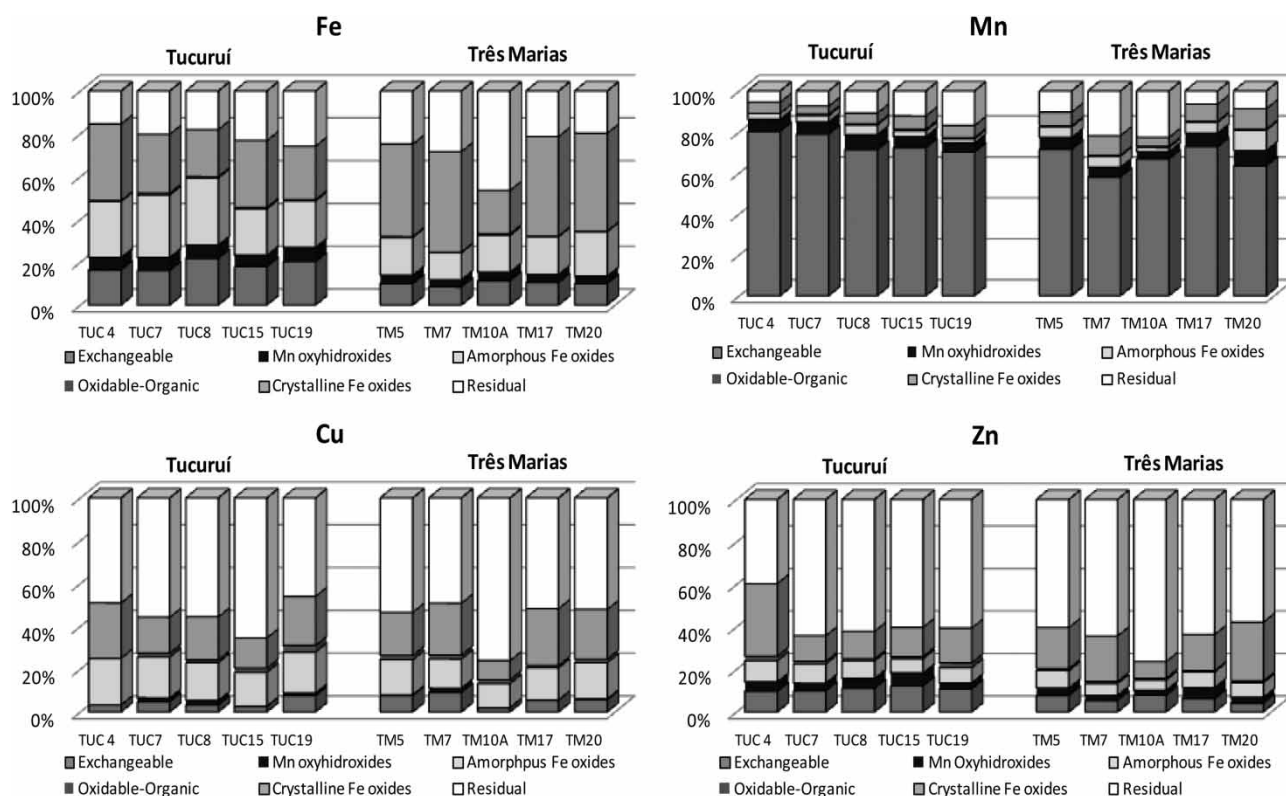
Previous studies using data from physical and chemical characterization of the water column conducted by [Morais \*et al.\* \(2009\)](#), showed the marked influence of climate on the physical and chemical dynamics of these hydrological systems. According to these studies, the water circulation and the vertical mixture of the water column lead to the oxygenation of the deeper layers in the wet period (better observed in Três Marias). The seasonal changes in precipitation, runoff and hence, the oxygenation of the deeper layers, induce change in the redox conditions of the lake bottom, which in turn have a significant impact on the retention/release of metals in the sediments. The redox potential is

lower in the deeper layers in November (after the dry period), suggesting low oxygen saturation. This is also demonstrated by the lower values of nitrates in the same period. Under anoxic conditions, the release of nutrients, metals (e.g. Fe, Mn) and other chemical components from the lake bottom sediments is coupled with increase of their soluble counterparts in sediments (interstitial fluids) and in the overlying water (see the increase of soluble Fe and Mn in sediments – Table 1 and in the bottom water – Table 2, in November). Anoxic conditions seem to cause a transformation of Fe and Mn from rather stable to more labile fractions.

With the purpose of elucidating the behaviour of these metallic elements in these freshwater ecosystems and the role that the chemical conditions of the environment and the sediments may play in the solubility and flux of these elements to the water column, we have done selective chemical extraction for Fe, Mn, Cu and Zn, to associate each element at different metal bearing phases and to identify the main phases that are the potential carrier of trace elements in the sample (Table 3 and Figure 3). The adopted methodology confirmed the role of the lake sediments as an important sink for various trace metals.

**Table 3** | Sequential extraction data for Fe, Mn, Cu and Zn in selected samples of both reservoirs (values in  $\mu\text{g g}^{-1}$ )

	Tucuruí					Três Marias				
	TUC 4	TUC 7	TUC 8	TUC 15	TUC 19	TM5	TM7	TM10A	TM17	TM20
<i>Fe (<math>\mu\text{g g}^{-1}</math>)</i>										
Exchangeable	4,364	8,020	13,200	7,390	3,468	6,604	4,066	6,358	5,730	5,150
Mn oxyhydroxides	1,553	3,028	3,783	2,188	1,133	2,598	1,595	2,263	2,078	1,785
Amorphous Fe oxides	6,990	14,495	19,005	8,955	3,720	11,680	6,090	9,685	9,630	10,675
Oxidable-organic	97	435	353	291	101	246	129	420	176	149
Crystalline Fe oxides	9,560	13,700	13,375	12,875	4,283	28,650	22,650	11,405	25,375	23,500
Residual	4,113	10,050	10,910	9,548	4,413	16,450	13,650	26,166	11,638	10,165
<i>Mn (<math>\mu\text{g g}^{-1}</math>)</i>										
Exchangeable	220	400	240	200	142	440	232	265	500	294
Mn oxyhydroxides	16	30	25	15	9	35	19	14	46	35
Amorphous Fe oxides	8	16	16	8	4	32	22	8	36	46
Oxidable-organic	0	3	2	2	1	3	2	2	3	2
Crystalline Fe oxides	15	20	18	18	12	42	38	17	58	46
Residual	15	38	37	34	34	63	88	90	44	41
<i>Cu (<math>\mu\text{g g}^{-1}</math>)</i>										
Exchangeable	1	2	1	1	1	3	3	1	2	2
Mn oxyhydroxides	0	1	1	0	0	0.18	1	0	0	0
Amorphous Fe oxides	4	7	6	5	3	7	5	5	6	6
Oxidable-organic	0	1	0	1	0	1	1	1	0	1
Crystalline Fe oxides	5	6	6	5	3	8	8	4	10	8
Residual	9	19	17	21	6	21	16	34	19	19
<i>Zn (<math>\mu\text{g g}^{-1}</math>)</i>										
Exchangeable	4	8	9	10	4	7	4	10	5	3
Mn oxyhydroxides	2	3	4	5	1	3	2	3	4	2
Amorphous Fe oxides	5	8	7	6	3	7	5	6	6	5
Oxidable-organic	1	1	1	1	1	1	1	1	0	1
Crystalline Fe oxides	16	10	11	11	6	17	18	10	13	20
Residual	18	53	53	49	21	52	53	96	48	42



**Figure 3** | Sequential extraction data for Fe, Mn, Cu and Zn in selected samples of both reservoirs (relative percentages).

Having total contents with ranges of  $13\text{--}34\ \mu\text{g Cu g}^{-1}$  (Tucuruí)/ $33\text{--}45\ \mu\text{g Cu g}^{-1}$  (Três Marias),  $35\text{--}85\ \mu\text{g Zn g}^{-1}$  (Tucuruí)/ $73\text{--}126\ \mu\text{g Zn g}^{-1}$  (Três Marias),  $54\text{--}107\ \mu\text{g Mn g}^{-1}$  (Tucuruí)/ $132\text{--}187\ \mu\text{g Mn g}^{-1}$  (Três Marias), and  $17,117\text{--}63,292\ \mu\text{g Fe g}^{-1}$  (Tucuruí)/ $48,180\text{--}66,228\ \mu\text{g Fe g}^{-1}$  (Três Marias), the distribution of metals is strongly influenced by Fe-oxides/hydroxides. The abundance of amorphous and crystalline Fe and Al oxides/hydroxides had already been identified in the clay fraction of the sediments from both reservoirs, associated with clay minerals (Fonseca *et al.* 2011).

Although sediments show a relatively homogeneous texture with the major contribution of fine-grained material, a few samples of Tucuruí have a significant sandy component (e.g. TUC 4: 36.5% sand). However, the variation of the texture does not seem to affect the speciation of metals in the samples and a correlation between the percentage of clay or silt and the more labile fraction of metals was not even found, with the exception of Cu. Only the residual fractions of Fe, Mn and Cu seem to increase with the increase of the silt fraction.

In Tucuruí, Fe is equitably distributed between crystalline (22.1–35.8%) and amorphous oxides (21.7–31.4%), while in Três Marias, Fe is more crystalline (~45%), hence

the composition of the main soil groups in the feeding area, mainly consisting of red dystrophic Latosols, resulting from intense weathering on dominant Fe-rich detrital lithology (Fonseca *et al.* 2007). As a consequence of this dissimilarity, in Tucuruí the soluble and exchangeable Fe forms are much more significant (16.1–22.8%) relative to Três Marias (8.44–11.29%). The lower degree of crystallinity affects their reactivity, easily releasing Fe to the more labile fractions.

Also, the redox potential in the bottom layers of Tucuruí, in the dry season, is lower (average value: 13 mv) than in the corresponding period in Três Marias (average value: 62 mv), enhancing the release of the Fe and Mn as exchangeable cations from the metal bearing-phases (Fe- or Mn-oxides). In both systems, oxidized ferric  $\text{Fe}^{3+}$  can precipitate to form a variety of relatively insoluble oxides, hydroxides and oxyhydroxides or they can enter into the lake in particulate forms resulting from erosion processes in the basin.

Mn oxides show low abundances and most Mn is associated with the more labile fractions, denoting the preponderance of reduced Mn forms in the sediments, which reflects the acidic and reducing conditions of the

bottom. The prevalence of this fraction discloses the higher levels of manganese found in the bottom water column (see Table 2). Reduced forms of Mn may be present in the clay minerals of sediments, dominated by kaolinite and illite (Fonseca *et al.* 2011), and could be slowly released through weathering, undergoing significant chemical transformations.

Iron and manganese exist in both oxidized and reduced oxidation states in these systems. Therefore the forms and cycling of these elements are strongly determined by the oxidation/reduction (redox) conditions in the environment (Giblin 2009). The redox conditions of Três Marias and Tucuruí (Table 2), with high values at the surface (>200 mv), obviously decreasing in depth, especially in Tucuruí, suggests essentially oxidized forms of Fe and Mn in the water column (Fe(III), Mn(III) and Mn(IV)). Considering the pH values of the water, near neutral values, the most important oxidant for  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  in the aquatic environment is oxygen. In contrast to  $\text{Fe}^{2+}$ , the chemical oxidation of  $\text{Mn}^{2+}$  is much slower, which allows for a much greater mobility for Mn than for Fe in these aquatic systems (Giblin 2009). The oxidized forms of these two elements in the aquatic environment, explain their low overall values throughout the water column, although there is an increase in their levels at the bottom, especially in Tucuruí, where reduced conditions are higher.

Sediments containing particles which offer surfaces for the (ad)sorption of ions (Chalar & Tundisi 2001) can play a major role in sequestering phosphorus from the water column (Mayer *et al.* 2006; Lake *et al.* 2007). Because iron is ubiquitous in the environment, in the sediments of these tropical lakes, rich in amorphous and crystalline iron oxides, these compounds could be an important factor in regulating the sediment's adsorption capacity (Zhang & Huang 2007; Crowe *et al.* 2008).  $\text{Fe}(\text{OH})_3$  has a strong binding capacity for inorganic phosphate in the water column and oxic sediments, so, it is not surprising that previous studies achieved in these reservoirs (Fonseca *et al.* 2011) showed that P is mainly retained in the bottom sediments by adsorption, fixation or precipitation on fine grained particles of Fe-oxides and hydroxides.

Cu and Zn have a distinct behaviour in relation to redox potential, from that of Fe and Mn. Under reduced conditions the solubility of both elements decreases and they usually precipitate as sulfides. This behaviour explains the low contents of Cu and Zn in the deeper water zones of both reservoirs where anoxia prevailed (<0.0003 mg/L). Only in the wet season in the Três Marias reservoir, do they have a slight increase due to the higher oxygenation of the

deeper layers (oxygen saturation: 44.19%, see Table 2) as a consequence of a higher water circulation and vertical mixture of the water column, observed in this system by Morais *et al.* (2009). Although under the oxidizing conditions of the surface, the adsorbed Cu and Zn on suspended particles may be solubilized and mobilized with a consequent increase of their bioavailability, the neutral pH of the water column reduces this solubility, which explains the low levels of these two elements on the water surface (see Table 2). Cu and Zn ranging from 40 to 70% are associated with the residual fraction of sediments, probably in the silicate matrix of illites or kaolinites (the predominant clay minerals in the sediments), or strongly adsorbed through its siliceous tetrahedral surfaces, explaining the low abundances (4–12%) of soluble and exchangeable forms in the deposited material. These labile fractions can also be absorbed and utilized by organisms in these aquatic environments (Campbell 1995). Iron and Mn oxide minerals and compounds have long been known to scavenge trace elements from solution. These materials, preponderant in the sediments of both reservoirs, are ubiquitous in aquatic environments and play an important role in the fate and transport of trace elements (McCarty *et al.* 1998). Thus, Cu and Zn could be easily retained from the water by adsorption or precipitation/co-precipitation onto fine-size charged amorphous and crystalline iron particles, which represent the second major fraction of these elements. Cu is equitably distributed between crystalline and amorphous Fe-oxides (average values: Cu in amorphous Fe-oxides – Três Marias = 18.7%, Tucuruí = 14.6%, Cu in crystalline Fe-oxides – Três Marias = 20.0%, Tucuruí = 20.6%), while Zn is mainly adsorbed by crystalline Fe-oxides (average values: Zn in amorphous Fe-oxides – Três Marias = 8.2%, Tucuruí = 6.5%, Zn in crystalline Fe-oxides – Três Marias = 17.9%, Tucuruí = 18.7%). Mn oxides only have a slight influence on the retention of Zn.

## CONCLUSIONS

This study aims to explain the reason why the water column of the tropical lakes of Três Marias and Tucuruí are relatively poor in dissolved metals (e.g. Fe, Mn, Cu, Zn), although the lithologies and soils in the hinterland associated with high rainfall and temperature throughout the annual cycle should allow high leaching rates and be sources of vast amounts of metals to these systems.

Although they are in general slightly stratified lakes, in the deepest areas of both reservoirs, there occurs



stratification of dissolved oxygen, especially after the dry period, when anoxic conditions prevail. Given the major mineral forms to which metals are associated by adsorption/precipitation with relatively weak bonding forces (Fe: amorphous and crystalline oxides; Mn: exchangeable and labile fractions; Cu, Zn: residual fractions), the acid and reducing conditions in the sediment–water interface affect the release and mobilization of a few elements such as Fe and Mn, leading to a significant increase of their soluble forms in the accumulated material. Under the oxidizing conditions of surface waters, only adsorbed Cu–Zn are released from their mineral/organic solid hosts and mobilized. However, the near neutral pH of the waters decreases the solubility of both elements which are thus retained in the aqueous phase of sediments and in the sediment–water interface.

In the dry period, the decrease of the redox potential and the low oxygen abundances (see Table 2) enhance the reduction of Fe(III) to the more soluble Fe(II) with subsequent release of the strongly retained phosphorus. As this element is a potentially limiting nutrient in most fresh-water environments, its release will strongly impact the primary productivity of the water column and will change the redox conditions in the surface sediment layer and in the bottom waters. Thus, through a close correlation between nutrient and metallic elements in these aqueous environments, the release of P bound to Fe-oxides, may reduce the redox conditions in the hypolimnia, which may in turn enhance the Fe reduction with subsequent solubility increase.

The geochemical behaviour of metals in the reservoir sediments influences their release to the water column, directly affecting water quality. In relation to the most abundant metallic elements (Fe, Mn, Cu, Zn) the strong retention by iron oxides of sediments and a near neutral water pH, explains their wide-ranging low values in the water column.

Although the two lake systems are located in different climatic regions, humid tropical climate (Tucuruí) and tropical dry savanna climate (Três Marias), and have different lithologic sources of sediments (most diverse, of finer texture and richer in basic materials, in Tucuruí), with the exception of iron (with higher amorphous contents in Tucuruí), most of the metallic elements have similar geochemical behaviour, either in the sediments or in the water column.

Given the significant relationship between sediments and the water column and its dependence on the chemical conditions of the environment, the geochemical study of the bottom sediments is crucial when trying to manage aquatic systems.

## ACKNOWLEDGEMENTS

This research was co-financed by FEDER (UE) and FCT (Portugal) through project SABRE (POCI/CTE-GEX/59277/2004) and by Eletronorte (Empresa Elétrica do Norte do Brasil), through the project ‘Progressive degradation of soils: geological challenges and strategies to a sustainable resolution of the problem’. The authors are grateful to four anonymous reviewers for providing comments and valuable suggestions on an earlier version of this paper.

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