Analysis of Mercury Grouping in Soil in the Foz of the Tapajós River, Amazonia-Brazil

Enilson da Silva Sousa ¹, Marcelo Augusto Machado Vasconcelos ², Joaquim Carlos Barbosa Queiroz³, Denison Lima Correa⁴

¹ Faculty of Technology in Geography - FTG / UFPA Ananindeua  
   Email: prof.enilson@gmail.com  
² Faculty of Technology in Geoprocessing - FTG / UFPA Ananindeua  
   Email: vasconcelos@ufpa.br  
³ Institute of Geosciences PPCCA  
   Email: joaquimqz@gmail.com  
⁴ Msc in Water Resources  
   Email: denison.singeo@gmail.com

Abstract— The region of Santarém, in the state of Pará, was chosen to carry out this research because it is at the center of discussions of mercury contamination in the Amazon. The objective of this paper is the analysis of Hg and Methyl-Hg speciation in soil. The methodological procedures to determine the total mercury and methylHg were carried out by means of samples, which were submitted to acid digestion and determinations of Hg performed by Atomic Absorption Spectrophotometry with cold vapor generation. The evaluation of the concentrations of mercury in the sampled and depth points was performed with the aid of cluster analysis, using the Hierarchical clustering method. The results obtained indicate that the total mercury in soil showed very high values in the analysis of total mercury with granulometry for fine fraction and gross fraction, indicating an urgent mobilization and political action in the municipal, state and federal spheres regarding the exposure of the environment environment to the mercury detected.

Keywords— Atomic Absorption, Granulometry, Environment.

I. INTRODUCTION

Mazonia is the region par excellence in the process of human environmental exposure, due to its geography and the presence of a vast hydrographic network. The monitoring and evaluation of the mercurial dynamics in the region and its consequences for local population, regional and global ecosystems are of great importance to suggest public policies and mitigate possible damages to health and the environment. An extensive literature deals with the possible effects of inorganic or methylated mercury on the local populations of the Tapajós region. The Amazonian populations, mainly riparian and indigenous, are potentially exposed to low concentrations of total mercury throughout their lives (PINHEIRO et al., 2007), and most studies show a positive relationship between fish consumption and high levels of Hg in hair (SANTOS et al., 1999; PASSOS et al., 2007). The highest concentrations (> 500 ppb) were found in carnivorous species, such as Plagioscion squamosissimus (white hake), Pseudoplatystoma spp. (surubim), Brachyplatystoma filamentosum (cub), B. fravicans (golden) and Cichlids Cichla spp. (TUCUNARÉ), among other carnivores (PINHEIRO et al., 2007), widely ingested and marketed by local communities. In this way, the commitment of the local fish will greatly affect the economic and environmental dynamics of these populations, especially the export trade that is controlled by the National Sanitary Surveillance Agency (ANVISA, 1998). Some of these studies refer to the effects on the cardiovascular system in these Amazonian populations and show that, for example, systolic and diastolic pressures are relatively low, however, there is evidence that this increases with age, and is related with high concentrations of total Hg in a population with minimal risk factors for hypertension and high environmental concentrations of Hg (FILLION et al., 2006). On the other hand, studies on age-related cataract (ARG) conducted in the lower Tapajós River (CARUSO PROJECT, 2010) indicated that one third (n = 69; 32.7%) of the participants presented ARG and presented individuals from this population with high levels of Hg, the cataratogenic effects of Hg can be reduced by the ingestion of selenium (Se) in their diets (LEMIRE et al., 2010). MeHg is primarily a neurotoxic agent, but its action could be antagonized by nutritional factors such as the ingestion of antioxidant vitamins present in Amazonian fruits (PASSOS et al., 2007), amino acids
(glycine, methionine, cysteine) (FARINA et al., LEMIRE et al., 2006), and minerals such as selenium (PINHEIRO et al., 2007).

The greater or lesser impact of high concentrations of total Hg in foods ingested by local populations and the ongoing study of neural diseases underscores the importance of implementing and maintaining public health programs for local people, especially riverine and indigenous peoples. As the inhabitants perceive this problem and how it will be the relation with the chronic mercurial disease, fact to be considered, is the other issue of the study here in focus from the application of IQ-MCS.

Thus, in this article, we seek to identify and analyze the speciation of Hg and Methyl-Hg in soil and particulate matter at the mouth of the Tapajós River, and the possible impacts on the health of the surrounding populations and the perception, mobilization capacity and political action on the contamination by this metal in the population of Santarém. This analysis will be carried out through the application of Integrated Questionnaires to Measure the Social Capital Index - QI-MCS, proposed by the World Bank, in 2003.

II. MATERIALS AND METHODS

The municipality of Santarém is located in the region of the mouth of the Tapajós river, confluence with the Amazon river, mesoregion of the Lower Amazon and the microregion Santarém, in the western portion of the state, with coordinates 02° 25'30" S and 54° 42'50" W (Figure 1). According to IBGE (2015), the municipality has a population of 294,580 habitants, an area of 22,887 km² and a population density of 12.8 hab./km².

The urban area of Santarém was chosen because it is the municipality directly associated to the contamination by this metal; the others were, the Village of Alter do Chão functions as an important tourist pole, in the state and national scenario and, therefore, an area directly impacted with possible dissemination of environmental contamination by Hg; The community of Arapixuna, located in the homonym hole, has its protein base in fish consumption, besides receiving seasonal influences from the waters of the Amazonas and Tapajós rivers; and communities along the Everaldo Martins Highway (Santarém-Alter-do-Chão), an area known as the Exo Forte.

For the soil sampling, the 6 points were selected, with a stratigraphic profile having 60 cm each, subdivided into fractions of 0-10, 10-20, 20-30, 30-40 and 40-60 cm, totaling 30 samples, for Fraction Grosso and 30 for Fine Fraction and collected during the dry season of the Amazon region (September and October). Samples of water and particulate material were collected at the six sampled sites.

At the end, statistical analyzes are performed by clusters (AC), which is a multivariate exploratory analysis technique that allows to separate or classify objects observed in a group or in a specific number of mutually exclusive subgroups or clusters of so that the subgroups formed have characteristics of great internal similarity and great external dissimilarity.

III. RESULTS

The dendogram of Figure 2 shows the groups formed for the localities in relation to the concentration of Hg Total, in soil in the Fina Fina at various depths. The method of grouping the averages (Average) presented better results, that is, the best ability to evidence the data structure, indicated by the correlation between the matrix of dissimilarity, or matrix of distances between each locality and the cofenetic matrix, generated by the dendogram. In this case, the correlation was 0.851, which characterizes a very good fit. Three homogeneous groups were formed: a group formed by the locality Alter-do-Chão (group 1), another by the localities Everaldo Martins and Lago Juá (group 2), and a third by the localities Lago Caranazal, Lake Itapari and Lago Caminho das Pedras (group 3).
For the concentration of HgTotal, in soil at the Coarse Fraction at various depths, the dendogram (Figure 3) showed 4 homogeneous groups: Everaldo Martins (group 1), Lake Caminho das Pedras (group 2), Itapari Lake (group 3) and Alter -do-Chão, Lago Juá and Lago Caranazal (group 4). The correlation between the distance matrix and the cofenetic matrix was 0.945, which indicates an optimal representation of the groups.

The analysis of the concentration of MeHg in soil in the fine fraction at various depths generated the dendogram (Figure 4). Four homogeneous groups were formed: Alter-do-Chão (group 1), Itapari Lake (group 2), Lake Caminho das Pedras (group 3) and Alter -do-Chão, Lago Juá and Lago Caranazal (group 4). The correlation between the distance matrix and the cofenetic matrix was 0.945.

Considering the concentrations of MeHg and HgTotal, in soil at the Fina Fina at various depths, the dendogram of Figure 5 was obtained and the same groups shown in the dendogram of Figure 3 were formed, that is, Alter-do-Chão (group 1), Lake Itapari (group 2), Lake Pedra (group 3) and Lake Juá, Everaldo Martins and Lake Caranazal (group 4). The correlation between the distance matrix and the cofenetic matrix was 0.956.

The evaluation of the depths in the various localities using the concentrations of MeHg and HgTotal in soil in the fine fraction generated the dendogram of Figure 6. In this case, the groups formed were: 40-60 Hg (group 1), 10-20 MeHg, 40-60 MeHg, 0-10 MeOH, 20-30 MeHg (Group 2), 30-40 MeHg (Group 3) and 0-10 Hg, 10-20 Hg, 20-30 Hg, 30-40 Hg (Group 4). It is observed that the concentrations of MeHg and Total Hg were in different groups. The correlation between the distance matrix and the cofenetic matrix was 0.943.
Techniques of multivariate statistics such as cluster analysis and discriminant analysis were used in geochemical studies (Moura, 1985; Oliveira; SHORE; CRUZ et al, 1998) and interrelationships between soil characteristics and crop productivity (Correia, 1993), and presented potential for use in the establishment and proposition of reference values of metals in soils. Fadigas (2006) used clustering analysis to separate polluted areas with heavy metal contents found in a given soil, with those in natural, ie non-polluted, or reference (standard) conditions. On the basis of soil characteristics present in each group, we could propose a model to obtain the heavy metal concentrations in soil from the correlation with other metals, and establish tolerance limit threshold and reference group, it was possible to propose a model to obtain the concentrations of heavy metals in soil from the correlation with other metals, besides establishing a tolerance limit and reference limit for the most diverse types of Brazilian soil. The groups obtained in soil studies, by similarity between the samples, also are composed of soils of different pedological classes, since soils of different pedological classes can present some chemical attributes and of granulometric composition in common (EMBRAPA, 2013); thus, samples of an A, B or transitional horizon of the same soil or of different soils may be present in the same group, provided that the concentrations of some of the variables considered in the cluster analysis are close. The groups for the analysis of the concentration of MeHg, in soil in the fine fraction, in the various depths, such as Alter-do-Chão (group 1), Lake Itapari (group 2), Lago Pedra (group 3) and Lake Juá, Everaldo Martins and Lago Caranazal (group 4). Considering the concentrations of MeHg and HgTotal in soil in the fine fraction at various depths, the correlation index was 95%, with the following grouping: Alter-do-Chão (group 1), Itapari Lake (group 2), Lago Caminho das Pedra (group 3) and Lake Juá, Everaldo Martins and Lago Caranazal (group 4).

Among the groups formed for the evaluation of the depths in the concentrations of MeHg and HgTotal, in soil in the fine fraction are: 40-60 Hg (group 1), 10-20 MeHg, 40-60 MeHg, 0-10 MeHg, 20 -30 MeHg (Group 2), 30-40 MeHg (Group 3) and 0 -10 Hg, 10-20 Hg, 20-30 Hg, 30-40 Hg (Group 4). The concentrations of MeHg and Total Hg were found to be in different groups. In all cases, the correlations were significant and the correlated environments presented characteristics of landscape, environment and geographical proximity very close.

### IV. CONCLUSION

With respect to contamination by Hg, were observed mean concentration values of Hg higher in the suspended particulate matter than in soil in fine fractions or crude fractions. However, most of the mercury in these waters is associated with the particulate fraction, indicating that the HgTotal in this river was derived predominantly from erosion. This particulate material rich in dissolved organic matter could be absorbing Hg0 and MeHg and distributing these chemical species along the biotic and abiotic compartments of the Amazonian ecosystem studied here.

### REFERENCES

[1] ANDRADE, H.; SCHAEFER, C.E. G. R.; DEMATTÉ, J. L. I.; ANDRADE, F. Vaz. Pedogeomorphology and micropedology of a hydroscopic quartz - sand latozol - sand sequence on crystalline rocks in the state of Amazonas. Geonomos, 5, 2010.

[2] WORLD BANK. Integrated Questionnaire to Measure Social Capital (QI-MCS). Thematic Group on Social Capital, July 2009.

[3] BOURDIEU, Pierre. The Symbolic Power. Publisher Bertrand Brazil S.A. Rio de Janeiro, 1989.

[4] BRAZIL. Brazilian Agricultural Research Corporation - EMBRAPA. Brazilian soil classification system. Humberto Goçalves dos Santos, 3 ed. Rio de Janeiro: National Soil Research Center, Embrapa Brasília, DF 2013.

[5] BRASIL, ANVISA - National Health Surveillance Agency. Portaria nº 685, of August 27, 1998. Available at: <http://www.anvisa.gov.br/ALIMENTOS/legis/especifica>. Accessed on June 29, 2016.

[6] CORREIA, J. R. Use of multivariate techniques in the study of interrelations of soil characteristics and eucalyptus productivity. Viçosa, UFV, 1993. Dissertation Master

[7] FADIGAS, F. S., Proposition of reference values for the natural concentration of heavy metals in Brazilian soils. Brazilian Journal of Agricultural and...
[8] FARINA, M.; ROCHA, J. B. T.; ASCHNER, M. Oxidative stress and methylmercury-induced neurotoxicity. Indianapolis: John Wiley & Sons; 2011. pp. 357-385.

[9] FOSTIER, A.H. et al. Mercury accumulation in natural forested Amazonian soils. In: INTERNATIONAL CONFERENCE ON MERCURY AS A GLOBAL POLLUTANT, 15. 1999. Rio de Janeiro. Proceedings ... Rio de Janeiro, 1999.

[10] FOSTIER, A. H.; OLIVEIRA, S. M. B.; GUIMARÃES, J. R. D. et al. Mercury accumulation in natural forested Amazonian soils. In: Proceedings of the Fifth International Conference on Mercury as a Global Pollutant. Rio de Janeiro, RJ, 1999.

[11] GUIMARÃES, J. R. D.; MEILI, M.; HYLANDER, L. D.; SILVA, E. D. E.; ROULET, M.; MAURO, J.B. N. et al. Hg net methylation in five tropical flood plain regions of Brazil: high in the root zone of floating macrophyte mats but low in surface sediments and flooded soils. Sci Total Environ, 2000a.

[12] IBGE, Technical notes: History of the investigation of color or race in the IBGE domiciliary surveys, Ethnic-racial characteristics of the Population: a study of the categories of color or race classification 2008. Web: http://www.ibge.gov.br . Accessed on February 10, 2015.

[13] LEMIRE, M.; FILLION, M.; FRENETTE, B.; PASSOS, C.J.; GUIMARÃES, J.R.; BARBOSA Jr, F. et al. Selenium from dietary sources and motor functions in the Brazilian Amazon. Neurotoxicology 2011; 32 (6): 944-53. (Electronic publication ahead of print). PubMed PMID: 21571000.

[14] LEMIRE, M.; FILLION M.; FRENETTE B.; MAYER A., PHILIBERT A., STEPS CJ, et al. 2010. Selenium and mercury in the Brazilian Amazon: opposing influences on age-related cataracts. Environ Health Perspect 118: 1584-1589.

[15] LEMIRE, M.; MERGLER, D.; FILLION, M.; PASSOS, C. J.; Page 2 DAVIDSON, R. et al. Elevated blood selenium levels in the Brazilian Amazon. Sci Total Environ 2006; 366: 101-11.

[16] LUCAS, Y.; BOULET, R.; CHAUVEL, A.; VEILLON, L. Systèmes Sols Ferralitiques-Podzols in Region Amazounienne, in D. Righi and A. Chauvel (eds.), Podzol et Podzolsisation, AFES / INRA, Poitiers, France, 1986.

[17] MOURA, C. V. A. Application of multivariate statistical treatment to soil geochemical data on geological mapping in the province of Carajás (target 2 - body 4). Brazilian Journal of Geosciences, São Paulo, v.15, 1985.

[18] OLIVEIRA, T. S.; COSTA, L. M.; CRUZ, C. D. Relative importance of the heavy metals of the soil in the identification and separation of source materials. Revista Ceres, Viçosa, v.45, n.260, 1998.

[19] PASSOS, C. J., MERGLER, D., FILLION, M., LEMIRE, M., MERTENS, F., GUIMARÃES, J. R. D., PHILIBERT, A. Epidemiologic confirmation that fruit consumption influences mercury exposure in riparian communities in the Brazilian Amazon. Environmental Research 105: 183-193, 2007.

[20] PINHEIRO, M. C. N.; CRESPO-LÓPEZ, M. E.; VIEIRA, J. L. F. T.; OKAWA, G.A.; GUIMARÃES, C. C.; ARAÚJO, W. W.; AMORAS, D. R.; RIBEIRO, A. M.; HERCULAN, J. L. M.; DO NASCIMENTO SILVEIRA, L. C. L. Mercury pollution and childhood in Amazon riverside villages. Environment International 33 56-61, 2007.

[21] ROULET, M.; GUIMARÃES, R. R. D.; LUCOTTE, M. Methyl Hg production and accumulation in sediments and soils of an Amazonian floodplain - effect of seasonal inundation. Water Air Soil Pollut, 2001a.

[22] SANTOS, ECO, Jesus, IMD, Brabo, EDS, Câmara, VDM, Loureiro, EC, Silva, DDFLD, ... & Cleary, D. Health Study and Mercury Exposure of the Ribeirinha Community of Brasília Legal, State of Pará, Brazil. Cad. Saúde Colet. 7 (2), José Bonifácio Foundation, Rio de Janeiro, 1999.

[23] SOUSA, S.E., et al. "Assessments of total mercury concentration in soil and particulate matter in floodable areas at the mouth of the Tapajós-PA, Fm. Alter do Chão, using remote sensing techniques." New NAEA Notebooks, 20