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Assessment of the Heavy Metal Pollution in a Gold "Garimpo"

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PRESENTATION

The assessment of the presence and concentration of heavy metals in active mining areas is one of the concerns of the geochemistry and environmentalists.

Which effects, if any, the drainage waters of the Brazilian wetlands, the "Pantanal", are to exist when gold mining is in operation in a very sensitive ecological area.

This work of Geol. Saulo Rodrigues Filho and Prof. John Maddock was presented at the "International Symposium on Perspectives for Environmental Chemistry in Tropical Countries" held in Niteroi, Brazil, in December of 1993, at the UFF - Fluminense Federal University.

Editing problems hindered the publication of this work up to now.

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Roberto C. Villas Boas
Director

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ABSTRACT

Gold has been exploited in the Poconé region, in Mato Grosso State in Brazil, during the past 13 years using “garimpo” methods. In this research, background levels of metals were determined by analyzing sediments and soils unaffected by mining activities, located upstream of the anthropogenic inputs. The study made in Poconé focuses on Hg, Cu, Pb, Zn, Fe and Mn.

In addition, the study aims to evaluate the level of contamination in sediments, soils and water, taking into account drainage waters directly affected by gold mining.

As the physical-chemical parameters of the waters are subjected to seasonal variations, they were monitored throughout the year for interpreting the behavior of the metals in the studied environments.

In general, the concentrations of Cu, Pb, Zn, Fe and Mn presented values very close to the background in sediments, while the concentrations of mercury in sediments showed anomalous geoaccumulation indexes.

Key words: *Poconé, environmental, gold mercury, heavy metals*

1. INTRODUCTION

Mining inevitably involves upsetting the balance between the various environmental compartments lying in the area of influence. This environmental impact can, however, be minimized by using environmentally compatible mining and ore dressing techniques, and by developing new technologies for treating ores, effluents and contaminated solid tailings.

Informal mining, in the form of *garimpos*, as a rule uses rudimentary mining and processing methods, which reflect the unreliable environmental control practised by the *garimpeiros*.

The *garimpo* region of Poconé-MT was originally founded on the discovery of goldbearing occurrences in 1777, by the *bandeirantes* (bands of explorers). After the main occurrences had been depleted, the founders of the town then took to cattle-raising, which has been an important activity in the region until today (CETEM/CNPq, 1991).

With the rise in the price of gold in the international market in the early 80s, a second gold cycle began in the region, when the development of the hitherto antieconomic mineral deposits became promising. The traces left by the *bandeirantes*, such as the horizons of reworked rocky fragments, were used in many cases as a reference when prospecting orebearing areas.

This study was developed under the "Environmental Technology Development-DTA", Program, set up at CETEM/CNPq - Centro de Tecnologia Mineral - in 1989, which focuses on harmonizing mining activities with environmental protection.

Researchs on environmental geochemistry presuppose the establishment of a reference level which expresses the natural concentration of a given element in the environment, commonly

known as the background level. For such a regional standard to be established, analyses of traces are necessary in samples that are free from anthropogenic inputs.

While the concentrations of trace metals in aquatic systems are extremely variable, as much on a global as on a local scale, besides analytical conclusions, geological reconnaissance of the watershed is necessary, paying special attention to mineralogy, so that it is possible to estimate the availability of each element with regard to the action of weathering (Salomons & Förstner, 1984).

Many possibilities have been proposed for establishing background values for trace metals in sediments. Förstner & Wittman (1979) have described the following alternatives:

a) Average concentration in schists as a standard value at global level.

b) Average concentration in sedimentary rocks, typifying the deposition environment and taking into consideration autochthonous and allochthonous natural mechanisms and factors.

c) Average concentration in recent unpolluted sediments.

d) Concentration and dating in sediment layers, making it possible to identify the historical record of the natural events that occurred in a certain drainage water.

The purpose of this study is to determine the distribution of the natural background concentrations of mercury (total Hg) and other heavy metals (Cu, Pb, Zn, Fe and Mn), found in soils, sediments and water of the *garimpo* region of Poconé-MT, using that distribution as a reference for assessing the degree of contamination of the aquatic system by heavy metals.

For recognizing the background levels, drainage waters were chosen which had not been directly affected by gold mining, so as to avoid the occurrence of anomalies resulting from mineral dressing (concentration of minerals rich in heavy metals, addition of mercury, etc...).

Additionally, the study seeks to assess the degree of contamination in soils, sediments and water, using as a reference drainage waters that have been clearly affected by the *garimpo* activity.

2. AREAS STUDIED

The municipality of Poconé-MT is in the region of the upper stretch of the Paraguay River, along the northern edge of the Pantanal Matogrossense, 100 km southwest of Cuiabá, the state capital.

The subject of the study was the subbasin of the Bento Gomes River, whose main tributaries are the streams Guanandi, Formiga and Piraputanga, lying in an area of approximately 1700 km² of the Poconé Sheet (SE.21-X-A-1/DSG), with latitudes between 16°00' and 16°30'S and longitudes between 56°30' and 57°00'W.

The Poconé region is represented by the detritic metasedimentary sequence of the Cuiabá Group, of older proterozoic age (800 to 600 m.y.), composed of sericitic, graphitic and pyritic phyllites, micaceous ferruginous quartzites and metaconglomerates showing flattened pebbles suboriented parallel to the schistosity, imposed by metamorphism in the green schist facies.

In that region, the *garimpeiros* have mined gold from both lateritic overburden and from quartz veins rich in gold which, as they are hydrothermal in origin, concentrated the gold found in the surrounding rocks of the Cuiabá Group. It is, therefore, a primary gold deposit with supergenic enrichment.

The mining is usually done jointly by the owners of the heavy machinery (loader, drag-line, hammer mill, centrifuge, etc.) and the manual workers. The former are responsible for working the surface layers of alteration of rocks ("bench") and for dressing the ore, whereas the latter are in charge of opening trenches along the orebearing veins. This joint work in some cases can go down

as deep as 50 meters, and is predominantly marked by the following characteristics:

- a) Exploration of "dry" areas, disassociated from the drainage waters;
- b) The use of grinding in the dressing process;
- c) Deposition of tailings in containment dams;
- d) Closed-circuit amalgamation (using water tanks); and
- e) Retorts are not used.

3. MATERIALS AND METHODS

The sampling campaign at Poconé was planned to cover areas where there were different variables that would affect the concentration of heavy metals in sediments, soils and water, that is, differentiations with regard to the rocky substrate, characteristic of the drainage waters, vegetation, pedological horizon (soils) and nearness to the *garimpos*. Hence, the points where sampling of sediments and water (PG notation) and soils (GB notation) was to be done were selected by identifying places with distinct characteristics in relation to such factors, amounting to a total of 21 samples of current sediments, 13 samples of water and 27 soil samples.

The current sediment samples were collected in compound form, that is, at the same collection station an average of 5 aliquot parts of samples were removed in a radius of approximately 10 meters. The soil and sediment samples were cooled (0°C) after collection, and packed in plastic bags, whereas the filtered water samples were acidified with concentrated HNO₃, in the proportion of 2 ml of acid for each liter of water, and stored in polyethylene bottles.

The subject of the study was the grain size fraction <74 µm of sediments (silt and clay), because this fraction most represents the solid-liquid interaction processes (Salomons & Förstner, 1984). Furthermore, that fraction had been used by other authors in studies for assessing contamination by heavy metals in water, thereby representing a good correlation parameter (Lacerda et al., 1991; Malm et al., 1989; Ackermann, 1980).

At all the sampling points (PG notation) *in situ* measurements of temperature, pH, Eh and drainage conductivity were taken. The physical-chemical parameters were determined using special

DIGIMED models DMPH-PV and CD-2P pH, redox potential and conductivity meters.

The volume of filtered water at each point, averaging 0.5 liter, was used to assess metals in the dissolved phase.

The analytical methodologies used in this study were divided according to the chemical element involved and the type of sample to be assessed. All the analytical determinations were made in duplicate.

The assessments of total mercury in soils and sediments were done using an atomic absorption spectrophotometer with cold vapor generation, a CG 7000 MAX 8 spectrophotometer belonging to CETEM/CNPq's analytical chemistry laboratory. The methodology used followed that optimized by Malm et al. (1989), where the samples are dried in an oven (50°C). After cooling, the samples are oxidized with potassium permanganate 5% for 30 minutes at 60°C and neutralized with hydroxylamine hydrochloride 12% (EPA, 1983).

Additionally, interlaboratory calibration was done between CETEM and the Sedimentology Institute of Heidelberg University, where the mercury analyses are done with an atomic absorption spectrometer used only for mercury analysis - "Mercury Analyser Hg-254 A" Seefelder Messtechnik. This analytical method was originally developed by Poluektov and Vitkun 1963 (in Welz, 1985) and is based on mercury vapor generated by a nebulizer immersed in an aqueous medium, through reduction of the ionic mercury by a stannous chloride solution. The mercury vapor is then taken to the absorption cell by the air flow produced by a peristaltic pump.

The sediment samples digestion procedure used by the Sedimentology Institute uses aqua regia for 3 hours at 150°C, while each reaction tube has a condenser to avoid losses during digestion.

The water samples were analyzed for mercury, using the Hg-254 A mercury analyzer, and for Pb, Cu and Ni, using a Perkin-Elmer 3030 B atomic absorption spectrometer and a HGA-600 graphite furnace.

The methodology used for analyzing the mercury in water is based on oxidation of the metal by adding potassium permanganate, nitric acid, sulfuric acid and potassium persulfate. It is left in a double boiler for 2 hours at 95°C. Then neutralization by hydroxylamine hydrochloride follows and reduction by stannous chloride. After which a reading is taken (methodology suggested by the manufacturer).

In the graphite furnace analysis of the metals in water does not require any preliminary treatment, because the sample is submitted to a series of temperatures rises before atomization, which frees it from interfering substances.

The methodology used for analyzing Cu, Pb, Zn, Fe and Mn, in sediments, soils and rocks, uses the atomic absorption spectrometry technique, while the samples are digested in a triacid solution of HNO₃, HCl and HF (2:2:1) at 120°C in teflon crucibles and recovered with HCl (Welcher, 1975).

4. RESULTS AND DISCUSSION

4.1 Physical-Chemical Description of the Poconé Drainage Waters

As they are subject to seasonal variations, the physical-chemical variables were determined at different times of the year, so that their variation intervals could be known. In this study, the field stages contemplated the dry season from September to November, and rainy season from January to May.

The pH values recorded in Poconé during the dry season (September, 1992) showed slightly alkaline neutrality conditions, varying from 6.9 to 8.0. The highest pH values (7.8 and 8.0) were recorded in drainage waters which cross the savannah, particularly in the Formiga stream and at the point PG-04 of the Bento Gomes River.

During the rainy season (January, 1992), the pH values were slightly acid, varying from 6.1 to 6.9, while the biggest drops in pH were noted in the drainage waters of the savannah, whose volume is much less than the drainage waters of the lowlands of the "Pantanal". Hence, it is rightful to expect that these drainage waters would be more subject to the influence of rain water containing dissolved CO₂, and leached humic substances.

The Eh values revealed a more oxidizing potential in the dry season, both in savannah and "Pantanal" drainage waters, varying from 193 to 260 mV. During the rainy season, slightly less oxidizing conditions were found, with Eh values varying from 163 to 210 mV.

Data obtained on the electrical conductivity as a rule showed low values, oscillating between 48 and 124 µS/cm. There was an exception at some sampling points in a savannah environment:

PG-04 in the Bento Gomes River, Formiga stream and Japão stream. In those places the concentrations of dissolved salts were considerably higher, with conductivity values of up to 1000 μ S/cm. In September, 1990, the waters of the Formiga stream showed 770 and 1000 μ S/cm. The decline of these values in the rainy seasons (400 and 250 μ S/cm) showed a strong seasonal dependence which in this case is represented by the effect of dilution caused by the rains. The experimental error involved in the electrical conductivity measurements may reach variations of up to 2 μ S/cm around each determination.

The Eh-pH stability diagram of the mercury, according to Hem, 1970, reveals the stability of the metallic mercury, aqueous Hg^0 , for the conditions found in the Poconé drainage waters, imparting low solubility (<25 ppb) to the metal which is poured directly into the rivers and streams as liquid effluent from the gold concentration amalgamation process. Even with the minor Eh and pH variations resulting from seasonality, all the measurements lay within the stability field of the Hg^0 . However, it is possible to note a tendency of the measurements made in the dry season as they approached the high solubility region, where the stable forms of the metal are Hg_2^{2+} and $Hg(OH)_2$.

Very little is yet known about the oxidation of Hg^0 to Hg^{2+} and the subsequent methylation to CH_3Hg^+ and $(CH_3)_2Hg$. It is known that microbial activity is related to the two reactions, but the bacteria which is able to oxidize the Hg^0 , in general, is not the same one which causes the methylation of the Hg^{2+} (Silver, 1984). Therefore, the stability diagram of the mercury must be analyzed as a means of partial interpretation, because it does not consider the biotic component (microbial) which can intermediate the metal's oxidation reaction.

According to Salomons & Förstner (1984), the monomethylation of mercury phenomenon is accelerated under mildly acid and low electrical conductivity conditions, while under alkaline and high conductivity conditions, the main product of the

methylation is dimethylmercury, which is highly volatile and much less stable than the monomethylated form.

Besides mercury, lead and copper were also considered for interpreting the thermodynamic equilibrium of these elements, under the physical-chemical conditions found in the drainage waters of the Poconé region.

In the lead stability diagram, according to Rose et al (1979), we noted that the values obtained in the dry season are included in the stability field of cerussite (PbCO_3) with low solubility ($<10^{-6}$ M). During the rainy season, however, the values obtained favored the stability of the Pb^{+2} ion, making the metal more mobile. Although in the presence of the Cl^- ion, the formation of PbCl_2 would occur, which shows low solubility.

In the Eh-pH stability diagram of copper we noted behavior similar to that of lead. During the dry season there is a predominance of measurements in the stability fields of tenorite (CuO) and cuprite (Cu_2O), where the molarity of the dissolved copper is lower than 10^{-7} . During the rainy season we noticed a shift to the stability field of the Cu^+ ion, where the molarity of the dissolved copper increases.

4.2 Distribution of Heavy Metals in Subdrainage Basins of the Poconé Region

4.2.1 Subbasin of the Formiga Stream

The concentrations of heavy metals found in samples of bottom sediment - fraction $<74 \mu\text{m}$ - of the Formiga and Japão streams, showed values compatible with the background levels known at world level, except for mercury which showed considerably high values, with an average of 0.91 ppm.

Assessments of the concentration of heavy metals made by Förstner & Müller (1974), in subrecent sediments of the Rhine river in Germany, that were free from anthropogenic inputs, showed levels compatible with the values found in the Formiga stream for Cu, Pb, Zn, Fe and Mn. The average concentration of mercury, however, is almost five times higher in the sediments of the Formiga stream.

In this study, a comparison will be made of the "Geoaccumulation Indexes" (Igeo) of metals in sediments, as a methodology for assessing the pollution level of heavy metals in an aquatic environment (Müller, 1979). The "Igeo" is defined by the following expression:

$$I_{geo} = \frac{\log_2 C_n}{1.5 \times B_n} \text{ where,}$$

C_n is the measured concentration of the element in the fraction <2 μm (clay) and B_n is the background value of the element found in subrecent clayey sediments and schists. Hence, the "Igeo" in class 0 indicates absence of contamination, and the "Igeo" in class 6 represents the upper limit of maximum contamination.

The grain size fraction <74 μm (silt and clay) used in this study can also be applied to the "Igeo", according to Salomons & Förstner (1984), provided there is a definition of the background values existing in that grain size fraction.

4.2.2 Subbasin of the Guanandi Stream

The Guanandi stream, which flows into the Bento Gomes River, is the drainage water most directly affected by the physical and chemical disturbances resulting from *garimpo* activity in Poconé. The principal mining and ore dressing fronts of the *garimpos* are scattered through areas near the spring, and

principally in the last 10 km of its course, downstream of the MT-111 highway.

It is interesting to note the concentrations of mercury in the PG-01 and PG-03 stations. At these sites, the samples were essentially formed of sandy sediments and rocky fragments (tailings), due to the nearness of the dressing fronts of the *garimpos*. The concentration troughs ("cobra fumando"), which are particularly prevalent in those areas, besides concentrating the ore, cause the remobilization of fine particles which end up being deposited in stretches downstream of the *garimpos*. It was found that the concentrations of mercury in these samples were as low as the detection limit, of 0.04 ppm, while the samples originating in areas further away from the ore dressing fronts, and rich in silty-clayey fraction, showed mercury concentrations corresponding to the "Igeo" in classes 1 and 2 (Table 1).

The fact that the mercury concentrations are so low in areas near the sources of mercury emission of the *garimpos*, seems to be due to the coarse grain size of those sediments which, because they do not participate significantly in the solid-liquid interaction processes, of the physical and/or chemical adsorption type, give the mercury emitted by the amalgamation process an accentuated heterogeneous distribution. Such evidence strengthens that presented by other authors, who claim that the transportation of mercury in an aquatic medium is controlled by the suspended sediments (Lacerda et al., 1991; Murdoch & Clair, 1986 and Silva et al., 1991).

Table 1 - Concentration of Heavy Metals in Bottom Sediments - <74 μ m - of the subbasin of the Guanandi Stream - Poconé

Sediments	Hg		Cu		Pb		Zn		Fe		Mn	
	ppm	Igeo	ppm	Igeo	ppm	Igeo	ppm	Igeo	%ppm	Igeo	ppm	Igeo
Guanandi Stream												
PG-01	<0.04	0	324	5	45	0	35	0	4.7	1	790	2
PG-02	0.08	0	8.0	0	28	0	46	0	3.2	0	130	0
PG-03	0.04	0	32	2	52	1	76	1	2.6	0	820	2
PG-11	0.50	2	41	2	28	0	60	0	2.9	0	1100	2
PG-12	0.60	2	40	2	36	0	120	1	4.3	1	1780	3
PG-14	0.20	1	12	0	32	0	106	1	1.7	0	420	1
PG-15	0.15	1	15	0	20	0	95	1	2.4	0	330	0
PG-16	0.04	0	24	1	36	0	70	1	2.5	0	410	1
Average	0.21	1	62	3	35	0	76	1	3.0	0	722	1
Standard Deviation	0.21		98		11		31		1.0		442	
Local Background	0.10		10		32		43		2.6		260	

Igeo = Geoaccumulation Index

With regard to copper and lead, entirely distinct behavior was noted. The greatest concentrations of these metals were found mostly in the PG-01 and PG-03 stations, where there is a predominance of tailings from the *garimpos*. In those cases, the source of emission was said to be partly anthropogenic and partly lithogenic, because the gravity concentration process used by the *garimpeiros* retains not only the gold, but also all the high density minerals, i.e. oxides, sulfides and ferromagnesium silicates. These minerals may contain anomalous concentrations of copper, lead and iron, among other metals (Loring, 1978). After the ore concentrate amalgamation stage, these accessory minerals then form part of the amalgamation tailings, which often pass through the trough again, and are then mixed with the gravity concentration tailings.

Although the concentrations of these metals in sediments may be somewhat high, the sediments cannot be considered absolutely polluted, due to a probably low bioavailability of the metals they contain. These elements would have reached the

drainage waters not only due to weathering of their minerals, which would increase mobility and possibly their bioavailability, but by the mechanical action of mining and dressing in the *garimpos*.

The low mobility of trace metals in the subbasin of the Guanandi stream is indicated by the low concentrations obtained in filtered water samples (dissolved phase). Only the PG-12 sample showed an anomalous concentration of copper (Table 2).

Table 2 - Concentrations of Heavy Metals in Drainage Waters of the Guanandi Stream Subbasin Compared with Uncontaminated Rivers.

Drainage Waters	Hg (ppb)	Cu (ppb)	Pb (ppb)	Autor
Guanandi				This study
PG-01	nd	nd	1.0	
PG-02	nd	nd	nd	
PG-03	nd	nd	nd	
PG-11	nd	nd	nd	
PG-12	nd	9.2	0.9	
PG-13	nd	0.4	nd	
PG-15	nd	nd	nd	
Uncontaminated Rivers	0.01	1.0	0.2	Salomons & Förstner (1984)
at world level	0.07	7.0	1.0	Drever (1982)
Uncontaminated rivers of the amazon	<0.04	-	-	Pfeiffer et al. (1989)

nd = 0.1 ppb (not detectable)

As to the soils of that subbasin, no significant differences were noted in the behavior of heavy metals, compared with soils of the Formiga stream subbasin. Nonetheless, for all the metals, the average concentrations found at horizon A of the Guanandi subbasin were slightly higher. Whereas at horizon B, the average concentrations of Hg and Cu were slightly lower than those noted in the Formiga stream (Table 3).

It is also possible to identify a direct correlation between the Hg and Cu concentrations in the soils of the Guanandi subbasin

(Figure 1). This correlation seems to indicate a common lithological origin for those elements, possibly related to weathering of sulfide rocks. The coefficient of correlation between the Hg and Cu concentrations in the soils, calculated at 0.765, confirms the existence of a marked correlation between those two elements in the samples studied.

Table 3 - Concentrations of Heavy Metals in Soils of the Guanandi Stream Subbasin Compared with Background Concentrations Found in the Formiga Stream Subbasin

Soils	Type of Soil	Hg (ppm)	Cu (ppm)	Pb (ppm)	Zn (ppm)
Guanandi	(Horizon)				
GB-1B	Organic (A)	0.07	10	25	13
GB-1C	Lateritic (B)	0.05	16	69	28
GB-1D	Saprolitic (C)	0.06	23	50	17
GB-3B	Organic (A)	nd	15	37	58
GB-4A	Organic (A)	nd	35	50	60
GB-4B	Lateritic (B)	nd	40	53	42
GB-9A	Organic (A)	0.07	76	112	64
GB-9B	Lateritic (B)	0.08	110	71	81
GB-9C	Lateritic (B)	0.07	62	32	50
GB-12B	Organic (A)	nd	35	26	20
GB-20A	Organic (A)	0.17	40	4.4	26
GB-20B	Lateritic (B)	0.14	96	5.6	19
GB-20C	Saprolitic (C)	0.24	54	32	21
GB-21B	Organic (A)	0.12	74	22	32
GB-22B	Sandy (B)	0.32	136	5.2	84
Average	Horizon A	0.08	41	39	38
Average	Horizon B	0.12	77	39	50
Background	Horizon A	0.05	28	34	29
Background	Horizon B	0.15	89	21	5

nd < 0.04ppm

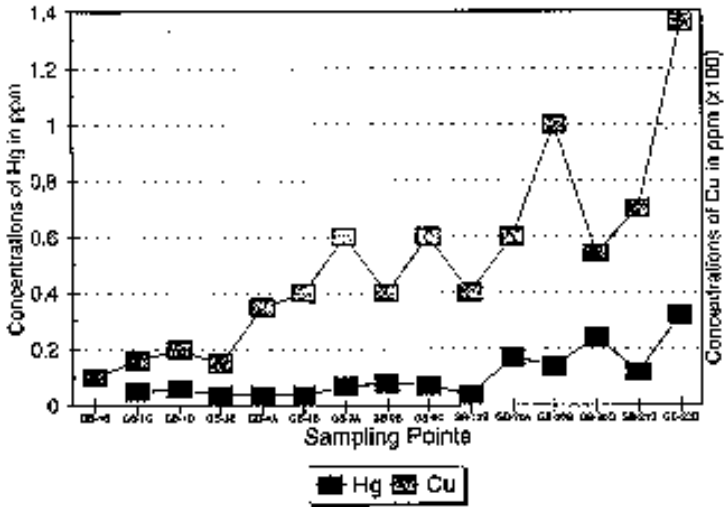


Figure 1 - Correlation between the Hg and Cu concentrations in the soils of the Guanandi stream subbasin.

4.2.3 Subbasin of the Bento Gomes River

As the main drainage water of the Poconé region, the Bento Gomes River receives the flows of all the drainage waters described above, except for the Formiga stream (Map 1). Hence, it is the final depository of the matter carried by the tributary drainage waters and, therefore, is the main focus of this study.

At the lake where station PG-24 is situated, there is an accentuated drop in the carrying capacity of the Bento Gomes River, where the land slopes gradually to then form part of the wetlands of the Pantanal Matogrossense.

The reduced carrying capacity results in higher sedimentation rates, particularly of suspended sediments. This means that the waters in such places have very low turbidity. This is a characteristic of the Pantanal Matogrossense and consists essentially of suspended organic particles.

Approximately 40 km upstream of station PG-24 is station PG-04, where the Bento Gomes River drains a typical savannah environment without impacts caused by *garimpeiro* activity. The concentrations of metals in that station are very similar to the concentrations found at station PG-02, in the Traíras stream, where also there are no activities related to the *garimpo*.

The average concentrations noted using stations PG-04 and PG-02 as a basis, must therefore reflect the natural levels of occurrence of heavy metals in sediments (background). The mercury background, equivalent to 0.10 ppm, found in current sediments in the fraction $<74 \mu\text{m}$, was higher than the value found in lacustrine sediments in remote areas of the Pantanal Matogrossense, which is equivalent to 0.02 ppm of Hg (Lacerda et al., 1991). Probably, this lower value in lacustrine sediments is due to the great distance from the main lithogenic sources of mercury, allied to the extremely low carrying capacity of the waters throughout the Pantanal lowlands. On the other hand, the local Hg background corresponds to half the average

concentration noted in uncontaminated clayey sediments (fraction $<2 \mu\text{m}$) of the Rhine, in Germany, of 0.20 ppm (Förstner & Müller, 1974).

The relatively high local background concentration of mercury seems to be related mainly to the dissemination of pyrites in the metasedimentary rocks of the Cuiabá Group, which make up the region's rocky substrate, and which as verified, can contain anomalous mercury concentrations (the weathered pyrite crystals contain an average 0.13 ppm).

The study done by Andrade et al. (1988), in the *garimpeiro* region of Pilar de Goiás, shows the occurrence of a very high (0.77 ppm) mercury background level in sediments, in the fraction $<106 \mu\text{m}$. That region is included in the Crixás Greenstone Belt, formed of basic and ultrabasic metasedimentary and metamorphic rocks, among others. The gold mineralization is associated with the occurrence of arsenopyrites and chalcopyrites.

The local background levels of the other metals studied in the Poconé region revealed concentrations that were still lower than those reported by Turekian & Wedepohl (1961) for uncontaminated clayey sediments at world level, except for lead (Table 4).

It is noted that starting from Station PG-19, near the *garimpo* called "Fazenda Salinas", as far as the vicinity of the confluence of the Guanandi stream, stations PG-08, PG-17 and PG-18, the concentrations of metals in the sediments of the Bento Gomes River become higher, showing the ingress of sediments more polluted by heavy metals (Map 1).

Table 4 - Concentrations of heavy metals in bottom sediments of the Bento Gomes river subbasin and geoaccumulation indexes.

Sediments	Hg		Cu		Pb		Zn		Fe		Mn	
	ppm	Igeo	ppm	Igeo	ppm	Igeo	ppm	Igeo	ppm	Igeo	ppm	Igeo
Bento Gomes												
PG-04	0.12	0	12	0	36	0	40	0	2.0	0	390	0
PG-06	0.30	1	25	1	28	0	46	0	1.9	0	180	0
PG-08	0.10	0	23	1	29	0	32	0	1.7	0	640	1
PG-17	1.10	3	40	2	44	0	90	1	3.1	0	820	2
PG-18	0.25	1	24	1	36	0	60	0	1.9	0	470	1
PG-19	1.85	4	36	2	58	1	76	1	4.2	1	840	2
PG-24	0.70	3	92	3	76	1	120	1	2.8	0	1340	2
Average	0.63	3	36	2	44	0	66	1	2.5	0	668	1
Standard Deviation	0.60		24		16		29		0.8		350	
Local Background	0.10		10		32		43		2.6		260	
World Background ⁽¹⁾ C.S. ^(*)	0.20		45		20		95		4.7		600	

(1) Turekian & Wedepohl (1961)

(*) Clayey Sediments

At station PG-24, where the river forms a large lake, high concentrations of all the metals were observed, denoting a sink for heavy metals, because downstream of the lake the concentrations in sediments are considerably reduced, coming close to the background levels (Figure 2). This is further evidence that the transportation in an aquatic medium not only of mercury, but also of the other metals studied, is mainly related to the suspended sediments.

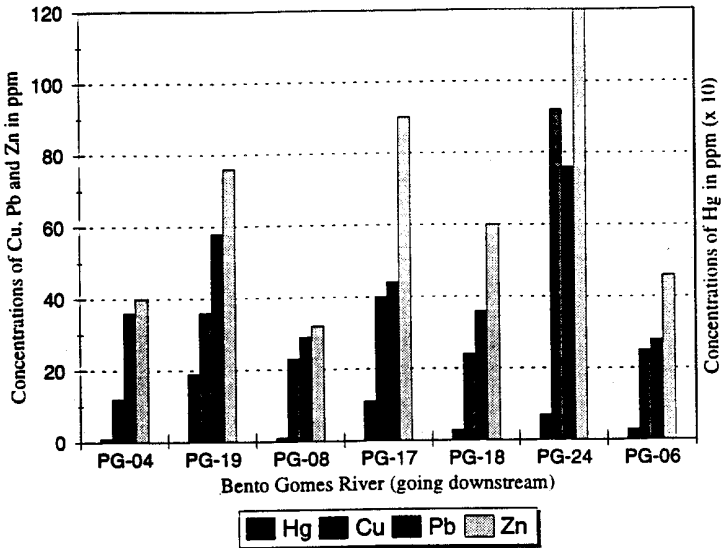


Figure 2 - Distribution of heavy metal concentrations in bottom sediments along the Bento Gomes River

When the correlation is established between the concentrations of mercury and iron found in current sediments, grouping together all the affected drainage waters, it is noted that there is a clear affinity in the behavior of the two elements, with a coefficient of correlation of 0.717. This shows that the iron oxides and hydroxides play an important role in retaining/transporting the mercury present in such drainage waters (Figure 3).

The "Geoaccumulation Index" noted at that site were the highest of these drainage waters, but even so they indicate, by and large, an only moderate degree of pollution (Table 4 and Figure 4).

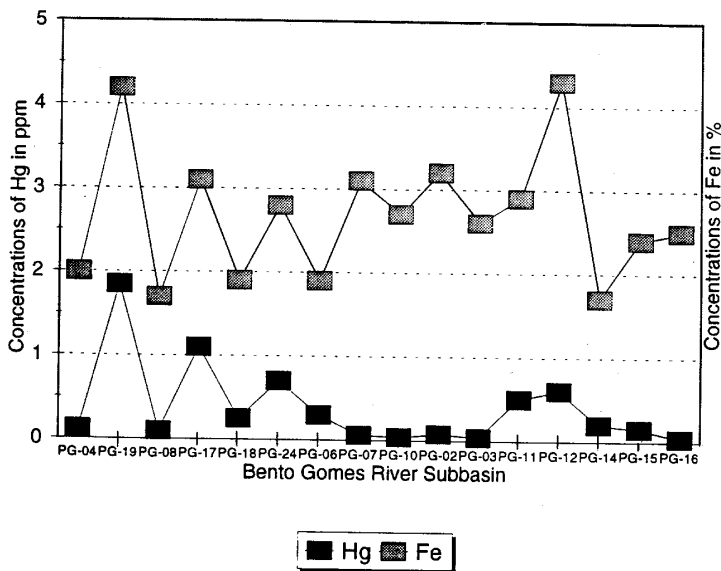


Figure 3 - Correlation between the Hg and Fe concentrations in bottom sediments of the affected drainages

If the origin of the mercury found in these samples is to be investigated, that is, to find out the extent to which they contribute to the anthropogenic and lithogenic sources, it would be necessary to make analytical determinations using selective extraction methods. However, the reliability of the results of these methods is still subject to verification, with regard to mercury (Veiga & Fernandes, 1990).

With regard to the concentrations of metals dissolved in samples of water from the Gomes River, low values were noted for all the metals, except for the PG-08 samples which showed

2.0 ppb of mercury and 1.5 ppb of copper, and PG-24 with 3.9 ppb of copper. Due to the nearness of that sampling station to the *garimpos* and to the gold buying shops, one could attribute this mercury anomaly to the atmospheric deposition of the metal which is emitted as vapor from the amalgam burning places (Table 5).

Table 5 - Concentrations of heavy metals in river waters of the Bento Gomes river subbasin compared with uncontaminated rivers.

Drainage Waters	Hg (ppb)	Cu (ppb)	Pb (ppb)	Autor
Bento Gomes				This study
PG-04	nd	nd	nd	
PG-06	nd	nd	nd	
PG-08	2.0	1.5	nd	
PG-24	nd	3.9	nd	
Uncontaminated Rivers at world level	0.01	1.0	0.2	Salomons & Förstner (1984)
Uncontaminated rivers of the amazon	<0.04	-	-	Pfeiffer et al. (1989)

nd < 0.1 ppb

5. CONCLUSIONS

It was noted that the concentrations of mercury in bottom sediments, water and soils of the drainage subbasins studied in the Poconé region showed anomalous indexes, compared with the local background values for sediments and soils, and compared with the known mercury concentrations for waters of uncontaminated rivers. In general, the metals Cu, Pb, Zn, Fe and Mn showed concentrations in sediments very close to the background values. The same occurred in the soils for Cu, Pb and Zn, and in waters for Cu and Pb.

In the subbasin of the Formiga stream, the anomalous concentrations of mercury in sediments, with an average "Igeo" in class 3, seem to be related to the marked occurrence of pyrite mineralizations in the phyllites, which were probably releasing the metal from their crystalline structure through weathering processes.

The electrical conductivity values found in the subbasin of the Formiga stream were high, reaching up to 1000 $\mu\text{S}/\text{cm}$, as well as in the other stations in the savannah environment. The pH values also were higher in those places, compared with the Pantanal environments, particularly during the dry season.

Considering all the physical-chemical measurements carried out in the Poconé region, it was noted that in the rainy season (January, 1992) there is more acidity, pH of 6.1 to 6.9, and a less oxidizing potential in the runoff waters, 163 to 210 mV. Although the Eh and pH values may indicate more Cu and Pb solubility in the rainy season, anomalous values were not found in the region's drainage waters, using as a reference the known values for uncontaminated river waters at world level. Only two water samples from the Bento Gomes River and one from the Guanandi stream showed slightly higher concentrations of copper, 1.5, 3.9 and 9.2 ppb, respectively.

In the subbasin of the Guanandi stream, where the presence of *garimpo* activities is strong, fairly high concentrations of mercury were noted, of 0.2 to 0.6 ppm, associated with sediments further away from the gold ore dressing fronts, with an "Igeo" in classes 1 and 2. The samples collected at points near the *garimpo* tailings showed minimum concentrations, of around 0.04 ppm, which may be explained by the predominance of quartz in those tailings whose grain size is coarse, and by the allochthonous origin of those materials.

With regard to copper and lead, the opposite behavior was noted, that is, the higher concentrations were associated with sediments near the gravity concentration tailings. The accumulation of copper and lead in those places could therefore be the consequence of the concentration of accessory minerals (more dense) from the gold ore dressing. The indication that these elements are contained in the crystalline structure of heavy minerals points to a low bioavailability of copper and lead in that drainage water.

A direct correlation was found between the Hg and Cu concentrations in the soils of this subbasin, indicating a common mineralogical origin for the two elements, possibly associated to the iron sulfides.

The geoaccumulation indexes of mercury in sediments of the Bento Gomes River indicate a relatively high degree of contamination at some points, even reaching class 4 (1.85 ppm) at the PG-19 station, near the *garimpo* of the Salinas ranch. However, when they reach the Pantanal Matogrossense, the mercury concentrations drop considerably, reaching 0.30 ppm. This is due to the accumulation of metals observed in the sediments of the lake of the Ipiranga ranch (PG-24), which retains a large part of the sediments transported by the Bento Gomes River. The preferential accumulation noted in that lake also occurred for the metals Cu, Pb, Zn, Fe and Mn.

A great affinity was noted between the Hg and Fe concentrations in sediments of this subbasin, indicating that the iron oxides and hydroxides play an important role in transporting mercury along the Bento Gomes River.

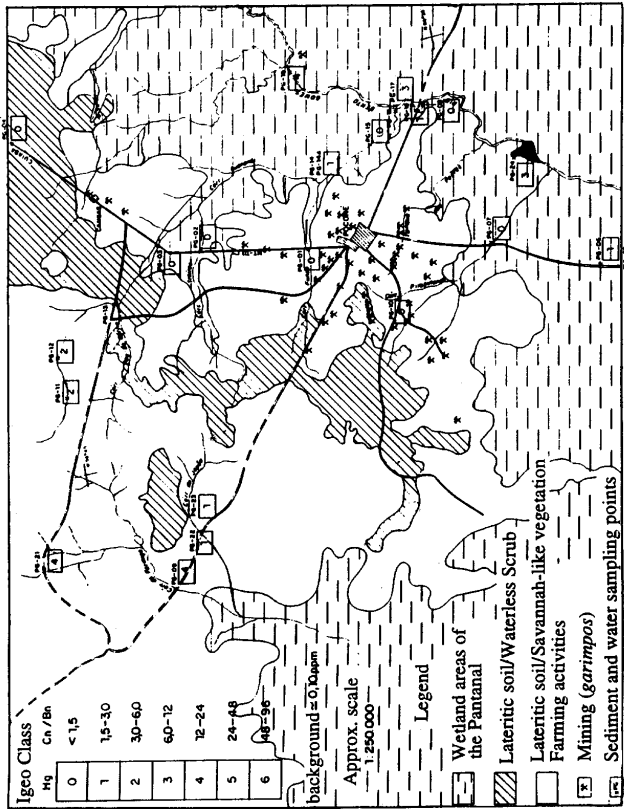


Figure 4 - Map of distribution for Mercury geoaccumulation indexes in sediments of the Poconé Région.

REFERENCES

1. ACKERMANN, F. (1980) A procedure for correcting the grain size effect in heavy metal analysis of estuarine and coastal sediments. *Environmental Technology Letters*. 1:518-527.
2. ANDRADE, J.C.; BUENO, M.I.M.S., SOARES, P.V. e CHOUDHURI, A. (1988) The fate of mercury released from prospecting areas (garimpos) near Guarinos and Pilar de Goiás, Go (Brazil). *An. Acad. Bras. Cienc.* 60:293-303.
3. CETEM/CNPq (1991) Poconé: um campo de estudos do impacto ambiental do garimpo (seg. ed. rev.). Org. por M.M. Veiga e F.R.C. Fernandes (*Tecnologia Ambiental*, 1). Rio de Janeiro. 113p.
4. DREVER, J.I. (1982) The geochemistry of natural waters. New York: Prentice-Hall. 387 p.
5. EPA-Environmental Protection Agency (1983) Methods for chemical analysis of water and wastes. Cincinnati. (EPA 600/4-79/020).
6. FÖRSTNER, U. & MÜLLER, G. (1974) Shwermetalle in Flüssen und Seen als Ausdruck der Umweltverschmutzung. Berlin: Springer. 225p.
7. FÖRSTNER, U. & WITTMANN, G.T.W. (1979) Metal pollution in the aquatic environment. Berlin: Springer. 486 p.
8. HEM, J.D. (1970) Chemical behaviour of mercury in aqueous media. In: U.S. Geol. Survey. *Mercury in the Environment (Professional Paper, 713)*. Washington. 67 p.p. 40-46.
9. LACERDA, L. D.; PFEIFFER, W. C.; MARINS, R. V.; RODRIGUES, S.; SOUZA, C. M. M. e BASTOS, W.R. (1991) Mercury dispersal in water, sediments and aquatic biota of a gold mining tailing deposit drainage in Poconé, Brazil. *Water, Air and Soil Pollution*. v.55, p.283-294.

10. LORING, D. H. (1978) Geochemistry of zinc, copper and lead in the sediments of the estuary and gulf of St. Lawrence. *Can. J. Earth Science*. v.15 p.757-772.
11. MALM, O.; PFEIFFER, W.C.; BASTOS, W.R. e SOUZA, C.M.M. (1989) Utilização do acessório de geração de vapor frio para análise de mercúrio em investigações ambientais por espectrofotometria de absorção atômica. *Ciência e Cultura*, v.41, n.1, p.88-92.
12. MUDROCH, A. & CLAIR, T.A. (1986) Transport of arsenic and mercury from gold mining activities through and aquatic system. *Science of Total Environment*. v.57 p.205-216.
13. MÜLLER, G. (1979) Schwermetalle in sedimenten des Rheins - Veränderungen seit 1971. *Umschau*. v.79 p.778-783.
14. PFEIFFER, W. C.; LACERDA, L.D.; MALM, O.; BASTOS, W.R.; SOUZA, C. M. M. and SILVEIRA, E.G. (1989) Mercury contamination in inland waters of Rondônia, Amazon, Brazil. *Science of Total Environment*. v.87/88 p.223-240.
15. ROSE, A.W.; HAWKES, H.E. and WEBB, J.S. (1979) Geochemistry in Mineral Exploration. London: Academic Press. 658p.
16. SALOMONS, W. & FÖRSTNER, U. (1984) Metals in the Hydrocycle. Berlin: Springer-Verlag. 349 p.
17. SILVA, A.P. (1991) Estudos biogeoquímicos sobre o mercúrio em ambientes aquáticos de Poconé. Rio de Janeiro: CETEM/CNPq (Série Tecnologia Ambiental, 1) p.61-83.
18. SILVER, S. (1984) Bacterial transformations of and resistance to heavy metals. In: NRIAGU, J. O. (ED.) Changing metal cycles and human health. Berlin: Springer-Verlag. p.199-224.
19. TUREKIAN, K.K. & WEDEPOHL, K.H. (1961) Distribution of the elements in some major units of the earth's crust. *Bull. Geol. Soc. Am.* v.72 p. 175-192.

20. VEIGA, M. M. & FERNANDES, F. R. C. (1990) Poconé: an opportunity for studying the environmental impact of the gold fields. In: INTERN. SYMP. ENVIRONM. STUD. TROPIC. RAIN FORESTS, 1, 1990, Manaus. Proceedings... v.1 p.185-194.
21. WELCHER, F.J., ed. (1975) Standard Methods of chemical analysis. 6 ed. Robert E. Krieger Publ. v. IIA, IIB, IIIA.
22. WELZ, B. (1985) Atomic Absorption Spectrometry. Weinheim: VHC Publishers. 506p.