

A REVIEW OF USE OF GIS FOR THE EVALUATION OF HEAVY METAL AND WATER QUALITY PARAMETERS IN THE CANAL DO CUNHA WATERSHED AND WEST OF THE GUANABARA BAY, RIO DE JANEIRO (BRAZIL)

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Abstract

As well as other sub-basins of the Guanabara Bay, the Canal do Cunha watershed, located in the Rio de Janeiro city, has suffered severe environmental degradation since the 50s, due to accelerated urban-industrial development. The fluvial dynamics has changed by the deforestation, landfill constructions, drainage and vale occupation. Canal do Cunha deliver wastewaters and sediments at the western side of Guanabara Bay. Contribute to the environmental degradation and has direct influence on the water quality indexes and heavy metal contamination at the western side of Guanabara Bay. This study intends to evaluate, through geoprocessing techniques, the spatial distribution of Lead (Pb), Zinc (Zn), dissolved oxygen (DO) and total phosphorus (total P) concentrations and pH values, using data provided by six monitoring stations of the Instituto Estadual do Ambiente – INEA (State Environmental

Institute). This work allows to observe the influence of weather conditions on Pb and Zn concentrations in superficial waters and surface sediments and the behavior of DO, pH and total P of superficial waters before and after the implementation of the remediation program: Programa de Despoluição da Baía de Guanabara (PDBG; Pollution Remediation Program of Guanabara Bay). Canal do Cunha flow has direct influence on the low quality indexes of water and contributes to the heavy metal contamination and environmental degradation of the western region of Guanabara Bay.

Keywords: Water contamination. Sediments contamination. Metals. Quality parameters. GIS.

1. Introduction

The waterways of metropolitan areas in various parts of the world, such as areas in which a vast contribution of domestic and industrial effluents causes degradation of these waterways are impacted by various anthropic activities.

The contamination of aquatic ecosystems by heavy metals is of great importance due to the negative effects on trophic chains, with a direct and immediate influence on human health (Cowen and Silver, 1984).

Remediation process remains challenging due to the lack of knowledge on the behavior of metals in aquatic ecosystems (Warren and Haak, 2001). According to Warren and Haak (2001), metals can exist in various forms in water; however, all metals are not equally toxic, mobile or bioavailable. Metal associations are dynamic, reversible and reflect physicochemical changes in the water. Consequently, potential effects from metals released from sediment exist even with reduced amounts of metals (Fonseca et al., 2013).

The degradation in water quality can be caused by a result of human made pressure as well as natural factors which are mostly accelerated by human activities (rock and soil erosion).

However, the watercourses of the metropolitan area have suffered, heavily, with many human activities (with the contribution of domestic and industrial effluents) established in their proximity. According to Pesquisa Anual de Amostras de Domicílio (PNAD; Annual Survey of Household Sample of 2009) 72.7% of the households were provided by the state's sewerage network (IBGE, 2010). In 2011, the coverage data presented the result of 70% (IBGE, 2012), showing a raise in household numbers and, consequently, an aggravation in environmental pollution due to the raise of untreated waste. The effluents which most affect the water resources are the organic components, heavy metals and nutrients which come from domestic and industrial waste.

Lead (Pb) and zinc (Zn) even though they are essential for some of modern society activities, they can harm health and provoke stress in coastal ecosystems (Rocha et al., 2010). Lead has as a main source the urban superficial outflow contribution, associated to the additives of automotive fuels.

Zinc is supplied from many kind of industries, such as: metallurgical, electroplating, painting, insecticide, pharmaceutical, luminescent products and fibril. It can even come from mining wastes and untreated domestic effluents (Martin et al., 1976).

The lack of criteria to measure the superficial contamination in the sediments and in superficial waters led Conselho Nacional do Meio Ambiente (CONAMA) to establish the Sediment Quality Value Guide (VGQS), with the resolution 344/2004, and in water, with the resolution 357/2005.

This work used an interpolation technique aiming to evaluate – the pollution degree by heavy metals and to determine some quality parameters from water around the Canal do Cunha watershed and west of the Guanabara Bay.

2. Material and methods

According to INEA (2003), the Canal do Cunha watershed (Fig. 1) is situated in Rio de Janeiro State (between the latitudes 22° 51' and 22° 55' S and the longitudes 43° 15' and 43° 20' W). It has 84% of its area (approximately 62.85 km²) in a densely urbanized area, including slums, clandestine or irregular allotment. The only existent natural area is the Tijuca Park which has secondary forests in good shape. Faria river mouth is located at the west region of Guanabara Bay, next Fundão Island (University city; Fig. 1B).

The metal distribution in water and on sediment, discussion and the water quality parameters in Canal do Cunha and in the west part of the Guanabara Bay is grounded on data provided by the Instituto Estadual do Ambiente (INEA; State Environmental Institute). Since the 70s the Fundação Estadual de Engenharia do Meio Ambiente (FEEMA; State Foundation of Environmental Engineering) monitored the main water bodies of the Rio de Janeiro state, providing historical series which allows the analysis of the evolution of environmental conditions of the fluvial ecosystem of this study.

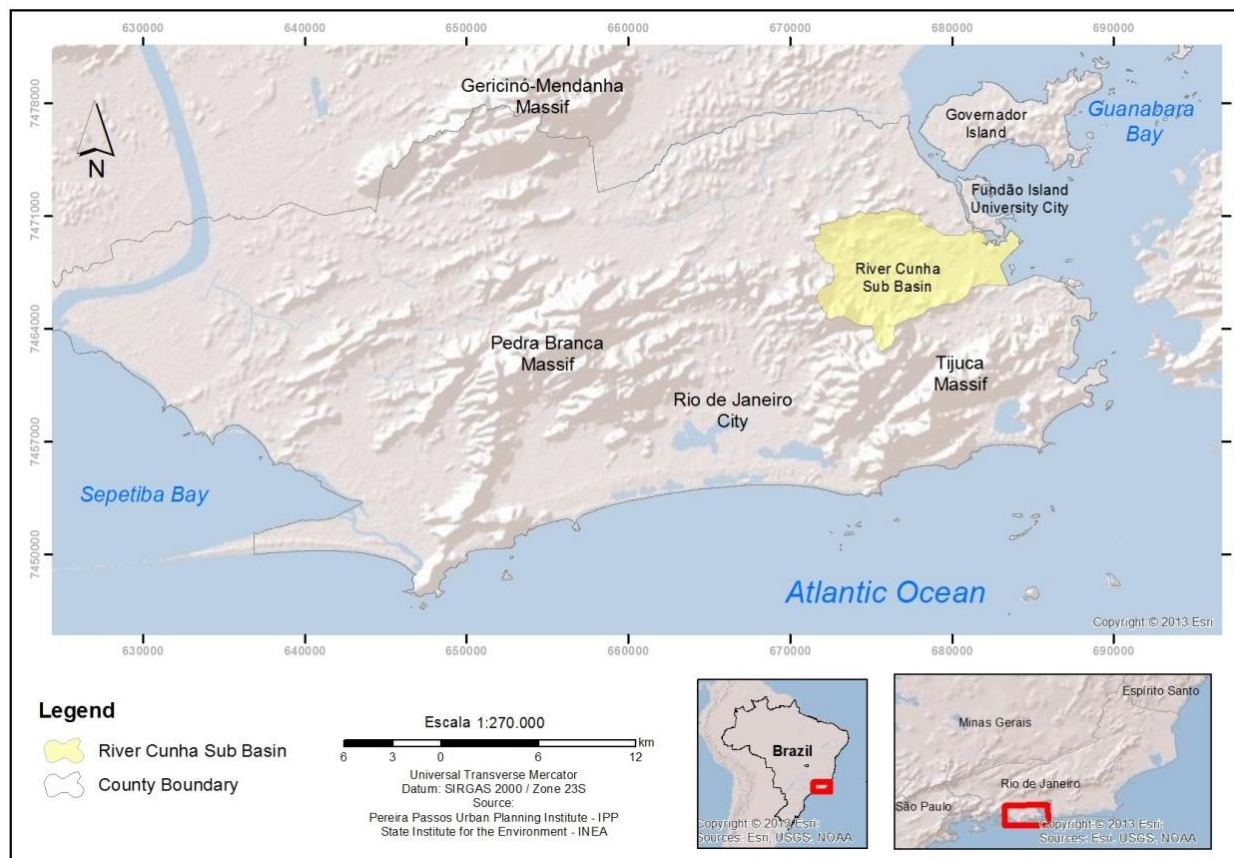
Data of six monitoring stations were selected to be analysed in this work (Fig. 2): CN100, FR142, GN22, GN43, GN48 and GN50. In the station GN43 were not recorded sedimentological data.

Data of surface water were obtained by collecting samples with a Van Dorn bottle, stored in 500 mL polyethylene bottles, cooled at 4°C and protected from light, for further filtration (INEA, 2003).

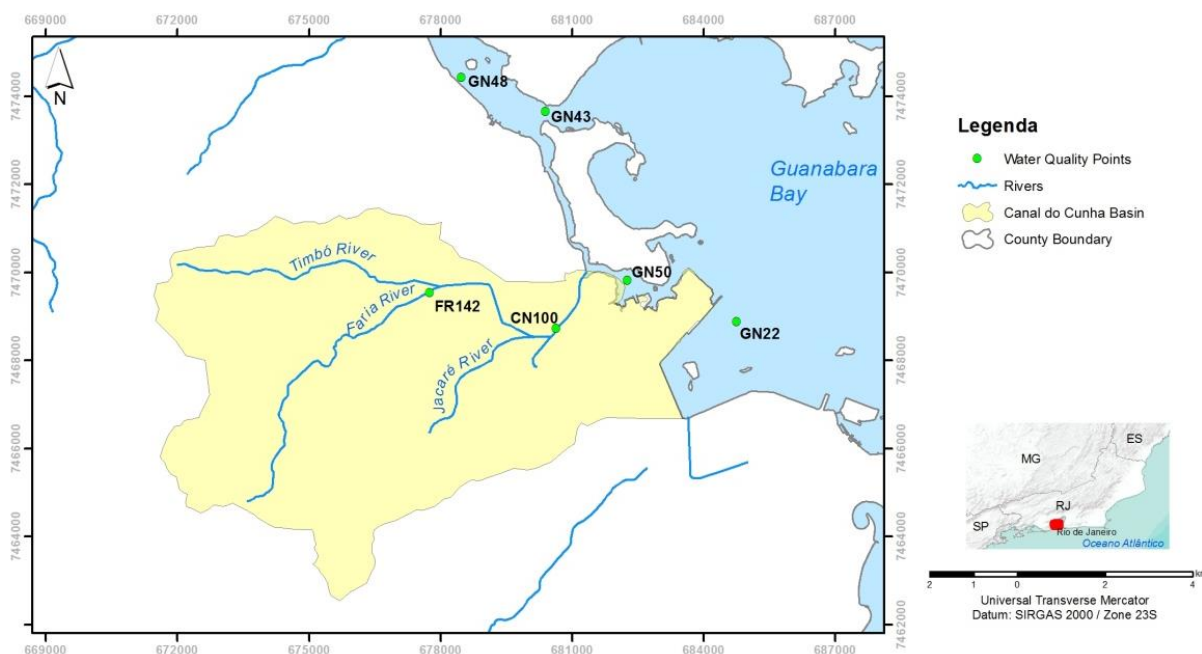
Sediments were recovered with a Van Veen grab. Sediment samples were stored on sanitized flasks. A Styrofoam cooler with ice was used to store and to transport these samples. The samples were sent to TASQA-Serviços Analíticos, Ltda. in Campinas, São Paulo, to perform the stages of openness of samples and analysis of extracts by inductively coupled plasma-optical emission spectrometry (ICP-OES).

The digestion of the sediment samples (0.5 g) for the metal analysis was performed according to EPA method 3051, using HCl and HNO₃, 3:1, respectively (EPA, 2007). The digestion was performed in a microwave oven. After the digestion, the liquid phase was filtered and transferred to polyethylene tubes. The obtained solution was subsequently diluted with deionized water to 20 ml. The analysis was performed using ICP-OES.

The water quality parameters were determined using the methodology described in Borges et al. (2015).



A



B

Fig. 1. (A) Canal do Cunha watershed. (B) Location of collection points in the river Canal Cunha Basin and west of Guanabara Bay.

Once georeferenced according to its coordinates in the sampling stations of INEA, these data were converted in vector format of points and interpolated with the technique Inverse Distance Weighted (IDW), available in the ArcGIS 10 software (ESRI, 2011). The mathematical method used by the interpolator IDW is represented on equation 1, were: z = interpolated value; n = number of observed individuals; z_i = values attributed to the observed individuals; d_i = distance between the observed and interpolated individuals (Varella and Junior, 2008):

$$x = \frac{\sum_{i=1}^n \frac{1}{d_i^p} z_i}{\sum_{i=1}^n \frac{1}{d_i^p}}$$

The criteria to choose this method was given by its properties. It does not estimate values higher or lower than

the maximum and minimum recorded in the sampling points, which does not happen in methods such as Kernel.

The used basemap was provided by the Department of Geosciences at UFRJ, Cartography Laboratory (Geocart), as a result of the project "Implementation of information network for the environmental management of the Guanabara Bay basin, based on geographic information system - GIS" developed for the Instituto Brasileiro de Administração Municipal (IBAM; Brazilian Institute of Municipal Administration) and for Instituto Brasileiro de Meio Ambiente e Recursos Naturais Renováveis (IBAMA, 2002; Brazilian Institute of Environment and Renewable Natural Resources). This consisted of an edition of a mosaic of sheets 1:50.000 from IBGE and Diretoria de Serviço Geográfico (DSG; Direction of Geographic Service). Among the plans of information developed by the project, only the data related to hydrography and coastline was adopted.

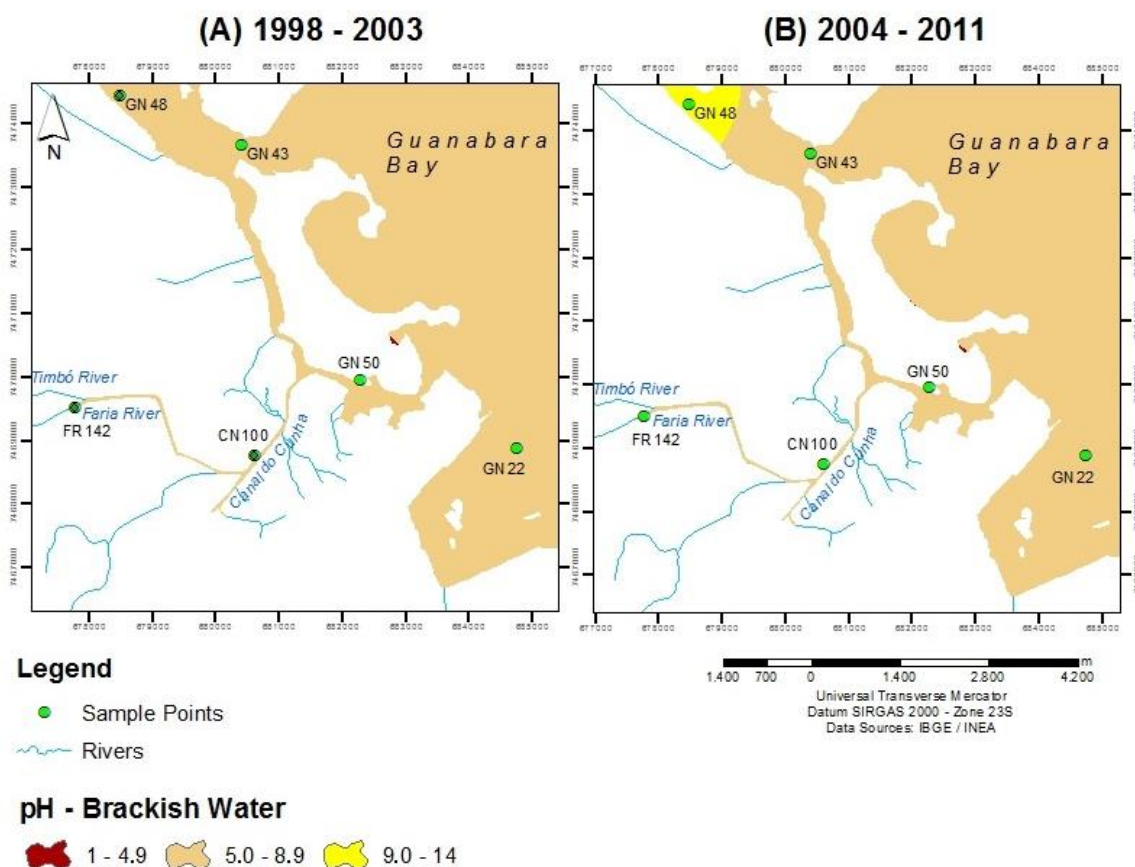


Fig. 2. Distribution of the pH values before and after the PDBG (Programa de Despoluição da Baía de Guanabara).

Considering the complexity and high variability normally observed in environmental studies (Einax and Soldt, 1999), it is frequent in these types of studies to use multivariate statistical methods to identify and differentiate natural levels of heavy metals from anthropogenic contamination.

In order to verify the parameters that contribute the most to such a characterization and how they are related to the methods used, cluster analysis was performed using the software STATISTICA 7 (Copyright 1984–1987, Stat-Soft, Inc. 2300 East 14th Street Tulsa, OK 74104, USA).

4. Results

Table 1 shows the results of water quality parameters in two time periods before (1998-2003) and after (2004-2011) the PDBG. These results represent the average

concentrations of monthly values for each station, which were subsequently grouped in years and finally transformed in the periods used in this work.

The pH values varied between 6.72 -9.24, though not vary greatly in both time periods, except in GN48. The lowest pH values was found in the FR142 point in Faria River. The highest pH value was obtained in GN48 point in the Guanabara Bay.

The DO values vary between 0.23-7.84 mg L⁻¹. The DO concentrations are critical in CN100 and FR142 and below the minimum required to maintain aquatic life (4 mg L⁻¹, according to CONAMA, 2005). GN43 and GN50 points located in Guanabara Bay, are also below the minimum set by CONAMA (2005) for saline water 6 mg L⁻¹. Regular concentrations are found in GN22 on both periods.

Tab. 1. Average concentrations of monthly values for each station of Water Quality Parameters for the periods 1998-2003 and 2004-2011. DO – dissolved oxygen.

Station	DO (1998-2003) (mg L ⁻¹)	DO (2004-2011) (mg L ⁻¹)	Total P (1998-2003) (mg L ⁻¹)	Total P (2004-2011) (mg L ⁻¹)	pH (1998-2003)	pH (2004-2011)
CN100	0.23	0.35	1.93	1.81	6.90	6.88
FR142	0.96	0.80	1.90	4.95	6.88	6.72
GN22	6.99	7.84	0.18	0.21	8.27	8.03
GN48	6.06	6.14	0.51	0.69	7.61	9.24
GN50	4.16	4.17	0.98	0.76	7.41	7.55
GN43	3.92	5.88	0.44	0.48	7.93	7.84

The values of total P vary between 0.18-4.95 mg L⁻¹. The total P levels were above 0.186 mg L⁻¹ in all the analyzed points. This is considered the maximum limit permitted by CONAMA (2005).

Table 2 shows the concentrations of heavy metals in water and sediment. The Pb concentrations in the sediments are much higher than in water, regardless of the evaluated period, dry or rainy season.

Tab. 2. Average concentrations of monthly values for each station of concentrations of heavy metals in water and sediment. Legend: RS - Rainy Season; DS - Dry Season

Station	Pb - water RS (mg kg ⁻¹)	Pb - water DS (mg kg ⁻¹)	Pb - sediment (mg kg ⁻¹)	Zn - water RS (mg kg ⁻¹)	Zn - water DS (mg kg ⁻¹)	Zn - sediment (mg kg ⁻¹)
CN100	0.04000	0.0300	21	0.00013	0.00005	20111
FR142	0.01625	0.0100	10	0.00004	0.00005	37
GN22	0.01150	0.0051	60	0.03480	0.02252	174
GN48	0.00607	0.0050	50	0.01225	0.02647	250
GN50	0.00555	0.0050	70	0.01200	0.03491	270

Lead concentrations vary between 0.0055-0.0400 mg L⁻¹ and between 0.0050-0.0300 mg L⁻¹ in water, during the rainy and dry seasons respectively. Lead concentrations vary between 10-70 mg L⁻¹ in the sediment. Zinc concentrations, on the other hand, had a homogeneous variation in the

evaluated stations. Zinc concentrations ranged from 0.00004-0.0348 mg L⁻¹ in the rainy season. In the dry period, Zn concentrations varied between 0.00005-0.03491 mg L⁻¹. However the sediment present a wide variation (between 37-20111 mg kg⁻¹) of Zn content.

5. Discussion

The pH directly influences the mobility, precipitation and adsorption of heavy metals in acidic environments. The tendency of metals is to be soluble in the water column (Warren and Haak, 2001); however alkaline environments promote precipitation and adsorption of these elements (Warren and Haak, 2001).

Fig. 3 shows the distribution of pH before and after the remediation works of Guanabara Bay. The pH values do not change much from one period to another. The lowest value was observed in point FR124 (6.2).

This low value is not relevant because, according to Resolution 357 of CONAMA (2005), the pH of fresh water can range from 6-9. The largest pH value in GN48 point exceeds the allowed limit for saline water (between 6.5 and 8.5).

These values are influenced by human activities. It can be stated that these values are mostly neutral or alkaline. Under these conditions the metals are probably precipitated or adsorbed in the sediments.

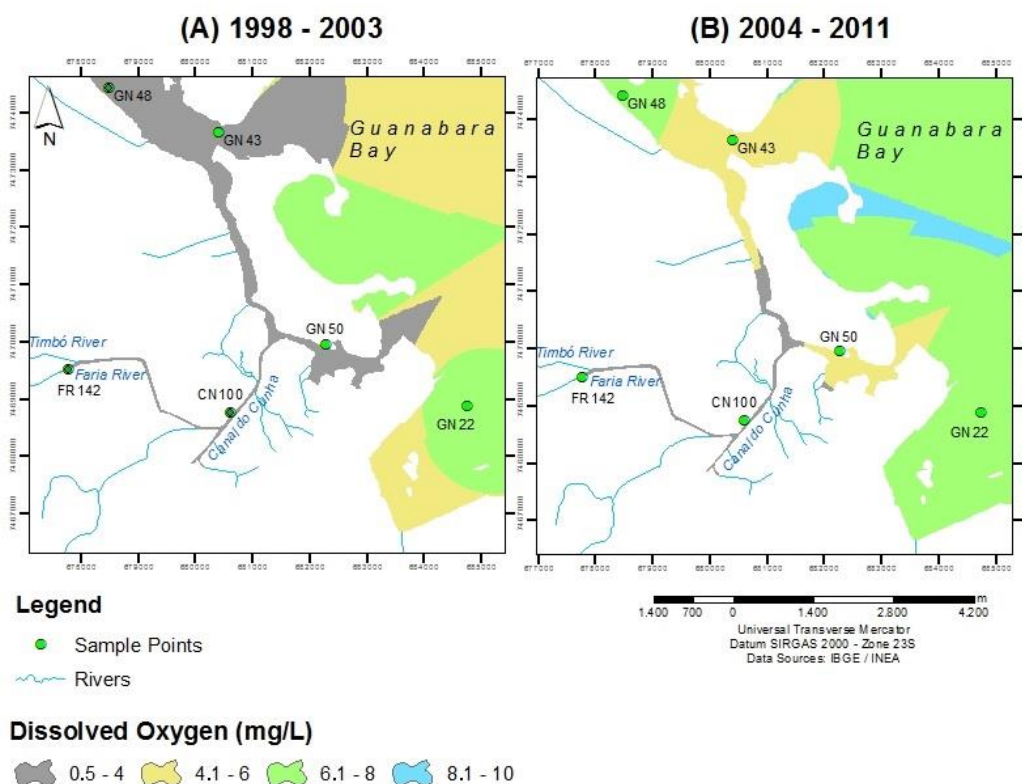


Fig. 3. Variation in concentration of dissolved oxygen in two periods before and after the PDBG.

Regarding water quality parameters, DO concentrations were in critical condition (Fig. 4), that is far from the below levels of 4 mg L⁻¹, the minimum values established by resolution 357 of CONAMA (CONAMA, 2005) for maintenance of aquatic life. The lowest values occurred at CN100 and FR142 stations, with 0.55 and 0.80 mg L⁻¹, respectively. The stations located in Guanabara Bay were also critical, with the exception of GN22 which was within the standards. These results indicate that the works promoted by the PDBG acted positively in this parameter, contributing to improving water quality in the Guanabara Bay. However the water quality in the Canal do Cunha watershed remained critical.

For total P (Fig. 5) the maximum limit established by the resolution 357 of CONAMA (CONAMA, 2005) is 0.186 mg L⁻¹. In the evaluated area before sanitation projects promoted by the PDBG the total P concentrations exceeded the limit on all points except in GN22. This fact can be associated with the water circulation in Guanabara Bay where the water is more quickly renewed. In the second period there was a worsening of total P levels and this may be occurring due to the increase in population on the slums of the region. In addition, even with the structuring of sewage networks in these slums, these are still released of untreated wastewater into rivers and streams of Canal do Cunha watershed.

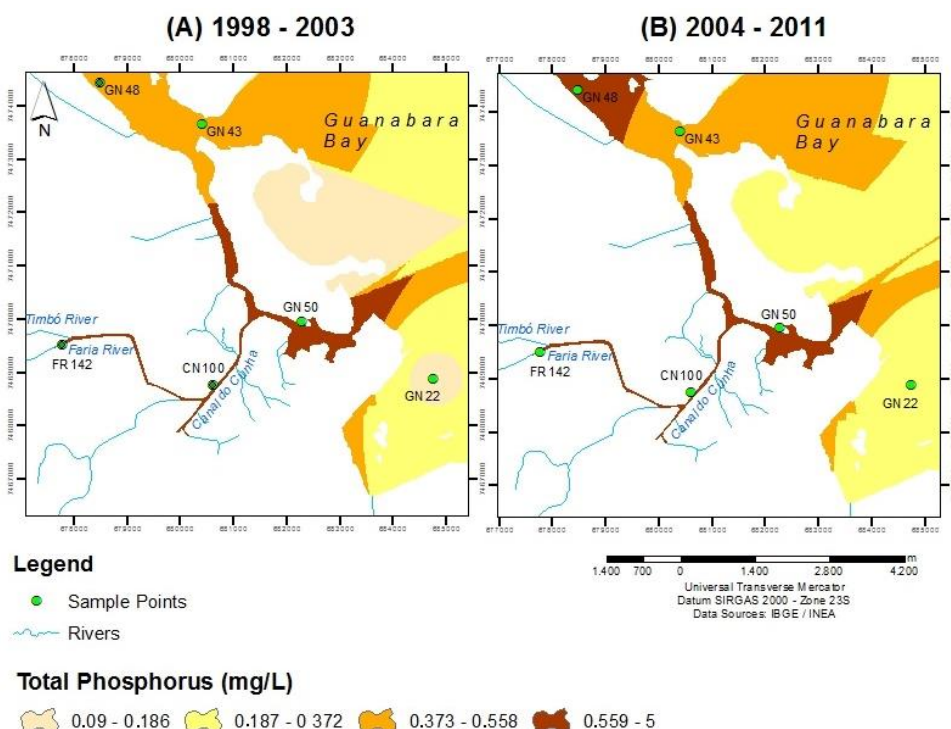


Fig. 4. Variation on P total concentration on periods before and after PDBG.

The distribution of Pb, Fig. 6, indicates that the concentrations of this element in surface water were higher during the rainy season compared to the dry season. These data suggest that urban shallow continental runoff is a major source of Pb and the rains potentiate their discharge on rivers of the Canal do Cunha watershed and consequently in Guanabara Bay. The sampling stations located on the Canal do Cunha watershed and Faria river have the highest Pb concentrations in water compared with the stations of Guanabara Bay. This is due to dilution caused by circulation and hydrodynamics in Guanabara Bay. However, all Pb

concentrations in surface waters are below the maximum extent permitted by the resolution 357 of CONAMA (CONAMA, 2005).

The concentration of Pb in sediments was much higher than that found in surface waters; this fact is probably associated with the adsorption of this metal by organic matter and fine sedimentary particles, which is facilitated in alkaline environments. However, Pb concentrations in sediments did not exceed the limit established by resolution 344 of CONAMA (CONAMA, 2004).

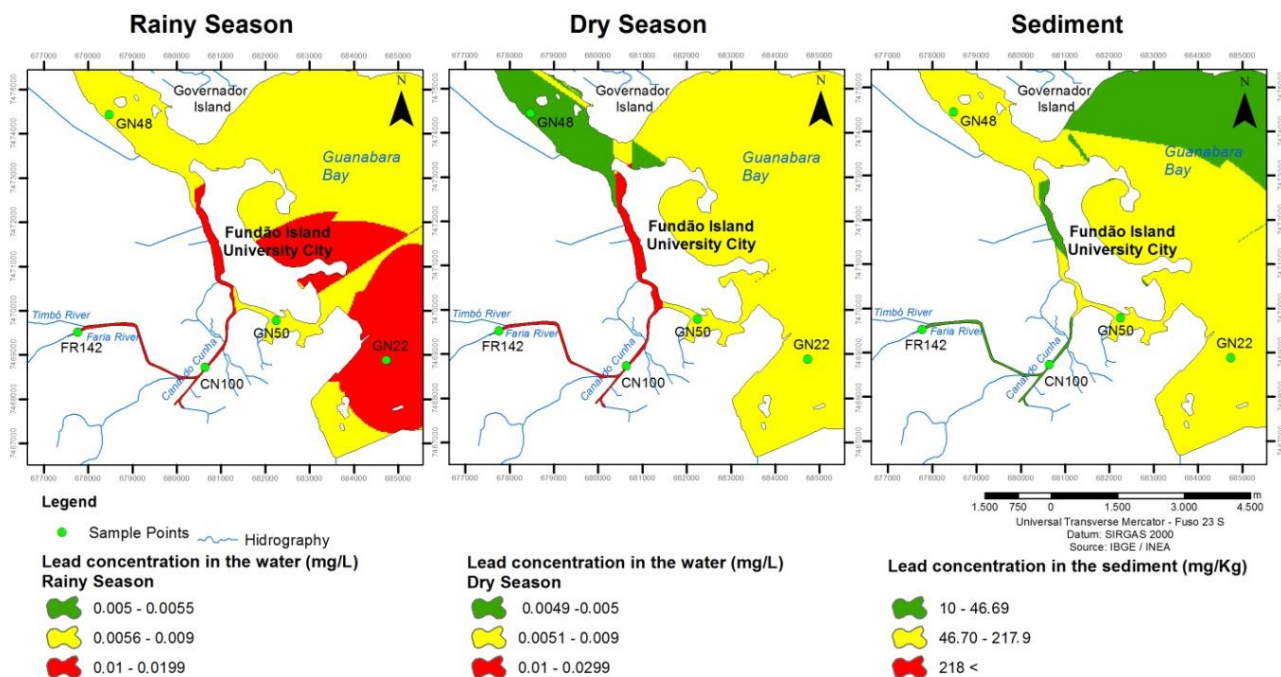


Fig. 5. Maps of distribution of Pb concentrations in water and sediment.

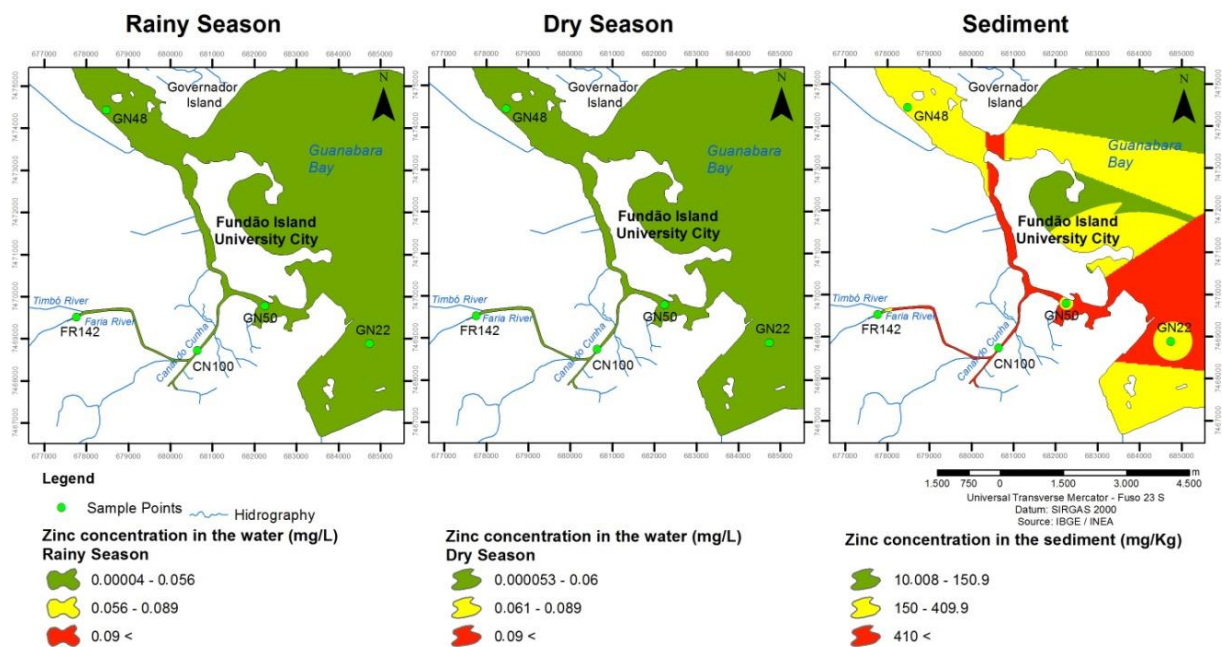


Fig. 6. Variation in Zn concentration in water and in sediment.

Hatje et al. (2001) studying Port Jackson in Australia found a Pb range between 110 and 240 mg.kg⁻¹ in sediment. Regnier and Wallast (1993) studying the Scheldt Estuary in northern France, Germany and Netherlands found Pb concentrations of about 185 mg.kg⁻¹ in sediment. The values presented in these works are above that obtained in the study area.

The seasonal variation of Zn concentration in surface water (Fig. 7), showed no significant differences between the rainy and the dry season. This fact shows that Zn is not from the urban continental runoff, but is supplied by several industries operating in the region, so the rains do not interfere with their distribution. In addition, Zn values in water were below the maximum limit permitted by resolution 357 of CONAMA (CONAMA, 2005).

The Zn concentrations in the sediment was much higher than in water, probably due to the alkaline environment favoring its adsorption. However, the concentration of this element in the sediment exceeded the maximum limit established by resolution 344 of CONAMA (CONAMA, 2004), indicating that this metal may be a risk to the environment of Guanabara Bay.

The Zn concentrations in the station CN100, located in the outer sector of the Canal do Cunha (20111 mg.kg⁻¹) are much higher than those reported in the international

literature. Hatje et al. (2001) studying the sediments of Port Jackson Australia found Zn concentrations between 400 and 800 mg.kg⁻¹. Stecko et al. (2000) studying Fraser Estuary River (Canada) obtained Zn values between 50 and 700 mg.kg⁻¹ in the sediment.

Figure 7 shows the statistical analysis of the distribution of heavy metals and water quality parameters, respectively. The results are similar in both analysis (the same groups of stations are recognized) for the studied sets of variables. Occurs the formation of two large groups of stations. The first formed by the stations located on the watershed of the Canal do Cunha. These stations are experiencing the highest level of contamination for both analyzed metals and for the water quality parameters. This fact is directly associated with the local hydrological characteristics, where the channeling of rivers contributed to the silting and, consequently, to a poor circulation and a highest concentration of metals and total P.

The second large group established by cluster analysis is formed by the stations located on the western side of Guanabara Bay. There is a greater similarity between the GN50, GN48 and GN43, probably due to hydrological conditions, as they are stations where there is a poor water circulation. The GN22 station displayed a more differentiated behavior since it is less affected both by metal contamination and for low quality water.

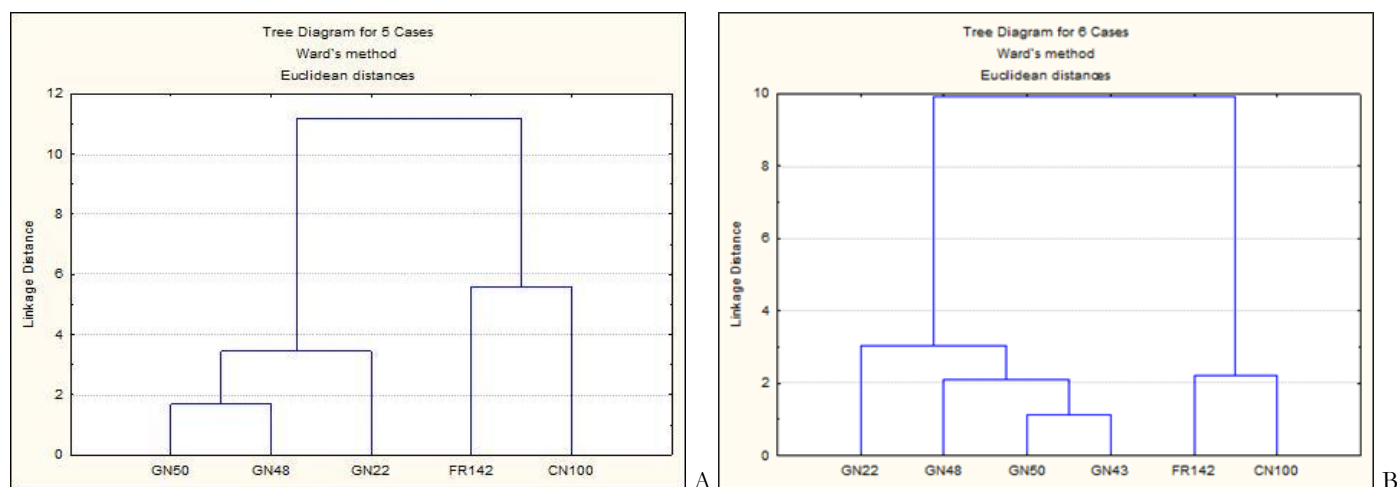


Fig. 7. Cluster analysis. (A) Dendrogram of stations evaluated for heavy metals. (B) Dendrogram of stations evaluated for water quality parameters.

6. Conclusion

In the study area, the pH varied in an alkaline range in most of the sites, in both analyzed periods, which favors precipitation and adsorption of metals.

The concentrations of Pb and Zn in surface water are substantially lower than the concentrations of these elements in the sediment. The deposition of great amount of organic matter and fine grained particles in the Canal do Cunha watershed and the western side of Guanabara Bay should promote the adsorption of metals.

The results indicate that the amount of Pb reaching the Canal do Cunha watershed and the western part of Guanabara Bay exponentially increase during the rainy season. The Zn concentrations in sediment exceeded the maximum extent permitted by resolution 344 of CONAMA.

According to the water quality parameters, the Canal do Cunha watershed can be classified as Class 4, in other words, the water is so altered and degraded that only can be used for navigation and landscape harmony, according to CONAMA Resolution No. 357/05.

Even after the works of sanitation held in the slums of the watershed Canal do Cunha through the Favela-Bairro Project, the improvement on water quality was not observed. This fact is due to an increase in population in these slums and also even after the construction of sewage networks, there was no treatment of this sewage before being released into rivers and streams of the region.

Acknowledgments

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