DOI: 10.5327/Z0102-9800201400020004

Mercury distribution in sediments of a shallow tropical reservoir in Brazil

Vinicius Andrade Souza[1]
Julio Cesar Wasserman[1]*

[1]Department of Geoenvironmental Analysis, Universidade Federal Fluminense – Niterói (RJ), Brazil.

*Corresponding author: geowass@vm.uff.br

Resumo

O mercúrio é um elemento tóxico distribuído globalmente em áreas contaminadas e também em ambientes remotos. No caso do Lago de Juturnaíba (Estado do Rio de Janeiro, Sudeste do Brasil), parte da paisagem foi submergida após a construção de uma represa, favorecendo a geração de condições anóxicas e baixo potencial redox e modificando as características geoquímicas. O entendimento do comportamento dos poluentes em Juturnaíba é necessário, pois o sistema é utilizado para vários propósitos, inclusive captação de água para consumo humano, irrigação, lazer e pesca amadora. No presente estudo, a distribuição das concentrações de mercúrio foi avaliada em sedimentos de superfície do reservatório de Juturnaíba, a qual foi interpretada à luz da granulometria e de concentrações de nitrogênio e carbono. Trinta e duas amostras de sedimento de superfície foram coletadas em março de 2011 a fim de se determinar as concentrações de mercúrio por espectrofotometria de absorção atômica com acessório vapor frio (CV-AAS). O mapa de distribuição indica que os maiores valores de mercúrio (211 ng/g) são associados com a presença de bancos de macrófitas aquáticas. Os valores mais baixos (58 ng/g) foram observados na porção Norte, associados com os aportes do Rio São João que drena uma região mais bem preservada. Deve ser sublinhado que as maiores concentrações associadas à maior produção de macrófitas é exatamente onde é mais intenso o processo de metilação, constituindo uma ameaça às populações humanas e ao meio ambiente.

Palavras-chave: reserva tropical, mercúrio total, contaminação ambiental, carbono orgânico total, nitrogênio total.

Abstract

Mercury is a toxic element that is globally distributed in contaminated areas, as well as remote environments. In the case of the Juturnaíba Lake (State of Rio de Janeiro, Southeastern Brazil), part of the landscape was flooded after the construction of a dam, favoring the development of anoxic conditions, reducing the redox potential within the sediments and modifying the geochemical conditions. The understanding of the pollutants behavior in the Juturnaíba is necessary, because the system is a multi-purpose environment that is used for water supply, agricultural irrigation, leisure and fishing. In the present study, we evaluated the mercury distribution of superficial sediments of the Juturnaíba reservoir that was interpreted in the light of granulometry and concentrations of carbon and nitrogen. Thirty-two surface sediment samples were collected in March 2011 in order to carry out the total mercury analyses with Cold

Vapor Atomic Absorption Spectrophotometry (CV-AAS). The distribution map indicates that the highest mercury values (211 ng/g) are associated with the presence of the aquatic macrophytes banks. The lowest values (58 ng/g) were observed in the Northern portion, associated with the inputs of the São João River that drains a better preserved area. It is necessary to underline that the highest concentrations occur in an area of significant macrophyte production, where methylation process may be more significant, constituting a threat for humans and the environment.

Keywords*: tropical reservoir, total mercury, environmental contamination, total organic carbon, total nitrogen.*

1. INTRODUCTION

Mercury (Hg) is a pollutant of worldwide human health concern due to its toxicity and capability for long-range atmospheric transport (USEPA 1997, Knightes *et al.* 2014). Indeed, the release of this pollutant from anthropogenic activities and its long range atmospheric transport have significantly increased its concentrations in the aquatic environment and consequently in the biota (Temme *et al.* 2003). Lindqvist (1994) estimated that only 10-20% of the Hg emitted from point sources is deposited in the neighborhood of its emission, the remainder being deposited regionally or globally. Toxicological concern about mercury bioaccumulation in aquatic food chains, especially of methylmercury (MeHg), has led to extensive research, mainly in the temperate regions and in the Amazon region. The studies were focused on the concentrations of Hg and its speciation in different environmental compartments including water, sediment and biota (Wasserman *et al.* 2003, Stoichev *et al.* 2004, Knightes *et al.* 2014, Small & Hintelmann 2014).

Considering the biogeochemical cycle of the mercury, sedimentary environments draw particular attention, because in such conditions mercury accumulation and transformations are favored by the lack of a strong hydrodynamic flow, generating conditions for fine sediment setting, stratification and oxygen depletion (Peretyazhko *et al.* 2006). Anoxic sediments also favor the development of sulfate-reducing bacteria, which have been described as important mercury methylators (Duran *et al.* 2008, Achá *et al.* 2011). Besides bacterial methylation, other chemical controls of the mercury speciation may occur in anoxic conditions (Muresan *et al.* 2008), and the geochemical partitioning is severely affected (Barrocas & Wasserman 1998).

The concern of reservoirs for the biogeochemistry of mercury arises from the fact that, as described above, flooding may considerably change the redox conditions, favoring the methylation process. For instance, the construction of a dam in the French Guiana (Petit-Sault Lake) to produce electric energy promoted the increase in concentrations of fish (Richard *et al.* 2002) and, therefore, increased risk of human contamination. In this same environment, a strong degassing process of metallic mercury was observed by Amouroux *et al.* (1999), a mercury that could only be generated from the upstream artisanal gold mining activities. Muresan *et al.* (2008) calculated an internal methylation rate in the Petit-Sault Lake of the order of 8.1 Molar year^{-1}. Although these figures are preoccupying, biomagnification rates through the trophic chain may be still higher as shown in the extensive work of Aula *et al.* (1994) in the Amazonian Tucuruí Reservoir and in the relatively pristine environment of Ilha Grande Bay in Rio de Janeiro (Guedes Seixas *et al.* 2014).

Although the methylation of mercury is consistently recorded in reservoirs, the processes are still barely known. The role of bacteria associated with aquatic macrophytes in freshwater environments has been established in *in vitro* radio-assays, showing that methylation rates may attain 36% (Achá *et al.* 2005, Correia *et al.* 2012). After Guimarães *et al.* (2000). This may be the most important methylation processes in the Amazonian environment and is probably very important in freshwater reservoirs.

In the early 1970s, the Brazilian Government established a policy for the occupation of the territory that, among many actions, planned the construction of dams and reservoirs for the storage of water and for the production of energy. The Tucuruí Reservoir is one of these constructions that alone was responsible for the flooding of over 2,400 km^2 (Brasil & ELETROBRAS 1987). Besides the significant deforestation, the construction of the dam modified the whole sedimentological and chemical setting of the region (Fearnside 2001). Following the same philosophy, DNOS (National Department of Sanitation Works) proposed the construction of a dam in the São João Basin (70 km, East of Rio de Janeiro) with the aim of providing abundant water for an agricultural settlement downstream of the Basin (Binzstok 1999). The whole project has certain similarities with what has been irresponsibly done throughout the world, and a good example was described by Aldhous (2004) in the Island of Borneo, where soil acidification due to organic matter oxidation hinder further agricultural developments and the peat formed under anoxic conditions started to burn periodically.

Presently, the Juturnaíba Lake provides treated water for a population of over one million inhabitants and is the second most important reservoir of clean fresh water in the State of Rio de Janeiro. Due to the construction of the dam, the water renewal time increased to almost 40 days (Bidegain & Völcker 2003), favoring the concentration of nutrients, stimulating the proliferation of aquatic macrophytes, among them *Egeria densa, Ceratophyllum demersum, Salvinia auriculata* and less frequent *Eichhornia crassipes*, which is indicative of the eutrophic environments. These aquatic plants may be responsible for various chemical changes, including the methylation of mercury, as described above. The southern and eastern shores of the dam are also covered with thick stands of the cattail *Typha domingensis*, which present the important role of purification of polluted water by absorbing heavy metals and other pollutants (Millán *et al.* 2014).

In this environment, the superficial sediment may be considered the ultimate deposit for heavy metals, due to the fact that it is a low hydrodynamic environment which serves as a geochemical barrier (sink) for metals (Machado *et al.* 2002, Cosio *et al.* 2014). The sediment shows less variation with time and space compared with water, and can provide an excellent proxy for anthropogenic impacts, allowing a more consistent evaluation of the spatial and temporal variability of the contamination (Guevara *et al.* 2005).

In the Juturnaíba reservoir, flooding occurred without the removal of the riparian vegetation, favoring the development of anoxic conditions, reducing the redox potential and modifying the geochemical conditions. The rectification of the tributaries had also a direct impact on physical parameters, such as channel geometry, bed elevation, composition and stability of the substrate, velocity, turbidity, sediment transport, flow and temperature (Batalla 2003).

Once inside the epilimnion of the reservoir, Hg can either be eliminated towards the atmosphere after photochemical reduction (Xiao *et al.* 1995, Peretyazhko *et al.* 2006), transferred to the hypolimnion after adsorption on particulate matter (like other heavy metals), or undergo further transformations such as methylation (Guimarães *et al.* 2006) or (co)precipitation (*e.g.*, with Fe species; Bura-Nakić *et al.* 2013).

In the present study, our objective was to evaluate the mercury distribution in superficial sediments of the Juturnaíba reservoir, using the model of attenuation of the concentration proposed by Wasserman and Queiroz (2004) and Ribeiro *et al.* (2013), which consists of an evaluation of the mobility of the metal based on its spatial distribution in surface sediments. Furthermore, the behavior of this metal was evaluated in the light of total carbon, total nitrogen concentrations and granulometry of the sediments.

2. MATERIALS AND METHODS

2.1. Study area

The Juturnaíba Lake (Figure 1) was built at the beginning of the 1980s in the municipality of Silva Jardim, in the state of Rio de Janeiro. According to FEEMA (1986), the reservoir is classified as mesotrophic, and the annual precipitation in the region varies between 1,500 and 2,500 mm. The surface of the dam is 43 km^2, 85 km perimeter, with a maximum width of 4 km and a maximum length of 15 km. The dam has a water storage capacity of 100 million m^3 and the amount of total solids received by the reservoir is approximately 100 mg/L, of which 35% are organic residues (Barcellos *et al.* 2012). For this reason, the water transparency is low, circa 0.75 m on average as inferred from Secchi disc measurements (Wasserman 2012).

In a recent study, Wasserman (2012) sampled monthly the water for two years and observed that the pH is neutral with an average value of 6.5, indicating that the area is not greatly affected by any chemical process that would modify acidity, like intense primary phytoplankton production (that would increase the pH) or significant loads of organic acids or other substances that would decrease the pH. Juturnaíba Lake is a shallow system characterized by depths reaching 6 meters, which occurs mainly in the area of the former Juturnaíba Lagoon (before flooding). In other areas, depths do not exceed 3 meters. Nevertheless, the lake has a relative stratification, which allows a distinct epilimnion and hypolimnion that do not entail the occurrence of a thermocline. After this same author, the average water temperature is 24.6ºC.

The soils in the region are extremely weathered, composed mainly of aluminum and iron oxi-hydroxides, brown to red colored and characterized by a clayey and silty texture. The low cohesion of the soil makes it susceptible to erosion. Moreover, the artificial rectification of the rivers improved soils draining, accelerated the water flow, increasing the erosion of banks and the sediment transport, causing changes in water quality in the Reservoir (Bidegain & Völcker 2003). All these processes may promote changes in the sedimentary and chemical characteristics of the sediments that may affect the mobility, speciation and availability of mercury.

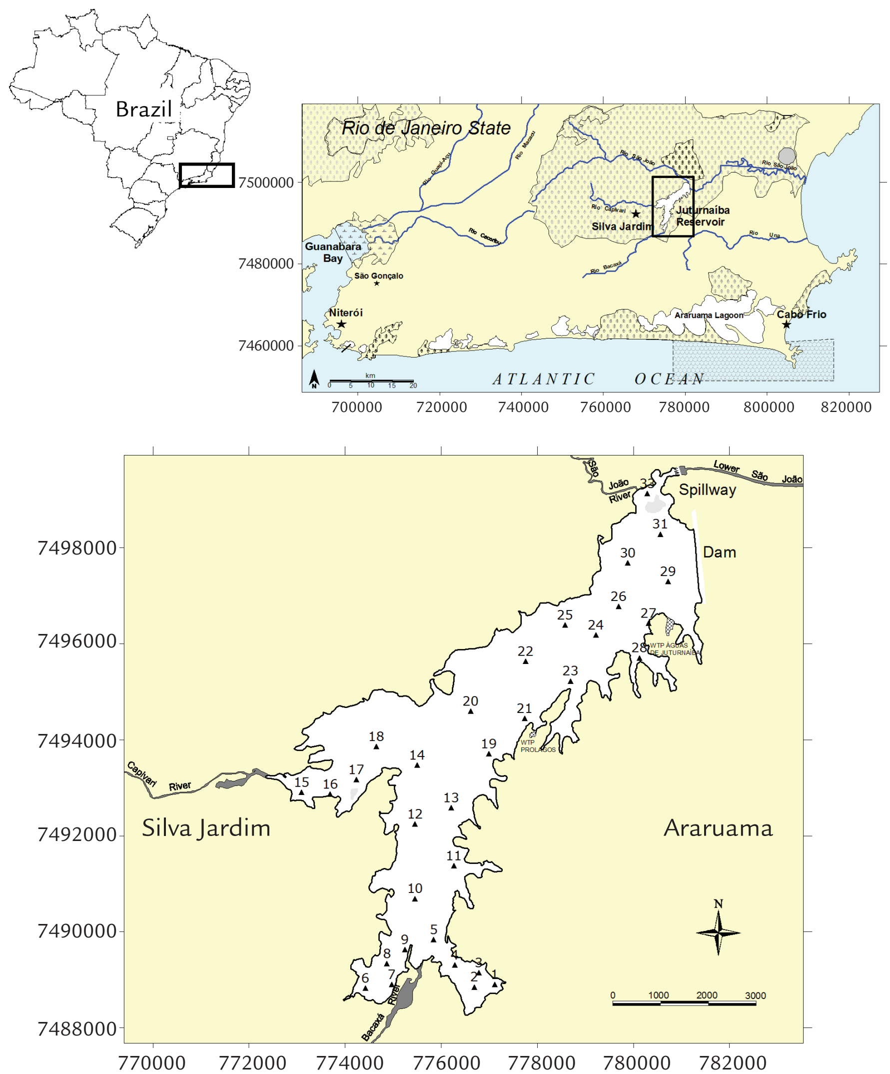

Figure 1
Location of sediment sampling stations in the State of Rio de Janeiro, southeastern Brazil.

2.2. Sampling and analytical procedures

Thirty two surface sediment samples were collected from Juturnaíba Lake in March 2011 in the stations depicted in Figure 1. All sampling site positions were determined with a global positioning system tracker (GPS). Collection was carried out with a Van-Veen grab and immediately placed in zip-lock plastic bags, and stored under refrigeration for transportation to the laboratory, where they were placed in a freezer until analysis. Besides the samples used for the mercury analysis, 300 g of each sample were stored in plastic bags as counter sample for other future analysis.

Sediment samples were analyzed for granulometry by wet sieving in a 63 mm aperture sieve, yielding the percentage of the silt-clay fraction. The analysis of Total Organic Carbon and Nitrogen was determined by the "Laboratório Bioagri" using an elemental analyzer LECO CHN-1000 that quantifies CO_2 and NO_2 unfastened from the combustion of the solid samples using O_2 as an oxidizing gas, at temperatures above 950°C. A catalyst converts CO to CO_2 and its quantification is done by an infrared detector (Nelson & Sommers 1996). Nitrogen was extracted by autoclaving samples with a persulfate solution as described by Valderrama (1981), and the resulting dissolved nitrate was measure after Grasshoff *et al.* (1983).

The quantification of total mercury in the sediments was carried out with an acid leaching with 50% *aqua regia* ($HCl:HNO_3$, 3:1) using the thermo-kinetic reactor (cold finger) containing distilled water, to prevent loss of mercury by volatilization (Malm *et al.* 1989). In each of the 32 extracts, 5 mL of sample were mixed with 5 mL of a 2% solution of $SnCl_2$, a reducing agent and purged with air to the detector. Mercury detection was carried out with a Coleman Bacarach cold vapor atomic absorption spectrophotometer. The certified material used was a PACS 2 with a reference value of 3.04 ng/g. The detection limit was determined as 0.002 ng/g, and the quantification limit was 0.003 ng/g. The overall accuracy of this method was determined with a recovery assay, where 98% of the introduced mercury was recovered.

The results of concentrations in the Juturnaíba Lake were plotted in a contour (iso-concentrations) maps with the software Surfer using the Krigging method of interpolation. Starting from this distribution map, the model of attenuation of concentrations was constructed (Wasserman & Queiroz 2004, Ribeiro *et al.* 2013). The attenuation of concentrations is based on the distance between contours. The larger is the distance the more mobile is the element in that region. To construct the attenuation model, it is necessary to determine pairs of positions, one in a contour and another in the immediately lower contour. Pairs must be located in a perpendicular line that crosses both contours. The distance between both contours is calculated and divided by the difference between the upper contour and the lower contour. The result is the attenuation of the concentration *A*, that is plotted in the median of the pair of points. This procedure is repeated until the whole map present attenuation points. Then, another distribution (contour) map is constructed, showing the mobility of the element in the studied area.

3. RESULTS AND DISCUSSION

Little is known about the sedimentary processes in Juturnaíba reservoir; however, it is possible to consider some sources of allochthonous and autochthonous sedimentary particles. The first group is from river sources and consists of detrital material and eroded soils that flow into the reservoir. The autochthonous sources are mainly from the erosion of the margins (Figure 2) or from resuspension of bottom sediments, a process that was observed by Wasserman (2012). In the study of this author, high concentrations of suspended particulate material, with high turbidity, were recorded, which were associated with the wave action in the margins. Since the reservoir was formed in the early 1980s, the drowning of large areas modified the erosional processes in the new formed margins, now submitted to the strength of wind formed waves, enhancing significantly the erosion. He also observed that extensive bancs of macrophytes in the mouth of the rivers function as barriers retaining sediments originated from the rivers.

The dominant sediment grain size in the reservoir is clay and silt (%< 63 μm) averaging 92.5% of the total. These fine grained sediments entered the system through the São João, Bacaxá and Capivari Rivers, promoting silting of the dam especially in their mouths (Figure 3). According to Förstner and Wittmann (1983) and more recently Dung *et al.* (2013), this grain size favors the accumulation of contaminants through surface chemical processes. The homogeneity shown in Figure 3 is probably a hydrodynamic response that is due to wind induced currents that should present very low velocities. The most reliable hypothesis for the sandier spots in the northern portion of the lake is the landslides of marginal cliffs that yielded the mixture of various granulometries.

The concentrations of Total Organic Carbon are presented in Figure 4, and the average in Juturnaíba was 7% (w/w), ranging from 0.8 to 27% (w/w). Sample 2 shows unusually high concentrations (27%), which can be associated with the low hydrodynamics of the region, and also a significant accumulation of organic matter from the aquatic macrophytes decomposition, in an effectively reducing environment.

One of the reasons for the appearance of generalized higher levels of organic carbon in the Juturnaíba Lake could be the fact that flooding caused submergence of the vegetation that was preserved in the bottom of the environment. In order to identify the type of the organic matter in the Reservoir, the nitrogen results were used to calculate the ratio carbon/

Figure 2
Cliffs formed in the margin of the lake due to wave beating.

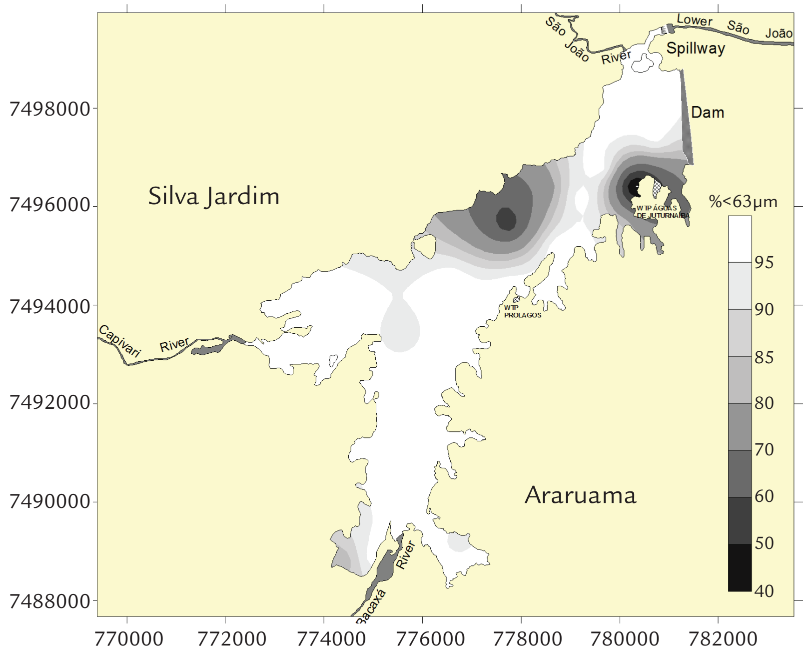

Figure 3
Distribution of the granulometry as indicated by the percentages of the fraction smaller than 63 µm.

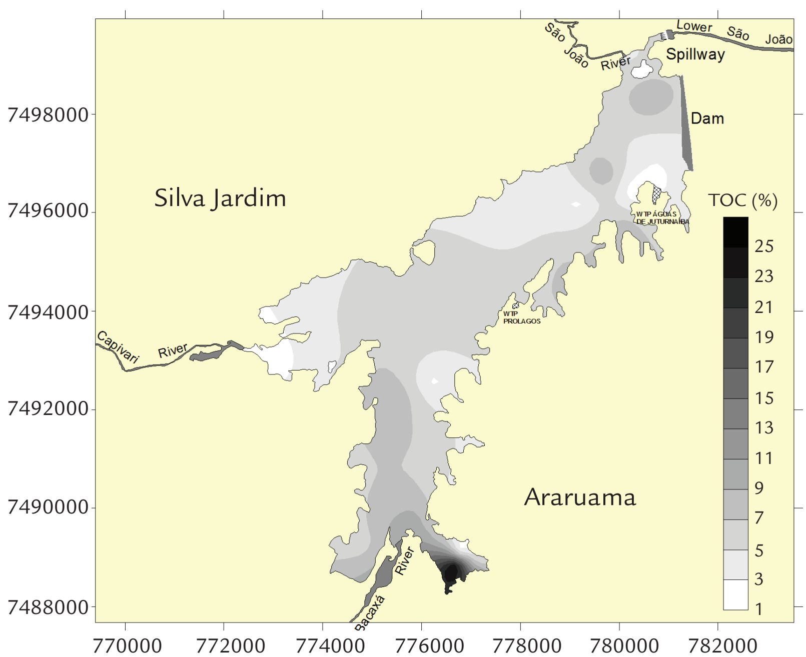

Figure 4
Distribution of the concentrations of organic carbon (TOC) given as percentage (w/w) in the sediments of the Juturnaíba Lake.

nitrogen (Figure 5). After Das *et al.* (2008), C/N ratios greater than 30 correspond to freshwater environments and values of up to 100 indicate low concentration of dissolved salts or a sharp input of organic matter from higher plants. Lower ratios of C/N (4 to 10) in lake sediments distinguish organic matter originated from weeds and phytoplankton (unstructured cellulose; Meyers & Ishiwatari 1993, Meyers 2003).

Based on the C/N ratios presented in Figure 5, it can be established that São João River has a strong contribution on organic matter from higher plants. In this sense, Das *et al.* (2008) argues that the input of sewage material rich in nitrogen, near the mouths of rivers, can mask the C/N ratio, suggesting the accumulation of organic matter despite the alteration of physico-chemical conditions in these ecosystems. Menor *et al.* (2001) speculated that the geochemical combination of several factors involved in an ecosystem influences C/N distribution patterns and must be considered in the data interpretations.

It is recognized that the presence of humic substances originated from litter leaching in the neighboring vegetated areas, under reducing environmental conditions, would promote a slight acidification of the water (Aiken *et al.* 1985).

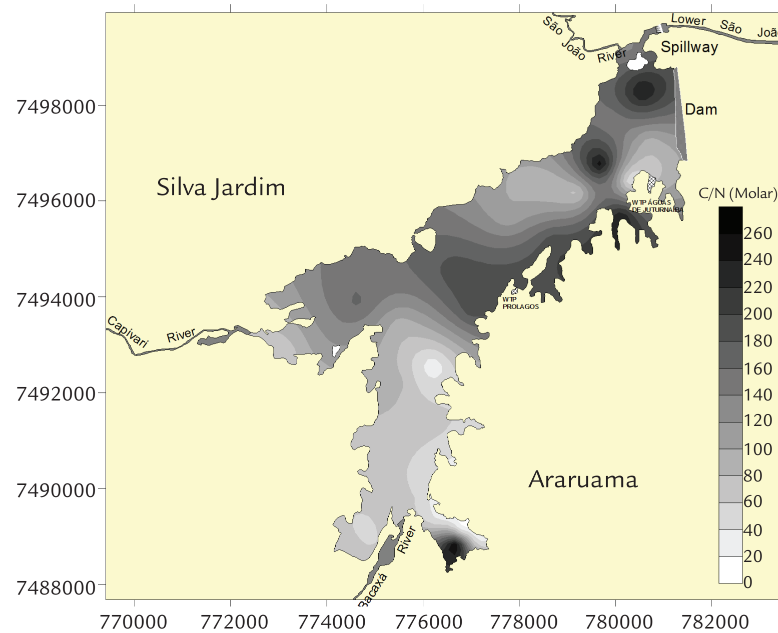

Figure 5

Distribution of the C/N ration in the sediments of the Juturnaíba Lake.

Both the acidification and the presence of dissolved organic matter may affect the behavior of the mercury in the sediments (Wallschläger *et al.* 1996). It is noteworthy that, on the other hand, algal blooms that may occur periodically in the environmental conditions of the reservoir slightly increase the pH in Juturnaíba (Pinilla-Agudelo 2009). Under such situations, the behavior of mercury would also be affected. These algal blooms have been registered mainly in the months of July, August, November and February (Wasserman 2012).

In a tropical hydroelectric plant reservoir of the French Guiana, the main flux of dissolved Hg to the hypolimnion was observed to be originated from both degradation of flooded vegetation and partial dissolution from ferralitic oxidized soils (made reducing due to flooding; Peretyazhko *et al.* 2005). In fact, the flooding of these types of soils, like in Juturnaíba, leads to a reductive dissolution of Fe oxi-hydroxides (FeO_x) and the migration of the released Hg into the aquatic ecosystem (Roulet *et al.*, 1998).

The average concentration of mercury in Juturnaíba was 0.148 mg/kg, but in three sampling points of the reservoir, 18, 19 and 23 (Table 1), the mercury concentrations reach values above the average concentration of reference materials such as mean shale or upper continental crust concentration, with 0.18 and 0.056 mg/kg, respectively (Reimann & De Caritat 1998). The average levels of Hg in the sediments of the Juturnaíba Lake were 0.211±0.058 mg/kg, which are smaller than 0.257±0.061 mg/kg, observed in the Wujiangdu Reservoir, China (Jiang *et al.* 2007) and higher than 0.039 mg kg^{-1} in the Newfoundland lakes, Canada (French *et al.* 1999), and 0.004–0.09 mg/kg in other uncontaminated reservoirs such as Lake Gordon and Lake Pedder, Australia (Bowles & Apte 1998).

The high concentrations of Hg (around 0.200 mg/kg; Figure 6) seem to be associated with the indentations of the reservoir, where reduced hydrodynamic conditions favor the settlement of aquatic macrophytes stands, constituting a suitable environment for the accumulation of this metal. The higher concentrations are not influenced by the particle size ($r=0.31$, $p<0.05$, $n=32$), however the inputs of the Capivari River, from the city of Silva Jardim (four km upstream), which may contain some mercury from domestic sewages and wastes, can contribute. In the central portion of the lake, some relatively high values were also observed (stations 11 and 12; Table 1) that could not be associated with fine grained sediments (Figure 3), neither

Table 1

Mercury (Hg) concentrations in the sampling points of the Juturnaíba Lake.

Station	Hg (mg/kg)	Station	Hg (mg/kg)	Station	Hg (mg/kg)	Station	Hg (mg/kg)
1	0.087	9	0.133	17	0.195	25	0.146
2	0.085	10	0.159	18	0.211	26	0.082
3	0.06	11	0.199	19	0.203	27	0.087
4	0.058	12	0.197	20	0.171	28	0.193
5	0.107	1 3	0.15	21	0.176	29	0.148
6	0.15	14	0.153	22	0.113	30	0.148
7	0.171	15	0.173	23	0.209	31	0.148
8	0.199	16	0.182	24	0.13	32	0.101

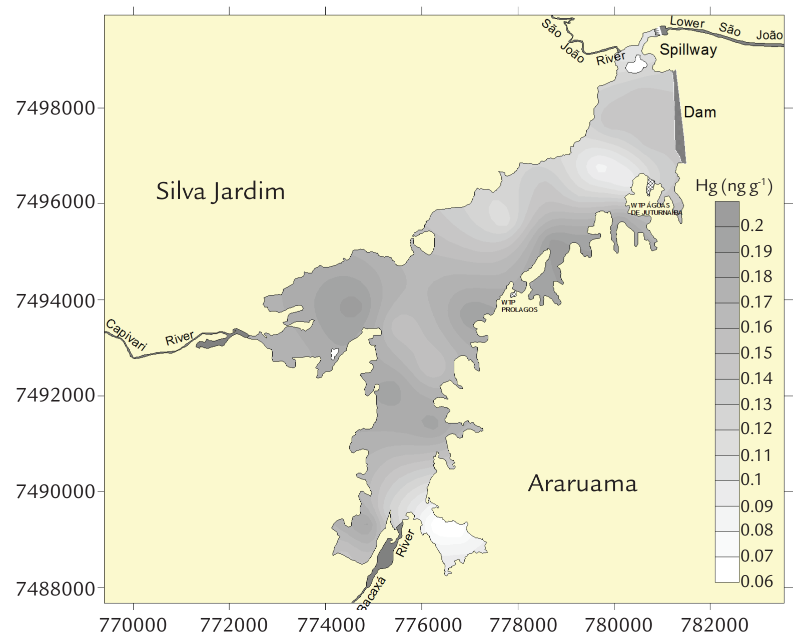

Figure 6
Distribution of concentrations of Hg (in ng/g).

with organic matter enrichment (Figure 4). Furthermore, this area did not show any sign of the presence of extensive aquatic macrophytes banks, like it was observed in the indentations of the reservoir. This enrichment in mercury concentrations could only be explained by ancient sedimentation condition, from the time when the dam was not yet constructed (early 1980s), that could not be detailed with the data presented in this work. The lowest values (0.058 mg/kg) were observed in the Southern portion, associated with the inputs of the Bacaxá River that drains a better preserved basin, with no human agglomeration or industries (Figure 6). This value is coherent with background concentrations observed in the region, reported for the Guanabara Bay (0.051 mg/kg) by Wasserman *et al.* (2000) and for the Sepetiba Bay (0.030 mg/kg), by Silva *et al.* (2003).

It is interesting to note that little accumulation of mercury was observed in the stations close to the dam and to the outlet of the São João River (Northern portion of the reservoir), indicating that, on the one hand, this river does not represent a significant source of mercury for the ecosystem (similarly to the Bacaxá River). On the other hand, it is interesting to note that the mercury that enters the ecosystem do not tend to accumulate around the spillway of the dam, indicating that the mercury is efficiently retained upstream in the reservoir. This can be better observed with the attenuation model (Figure 7), showing that the darker areas constitute barriers where mercury evolves more difficultly. In the reservoir (Figure 7), four spots of higher attenuation are responsible for the retention of mercury within the system. The association

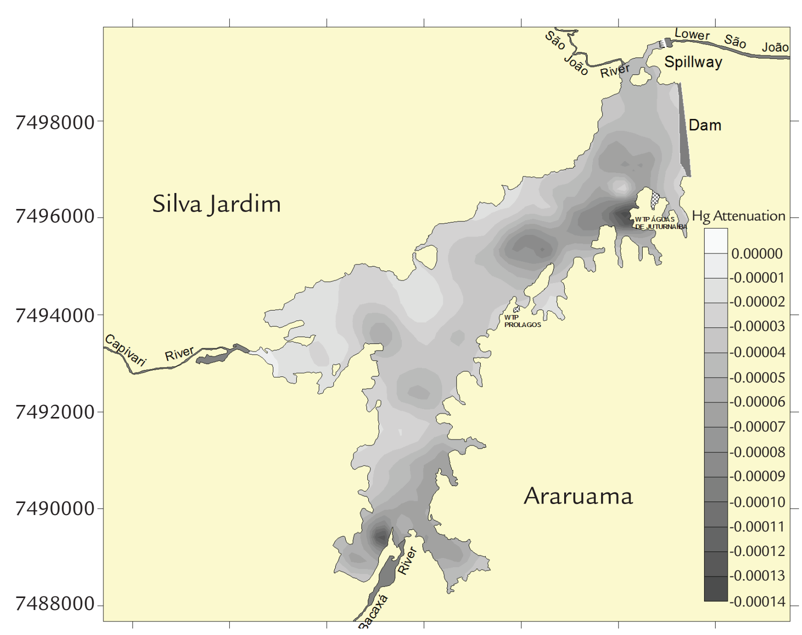

Figure 7
Hg attenuation in the Juturnaíba reservoir. The values of attenuation are dimensionless.

of these spots with physicochemical parameters was not demonstrated in the present work (Figures 3, fine grained sediments and Figure 4, total organic carbon), so it can be suggested that further studies on the hydrodynamics of the reservoir should be a significant contribution for the understanding of the mercury behavior.

4. CONCLUSION

Currently, despite the actions of constant maintenance and operation of the Juturnaíba reservoir, it is threatened by the impact of the use of their surroundings, caused mainly by farming and peri-urban occupation. It is still possible to observe the accumulation of domestic wastes in some parts of the lake, and also the disposal of sewage directly into the water. The improper management of the surrounding lands, plus the agricultural supplies, has generated exceeding inputs of nutrients and sediments.

In recent years, especially in periods between July, August, November and February, the concentration of algae in the Juturnaíba Lake promotes the reduction of the water quality. According to the water treatment companies Águas de Juturnaíba and Prolagos, the frequency and concentration of chemicals for the water treatment are continuously increasing in the recent years, highlighting the inappropriate use and occupation of the drainage basin.

Considering the historical evolution of the occupation of the drainage basin and the results obtained, we cannot indicate with precision the origin of organic matter deposited in sediments, but a few reduced values of the C/N molar ratio may be related with the greater influence of sewage from the tributary Capivari River.

Although the degradation processes and occupation around the Juturnaíba Lake are intensifying, the system has not exceeded its loading capacity, since the concentrations of mercury are still below the shale background (0.18 mg kg^{-1}), with the exception of six sampling points.

It is necessary to underline that the highest mercury concentrations occur in an area of significant macrophyte production, where methylation process may be more significant, constituting a threat for humans and the environment. Moreover, in Juturnaíba, the formation and dissolution of oxi-hydroxides combined with intense microbial activity, high temperatures and the presence of organic substrate for bacteria can accelerate the methylation of mercury.

An important measure of management of the reservoir is the intensification of recuperation of the riparian forests. This program should be expanded to the reforestation of the riparian areas of the tributaries of the lake. This will decrease the amount of suspended material and improve the water quality.

5. ACKNOWLEDGEMENTS

Thanks are due to CNPq, for a scholarship research in productivity granted to JCW. The Mico Leão Dourado Association and the Petrobras Environmental Programme created conditions for the implementation of sampling and laboratory analysis. Thanks are also due to Professor Emmanoel V.S. Filho for granting the laboratory to perform the mercury analyzes.

6. REFERENCES

Achá D., Hintelmann H., & Yee J. 2011. Importance of sulfate reducing bacteria in mercury methylation and demethylation in periphyton from Bolivian Amazon region. *Chemosphere*, **82**:911-916.

Achá D., Iñiguez V., Roulet M., Guimarães J.R.D., Luna R., Alanoca L. & Sanchez S. 2005. Sulfate-reducing bacteria in floating macrophyte rhizospheres from an Amazonian floodplain lake in Bolivia and their association with Hg methylation *Applied Environmental Microbiology*, **71**:7531-7535.

Aiken G.R., Mcknight D.M., Wershaw R.L. & Maccarthy P. 1985. Humic Substances in Soil, Sediment, and Water: Geochemistry, Isolation, and Characterization. New York, John Wiley & Sons, 692 p.

Aldhous P. 2004. Borneo is burning. *Nature*, **432**:144-146.

Amouroux D., Wasserman J.C., Tessier E. & Donard O.F.X. 1999. Elemental mercury in the atmosphere of a tropical Amazonian forest (French Guiana). *Environmental Science and Technology*, **33**:3044-3048.

Aula I., Braunschweiler H., Leino T., Malin I., Porvari P., Hatanaka T., Lodenius M. & Juras A. 1994. Levels of mercury in the Tucuruí Reservoir and its surrounding area in Pará, Brazil. *In:* C.J. Watras & J.W. Huckabee (eds.). *Mercury Pollution: Integration and Synthesis*. Lewis Publishers, p. 21-40.

Barcellos R.G., Barros S.R.D.S., Wasserman J.C., Lima G.B.A. & Chicayban M.D. 2012. Availability of water resources from the São João River basin for a petrochemical complex of Rio de Janeiro, Brazil. *In:* C. Bilibio, O. Hensel & J. Selbach. (eds.) *Sustainable Water Management in the Tropics and Subtropics and Case Studies in Brazil*. Vol. 3, FUFPampa, Unikassel, PGCult, UFMA, p. 653-683.

Barrocas P.R.G. & Wasserman J.C. 1998. Mercury behaviour in sediments from a subtropical coastal environment in SE Brazil. *In:* J.C. Wasserman, E.V. Silva-Filho & R. Villas-Boas (eds.). *Environmental Geochemistry in the Tropics*. Vol. 72, Springer-Verlag, p. 171-184.

Batalla R.J. 2003. Sediment deficit in rivers caused by dams and instream gravel mining. A review with examples from NE Spain. *Revista del Cuaternario y Geomorfología*, **17**:79-91.

Bidegain P. & Völcker C.M. 2003. *Bacia Hidrográfica dos rios São João e Ostras - Águas, Terras e Conservação Ambiental*. Araruama, Consórcio Intermunicipal Lagos São João, 177 p.

Binzstok J. 1999. Vale do São João, um empreendimento "fracassado" da agricultura comercial no Estado do Rio de Janeiro. Instituto de Geociências, Universidade Federal Fluminense, 65 p.

Bowles K.C. & Apte S.C. 1998. Determination of methylmercury in natural water samples by steam distillation and gas chromatography-atomic fluorescence spectrometry *Analytical Chemistry*, **70**:395-399.

Brasil & ELETROBRAS. 1987. Plano 2010: Relatório Geral. Plano Nacional de Energia Elétrica 1987/2010 (dezembro de 1987). Centrais Elétricas do Brasil (ELETROBRAS), 269 p.

Bura-Nakić E., Viollier E. & Ciglenečki I. 2013. Electrochemical and colorimetric measurements show the dominant role of FeS in a permanently anoxic lake. *Environmental Science and Technology*, **47**:741-749.

Correia R.R.S., Miranda M.R. & Guimarães J.R.D. 2012. Mercury methylation and the microbial consortium in periphyton of tropical macrophytes: Effect of different inhibitors. *Environmental Research*, **112**:86-91.

Cosio C., Flück R., Regier N., Slaveykova V.I. 2014. Effects of macrophytes on the fate of mercury in aquatic systems. *Environmental Toxicology and Chemistry*, **33**:1225-1237.

Das B., Nordin R. & Mazumder A. 2008. An alternative approach to reconstructing organic matter accumulation with contrasting watershed disturbance histories from lake sediments. *Environmental Pollution*, **155**:117-124.

Dung T.T.T., Cappuyns V., Swennen R., Phung N.K. 2013. From geochemical background determination to pollution assessment of heavy metals in sediments and soils. *Reviews in Environmental Science and Biotechnology*, **12**:335-353.

Duran R., Ranchou-Peyruse M., Menuet V., Monperrus M., Bareille G., Goñi M.S., Salvado J.C., Amouroux D., Guyoneaud R. & Donard O.F.X., Caumette P. 2008. Mercury methylation by a microbial community from sediments of the Adour Estuary (Bay of Biscay, France) *Environmental Pollution*, **156**:951-958.

Fearnside P.M. 2001. Environmental impacts of Brazil's Tucuruí Dam: Unlearned lessons for hydroelectric development in Amazonia. *Environmental Management,* **27**:377-396.

FEEMA. 1986. Levantamento de Metais Pesados no Estado do Rio de Janeiro. Fundação Estadual de Engenharia do Meio Ambiente.

Förstner U. & Wittmann G.T.W. 1983. *Metal Pollution in the Aquatic Environment*. Springer-Verlag, Heidelberg, 486 p.

French K.J., Scruton D.A., Anderson M.R. & Schneider D.C. 1999. Influence of Physical and Chemical Characteristics on Mercury in Aquatic Sediments. *Water Air and Soil Pollution*, **110**:347-362.

Grasshoff K., Ehrhardt M. & Kremling K. 1983. *Methods of Sea Water Analysis*. Verlag-Chemie, Weinhein, 419 p.

Guedes Seixas T., Moreira I., Siciliano S., Malm O. & Kehrig H.A. 2014. Mercury and selenium in tropical marine plankton and their trophic successors. *Chemosphere*, **111**:32-39.

Guevara R., Rizzo A., Sanchez R., Arribere M. 2005. Heavy metal inputs in northern Patagonia lakes from short sediment core analysis. *Radioanalytical and Nuclear Chemistry*, **265**:481-493.

Guimarães J.R., Meili M., Hylander L.D., Silva E.C., Roulet M., Mauro J.B.N. & Lemos R.A. 2000. Mercury net methylation in five tropical flood plain regions of Brazil: high in the root zone of floating macrophyte mats but low in the surface sediments and flooded soils. *Science of the Total Environment*, **261**:99-107.

Guimarães J.R.D., Mauro J.B.N., Meili M., Sundbom M., Haglund A.L., Coelho-Souza S.A. & Hylander L.D. 2006. Simultaneous radioassays of bacterial production and mercury methylation in the periphyton of a tropical and a temperate wetland *Journal of Environmental Management*, **81**: 95-100.

Jiang H., Feng X., Li G., Qiu G., Yan H. 2007. Seasonal distribution of total mercury and methylmercury in sediments of the Wujiangdu Reservoir, Guizhou, China. *Chinese Journal of Geochemistry*, **26**:414-417.

Knightes C.D., Golden H.E., Journey C.A., Davis G.M., Conrads P.A., Marvin-Dipasquale M., Brigham M.E., Bradley P.M. 2014. Mercury and methylmercury stream concentrations in a Coastal Plain watershed: A multi-scale simulation analysis. *Environmental Pollution*, **187**:182-192.

Lindqvist O. 1994. Atmospheric cycling of mercury: an overview. *In:* C.J. Watras & J.W. Huckabee (eds.). *Mercury Pollution: Integration and Synthesis*. Lewis Publishers, p. 181-185.

Machado W., Moscatelli M., Rezende L.G. & Lacerda L.D. 2002. Mercury, zinc, and copper accumulation in mangrove sediments surrounding a large landfill in southeast Brazil. *Environmental Pollution*, **120**:455-461.

Malm O., Pfeiffer W.C., Bastos W.R. & Souza C.M.M. 1989. Utilização do acessório de geração de vapor a frio para análise de mercúrio em investigações ambientais por espectrofotometria de absorção atômica. *Ciência e Cultura, Journal of the Brazilian Association of the Advancement of Science*, **41**:88-92.

Menor E.A., Menezes P., Santos A. & Moraes A.S. 2001. Relações C/N da matéria orgânica em Pelitos de um Ecossistema Lacustre Insular: Lagoa da Viração, Ilha de Fernando de Noronha, Brasil. *In:* VIII Congresso Brasileiro de Geoquímica, Vol. CD, p. 1-4. SBGq.

Meyers P.A. 2003. Applications of organic geochemistry to paleolimnological reconstructions: a summary of examples from the Laurentian Great Lakes. *Organic Geochemistry.*, **34**:261-289.

Meyers P.A. & Ishiwatari R. 1993. Lacustrine organic geochemistry-an overview of indicators of organic matter sources and diagenesis in lake sediments. *Organic Geochemistry*, **20**:867-900.

Millán R., Lominchar M.A., Rodríguez-Alonso J., Schmid T., Sierra M.J. 2014. Riparian vegetation role in mercury uptake (Valdeazogues River, Almadén, Spain). *Journal of Geochemical Exploration*, **140**:104-110.

Muresan B., Cossa D., Richard S. & Dominique Y. 2008. Monomethylmercury sources in a tropical artificial reservoir. *Applied Geochemistry*, **23**:1101-1126.

Nelson E.W. & Sommers L.E. 1996. Total Carbon, Organic Carbon, and Organic Matter. *In:* Sparks, D.L. (eds.). *Methods of Soil Analysis. Part 3. Chemical Methods*. Vol. 3 Soil Science Society of America.

Peretyazhko T., Charlet L., Muresan B., Kazimirov V. & Cossa D. 2006. Formation of dissolved gaseous mercury in a tropical lake (Petit-Saut reservoir, French Guiana). *Science of the Total Environment*, **364**:260-271.

Peretyazhko T., Van Cappellen P., Meile C., Coquery M., Musso M., Regnier P. & Charlet L. 2005. Biogeochemistry of major redox elements and mercury in a tropical reservoir lake (Petit Saut, French Guiana). *Aquatic Geochemistry*, **11**:33-55.

Pinilla-Agudelo G.A. 2009. Primary production in a clear water lake of Colombian Amazon (Lake Boa). *Acta Biologica Colombiana*, **14**:21-30.

Reimann C. & De Caritat P. 1998. *Chemical Elements in the Environment: Factsheets for the Geochemist and Environmental Scientist*. Springer-Verlag, Heidelberg, Germany, 398 p.

Ribeiro A.P., Figueiredo A.M.G., Dos Santos J.O., Dantas E., Cotrim M.E.B., Figueira R.C.L., Silva E.V. & Wasserman J.C. 2013. Combined SEM/AVS and attenuation of concentration models for the assessment of bioavailability and mobility of metals in sediments of Sepetiba Bay (SE Brazil). *Marine Pollution Bulletin*, **68**:55-63.

Richard S., Arnoux A., Cerdan P., Reynouard C., Horeau V. & Vigouroux R. 2002. Influence of the setting up of a man-made lake on mercury levels in the flesh of fish in a neotropical habitat: The Sinnamary River (French Guiana). *Revue D Ecologie-La Terre Et La Vie*, p. 59-76.

Roulet M., Lucotte M., Saint-Aubin A., Tran S., Rheault I., Farella N., Da Silva E.D., Dezencourt J., Passos C.J.S., Soares G.S., Guimaraes J.R.D., Mergler D. & Amorim M. 1998. The geochemistry of mercury in central Amazonian soils developed on the Alter-do-Chão formation of the lower Tapajos River Valley, Pará state, Brazil. *Science of the Total Environment*, **223**:1-24.

Silva L.F.F., Machado W., Lisboa S.D. & Lacerda L.D. 2003. Mercury accumulation in sediments of a mangrove ecosystem in SE Brazil. *Water Air and Soil Pollution*, **145:**67-77.

Small J.M. & Hintelmann H. 2014. Sulfide and mercury species profiles in two Ontario boreal shield lakes. *Chemosphere*, **111:**96-102.

Stoichev T., Amouroux D., Wasserman J.C., Point D., De Diego A., Bareille G. & Donard O.F.X. 2004. Dynamics of mercury species in surface sediments of a macrotidal estuarine coastal system (Adour River, Bay of Biscay). *Estuarine, Coastal and Shelf Science*, **59**:511-521.

Temme C., Einax J.W., Ebinghaus R. & Schroeder W.H. 2003. Measurements of atmospheric mercury species at a coastal site in the Antarctic and over the south Atlantic Ocean during polar summer. *Environmental Science and Technology*, **37**:22-31.

USEPA (United States Environmental Protection Agency). 1997. Fate and transport of mercury in the environment. Mercury Study Report to the Congress, Vol. III, p. R-97-005. United States Environmental Protection Agency.

Valderrama J.C. 1981. The simultaneous analysis of total nitrogen and total phosphorus in natural waters. *Marine Chemistry*, **21**:109-122.

Wallschläger D., Desai M.V.M., & Wilken R.D. 1996. The role of humic substances in the aqueous mobilization of mercury from contaminated floodplain soils. *Water Air and Soil Pollution*, **90**:507-520.

Wasserman J.C. 2012. Programa de Monitoramento físico-químico, bacteriológico e de sedimentos no reservatório de Juturnaíba e em seus contribuintes (Rios Bacaxá, Capivari e São João), p. 169. UFF Network of Environment and Sustainable Development/Golden Lion Tamarin Association.

Wasserman J.C., Freitas-Pinto A.A.P. & Amouroux D. 2000. Mercury concentrations in sediment profiles of a degraded tropical coastal environment. *Environmental Technology*, **21**:297-305.

Wasserman J.C., Hacon S. & Wasserman M.A. 2003. Biogeochemistry of mercury in the Amazonian environment. *Ambio*, **32**:336-342.

Wasserman J.C. & Queiroz E.L. 2004. The attenuation of concentrations model: A new method for assessing mercury mobility in sediments. *Química Nova*, **27**:17-21.

Xiao Z.F., Strömberg D. & Lidqvist O. 1995. Influence of humic substances on photolysis of divalent mercury in aqueous solution. *Water Air and Soil Pollution*, **80**:789-798.