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Land-Sea Link in Asia

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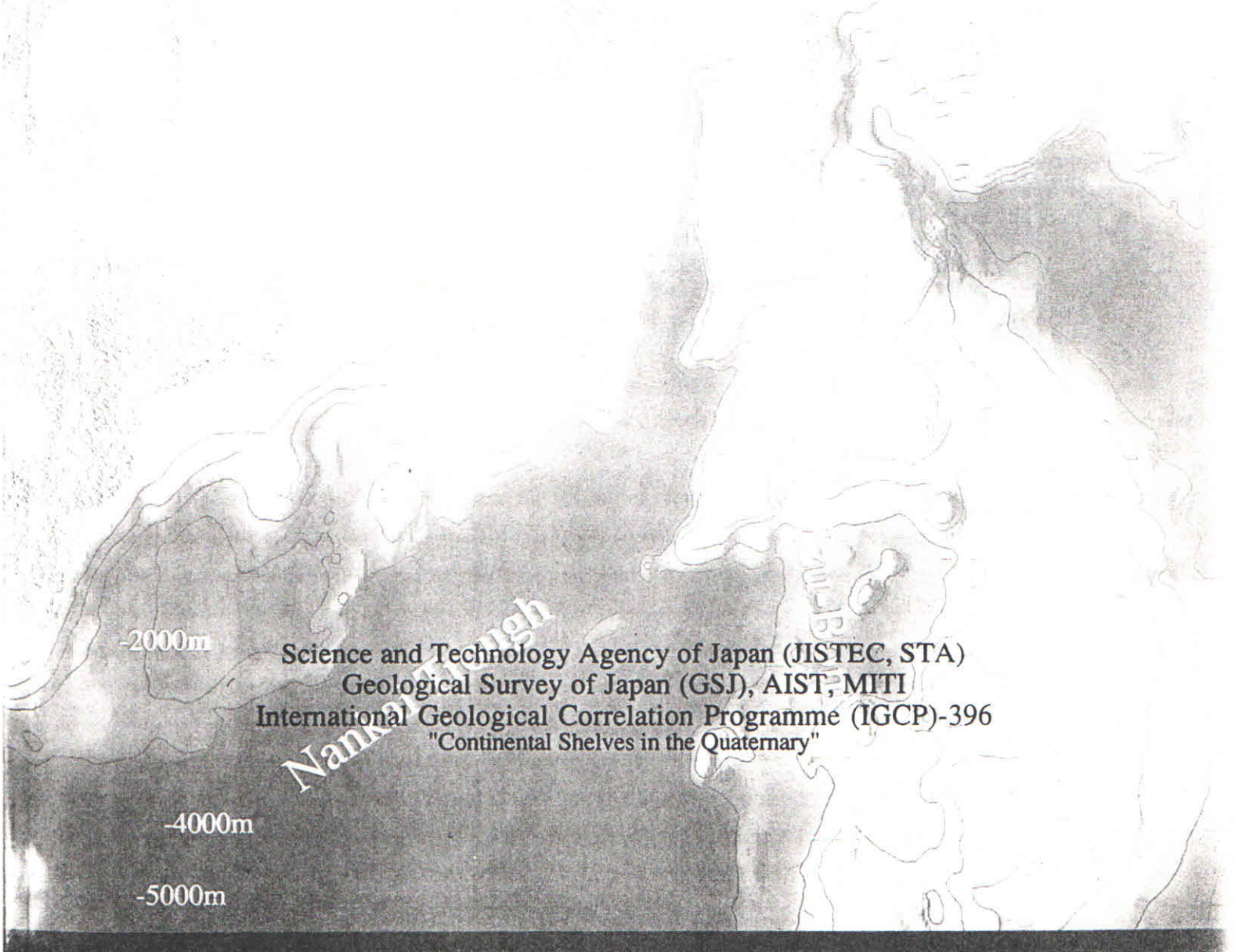
Tsukuba, Japan, March 15-19, 1999



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Mercury in eroded, river transported material and in sediments from the Cuiabá river, Brazil

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Abstract

Artisan gold mining with mercury is commonly practised in Brazil and many other tropical countries. The mercury used is lost to the surrounding water, soil and air. The losses occur both at the initial treatment, when mercury is mixed with soil and water, and subsequently, when purifying the formed gold amalgam by heating to volatilize the mercury. We studied the mercury contamination of waters and sediments around a gold mining area situated at the margin of the Pantanal floodplain in central western Brazil. Sediment cores were taken in rivers and floodplain lakes with a tube corer, divided into 2- to 5-cm thick horizons and the subsamples sieved (< 74 μm). Material suspended in the water was collected by precipitation with aluminium sulphate at a controlled pH. The fine fraction of sediments and the precipitated material were analysed for total mercury and for amorphous iron, aluminium and manganese. The mercury content was substantially elevated in the surface horizons of sediment collected downstream in the vicinity of gold mines. The mercury content declined at increasing distances from known point sources. Profiles without direct influence of mine water discharge but possibly influenced by long-range atmospheric Hg deposition indicated a moderate enrichment of Hg in the upper layers, which partly coincided with elevated concentrations of Fe and Mn oxides.

Introduction

The alluvial plain of Pantanal (Fig. 1) facing the border of Bolivia and Paraguay in Brazil is truly unique in the world, having an abundance of birds (more than 650 species), fish and caimans like the endangered spectacled caiman *(Caiman sclerops or crocodilus)*. Pantanal is formed by sedimentary deposits of mainly quartz sand and aluminium silicate clay sediments. The 300,000 km^2 great plain has an average slope north to south of only 2 cm per km and west to east of 6 cm per km. Some 144 000 km^2 of the plain is yearly flooded from December to March. The Alto Pantanal (app. 15.5°-17.5°S and 55°-59°W) is the northernmost part of the Paraguay River basin, including the tributary Rio Cuiabá. The rivers run southwards, and are to the north separated from the Amazon basin by the Serra dos Parecis and Serra Azul

Table 2. Mercury content in suspended matter in water and in the fine fraction of lake sediments sampled in March 1998. Duplicate samples and analyses in most cases.

Sampling site	Suspended matter	SD	Surface sediment (Ekman)	SD	Sediment profile 0-2 cm	SD	21-24 cm	SD
	ng Hg g^{-1} (dw)							
Volta Grande	132	16	39	5	35	9	22	8
Baía Siá Mariana	277	46	56	14	n.a.		n.a.	
Baía Chacororé	153	50	29	9	23	s.s.	16	s.s.
Baía Jofre	186	33	27	s.s.	24	20	20	s.s.
Baía do Burro	82	s.s.	20	12	32	8	7	s.s.

n.a. = not analysed
s.s. = single sample

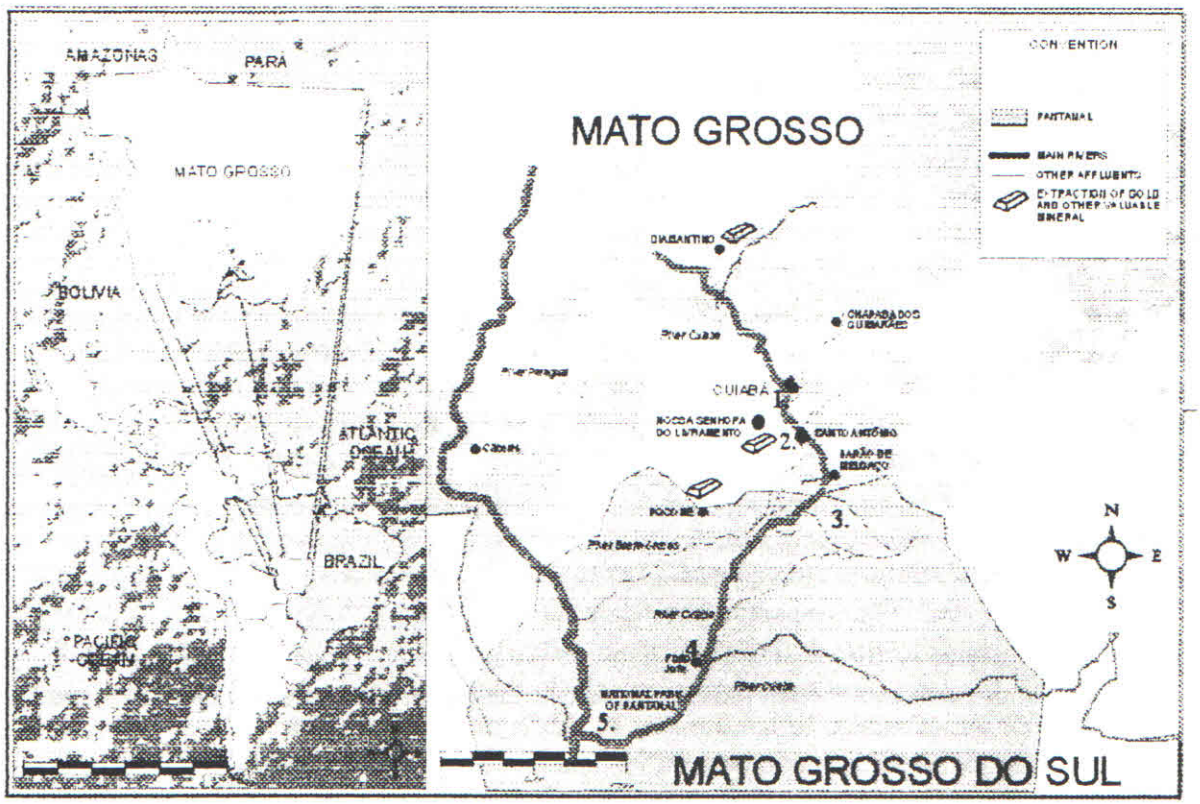

Figure 1. Study area with location of sampling sites. 1. RiverCuiabá at Cuiabá; 2. Volta Grande; 3. Bog stream at Mimoso, River Mutum, Baía Siá Mariana, Baía Chacororé, north and south; 4. River Cuiabá at Porto Jofre, Baía Jofre; 5. River Cuiabá at Baía do Burro and Baía do Burro.

can be estimated. An estimated typical dissolved Hg concentration of around 1 ng L^{-1} (cf. Meili 1997) suggests that the transport of particulate Hg may dominate the total Hg transport in the river. Estimating the river transport of total Hg yields values on the order of 1-100 kg $year^{-1}$, of which an unknown fraction is anthropogenic. The higher Hg 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 superficial horizons.

mountain chains. (Banks, 1991; Estudos hidrológicos da bacia do Alto Paraguai, 1974.)

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 (Gercino, 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 (Hylander et al., 1994; Lacerda and Salomons, 1991; Veiga et al., 1991).

Another serious problem is 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 gold mining and dredging for construction sand from the river bottom contribute to erosion.

This paper deals with the impact of Hg contamination and erosion in the Rio Cuiabá river basin. The aim of our studies is to quantify the Hg contamination and its relation to soil erosion and sediment transport.

Methods

Two sediment cores were taken each time with a tube corer from the river or lake bottom in March (rainy season) and August (dry season) 1998. The cores were divided into 2 to 5 cm thick horizons, dried (<50 °C) and sieved (<74 μm). Surface sediment was also collected with an Ekman grab sampler, dried and sieved. Material suspended in the water was flocculated and precipitated by addition of aluminium sulphate, $Al_2(SO_4)_3$, (Silva et al., 1993). About 20 mL of a 10% $Al_2(SO_4)_3$ solution and about 20 mL of sodium hydroxide (NaOH, 1 N) was added to 20 L of water. The fine fraction of sediments and the precipitated material were analysed for total content of mercury (Hg), and for reactive (amorphous) iron (Fe), aluminium (Al) and manganese (Mn). Total Hg was determined by cold vapor atomic absorption spectrophotometry after sample digestion in nitric acid (Gonçalves and Paiva, 1995; Malm et al., 1989). Water pH, dissolved oxygen, temperature, conductivity and turbidity were measured in field with a multipurpose field instrument (Horiba U-10). Total carbon (C) was determined by dry combustion and subsequent determination on a gas chromatograph. Acid ammonium oxalate (0.2 *M*, pH 3) was used for the extraction of reactive Al, Fe and Mn (Klute, 1986), followed by flame AAS determination.

Results and Discussion

Rio Cuiabá is a white water river with a high load of suspended material, which increases downstream the city of Cuiabá (Table 1). With a water flow during the dry season of more than 100 $m^3 s^{-1}$ (130 $m^3 s^{-1}$ measured downstream Porto Jofre in Oct. 1997, Maranhão, 1998), and a suspended matter content of around 50 mg L^{-1} (Table 1) at least 500 tonnes of eroded material is daily transported by the river past Porto Jofre. During the rainy season the daily transported load is much larger (unpubl. data). 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 the Cuiabá river before the confluence with Paraguay river (Godoi Filho, 1986).

Table 1. Suspended matter (0.45 µm filter), turbidity, pH, conductivity, dissolved oxygen, and dissolved organic carbon in the water of floodplain lakes (Baía) and rivers of the Pantanal (Brazil) in August 1998.

Sampling site	Coordinates South	Coordinates West	Susp. mg L^{-1}	Turb. NTU	pH	Cond. µS cm^{-1}	DO mg L^{-1}	DOC mg L^{-1}
RiverCuiabá,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
River 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
River Cuiabá, Jofre	17° 22'	56° 46'	50 [a)]	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
River Cuiabá, Burro	17° 51'	57° 24'	55 [a)]	47	6.5	27	7.0	3.3

n.a. = not analysed

[a)] Estimated from adjusted turbidity measurements and from the amount of material precipated with $Al_2(SO_4)_3$, corrected for added chemicals.

Some of the tributaries (e.g. Rio Mutum, Table 1) have dark water, dominated by a high content of dissolved organic matter but with an insignificant load of suspended material, and with signs of oxygen depletion (Table 1). This type of water is known to increase the mobility and probably also the bioavailability of Hg (Meili, 1991, 1997).

The Hg concentration in the sediments ranged from below 10 ng Hg g^{-1} (dw) in deeper horizons to above 50 ng Hg g^{-1} at the surface (Table 2). Lacerda et al. (1991) also found higher Hg content in the surface horizons than in deeper horizons. The Hg content in surface sediment was highest in upstream lakes, which can be interpreted as an effect of the vicinity to gold mining fields, where Hg is used and discharged. River bottom sediments sampled in 1992 from the same area as the present lake sediments, contained between 10.6 and 39.4 ng Hg g^{-1}, with an avearge of 24.7 ng Hg g^{-1} (Hylander et al., 1994). The somewhat lower Hg content than in the present samples might be explained by that bulk samples were analysed, and not only the fine fraction, and by the different sediment type. The Hg content is higher in the immediate vicinity of present or former gold mining sites, where bottom sediments (<74 µm) sampled in August 1998 contained between 18 and 348 ng Hg g^{-1} with an average of 91.5 ng Hg g^{-1} (Oliveira et al., 1999). Yet, the Hg concentrations encountered in sediments in that area during the liberal use of Hg in gold mining during the eighties were often higher. Rodrigues P. Filho (1995) encountered Hg concentrations in the <74 µm-fraction of sediments ranging from <40 up to 1850 ng Hg g^{-1} with an average from 17 sites of 342 ng Hg g^{-1}. Tümpling, et al., (1995) encountered 23 - 198 ng Hg g^{-1} in river sediment (not sieved) collected 1992 - 1993.

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 oxidised Hg binds strongly to the oxyhydroxides of other metals, which reduces its mobility. The mechanical relocation of particle-bound Hg depends among other on the vulnerability to erosion of formed sediments. Assuming that the Hg concentration in suspended matter is the same as in the sediment (Table 2), a mean concentration of around 1-10 ng L^{-1} particulate Hg

Oxalate extractable Fe was above 0.5% at the surface, but this fraction is reduced to half at 15 cm depth in the studied lake sediments. Oxalate extractable manganese reached 0.02-0.03% in the surface sediments of the lakes Baía Siá Mariana, Baía Chacororé and Baía Jofre, but was 10 times lower at 15-30 cm depth. Baía do Burro had a low content of reactive Mn throughout the profile.

In Baía Siá Mariana and some locations in the Cuiabá river, some carnivorous fishes have a Hg content above 0.5 μg Hg g^{-1} (Hylander et al., 1994; Pinto et al., 1999), indicating that they are not suitable for consumption. If discharged Hg is chemically or mechanically demobilised and relocated, fish in larger and more remote areas will also be contaminated. Reducing the effects of Hg discharges can be costly, as shown in the Minamata case where the restoration costs widely exceeded the benefits of using Hg, human suffering not accounted for (Laws, 1993). Reduction of both Hg use and anthropogenic erosion will contribute to protect the unique fauna of the Pantanal floodplain from Hg contamination.

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