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Sedentary nestlings of Wood Stork as monitors of mercury contamination in the gold mining region of the Brazilian Pantanal

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ABSTRACT

Sedentary organisms that are at top trophic levels allow inference about the level of local mercury contamination. We evaluated mercury contamination in feather tissue of nestling Wood Storks (*Mycteria americana*), sampled in different parts of the Brazilian Pantanal that were variably polluted by mercury releases from gold mining activities. Levels of mercury in feathers sampled in seven breeding colonies were determined by atomic absorption spectroscopy, and the mean value of mercury concentration was 0.557 $\mu\text{g/g}$, dry weight ($n=124$), range 0.024–4.423 $\mu\text{g/g}$. From this total sample, 21 feathers that represent 30% of nestlings collected in Porto da Fazenda and Tucum colonies, in the northern region, ranged from 1.0 to 4.43 $\mu\text{g/g}$, dry weight (median value=1.87 $\mu\text{g/g}$). We found significant differences among regions ($H=57.342$; $p=0 < 0.05$). Results suggest that permanently flooded areas, or along mainstream rivers are more contaminated by mercury than dry areas, regardless of the distance from the gold mining center, which is located in the northern Pantanal. Highest values found in nestlings feathers were similar to those found in feathers of adult birds and in tissues of adult mammals that are less sedentary and were captured in the same region of Pantanal. These findings indicate that mercury released has been biomagnified and it is present in high concentrations in tissues of top consumers. We suggest a program to monitor mercury availability in this ecosystem using sedentary life forms of top predators like Wood Storks or other piscivorous birds.

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1. Introduction

Aquatic food webs are typically longer than those in terrestrial systems and consequently have higher bioaccumulative potential (Weisbrod et al., 2009). Mercury, particularly in its methylated form (MeHg), is a globally distributed, bioaccumulative contaminant that is often associated with wetland ecosystems (Zillioux et al., 1993).

One of the most important anthropogenic sources of mercury pollution in aquatic systems is gold mining (Wang et al., 2004). The Brazilian Pantanal region has been the focus of gold mining activities, mainly at its northern margins, near the Poconé region where 10–15 t of mercury were used in the gold recovery and amalgamation process during the last two centuries (CETEM/CNPq, 1989). The mercury was liberated either by volatilization in the burning of the amalgam or from spillage of storage tanks

(Nogueira et al., 1997; Callil and Junk, 2001). Although there is an evidence of mercury contamination in sediments, water, and fish, it is not clear how piscivorous birds have been affected either in level of exposure or geographic extent of exposure.

Aquatic and particularly piscivorous birds are known to be at high risk of exposure to MeHg because of their trophic position (Frederick et al., 2002; Scheuhammer et al., 2007) and their populations have often been used to monitor heavy metal contamination (Kushlan, 1993; Frederick and Ogden, 2003; Zamani-Ahmadmoodi et al., 2010).

Wood Storks (*Mycteria americana*) are predators of small to moderate sized fish, and their primary source of mercury is through diet. Wood Stork adults are not sedentary but their nestlings remain for approximately seven weeks inside nests, and during this period they receive food brought by their parents. Determining concentrations of mercury in feathers of nestling birds before their first molt is a strategy to evaluate the level of local contamination, and concentrations of mercury in the young, therefore, are reflective of local sources of contamination. Wood Stork breeding colonies are established annually in different

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regions of the Pantanal during the dry season. These colonies occupy a large range (Yamashita and Valle, 1990) that includes wetland areas, both close to and distant from gold mining activities.

While there is an indication that high trophic level predators in the Pantanal may be exposed to mercury (Hylander et al., 1994, 2000; Leady and Gottgens, 2001; Vieira et al., 2004; Fonseca et al., 2005), those organisms sampled in previous studies were neither sedentary, and nor extensively sampled enough to characterize regional differences. In this paper, we document mercury contamination in feather tissue of nestling Wood Storks sampled in breeding colonies located in different regions of the Brazilian Pantanal, and we compare these levels with other top predators sampled in the same region.

2. Material and methods

We collected feathers during the dry season in the Pantanal from 124 Wood Stork nestlings 14–56 days age in seven colonies (Fig. 1A and B). The age of nestlings sampled was inferred based on a growth curve tarsus length (mm) = 21.12 + 3.60 (age in days) (Mattos et al., 2001), determined using 157 nestlings data collected after direct observation of nests. At 50–55 d, chicks fledge, but they travel from colony and return for feeding with decreasing frequency during the period of 55–70 d (Kahl, 1972). One chick from each nest was captured by hand, and we collected whole feathers (4–8) by pulling from scapular regions on both sides of the back.

Feathers were stored in paper bags at -20°C until analysis. For determination of total Hg concentration, feathers were digested with nitric acid for two hours at 65°C and diluted in ultrapure water. Samples were reduced with SnCl_2 and the levels of mercury were determined by cold vapor atomic absorption spectrometry (Buck Scientific 400-A) coupled to a flow injection analysis system. At the time the

determinations were carried out in the biological material, the laboratory was participating in the Mercury Quality Assurance proficiency test provided by the Canadian Food Inspection Agency. Samples were digested in batches containing a blank. Maximum standard error among triplicate samples was calculated for 20% of the samples. Mercury concentrations were expressed as μg total Hg/g on dry weight basis, though the majority of mercury in feathers is probably in the methylated form. Mercury concentrations among colonies were compared using the Kruskal–Wallis nonparametric test and results were considered significant when $p < 0.05$. Comparisons by a nonparametric multiple test were done to evaluate differences among ranks of different levels. Based on foraging flight data (Bryan and Colter, 1987; Bryan et al., 1995), we quantified the percentage of flooded area within 25 km buffer from each colony during wet and dry seasons.

3. Results and discussion

No differences in mercury concentrations were found among samples collected during three consecutive annual reproductive cycles in the Porto da Fazenda colony (Kruskal–Wallis, $n = 15$ samples per year, $H = 2.723$, $p = 0.256$), and these 45 samples were therefore pooled to represent this site. The mean value of mercury concentration based on samples from seven sites was $0.557 \mu\text{g/g}$, dry weight ($n = 124$), range 0.024 – $4.423 \mu\text{g/g}$. Our extensive sampling revealed some particularly high levels in two colonies that may be cause for concern. We found mercury concentrations exceeding $1.0 \mu\text{g/g}$ in 15 individuals from the Porto da Fazenda colony (1.00 – $4.43 \mu\text{g/g}$) and in six individuals from the Tucum colony (1.25 – $2.48 \mu\text{g/g}$).

There were significant differences among values of mean mercury concentrations of Wood Stork nestling feathers sampled in different regions of the Pantanal ($H = 57.342$; $p < 0.05$) (Fig. 1A and B).

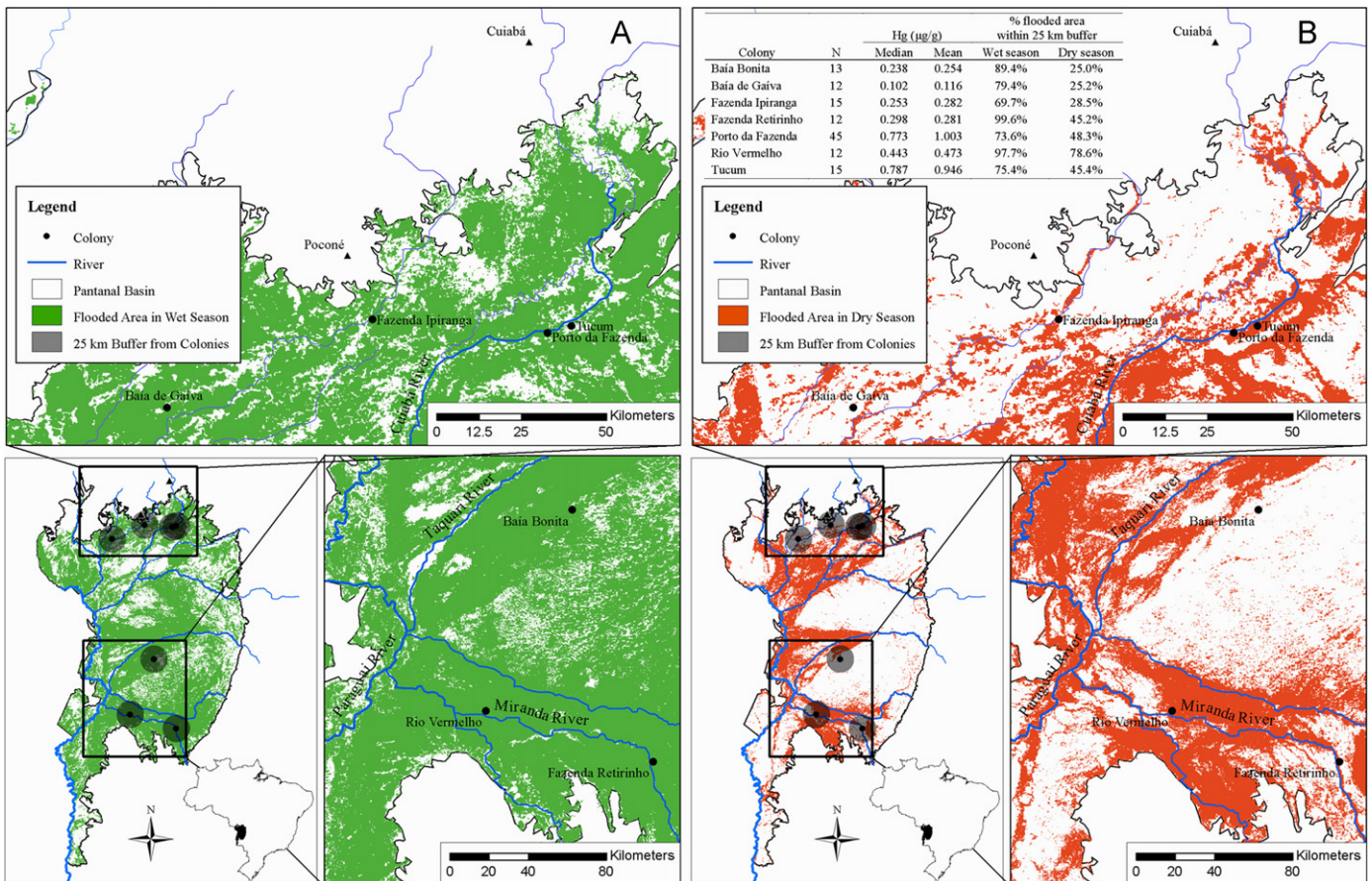


Fig. 1. Location of Wood Storks (*Mycteria americana*) breeding colonies where nestlings were sampled during (A) and dry season (B). Colonies sampled were: Baía Bonita ($18^{\circ}40'S$, $56^{\circ}26'W$; 1999), Baía de Gaíva ($16^{\circ}39'S$, $57^{\circ}10'W$; 1999), Fazenda Ipiranga ($16^{\circ}25'S$, $56^{\circ}36'W$; 2000), Fazenda Retirinho ($19^{\circ}50'S$, $56^{\circ}02'W$; 1999), Porto da Fazenda ($16^{\circ}27'S$, $56^{\circ}07'W$; 1998–2000), Rio Vermelho ($19^{\circ}36'S$, $56^{\circ}51'W$; 1999), and Tucum ($16^{\circ}26'S$, $56^{\circ}03'W$; 2000). Levels of mercury concentration determined in feathers and percentage of flooded area in wet and dry season are expressed in Fig. 1A and B.

Specifically, we found differences between colonies with highest mercury concentrations (Porto da Fazenda, Rio Vermelho, and Tucum colonies), and those with a more intermediate level of mercury concentration (Baía Bonita, Fazenda Ipiranga, and Fazenda Retirinho). The lowest mercury concentration was found in Baía de Gaíva, and this colony was significantly different from all of the six other breeding colonies. Significant association was found between mercury concentrations and flooded area 25 km radius during dry Pantanal season ($rS=0.821$; $p=0.023$). Our findings were compared to average mercury concentrations reported for adult predatory birds, mammals and fishes, captured in the Pantanal (Table 1).

We found little evidence to support the hypothesis that the distance from gold mining activity alone could explain contamination levels in Wood Storks. While we found high concentrations in some colonies close to the source (Porto da Fazenda and Tucum), we also found low levels in the nearby colony (Fazenda Ipiranga). Our data suggested that colonies in permanently flooded areas or along mainstream rivers may be more contaminated than those in the area of periodic flooding (Fig. 1A and B). Colonies with intermediary (Baía Bonita, Fazenda Ipiranga, and Fazenda Retirinho) and lowest level (Baía Gaíva) of mercury contamination were located at the margins of the permanently flooded area, or in area that were only periodically flooded. In relation of lowest level of mercury found in the Baía Gaíva, it is interesting to point that this colony is located in the Northwestern region of the Pantanal, inside the Paraguai river basin, and not to Cuiaba river basin.

Moreover, previous studies have shown that flooding increases the production of MeHg as flooding increases the decomposition of terrestrial organic matter. Flooding condition also contributes to the development of poor oxygen conditions and the activity of bacteria that are mercury-methylating (Heyes et al., 2000; Hall and Louis, 2004). Sorensen et al. (2005) has demonstrated the direct relationship between the changes in water levels and the content of MeHg in fishes. The bioaccumulation of monomethyl mercury MeHg, the neurotoxic form of mercury in biota can be affected by several factors. As hydrology, water quality, trophic structure, and temperature are similar in the Pantanal regions, we can hypothesize that the flooding percentage of area is the main factor that explains the detected variation in the level of mercury contamination among areas studied.

Our results also suggested that mercury may have accumulated in the Southern part of the Pantanal. Rivers in the Pantanal region flow from North to South and from East to West, and the extreme Southern region has the lowest elevation (Ponce, 1995). Concentrations varied in general along an elevation gradient within the same rivers, with lower elevation colonies being more contaminated: Fazenda Retirinho (upstream Miranda river) was lower than Rio Vermelho (downstream basin of Miranda river), and Tucum (upstream Cuiabá river) was lower than Porto da Fazenda (downstream Cuiabá river).

The highest mercury concentrations were found in two colonies located on the banks of the Cuiabá river (Porto da Fazenda

Table 1
Concentrations of mercury in feathers of Wood Stork (*Mycteria americana*) and in organisms that are on top of trophic web sampled in the Pantanal.

Sample (tissue)	Sampling period	Pantanal location	Geographic coordinates	N	Average concentration of Hg $\mu\text{g g}^{-1}$ (d w^{-1}) ^a	Ref.
Birds						
Cormorant <i>Phalacrocorax brasiliensis</i> (adult feathers)	08/1989	Rod. Transpantaneira		6	2.787 ± 0.298	Vieira (1991)
Great egret <i>Ardea alba</i> (adult feathers)	08/1989	Rod. Transpantaneira		9	2.575 ± 0.493	Vieira (1991)
Wood Stork <i>Mycteria americana</i> (nestling feathers)	09/1998	Pantanal ^b	–	124	0.557 ± 0.627 (0.339) ^c	This study
	09/1999					
	10/2000					
Mammals						
Giant otter <i>Pteronura brasiliensis</i> (hair)	11/2002	Rio Negro Mato Grosso do Sul		2	2.940–3.680	Fonseca et al. (2005)
(liver)	11/2003				1.520–4.300	
(muscle)					0.170	
Fishes						
Cachara <i>Pseudoplatystoma fasciatus</i> (muscle)	1998/1999	Bento Gomes river (near Poconé city)		15	0.435 ± 0.097	Vieira et al. (2004)
Cachara <i>Pseudoplatystoma fasciatus</i> (muscle)	08/1998	Baía Siá Mariana	16°20'S, 55°53'W	2	0.738 ± 0.532	Hylander et al. (2000)
Pintado <i>Pseudoplatystoma coruscans</i> (muscle)	09–12/1992	Santo Antônio Leverger	15°53'S, 56°07'W	5	0.190	Hylander et al. (1994)
Pintado <i>Pseudoplatystoma coruscans</i> (muscle)	09–12/1992	Barão de Melgaço (Cuiabá river)	16°12'S, 55°58'W	5	0.300	Hylander et al. (1994)
Pintado <i>Pseudoplatystoma coruscans</i> (muscle)	09 a 12/1992	Porto Cercado (Cuiabá river)	16°30'S, 56°23'W	5	0.250	Hylander et al. (1994)
Pintado <i>Pseudoplatystoma coruscans</i> (muscle)	08/1998	Barão de Melgaço (Cuiabá river)	16°12' , 55°58'W	4	0.281 ± 0.103	Hylander et al. (2000)
Piranha <i>Serrasalmus nattereri</i> (muscle)	1998/1999	Cuiabá river		3	0.338 ± 0.085	Vieira et al. (2004)
Piranha <i>Pygocentris nattereri</i> (muscle)		Poconé (northern Pantanal)		16	0.302 ± 0.159	Leady and Gottgens (2001)
Piranha <i>Pygocentris nattereri</i> (muscle)		Acurizal (center of Pantanal)		16	0.172 ± 0.115	Leady and Gottgens (2001)

^a Mercury concentration expressed as $\mu\text{g/g}$, dry weight and values of standard deviation reported in citation were expressed after \pm .

^b Total sample of Wood Stork from seven colonies.

^c Median value.

and Tucum). Hylander et al. (2000) found high levels of mercury contamination in fishes from the Cuiabá river, in comparison with those collected from Paraguay river. The authors supposed that this result was a consequence of (1) the contribution of sewage and day water from Cuiabá city and (2) the larger load of suspended particulate matter in the Cuiabá river due to erosion caused by agriculture, dredging, and clear cutting of the riverbanks. The activity of a gold mine at Nossa Senhora do Livramento, a city that is located at the banks of the Cuiabá river (Vieira, 1991), may also have contributed directly to the high level of mercury in the biota of the Cuiabá river.

The Pantanal is a large alluvial plain that receives water from a surrounding upland drainage basin. Release of water during the annual flood pulse occurs only through a single, downstream channel in the Paraguay river (Da Silva and Girard, 2004). This hydrological characteristic with slow drainage of water to outside the alluvial plain may favor the accumulation of mercury in this region. The primary source of mercury contamination in the Pantanal is gold mining. In wetlands, inorganic mercury may be readily and quickly converted to methylmercury through the metabolism of sulfur reducing bacteria (Snodgrass et al., 2000). Due to its long residence time in tissue, methylmercury is biomagnified in the food web, and reaches its highest concentrations in top aquatic predators (Cabana et al., 1994; Leady and Gotgens, 2001).

Blood and feather tissue have advantages and disadvantages as sampling media for mercury determination in birds. Previous studies have found strong relationship between levels of mercury determined in blood and in feathers of Wood Stork nestlings (Gariboldi et al., 2001; Hylton et al., 2006). Mercury sequestered into feathers becomes highly stable (Burger, 1994; Dauwe et al., 2003) and is reflective of diet during the period of feather growth. Our results in feathers of Wood Stork nestlings agree with the expectation that feathers of adult piscivorous birds (Cormorant, *Phalacrocorax brasilianus*, and Great egret, *Ardea alba*) will present a higher level of contamination than nestlings, due to a much longer period of exposure and accumulation. Predatory fishes and Wood Storks may not have exactly the same diet, but both are predatory animals foraging high in the trophic web, thus it was expected an agreement in relative contamination detected by these bioindicators. Moreover, Pintado (*Pseudoplatystoma coruscans*) and Cachara (*Pseudoplatystoma fasciatum*) are migratory fishes, and therefore may not represent the local pattern of contamination. Tissues of two giant otters (*Pteronura brasiliensis*) sampled in the Rio Negro (Southern Pantanal) showed similar levels of contamination compare to those found in feathers of adult piscivorous birds (Vieira, 1991; Fonseca et al., 2005) and Wood Stork nestling feathers from the Porto da Fazenda and Tucum colonies. Levels detected in these different tissues of mammals and birds indicated that mercury released in this Pantanal region was biomagnified and it was incorporated in different organisms at top of the food web.

Mercury cycling and availability in wetlands is known to be influenced by hydrology of the contaminated region, and may respond both seasonally, and in relation to longer term patterns of global change. For example, prolonged droughts may serve to solubilize mercury trapped in sediments, and inundation cycles may affect methylation patterns. The hydrologic cycles of the Pantanal may undergo strong alteration in its cycles in response to globally induced climate changes (Loarie et al., 2009). We suggest that mercury contamination in the ecosystem may be dynamic in coming decades, and a program to monitor these changes is necessary. We propose that such a program could economically use sedentary life stages of far-ranging top predators like piscivorous birds to monitor methylmercury availability to the food web.

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