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The Science of the Total Environment 260 (2000) 97–107

**the Science of the  
Total Environment**

An International Journal for Scientific Research  
Into the Environment and its Relationship with Man

www.elsevier.com/locate/scitotenv

## Relationship of mercury with aluminum, iron and manganese oxy-hydroxides in sediments from the Alto Pantanal, Brazil

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Received 27 September 1999; accepted 30 April 2000

### Abstract

Sediments from nine floodplain lakes in Pantanal were analyzed for a large-scale (300 km) survey of mercury (Hg) load in sediments and soils of the Alto Pantanal and to study the relationship between Hg and reactive aluminum, iron, and manganese oxy-hydroxides. The results were compared with the Hg content in river and stream sediments from the Poconé gold mining area, where Hg has been extensively used and still is in use. The results indicate that the Hg concentrations were elevated in river sediment close to the mining area in Bento Gomes river basin (average in the < 74- $\mu$ m fraction 88.9 ng Hg g<sup>-1</sup> dry wt.; interquartile range 50.3–119.5), but there was no clear indication that the local Hg emissions have contaminated the remote floodplain lakes, where concentrations were surprisingly low (average in the < 74- $\mu$ m fraction 33.2 ng Hg g<sup>-1</sup> dry wt. sediment; interquartile range 18.4–46.8), in particular

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when considering geochemical characteristics of the sediment. The sediment from the floodplain lakes contained less Hg-tot and more reactive iron oxy-hydroxides than soils from the Tapajós area in the Amazon basin. This resulted in a mass ratio between Hg and amorphous oxy-hydroxides of only  $5 \times 10^{-6}$  for Hg-tot/Fe-oxa (interquartile range  $3\text{--}7 \times 10^{-6}$ ). © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Mercury; Iron; Aluminum; Manganese; Suspended particulate matter; River sediments; Floodplain lakes

## 1. Introduction

Artisanal gold-mining has been suspected to be responsible for the release of much of the mercury encountered in tropical floodplains such as the Amazon and the Pantanal in Brazil (e.g. Lacerda et al., 1990). During the goldrush of the past decades, an estimated 2000 t of Hg has been released in the Amazon region (Veiga et al., 1995). Furthermore, the Spaniards brought another estimated 260 000 t of Hg into Latin America between 1550 and 1930, mostly used for silver amalgamation (Nriagu, 1993; Lacerda, 1997). On the other hand, most Hg in remote soils and sediments is supplied by atmospheric deposition (Fitzgerald et al., 1998), which can be of natural or anthropogenic origin. Large quantities of Hg can be accumulated in some soils and can eventually reach surface waters, in particular at improper management. Forsberg et al. (1999) estimated that the soils in the Rio Negro basin (a tributary to the Amazon river) contains considerably more Hg than could possibly be of anthropogenic origin, in spite of three times higher global Hg deposition nowadays compared to preindustrial deposition. This Hg is leached from the soil by organic acids and can cause Hg concentrations in fish to exceed the limit for safe consumption (Nakazono et al., 1999). Roulet et al. (1998a,b) suggested that Hg entering the Amazon soil is initially firmly bound to soil constituents such as sesquioxides and crystalline Fe and Al oxy-hydroxides. It is first when the soil or sediment reaches saturation that Hg leaks into the water courses in potentially bioavailable forms. The bound Hg can also reach rivers if the soil constituents themselves are relocated to the water courses due to erosion or wash out of soil particles. Roulet et al. (1998a,b) estimated that 97% of the Hg burden to the lower Tapajós river

(a tributary to the Amazon river) originates from soil eroded Hg, in spite of direct pollution from upstream (> 50 km) gold mining using Hg. They also demonstrated that the Hg burden is not related to organic matter content in the oxisols and spodosols under rainforest in the Tapajós valley, contrary to what is known from temperate areas with boreal forests (e.g. Meili, 1997). Instead they identified crystalline Al and Fe oxy-hydroxides to be the soil constituents determining the capacity to sorb Hg. Also amorphous Al and Fe oxy-hydroxides as well as Mn oxy-hydroxides have capacity to sorb heavy metals (McKenzie, 1980), but were not as abundant in the actual soils.

The aim with the present study was to survey the Hg levels in sediments and soils of the Alto Pantanal and to quantify relationships between the sediment Hg content and the abundance of amorphous and crystalline Al, Fe, and Mn oxy-hydroxides in Alto Pantanal. An additional aim was to estimate Hg amounts relocated by water courses from gold mining areas, where Hg has been extensively used and still is in use. The presented data are obtained in a project financed by Sida/SAREC (Swedish International Development Co-operation Agency/Department for Research Co-operation) with the aim to study the accumulation and transformation of mercury in tropical rivers and wetland in Brazilian Pantanal and in the environmental monitoring program run by FEMA (the governmental, environmental foundation of Mato Grosso state) in the Bento Gomes river basin, Brazil.

## 2. Study area

The savanna wetland Pantanal is a 137 000-km<sup>2</sup>

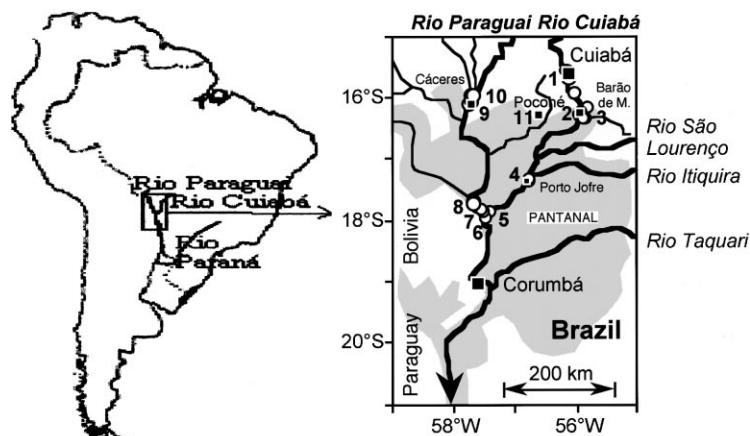


Fig. 1. Location of sampling sites in the Alto Pantanal (Brazil). (1) Rio Cuiabá at Cuiabá; (2) Volta Grande; (3) Bog stream at Mimoso, Rio Mutum, Baía Siá Mariana, Baía Chacororé, north and south; (4) Rio Cuiabá at Porto Jofre, Baía Jofre; (5) Rio Cuiabá at Baía do Burro, Baía do Burro; (6) Rio Paraguai at Baía Amolar, Baía Amolar; (7) Rio Paraguai at Baía Paraíso and Acurizal, Baía Paraíso; (8) Rio Paraguai at Baía Cachorada, Baía Cachorada; (9) Rio Paraguai south and west of Cáceres, Baía da Cidade Cáceres; (10) Rio Paraguai at Baía Ximbuva, Baía Ximbuva; (11) Bento Gornes river basin (< 30 km from Poconé).

large alluvial plain in central-western Brazil facing the border of Bolivia and Paraguay, receiving water from a surrounding upland drainage basin that occupies 359 000 km<sup>2</sup> (Hamilton et al., 1996). The area is hydrologically divided into the Alto (high), Médio and Baixo (low) Pantanal. Floodplains make up approximately 20% of the upstream watershed (Alto Pantanal) and most of the area in the Baixo Pantanal (Alho et al., 1988). The rain falling from October to March results in an annual flooding of usually more than half and often more than 90% of the alluvial plain, while on the other hand permanent open-water areas are minimal (Hamilton et al., 1996). The annual fluctuation of the inundation area is most extreme in the Alto Pantanal, where the inundation is maximal in March–April and minimal in October–November (Hamilton et al., 1996). The Alto Pantanal (Fig. 1) is the northernmost part of the Paraguay River basin, including the tributary Rio Cuiabá (approx. 15.5–17.5°S and 55–59°W). The rivers run southwards, and are to the north separated from the Amazon basin by the Serra dos Parecis and Serra Azul mountain chains (Estudos hidrológicos da bacia do Alto Paraguai, 1974). Rio Paraguai has within the studied area a slope of 0.03–0.15 m km<sup>-1</sup>, while the east–west slope for the plain is 0.3–0.5 m km<sup>-1</sup> (Zeilhofer, 1996),

causing Rio Cuiabá to flow faster than Rio Paraguai through the plain, before they join in the southern part of the study area. Rio Cuiabá originates in the Chapada dos Guimarães highlands of crystalline bedrock (mainly sandstone and magmatite) with an altitude of 600–700 m above sea level (Godoi Filho, 1986), and when entering the Pantanal at an altitude of 100 m above sea level, this river does not transport sand but clay from the surrounding plain (Zeilhofer, 1996). The Pantanal basin was created more than 100 million years ago and has subsequently been filled up by deposits of quartz sand and aluminum silicate clay sediments, with a depth of 100 m or more over large areas (Godoi Filho, 1986).

Alto Pantanal houses gold miners, since veins of gold-containing coarser material are found in the clay layers at some places on the margin of the plain (Rodrigues Filho, 1995). This material is excavated in huge open cast mines as well as small pits and processed for gold extraction. During this process mercury (Hg) is used as an amalgamating agent, which results in Hg losses to the air and the water of the wetland (Lacerda et al., 1991; Veiga et al., 1991; Hylander et al., 1994; Rodrigues Filho, 1995; von Tümpling et al., 1995; Alho and Vieira, 1997). One of the oldest (> 100 years) and largest gold mines in the area is

located in Poconé, around which the present study was focused (Fig. 1).

Another source of Hg to the flood plain is Hg dissolved in river water or sorbed to soil particles and brought there by the rivers, eventually with increased Hg burdens as a result of the extensive erosion. The water, falling as rain on the surrounding Guimarães Plateau, carries a large burden of suspended material on its route down to the plain. The erosion is mainly caused by large-scale agriculture and by cutting trees and bushes on the river banks and other areas sensitive to erosion (Gonçalves, 1996). Also uncontrollable secondary gold mining and dredging for construction sand from the river bottom contribute to the erosion.

### 3. Material and methods

The samples were collected during three campaigns, two at the end of the dry seasons in August–September/October 1997 and 1998, and the third campaign at the end of the rainy season in March 1998. Water pH, dissolved oxygen, temperature, conductivity and turbidity were measured in the field with a multipurpose field instrument (Horiba U-10) at all sampling locations.

Superficial stream sediment was collected at 40 sites in the Bento Gomes river basin around Poconé (< 30 km) at the end of the dry season 1997 and 1998. In March (rainy season) and August (dry season) 1998, rivers and floodplain lakes were studied covering a much larger area (< 150 km in a beeline from Poconé). Two replicate sediment cores were collected with a tube corer, divided into 2–5-cm-thick horizons in the field, and frozen until preparation for analyses. In the laboratory, all sediment samples (cores and superficial sediment) were thawed and dried (< 50°C) and dry sieved (< 74  $\mu\text{m}$ ) with nylon mesh sieves.

The fine fraction of sediments were analyzed for total content of Hg (Hg-tot), determined by cold vapor atomic absorption spectrophotometry (CVAAS) after sample digestion in nitric acid

(Gonçalves and Paiva, 1995; Companhia de Pesquisa Recursos Minerais, 1987). A sample of 2 g was digested with 10 ml, conc.  $\text{HNO}_3$  in a glass tube covered by a glass pear to prevent evaporation in a hot block digester at 120°C for 2 h. After cooling, water was added, and after settling of remaining solid particles the Hg-tot concentration was determined by CVAAS (Varian model VGA 77 coupled to a Varian AAS model 200).

Acid ammonium oxalate (0.2 M, pH 3) was used for the extraction of amorphous Al, Fe and Mn (Klute, 1986). We used a 0.5-g sediment sample (< 74  $\mu\text{m}$ ) and 20 ml ammonium oxalate solution, 30 min shaking in the dark at room temperature, followed by centrifugation and determination of Al, Fe and Mn in the supernatant by flame AAS. The sediment was also analyzed for nitric acid extractable Al, Fe and Mn by extracting a 0.2-g sediment sample (< 63  $\mu\text{m}$ ) with 3 ml conc.  $\text{HNO}_3$  in closed quartz tubes in an oven at 160°C for 2 h, diluted 30 times and analyzed for Al, Fe and Mn by inductively coupled plasma atomic emission spectrophotometer (ICP-AES Perkin-Elmer Optima 3000 DV, 1995).

Distilled and deionized water and laboratory grade chemicals were used in all experiments and for preparing solutions. Accuracy of the Hg analyses was checked by comparison with certified reference materials (GBW 07309 stream sediment with 83 ng Hg-tot  $\text{g}^{-1}$  dry wt., NIST Buffalo river sediment 2704 with 1470 ng Hg-tot  $\text{g}^{-1}$  dry wt.) and with selected samples run also at an independent laboratory. All samples were digested at least in duplicates, and each extract was analyzed twice. Precision of all metal analyses was verified by internal standards and replicated analyses. The detection limit (3 S.D.) for Hg was 0.5  $\mu\text{g l}^{-1}$  Hg in the extract, and 5 ng Hg-tot  $\text{g}^{-1}$  dry wt. in the sediment when using 2-g samples and 20 ml extractant. The precision (1 S.D.) was approximately 10% in typical samples containing 10–100 ng Hg-tot  $\text{g}^{-1}$  dry wt.

### 4. Results

A wide variety of surface waters was found in

Table 1

Suspended matter (0.45  $\mu\text{m}$  filter), turbidity, pH, conductivity, dissolved oxygen, and dissolved organic carbon in the water of floodplain lakes (Baía) and rivers (Rio) of the Alto Pantanal (Brazil) in August 1998<sup>a</sup>

Sampling site	Co-ordinates		Susp. (mg l <sup>-1</sup> )	Turb. (NTU)	pH	Cond. ( $\mu\text{S cm}^{-1}$ )	DO (mg l <sup>-1</sup> )	DOC (mg l <sup>-1</sup> )
	South	West						
Rio Cuiabá, Cuiabá	15°37'	56°06'	34	8	6.9	77	7.4	3.9
Bog stream, Mimoso	16°10'	55°48'	1	< 1	5.1	14	3.9	4.4
Rio Mutum	16°20'	55°50'	9	27	4.5	3	5.6	3.7
Baía Siá Mariana	16°20'	55°53'	34	23	5.3	4	6.5	5.1
Baía Chacororé, N.	16°14'	55°55'	120	105	6.7	44	6.0	n.a.
Baía Chacororé, S.	16°19'	55°55'	340	203	7.1	41	5.6	5.2
Rio Cuiabá, Jofre	17°22'	56°46'	50 <sup>b</sup>	35	6.1	27	6.3	3.1
Baía Jofre	17°20'	56°46'	87	77	6.3	37	5.6	8.9
Baía do Burro	17°50'	57°24'	50	38	6.4	31	7.1	5.6
Rio Cuiabá, Burro	17°51'	57°24'	55 <sup>b</sup>	47	6.5	27	7.0	3.3
Baía do Amolar	17°57'	57°28'	37	26	6.4	47	6.5	6.7
Rio Paraguai, Amolar	17°57'	57°28'	48	32	6.4	45	6.5	6.5
Baía Paraíso	17°52'	57°30'	13	3	6.6	59	2.7	7.7
Rio Paraguai, Paraíso	17°52'	57°31'	28	19	6.3	58	6.8	8.1
Rio Paraguai, Acurizal	17°47'	57°37'	n.a.	22	6.9	58	6.7	7.3
Baía Cachorrada	17°44'	57°40'	n.a.	25	6.3	53	6.2	5.6
Rio Paraguai, Cachor.	17°44'	57°39'	n.a.	22	6.7	59	6.9	6.4
Baía da Cidade Cáce.	16°04'	57°42'	25	20	5.8	35	7.6	3.6
Rio Paraguai, S Cáce.	16°08'	57°44'	24	28	6.1	34	7.7	3.3
Rio Paraguai, W Cáce.	16°04'	57°42'	45	24	6.1	35	7.7	3.4
Baía Ximbuva	15°59'	57°41'	18	20	7.9	460	8.9	19.1
Rio Paraguai, Ximbuva	15°58'	57°41'	5	24	6.1	22	7.3	3.9

<sup>a</sup> n.a., not analyzed.

<sup>b</sup> Estimated from the amount of material precipitated with  $\text{Al}_2(\text{SO}_4)_3$ , corrected for added chemicals.

the Alto Pantanal. Rio Cuiabá is a white water river with a high load of suspended material, which increases downstream from the city of Cuiabá (Table 1). The tributary Rio Mutum has dark water with signs of oxygen depletion, and with an insignificant load of suspended material so the dissolved organic matter will dominate its characteristics (Table 1). This type of water is known to increase the mobility and probably also the bioavailability of Hg (Meili, 1991, 1997). The gently flowing Rio Paraguai has a lower load of particulate matter in suspension than Rio Cuiabá (Table 1). The brooks, ponds and rivers in the Bento Gomes river basin have quite varying loads of suspended matter, largely influenced by adjacent mining activity (Table 2).

The average Hg-tot concentration in the fine sediments (< 74  $\mu\text{m}$ ) from the studied lakes was 33.2 ng Hg g<sup>-1</sup> dry wt., the median 26.9, the first

quartile 18.4 and the third quartile 46.8 ng Hg g<sup>-1</sup> dry wt. sediment (Fig. 2). The average Hg-tot concentration in surface sediment sampled in the Bento Gomes river basin was 88.9 ng Hg g<sup>-1</sup> dry wt., the median 69.7, the first quartile 50.3 and the third quartile 119.5 ng Hg g<sup>-1</sup> dry wt. sediment (< 74  $\mu\text{m}$ ; Table 2), indicating clearly elevated Hg-tot concentrations in the gold mining area.

The concentration of oxalate extractable Al (Al-oxa) in fine sediment (< 74  $\mu\text{m}$ ) was on average 620  $\mu\text{g Al g}^{-1}$  dry wt. It was highest in sediment from the lake Baía da Ximbuva, which had highly alkaline water and water apparently rich in clay (Fig. 3, Table 1). The amount of oxalate extractable Fe was approximately 10 times higher, that is on average 8760  $\mu\text{g Fe g}^{-1}$  dry wt. Generally the surface horizons contained most Fe-oxa, which was reduced to approximately half

Table 2

Turbidity, water pH, conductivity, dissolved oxygen, and total Hg in surficial (river and) stream sediments (in water courses) in the Bento Gomes river basin, Alto Pantanal (Brazil)<sup>a</sup>

Sampling site	Co-ordinates		Turbidity (NTU)	pH	Cond. ( $\mu\text{S cm}^{-1}$ )	DO ( $\text{mg l}^{-1}$ )	Hg in sediment ( $\text{ng g}^{-1}$ dw)
	South	West					
ANT 01	16°16'	56°40'	9 ± 13	6.2 ± 0.4	66 ± 8	4.9 ± 2.1	74 ± 62
BNG 01	15°59'	56°28'	35 ± 2	7.1 ± 0.6	136 ± 55	6.6 ± 1.3	24 ± 1
BNG 02	16°19'	56°32'	5	7.2	165	4.0	35
BNG 05	16°19'	56°33'	8 ± 3	6.9 ± 0.3	135 ± 13	4.8 ± 0.6	39 ± 1
BNG 07	16°23'	56°36'	9 ± 2	6.5 ± 0.3	97 ± 9	4.4 ± 2.1	79 ± 76
BNG 08	16°26'	56°40'	5 ± 4	6.5 ± 0.0	153 ± 9	2.2 ± 1.1	127 ± 100
CAA 01	16°16'	56°36'	9 ± 2	6.0 ± 0.5	42 ± 15	4.4 ± 1.1	91 ± 17
CCO 01	16°15'	56°39'	2 ± 0.0	6.3 ± 0.2	100 ± 71	4.4 ± 4.2	118 ± 85
CCO 02	16°15'	56°39'	7 ± 5	6 ± 0.4	47 ± 10	5.9 ± 0.1	121 ± 36
CDC 01	16°17'	56°41'	6 ± 3	6.4 ± 0.4	113 ± 42	3.7 ± 2.5	51 ± 10
CFU 01	16°13'	56°40'	10 ± 5	6.7 ± 0.1	79 ± 26	7.9 ± 0.0	29 ± 15
CFU 02	16°13'	56°38'	5	7.0	50	7.8	169
CFU 03	16°13'	56°36'	10 ± 0.0	6.7 ± 0.1	72 ± 23	7.7 ± 0.1	82 ± 23
CLO 01	16°14'	56°39'	1 ± 1.4	6.9 ± 0.4	39 ± 13	6.8 ± 1.5	119 ± 30
DCI 01	16°13'	56°36'	8 ± 2.8	6.4 ± 0.5	65 ± 12	7.0 ± 1.0	63 ± 21
PIM 01	16°07'	56°36'	2	5.2	112	2.7	164 ± 149
PIM 02	16°14'	56°35'	5 ± 2	6.6 ± 0.2	79 ± 20	5.0 ± 0.9	50 ± 4
PIM 03	16°15'	56°35'	17 ± 18	6.7 ± 0.2	73 ± 18	5.4 ± 1.6	65 ± 25
PIM 04	16°18'	56°32'	14 ± 16	6.7 ± 0.1	88 ± 11	4.8 ± 0.6	62 ± 50
PRT 01	16°16'	56°40'	4 ± 3	6.7 ± 0.1	90 ± 28	5.8 ± 2.3	50 ± 27
PRT 02	16°16'	56°40'	2 ± 0.0	6.5 ± 0.1	87 ± 23	7.6 ± 0.3	48 ± 30
PRT 03	16°17'	56°40'	2 ± 0.0	6.5 ± 0.1	78 ± 11	6.9 ± 0.1	86 ± 49
PRT 04	16°19'	56°40'	19 ± 13	6.8 ± 0.4	72 ± 3	7.5 ± 0.6	53 ± 33
PRT 05	16°21'	56°39'	8 ± 4	6.5 ± 0.1	72 ± 6	5.2 ± 1.7	348
PRT 06	16°23'	56°39'	4 ± 0.7	7.0 ± 0.4	71 ± 1	6.5 ± 1.6	39 ± 16
RAB 01	16°20'	56°44'	2 ± 3	7.4 ± 0.2	125 ± 33	7.2 ± 0.8	36 ± 7
TAL 01	16°16'	56°39'	10	6.3	80	6.1	59 ± 16
TEB 01	16°15'	56°36'	17 ± 1	6.2 ± 0.7	87 ± 35	6.3 ± 1.6	125
TEB 02	16°17'	56°39'	4 ± 3	6.4 ± 0.3	104 ± 95	6.0 ± 0.1	165 ± 13
TQP 01	16°17'	56°38''	3 ± 1	5.8 ± 1.1	29 ± 25	5.2 ± 1.8	167
TQP 02	16°20'	56°36'	0.5 ± 0.7	5.7 ± 0.7	31 ± 31	6.1 ± 0.8	136 ± 62
TQP 03	16°20'	56°37'	4 ± 4	7.4 ± 1.8	51 ± 1	7.3	52 ± 8
TRA 01	16°09'	56°37'	16 ± 16	6.0 ± 1.5	60.5	5.7 ± 0.8	98
VGC 01	16°19'	56°43'	6 ± 6	6.6 ± 0.3	69 ± 25	7.3 ± 0.7	53 ± 3

<sup>a</sup>Average ± S.D. from 2 years of sampling (September 1997 and September–October 1998).

at 0.5 m depth in sediments from Baía Siá Mariana, Baía Chacororé and Baía Cachorada. The differences in Fe-oxa concentrations between the surface horizon and deeper horizons were smaller in the other lakes. Also the concentration of oxalate extractable Mn was highest in the surface sediments. Mn was the least abundant of the studied oxy-hydroxide metals with an average concentration of 223  $\mu\text{g Mn g}^{-1}$  dry wt. The total amount of these elements in the sediment was on average 41.6 (interquartile range 32.3–55.0) mg

Al-tot  $\text{g}^{-1}$  dry wt., 23.1 (interquartile range 18.6–28.3) mg Fe-tot  $\text{g}^{-1}$  dry wt., and 0.4 (interquartile range 0.5–0.3) mg Mn-tot  $\text{g}^{-1}$  dry wt.

The concentration of Hg-tot was correlated to all three oxy-hydroxide metals (Fig. 3). The mass ratio between Hg-tot and the oxy-hydroxide metals was  $89 \times 10^{-6}$  for Hg-tot/Al-oxa (interquartile range  $46\text{--}65 \times 10^{-6}$ ),  $5 \times 10^{-6}$  for Hg-tot/Fe-oxa (interquartile range  $3\text{--}7 \times 10^{-6}$ ), and  $290 \times 10^{-6}$  for Hg-tot/Mn-oxa (interquartile range  $116\text{--}348 \times 10^{-6}$ ).

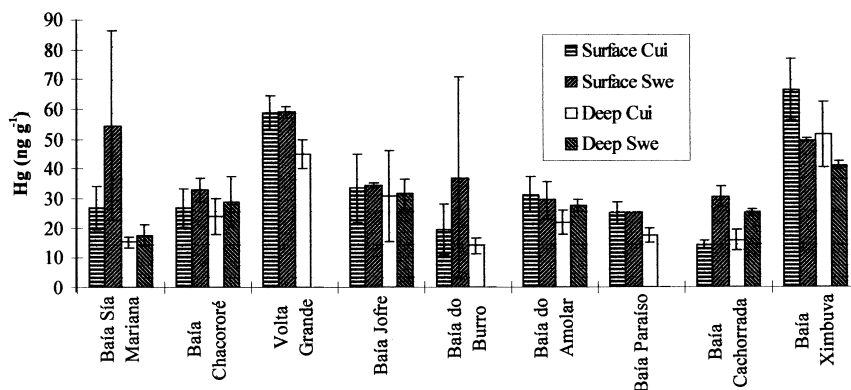


Fig. 2. Total Hg concentration in the surface horizons (0–6 cm) and in deep horizons ( $\approx 0.5$  m) of sediment profiles from floodplain lakes in the Alto Pantanal, Brazil. Averages of three strata from each of two profiles sampled in March and August 1998, analyzed at a laboratory in Cuiabá (Cui) and averages of one stratum from each of two profiles sampled in August 1998, analyzed at a laboratory in Sweden (Swe). Vertical bars indicate  $\pm 1$  S.D.

## 5. Discussion

Low Hg-tot concentrations were found in sediments of the Alto Pantanal, except in the immediate vicinity of a major gold-mining site. Also relative to the abundance of sesquioxide forming metals, Hg-tot concentrations were lower than in other tropical floodplain areas. The Hg-tot concentration in the lake sediments ranged from below  $10 \text{ ng Hg g}^{-1}$  dry wt. in some deep sandy horizons to above  $50 \text{ ng Hg g}^{-1}$  dry wt. (Fig. 2). River bottom sediments sampled in 1992 from the same area as the present lake sediments contained between  $10.6$  and  $39.4 \text{ ng Hg-tot g}^{-1}$  dry wt., with an average of  $24.7 \text{ ng Hg g}^{-1}$  dry wt. (Hylander et al., 1994). The somewhat lower Hg-tot content than in the present samples might be explained by the fact that bulk samples were analyzed, and not only the fine fraction, and by different sediment types (river vs. lake sediment). Lacerda et al. (1991) found higher Hg-tot content in the surface horizons than in deeper horizons in two studied lakes of the same area, which they ascribed to atmospheric deposition of Hg originating from the gold mining activities in Poconé. They encountered  $62$ – $80 \text{ ng Hg g}^{-1}$  dry wt. in the upper 2 cm, but only  $12$ – $30 \text{ ng Hg g}^{-1}$  dry wt. below 3-cm depth. However, since the organic matter content showed a similar pattern, that also may apply to other constituents of fine sediments

as was often the case in our profiles, it is difficult to interpret an increasing Hg-tot level as an increasing Hg-tot deposition without a careful study of sediment properties and turnover.

In the present study the surface sediments were generally enriched in amorphous Al, Fe, and Mn oxy-hydroxides. This was most pronounced for Mn, which is known to be greatly influenced by the redox potential and easily mobilized at anoxic conditions (Bartlett, 1988). The reduced Mn ions can be leached or washed out from the deep sediment, which may result in a lower future capacity to sorb Hg-tot in case the subsurface horizons would get oxygenated again.

Iron is in the same way affected by redox reactions, which may cause leakage of Fe and formation of laterite rock or soils with clay texture. In the Poconé area the gold miners are digging in huge laterite layers to the depth of more than 50 m in the search for gold-containing quartz veins embedded in laterite. The total Fe content in the sediments in Alto Pantanal is approximately  $25 \text{ mg g}^{-1}$  dry wt. and on average one-third of Fe-tot was available as reactive oxides or hydroxides determined by oxalate extraction (Fig. 3). The acid oxalate solution extracted about half of Mn-tot and less than 5% of Al-tot (Fig. 3). Reactive oxy-hydroxides have by some authors been shown to sorb Hg (Forbes et al., 1974; Roulet et al., 1998a) while others (Semu et

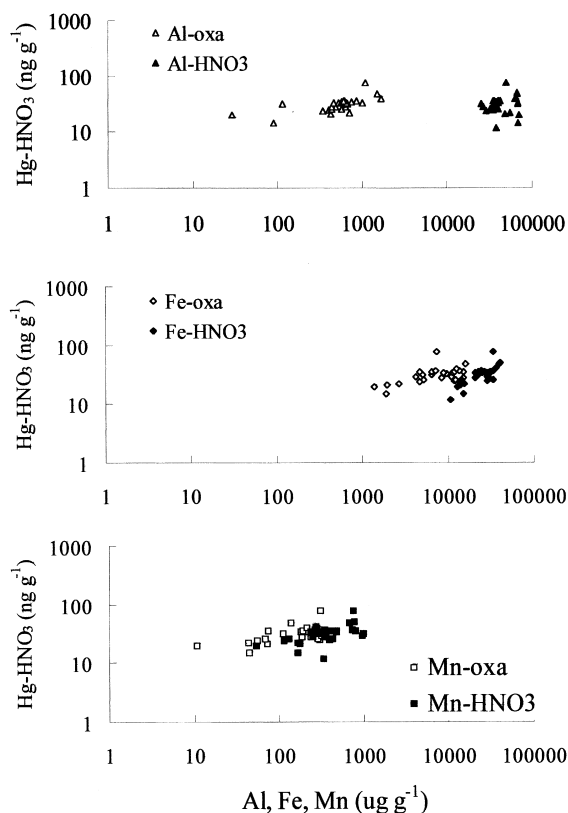


Fig. 3. Concentrations of total Hg ( $\text{ng g}^{-1}$  dry wt.) vs. oxalate extractable and total (nitric acid extractable) Al, Fe and Mn ( $\mu\text{g g}^{-1}$  dry wt.), respectively, in sediments from floodplain lakes in the Alto Pantanal, Brazil. Oxalate extractable data from three surficial horizons and from three deep horizons ( $\approx 0.5$  m) and nitric acid extractable data from one surficial horizon (2–4 cm) and one deep horizon of profiles sampled in August 1998.

al., 1986) showed that it is not always true for tropical soils. In the present study there was a weaker correlation between Hg-tot content in sediment and reactive Al, Fe or Mn oxy-hydroxides than demonstrated in the Tapajós area, based on extraction with citrate-dithionite-bicarbonate buffered extract (cdb), which in addition to amorphous compounds also extract some crystalline Fe and Al (Roulet et al., 1998a). For the Pantanal sediments the difference between Al-oxa and Al-cdb was a few percent, while Fe-cdb on average counted for approximately half of Fe-tot and Mn-cdb for approximately 80% of Mn-tot (unpublished data). The differences in soil and sediment

types between Pantanal and Tapajós are evident, for example demonstrated in lower mass ratio between Hg-tot and Fe in the Tapajós compared to Pantanal, mainly caused by lower Hg-tot content in the Pantanal sediments.

The used oxalate solution will not extract crystalline Al and Fe oxy-hydroxides such as gibbsite and goethite, but will extract amorphous Al, Fe, and Mn oxy-hydroxides and also organically bound Al, Fe, and Mn (Klute, 1986). However, in our samples, as well as in many other tropical soils and sediments, organically bound Al, Fe, and Mn probably makes up only a minor fraction of the extracted elements, since the C content was only 0–5% dry wt. in the fine fraction ( $< 74 \mu\text{m}$ ) determined by dry combustion and IR-detector (unpublished data).

The Hg-tot content of bottom sediments ( $< 74 \mu\text{m}$ ) from water courses in the immediate vicinity of present or former gold mining sites was higher than in the lake sediment. The FEMA sediments around Poconé contained between 18 and 348  $\text{ng Hg-tot g}^{-1}$  dry wt. with an average of 91.5  $\text{ng Hg g}^{-1}$  dry wt. Yet, the Hg-tot concentrations encountered in sediments in that area during the liberal use of Hg in gold mining during the 1980s were higher. Silva (1996) sampled in 1993–1994 one-third of the sites that are included in the present monitoring program and encountered 92–880  $\text{ng Hg-tot g}^{-1}$  in not sieved river sediment, with an average from 13 sites of 428  $\text{ng Hg g}^{-1}$ . von Tümpling et al. (1995) encountered 23–198  $\text{ng Hg-tot g}^{-1}$  in river sediment (not sieved) collected in 1992–1993. Rodrigues Filho (1995) encountered Hg-tot concentrations in the  $< 74\text{-}\mu\text{m}$  fraction of sediments ranging from  $< 40$  up to 1850  $\text{ng Hg g}^{-1}$  with an average from 17 sites of 342  $\text{ng Hg g}^{-1}$ . The present, lower Hg-tot concentrations may be a result of enforcement of the legislation protecting the environment from contamination and a sharp reduction in gold mining activity. In May 1987, 70 gold mining sites (garimpos) were working, but only seven in May 1999, due to the falling gold price on the world market (site study by L.J. Oliveira in May 1999).

With a water flow in Rio Cuiabá during the dry season of more than  $100 \text{ m}^3 \text{ s}^{-1}$  ( $130 \text{ m}^3 \text{ s}^{-1}$  measured downstream Porto Jofre in October



1997; Ministério do Meio Ambiente, 1997) and a suspended matter content of around  $50 \text{ mg l}^{-1}$  (Table 1), at least 500 tons of eroded material is daily transported by the river past Porto Jofre. During the rainy season the daily load is much larger. Part of the load settles in lakes and marshlands, especially during the rainy season when large water quantities are not conducted in the river channel but inundate surrounding areas, which results in a reduced water velocity. Presently, the main area of sedimentation is to the south of Rio Cuiabá before the confluence with Rio Paraguai (Godoi Filho, 1986). The total burden of particulate matter in suspension, and probably also of Hg-tot transported by Rio Paraguai is larger than those in Rio Cuiabá due to the nearly three times larger water flow ( $374 \text{ m}^3 \text{ s}^{-1}$  measured downstream Ilha de Taiamã in October 1997; Ministério do Meio Ambiente, 1997).

The mobility and transport of dissolved and particulate Hg is largely dependent upon binding forms of accumulated Hg. Mercury can be relocated by leaching of dissolved Hg. Elemental Hg forms an alloy with most other metals, iron being a notable exception, and oxidized Hg binds strongly to the oxy-hydroxides of other metals, which reduces its mobility. The mechanical relocation of particle-bound Hg depends among others on the vulnerability to erosion of formed sediments. Assuming that the Hg-tot concentration in suspended matter is the same as in the sediment (Fig. 2), a mean concentration of approximately  $1\text{--}10 \text{ ng l}^{-1}$  particulate Hg can be estimated from the suspended load. An estimated typical dissolved Hg concentration of approximately  $1 \text{ ng l}^{-1}$  (cf. Meili, 1997) suggests that the transport of particulate Hg may dominate the total Hg transport in the Rio Cuiabá. Estimating the river transport of total Hg yields values in the order of  $1\text{--}100 \text{ kg year}^{-1}$  in Rio Cuiabá at Porto Jofre, of which an unknown fraction is anthropogenic.

The higher Hg-tot content in the surface horizons than in deeper horizons may indicate an anthropogenic enrichment, but may on the other hand also be related to the higher content of

reactive Mn and Fe encountered in surficial horizons.

## 6. Conclusions

The Hg-tot content in fine sediments ( $< 74 \mu\text{m}$ ) of the Alto Pantanal, apart from the immediate vicinity of present or former gold mining activities, is generally below  $50 \text{ ng Hg g}^{-1}$  dry wt., which is lower than in the Amazon region as well as in many temperate areas. Hg-tot/Al and Hg-tot/Fe ratios were lower than those presented by Roulet et al. (1998a) for soils and sediments in the Tapajós basin and other tropical areas of South America, even though only amorphous metal oxy-hydroxides were considered in our study. This suggests that the Hg cycle in the Pantanal may be governed by other parameters than in the Amazon basin, where the soils are younger and of different origin.

## Acknowledgements

Work supported by Sida/SAREC (Swedish International Development Co-operation Agency/Department for Research Co-operation), PRODEAGRO (the program for agro-environmental development in Mato Grosso state, Brazil), and the Federal University of Mato Grosso, Brazil. We thank Leila M.C. Singulane, Sandra M. Laet, Luis B. Barreto, and Salatiel A. Araujo at the mining division of FEMA (the governmental, environmental foundation of Mato Grosso state) for technical support. A special thanks to Ecotropica for logistical support, Marco Maia for boat and lodging, Angelika Jünker, Paulo Alvarez, and Projeto Gran Pantanal at UFMT for boat, Domingos Godoi Filho for explaining the geology of Pantanal and IBAMA for permits.

## References

- Alho CJR, Vieira LM. Fish and wildlife resources in the Pantanal wetlands of Brazil and potential disturbances from the release of environmental contaminants. *Environ Toxicol Chem* 1997;16:71–74.
- Alho CJR, Lacher TE, Goncalves HC. Environmental degra-

- duction in the Pantanal ecosystem. *BioScience* 1988;38(3): 164–171.
- Bartlett RJ. Manganese redox reactions and organic interactions in soils. In: Graham RD, Hannam RJ, Uren NC, editors. *Manganese in soils and plants*. Dordrecht, Boston and New York: Kluwer Academic Publishers, 1988:59–73.
- Companhia de Pesquisa Recursos Minerais. *Manual Técnico do LAMIN* [In Portuguese]. LAMIN, Rio de Janeiro, Brazil, 1987.
- Estudos hidrológicos da bacia do Alto Paraguai. Ministério do Interior. Departamento Nacional de Obras de Saneamento. *Rel. Téc. UNESCO/PNUD. BRA-66.521, vol. I* [In Portuguese], Brasília, Brazil, 1974:284.
- Fitzgerald WF, Engstrom DR, Mason RP, Nater EA. The case for atmospheric mercury contamination in remote areas. *Environ Sci Technol* 1998;32:1–7.
- Forbes EA, Posner AM, Quirk JP. The specific adsorption of inorganic Hg(II) species and Co(III) complex ions on goethite. *J Colloid Interface Sci* 1974;49:403–409.
- Forsberg BR, Jardim WF, Zeidemann VK et al. The biogeochemistry of mercury in the Negro river basin (Brazilian Amazon). In: Barbosa J, Melamed R, Villas Bôas R, editors. *Mercury as a global pollutant — 5<sup>th</sup> International Conference, 23–27 May 1999, Rio de Janeiro, Brazil*. CETEM-Center for Mineral Technology. Rio de Janeiro, Brazil, 1999;153:592.
- Godoi Filho JD. Aspectos geológicos do Pantanal Mato-Grossense e de sua área de influência. In: *Anais do 1. Simpósio sobre Recursos Naturais e Sócio-econômicos do Pantanal* [In Portuguese, English summary]. Centro de Pesquisa Agropecuária do Pantanal/Universidade Federal de Mato Grosso do Sul, Brasília, Brazil, 1986:63–76.
- Gonçalves LL. Diagnóstico das influências hidro-sedimentológicas das Sub Bacias dos Rio Aricá-Açú e Aricá-Mirim na Bacia do Cuiabá River, no trecho Compreendido entre Santo Antônio do Leverger — Barão Melgaço [In Portuguese]. UFMT. Depto Engenharia Sanitária e Ambiental, Cuiabá, Brazil, 1996:134 + annex.
- Gonçalves GO, Paiva EC. Otimização da Metodologia para Determinação de Mercúrio Total em Rochas, Solos e Sedimentos. Depto de Química. CETEM/CNPq, Rio de Janeiro, Brazil, 1995.
- Hamilton SK, Sippel SJ, Melack JM. Inundation patterns in the Pantanal wetland of South America determined from passive microwave remote sensing. *Arch Hydrobiol* 1996; 137:1–23.
- Hylander LD, Silva EC, Oliveira LJ, Silva SA, Kuntze EK, Silva DX. Mercury levels in Alto Pantanal — a screening study. *Ambio* 1994;23(8):478–484.
- Klute A, editor. *Methods of soil analysis*. Part 1. Physical and mineralogical methods. Madison, Wisconsin, 1986.
- Lacerda LD. Global mercury emissions from gold and silver mining. *Water Air Soil Pollut* 1997;97:209–221.
- Lacerda LD, Pfeiffer WC, Bastos WR. Mercury dispersal in water and sediments draining a gold mining tailing deposit in Poconé, Brazil. *Univ. Fed. Fluminense and Univ. Fed. do Rio de Janeiro*, 1990.
- Lacerda LD, Salomons W, Pfeiffer WC. Mercury distribution in sediment profiles from lakes of the high Pantanal, Mato Grosso State, Brazil. *Biogeochemistry* 1991;14:91–97.
- McKenzie RM. The adsorption of lead and other heavy metals on oxides of manganese and iron. *Aust J Soil Res* 1980; 18:61–73.
- Meili M. Mercury in boreal forest lake ecosystems. *Acta Universitatis Upsaliensis, Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science*, vol. 336. Uppsala University, Sweden, 1991.
- Meili M. Mercury in lakes and rivers. In: Sigel A, Sigel H, editors. *Mercury and its effects on environment and biology*, vol. 34. New York, USA: Metal Ions in Biological Systems, Marcel Dekker Inc, 1997:21–51.
- Ministério do Meio Ambiente. *Plano de Conservação da Bacia do Alto Paraguai — PCBAP, vol. II* [In Portuguese], PNMA. Brasília — DF, 1997.
- Nakazono EM, Forsberg BR, Martins AE, Padovani CR. Factors controlling mercury contamination in tucunarés (*Cichla* sp.) from the Negro and Tapajós river basins, Brazilian Amazon. In: Barbosa J, Melamed R, Villas Bôas R, editors. *Mercury as a global pollutant — 5<sup>th</sup> International Conference, 23–27 May 1999, Rio de Janeiro, Brazil*. CETEM-Center for Mineral Technology. Rio de Janeiro, Brazil, 1999;212:592.
- Nriagu JO. Mercury pollution from silver mining in colonial South America. In: Abrão J, Wasserman JC, Silva-Filho EV, editors. *Proc. Int. Symp. Perspect. Environ. Geochem. Trop. Countries, Niterói, Brazil, 1993*:365–368.
- Rodrigues Filho S. Metais pesados nas sub-bacias hidrográficas de Poconé e Alta Floresta [in Portuguese; English summary]. *Série Tecnologia Ambiental 10*. CETEM/CNPq, Rio de Janeiro, 1995:90.
- Roulet M, Lucotte M, Saint-Aubin A et al. The geochemistry of mercury in central Amazonian soils developed on the Alter-do-Chão formation of the lower Tapajós River Valley, Pará state, Brazil. *Sci Total Environ* 1998a;223:1–24.
- Roulet M, Lucotte M, Canuel R et al. Distribution and partition of mercury in waters of the Tapajós River basin, Brazilian Amazon. *Sci Total Environ* 1998b;213:203–211.
- Semu E, Singh BR, Selmer-Olsen AR. Adsorption of mercury compounds by tropical soils. *Water Air Soil Pollut* 1986; 27(1–2):19–27.
- Silva AP. *Mercúrio em ambientes aquáticos de Poconé, MT*. Doctoral thesis. Programa de Pós Graduação em Mineralogia e Petrologia [In Portuguese], Universidade de São Paulo, Instituto de Geociências, São Paulo, Brazil, 1996.
- Veiga MM, Fernandes FRC, Farid LH et al. Poconé: Um campo de estudos do impacto ambiental do garimpo [In Portuguese]. *Tecnologia Ambiental 1*, CETEM/CNPq, Rio de Janeiro, 1991:113.
- Veiga MM, Meech JA, Hypolito R. Educational measures to address mercury pollution from goldmining activities in the Amazon. *Ambio* 1995;24(6):371–375.

von Tümpling Jr. W, Wilken R-D, Einax J. Mercury contamination in northern Pantanal region Mato Grosso, Brazil. *J Geochem Explor* 1995;52:127–134.  
Zeilhofer P. Geökologische Charakterisierung des nördlichen

Pantanal von Mato Grosso, Brasilien, anhand multitemporaler Landsat Thematic Mapper-Daten [In German]. Herbert Utz Verlag Wissenschaft, München, 1996:225 + app.