Mercury bioaccumulation in fishes of a paddy field in Southern of Brazil

Bioacumulação de mercúrio em peixes em uma lavoura de arroz no Sul do Brasil

Vinicius Tavares Kütter¹, Mateus Tavares Kütter², Emmanoel Vieira Silva-Filho¹,

Eduardo Duarte Marques³, Olga Venimar de Oliveira Gomes¹ and Nicolai Mirlean⁴

¹Departamento de Geoquímica, Universidade Federal Fluminense – UFF, Outeiro São João Batista, s/n, CEP 24020141, Niterói, RJ, Brazil e-mail: viniciuskutter@yahoo.com.br; geoemma@vm.uff.br; olgagomes@id.uff.br

²Instituto de Biologia, Universidade Federal do Rio Grande – FURG, Av. Itália, Km 8, CEP 96201900, Rio Grande, RS, Brazil e-mail: kutter.m.t@gmail.com

³Escritório Regional Belo Horizonte, Serviço Geológico do Brasil – CPRM, CEP 30140-002, Belo Horizonte, MG, Brazil e-mail: Eduardo.marques@cprm.gov.br

⁴Instituto de Oceanografia, Universidade Federal do Rio Grande – FURG, Av. Itália, Km 8, CEP 96201900, Rio Grande, RS, Brazil e-mail: dgeonmir@furg.br

Abstract: Aim: The aim of present study was to evaluate the Hg concentration in two species of fish (Astyanax sp and Corydoras paleatus) and its potential use as a biomonitor, in order to know if the use of pesticides and fertilizers in paddy can enhance the Hg contamination to adjacent aquatic environment. Methods: Soil, suspended particulate matter and fish samples were sampled in a paddy field in South Brazil A cold vapor system, coupled with a GBC 932 atomic absorption spectrophotometer was used for total Hg determinations in samples. Results: The paddy soil shows Hg concentration 2-fold higher (mean 31 ng g⁻¹) in comparison to background areas (not cultivated). Suspended particle matter Hg concentration in paddy channels (mean $232.5 \pm 44.2 \text{ ng g}^{-1}$) are 1.5 times higher than the regional background. The analyzed fish specimens Astyanax sp in paddy showed Hg concentration 4-fold higher and significant different to background area. The mean Hg concentration in fish was: $51.7 \pm 19.5 \text{ ng g}^{-1}$ in Astyanax sp and 156.8 \pm 44.0 ng g⁻¹ in *Corydoras paleatus*. **Conclusions:** Considering the linear regression and Man whitney test hypothesis to Hg concentration in fish tissue from paddy suggests that Astyanax sp. can be a good biomonitor of Hg contamination, whereas Corydoras paleatus is a potential biomonitor. However, more studies with Corydoras are necessary in order to aggregate consistency to this hypothesis.

Keywords: biomonitoring; fish; mercury; contamination; Pampa biome.

Resumo: Objetivo: O objetivo do presente estudo foi avaliar a concentração de Hg em duas espécies de peixes (Astyanax sp e Corydoras paleatus) e seu uso potencial como biomonitor, a fim de saber se o uso de pesticidas e fertilizantes na lavoura pode levar a contaminação por Hg ao ambiente aquático adjacente. **Métodos:** Solo, material particulado em suspensão e amostras de peixes foram coletadas em um campo de arroz no sul do Brasil. Um sistema de vapor frio acoplado a um espectrofotômetro de absorção atômica (GBC 932) foi usado para as determinações de Hg total nas amostras. **Resultados:** O solo da lavoura de arroz apresentou concentração de Hg 2 vezes mais elevada (média de 31 ng g⁻¹), em comparação com a área controle (não cultivado). A concentração de Hg no material particulado em suspensão dos canais de irrigação do arroz (média de 232,5 ± 44,2 ng g⁻¹) é 1,5 vezes mais elevada do que na área controle. Os espécimes de peixes *Astyanax sp* analisados na área de cultivo mostraram concentração de Hg 4 vezes maior e, significativamente diferentes da área controle. A concentração média de Hg em peixes foi: 51,7 ± 19,5 ng g⁻¹ em *Astyanax sp* e 156,8 ± 44,0 ng g⁻¹ em *Corydoras paleatus*. **Conclusões:** Considerando a regressão linear e o teste de hipótese de de Man Whitney para a concentração de Hg em tecidos de peixes da lavoura de arroz, sugere que *Astyanax sp.* pode ser uma bom biomonitor de contaminação Hg, enquanto *Corydoras paleatus* é um biomonitor potencial. No entanto, mais estudos com *Corydoras* são necessárias, a fim de agregar consistência a este estudo.

Palavras-chave: biomonitoramento; peixe; mercúrio; contaminação; bioma Pampa.

1. Introduction

Mercury (Hg) is considered a highly toxic metal and has been used in the composition of pesticides utilized in rice fields (Smart & Hill, 1968). In Brazil, the use of pesticides containing Hg was banned in the 70's. Although the input of anthropogenic Hg had been stopped at these sites after the banishment, its effects persist in the environment and biota. Studies on paddies in Japan have reported an insignificant reduction of Hg soil contamination over eight years of study (Nakagawa & Yumita, 1998). Furthermore, more recent studies in paddies reported high concentration of methylmercury (MeHg) in rice grains (Zhang et al., 2010a,b; Zhao et al., 2010; Zhu et al., 2011; Peng et al., 2012; Rothenberg et al., 2012; Li et al., 2013).

In Brazil, the study developed by Silva et al. (2010) found Hg concentrations ranging from 2.2 to 4.4 ng g^{-1} in rice grains. Actually the large use of fertilizers in the rice production can intensify the methylation process in paddy fields due to bacteria growth stimulation.

Amongst the three Hg forms, the organic form MeHg is the most toxic to humans even in low concentrations (Zahir et al., 2005). Although Hg presents low concentration in water, it can be potentially biomagnified, reaching very higher concentrations in predatory fish, which can result in an increased risk of developing health problems when consumed by humans (NRC, 2000).

According to the report of the Committee on the Toxicological Effects of Methylmercury in the United States, the major source of human exposure to MeHg is the consumption of contaminated fish (NRC, 2000). Innumerous studies have been demonstrated that more than 80% of the total Hg present in fish tissue is in the form of MeHg (Silva et al., 2011; Kannan et al., 1998).

The characteristics of paddy are favorable to the process of Hg conversion into MeHg by anaerobic microorganisms (Rothenberg & Feng, 2012). Moreover, some studies have demonstrated that this process can also occur in the intestine of some fish species when they are fed with inorganic mercury (Rudd et al., 1980; Leaner & Mason, 2002). Since 1908, the rice production is cultivated in paddies in the Southern Brazil (Beskow, 1986). Nowadays, Brazil is the ninth largest rice producer in the world (Wong, 2004). The Rio Grande do Sul State produces 68% of the national production (CONAB, 2013). This region is part of the Pampa Biome that covers about 63% of Rio Grande do Sul State (IBAMA, 2004).

The Pampa has a great biodiversity including endemic species, some of them endangered or at risk of extinction (Marques et al., 2002). Notwithstanding the considerable number of endangered species, this region has received little attention in terms of environmental research (Bencke, 2010).

The paddy has a considerable impact on aquatic animals, since many species that inhabit nearest areas, swamps and lagoons, move to them after the flood. Furthermore, this environment has great ecological significance because it represents an important feeding, resting and breeding area for birds, including migratory species that comes from North and South America's (Dias & Burger, 2005).

Studies with fish demonstrated that this animal group is a good indicator of environmental health (Van der Oost et al, 2003; Raimundo et al., 2011). In this group, the main Hg incorporation in tissue occurs through feeding (Kidd et al., 1995; Snodgrass et al., 2000). The MeHg is absorbed by the gut and accumulated in tissues, where it can be biomagnified because of the long half-life of this compound (Lacerda & Malm, 2008). Therefore, as predator fish are in the top of the food web, they have the highest concentrations of this metal in relation to species which are at the bottom.

Mirlean et al. (2005), who investigated Hg levels in lakes near the paddy region in the Southern Brazil, found that the main source of Hg in this area is the atmospheric deposition. In this same study, the authors have proposed the use of *Astyanax sp* as a bioindicator of Hg contamination in studied area, once these species have shown a good correlation with Hg levels in the environment.

The genus *Astyanax* has been appointed by several authors as an excellent biomonitor of aquatic ecosystems, responses of countless biomarkers, such as histopathological assays (Prado et al., 2011;

Flores-Lopes & Thomaz, 2011; Schulz & Martins-Junior, 2001), micronucleus genotoxicity tests (Bogoni et al., 2014; Pantaleão et al., 2006) comet assay (Ramsdorf et al., 2012), and also hepatic porphyrin (Carrasco-Letelier et al., 2006).

The *Astyanax* sp and *Corydoras paleatus* are widely found in paddies in Southern Brazil, and are a food source to a large number of birds and mammals that use the paddy as a feeding area. These fish species are in the base of the aquatic food web. Therefore, they occupy a key position in the Hg bioaccumulation and transfer in the food web of this environment.

The aim of present study was to evaluate the Hg concentration in two species of fish (*Astyanax* sp and *Corydoras paleatus*) and its potential use as a biomonitor, in order to know if the use of pesticides and fertilizers in paddy can enhance the Hg contamination to adjacent aquatic environment.

We hypothesize the use of pesticides and fertilizers in rice paddy fields are a potential Hg source to adjacent aquatic environment.

2. Material and Methods

2.1. Study sites and species

The studied site is located at the municipality of Rio Grande-RS, in the region of the swamppampas, Coastal Southern Brazil (Figure 1). This region is characterized by a coastal plain where major soil types are Planosol, Gleysol, Podzol and quartz sands, comprised of medium/fine sand and clay (Tagliani, 1997). Around the paddy fields, there are artificial channels used for drainage and irrigation, connecting this environment to natural lakes and wetlands with great biodiversity (fish, crustaceans, amphibians, aquatic birds, etc.) and allows the migration of the aquatic fauna between these sites.

During the growth period, the rice farms remain flooded for 80-100 days and many wild aquatic organisms inhabit this environment. Also in this period fertilizers, pesticides and herbicides are applied into the crops. In the harvest period the crops are drained and the animals are found in the channel, lakes and wetlands.

The sampling campaign was carried out in the summer of 2005, in a farm located at the boarder of the highway RS-473 in the period immediately after the rice harvest. The water used for rice irrigation comes by diversion from São Gonçalo River. One 40 cm core of paddy soil was collected. In the paddy drainage channel, four samples of suspended particulate matter (SPM) and the two wild fish species (*Astyanax sp* and *Corydoras paleatus*) were collected.

Regarding the biology of the fish species, the *Astyanax* genus feeding in the water column,

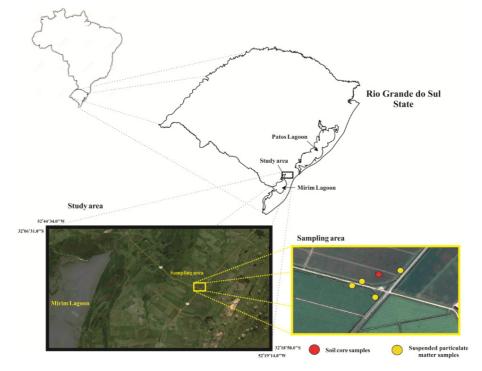


Figure 1. Location of the sampling area.

consuming mainly zooplankton, fish eggs, and insects, whereas the *Corydoras paleatus* are bottom feeders, eating insects, small invertebrates and organic detritus (Moresco & Bemvenuti 2005). In the swamp-pampas of Southern Brazil the most abundant species are: *Astyanax jacuhiensis, Astyanax eigenmanniorum* and *Astyanax fasciatus* (Moresco & Bemvenuti 2005).

The paddy soil core was obtained employing acrylic tube sampler. In the laboratory, the soil core was fractionated in: 0-15 cm, 15-30cm and 30-40cm. Each part of the soil core was homogenized and an aliquot of this homogenates were utilized in the total and $<63\mu$ m fractions for mercury determination.

The paddy drainage water was sampled in 1.5 L plastic bottles previous cleaned with HCl 10% (v/v). The water was maintained at temperature of 4 °C in cooler boxes until arrival to laboratory. At the laboratory, the water was filtered in acetate cellulose membranes $(0.45 \mu m)$ in a vacuum system for suspended particulate matter (SPM) quantification.

The fish species were collecting by netting. A total of 25 specimens of *Astyanax sp* and 10 of *Corydora paleatus* were obtained. In the laboratory, the fork lengths were determined, and then muscle tissue samples were removed for Hg analysis.

The results obtained in the present study were compared to literature data from background area (Federally-protected Taim Ecological Station). This area is located 80 Km away from farming investigated in the present work.

2.2. Sample digestion and total mercury analysis

Digestion methods for soil, SPM and fish tissues were the same proposed by Zhou & Wong (2000). Briefly, aliquots (0.5 g) of the soil and SPM samples were digested in 15 ml of concentrated H_2SO_4 and HNO_3 (2:1 v/v) in a 60 °C water bath. Digestion was proceeded until the solution was clear, then the digestion flasks were transferred to an ice bath, and 6% KMnO₄ solution was added slowly, until the digest turned purple. Five milliliters of 5% $K_2S_2O_8$ was then added to each flask to ensure complete oxidation of organic mercury compounds.

Fish tissue samples were pre-digested in 8 ml of concentrated HNO₃ and H_2SO_4 (2:1 v/v) at 25 °C for 3h, then at 60 °C for 5 h. Five milliliters of 30% H_2O_2 were added to the samples in 0.5 ml increments, with time enough for decreasing of foaming between additions. The temperature was then raised to 65 °C, and digestion proceeded until the samples turned colorless or light yellow. A cold

vapor system, coupled with a GBC 932 atomic absorption spectrophotometer, was used for total Hg determinations in digested soil, SPM and fish samples.

During the analysis, the Hg liberated by the reduction was purged with argon, and collected on a gold wool trap connected to a GBC HG3000 hydride generation system. An additional gold trap in the gas line stripped mercury from the carrier gas. Concentrations were then determined with the GBC atomic absorption spectrophotometer. The spectrophotometer has a detection limit of $0.4 \text{ ng } \text{L}^{-1}$.

All samples were analyzed in triplicate. Coefficients of variation for all triplicates were <6%. The accuracy and precision of Hg analysis were verified by sequential digestion and analysis of certified reference materials (PACS-2 for sediment, and IAEA 350 tuna homogenates for fish muscle). Mean Hg recovery was within the 97% confidence interval for both materials, indicating high accuracy, and the coefficient of variation for six analysis was <5%, indicating high precision.

Mercury concentrations in fish are expected to increase with age due to cumulative exposure; however, to determine fish ages is not often possible. Fish lengths and weights are typically used as surrogates for age, and positive relationships between Hg concentrations and both size and age have been reported for lake fishes (Grieb et al., 1990). A linear regression was computed to assess the relationship between tissue Hg and fork length. Furthermore, a Man Whitney test was employed in Statistica 8.0 to test the differences of Hg concentration in fish from different areas are significant.

3. Results and Discussion

3.1. Mercury in the Soil and Suspended particulate matter

The mercury concentration in the soil (fraction $<63 \ \mu\text{m}$) was around 2 times higher than found in the total fraction (Table 1).

This result agrees with that found by Conceição (2005) for the regional background. It was not found any considerable variability in the Hg concentration in the different soil depths evaluated. This is probably because the soil is plowed every year for rice planting, leading to a homogenization among the soil layers.

According to Mirlean & Oliveira (2006), the unpolluted soils (fraction <63 μ m) in this region presents average Hg concentration of 27 ng g⁻¹ (ranging from 10 to 50 ng g⁻¹). The results found in the paddy soil indicate that it contains a small enrichment in Hg in comparison to the regional background. The same result is found in the total soil fraction, since Conceição (2005) found a mean Hg concentration of 15 ng g^{-1} in this fraction.

The probable source of mercury enrichment in the paddy soil is the use of fertilizers and/or pesticides. Some studies with fertilizers described mercury concentrations of 147,000.0 \pm 38, 235,000.0 \pm 98 and 196,000.0 \pm 65 ng g⁻¹ in superphosphate, triple superphosphate, and NPK fertilizer, respectively (Mirlean et al., 2008). The low Hg enrichment of the soil could be related to the leaching process.

After the soil fertilization and rice planting, the area is flooded and due to the predominance of fine grained soil, the SPM in water column allows the Hg transport to adjacent aquatic environments. These processes were found by Aomine et al. (1967), which showed the mercury sprayed onto crops would be partly retained by the soil in paddy conditions for a considerable period whereas another fraction would be removed with percolation and run-off water and also be absorbed by plant roots. Moreover, Aomine et al. (1967) showed that largest part of Hg applied in the paddy is transported by and deposited in the rivers bottom sediment from the adjacent watershed.

The mean Hg concentration in suspended particulate matter in the paddy was 232.5±44.2

ng g⁻¹. This value is about 5 times higher than that found in the fine soil fraction (<63 μ m) and lower than that found in SPM at hydric compartments contaminated by gold mining and urban effluent (Table 2). However, it is similar to that found by Kütter (2006) from an industrial area in the same region (Table 2). The Hg concentrations in SPM paddy was about 1.5 times higher than the regional background and up to 4 times higher compared to remote areas in Amazon (Brabo et al., 2003).

Silva et al. (2009) demonstrated that watershed land use influences Hg levels in fishes of Amazon biome. According to this work, watershed with highest aquatic vegetation density and lowest forest cover showed ichthyofauna with highest Hg concentration. Conversely, the watershed with the highest forest cover and low aquatic vegetation density showed the lowest mercury concentration in fish community.

Lacerda et al. (2012), demonstrated that the change of land use in Amazon region is the main cause of Hg increase in top food web predatory fish. Furthermore, the SPM represents 90% of the total Hg present in the water river. According to Lacerda et al. (2012) the SPM has a key role in the process of fish Hg increase.

In Amazon biome, soils under any type of local cultivation (fallow, pasture, orchards, banana plantations) were characterized by cation enrichment

,		,	
		Hg concentrati	on (ng g ⁻¹)
Site	Deep (cm)	Soil (fraction <63 µm) (n=3)	Soil (Total) (n=3)
	0-15	57.0 ± 4.0	28.5 ± 4.1
Paddy field	15-30	63.5 ± 2.7	29.5 ± 3.6
	30-40	54.3 ± 3.3	34.8 ± 1.2

Table 1. Mercury concentration (ng g⁻¹) in soils from the study area.

Table 2. Comparison among different sources of Hg in SPM for different sites in Brazil.

Site	Hg ng g⁻¹ average (range)	Reference
Domestic effluent – Rio Grande City	5530 (460 - 21140)	Mirlean et al. (2003)
Mixes effluent – Rio Grande City	1180 (120 - 3970)	Mirlean et al. (2003)
Industrial effluent – Rio Grande City	650 (140 - 1940)	Mirlean et al. (2003)
Rain water runoff – Rio Grande City	350 (70 - 1100)	Mirlean et al. (2003)
Paddy channel - Rio Grande City	232.5 (170.3 - 275)	This work
Industrial Area – Pelotas RS	258.8	Kütter (2006)
Natural Reserve (background regional) - Rio Grande City	163.4	Kütter (2006)
Gold mining area – Viseu City – Pará	201.5 (< 8 - 900)	Vieira & Passarelli (1996)
Acre State rivers – Amazon Forest	60 (1 - 220)	Brabo et al. (2003)
Gold mining tailing deposit – Poconé city	(< 20 - 610)	Lacerda et al. (1991)
Paraíba do Sul River – Rio de Janeiro	522.8 (233 - 964)	Molisani et al. (2007)
Acre River – Amazon Forest	98 (67 – 220)	Mascarenhas et al. (2004)

associated with slash-and-burn activities, leading to loss of Hg, compared to levels measured in soils under forest cover (Farella et al., 2006, 2007). Pampa biome soils under rice cultivation are characterized by adduction of fertilizers and calcareous (pH soil corrector) by the periodic flooding, leading to Hg availability for biota incorporation.

3.2. Mercury in fishes

The linear regression of Hg concentrations in the fish tissue versus fish size show an increasing trend to bioaccumulation in both species investigated (Figure 2).

In Astyanax sp the Hg average concentration was 51.7 \pm 19.5 ng g⁻¹ (26.1 to 51.7 ng g⁻¹), whereas Corydoras paleatus has averaged of 156.8 \pm 44.0 ng g⁻¹ (ranging from 85.4 to 222.3 ng g⁻¹). This difference in Hg concentration between Astyanax sp and Corydoras paleatus may be related to feed habits as well as to distinct physiological characteristics of the two species. The Corydoras *paleatus* is detritivorous feeding organic matter and invertebrates from bottom, on the other hand, the *Astyanax sp* is omnivorous feeding plankton and invertebrates from water (Moresco & Bemvenuti, 2005).

The maximum size attained by *Astyanax sp* as an adult is greater than the *Corydoras paleatus*. The highest concentration of Hg found in *Corydoras paleatus* may be related to the fact that this fish species grows less in comparison to *Astyanax sp*.

The Hg concentration in *Astyanax sp* is approximately 4-fold higher in the paddy area when compared to individuals of the same size of the background area (Mirlean et al., 2005) (Figure 3). Moreover, these differences between the paddy field and background area are significantly different p< 0.05 (Man-Whitney test). However, the Hg concentration in *Astyanax sp* from paddy is 2.6 and 1.3 times lower than observed in individuals from industrial and suburban areas, respectively (Table 3).

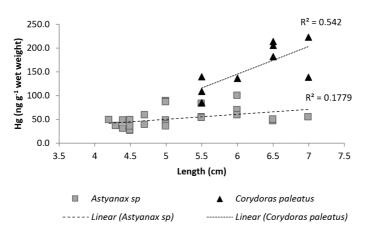


Figure 2. Relation between Hg concentration in *Astyanax sp* (n = 25) and *Corydoras paleatus* (n = 10) tissues and sizes sampled from a paddy.

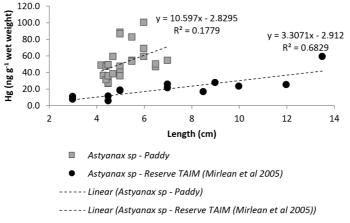


Figure 3. Mercury concentration in *Astyanax sp* from paddy in comparison to data from Mirlean et al. (2005) nature reserve.

Specie	Tropic class	Fork length, Range (cm)	Hg concentration Mean ± SD (range)	Site	Biome	Reference
Astyanax sp (n=25)	Omnivore	4.2 -7.0	51.7 ± 19.5 (26.1 - 51.7)	Paddy field-RS Brazil	Pampa	Present work
Astyanax sp (n=18)	Omnivore	2.5 -14.0	134.9 ± 32.8 (89.4 - 195.8)	Industrial area-RS, Brazil	Pampa	Mirlean et al. (2005)
Astyanax sp (n=15)	Omnivore	2.5 -14.0	69.1 ± 50.5 (14.1 -166.2)	Suburban area-RS, Brazil	Pampa	Mirlean et al. (2005)
Astyanax sp (n=13)	Omnivore	2.5 -14.0	20.5 ± 13.4 (7.0 - 58.5)	Taim Reserve-RS, Brazil	Pampa	Mirlean et al. (2005)
Astyanax sp (n=3)	Omnivore	29.0	203.6 (76.3 - 346.6)	Patos Lagoon-RS, Brazil	Pampa	Kütter et al. (2009)
Atyanax aff bimaculatus (n=22)	Omnivore	9.7 -11.0	(96.0 - 157.0)	Vigário Reservoir-RJ, Brazil	Atlantic Forest	Kasper et al. (2009)
Astyanax integer (n=4)	Omnivore		277.5*	Las Marías River - Venezuela	Amazon Forest	Kwon et al. (2012)
Astyanax/Moenkhausia spp (n=1)	Omnivore	16.7	180.0	Maroni River, French Guiana	Amazon Forest	Fujimura et al. (2012)
Astyanax Bimaculatus (n=6)	Omnivore	9.2	547.5*	Petit-Saut reservoir – French Guiana	Amazon Forest	Durrieu et al. (2005)
Corydoras paleatus (n=10)	Detritivore	5.5 - 7.0	156.8 ± 44.0 (85.4 - 222.3)	Paddy field-RS, Brazil	Pampa	Present work
Rineloricaria cadeae (n=46)	Detritivore	9.0-12.4	59.0 (46.0-71.0)	Cadeia and Feitosa Rivers- RS, Brazil (Impacted area)	Pampa	Rodrigues & Formoso (2006)
Rineloricaria cadeae (n=22)	Detritivore	9.4-12.8	222.0 (178.0-355.0)	Cadeia and Feitosa Rivers- RS, Brazil (unpolluted area)	Pampa	Rodrigues & Formoso (2006)
Hypostomus affinis (n=30)	Detritivore	18.0-28.0	(<17.9 - 33.4)	Muriaé River-RJ, Brazil	Atlantic Forest	Araujo et al. (2010)
Hypostomus c.f.luetkini (n=30)	Detritivore	12.0-28.0	(<17.9 -39.5)	Muriaé River-RJ, Brazil	Atlantic Forest	Araujo et al. (2010)

Table 3. Mercury concentration (ng $\mathrm{g}^{\text{-1}}$ wet weight) in fish.

The highest Hg concentrations in *Astyanax sp* are reported in hydroelectric reservoir from Amazon region (Durrieu et al., 2005). These values are related to methylation process that is increased in those environments (Hylander et al., 2006; Montgomery et al., 2000). Even in the background areas from the Amazon region the Hg values in *Astyanax sp* are at least 5 times higher than that found in paddy fields in Southern Brazil (Kwon et al., 2012; Fujimura et al., 2012) (Table 3).

In another study developed in a reservoir in Southeastern Brazil, Kasper et al. (2009) found Hg concentration 1.8 to 3.0 times higher in *Astyanax sp* in comparison to paddy field from Pampa (Table 3). These reservoirs receive water from a polluted river, Paraíba do Sul, that cross the biggest Brazilian industrial park.

Due to the fact that the present work is the first study to show data on Hg accumulation in *Corydoras paleatus*, we opted to compare the data from paddy field with others detritivores species. The *Corydoras paleatus* from paddy showed Hg concentration 3 times higher than that found in *Rineloricaria cadeae* in an unpolluted area from Pampa biome (Rodrigues & Formoso, 2006). On the other hand, tissue Hg concentrations in *Rineloricaria cadeae* from tanneries impacted area are 1.4 times higher than *Corydoras paleatus* (Table 3) in our study. Other detritivorous fish, *Hypostomus sp* showed tissue Hg concentration 4 times lower in unpolluted area than *Corydoras paleatus* from paddy (Table 3).

4. Conclusion

The results demonstrated that the levels of Hg in fish found in the paddy are higher than in near sites without human activities (control area, Taim reserve). This result, suggest that the use of pesticides and fertilizers in paddy fields can enhance the mercury contamination to adjacent aquatic ecosystems. Furthermore, considering the linear regression and Man whitney test hypothesis to Hg concentration in fish tissue from paddy suggests that *Astyanax sp.* can be a good biomonitor of Hg contamination, whereas *Corydoras paleatus* is a potential biomonitor. However, more studies with Corydoras are necessary in order to aggregate consistency to this hypothesis.

References

AOMINE, S., KAWASAKI, H. and INOUE, K. Retention of mercury by soils. *Soil Science and Plant Nutrition*, 1967, 13(6), 187-188. http://dx.doi.org/ 10.1080/00380768.1967.10431994.

- ARAUJO, B.F., CARVALHO, C.E.V., ANDRADE, D.R. and GOMES, R.S. Distribuição de mercúrio em tecido muscular de *Hypostomus affinis* (Steindachner, 1877) e *Hypostomus c.f.luetkini* (Barlenger, 1887) do Rio Muriaé, Itaperuna-RJ. *Journal of the Brazilian Society of Ecotoxicology*, 2010, 5(1), 49-54. http:// dx.doi.org/10.5132/jbse.2010.01.008.
- BENCKE, G. New and significant bird records from Rio Grande do Sul, with comments on biogeography and conservation of the southern Brazilian avifauna. *Iheringia Série Zoologia*, 2010, 100(4), 391-402. http://dx.doi.org/10.1590/S0073-47212010000400014.
- BESKOW, PR. O arrendamento capitalista na agricultura: evolução e situação atual da economia do arroz no Rio Grande do Sul. *Cadernos de Difusão de Tecnologia*, 1986, 3(2), 343-350 [viewed 16 Aug. 2014]. Available from: https://seer.sct.embrapa.br/index. php/cct/article/viewFile/9216/5253.
- BOGONI, J.A., ARMILIATO, N., ARALDI-FAVASSA, C.T. and TECHIO, V.H. Genotoxicity in Astyanax bimaculatus (Twospot Astyanax) exposed to the waters of Engano River (Brazil) as determined by micronucleus tests in erythrocytes. Archives of Environmental Contamination and Toxicology, 2014, 66(3), 441-449. http://dx.doi.org/10.1007/s00244-013-9990-5. PMid:24435477
- BRABO, E.S., ANGÉLICA, R.S., SILVA, A.P., FAIAL, K.R.F., MASCARENHAS, A.F.S., SANTOS, E.C.O., JESUS, I.M. and LOUREIRO, E.C.B. Assessment of Mercury levels in soils, Waters, bottom sediments and fishes of Acre state in Brazilian Amazon. *Water, Air, and Soil Pollution*, 2003, 147(1-4), 61-77. http://dx.doi.org/10.1023/A:1024510312250.
- CARRASCO-LETELIER, L., EGUREN, G., DE MELLO, F.T. and GROVES, P.A. Preliminary field study of hepatic porphyrin profiles of Astyanax fasciatus (Teleostei, Characiformes) to define anthropogenic pollution. *Chemosphere*, 2006, 62(8), 1245-1252. http://dx.doi.org/10.1016/j. chemosphere.2005.07.005. PMid:16153685
- COMPANHIA NACIONAL DE ABASTECIMENTO - CONAB. Acompanhamento da safra brasileira de grãos 2012/13- Décimo levantamento - julho. Brasília, 2013 [viewed 16 Aug. 2014]. Available from: http://www.conab.gov.br/OlalaCMS/uploads/ arquivos/13_07_09_09_04_53_boletim_graos_ junho_2013.pdf.
- CONCEIÇÃO, C.O. Contaminação dos aterros urbanos por metais pesados no município de Rio Grande - RS [Master thesis]. Rio Grande: Fundação Universidade Federal do Rio Grande, 2005, 108 p. [viewed 16 Aug. 2014]. Available from: http://repositorio.furg. br:8080/handle/1/3527.
- DIAS, R.A. and BURGER, M.I. A assembléia de aves de áreas úmidas em dois sistemas de cultivo de arroz

irrigado no extremo sul do Brasil. *Ararajuba*, 2005, 1(13), 63-80.

- DURRIEU, G., MAURY-BRACHET, R. and BOUDOU, A. Goldmining and mercury contamination of the piscivorous fish Hoplias aimara in French Guiana (Amazon basin). *Ecotoxicology and Environmental Safety*, 2005, 60(3), 315-323. http://dx.doi.org/10.1016/j.ecoenv.2004.05.004. PMid:15590010
- FARELLA, N., DAVIDSON, R., LUCOTTE, M. and DAIGLE, S. Nutrient and mercury variations in soils from family farms of the Tapajós region (Brazilian Amazon): recommendations for better farming. Agriculture, Ecosystems & Environment, 2007, 120(2-4), 449-462. http://dx.doi.org/10.1016/j. agee.2006.11.003.
- FARELLA, N., LUCOTTE, M., DAVIDSON, R. and DAIGLE, S. Mercury release from deforested soils triggered by base cation enrichment. *The Science* of the Total Environment, 2006, 368(1), 19-29. http://dx.doi.org/10.1016/j.scitotenv.2006.04.025. PMid:16781764
- FLORES-LOPES, F. and THOMAZ, A.T. Histopathologic alterations observed in fish gills as a tool in environmental monitoring. *Brazilian Journal of Biology*, 2011, 71(1), 179-188. http:// dx.doi.org/10.1590/S1519-69842011000100026. PMid:21437416
- FUJIMURA, M., MATSUYAMA, A., HARVARD, J.P., BOURDINEAUD, J.-P. and NAKAMURA, K. Mercury contamination in humans in Upper Maroni, French Guiana between 2004 and 2009. *Bulletin of Environmental Contamination and Toxicology*, 2012, 88(2), 135-139. http://dx.doi.org/10.1007/s00128-011-0497-3. PMid:22147084
- GRIEB, T.M., DRISCOLL, C.T., SCHOFIELD, C.L., BOWIE, G.L. and PORCELLA, D.B. Factors affecting mercury accumulation in fish in the upper Michigan peninsula. *Environmental Toxicology and Chemistry*, 1990, 9(7), 919-930. http://dx.doi. org/10.1002/etc.5620090710.
- HYLANDER, L.D., GRÖHN, J., TROPP, M., VIKSTRÖM, A., WOLPHER, H., DE CASTRO E SILVA, E., MEILI, M. and OLIVEIRA, L.J. Fish mercury increase in Lago Manso, a new hydroelectric reservoir in tropical Brazil. *Journal of Environmental Management*, 2006, 81(2), 155-166. http://dx.doi.org/10.1016/j.jenvman.2005.09.025. PMid:16797830
- INSTITUTO BRASILEIRO DO MEIO AMBIENTE E DOS RECURSOS NATURAIS RENOVÁVEIS - IBAMA. *Estatísticas sobre Unidades de Conservação nos Biomas Brasileiros.* 2004 [viewed 16 Aug. 2014]. Available from: http://www.ibama.gov.br.
- KANNAN, K., SMITH JUNIOR, R.G., LEE, R.F., WINDOM, H.L., HEITMULLER, P.T., MACAULEY, J.M. and SUMMERS, J.K.

Distribution of total mercury and methyl mercury in water, sediment, and fish from south Florida estuaries. *Archives of Environmental Contamination and Toxicology*, 1998, 34(2), 109-118. http://dx.doi. org/10.1007/s002449900294. PMid:9469852

- KASPER, D., PALERMO, E.F.A., DIAS, A.C.M.I., FERREIRA, G.L., LEITÃO, R.P., BRANCO, C.W.C. and MALM, O. Mercury distribution in different tissues and trophic levels of fish from a tropical reservoir, Brazil. *Neotropical Ichthyology*, 2009, 7(4), 751-758. http://dx.doi.org/10.1590/ S1679-62252009000400025.
- KIDD, K.A., HESSLEIN, R.H., FUDGE, R.J.P. and HALLARD, K.A. The influence of trophic level as measured by delta-15N on mercury concentrations in freshwater organisms. *Water, Air, and Soil Pollution*, 1995, 80(1-4), 1011-1015. http://dx.doi. org/10.1007/BF01189756.
- KÜTTER, V.T. Aspectos da biogeoquímica do mercúrio em lagos na planície costeira do sul do Rio Grande do Sul [Master Thesis]. Rio Grande: Fundação Universidade Federal do Rio Grande, 2006, 93 p. [viewed 16 Aug. 2014]. Available from: http://www. argo.furg.br/bdtd/tde_arquivos/3/TDE-2007-09-27T195352Z-50/Publico/Kutter.pdf.
- KÜTTER, V.T., MIRLEAN, N., BAISCH, P.R., KÜTTER, M.T. and SILVA-FILHO, E.V. Mercury in freshwater, estuarine, and marine fishes from Southern Brazil and its ecological implication. *Environmental Monitoring and Assessment*, 2009, 159(1-4), 35-42. http://dx.doi.org/10.1007/s10661-008-0610-1. PMid:19011981
- KWON, S.Y., MCINTYRE, P.B., FLECKER, A.S. and CAMPBELL, L.M. Mercury biomagnification in the food web of a neotropical stream. *The Science of the Total Environment*, 2012, 417-418, 92-97. http://dx.doi.org/10.1016/j.scitotenv.2011.11.060. PMid:22257508
- LACERDA, L.D. and MALM, O. Contaminação por mercúrio em ecossistemas aquáticos: uma análise das áreas críticas. *Estudos Avançados*, 2008, 22(63). http:// dx.doi.org/10.1590/S0103-40142008000200011.
- LACERDA, L.D., BASTOS, W.R. and ALMEIDA, M.D. The impacts of land use changes in the mercury flux in the Madeira River, Western Amazon. *Anais da Academia Brasileira de Ciencias*, 2012, 84(1), 69-78. http://dx.doi.org/10.1590/S0001-37652012000100007. PMid:22441596
- LACERDA, L.D., PFEIFFER, W.C., MARINS, R.V., RODRIGUES, S., SOUZA, C.M.M. and BASTOS, W.R. Mercury dispersal in water, sediments and aquatic biota of a gold mining tailing deposit drainage in Poconé, Brazil. *Water, Air, and Soil Pollution*, 1991, 55(3-4), 283-294. http://dx.doi.org/10.1007/ BF00211194.
- LEANER, J.J. and MASON, R.P. Methylmercury accumulation and fluxes across the intestine of

channel catfish, Ictalurus punctatus. *Comparative Biochemistry and Physiology Part C Toxicology & Pharmacology*, 2002, 132(2), 247-259. http:// dx.doi.org/10.1016/S1532-0456(02)00072-8. PMid:12106901

Kütter, V.T. et al.

- LI, B., SHI, J.B., WANG, X., MENG, M., HUANG, L., QI, X.L., HE, B. and YE, Z.H. Variations and constancy of mercury and methylmercury accumulation in rice grown at contaminated paddy field sites in three Provinces of China. *Environmental Pollution*, 2013, 181, 91-97. http://dx.doi. org/10.1016/j.envpol.2013.06.021. PMid:23838485
- MARQUES, A.A.B., FONTANA, C.S., VELEZ, E. BENCKE, G.A. and REIS, RE. Lista das espécies da fauna ameaçada de extinção no Rio Grande do Sul: Decreto estadual n. 41.672. Porto Alegre, 2002. [viewed 16 Aug. 2014]. Publicações Avulsas FZB, no. 11. Available from: http://www.fzb.rs.gov.br/ upload/1396361091_preliminares.pdf.
- MASCARENHAS, A.F.S., BRABO, E.S., SILVA, A.P., FAYAL, K.F., JESUS, I.M. and SANTOS, E.C.O. Mercury concentration assessment in botton sediments and suspended solids from the Acre river, in the State of Acre, Brazil. *Acta Amazonica*, 2004, 34(1). http://dx.doi.org/10.1590/S0044-59672004000100008.
- MIRLEAN, N. and OLIVEIRA, C. Mercury in coastal reclamation fills in Southernmost Brazil: Historical and environmental facets. *Journal of Coastal Research*, 2006, 22(6), 1573-1576. http://dx.doi. org/10.2112/04-0352.1.
- MIRLEAN, N., ANDRUS, V.E. and BAISCH, P. Mercury pollution sources in sediments of Patos Lagoon Estuary, Southern Brazil. *Marine Pollution Bulletin*, 2003, 46(3), 331-334. http:// dx.doi.org/10.1016/S0025-326X(02)00404-6. PMid:12604067
- MIRLEAN, N., BAISCH, P., MACHADO, I. and SHUMILIN, E. Mercury contamination of soil as the result of long-term phosphate fertilizer production. *Bulletin of Environmental Contamination and Toxicology*, 2008, 81(3), 305-308. http://dx.doi. org/10.1007/s00128-008-9480-z. PMid:18587516
- MIRLEAN, N., LARNED, S.T., NIKORA, V. and KÜTTER, V.T. Mercury in lakes and lake fishes on a conservation-industry gradient in Brazil. *Chemosphere*, 2005, 60(2), 226-236. http:// dx.doi.org/10.1016/j.chemosphere.2004.12.047. PMid:15914242
- MOLISANI, M.M., KJERFVE, B., BARRETO, R. and LACERDA, L.D. Land-sea mercury transport through a modified watershed, SE Brazil. *Water Research*, 2007, 41(9), 1929-1938. http://dx.doi. org/10.1016/j.watres.2007.02.007. PMid:17382988
- MONTGOMERY, S., LUCOTTE, M. and RHEAULT, I. Temporal and spatial influences of flooding on dissolved mercury in boreal reservoirs. *The Science*

of the Total Environment, 2000, 260(1-3), 147-157. http://dx.doi.org/10.1016/S0048-9697(00)00559-3. PMid:11032123

- MORESCO, A. and BEMVENUTI, M.A. *Peixes: áreas de banhado e lagoas costeiras do extremo sul do Sul do Brasil.* Porto Alegre: ABRH, 2005, 63 p.
- NAKAGAWA, R. and YUMITA, Y. Change and behavior of residual mercury in paddy soils and rice of Japan. *Chemosphere*, 1998, 37(8), 1483-1487. http://dx.doi.org/10.1016/S0045-6535(98)00138-6. PMid:9753762
- NATIONAL RESEARCH COUNCIL NRC. *Toxicological effects of methylmercury*. Washington: Committee on the Toxicological Effects of Methylmercury, Board on Environmental Studies and Toxicology, Commission on Life Sciences, National Research Council, National Academy Press, 2000.
- PANTALEÁO, S.M., ALCÂNTARA, A.V., ALVES, J.P. and SPANÓ, M.A. The piscine micronucleus test to assess the impact of pollution on the Japaratuba river in Brazil. *Environmental and Molecular Mutagenesis*, 2006, 47(3), 219-224. http://dx.doi.org/10.1002/ em.20188. PMid:16388529
- PENG, X., LIU, F., WANG, W.-X. and YE, Z. Reducing total mercury and methylmercury accumulation in rice grains through water management and deliberate selection of rice cultivars. *Environmental Pollution*, 2012, 162, 202-208. http://dx.doi.org/10.1016/j. envpol.2011.11.024. PMid:22243865
- PRADO, P.S., SOUZA, C.C., BAZZOLI, N. and RIZZO, E. Reproductive disruption in lambari Astyanax fasciatus from a Southeastern Brazilian reservoir. *Ecotoxicology and Environmental Safety*, 2011, 74(7), 1879-1887. http://dx.doi. org/10.1016/j.ecoenv.2011.07.017. PMid:21831433
- RAIMUNDO, J., PEREIRA, P., CAETANO, M., CABRITA, M.T., VALE, C. Decrease of Zn, Cd and Pb concentrations in marine fish species over a decade as response to reduction of anthropogenic inputs: the example of Tagus estuary. *Marine Pollution Bulletin*, 2011, 62(12), 2854-2858.
- RAMSDORF, W.A., VICARI, T., DE ALMEIDA, M.I., ARTONI, R.F. and CESTARI, M.M. Handling of Astyanax sp. for biomonitoring in Cangüiri Farm within a fountainhead (Iraí River Environment Preservation Area) through the use of genetic biomarkers. *Environmental Monitoring and* Assessment, 2012, 184(10), 5841-5849. http://dx.doi. org/10.1007/s10661-012-2752-4. PMid:22821320
- RODRIGUES, M.K. and FORMOSO, M.L.L. Heavy metals in recent sediments and bottom-fish under the influence of tanneries in South Brazil. *Water, Air, and Soil Pollution,* 2006, 176(1-4), 307-327. http:// dx.doi.org/10.1007/s11270-006-9170-6.

- ROTHENBERG, S.E., FENG, X. Mercury cycling in a flooded rice paddy. *Biogeosciences*, 2012, 117(G3), 1-16. http://dx.doi.org/10.1029/2011JG001800.
- ROTHENBERG, S.E., FENG, X., ZHOU, W., TU, M., JIN, B. and YOU, J. Environment and genotype controls on mercury accumulation in rice (Oryza sativa L.) cultivated along a contamination gradient in Guizhou, China. *The Science of the Total Environment*, 2012a, 426, 272-280. http://dx.doi.org/10.1016/j. scitotenv.2012.03.024. PMid:22513403
- RUDD, J.W., FURUTANI, A. and TURNER, M.A. Mercury methylation by fish intestinal contents. *Applied and Environmental Microbiology*, 1980., 40(4), 777-782. PMid:7425625.
- SCHULZ, U.H. and MARTINS-JUNIOR, H. Astyanax fasciatus as bioindicator of water pollution of Rio dos Sinos, RS, Brazil. *Brazilian Journal of Biology*, 2001, 61(4), 615-622. http://dx.doi.org/10.1590/S1519-69842001000400010. PMid:12071317
- SILVA, C.A., TESSIER, E., KÜTTER, V.T., WASSERMAN, J.C., DONARD, O.F.X. and SILVA-FILHO, E.M. Mercury speciation in fish of the Cabo Frio upwelling region, SE-Brazil. *Brazilian Journal of Oceanography*, 2011, 59(3), 259-266. http://dx.doi. org/10.1590/S1679-87592011000300006.
- SILVA, D., LUCOTTE, M., PAQUET, S. and DAVIDSON, R. Influence of ecological factors and of land use on mercury levels in fish in the Tapajós River basin, Amazon. *Environmental Research*, 2009, 109(4), 432-446. http://dx.doi.org/10.1016/j. envres.2009.02.011. PMid:19356749
- SILVA, M.J., PAIM, A.P.S., PIMENTEL, M.F., CERVERA, M.L. and DE LA GUARDIA, M. Determination of mercury in rice by cold vapor atomic fluorescence spectrometry after microwaveassisted digestion. *Analytica Chimica Acta*, 2010, 667(1-2), 43-48. http://dx.doi.org/10.1016/j. aca.2010.04.016. PMid:20441864
- SMART, N.A. and HILL, A.R.C. Pesticides residues in foodstuffs in Great Britain. VI. Mercury residues in rice. *Journal of the Science of Food and Agriculture*, 1968, 19(6), 315-316. http://dx.doi.org/10.1002/ jsfa.2740190606. PMid:5659586
- SNODGRASS, J.W., JAGOE, C.H., BRYAN JUNIOR, A.L.B., BRANT, H.A. and BURGER, J. Effects of trophic status and wetland morphology, hydroperiod, and water chemistry on mercury concentrations in fish. *Canadian Journal of Fisheries and Aquatic Sciences*, 2000, 57(1), 171-180. http://dx.doi. org/10.1139/f99-199.
- TAGLIANI, C.R.A. Proposta para manejo integrado da exploração de areia no município costeiro de Rio Grande-RS, dentro de um enfoque sistêmico [Master Thesis]. São Leopoldo: UNISINOS, 1997; 157 p.

- VAN DER OOST, R., BEYER, J. and VERMEULEN, N.P.E. Fish bioaccumulation and biomarkers in environmental risk assessment: a review. *Environmental Toxicology and Pharmacology*, 2003, 13(2), 57-149. http://dx.doi.org/10.1016/S1382-6689(02)00126-6. PMid:21782649
- VIEIRA, J.L.F. and PASSARELLI, M.M. [Determination of total mercury in water samples, sediments and solids in suspension in aquatic systems by cold-vapor atomic absorption spectrophotometry]. *Revista de Saude Publica*, 1996, 30(3), 256-260. http:// dx.doi.org/10.1590/S0034-89101996000300008. PMid:9110471
- WONG, L.C.Y. Future Challenges for the global rice market: a worm's eye view. In FAO Rice Conference. Rome, 2004.
- ZAHIR, F., RIZWI, S.J., HAQ, S.K. and KHAN, R.H. Low dose mercury toxicity and human health. *Environmental Toxicology and Pharmacology*, 2005, 20(2), 351-360. http://dx.doi.org/10.1016/j. etap.2005.03.007. PMid:21783611
- ZHANG, H., FENG, X., LARSSEN, T., QIU, G. and VOGT, R.D. In inland China, rice, rather than fish, is the major pathway for methylmercury exposure. *Environmental Health Perspectives*, 2010a, 118(9), 1183-1188. http://dx.doi.org/10.1289/ ehp.1001915. PMid:20378486
- ZHANG, H., FENG, X., LARSSEN, T., SHANG, L. and LI, P. Bioaccumulation of methylmercury versus inorganic mercury in rice (Oryza sativa L.) grain. *Environmental Science & Technology*, 2010b, 44(12), 4499-4504. http://dx.doi.org/10.1021/es903565t. PMid:20476782
- ZHAO, K., LIU, X., XU, J. and SELIM, H.M. Heavy metal contaminations in a soil-rice system: identification of spatial dependence in relation to soil properties of paddy fields. *Journal of Hazardous Materials*, 2010, 181(1-3), 778-787. http://dx.doi.org/10.1016/j.jhazmat.2010.05.081. PMid:20561748
- ZHOU, H.Y. and WONG, M.H. Mercury accumulation in freshwater fish with emphasis on dietary influences. *Water Research*, 2000, 34(17), 4234-4242. http:// dx.doi.org/10.1016/S0043-1354(00)00176-7.
- ZHU, J., WANG, D., LIU, X. and ZHANG, Y. Mercury fluxes from air/surface interfaces in paddy field and dry land. *Applied Geochemistry*, 2011, 26(2), 249-255. http://dx.doi.org/10.1016/j. apgeochem.2010.11.025.

Received: 05 October 2014 Accepted: 24 February 2015