SPATIAL DISTRIBUTION OF METALS IN SEDIMENTS FROM GUARAPIRANGA DAM, SAO PAULO-SP/BRAZIL

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Spatial distribution of metals in sediments from Guarapiranga Dam, Sao Paulo-SP/Brazil.

Abstract:
Guarapiranga Dam is one of the most important water catchment sites in Sao Paulo City. Around 3.8 million inhabitants are supplied by this water system. The reservoir has continuously presented signs of water quality degradation by untreated domestic and industrial sewage spilling. The soil use and occupation interfere dynamically in the water quality, changing the biotic community established in the hydric system. In the present study, it was collected in 14 points Guarapiranga bottom sediments for geochemical evaluation of environmental available metals in this compartment. Results were comparable with TEL and PEL values established by Canadian Council of Ministers of the Environment (CCME). Sediments presented high concentrations of Cu, Zn, Cr, As, Mn, V and Ti. Copper average concentration was several times higher than TEL and PEL values. In some points the Zn, Cr, and As average concentration exceeded TEL values. By these elements spatial distribution it was possible to locate some probable sources and the correlation between the evaluated elements.
Keywords: Metals in sediments, Guarapiranga Dam, Brazil

Resumen:

Distribucion espacial de metales em sedimentos em la Represa del Guarapiranga, São Paulo – Brasil.

La represa del Guarapirang es uno de lós más importantes sítios de captación de água para en la ciudad de São Paulo. Alrededor de 3,8 milliones de habitantes son servidos por este sistema. La represa presenta evidencias de degradación de la calidad del agua causada por la descarga de aguas residuales domésticas e industriales. El uso y ocupación del suelo interfiere de forma dinámica en la calidad del agua, llevando a cambios en la comunidad béntica. En el presente estudio, se tomaron muestras de sedimentos de fondo en 14 localidades en la represa del Guarapiranga para la evaluación geoquímica de metales ambientalmente disponibles. Los resultados son comparados con los valores de TEL y PEL del Consejo Canadiense del medio Ambiente (CCME). Los sedimentos presentan altas concentraciones de Cu, Zn, Cr, Mn, V y Ti. La concentración del Cu fue varia veces mayor que los valores de Tel y PEL. En algunos locales la concentración de Zn y Cr presentaron valores superiores al PEL. Tales para estos fueron utilizados para evaluar la distribución espacial y establecer correlaciones.
Palabras Clave: metales, sedimentos, represa Guarapiranga, Brasil.

INTRODUCTION

Dam sediments usually accumulate many types of compounds and are a useful tool to evaluate the lake environmental status (Margalef, 1983; Mozeto, 2004; Smol, 2008). Nutrients, metals and organic chemicals can be absorbed in organic and inorganic material that eventually settle as bottom sediments (Burton, 2002). These sediments can be immobilized by sulfide presence or can be eventually re-suspended and be bioavailable. The elemental behavior will depend on the lake biogeochemical condition (Burton, 2002; Champan *et. al.*, 1999).

Guarapiranga Dam is one of the most important aquatic ecosystems, near Sao Paulo City, a highly industrialized and urbanized area supplying water to 3.8 million people (Guimarães, 2012). Several studies have reported metal content at Guarapiranga Dam exceeding the most common Sediment Quality Guidelines -SQGs (Guimarães, 2012; Padial, 2008; Whately & Cunha, 2005; Jesus, 2008). Some elements (such as As, Cd, Cr, Cu, and Zn) are known to be potentially toxic to the aquatic biota (Burton, 2002; Chapman *et al.*, 1999) will be evaluated in this study of 14 sediments collected in Guarapiranga Dam. It was intended to obtaining a spatial distribution of elements, in the bottom sediment, in order to identify the sensitive areas. By knowing these critical areas, adequate basin management actions could be taken to prevent the increase of these elements content in the sediment, such as sewer collection and treatment, identification and prevention of industrial activity and any other action that lead to this elements mobilization in Guarapiranga water.

METHODS

The Guarapiranga Hydrographic Basin is located at the portion southwest from the Sao Paulo Metropolitan Region (Figure 1). The collection campaign was performed in august 2011, corresponding to winter (most dried season). The 14 sediment collection points from Guarapiranga Dam can be seen in Figure 2. The location description and GPS coordinates are presented in Table 1. A modified gravity sampler was used (Esteves & Camargo, 1982). After collection, the sample was cooled to preserve the interest analytes, and kept at up to 4°C. Later in the laboratory, the samples were dried at 60°C for 5 days, grinded and sieved at 80 mesh (1 mm). The metal and semi-metal digestion was in accordance to the EPA 3051 method (USEPA, 1994). Analysis of As, Cr, Cu, Mn, Pb, V and Zn was performed by ICP-OES (Spectraflame, SPECTRO Analytical Instruments GmbH, Germany).

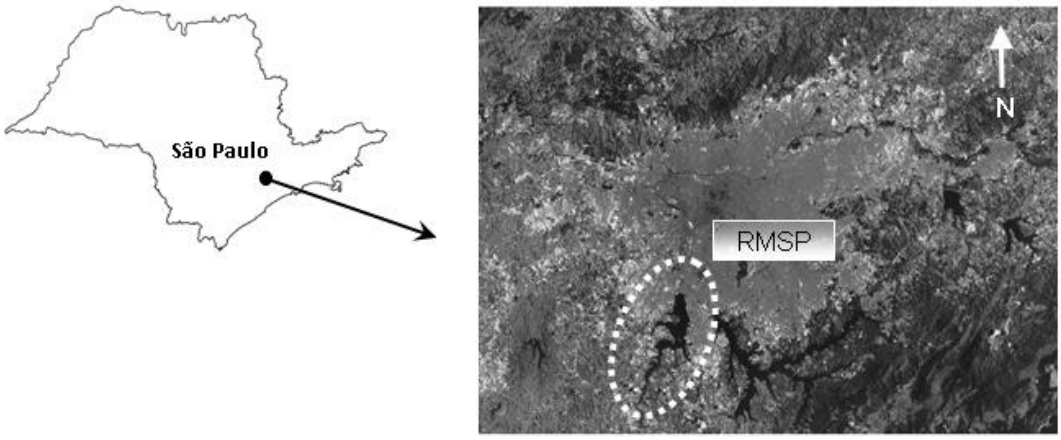

Figure. 1: Location of Guarapiranga Dam.

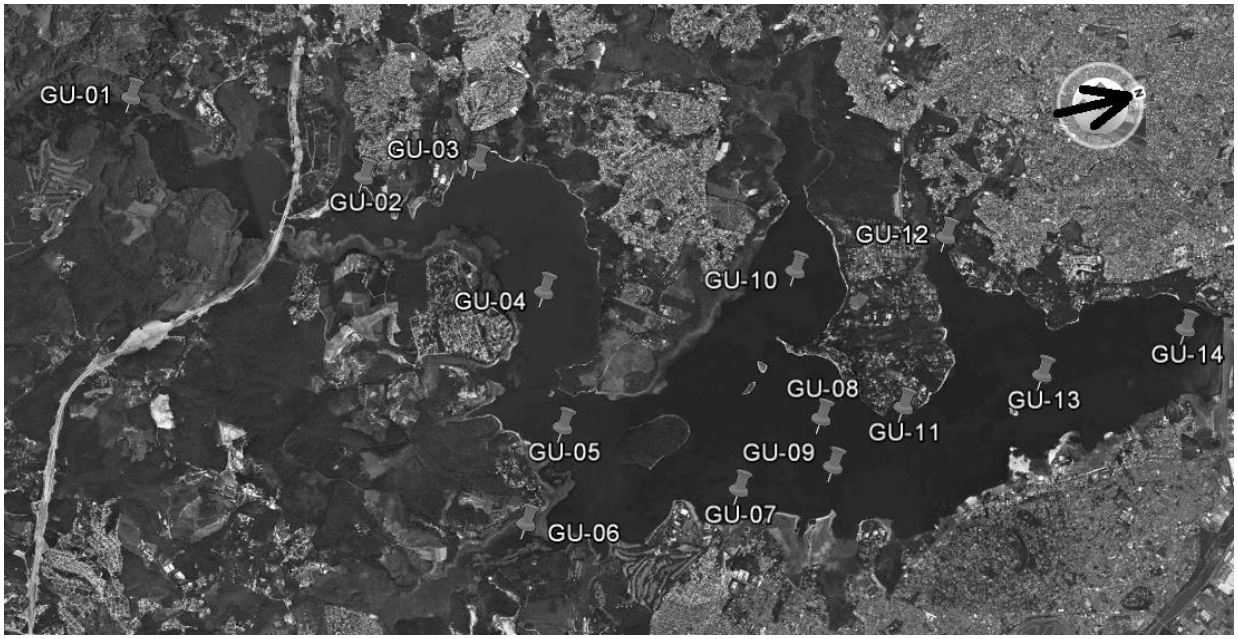

Figure. 2: Location of 14 Collection points.

Table 1: Collection points and geographical coordinates.

Collection point	Geographical coordinates
GU-01	23º46,496'S 46º47.220'W
GU-02	23º45,295'S 46º46.187'W
GU-03	23º 44.522'S 46º46.136'W
GU-04	23º44,446'S 46º45.258'W
GU-05	23º44,575'S 46º44.242'W
GU-06	23°45.012´S; 46°43.615´W
GU-07	23°43.647´S; 46°43.423´W
GU-08	23º42,969'S 46º43,612'W
GU-09	23º43,046'S 46º43,340'
GU-10	43º42,899'S 46º44,687'W
GU-11	23º42,534'S 46º43,449'W
GU-12	23º41,885'S 46º44,673'W
GU-13	23º41,580'S 46º43,573'W
GU-14	23º40,782'S 46º43,559'W

RESULTS

Nowadays it is currently adopted the Threshold Effect Level – TEL. Toxic effects are unlikely to occur below TEL values. Also, there is also considered the Probable Effect Level – PEL, that upon these values adverse biologic effects are likely to occur (Burton, 2002; Chapman *et al.*, 1999). The copper concentration found in twelve from fourteen points exceeded the TEL. Also in eleven points, the copper concentration exceeded up to 28 times PEL values (Figure 3). The higher levels were found at GU-13 and GU-14 that is near the water cachment point managed by the State water suply company. High

copper concentration in the sediment is related to the use of copper sulfate as algicidae applied systematically at Guarapiranga since the first bloom reported (Rodrigues, 2008) in 1990.

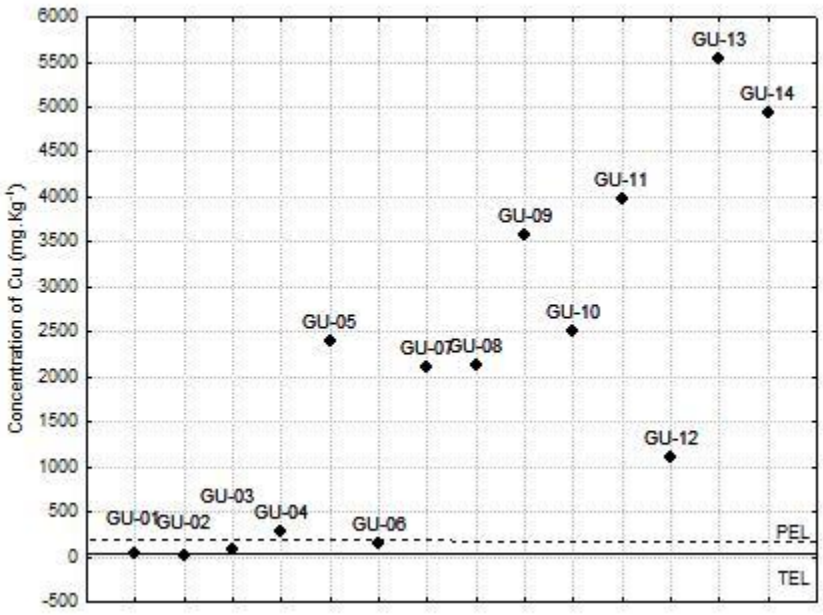

Figure 3: Copper Concentration (mg/kg) in each collection point.

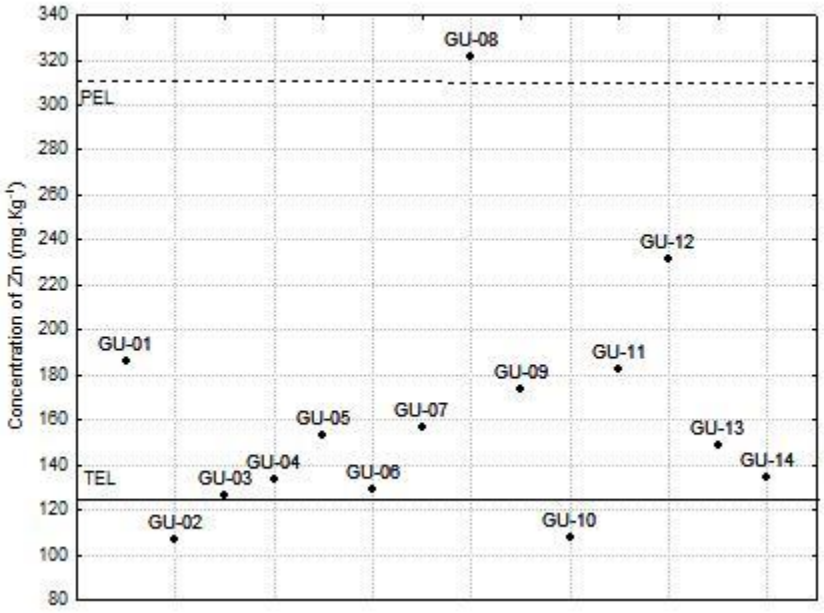

Figure 4: Zinc Concentration (mg/kg) in each collection point.

Zinc concentrations exceeded the TEL values in eleven of the fourteen monitored points (see Figure 4).The overall Zinc distribution could be originated by the long term populational growth around the Guarapiranga Dam and the untreated sewer release in different streams release at Guarapiranga.

In all points, exception to GU-02, the chromium concentration exceeded the TEL values (see Figure 5). However the dispersion of chromium was found between 34 to 59 mg/kg that corresponds to quite narrow range to propose a spatial distribution. The same occurred to As and V. Concerning As results, 5 points exceeded the TEL values however the values range was from 2 to 8 mg/kg.

The manganese is not a conservative element in bottom sediment (Harvey, 1998). Manganese affects the trace elements transport. The removal of manganese is enhanced by microbial oxidation and is related with bottom layer anoxia that occurs in summer cycles. In Figure 6 it is presented the Mn concentration at Guarapiranga Dam. It was observed that Manganese concentration in sediments presents a high correlation with depth in each collection point (Mn = -5.99+140.31*depth, r = 0.7892; p = 0.0008). The manganese high concentration may in the future helps in the fixation of heavy metals by sulfide formation under this anoxia condition.

Titanium and Vanadium are relatively abundant elements widely spread. Usually these elements are related with Al, Fe, K, Na, Si and Cr, that shared the natural origin in granitic rocks (US Geological Survey, 2000). Titanium and Vanadium ranges at Guarapiranga were 593 to 978 mg/kg and from 45 to 94 mg/kg respectively. The Mn, V and Ti values observed in this collection campaign could be used as a reference in future studies.

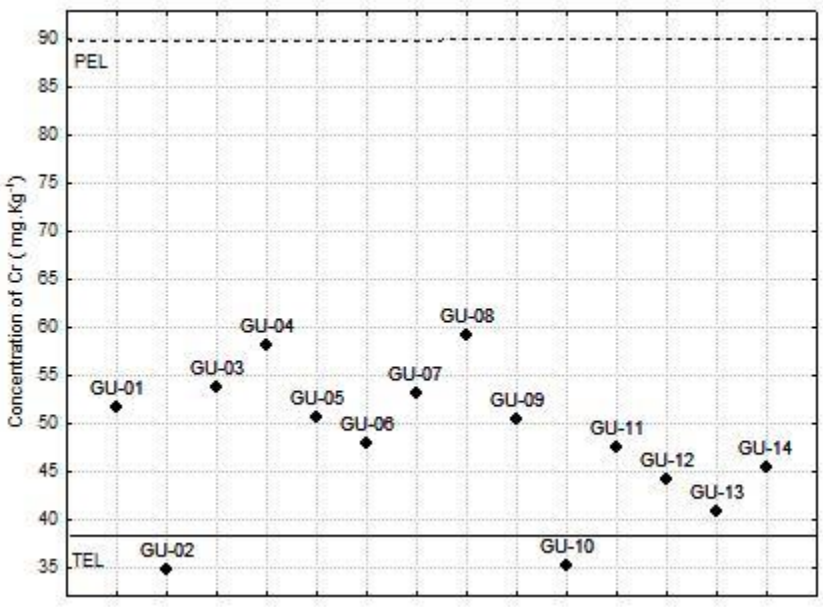

Figure 5: Chromium Concentration (mg/kg) in each collection point.

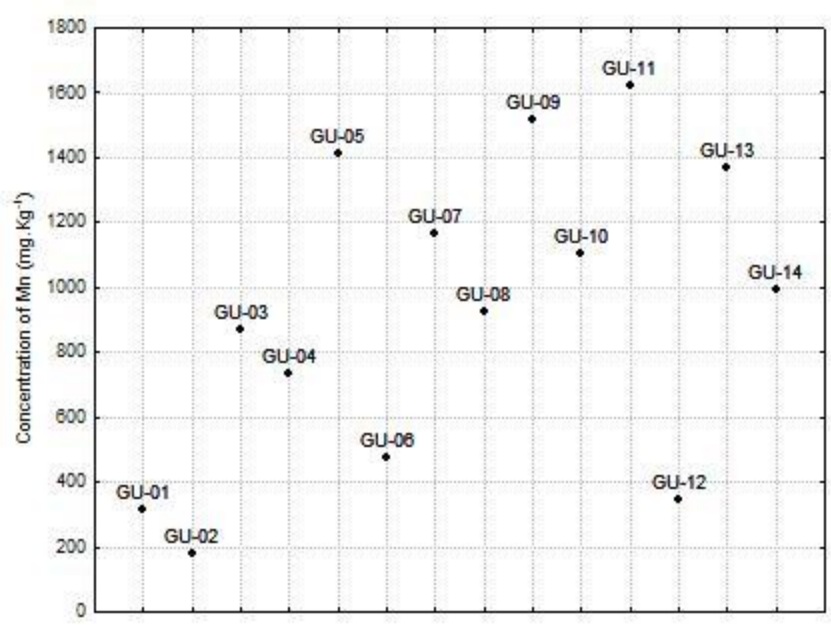

Figure 6: Manganese Concentration (mg/kg) in each collection point.

CONCLUSION

The sediment As and metal content evaluation was conducted to identify the most sensitive areas in Guarapiranga Dam. In several collection points, Cu, Zn, Cr and As content in Guarapiranga Dam sediments exceeded TEL values. Copper content in sediments exceed the PEL values in the majority of Guarapiranga collection points. By zinc distribution, it is possible to recommend increase the sewer collection and treatment in the areas that came from Rio das Pedras and Rio Bonito. By copper distribution, it is recommended to diminish the copper sulfate use as algaecide in the area close to the water catchment point. It is known these elements can be re-suspended in water column by sudden flow increase related with heavy rain events and or floods. It was identified one sensitive area. This area can be described as a canal where the water flows from the center of the Dam to the municipal water catchment site (from GU-07 to GU-14).

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REFERENCES

BURTON, G. A. Sediment Quality criteria in use around the world. *Liminology,* 3: 65-75.

CHAMPMAN, P. M.; WANG, F.; ADAMS, W.J.; GREEN, A. Appropriate applications of sediment quality values for metals and metalloids. *Environmental Science and Technology,* 33(22): 3937-3941.

ESTADO DE SAO PAULO. "Guarapiranga- Caderno Ambiental" 2008, Acessed in Feb 28, 2012 at. http://homologa.ambiente.sp.gov.br/EA/adm/admarqs/Guarapi_cad_baixa.pdf

ESTEVES, F.A.; CAMARGO, A.F.M. "Caracterização de sedimentos de 17 reservatórios do estado de São Paulo com base no teor de feopigmentos, carbono orgânico e nitrogênio orgânico" *Ciência e Cultura, 34(*5): 669-674.

GUIMARAES, G. M.;ZAHN, G.S.; FRANKLIN, R. L.; SILVA, P.S.C.; FÁVARO, D. I. T "Neutron Activation Analysis applied in sediment samples from the Guarapiranga Reservoir for metals and trace elements assessment" *J. Radioanal. Nucl. Chem*. 291: 155-161.

HARVEY, J. W. "Effect of enhanced manganese oxidation in the hyporheic zone on basin-scale geochemical mass balance" Water resources Research, 34(4): 623-636.

JESUS, T.A. "Avaliação do histórico de impactos antrópicos na bacia de drenagem do Lago das Garças (São Paulo-SP), durante o século XX, com base nos estoques de nutrientes, metais pesados e compostos orgânicos em sedimento lacustre" Ph.D. Thesis Universidade de São Paulo, Escola de Engenharia de São Carlos, Brazil.

MARGALEF, R.*1983, Liminología*. Ed. Ômega: Barcelona, Spain.

MOZETO, A.A. 2004. Sedimentos e Particulados Lacustres: Amostragens e Análises Biogeoquímicas. In: *Amostragem em Limnologia*. Bicudo C.E.M. & Bicudo, D. C. (Org.) 295 – 320. RIMA, São Carlos-SP, Brazil.

PADIAL, P. R. 2008. *Qualidade, heterogeneidade espacial e biodisponibilidade de metais no sedimento de um reservatório tropical urbano eutrofizado (Reservatório Guarapiranga, SP)* Master Thesis. Universidade de São Paulo, Instituto de Biociências, São Paulo,Brazil.

RODRIGUES, L.L 2008. *Biodiversidade de Cianobactérias e algas das represas Billings (Braço Taquacetuba) e Guarapiranga, SP, Brasil*. Master Thesis, Universidade de São Paulo, Instituto de Biociências, Brazil.

SMOL, J.P. 2008. *Pollution of lakes and rivers – A Paleoenviron-mental Perspective.* 2a ed. Blackwell Publishing.

USEPA [United States Environmental Protection Agency]. *Method 3051. Microwave assisted acid digestion of sediments sludge's, soils and oils*, 1994, 12 p.

US GEOLOGICAL SURVEY. *Great Salt Lake Basins NAWQA Chief.* 2000, Accessed in Feb 28, 2012 at http://ut.water.usgs.gov

WHATELY, M.; CUNHA, P. M. *Guarapiranga 2005 Como e por que São Paulo está perdendo este manancial: resultados do diagnóstico socioambiental participativo da Bacia Hidrográfica do Guarapiranga.* ISA - Instituto Socioambiental, 2006, 51.