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Mercury contamination in the northern Pantanal region Mato Grosso, Brazil [1]

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Abstract

In gold mining areas around the world, mercury is used to separate gold by amalgamation. This often causes mercury contamination. Such a situation near the goldmines in the Poconé area, Mato Grosso, Brazil was investigated. Concentrations of mercury were determined in water, sediment and air. The results obtained in water showed elevated mercury concentrations of between 18 and 160 ng/l (filtered) compared to 25 ± 0.9 ng/l in a reference site. In sediments, total mercury concentrations were in the range from 23 to 198 ng/g (dw). Results of speciation analyses in water and sediment samples from two small rivers showed that only 10 to 50% of the mercury is easily reducible. At the beginning of the rainy season, volatile mercury concentrations of up to 8 ng/l resulted from leaching the tailings by the rain. In the ambient air near the gold mine region, concentrations of up to 6 ng/m^3 mercury were detected. Two meters above contaminated tailings, the values found were ten times higher. These results provide first information on transformations of mercury species and their pathways under tropical conditions.

1. Introduction

Since the 1980s, about 5000 workers have been employed in about 130 gold mines, called garimpos, near Poconé, Mato Grosso, in the centre of Brazil. The gold ore is mined as bedrock, which is crushed and then concentrated in centrifuges. Mercury is then used to amalgamate the gold particles and separate the gold from the waste. The waste from this separation process is contaminated with mercury and is collected in the tailings. Thus, a

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great deal of the mercury from the gold purification process ends up deposited in the slag piles. We estimate the amount to be about 2 tons (von Tümpling and Zeilhofer, 1994). Overall, it is estimated that during the 1980s between 10 and 15 t of mercury were used in the region of Poconé (CETEM, 1989, CETEM, 1991, Lacerda et al., 1991).

The results of several previous investigations near Poconé have dealt only with the total concentrations of mercury. However, mercury is an element that can pass through various cycles in the environment, successively forming different compounds, each with its own environmental behaviour. Thus, to determine its actual behaviour under tropical conditions, we studied mercury in its various forms. The results facilitate an evaluation of the effects mercury can have as an environmental contaminant. This can then form the basis for a description of the pathways of mercury in tropical regions such as Poconé.

2. Materials and methods

For one year at bimonthly intervals, 14 samples of bottom sediment combined from five points in a horizontal cross sectional profile from left to right bank were taken together with the same number of water samples from a ditch called Corrego Fundo which has a cross section between one and three square metres. The ditch passes through a gold mining region before it confluences with the Piranema River. Samples were also collected from the Piranema River at bimonthly intervals.

Samples of water, sediment and air were in an area of the National Park "Serra das Araras", which is located about 100 km north West of the mining area collected for comparison. This park is free of gold mines and other possible direct industrial mercury emission influences.

The water samples were filtered through 0.45 μm Millipore filters and stored in brown glass bottles. The sediment samples were transported in brown glass bottles and sieved in the laboratory. All water samples were treated with nitric acid and stabilised by cooling.

Each of the species groups of mercury was determined individually by atomic fluorescence spectroscopy (AFS) (Brooks Rand Ltd., 1990) The Hg^0 content was determined first by purging the water samples only with argon. Next, the easily reducible fractions of mercury were determined after reduction with stannous chloride. Finally, the samples were oxidised using a solution of 0.2 M BrCl (Bloom and Crecelius, 1983). The remaining fraction was analysed after reduction with stannous chloride. The total mercury could then be calculated (Bloom and Crecelius, 1983). For sediment samples, the same procedure was used to determine the total concentration of mercury, the sediments were first digested in nitric acid (Nagase et al., 1980).

To collect air samples, gold traps and a Carbotrap® adsorber device were connected to a "Quantimeter 1000" (Dräger, Lübeck) air pump. To determine content of mercury in these samples, the traps were attached to a heating device at the input point of the AFS (Wilken, 1992).

Certified material was used for quality control of the results. The results were also qualified by participation in an intercalibration test with other German environmental laboratories (Wilken et al., 1994).

3. Results

3.1. Mercury in waterbodies and river sediments

Investigated area

The investigated area is shown in Fig. 1.

Preliminary examinations

In June and August 1992, the first samples of water and sediment were taken every 200 m in the Corrego Fundo ditch and at 4 points in the Piranema River (Fig. 1), to provide orientation values on the regional contamination and to establish representative permanent observation points. Samples were to be taken regularly at these observation points throughout the year to describe the behaviour of mercury and its species in a tropical surface water.

In any investigation, the number of samples is limited. Therefore, multivariate statistical methods, such as methods of cluster, variance, and discriminant analysis had to be used to determine the similarities and/or differences between the sampling sites and to optimise the sampling strategy. Fig. 2, with the results of cluster analyses, shows clearly that changes were occurring near the gold mines, while along the middle course of the stream, the degree of similarity was much greater. In contrast, near the confluence of the stream and the river, the results were very dissimilar, making it necessary to establish a set of sampling points much closer together than those along the middle section of the stream. From the findings of these studies, it was possible to designate the sampling points within the squares as permanent observation points in the Fundo ditch at which samples were then taken regularly throughout the year.

Results of the annual cycle in the water

The results of the water, sediment, and suspended matter analyses showed that the mercury contamination at the sampling sites was higher than the reference values. This could be explained by the collapse of a dam in March 1992, three months before sampling began.

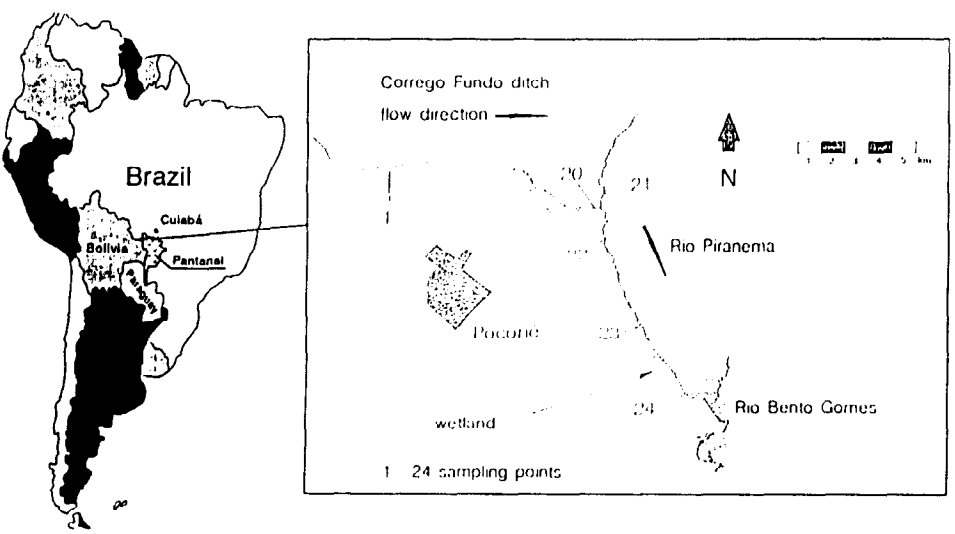

Fig. 1. Study area near Poconé, Mato Grosso, Brazil.

sampling points	June	1	3	5	7	9	11	13	15	17	19	
	August	2	4	6	8	10	12	14	16	18	20	
cluster	June	1	2	2	3	3	3	3	3	4	5	
	August	1	1	1	1	1	2	3	3	4	5	

☐ sampling points after cluster analysis

Fig. 2. Results of cluster analysis according to the algorithm of Wards.

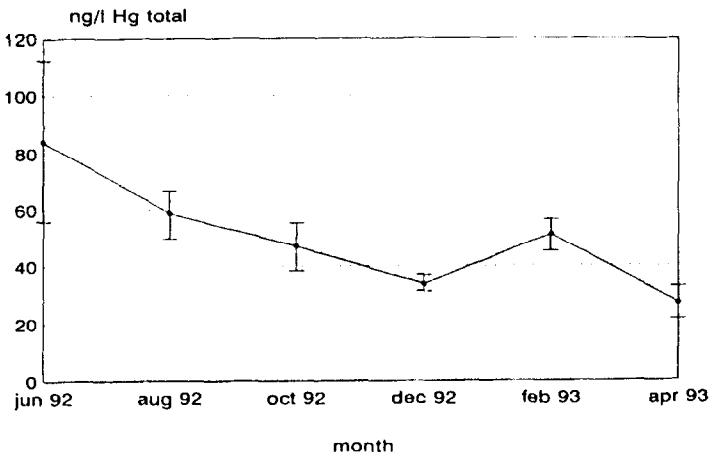

Fig. 3. Concentrations of total Hg in river water vs. time.

(1) Total mercury in the water phase

The annual cycle of the total mercury concentration represented in Fig. 3 shows that the values recorded in the ditch were relatively high.

After the dam was reconstructed in July, these values showed a steady decrease. At the end of the rainy season, the concentrations slightly increased again as the water level and movement of sediment in the ditch decreased. When the water current increased again, the sediment was carried downstream, and the values resumed their decrease once again.

(2) Volatile elemental mercury in the water phase

In Fig. 4 the results of volatile mercury in the water phase are shown.

This figure can be interpreted as an effect of leaching of mercury from contaminated tailings by rain water. This was confirmed by the calculation of a correlation coefficient between the elemental mercury ($n=76$) in the water and mercury in the suspended matter ($n=76$) at the beginning of the rainy season. This correlation coefficient was 0.71, which is statistically significant with a first kind error probability of less than 1%.

(3) Reactive mercury in the water phase

The concentrations of the determined reactive mercury in the water phase are shown in Fig. 5.

Only 20% to 40% of the total mercury in these waters is easily reducible. During this entire period, the amount of reactive mercury showed a steady decrease. The reason for this could be a transformation to more inert compounds.

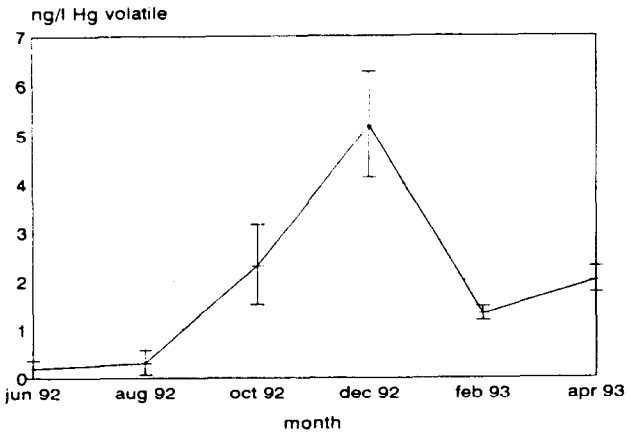

Fig. 4. Concentrations of Hg^0 in river water vs. time.

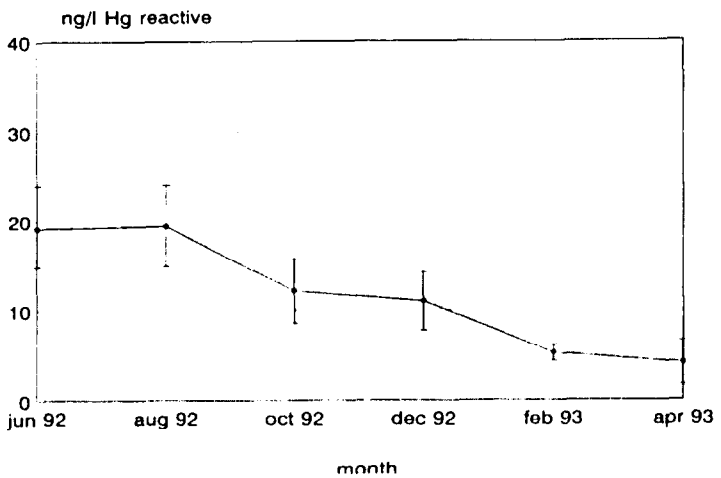

Fig. 5. Concentrations of reactive Hg in river water vs. time.

(4) Nonreactive and inert mercury in the water phase

Between 55% and 75% of the total mercury forms compounds which are not reactive or inert and may associated with humic substances.

Results of the annual cycle in surface river sediments

(1) Total mercury in surface sediments

The results of total mercury obtained during the entire seasonal cycle are shown in Fig. 6.

Tailing particles contaminated with mercury are mobilised and enter the river system during the rainy season which starts in October. These particles are deposited in the river system, depending on water velocity. When the water velocity decreases, sedimentation increases and the wetlands are flooded. Near the end of the rainy season, the discharge is so low that the river flows once more with higher velocity in its bed. These process explain

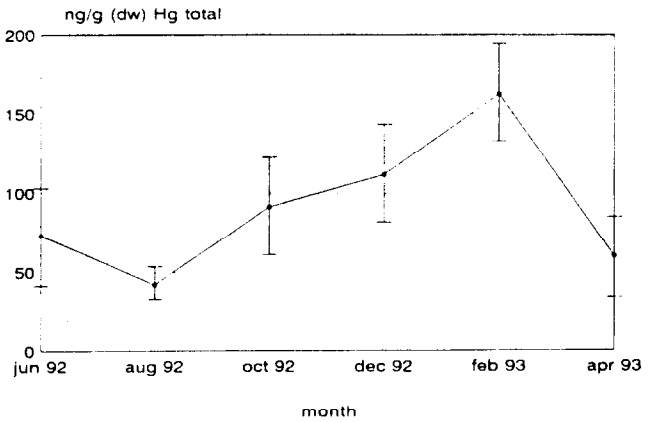

Fig. 6. Concentrations of total Hg in river sediment vs. time.

the lower concentrations of mercury recorded in the surface sediments during April, at the end of the rainy season, and from June through August, the dry season.

(2) Volatile elemental mercury in surface sediments

Elemental mercury and its volatile organic compounds were below the detection limit of 0.5 ng mercury/g dry sediment. One possible explanation for this result is the adsorption of mercury and its compounds on sediment particles.

(3) Reactive mercury in surface sediments

The percentage of the total mercury content in the sediment that belongs to the easily reducible fraction proved to be 18%. This fraction was therefore less abundant in the sediment than in the water.

(4) Non-reactive and inert mercury in surface sediments

Nearly 80% of the total mercury in these sediments is immobilised by forming non-reactive and inert compounds. Only at the end of the rainy season, with a high current in the rivers, did demobilisation and transport of these particles take place in the water phase.

4. Mercury in the ambient air

The mercury concentrations determined in the ambient air near Poconé were higher than the natural background level recorded in the Serra das Araras National Park (Table 1).

One possible source of atmospheric mercury is the contaminated tailings in the gold mines. Near these tailings, values of mercury in the air as high as 80 ng/m^3 were detected. In the Pantanal, 100 km from the mines, total concentrations of about 3 ng/m^3 were determined in the air. Thus, the Pantanal concentrations are lower than the concentrations in the Poconé region but higher than the background values in the Serra das Araras National Park. The transport of mercury from the Poconé area away into the Pantanal could be a possibility.

Table 1
Concentrations of mercury and volatile organic mercury compounds in the air

	Hg-total in ng/m^3				Organomercurials in ng/m^3			
Investigated area	range	SM	SD	*n*	range	SM	SD	*n*
Surrounding of Poconé	4.1–6.3	5.3	0.7	8	0.4–0.6	0.5	0.1	8
100 km south of Poconé in the Pantanal wetland	2.5–3.0	2.8	0.3	3	0.3–0.5	0.4	0.1	3
Serra das Araras	1.9–2.1			2	0.4–0.5			2
Above contaminated tailings	76–85			2	0.3–0.6			2

SM = statistical mean; SD = standard deviation; *n* = number of samples.

5. Conclusion

Mercury concentrations in the water and sediment samples were relatively low compared to corresponding values from other regions such as the Amazon basin, Brazil (Lacerda and Salomons, 1991). However, they are significantly higher than those in the Serra das Araras National Park. Therefore, mercury has a hazardous influence on the Pantanal, one of the largest wetland areas in the world, and on its unique flora and fauna.

The mercury that enters the ditch near the gold mines probably becomes immobilised in the sediment several kilometres from its site of release. This would explain the failure to detect volatile mercury in the study area. At the beginning of the rainy season, elemental mercury from contaminated tailings was found to be transported with the rain water into the river system.

In the ambient air near Poconé, higher mercury concentrations were found in comparison to the Pantanal area, 100 km away from the garimpos (small gold mines). Therefore, there is a possible atmospheric transport of mercury from the Poconé area into the Pantanal through the atmosphere.

Compared to other sources of contamination, such as during the burning of gold amalgam in the open air, the estimated maximum mercury levels which can evaporate from the main tailings are low at present and, generally speaking, should not pose a threat to the local surroundings.

The results above contribute to a better understanding of the main pathways of mercury in the tropical Pantanal aquatic system. The ultimate goal of this research is the prevention of future mercury pollution and reduction of the problems that are being caused by the past and present release of mercury and its species in the past.

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