

# Geochemistry of metals in the bottom sediments of tropical dam reservoirs in San Francisco River (Três Marias, MG) and Tocantins River (Tucuruí, PA), Brazil

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## 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 easiness 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 at 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 assess 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 solid hosts and mobilized to the aqueous phase of sediments, which show high levels of soluble forms of these elements. However, the solubilisation process and the release to the water column are not very extensive, as abundances of metals such as Fe and Mn in water are low, although increasing with depth.

**Keywords:** aquatic systems management, metals speciation, reservoir sediments, water quality.

## 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, 2003). Due to the toxicity and ability of the heavy metals to accumulate in the biota, pollution by these elements is a serious problem.

In lacustrine systems, concentrations of metals in the water result from (1) entry into the basin through point and diffuse sources, (2) transport under dissolved and particulate forms outcoming from erosion processes in the basin, (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 forms, including different oxidation states, a wide variety of organic and inorganic complexes in the dissolved, colloidal and solid phases. Considering the metals with higher concentrations in the freshwaters ecosystems, 90-99% of the total Fe and more than 80% of the Mn are found in particulate form. Only a minor amount is transported in dissolved forms as they quickly precipitate upon reaching oxic water, except under acidic conditions (Giblin, 2009).

These metallic elements undergo extensive cycling within lake sediments and within the water column. In spite of this extensive recycling, many lakes are extremely retentive of metals and often the majority of elements coming into a lake are lost to the sediments. However, the retention rate depends on the lake mixing, the lake trophic status and the lake chemistry (Giblin,

2009). Even considering that sediments are the main sink for these elements, when environmental conditions change (pH, sediment redox potential, etc.), sediments can act as a source of metals.

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, given the inputs of these elements into the hydrological system, due to the easiness of 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, which may reduce the oxygen levels (Crowe et al., 2008).

A wide 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 of sediments, much higher than the corresponding levels in the parent soils (Fonseca et al., 2007, 2009), not showing, however, high concentrations in the water column (Morais et al. 2009). We have analyzed *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 and by sequential extraction methods, with the purpose of elucidating 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 is a large lake, with 1,050 km<sup>2</sup> of inundated area, volume of 17.8 km<sup>3</sup>, main axis 150 km long; average depth is 16.8 m. The climate is tropical climate savanna (Aw type, Köppen classification), characterized by very dry winters and rainy summers, with an average annual precipitation near 1200-1300 mm. It is fed by a large variety of waterways, tributaries of the main watercourse, and the average residence time is about 90 days.

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 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, in the Amazon basin and has a wet tropical climate. It is the second largest reservoir in Brazil, with 2,850 km<sup>2</sup> of inundated area, watershed with 758,000 km<sup>2</sup> of area and 45.5 km<sup>3</sup> of maximum volume. The air temperature and the rain are higher throughout the annual cycle (precipitation up to 2400 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 to the Três Marias reservoir and belong to three large geological unities: Cráton Amazônico, Araguaia Belt and Sedimentary Basin of Parnaíba (Tassinari and 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; 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 on the structure and behaviour of these reservoirs, in both periods, we have collected 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). 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 two meters, using a multiparameter probe TURO T611, of the following physical and chemical parameters: pH, dissolved O<sub>2</sub> concentration, O<sub>2</sub> saturation and Eh.

**Water analysis:** The concentrations of Fe and Mn were determined by 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 “masters metals” owing to their ability to strongly influence the cycles of other biologically important elements.

**Sediment analysis:** In both reservoirs and in each sampling period, in preserved samples (cooling at 4±2°C), we have performed analysis of total contents of major elements, grain-size, pH (H<sub>2</sub>O) and soluble contents 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 (easily exchangeable ions, metal carbonates, oxides, sulfides, organometallic compounds, ions in crystal lattices of minerals, etc.), which determine their mobilization capacity and bioavailability. In order to study metals speciation, selected samples (based on total and soluble metals contents and textural characteristics), 5 from Três Marias and 5 from Tucuruí, were submitted to a series of 6 extractions, 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 (Fe<sub>2</sub>O<sub>3</sub>, 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:** This 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 (H<sub>2</sub>O) was measured by a potentiometer in a water-sediment suspension.

**Soluble contents of Fe, Mn, Cu and Zn:** evaluation of the soluble contents was based on Lakanen and Ervio method (Cottenie et al., 1980).

**Sequential chemical extraction:** The procedure of sequential chemical extraction of a series of 6 fractions and subsequent AAS analysis has been discussed by Cardoso Fonseca et al., (1998). The chemical fractions dissolved by selected mixture of reagents are the follow: F1- water soluble metals and dissolved exchangeable ions, specifically adsorbed and bound to carbonates; F2- metals bound to Mn oxyhydroxides; F3- metals bound to amorphous Fe oxides; F4- metals

bound to organic matter; sulphide (primary sulphide minerals could not be totally leached out in this step); F5- metals bound to crystalline Fe oxides; F6- Residual metals: matrix bound in lattice positions, in resistant oxides and sulphides.

The accuracy and analytical precision of the sequential analysis have been checked by the analysis of reference materials and duplicate samples (a split of sample, submitted as two separate samples) in each analytical set. The precision 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 6 fractions / the independent total concentration) ranged from 80 to 115%.

## Results and Discussion

In both systems, the grain-size distribution of the bottom sediments clearly evidences the selective erosion of the fine-grained soil particles of the drainage basins. 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 fall 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.

Iron and manganese are present in relatively high concentrations in these freshwater (Table 1) ecosystems and they can be viewed as “master metals” owing to their ability to strongly influence the cycles of other biologically important elements through microbially mediated and abiotic chemical reactions (Giblin, 2009). Both elements are abundant in the soils of the catchment area of both reservoirs, dominated by strongly acidic latosols containing gibbsite and/or iron oxide (Fonseca et al., 2007). Thus, Fe and Mn redox cycling may play important roles in determining the forms and cycling of trace metals in the lakes (Giblin, 2009), being especially important in regulating the chemical composition of the water column.

Três Marias (November 2005)										Tucuruí (November 2006)									
#	Fe <sub>2</sub> O <sub>3</sub> (%)	MnO (%)	Cu (ppm)	Zn (ppm)	Fe sol (ppm)	Mn sol (ppm)	Cu sol (ppm)	Zn sol (ppm)	pH (H <sub>2</sub> O)	#	Fe <sub>2</sub> O <sub>3</sub> (%)	MnO (%)	Cu (ppm)	Zn (ppm)	Fe sol (ppm)	Mn sol (ppm)	Cu sol (ppm)	Zn sol (ppm)	pH (H <sub>2</sub> O)
TM1	7.84	0,058	30	90	667	214	5,4	3,1	4.98	TUC 1	8.32	0,056	30	70	3316	251	7,5	5,5	5.34
TM2	10.7	0,055	40	100	2356	194	9,7	13,8	4.60	TUC 2B	9.28	0,083	320	260	6744	478	12,6	28,8	4.72
TM3	10.42	0,037	40	80	1916	98	9,6	7,6	4.68	TUC 3	13.04	0,199	40	80	7592	1260	8,5	6,6	4.63
TM4	11.27	0,037	40	90	762	99	10,7	8,8	4.74	TUC 4	5.7	0,053	20	50	2236	307	6,9	6,3	8.00
TM5	11.2	0,09	30	70	842	412	9,4	6,3	4.76	TUC 4B	3.84	0,018	20	40	608	62	3,9	1,6	6.73
TM6	7.31	0,013	< 10	< 30	186	16	2	0,4	4.48	TUC 4C	16.45	0,534	90	170	510	2532	16,6	2,8	6.37
TM7	9.98	0,069	30	60	1672	230	8,4	3,7	4.88	TUC 5A	12.46	0,105	40	80	9496	481	6,1	7,7	4.75
TM8	11.26	0,05	30	50	2096	180	8,5	5	4.60	TUC 7	9.11	0,075	40	90	3488	414	8	8,2	4.83
TM9	11.14	0,04	30	50	2524	122	9,5	5,1	4.61	TUC 8	9.64	0,064	30	80	5776	340	6,6	9,5	4.76
TM10A	10.91	0,099	20	60	2048	493	8,3	4,7	4.81	TUC 11	9.53	0,099	40	100	4192	580	9,7	6,2	4.92
TM11C	10.92	0,048	30	70	3592	149	10	5,9	4.57	TUC 12	10.34	0,067	40	80	6280	351	6,7	9,4	4.64
TM12	9.83	0,112	20	50	740	338	5,7	2	4.86	TUC 13A	10.79	0,088	40	80	6744	449	7	6,9	4.91
TM13	10.83	0,042	30	60	148	139	9,5	4,3	4.58	TUC 14	8.65	0,111	30	70	3796	700	6,4	7,3	5.43
TM14	11.04	0,061	30	60	3020	232	10,3	4,8	4.91	TUC 15	7.00	0,046	30	90	2636	232	7	10,8	4.72
TM16	8.09	0,074	20	50	636	355	5,2	3	5.19	TUC 16	8.11	0,123	30	80	2256	764	6,9	5,2	5.50
TM17	10.67	0,109	30	60	2028	518	9,8	5,3	4.84	TUC 17	5.92	0,101	20	70	2548	503	5,5	4,5	6.51
TM20	9.06	0,067	30	60	1340	267	7,4	3,5	5.04	TUC 18	5.48	0,125	20	70	1464	744	4,2	3,6	6.23
										TUC 19	5.09	0,06	20	70	1476	257	5,4	5,7	4.91
										TUC 20	0.55	0,01	< 10	< 30	31	3	0,1	0,1	7.12

Table 1 – Contents of the total and soluble fractions of the major metallic elements, Fe, Mn, Cu and Zn, for each sample and for each reservoir in the period in which the redox conditions are more unstable and lower (after drought, in November).

Iron and manganese, as well as copper and zinc, have similar distribution patterns in each reservoir, denoting (1) their provenance from the same sources in the drainage areas and (2) occurrence in the sediments under similar inorganic/organic forms and having preferential association to the same mineral and organic compounds. The higher values of these metallic elements in the sediments when comparing with data achieved in similar systems under Mediterranean climate (e.g. Fonseca et al., 2003) can be a consequence of (1) higher values of temperature and precipitation throughout the annual cycle, which lead 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, (3) predominance of kaolinite in the clay fraction of sediments (Fonseca et al., 2007, 2009); though it is the clay mineral having lower cationic exchange capacity, it strongly adsorbs metallic elements through its siliceous tetrahedral surfaces.

Some heavy metals outcoming 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. Under the acidic conditions of sediments of both reservoirs (medium values: Três Marias- pH(H<sub>2</sub>O)- 5,1; Tucuruí- pH(H<sub>2</sub>O)- 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. This solubilisation process can probably explain the high solubility of these elements (particularly Fe and Mn) found in the studied sediments (see table 1). Although there is an obvious increase of metals solubility with decreased pH, there is no proportionality between both variables because the solubility is 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, as they precipitate as sulphide constituents. However, even, considering the relatively high metal content, both in the total and in the soluble fractions of sediments, their concentration in natural waters are lower than expected (Table 2).

Parameters	Três Marias Reservoir							
	May 2005				November 2005			
	Surface		Bottom		Surface		Bottom	
	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.
Oxygen saturation (%)	92,62	11,06	44,19	22,13	78,22	2,63	21,51	25,52
Dissolved Oxygen	6,99	0,77	3,44	1,73	6,16	0,23	1,75	2,06
pH	7,49	0,15	6,98	0,38	7,15	0,29	6,44	0,31
Redox Potential (mV)	225,56	28,26	194,83	62,68	185,82	38,40	62,36	168,37
Iron (mg/l Fe)	0,004	0,005	0,004	0,004	0,002	0,003	0,068	0,166
Manganese (mg/l Mn)	0,010	0,004	0,107	0,004	<0,06		0,005	0,005
Parameters	Tucuruí Reservoir							
	April 2006				November 2006			
	Surface		Bottom		Surface		Bottom	
	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.
Oxygen saturation (%)	72,83	7,81	25,41	23,73	70,56	10,53	29,29	30,98
Dissolved Oxygen	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)	251,83	64,59	118,00	184,41	160,13	64,70	12,91	153,54
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

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

Previous studies using data from physical and chemical characterization of the water column conducted by Morais (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 Tucuruí), conditioning the oxidation-reduction of the environment. The redox conditions in the sediment-water interface and consequently, the major or minor solubility of nutrients and metals in the sediments are followed, respectively, by their diffusion or no-diffusion to the water column. In the dry periods (represented by November in these systems), under anoxic conditions, the release of nutrients, metals and other chemical components from the bottom lake sediments is coupled with increase of their soluble counterparts in sediments (interstitial fluids) and in the overlying water.

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 performed sequential extraction methods, and obtained six different fractions for each element (Fig. 1).

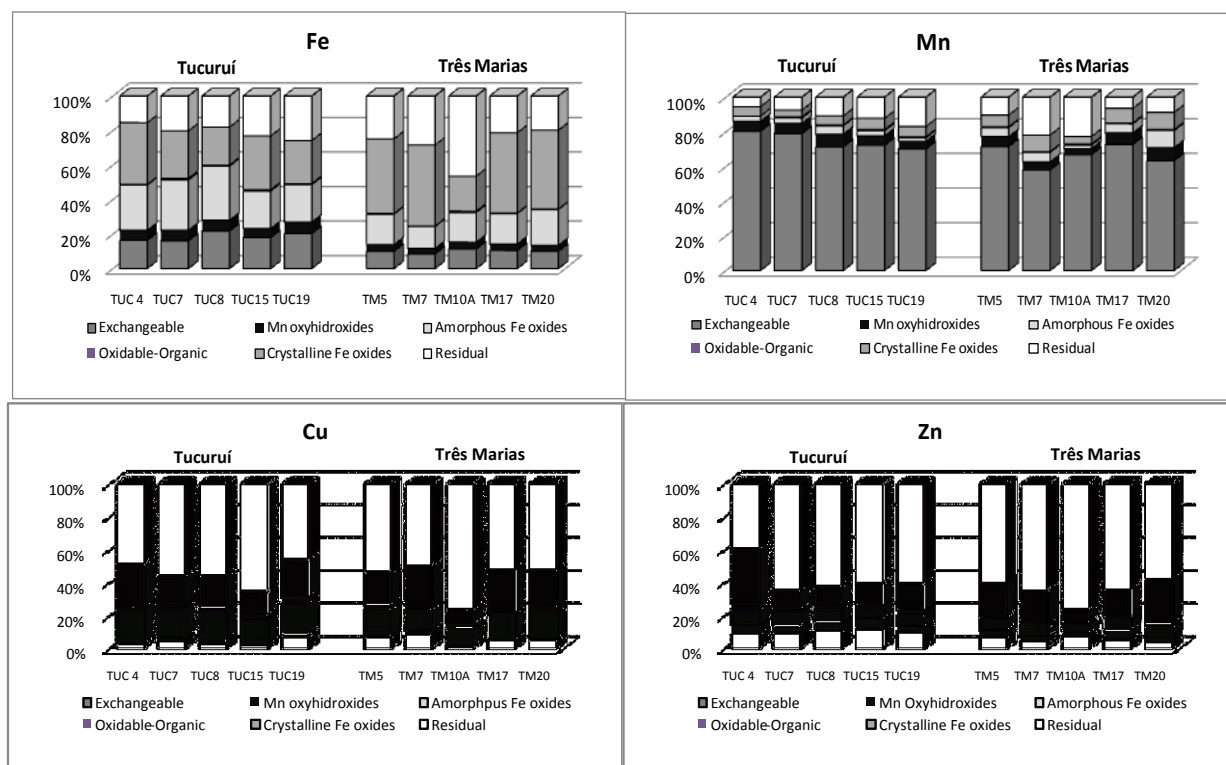


Fig. 1 – Sequential extraction data for Fe, Mn, Cu and Zn in selected samples of both reservoirs

Having total contents ranging between 13-34  $\mu\text{gCu g}^{-1}$  (Tucuruí)/33-45  $\mu\text{gCu g}^{-1}$  (Três Marias), 35-85  $\mu\text{gZn g}^{-1}$  (Tucuruí)/73-126  $\mu\text{gZn g}^{-1}$  (Três Marias), 54-107  $\mu\text{gMn g}^{-1}$  (Tucuruí)/132-187  $\mu\text{gMn g}^{-1}$  (Três Marias), and 17117-63292  $\mu\text{gFe g}^{-1}$  (Tucuruí)/ 48180-66228  $\mu\text{gFe g}^{-1}$  (Três Marias), the distribution of metals is strongly influenced by Fe-oxides/hydroxides.

In Tucuruí, Fe is equitably distributed between crystalline (22.1 to 35.8%) and amorphous oxides (21.7 to 31.4%), while in Três Marias, with the exception of coarser samples, Fe is more crystalline (~ 45%), hence the composition of the main soil groups in the feeding area, mainly consisting of red dystrophic Latosols, outcoming 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%) relatively to Três Marias (8,44-11,29%). The lower degree of crystallinity affects their reactivity, easily releasing Fe to the more labile fractions. 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 under particulate forms outcoming 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., 2007, 2009), 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. 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. 40% to 70% of Cu and Zn are associated to the residual fraction, probably in the silicate matrix of sediments, or strongly adsorbed through its siliceous tetrahedral surfaces, explaining the low abundances (4-12%) of soluble and exchangeable forms. These labile fractions can also be absorbed and utilized by organisms in these aquatic environments (Campbel, 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 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, while Zn is mainly adsorbed by crystalline Fe-oxides. Mn oxides only have a slightly importance on the retention of Zn.

## Conclusions

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, the acid and reducing conditions in the sediment-water interface affect their release and mobilization, leading to a significant increase of the soluble forms in the accumulated material. The geochemical behavior of metals in the reservoir sediments influences their release to the water column, directly affecting water quality. Being directly influenced by soil type and land use of drainage basins, as well as by chemical conditions of the environment, the geochemical study of the bottom sediments is crucial when trying to make a proper management of aquatic systems.

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