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Development of water parameters and changes in fish mercury concentrations a decade after creating a tropical reservoir



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Abstract

In this study, total mercury (tot-Hg) levels in fish and a number of water quality parameters have been determined in the tropical hydroelectric reservoir Lago Manso, Brazil. In spite of several studies related to Hg levels in fish from temperate reservoirs, few studies have earlier been performed in fish from tropical hydroelectric reservoirs. It is believed that the speed of the methylation process is different in temperate and tropical areas, as a result of the difference in temperature and other parameters. This study is unique since it was the fifth sequential study performed in a tropical reservoir (Lago Manso), resulting in important time series of mercury levels in fish after the completed construction of the reservoir in 1999. At present, nearly eleven years after inundation, the mercury levels in fish from Lago Manso are higher than ever before. The mean Hg levels from all species analyzed in this study exceeded the fish mercury limits recommended by the WHO (500 ng Me-Hg g⁻¹ f.w. for non-predatory fish and 1000 ng Me-Hg g⁻¹ f.w. for predatory fish). The species with the highest average mercury level in the study was *Salminus brasiliensis*, which had a mean higher than 6000 ng tot-Hg g⁻¹ f.w. The water parameters analyzed showed that the levels of dissolved oxygen (DO) have decreased during the latest years and is now lower than ever. At the same time, the secchi depth has increased in the reservoir and is now greater than ever. In conclusion, fish from Lago Manso should not be consumed and appropriate recommendations should be announced until future studies eventually demonstrate the return of fish Hg concentrations to acceptable levels.

Keywords

Mercury in fish, bioaccumulation, secchi depth, DOC, dissolved oxygen, hydroelectric reservoir

Resumo

Neste estudo, os níveis de mercúrio total em peixes (tot-Hg) e alguns parâmetros aquáticos foram determinados no reservatório hidrelétrico tropical Lago Manso, Brasil. Apesar dos diversos estudos relacionados aos níveis de Hg em peixes de reservatórios em áreas temperadas, poucos estudos foram realizados previamente em peixes de reservatórios hidrelétricos tropicais. Acredita-se que a velocidade do processo de metilação é diferente em áreas temperadas e tropicais, como um resultado da diferença de temperatura, bem como, outros parâmetros. Este estudo é pioneiro, uma vez que é o quinto estudo sequencial realizado em um reservatório tropical (Lago Manso), resultando em um importante histórico dos níveis de mercúrio em peixes desde a construção do reservatório em 1999. Atualmente, aproximadamente onze anos após a inundação, os níveis de Hg em peixes do Lago Manso apresentam-se mais altos do que nunca. A média de Hg total das espécies analisadas neste estudo excederam os limites de Hg em peixes, recomendados pela OMS (500 ng MeHg g⁻¹ f.w. para peixes não-predadores e 1000 ng MeHg g⁻¹ f.w. para peixes predadores). A espécie que apresentou a média mais alta de mercúrio neste estudo foi *Salminus brasiliensis*, com média acima de 6000 ng tot-Hg g⁻¹ f.w. Os parâmetros aquáticos analisados mostraram que os níveis de oxigênio dissolvido (DO) sofreram um decréscimo durante os últimos anos, apresentando os valores mais baixos já registrados. Ao mesmo tempo, a profundidade Secchi aumentou no reservatório e apresenta os valores mais altos já registrados. Em conclusão, os peixes do Lago Manso não devem ser consumidos e recomendações apropriadas devem ser feitas até que estudos futuros, eventualmente, demonstrem que as concentrações de Hg em peixes retornaram a níveis de consumo aceitáveis.

Palavras-chave

Mercúrio em peixes, bioacumulação, profundidade Secchi, DOC, oxigênio dissolvido, reservatório hidrelétrico

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1. Introduction

The purpose of this study was to determine the mercury levels of fish from a tropical hydroelectric reservoir, Lago Manso, ten years after inundation. Also, a number of water quality parameters were studied to see their change over time. Previously, there have been similar studies performed in the area: The first study was performed in 1999 (the same year as the construction of the reservoir was completed) and studies have been performed every third year ever since. This study was the fifth in order and it was performed in 2010. These studies are important because they increase the environmental knowledge of impacts from hydroelectric power stations in tropical areas.

In total, hydropower accounts for about 20 % of the world's electricity supply (The World Bank, 2010). In Brazil alone, 83.4 % of the electricity was generated through hydropower 2005 (Cateano de Souza A.C., 2008). Still, there is a big capability for building more hydroelectric power plants in Brazil, since only 27.2 % of the possible hydroelectric potential is currently being assimilated (Cateano de Souza A.C., 2008).

The hydropower potential presently being exploited in all developing countries is calculated to be 23 % (The World Bank, 2010). Therefore, there is a big potential to increase hydropower productivity in the world. Hydropower is often being seen as an environmentally friendly alternative to fossil fuelled electricity production. It is, though, a great mistake to believe that hydroelectric reservoirs (and thus hydropower) have no emissions at all of green house gases. New hydroelectric reservoirs are net emitters of carbon dioxide as well as methane. The amounts of gases may be substantial; In the year 1990, emissions from the Tucuruí reservoir in northern Brazil were equivalent to $7.0\text{--}10.1 \times 10^6$ tons of CO₂-equivalent carbon, which at that time was more than the fossil fuel emissions from the city of São Paulo (Brazil) (Fearnside, 2000). São Paulo has more than 10 million inhabitants. Another problem with creating reservoirs is that the people, who are living in the area where the reservoir is being flooded, have to be displaced. In the world in total, it is estimated that between 40 and 80 million people have been displaced as a consequence of construction of hydroelectric power plants (The World Commission on Dams, 2000).

However, dams do not only bring trouble. The World Commission on Dams says that considerable benefits have derived from creating dams, but that the social and environmental price for creating the dams in many cases have been unacceptable and unnecessary (The World Commission on Dams, 2000). Lerer et al. (1999) gives some examples of problems: "Water projects have resulted in vector-borne diseases, loss of food security, pollution, and social problems that negatively influence health".

One effect of creating dams is that mercury levels may increase in the biota of the dam. This could bring harm since mercury is toxic for both humans and the environment. One of the most famous cases of mercury poisoning is the Minamata disease which was officially reported in May 1956. The mercury poisoning was an effect of methyl mercury discharge from a chemical plant (Chisso Co. Ltd.). Of the 2252 officially recognized patients, 1043 died within 36 years (Harada, 1995). But the numbers of poisoned are thought to be more than the officially recognized; 12127 persons who claimed to have the disease were in 1995 not yet recognized as Minamata disease patients (Harada, 1995).

Presently, the largest anthropogenic emissions of mercury come from coal fired power plants (UNEP, 2008), but mercury is not only a by-product of coal fired power plants; it is also an element

internationally used in e.g. compact fluorescent lamps and in the process of gold extraction by small scale miners

Mercury occurs, to some extent, naturally in the atmosphere, e.g. because of eruptions from volcanoes. The natural emissions are difficult to calculate and the emissions could be bigger or smaller than what is known today, which implies that greater precaution regarding emissions should be made. If one does not consider the re-emissions (which half of can be seen as anthropogenic), the global anthropogenic emissions of mercury were estimated to 1930 (range 1230-2890) tonnes in 2005, while the natural emissions from land and oceans together are estimated to 900-2300 tonnes per year (UNEP, 2008). Since most of the mercury emissions are thought to be anthropogenic, there is a great opportunity to decrease the discharge of mercury.

The mercury that is emitted into the atmosphere is free to move with the winds over the globe – making mercury a global pollutant. This means that mercury can, and does indeed, deposit anywhere on our planet. Mercury is a serious problem; if the conditions are propitious, mercury can become more biologically available in the form of methyl mercury.

One of the biggest problems regarding hydroelectric reservoirs is the increased production of methyl mercury. The general increase of methyl mercury is due to changed environmental conditions, where the decrease of dissolved oxygen is one of the most crucial ones (Regnell, 1992, Driscoll et al., 1995). This means that mercury levels in organisms in the reservoir could rise even though there has been no direct discharge of mercury into the reservoir. In the Amazon River, the dominant stock of mercury is derived from erosion of natural soils (Roulet et al., 2001). The dominant stock of mercury in Lago Manso is, most probably, also derived from natural soils since there are no known sources of direct mercury pollution in the surroundings (Hylander et al., 2006).

World Health Organisation (WHO) has recommended limits for methyl mercury levels in fish for consumption. The limits for methyl mercury are 500 ng MeHg g⁻¹ f.w. for non-predatory fish and 1000 ng MeHg g⁻¹ f.w. for predatory fish (WHO, 2007). Methyl mercury makes up approximately 90 % of the total mercury in the region (Kehrig et al., 1998, Hylander et al., 2006). This makes the limits of total mercury 556 ng tot-Hg g⁻¹ f.w. for non-predatory fish and 1111 ng tot-Hg g⁻¹ f.w. for predatory fish, in the region.

Since methyl mercury is easily biomagnified, the top predators in the food chain get higher mercury levels than other organisms. The top predators are often fish consumed by humans, thereby being a human health problem. The number of studies on mercury levels in fish in hydroelectric reservoirs in tropical areas is scarce, but according to Verdon et al. (1991), it is suggested that elevated levels of mercury in fish could last for 20 to 30 years, based on studies on reservoirs in Canada that were 6 to 67 years old. In Finland, Porvari (1998) also found increased levels of mercury. In 18 Finnish reservoirs elevated levels of mercury occurred for 15-25 years before they returned to pre-impoundment levels.

In one laboratory experiment, the net methylation was highest at temperatures in the 33-45 °C range (Guimarães et al., 1998). This means that the methylation process could go faster in a tropical reservoir compared to a temperate reservoir. It is therefore reasonable to draw the conclusion that the increase of mercury levels in fish in a tropical reservoir is steeper than in a temperate reservoir,

but that the increased levels will last for a shorter time. The objective of this study is to bring light to the course of events of elevated levels of mercury in fish in tropical reservoirs.

2. Material and methods

2.1. Study area

Lago Manso is situated north east of Cuiabá, the capital of the state Mato Grosso in central western Brazil. The construction was finished in 1999 and a map over the reservoir can be seen in figure 1. The reservoir has a size of 427 km² between the coordinates S14°40′-15°20′ and W55°20′-60°00′ with a drainage area of 9365 km² (Furnas, 2010). The maximum water surface level is 289.8 meters above sea level and the water volume of the reservoir is 73*10⁸ m³ (Hylander et al., 2006). The reservoir was mainly flooded by the three rivers Rio Manso, Rio Casca and Rio Quilombo. Before the construction of the reservoir, the average flux from Rio Manso was 170 m³ s⁻¹, and after the construction of the reservoir, the flux from the entire reservoir was 135 m³ s⁻¹ (Hylander et al., 2006).

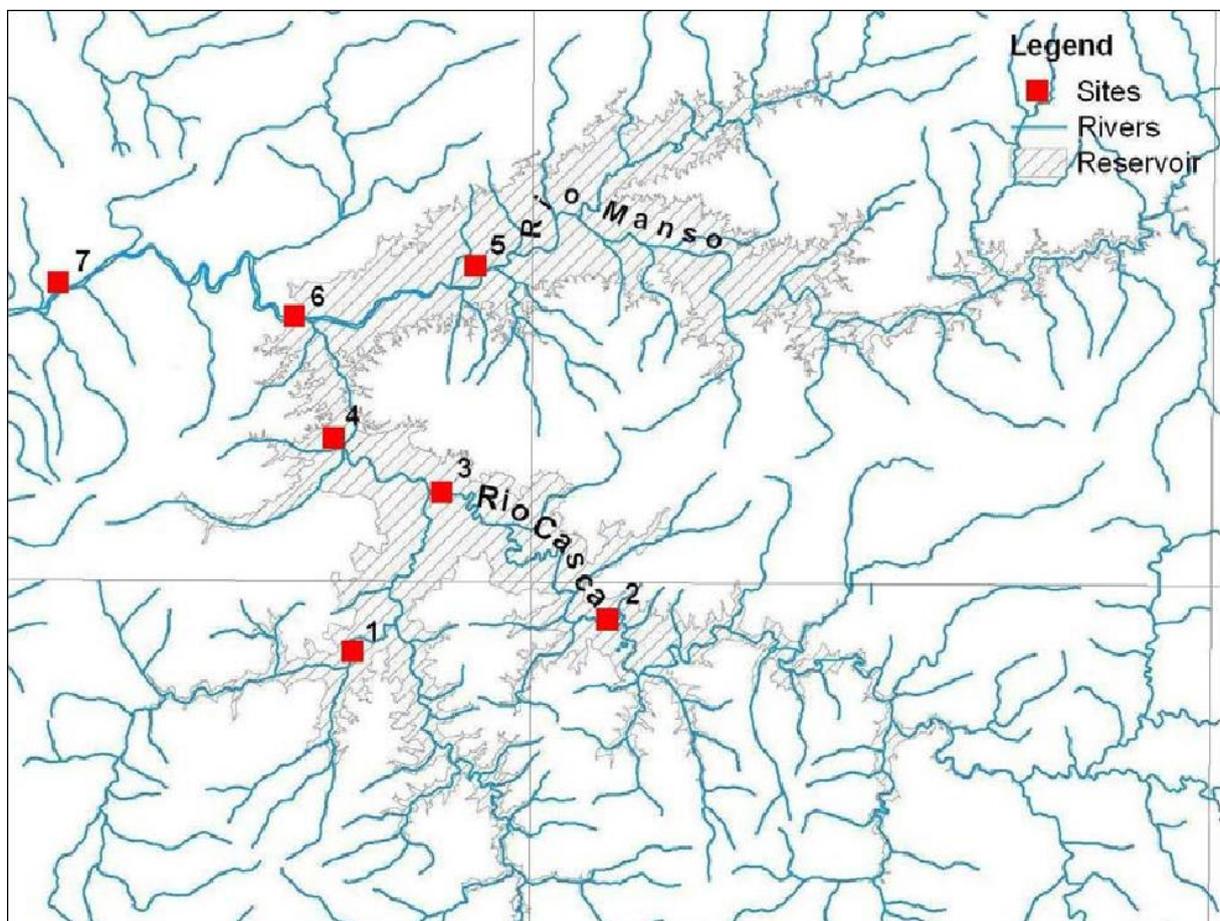


Figure 1. Map over Lago Manso where the measurement sites are shown.

The reservoir is situated 1670 km from the equator and there are two climate seasons; a dry season from April to August and a rainy season from September to March.

The landscape around the reservoir is dominated by sandy hills with drought resistant bush vegetation. When the area was flooded, trees were left standing and are, 11 years later, still partly

submerged in the water. The area is not highly populated, but some small scale farmers live permanently around the reservoir. Since the inundation, the tourism and the commercial hotels have increased as an effect of the creation of the lake, since lakes are unusual in the area.

2.2. Water analyses

Water samples in duplicates were collected on the 18th of April 2010 at seven different sampling sites. On every site the following parameters were determined: Dissolved oxygen, pH, conductivity, water temperature, air temperature and secchi depth. Six of the sampling sites are located in Lago Manso and one sampling site is located in Rio Manso, downstream the dam. In field, the positions of the sampling sites were found with a Global Positioning System (GPS) receiver.

Before going into the field, the Dissolved Oxygen (DO) meter, the pH meter and the conductivity meter were calibrated. Tap water from Federal University of Mato Grosso (UFMT) was then analysed to get a reference value.

At every sampling site, DO, pH and conductivity were measured in water from Lago Manso as well as the tap water from UFMT, to detect any deviations from the reference value, in order to secure data quality. The measurements were made in plastic cups with water collected at a depth of 20 cm. The water temperature was also measured in plastic cups and the air temperature was measured in the shade. The secchi depth was determined with a secchi disk. Furthermore, water was collected at a depth of 20 cm in duplicate clean 1500 mL water bottles for later analysis of water colour, turbidity and suspended matter.

In field, duplicate of 200 mL water sample for DOC were collected at a depth of 20 cm at each sampling site. The samples were conserved immediately according to Malm et al. (1989; 1 mL 4M H₂SO₄ per 100 mL water sample). The water was filtered through a 0.45 µm filter, according to Malm et al. (1989), with vacuum pump at lab, UFMT. Blank samples for all DOC samples were prepared the evening before going to field, in the volume of 20 mL. The blanks were also conserved in field and filtered in lab. All DOC samples and blanks were stored in a refrigerator at 0-5 °C for eleven weeks and then transported to Sweden with aviation. The content of DOC in the samples was then determined with high temperature combustion and IR-detection, Shimadzu TOC-5000, at Limnology Department, Uppsala University.

Water colour and turbidity were analysed at the department of sanitary engineering, UFMT. Water colour was determined with a digital spectrophotometer, HACH DR/2010, at a wavelength of 455 nm. Turbidity was determined with a turbidity meter, TECNOPON TB1000.

The amount of suspended matter was determined at the department of chemistry, UFMT. For the analysis, 0.45 µm filters were used, according to the method of Malm et al. (1989). First, the filters were dried in an oven at 60 °C for 6 hours. Then, the filters were individually weighed whereupon 0.5 L water from Lago Manso was filtered through them with a vacuum pump. Afterwards, the filters were stored in an oven for 36 hours in a temperature between 25 and 50 °C and then dried at 60 °C for 6 hours, whereupon each filter was weighed individually. The suspended material was determined from the difference of the filter's dry weight and the volume water that was filtered.

2.3. Mercury analyses

In this study, 30 different fishes (27 from the reservoir and 3 from the downstream area) were analysed for mercury (Hg) content. The fish were captured by local anglers between the 14th of April and the 22nd of April 2010. The fish consisted of two omnivore species; *Serrasalmus marginatus* (Valenciennes, 1837, with popular name "Piranha") and *Pygocentrus nattereri* (Kner, 1858, with popular name "Red Piranha"), one carnivore species; *Salminus brasiliensis* (Cuvier, 1816, with popular name "Dorado"), one piscivore species; *Pinirampus pirinampu* (Spix & Agassiz, 1829, with popular name "Flatwhiskered catfish") and one herbivore species; *Brycon hilarii* (Valenciennes, 1850, with popular name "Piraputanga") (Fishbase, 2010).

After each fish was collected, the gutted weight, the total and the standard lengths were determined. The total weight were only determined when the fish were collected unopened from fishermen. The fish was then stored in a freezer until the first step of preparation for mercury analysis; after each fish was completely thawed, a sample of the dorsal muscle was removed and grinded. The samples were then refrozen in plastic bags until the second step of the preparation.

The second step of preparation before mercury analysis was dissolving the fish samples; three subsamples (~2 g, weighed in Erlenmeyers on scales with a resolution of 100 µg) was taken from each fish and prepared according to Malm et al. (1989), in three different rounds. The Erlenmeyers were kept in an ice bath and totally 2 mL of concentrated hydrogen peroxide (H₂O₂) was added to each sample in two rounds (1+1 mL). After waiting for 10 minutes, totally 15 mL of concentrated sulphuric acid (H₂SO₄) was added to each sample in two rounds (5+10 mL). Afterwards, the Erlenmeyers were incubated in a 60 °C-water bath for 30 minutes. The Erlenmeyers were then kept in an ice bath and the samples were added with 25 mL 5 % (w/v) potassium permanganate (KMnO₄) in two different rounds (5+20 mL). After having waited for one hour, 40 mL 5 % (w/v) potassium persulfate (K₂S₂O₈) was added to each sample. The samples were then left to rest for 9 to 14 hours in a refrigerator, whereupon sufficient 12 % (w/v) hydroxyl ammonium chloride (HONH₂-HCl) was added, in small volumes, until the solution was clear. During the addition of the chemicals mentioned, the samples were shaken. After the sample preparation, the samples were stored (maximum 48 hours) in a refrigerator until the analyses.

When it was necessary for the analyses, samples were diluted with distilled water because of too high concentrations, which created problems for the spectroscopy readings.

Total mercury concentrations (a mean of three readings for each subsample) were analysed with cold vapour atomic absorption spectroscopy (CV-AAS) at IFMT, Federal Institute of Mato Grosso, Cuiabá (with a AA240FS, Varian Inc., USA) and at UFMT, Federal University of Mato Grosso, Cuiabá (with a SpectrAA 220, Varian Inc., USA).

2.4. Data quality

Certified external standard IAEA 350 (tuna fish homogenate with 4680 ng tot-Hg g⁻¹ d.w., International Atomic Energy Agency, Vienna, Austria) was used during the analyses. The reference material was prepared in the same way as the fish samples, parallel to those. In the first analysis round, two samples of the certified external standard were prepared and analysed both before and after the fish samples were analysed. In the second and third analysis round, four samples of the certified external standard were prepared each time, and analysed both before and after the fish

samples were analysed. The results from the reference analyses are shown in table 1 and imply that the measurement equipment was well working and well calibrated since the difference between the obtained mean and the established mercury content was only between 4 and 6 %. To further secure data quality, one of the *P. nattereri* was analysed in all three analyses as a reference, as can be seen in table 1, with a mean of 2799 ng tot-Hg g⁻¹ f.w. and a std of 3.6 %. Also, an inter-laboratory comparison of four fishes was made at Federal University of Rio de Janeiro. In four different analyses, there was a standard deviation between 11 % and 33 %. The mean value differed between -15 % and 3 % from the analysis at Federal University of Mato Grosso, Cuiabá (Appendix IV).

Table 1. Results from quality control of certified external standard and results from reference *P. nattereri*.

Round	n	Established total mercury [ng g ⁻¹ d.w.]	Obtained mean total mercury [ng g ⁻¹ d.w.]	STD [%]	Difference [%]
1	2	4680	4959	6	6
2	4	4680	4941	2	6
3	4	4680	4875	<1	4
Round	n	Mean value of reference <i>P. nattereri</i> [ng g ⁻¹ d.w.]	Obtained mean total mercury [ng g ⁻¹ d.w.]	STD [%]	Difference [%]
1	3	2799	2798	<1	0
2	1	2799	2699	0	-4
3	2	2799	2900	<1	4

3. Results

3.1. Water parameters

Water parameters from 2010 are shown in table 2 and parameters from earlier studies are represented in Appendix I. The weather was sunny and clear at the time of the measuring of water parameters and the collecting of water samples. The measurements were made between 7 am and 5 pm.

Table 2. Water parameters measured in field on the 18th of April 2010. Note that DO is corrected because deviation from reference tap water was more than 10 %.

Sample site	Time	Weather	Coordinates	Temp		pH	DO	Cond.	Secchi depth	Water colour	Turbidity	Susp. matter	DOC
				Air [°C]	Water [°C]								
1	09.15	sun, clear	S15°05.344 W55°43.389	29	29.4	7.3	3.6	25.7	3.65	14	0.8	1.9	0.4
Rio Quilombo													
2	11.24	sun, clear	S15°02.430 W55°37.379	32	30.9	7	2.6	24.5	4.3	10	0.6	1.45	0.5
Rio Casca													
3	12.30	sun, clear	S14°57.547 W55°43.267	32	31.4	7.6	3.9	25.8	4.75	8	0.6	0.75	0.2
Rio Casca													
4	13.15	sun, clear	S14°56.312 W55°45.963	35	30.4	7.3	4.1	23.4	4.7	7	0.6	1.2	0.2
Rio Casca													
5	06.55	sun, clear	S14°51.006 W55°42.544	25	27.1	7.8	2.4	43.6	3.59	9	0.6	1.4	0.6
Rio Manso													
6	07.30	sun, clear	S14°52.344 W55°46.600	26	27.5	7.6	3.2	44.3	6.05	5.5	0.6	1.2	0.8
Dam area													
7	17.15	clear	S14°51.120 W55°53.523	27	28.5	7.3	2.7	33.4	-	26.5	2.6	4.9	0.9
Downstream													

Water pH was just above 7 and could be considered as neutral. Since the inundation, the pH has been increasing (Figure 2). In 2008, there was a peak in pH and 2010 shows a start of a decreasing trend, but the values are still greater than in 2005. Water from Rio Manso has a slightly higher pH than water from Rio Casca and Rio Quilombo and the same results are shown in earlier studies.

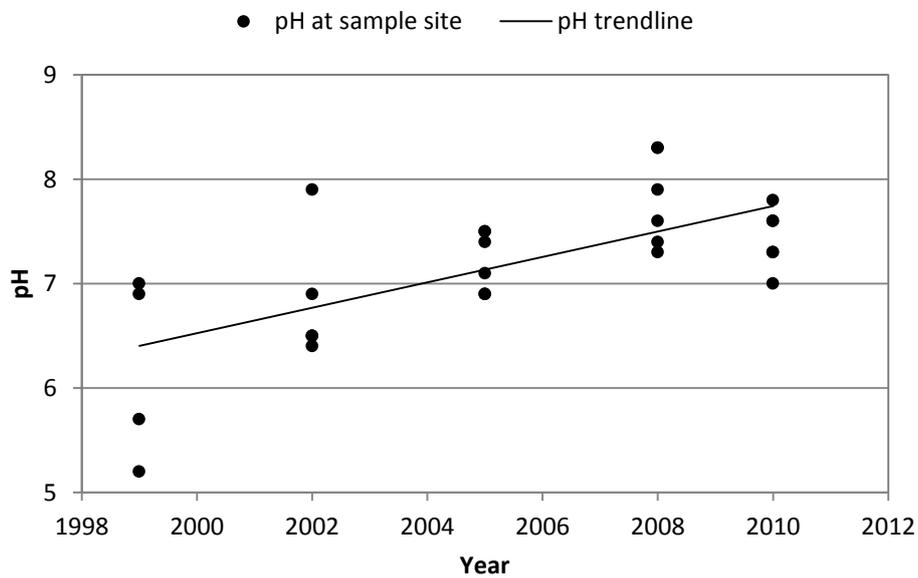


Figure 2. Trend line of pH in the reservoir Lago Manso, determined between 1999 and 2010. Measurements downstream are not included in the figure

The water contained about 3.2 mg L^{-1} dissolved oxygen (DO). To secure data quality, DO was also measured in tap water at every sampling site as a reference. Since the DO values fluctuated more than 10 % (between -23 % and 16 %) in the tap water, the DO values from Lago Manso were corrected according to the fluctuation within every site (Appendix V). DO has the opposite trend compared with pH and has decreased since 1999. Just like pH, there is a peak in 2008 which diverges from the trend (Figure 3).

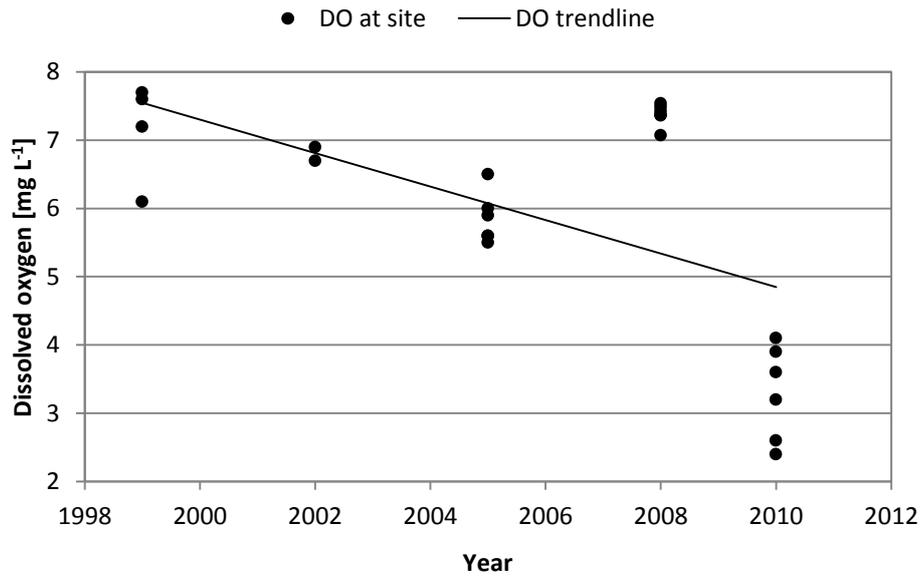


Figure 3. Trend line of dissolved oxygen in the reservoir Lago Manso, determined between 1999 and 2010. Measurements downstream are not included in the figure

Secchi depth has increased in every study since inundation, which can be seen in figure 4. The maximum secchi depth of this study was 6 m. Because of the strong current, it was not possible to measure the secchi depth downstream.

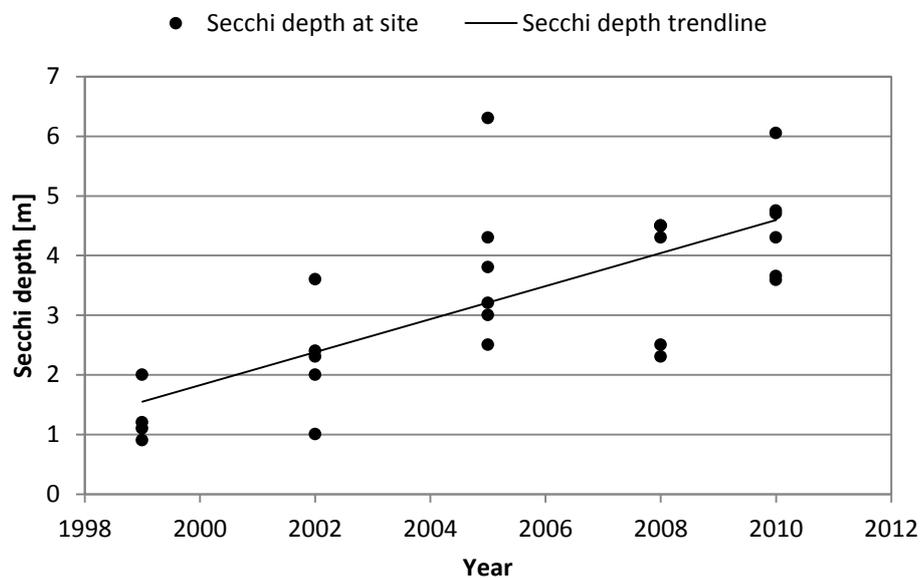


Figure 4. Trend line of secchi depth in the reservoir Lago Manso, determined between 1999 and 2010. Measurements downstream are not included in the figure.

The water colour was very low in the reservoir, between 6 and 14 mg PT L⁻¹. Downstream, the water colour was 26.5 mg PT L⁻¹. Turbidity was low, around 0.6 NTU, in the reservoir and 2.6 NTU downstream. DOC was low and close to detection limit. In the reservoir, DOC was in the range of 0.2 to 0.8 mg L⁻¹. Downstream, the DOC value was slightly higher than in the reservoir. Suspended matter was around 1 mg L⁻¹ with exception for downstream, which had a value of 4.9 mg L⁻¹. Since

inundation in 1999, the mean value of suspended matter in the dam has been reduced five times but almost all changes occurred up until 2005, and since then it has been relative stable downstream.

Conductivity varied from 23 $\mu\text{S cm}^{-1}$ to 44 $\mu\text{S cm}^{-1}$. There was a distinct difference between the water from Rio Casca and from Rio Quilombo, which had low values, while the water from Rio Manso and the dam area had higher values. Results from 2005 are slightly higher but show the same difference.

3.2. Fish

The mean values of mercury concentration, gutted weight and length of the 30 analysed fish are presented in table 3. In all fish, the mean value of mercury concentration varied between 218 ng tot-Hg g^{-1} f.w. and 6845 ng tot-Hg g^{-1} f.w. The carnivore specie *S. brasiliensis*, captured in the reservoir, had the highest mean value of mercury concentration. *S. brasiliensis* had almost two times higher concentration than the omnivore *P. nattereri*, who had the second highest. The lowest concentration was in the piscivore species *P. pirinampu*, captured downstream. It is notable that the concentration of mercury in *S. brasiliensis* was almost five times lower downstream than in the reservoir.

The captured number of each specie varied between 1 and 9. No significant relation was found between mercury concentration and gutted weight between each species.

Table 3. Mercury concentration, weight and length of fish collected between 14th of April and 22nd of April, 2010.

Fish	Location	N	Total mercury				Gutted weight				Average length	
			[ng tot-Hg g^{-1} f.w.]				[g]				[cm]	
			Min	Average	SD	Max	Min	Average	SD	Max	Full	Standard
<i>P. nattereri</i>	Lago Manso	9	1895	3146	882	4670	800	1000	173	1400	35	31
<i>S. marginatus</i>	Lago Manso	8	937	2205	616	3018	130	225	87	370	22	19
<i>B. hilarii</i>	Lago Manso	6	374	798	338	1313	800	1133	437	2000	43	39
<i>S. brasiliensis</i>	Lago Manso	4	5522	6064	558	6845	3500	4125	479	4500	71	62
	Downstream	2	1309	1323	19	1336	1800	5900	5798	10000	72	65
<i>P. pirinampu</i>	Downstream	1		218				2300			65	58

Variation of mercury concentration with time is presented in figure 5. The mercury concentration has increased in all species since the inundation 1999. Since 2005, all species are over the limit according to WHO, 556 ng tot-Hg g^{-1} f.w. for non-predatory fish and 1111 ng tot-Hg g^{-1} f.w. for predatory fish.

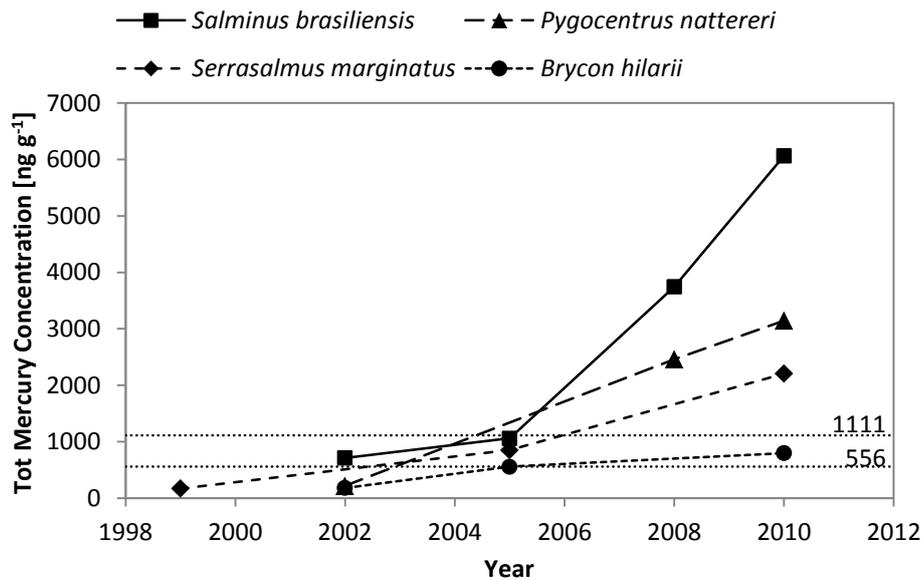


Figure 5. Change of mercury concentration in fish from the reservoir Lago Manso between 1999 and 2010. 1111 ng tot-Hg g⁻¹ is the above limit for predatory fish and 556 ng tot-Hg g⁻¹ for non-predatory fish according to WHO (2007).

S. brasiliensis had the steepest increasing slope of change in mercury concentration. *B. hilarii*, on the other hand, had a decreasing slope even if the value was still increasing. Both *P. nattereri* and *S. marginatus* seem to have a stable change of concentration. There have not been any known mercury analyses of *P. Pirinampu* from Lago Manso before, and it is therefore not possible to draw any conclusions of any change of mercury levels in *P. Pirinampu*.

4. Discussion

4.1. Water parameters

Mercury is transformed from inorganic mercury to methyl mercury by bacteria (Kehrig et al., 1998). The process of methylation is complex, since some of the bacteria carrying out the methylation in some circumstances also demethylate mercury (Pak et al., 1998). It is suggested that pH influences neither methylation nor demethylation (Pak et al., 1998, Regnell, 1992).

In this study, DO have decreased since the previous study and is now at all time low. Methylation is affected by oxygen levels and mercury methylation occurs in anoxic conditions (Regnell, 1992, Olson et al., 1976, Driscoll et al., 1995, Watras et al., 1995) and according to Pak et al. (1998), mercury methylation in anoxic aquatic sediments is performed by sulfidogens. The low DO values in the reservoir favours methylation of mercury and it is not surprising to see that the oxygen levels decrease at the same time as the mercury levels in fish increase, since the reservoir is relatively new and there is most likely a substantial amount of mercury stored in the upper sediment horizons. Because of large variation of DO in tap water, there is a big uncertainty of DO in this study. The reason is unclear but could be because of small differences in the handling of tap water under measurement. Even if the value is uncertain, it is still clear that DO have a decreasing trend.

Mercury methylation is also affected by organic matter (Olsen et al., 1976, Driscoll et al., 1995). Organic matter stimulate mercury methylation but only to some extent; when the organic

concentration is too high the mercury may become less available for methylation because of high affinity of mercury to particulate organic material (Hylander et al., 2006). The water is slightly coloured and has not changed significantly during the last years. Turbidity, suspended matter and DOC are low. All three of them together with water colour are close to the detection limits of the used instruments. Secchi depth is a result of turbidity, suspended matter and water colour and the tendency is that the secchi depth is increasing. This could, together with the turbidity, water colour, DOC and suspended matter imply that the lake is turning oligotrophic.

4.2. Fish

S. brasiliensis had the highest mercury levels in this study, with an average of 6064 ng tot-Hg g⁻¹ f.w. The increase from the last study is large; the average was 3744 ng tot-Hg g⁻¹ f.w. in 2008. It is not unexpected that it is the *S. brasiliensis* that had the highest mercury values since the *S. brasiliensis* is a top predator, which means it is biomagnifying more mercury than the other species in the study. The increase of mercury in *S. brasiliensis* since 2008 is substantial and could only partly be explained by the higher average weight of the specimen in this study than in the study performed in 2008 (a higher weight generally implies a higher mercury level).

Mercury levels of the other fish have also risen in this study. The increase must however be seen in the light of the specimens weight, as with *S. brasiliensis*. The average mercury level of *P. nattereri* and the average weight increased compared to 2008.

One interesting aspect is that the increase ratio of the mercury levels in *B. hilarii* is lower now than before. This could mean that the mercury levels in *B. hilarii* will be decreasing in the near future. On the other hand, the average weight of the specimens of *B. hilarii* in this study was lower than the average weight of the specimens of *B. hilarii* in the study 2005, meaning that the difference could also be due only to the different average weight.

The course of events of fish mercury changes is different for different species. Herbivore species do, in general, get increased mercury levels before predatory fish does. The reason for this is that the herbivores are below the predators in the food-web, thus consuming mercury rich biota before the predators do. In the same way, herbivore species are precursors when the mercury levels decrease, which is why the possible decrease of mercury levels in *B. hilarii* is expected. Regarding the carnivore species, it is not probable that the mercury levels will decrease within the near future, since they are predecessors in relation to herbivores when it comes to mercury levels.

Fish from Lago Manso should not be eaten, since all the fish captured in the reservoir have mercury levels which exceed the safety levels determined by WHO. Further studies are necessary to monitor the mercury levels in fish from Lago Manso. The mercury levels in fish could, if the fish is consumed, mean serious health problems for the consumers and especially to foetus and children.

The number of fish in the reservoir has decreased since the construction of the reservoir (personal communication). One possible reason for the decline is that the levels of dissolved oxygen have decreased since the construction and hypoxia could occur in deeper horizons. Another possible reason for the decline is that there is no passage for fish to get by the dam (Hylander et al., 2006).

An interesting continuation of this study would be to investigate the mercury levels of plankton – since they are primary producers and therefore – according to what is discussed above – precursors

to the fish regarding mercury levels change. Firstly, to investigate mercury levels of plankton would be interesting because when the mercury stock runs out, the mercury change in the biota will be seen in plankton before it is seen in fish. Secondly, if the environment of the reservoir makes it difficult for the fish to survive due to low feed production, it would be easier to find plankton than fish and it would thus be a more available measurement parameter.

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Appendix I: Water parameters measured at every site in previous studies from Lago Manso

Water parameters from Lago Manso measured between 1999 and 2008 according to Wolpher et al. (2003), Hylander et al. (2006), Tuomola et al. (2008) and Rönnbäck et al. (2010).

Sample site	Coordinates	Year	Temp		pH	DO	Cond.	Secchi depth	Water colour	Turbidity	Susp. matter	DOC
			Air [°C]	Water [°C]								
1 Rio Quilombo	S15°05.344	2002	22	25	6.4			1.0				
	W55°43.389	2005	26	25	6.9	5.6	28	2.5	6	0.7	1.5	2.3
		2008	32	30	7.3	7.1	15	2.5	22	<1		4.3
2 Rio Casca	S15°02.430	2002	34	28	6.5	6.7		2.0				
	W55°37.379	2005	27	23	6.9	5.6	27	3.2	8	0.9	2.2	6.2
		2008	26	30	7.4	7.5	14	2.3	15	2		4.8
3 Rio Casca	S14°57.547	1999	28	23	5.7	7.7		1.1		7	11	2.2
	W55°43.267	2002	29	27	7.9	6.9		2.4				
		2005	28	25	7.1	5.5	30	6.3	2	1.7	1.7	3.3
		2008	30	30	7.6	7.4	13	4.5	12	1		4.5
4 Rio Casca	S14°56.312	1999	28	24	5.2	7.6		0.9		7	5.1	1.5
	W55°45.963	2002	31	27	6.5			2.3				
		2005	23	24	7.5	6.5	30	3.0	1	1.9	1.8	2.5
		2008	35	32	7.9	7.4	13	4.3	17	3		4.3
5 Rio Manso	S14°51.006	1999	29	25	6.9	7.2		2.0		8	3.2	4.2
	W55°42.544	2002	36	28	6.9			3.6				
		2005	27	25	7.5	5.9	42	4.3	1	2.8	1.6	2.9
		2008	34	31	8.3	7.5	30	4.5	15	7		4.5
6 Dam area	S14°52.344	1999	29	27	7	6.1		1.2		3	7	2.3
	W55°46.600	2002										
		2005	26	24	7.4	6.0	48	3.8	5	2.7	1.8	2.7
		2008	35	31	8.3	7.4	20	4.5	19	21		3.4
7 Downstream	S14°51.120	1999	29	25	6.3	7.8				3	5.1	1.6
	W55°53.523	2002	37	25	6.8			1.5				
		2005	19	20	6.7	3.3	49		27	9.2	5.3	2.9
		2008	27	28	7.3	5.1	23		33	11		4.2

Appendix II: Fish collected in previous studies from Lago Manso

Four different fish species collected both in Lago Manso and downstream between 1999 and 2008 according to Wolpher et al. (2003), Hylander et al. (2006), Tuomola et al. (2008) and Rönnbäck et al. (2010). In 2008, the weight was measured as gutted weight.

Lago Manso

Fish	Year	N	Hg tot				Total weight				Length
			[ng g ⁻¹ f.w.]				[g]				[cm]
			Min	Average	SD	Max	Min	Average	SD	Max	Average
<i>P. nattereri</i>	2002	14	82	217	255	449	91	173	67	343	18
	2008	12	846	2461	888	3836	106*	478*	326*	1100*	
<i>S. marginatus</i>	1999	2	73	169	136	265	168	207	55	246	19
	2005	9	294	850	559	1996	500	640	130	850	14
<i>B. hilarii</i>	2002	10	88	180	106	285	464	688	209	1152	31
	2005	6	73	556	350	1030	500	1340	730	2700	40
<i>S. brasiliensis</i>	2002	5	377	712	624	938	2200	3430	1434	5700	55
	2005	2	501	1061	791	1620	6000	6500	710	7000	82
	2008	10	2870	3744	734	4947	3300*	3767*	1052*	6500*	

Downstream

Fish	Year	N	Hg tot				Total weight				Length
			[ng g ⁻¹ f.w.]				[g]				[cm]
			Min	Average	SD	Max	Min	Average	SD	Max	Average
<i>S. marginatus</i>	2005	6	319	1118	538	1464	160	338	120	5000	24
<i>B. hilarii</i>	2005	4	54	167	136	359	290	860	670	1800	38
<i>S. brasiliensis</i>	2005	8	623	1323	700	2847	1000	4694	2350	7500	69

* Gutted weight

Appendix III: Fish collected 2010

Five species distributed in 30 fishes, collected both in Lago Manso and downstream in April, 2010.

Lago Manso							
Specie	Fish no.	Hg tot	STD	Length		Weight	
		Average [ng g ⁻¹ f.w.]		Total [cm]	Standard [cm]	Total [g]	Gutted [g]
<i>P. nattereri</i>	1	2815	3	35	31		1000
	2	3007	8	35	31		900
	3	3072	4	37	33		1400
	16	3972	2	33	30		900
	17	4670	1	33	30		1000
	24	1895	1	35	32		1100
	25	2836	1	36	32		1000
	26	3858	10	36	31		900
	27	2192	19	35	30		800
<i>S. marginatus</i>	6	937	13	19	17	200	174
	7	2250	3	20	18	240	207
	10	2359	2	18	15	149	130
	11	1895	1	19	16	160	145
	12	2683	2	22	20	224	203
	13	2116	1	26	23	407	370
	14	2382	1	26	24	374	339
	15	3018	3	23	21	339	228
<i>S. brasiliensis</i>	9	5971	3	65	62		4500
	21	5522	1	68	60		3500
	22	6845	2	79	62		4000
	23	5918	1	71	64		4500
<i>B. hilarii</i>	4	801	3	46	41		1100
	5	647	13	41	38		800
	8	1052	5	51	45		2000
	28	1313	3	42	38		1000
	29	374	30	40	37		1000
	30	599	1	40	37		900

Downstream							
Specie	Fish no.	Hg tot	STD	Length		Weight	
		Average [ng g ⁻¹ f.w.]		Total [cm]	Standard [cm]	Total [g]	Gutted [g]
<i>S. brasiliensis</i>	18	1309	1	54	49	1940	1800
	19	1336	1	90	80		10000
<i>P. pirinampu</i>	20	218	2	65	58		2300

Appendix IV: Inter-laboratory comparison

Comparison between analysis at Federal University of Rio de Janeiro and Federal University of Mato Grosso. Difference show how much results from Rio de Janeiro differed from Mato Grosso.

Specie	Fish no.	Federal University of Rio de Janeiro						Federal University of Mato Grosso	
		Analysis [ng/g]				STD	Average	Average	Difference
		1	2	3	4	[%]	[ng g ⁻¹ d.w.]	[ng g ⁻¹ d.w.]	[%]
<i>P. nattereri</i>	17	5441	2403	3539	4397	33	3945	4670	-16
<i>P. nattereri</i>	27	2252	1914	1725	2051	11	1986	2192	-9
<i>S. brasiliensis</i>	22	9947	6448	5748	6141	27	7071	6845	3
<i>S. brasiliensis</i>	23	7445	5998	4480	4960	23	5721	5918	-3

Appendix V: Variation in DO measurements

Deviation in tap water at every site from reference measurement in tap water. Reference value was 3 mg L⁻¹.

Sample site	Tap	Difference	DO	
	[mg L ⁻¹]	from ref tap =3 [%]	Measured [mg L ⁻¹]	Corrected [mg L ⁻¹]
1 Rio Quilombo	2.6	-13	3.2	3.6
2 Rio Casca	3.2	7	2.8	2.6
3 Rio Casca	2.4	-20	3.3	3.9
4 Rio Casca	2.3	-23	3.4	4.1
5 Rio Manso	3.5	17	2.9	2.4
6 Dam area	3.3	10	3.5	3.2
7 Downstream	3	0	2.7	2.7