MERCURY CONCENTRATION IN MARGIN SOIL OF THE MADEIRA RIVER

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ABSTRACT. The extraction of gold in the Amazon, since 1970, has grown fast from a politic that was resulted in the creation of gold extraction reserves in this region. In the Madeira River the gold exploration is noticeable because of the deposition of mercury in the environment. This metal is toxic and it resists to degradation process, transforming itself chemically, till it gets to its organic form, known as very toxic. Its extensive usage in the gold recover has caused impacts to the environment and consequently to the population, according to studies already done. This study has as its goal to value the pollution by Hg in soils and the variation according to soil fractions. The soils were collected by profiles in 10 areas in the Madeira River. The determination of organic matter was done, according (BRASIL, 1999). To Hg determination it was selected the fraction <200 mesh (<74 m), analyzed by atomic absorption spectrophotometer coupled vapor cold generation (Bastos et. al, 1998). Soils of the kind Latosols and hydromorphic were identified. The Latosols presented from 288 to 641 $g.Kg^{-1}$ of clay and from 266 to 111 $g.Kg^{-1}$ of thin send, from the horizon A₁ (superficial) to B₂ (sub-superficial). The increase of values of clay makes the function of organic matter in the superficial horizon better (from 20,2 to 19.0 %). The Hg concentration in these horizons varies from 25,5 to 641,4 $g.Kg^{-1}$ in the superficial horizon. The hydromorphic, especially, the Fluvic Neosols, present thin area, 396 to 57 g.Kg⁻¹ and clay from 254 to 654 g.Kg⁻¹ from A_1 to A_2 . The horizon A_2 presents 467 g.Kg⁻¹ of silt, 13,6 % of OM and 147,31 gHg.Kg⁻¹. Among the soils groups of the studied area, it is noticed more Hg concentration with the increase of values of silt and clay, that consequently presents more tenor of OM, and that subsidizes the organic mercury forming.

Words-key: mercury, Madeira River, soil, Amazon

INTRODUCTION

After events occurred in Japan and Iraq, with the people's death and still health problems occurrences due to mercury contamination, specifically methyl-mercury compounds, researchers groups proceeded studying this metal in environmental and human compartments.

The study in Amazon it owes to the mineral resources historical exploration, from 70 decade, that configured an new expansion in Amazon Brazilian, your due potential mineral, allied the great projects (national or foreign) and mining groups (Becker, 1991). Vainer (1990) it highlights these projects like source of a territory administration new form and which ones has a new formatting in the environment, due to fast and profound modifications in the populations life means and manners of the direct or indirectly affected areas. In the gold mining specific case in the region in study it has mercury (Hg) pouring out, noxious metal to the human health and that presents high toxicity (Silveira, 1998). During gold mining it uses mercury for its amalgams capacity with gold. Its extensive use in the gold recovery has been causing impacts to the environment and consequently to the riverside population. Studies accomplished for researchers Amazon group (Federal University of Pará, Evandro Chagas Institute, Environmental Geochemistry Laboratory/UNIR) demonstrate that the critical population is the riverside, because your protean source has like base the fish. When available for the ecosystem, Hg can transform in methyl-mercury (CH₃-Hg), toxic form of this metal. The CH₃-Hg can incorporate easily to aquatic biota throught biomagnification process could arrive until the human beings (Malm et al, 1997).

This study in the soil matrix in the spill of the Madeira river, between Porto Velho and Humaita-AM cities, is an attempt to understand the behavior of this in tropical environment, and which the level in this compartment. In synthesis, the goal is to evaluate the pollution by Hg in soils and your variation according to granulometric.

Gold mining historical in Rondônia

The gold mining artesian in Rondônia had beginning in 1739, when mining discover gold sparks in the Corumbiara river, tributary of the Guaporé river (Teixeira & Fonseca, 1998), however, the first official registration regarding gold discovery in this region, exactly in the Madeira river, date of 1826 in aluvion deposits nearby Ribeirão waterfall. This affirmation Adamy & Pereira (1991) they sustain from the written of Luis D'Alincourt,

"Memory concerning province border of Mato Grosso". However, only in 1978 had beginning the extraction process by means of the manual method, and, at the beginning of decade of 80 arose rafts and afterwards the dredges (Figure 1). In this same period it intensified the auriferous exploration in every stretch that comprehends the high Madeira River, overcoat of the claims Piriquitos, Santo Antonio and Belmonte.

The auriferous sedimentary deposits in the Madeira River occur in alluvial environment Holocene recent and old, where the old are represented for alluvial terraces, denominated of paleovalleys. These reach several depth meters with materials silt-clay predominance could insert two mining levels of gold found in alluvial mining of the Madeira river, that belong to very fine granulation, or be, powdered gold, peculiarity that complicates the separation of this too much particles ore extracted in mining process. To depart of this characteristic the amalgamation technique with Hg is the preferred process by mining in the gold recovery (Adamy & Pereira, 1991).

The Hg input in the Amazon ecosystem, specifically in the Madeira river, reached your maximum point at the end of decade of 1980, in the auriferous extraction summit. For each Kg extracted gold were used 4 Kg de Hg and from this total 1,32 Kg lost was for the environment. Between 65 to 75% to atmosphere through the amalgam burning and of 25% to 35% release directly in the fluvial system and in the soil, that occurred during the concentration process in the box of filtration, location where Hg is added to avoid gold losses (Pfeiffer & Lacerda, 1988; Bezerra, *et. al*, 1998; Kitamura, 1994).



Figure 1 – Spare gold mining in the Madeira river.

Fisiographic aspects of the Madeira River

The Madeira River rises from the confluence amidst Beni and Mamoré Rivers in the area of Nova Mamoré County, at the zone of the international border that divides Brazil and Bolivia. It drains all the east part of Bolivia, as well as the northern and western parts of the Rondônia State and south of the Amazonas State, covering about 1.350 km, flowing into the right edge of Amazonas River (Mortatti, 1987). From the confluence to the city of Porto Velho, the Madeira River's course is imposed by the local tectonic (breakings and imperfections). First, it flows in the south-north direction to the Abuna District where the water flow inverts to the northeast direction in which it follows transposing many Precambrian Rocky Formations as the waterfalls Jirau, Teotônio and Santo Antônio. In this draught, the volume continues over the plain underneath sedimentary lands of Tertiary, Quaternary and the Holocene of the Solimões Formation as far as its estuary in Amazonas (Brasil, 1996). The Madeira river, in the study area, exhibits very particular fluvial dynamics, where two distinct hydrological phases are jut out: the overflow, that occurs in the period of December to May coinciding relatively with the rainy period whose maximum average drainage floats between 35.000m³/s and 30.000 m³/s; and the reflux (the ebb tide), that happens among June and November, correspondent to drought station or few rain incidence

on the region, consequently the outflow presents minimum values between 5.000 m³/s and 10.000 m^3 /s (Figure 2) (Brasil, Op. Cit.).



Figure 2: Madeira River's streamflow (Linhares, 2004).

METHODOLOGY

For organic matter's percentages determination, Hg concentration and granulometric analysis, it was opted for the collection of soil samples through pedologic profiles (minitrench), with depth varying from 0 to 130 cm in a 20 km interval between each point. In a passage of 240 km, between Porto Velho - RO and Humaitá - AM, 10 profiles had been built, totalizing 41 samples, weighing 900g, identified by horizons or layers in accordance with the morphological description, for posterior in-lab analysis.

In the biogeochemistry parameter analysis, two methodological procedures were used: in the first one, used up for Brasil (1999), 20g of dry-air thin sand were selected in a 80 mesh bolter. After that, 500 mg of this sample was put in a 500mL *erlenmeyer*. 10mL of potassium dichromate solution was added on 0,2M ($K_2Cr_2O_7$ 1N) and, carefully, put straight in the 20 mL sulfuric acid solution (H_2SO_4), the *erlenmeyer* was slowly shaken for a good homogeneity. After that procedure, the samples were put to rest for 30 minutes an then, when finished the rest, 150 mL of phosphoric solution (H_3PO_4) was additioned in 5% of each sample and placed to rest for 10 more minutes. Again, the sodium fluorid (NaF) was added alone with 5 drops of 1% difenilamin in all the samples. The solubilization was concluded,

increasing ammoniacal ferrous sulphate on 0,5N (Fe(NH₄)₂(SO₄)₂.6H₂O), titulating them until get dark green. To finish, the volume of the solution spent in the sample preparation was registered.

The percentage of organic matter is set by the equation $[1-T/S] \times 10,3g.10g/Kg$. Three blank tests had been constructed in order to give trustworthiness to the results.

The granulometric analyses had been carried through at the Soil Laboratory of the Brazilian Company of Farming Research - EMBRAPA/RO through the pipette method. The fractions had been selected according to diameter, in the following categories: Thick sand (2 - 0,2mm), Thin sand (0,2 - 0,05mm), Silt (0,05 - 0,002mm) and Clay (lesser that 0,002mm). In this study, it was considered the values amount of thick and thin sand, by doing that, the total sand value was obtained (Brasil, 1997).

The second procedure was developed by Bastos *et al* (1998) for the Hg concentrating determinations. In this one, the samples had passed through a granulometric process where with <200 mesh ($<74\mu$ m) of the material. After drying and macerating, the samples had suffered acid extraction (HNO₃ and HCL) and were analyzed by spectrophotometer of atomic absorption with cold vapor generation (Flow Injection Mercury System - FIMS - 400). The analyses were accomplished in duplicate with white controls and samples of certified reference (IAEA-356) for the analytical quality guarantee.

RESULTS AND DISCUSSION

Based on Brasil (1999) classification, the physic-chemistry results indicate two groups of soil with four pedologic classifications. The first group, represented by the soils in which genesis consists basically on the removing of the silica and bases of the profile after intemperism of the main minerals. In this case, the soils formed after these proceedings show well-developed latosolic B horizons. In general, they occupy higher surface (fluvial Terraces), generally plateaus. Deriving from this process, we found the group of PlinthicYellow Latosols located in the community of Cujubim Grande-RO (Profile - 01), and Yellow Latosols in Itacoã-RO (profile-02).

The second group is originated from the rework of soil particles (transported and deposited) because of the water courser action, it might present permanent or periodic swam pines, which could influence disposal of soils on layers or horizons, it comes in accordance with the regional and local hydrologic fluvial regimen, which is submitted to the study area. The water excess, confers soils originated for Hydromorphism, a deficient, with slow

decomposition of organic matter and an environment with low potential of *oxi-reduction*, peculiarity that can transform particles of *Fe* and *Mn* and other soluble metals into form, facilitating its migration for other environments (plants) (Cunha and Guerra, 1998). With these characteristics, three soil classes in the study area have been observed: the first, *Gleisols*, situated in the areas of *São Carlos-RO* and *Calama-RO* Districts (Profile - 04 and 08) and still on *Curicacas-RO* community (profile - 05). The second class is very common in the main gutter of the Madeira River, formed by Fluvic Neosols, there was identified in the communities of *Primavera-RO* (profile-03), *Papagaios-RO* (profile-07), *Ponta Pelada-AM* (profile-09) and close to the town of *Humaitá* (profile-10). Finally, the third class Plintosols, located in *Cavalcante's* island (profile -06).

The space and time distribution of the Hg in soil occurs in accordance with pedogenetic process, which constitute soils and geographic localization of the contamination source. In case of the study area, [Hg] is associated to gold mineral prospecting activity developed in the Madeira riverbed. In this context, it is important to clarify that the referring research, the contamination of the Hg in soil in the Amazonian basin, especially the hydrographic basin of Madeira river, is incipient, however studies developed by Lacerda *et. al.* (1999); Linhares *et. al.* (2003), affirm that the dynamics of levels of this metal in soil has as subsidy, the availability of organic matter - *OM*. Added to that factor, the Hg tends to add less soils sized fraction (texture) of intemperate minerals (soil) less than 0,45 µm.

At profile - 01 (table 1) Plinthic Yellow Latosol have been identified according with the granulometric composition, possess clay texture, predominated in the superficial horizon (depth enters the 06 cm) bigger percentages of sand (412 g/kg), *Hg* (641,4 mg.Kg-1) and organic matter (20 g/Kg) and minors of silt (300 g/kg) and clay (288 g/kg). Also It has been observed in this profile, a continuous and significant decrease of the sand percentage (146 g/Kg) in the subsuperficial horizon B2 (depth 80+) with an increase of the clay fraction to 621 g/Kg, trend that is observed for the concentrations of Hg (140,46 mg.Kg-1) in two profiles of *Yellow Latosols*. The high concentrations in the A horizon of this profile, derives of the activity of gold mineral prospecting, still present in the region.

CLAY SAND Horizon Depth (cm) SILT Hg (µg.Kg⁻¹) OM (g. Kg⁻¹) 0 a 6 412 А 300 288 641.4 20.2 AB 6 a 19 300 304 19.7 396 147.36 BA 19 a 60 346 300 354 112.5 4.5 B1 60 a 80 262 384 454 87.83 0 B² + de 80 146 233 621 140.46 0

Table I – Profile (01) Results – Cujubim Grande (RO)

Profiles 03, 09 and 10 (Figures 3, 4 and 5, respectively) from Fluvic Neosols, have been originated from deriving layers stratified of the particulate deposition process (sediments in suspension and dissolved) carried by Madeira river. In this pedologic class, the biggest average mercury levels had been detected, between 147 mg.Kg⁻¹ and 61,76 mg.Kg⁻¹ and, still, values average of OM, between 7,70 g/Kg and 12,35 g/kg in the subsuperficial layer (depth >30 with) where evidences of the biggest values of silt, varying enters 184 g/kg to 634 g/Kg and clay oscillating 288g/kg to 654g/kg and minors values of sand (12 g/kg to 546 g/kg).



Figure 3: Profile 3 (Primavera-RO). Figure 4: Profile 9 (Ponta Pelada-AM).



Figure 5: Profile 10 (Humaitá-AM).

Profile-07 (figure 6), also a Fluvic Neosol, however of sand-clay texture, presented relevance of the percentages % OM and the granulometric analysis determination for the studies of Hg, therefore, despite the high value of OM (20,0 g/Kg) in relation to the analyzed profiles of *Neosols*, the levels of Hg (47,52 mg.Kg-¹) had been low, respectively, as well in the superficial layer as subsuperficial. We attribute this decrease in [Hg] to the percentile sand raised one, varying enters 579 g/kg to 796 g/kg and lowly percentage of silt, oscillating between 50 g/Kg and 200 g/Kg and of clay, 171g/kg to 221g/Kg.



Figure 6: Profile 7 (Papagaios - RO).

At the profiles 04, 05 and 08 were identified with *Gleisols*, whose origin is associate to the recent deposition sedimentary process, natural or not, to constant or periodic rises of the under ground water. This pedologic type is subdivided in Humic Glei, which receives this classification when posses relatively high levels of % MO, diagnostic horizon superior to 20 cm of thickness and dark coloration. Little Humic Glei presents minor thickness, clearer coloration and lesser levels OM in the horizon (Cunha and Guerra, 1998). The profile - 04 takes advantage of Humic Glei, when superficial horizon registered the biggest %MO (43,9 g/kg) in the study area. At this profile, the biggest mercury levels (90,04 mg.Kg⁻¹) has been determined in subsuperficial horizon (depth of 13 to 29cm), trend that is directly related to the high percentages of silt (350 g/kg), clay (438 g/kg) and sand decrease (212 g/kg). Profiles 05 and 08 of Little Humic Glei has presented average value of OM, among 11,84g/Kg to 13,47g/Kg, inferior to the previous profile, however the graters registered [Hg] at the profile-05 (97,96 mg.Kg⁻¹) and in profile-08 (76,9 mg.Kg⁻¹) was detected in subsuperficial horizon, where the silt and clay fractions present superior values compared to the sand. And, finally, Perfil-06, classified with *Plintosol*, has its related origin to the presence of plinthization process, with or without presence of petroplinthite or litoplinthic horizon. This soil presented maximum levels of Hg (92,80 mg.Kg⁻¹) in horizon "AB", subsuperficial (depth 15 to 62cm), as well as the granulometric fraction clay (588g/Kg), despite the low trench of silt (266g/Kg) and OM (3,0g.Kg⁻¹), this in relation to the horizon, which OM was 15,01g.Kg⁻¹ and silt 433g.Kg-1.

CONCLUSION

The biggest concentrations of Hg, in soils samples at the studied area (city *Porto Velho - RO* to *Humaitá - AM*), indicates that the granulometer of profiles analyzed confers it,

an clay texture, physics characteristics which allow a relative accumulation of organic matter, as well as bigger particle aggregation of Hg (except profile - 07 that presented sand texture).

Based on results and in accordance with pedologic origin, *Fluvic Neosols*, represents, on the analyzed classes, the soil with better parameters to understand the dynamics of space and time dispersion of this pollutant at Amazonian Basin.

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