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Article

Assessment of Metal Concentration in the Billings Reservoir Sediments, São Paulo State, Southeastern Brazil

Marcos A. Hortellani,*[,a] Jorge E. S. Sarkis,[a] Luciana C. B. Menezes,[b] Renata Bazante-Yamaguishi,[a] Alder S. A. Pereira,[a] Priscila F. G. Garcia,[a] Lídia S. Maruyama[b] and Paula M. Gênova de Castro[b]

*[a]Centro de Química e Meio Ambiente, Instituto de Pesquisas Energéticas e Nucleares (IPEN),
Travessa R No. 400, Cidade Universitária, 05508-000 São Paulo-SP, Brazil*

*[b]Instituto de Pesca (IP-SP), Avenida Francisco Matarazzo 455,
Parque da Água Branca, Perdizes, 05001-900 São Paulo-SP, Brazil*

A contaminação por metais em 47 amostras de sedimentos (fração < 63 µm) coletadas em 13 pontos de pesca no reservatório Billings foi avaliada utilizando quatro metodologias: normas de qualidade de sedimentos (SQG_S), índice de geoacumulação (I_{Geo}), índice de poluição metálica (MPI) e análises estatísticas. Somente Fe e Co parecem estar associados com a composição natural do sedimento ou processos de intemperismo natural, enquanto Al, Cd, Cr, Cu, Hg, Mn, Ni, Pb, and Zn mostraram aumento em suas concentrações, sugerindo associação com fontes antropogênicas. MPI identificou as áreas mais críticas em relação à concentração total de metais enquanto I_{Geo} identificou o metal específico para cada área. A sazonalidade sobre os níveis dos metais foi avaliada usando análise de variância (ANOVA) e gráfico de caixa. Somente o gráfico de caixa sugeriu um pequeno aumento na contaminação por Hg and Pb durante o período com muita chuva e também indicou altas concentrações de Cu e Zn em um dos pontos analisados com a incidência de valores fora do normal e extremos. Portanto, políticas ambientais devem ser adotadas para reduzir a contaminação por metais.

Four approaches were applied to evaluate the metal contamination in 47 sediment samples (< 63 µm fraction) collected at 13 fishing points of the Billings Reservoir: sediment quality guidelines (SQGs), geoaccumulation index (I_{Geo}), metal pollution index (MPI) and statistical analyses. Only Fe and Co concentrations seemed to be associated with crustal material or natural weathering processes, while Al, Cd, Cr, Cu, Hg, Mn, Ni, Pb and Zn showed increases in their concentrations, which seemed to be associated with anthropogenic sources. MPI identified the most critical sites in relation to the total metal accumulation while I_{Geo} identified the specific metal accumulation for each site. Analysis of variance (ANOVA) and box plot method were performed to evaluate seasonal effects on the metal levels. Only box plot suggested a slight increase in Hg and Pb contamination during heavy rainy periods and also indicated high concentrations of Cu and Zn in one of the analyzed point, with incidence of outliers and extreme values. Thus, an environmental policy in order to reduce these metal contaminations must be adopted.

Keywords: sediments, metal contamination, geoaccumulation index, Billings Reservoir

Introduction

The Billings Reservoir is extremely important as it is the largest water reservoir for the Metropolitan Region of São Paulo, Brazil. The Billings Reservoir produces 12 m³ s^{-1} of water and supplies the ABC region, part of São Paulo City and the Baixada Santista region. The ABC region refers to three smaller cities bordering São Paulo City (Santo André, São Bernardo do Campo and São Caetano do Sul). The ABC area is well-known in Brazil because of the numerous automotive manufacturers located in the vicinity. The Baixada Santista Metropolitan region is a densely urbanized region in São Paulo State.[1] This reservoir is impacted by urban invasion, industrial and sewage waste, seriously affecting its ecosystems and quality of life of population in this region.[2,3]

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*e-mail: mahortel@ipen.br

The metal levels in the Billings Reservoir water presented concentration below the CONAMA (Brazilian National Council on the Environment) criteria,[4] according to studies carried out by the Environmental Control Agency of São Paulo State (CETESB).[5] However, some metal concentrations obtained by CETESB[5] for two sediment samples (BILL02100, Bororé on September 29, 2005) and (RGDE02900-Grande River on November 09, 2005) were above the levels frequently associated with adverse biological effects (PEL limit). This limit was established by the Canadian Ministry of the Environment (CCME)[6] and adopted by CETESB[5] and CONAMA[7] as standard for sediment quality monitoring.

Sediment pollution is considered by many regulatory agencies to be one of the main risks to the aquatic environment since many of its organisms spend the major portion of their lifecycle living on or in sediments.[8]

In aquatic ecosystems, in particular, inorganic mercury enters a complex cycle, in which it can be methylated in water and/or in sediments producing methylmercury, the most toxic form of Hg. Methylmercury level in sediments is controlled by competing and simultaneous methylation and demethylation reactions.[9,10] Methylmercury usually represents 1.5% of the total mercury present in sediments.[9] This organic-metallic compound present in sediments can be released by diffusion or resuspension, and upon entering the food chain causes an effective biomagnification in aquatic biota.[11,12] Methylmercury represents more than 85% of the total mercury present in fish.[13] Thus, human ingestion of fish is an important pathway to mercury intake.[14]

The goal of this work was to determine the levels of metallic elements in 47 surface sediment samples from 13 fishing points of the Billings Reservoir, collected in four sampling campaigns (2009/2010), after a first grain size normalization by wet sieving (< 63 µm fraction), assessing metallic element contamination in this reservoir. This was achieved by using sediment quality guidelines (SQGs), geoaccumulation index (I_{Geo}), metal pollution index (MPI) and statistical analyses to verify the seasonal effect over the metal accumulation and to study the behavior of sample sites and metal contaminants.

Experimental

Sampling and preparation

A total of 47 surface sediment samples was collected at four sampling campaigns in order to determine variations in the concentration of metals from 13 fishing points of the Billings Reservoir by a VanVeen sampler, packed in plastic bags and placed on ice (–5 ºC). To avoid metal contamination from the walls of the grab, only the inner and surface fraction parts (5 cm) were further processed. From theses 47 samples, 12 were collected during the dry winter period in July-2009 (1st sampling), 11 during rainy periods in October-2009 (2nd sampling), 13 during heavy rainy periods in January-2010 (3rd sampling) and 11 during the dry winter period in

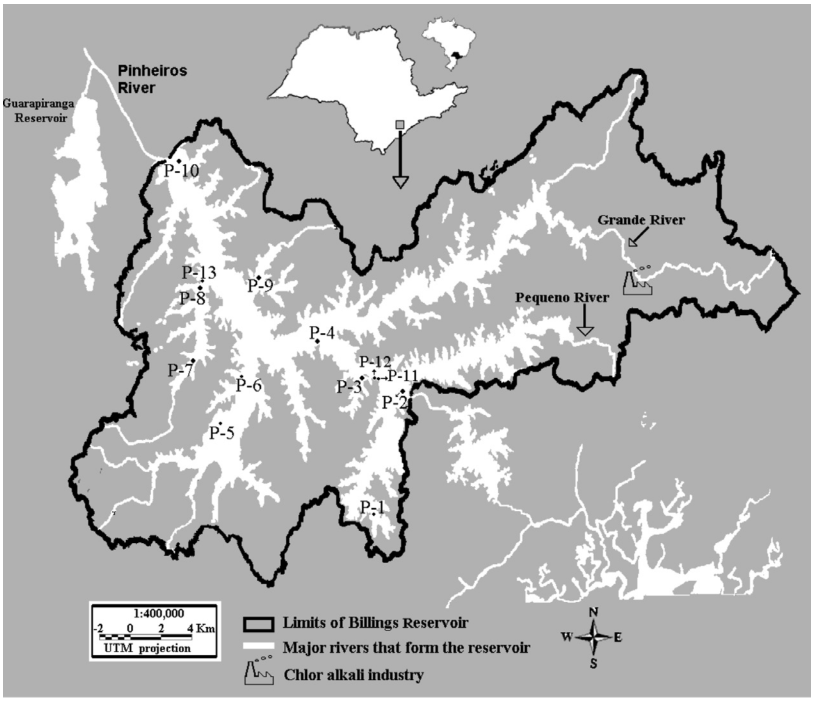

Figure 1. Map of the study area and location of the sampling sites (adapted from reference 15).

July-2010 (4th sampling). Figure 1 displays the localization of these sites and Table S1 in the Supplementary Information (SI) section shows site localizations in details.

Immediately after collection, samples were taken to the laboratory and stored at –20 °C. Prior to the metal analysis procedures, the samples were wet sieved at 63 µm and then dried at 40 °C. Thereafter, a known quantity (0.5-1.0 g) of sediment sample (< 63 µm fraction) was placed into a PFA tubing.

Metals were extracted for each sample and two certified reference materials (in triplicate and seven blanks) were processed as the samples, applying the EPA method 3051A.[16] This acid extraction solution consisted of an addition of 9 mL of HNO_3 sub-boiling and 3 mL of HCl sub-boiling to 0.5-1.0 g of sediment samples and/or certified material references in microwave HP-500 vessels (PFA Teflon, fluorocarbon polymer).The digestion was made in a microwave furnace model Mars 5 (CEM Corporation) according to the following parameters: power of 600 W, time of temperature ramp of 9 min, final temperature of 175 ºC and hold time of 4.5 min.

After cooling, the vessel content was transferred to a 50 mL centrifuge vial and the volume turned into 40 g with water (Milli-Q) with a resistivity of 18 MΩ cm at 25 °C. The metal analysis was performed after the decanting or centrifugation of residues of the vial content.

Mercury analyses

Total Hg concentrations were determined by cold vapor generation in an atomic absorption spectrometry Varian, model Spectr-AAS-220FS in a wavelength of 253.7 nm, slit width of 0.5R nm, lamp current of 4.0 mA with a deuterium lamp background correction. The spectrometer was coupled to a typical FIA (flow analysis injection) manifold, with a manual injection valve that injects 500 µL of digested sample at a flow of Milli-Q water (10 mL min^{-1}). Hg^{2+} was reduced on line by $SnCl_2$ 25% (m/v) in HCl 25% (v/v) at a flow of 1 mL min^{-1}. Argon was used as a carrier gas at a constant flow of 200 mL min^{-1}.[17,18] All reagents were of analytical grade with low levels of mercury (HNO_3 sub boiling and HCl sub boiling). High purity water of 18 MΩ cm resistivity was obtained using Milli-Q system. The Hg stock solution (1000 mg L^{-1}) was acquired by dissolving HgO (Johnson Matthey Chemicals Limited).

Other metal analyses

Al, Fe, Mn, Co, Cd, Cu, Ni, Pb, and Zn concentrations were determined by a fast sequential atomic absorption spectrometer Varian, model Spectr-AAS-220Fs,[17] using the flame mode, with deuterium lamp background corrections for Co, Ni and Pb.

Assessment of metal contamination

After determination of the metal concentrations, four approaches were applied in order to evaluate the metal contaminations: sediment quality guidelines (SQGs), the geoaccumulation index (I_{Geo}), metal pollution index and statistical analyses.

Sediment quality guidelines (SQGs)

Sediment quality guidelines (SQGs) were developed to support protection and management strategies for freshwater, estuarine and marine ecosystems. The Canadian legislation[6] developed the TEL and PEL reference values of the Sediment Quality Guidelines, which were also adopted by CONAMA.[7] Threshold effect level (TEL) is the limit below which no adverse effects on the biological community are observed. Threshold effect level and the Probable Effect Level (PEL) is the probable level in which an adverse effect in the biological community occurs. These limits for Hg, Cd, Cr, Cu, Ni, Pb and Zn concentrations in sediments from fresh water are shown in Table 2.

Index of geoaccumulation (I_{Geo})

To assess the intensity of metal contamination in the sediments of the Billings Reservoir, the geochemical accumulation index was calculated using the equation 1 proposed by Muller and co-workers:[19]

$$I_{GEO} = \log_2\left[\frac{Cn}{1.5\,Bn}\right] \qquad (1)$$

where, I_{Geo} is the geochemical accumulation index; Cn is the sediment metal concentration in the fraction < 63 µm; 1.5 is the factor for possible variations in background data due to lithological effects; Bn is the metal concentration in the shale.

Table 1 presents the seven I_{Geo} classes (0 to 6), I_{Geo} range and sediment quality according Muller and co-workers.[19]

Table 1. I_{Geo} classes, I_{Geo} range and sediment quality[19]

I_{Geo} class	I_{Geo} range	Sediment quality
0	< 0	background concentration
1	0-1	unpolluted
2	1-2	polluted to unpolluted
3	2-3	moderately polluted
4	3-4	moderately to highly polluted
5	4-5	highly polluted
6	> 5	very highly polluted

Metal pollution index (MPI)

The metal pollution index was applied to compare the total content of metals at the 13 fishing points of the Billings Reservoir. MPI was determined according to the following equation:[20,21]

$$\mathrm{MPI} = (\mathrm{Cf}_1\ \ \mathrm{Cf}_2\ \ldots\ \mathrm{Cf}_k)^{1/k} \qquad (2)$$

where, Cf_1 is the concentration value in ppm of the first metal; Cf_2 is the concentration value in ppm of the second metal; Cf_k is the concentration value in ppm of the kth metal.

Statistical analyses

Statistical differences among the metal concentrations in the sediments in four samplings were determined with analysis of variance (ANOVA) and considered significant at p-values < 0.05.

To better illustrate the changes in the metal concentrations in the sediments at four sampling campaigns, it was also used the box plot method, a useful visual technique to improve the interpretation of data, to compare seasonal metal distributions and to identify outliers and extreme concentrations.[22]

A correlation matrix of all studied variables was performed to recognize previous relationships among the metals concentration and cluster analysis was used to identify and study the interrelationships among variables (metals) and sites with similar behaviors. These statistical analyses were carried out using SSPSS 11.0 software package for Windows.

Results and Discussion

The validation of this method was performed by analyzing two certified reference materials (Buffallo River sediment (1) and San Joaquin soil (2)). Table S2 (in the SI section) shows the metal recovery for the two certified reference materials, the Z score, the limits of detection and determination for all metals established in agreement with Inmetro (National Institute of Metrology, Standardization and Industrial Quality, Brazil).[23] The metal recovery was > 80%, an indicative of a satisfactory method, except for elements Cr ((1)-56.7%, (2)-48.9%) and Al ((1)-38.4%, (2)-51.1%). These results are in agreement with other studies[24,25] and compliant with validation data presented by the method 3051A for Buffalo River sediment.[16] These (residual fraction from Cr and Al) are associated with the crystalline structures of minerals and thus are considered to be of natural origins.[26]

Our group intent was not to completely decompose the samples but nearly get a total digestion of the samples in order to obtain the elements that are associated with the adsorbed, exchangeable, oxidizable and reduced geochemical fractions and that can be considered anthropogenic in origin.[25]

The limits of detection for these metals were obtained based in a mean of determinations of seven blank preparations ($\overline{\mathrm{X}}$) plus t times the standard deviation determined by these seven preparations of the blanks ($\mathrm{LOD} = \overline{\mathrm{X}} + \mathrm{t}s$) were t = 3.143 value of student's *t* test for $p = 0.05$ and six degrees of freedom (n − 1). The limit of determination was obtained by an equation ($\mathrm{LOQ} = \overline{\mathrm{X}} + 5s$). The final LOQ of this procedure was obtained, considering sample mass and dilutions of solutions.

Metal concentrations in the studied area are shown in Table 2. The metal concentration values for some of the samples are compatible with findings of studies carried out by CETESB in the same reservoir in 2005 and 2006.[4]

After the determination of the metal concentrations, the following four approaches were applied:

Sediment quality guidelines (SQGs)

By applying SQGs, the results showed increases in the concentrations of Hg, Cd, Cu, Zn, Cr, Ni and Pb, suggesting the association with human activities. In several samples, these elements showed levels above PEL, levels frequently associated with adverse biological effects (Table 2), Hg with 55% of samples, Cu only four samples (8.5%), Zn with seven samples (14.8%), Cr with seven samples (14.8%), Ni with twenty nine samples (61.7%), Pb with four samples (8.5%) and Cd no samples (0%). The worst contamination site was P-10 with Hg, Cr, Cu, Ni, Pb and Zn levels above the PEL limit and Cd concentration above the TEL limit.

Only three samples, P-13 located in the margins near the ferry boat, P-3 in Biguás Island and P-7 in Bororé exit (in dry period) far from anthropogenic activities, presented mercury concentration below TEL (0.17 µg g^{-1}) levels, in which no adverse effect on the biological community was observed. These 3 samples were used for determination of background level ($\mathrm{Bg}_{\mathrm{Hg}}$ = 0.08 µg g^{-1}).

Only eight samples presented Cu concentration below TEL (35.7 µg g^{-1}) levels and were used for determination of background level for Cu ($\mathrm{Bg}_{\mathrm{Cu}}$ = 15.7 µg g^{-1}).

Eighteen samples presented Zn concentration below TEL (123 µg g^{-1}) levels and these were used for determination of background level for Zn ($\mathrm{Bg}_{\mathrm{Zn}}$ = 62.1 µg g^{-1}). Twenty samples presented Cr concentration below TEL (37.3 µg g^{-1}) levels and these were used for determination of background level for Cr ($\mathrm{Bg}_{\mathrm{Zn}}$ = 22.1 µg g^{-1}). Nine samples presented Ni concentration below TEL (18.0 µg g^{-1}) levels and these were used for determination of background level

Table 2. Trace elements (in μg g^{-1}) and major elements (Fe and Al expressed in %) in sediments (< 63 μm fraction) from Billings Reservoir

Station	Al	Fe	Mn	Co	Cd	Hg	Cu	Cr	Ni	Pb	Zn
P-1 - A	4.37	4.18	169.4	2.53	< 0.60	0.30	80.47	21.30	34.65	29.74	100.43
P-1 - B	5.39	4.01	190.1	3.44	< 0.60	0.36	32.20	21.43	**44.07**	31.49	72.24
P-1 - C	4.38	4.21	151.6	3.13	< 0.60	0.38	29.32	22.38	**40.80**	26.97	60.42
P-1 - D	3.31	3.95	174.3	1.85	< 0.60	0.28	22.96	24.87	34.46	27.44	59.01
P-2 - A	6.05	6.89	654.0	11.47	1.44	**0.80**	134.6	84.12	**101.88**	62.38	290.68
P-2 - B	6.14	6.24	631.6	12.57	1.73	**1.15**	139.1	**107.92**	**120.04**	76.33	**317.13**
P-2 - C	7.78	5.92	653.1	10.38	1.38	**1.61**	111.0	**112.00**	**97.12**	83.54	296.58
P-2 - D	6.49	7.64	1438	13.59	2.17	**0.81**	158.2	**178.07**	**128.39**	58.37	301.38
P-3 - A	9.53	6.89	502.7	7.97	0.98	**0.63**	136.9	69.4	**82.41**	48.04	219.6
P-3 - B	9.45	7.62	1040	3.01	< 0.60	**0.64**	47.42	21.5	30.71	39.67	156.0
P-3 - C	7.33	8.00	744.8	10.53	1.36	**0.99**	118.0	**96.8**	**102.1**	75.39	**330.2**
P-3 - D	1.42	3.54	359.8	< 1.0	< 0.60	0.05	9.22	10.5	8.63	< 2.00	28.20
P-4 - A	7.11	6.13	336.4	10.55	< 0.60	0.34	62.72	68.82	**76.87**	38.62	140.0
P-4 - B	12.9	6.01	1658	3.17	< 0.60	0.38	41.93	28.39	33.37	17.50	71.34
P-4 - C	3.65	6.16	1061	2.89	< 0.60	0.28	76.36	26.45	27.97	22.92	64.83
P-4 - D	6.03	5.80	994.8	6.2	1.12	**0.59**	88.06	37.02	**54.65**	51.56	240.9
P-5 - A	10.5	8.22	1215	6.69	< 0.60	**1.77**	**214.5**	48.88	**62.16**	48.90	312.1
P-5 - B	9.49	8.84	1471	32.06	< 0.60	0.27	92.90	**116.7**	**105.7**	42.91	98.41
P-5 - C	8.81	8.47	756.4	13.16	< 0.60	0.26	53.61	91.56	**71.79**	28.33	85.63
P-5 - D	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc
P-6 - A	7.01	6.02	517.9	6.96	1.06	0.47	98.7	44.73	**69.48**	58.44	255.6
P-6 - B	1.22	4.79	246.6	1.75	< 0.60	0.23	124.6	21.00	22.90	19.53	82.57
P-6 - C	4.64	4.66	449.5	5.08	0.60	**0.71**	94.45	38.08	**47.94**	36.44	166.4
P-6 - D	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc
P-7 - A	9.01	6.47	220.3	7.44	0.60	**0.60**	75.58	45.62	**62.43**	48.76	184.70
P-7 - B	6.64	6.09	301.0	7.06	1.28	**0.61**	91.78	57.63	**75.02**	50.11	245.70
P-7 - C	8.16	6.02	276.3	6.13	0.96	**0.58**	80.46	55.22	**72.11**	50.72	207.7
P-7 - D	2.19	1.30	118.2	2.63	< 0.60	0.16	10.27	11.48	9.42	13.325	32.05
P-8 - A	7.44	7.10	403.8	5.49	0.73	**0.67**	96.03	38.61	**53.31**	50.99	257.6
P-8 - B	4.17	4.25	258.4	6.88	1.20	**0.95**	112.8	41.02	**52.62**	47.87	268.1
P-8 - C	5.31	4.94	135.3	7.14	1.63	**2.50**	131.2	58.81	**45.13**	84.04	**318.1**
P-8 - D	4.10	6.90	890.0	13.11	2.34	**0.98**	163.7	**139.9**	**124.7**	57.05	**329.0**
P-9 - A	8.48	6.19	590.6	7.82	1.25	**0.75**	110.5	36.91	**58.99**	72.16	293.4
P-9 - B	7.21	6.27	534.1	10.31	2.08	**0.70**	151.2	61.94	**87.72**	79.15	**372.6**
P-9 - C	8.01	6.57	518.7	8.33	1.69	**0.72**	122.7	47.69	**73.43**	70.96	307.8
P-9 - D	10.0	6.75	1321.2	3.72	< 0.60	**0.86**	37.91	39.14	**42.82**	21.16	161.5
P-10 - A	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc
P-10 - B	7.13	6.20	431.5	9.89	2.96	**1.09**	**401.1**	**92.5**	**74.24**	**123.0**	**750.4**
P-10 - C	7.03	6.11	378.3	9.23	2.65	**1.50**	**358.6**	**107**	**67.27**	**144.3**	**670.9**
P-10 - D	8.54	6.30	384.8	10.31	2.25	**0.88**	**318.6**	74.7	**70.60**	**111.4**	**494.9**
P-11 - A	12.08	2.55	562.5	0.74	< 0.60	0.19	67.67	9.26	10.77	31.17	27.29
P-11 - B	8.05	9.51	152.1	2.19	< 0.60	0.48	86.31	34.0	15.30	41.53	116.6
P-11 - C	8.86	7.54	143.6	1.62	< 0.60	0.36	43.80	25.1	15.70	65.30	92.08
P-11 - D	2.37	10.33	82.60	1.10	< 0.60	0.22	10.20	38.6	4.14	6.13	31.12
P-12 - A	8.64	10.35	548.8	3.39	< 0.60	**0.88**	**598.7**	28.30	24.70	**178.6**	**458.3**
P-12 - B	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc
P-12 - C	3.93	6.70	596.9	5.70	< 0.60	**1.26**	120.1	27.1	24.78	84.72	261.3
P-12 - D	6.75	9.28	374.6	4.23	< 0.60	0.34	63.75	33.19	30.47	29.03	94.13
P-13 - A	4.90	12.45	364.4	1.71	< 0.60	0.30	149.9	20.83	16.26	7.11	75.60
P-13 - B	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc
P-13 - C	17.8	4.42	56.72	1.57	< 0.60	0.24	10.24	15.76	8.69	12.72	23.02
P-13 - D	2.24	1.09	27.68	< 1.00	< 0.60	< 0.03	0.83	2.25	< 2.00	2.83	2.79
$B_{Billings}$	nd	nd	nd	4.55	nd	0.08	15.7	22.1	10.1	19.4	62.1
B_{SE}	2.12	2.90	226	7.3	0.11	0.12	14.0	31.00	14.00	15	51.00
TEL					0.6	0.17	35.7	37.3	18	35	123
PEL					3.5	0.486	197	90	35.9	91.3	315

A: 1st sampling; B: 2nd sampling; C: 3rd sampling; D: 4th sampling; values above PEL are in bold font and these above TEL are in underline format; $B_{Billings}$: background levels for this study; B_{SE}: Background levels for a Santos Estuarine System;[27] nc: not collected samples; nd: not determined.

for Ni (Bg_{Ni} = 10.1 µg g^{-1}). Nine samples presented Pb concentration below TEL (18.0 µg g^{-1}) levels and these were used for determination of background level for Pb (Bg_{Pb} = 19.4 µg g^{-1}).

These results of background levels determined in this work are in accordance with the result of metal background presented by Luiz-Silva *et al.*[27] (Table 2) for Santos Estuarine System (São Paulo State), including samples in Cubatão River, Pedreira River, Capivari River and others.

For the elements Al, Fe and Mn that do not present PEL and TEL limits and for the Cd, in which values under TEL cannot be determined due to the limitations of our analytical procedure, metal background presented by Luiz-Silva *et al.*[27] was used to calculate the index of geoaccumulation I_{Geo}. For Co, it was (Bg_{Co} = 4.55 µg g^{-1}) obtained by the mean of the samples grouped by the cluster analysis in sediment samples with lower levels of contamination.

Index of geoaccumulation (I_{Geo})

By applying an index of geoaccumulation analysis, the I_{Geo} results were found for 47 samples and are presented in Table S3 (in the SI section).

Based on these results, no I_{Geo} class 6 was found. This class represents sediments very highly polluted. Therefore, I_{Geo} class 5 that represents highly polluted sediments was observed in only one of the samples for Hg, two samples for Cd and Cu. I_{Geo} class 4 that represents sediments moderately to highly polluted was found in 9 samples for Cd, 6 samples for Hg, three samples for Cu and only one sample for Ni and Al. I_{Geo} class 3 that represents sediments moderately polluted was found in 23 samples for Al, 19 samples for Hg, 16 samples for Cu, 9 samples for Cd, 4 samples for Zn, 3 samples for Pb, 3 samples for Mn and only one sample for Co.

In general terms, the most critical areas concerning metal accumulation are the sites P-2, P-8, P-9 and P-10. The P-2 site is influenced by chloralkali factories in which mercury cathodes were used for chlorine production until 2010. However, the study of mercury contamination in the Gulf of Trieste, [28] originating from Soca river in Slovenia (Isonzo in Italy) that drains the cinnabar deposits of the world's second largest Hg mining area, Idrija, Slovenia. Showed that even 10 years after closure of the Hg mine, Hg concentrations in river sediments are still very high and did not show the expected decrease. Sites P-10, P-9 and P-8 were also critical areas (getting disposal of solid wastes and liquid effluents) close to sewage wastes from Pinheiros River, swine waste liquid slurry and other industrial wastes (Figure S2 in the SI section).

Metal pollution index

MPI are illustrated in Figure 2. The average metal concentrations at each sampling site was calculated from the concentration levels obtained at the four sampling campaigns to determine the influence of total metal content at 13 fishing points of the Billings Reservoir.

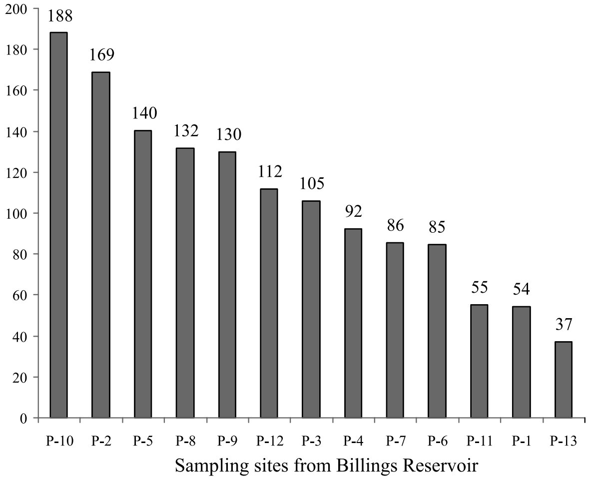

Figure 2. The metal pollution index (MPI) that determines the influence of total metal content at 13 fishing points of the Billings Reservoir.

Figure 2 shows that the most critical areas concerning the total metal accumulation are the sites P-10 and P-2. The most critical site P-10 presented total metal concentration 5 times above total metal concentration of P-13 and 3.7 times above P-1, sites that have the lowest total metal concentrations, which also suggest a contamination associated with anthropogenic sources.

Statistical analyses

Seasonal variations in metal levels among four sample campaigns were determined with ANOVA and considered statistically insignificant ($p > 0.05$), suggesting that seasonal variations may not contribute to the source of metals. However, seasonal changes of metal levels for each site were also compared using ANOVA and considered statistically significant ($p < 0.05$), suggesting that metal contamination can vary in a short space due to mineralogy differences or due to simple displacement of sediments by the Billings Reservoir while the grain-size differences were reduced by the utilization of sediments (< 63 µm fraction).

The box plot method was also used to better illustrate changes in the metal concentrations in sediments at four sampling campaigns. The box plot uses the median, the approximate quartiles, and the lowest and highest data points to convey the level, spread and symmetry of a distribution of data values.

The Hg, Pb, Co, Al and Fe levels and distribution in four sample campaigns are shown in box plot (Figure 3).

Overlap of the boxes that represent metal levels among the four sample campaigns confirms the results obtained by ANOVA, suggesting that the variations in metal levels were considered statistically insignificant ($p > 0.05$). However, as seen in Figure 3, the 3rd sampling box plot to Hg and Pb shows that the median value is slightly elevated and has a wide distribution of coefficients, while others have a compact distribution. Such fact suggests a slight increase in Hg and Pb contamination during the heavy rainy periods in January-2010.

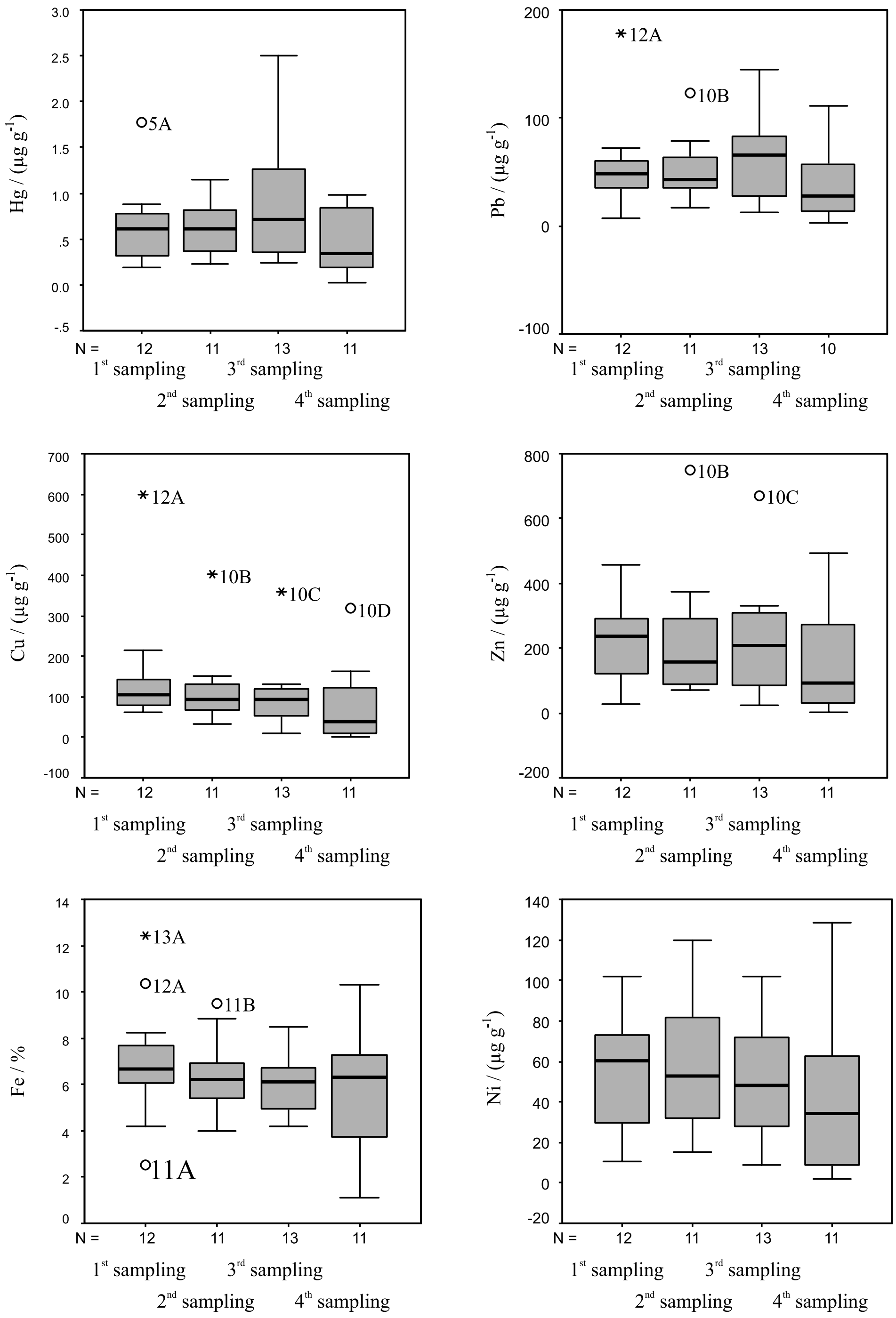

Figure 3. Box plot of Hg, Pb, Cu, Zn, Fe and Ni concentration for 47 sediment samples collected in four sampling campaigns. Solid line within the box indicates a median value. Horizontal lines in the boxes represent 25, 50 (median) and 75% of values; error bars indicate 5 and 105% of these values. Open circle represents outlying points, while (*) represents extreme points.

Also, outlier and extreme values were observed for Cu and Zn on P-10 in most sampling campaigns and Pb in 2nd sampling, suggesting that this is the most critical site to metal contamination.

Correlation matrix

Pearson's correlation is summarized in Table S4 (in the SI section). Al and Fe (commonly used for normalization) presented non-significant correlation ($p > 0.05$) with other metals and among them, except for Mn (with significant correlation, $p < 0.05$) and Fe whit Cr ($p < 0.05$).

The metals Hg, Cu, Cr, Ni, Pb and Zn presented high significant correlation ($p < 0.01$) among them and indicated to be strongly correlated, suggesting a generalized dissemination of these metals in the Billings Reservoir. However, groups of metals with similar behavior were not detected by this analysis.

Cluster analysis

Cluster analysis is a useful tool for grouping most similar metal behavior and sampling sites by generating a dendrogram which summarizes the similarity of variables (metals). This analysis examines distances between samples and data sets.

A dendrogram showing the metal and sample similarities are presented in Figure 4. The horizontal links correspond to sites or elements and the numbers on the top of the dendrogram correspond to similarity level, in a scale from 0 (maximum identity) to 25 (maximum dissimilarity).

The sites were clustered into two major groups (G-1 and G-2) separated by maximum dissimilarity among the metals (Figure 4a) and by maximum dissimilarity among the metal content of the samples (Figure 4b).

In Figure 4a, it can be observed a group G-2 whit the metals Hg, Cd, Cu, Pb and Zn grouping by their similarity, these metals showed the worst indices of metal geoacumulantion (Table S3 in the SI section). and the group G-1 was divided in 2 other groups by the maximum dissimilarity a group G-1B whit the metals Fe, Al and Mn with similar behavior and a group G-1A whit the metals Co, Cr and Ni with similar behavior.

The characterizations of groups shown in Figure 4b were made by average value and standard deviation of each analyzed metal (Table 3). G-2 (containing 15 samples) presented average metal concentrations from 1.42 to 2.92 times above metal concentration of G-1 (which contains 32 samples), suggesting that G-2 corresponds to sites with critical level of metal contamination of sediment whereas G-1 grouped sediment samples with lower levels of contamination.

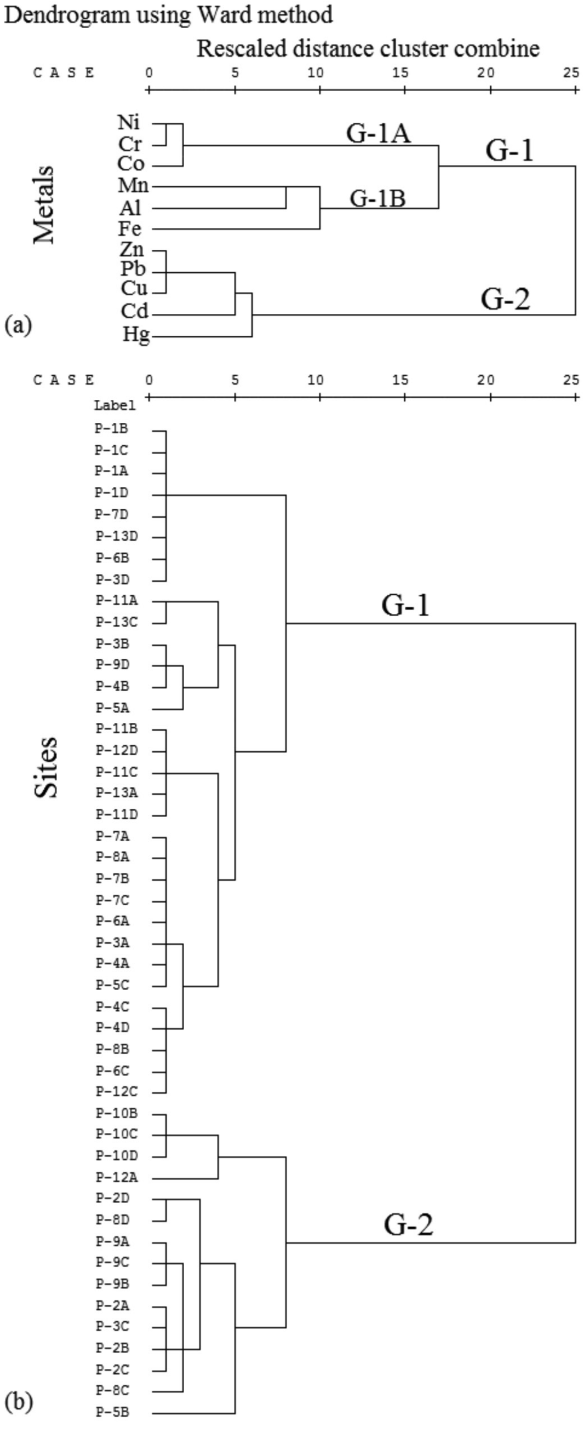

Figure 4. Dendrogram from the cluster analysis for metal concentrations in surface sediments collected from Billings Reservoir.

The dendrogram confirmed for the relation (G-2/G-1) that only Al (1.07) and Fe (1.15) presented concentration seemed to be associated with crustal material or natural weathering processes, while Mn (1.42), Cd (2.03), Hg (2.08), Ni (2.14), Co (2.49), Pb (2.50), Cr (2.63), Zn (2.86) and Cu (2.92) showed increases in their concentrations, which seemed to be associated with anthropogenic sources.

Table 3. Characterization of groups by metal content

Element	G-1[a] / (μg g^{-1})	G-2[a] / (μg g^{-1})	G-2/G-1
Cu	70.97 ± 47.64	207.3 ± 145.4	2.92
Zn	131.1 ± 89.3	375.5 ± 161.9	2.86
Cr	34.10 ± 19.40	89.54 ± 40.12	2.63
Pb	35.13 ± 18.70	87.97 ± 36.47	2.50
Co	4.55 ± 2.94	11.34 ± 6.28	2.49
Ni	39.9 ± 23.6	85.47 ± 29.90	2.14
Hg	0.50 ± 0.35	1.04 ± 0.52	2.08
Cd	0.95 ± 0.25	1.92 ± 0.54	2.03
Mn	471.4 ± 410.9	667.0 ± 364.5	1.42
Fe	6.02 ± 2.48	6.89 ± 1.34	1.15
Al	6.70 ± 3.69	7.18 ± 1.41	1.07

[a] Mean ± standard deviation.

However, the results presented by the dendrogram indicated two disabilities. The relation G-2/G-1 = 1.07 for the element Al presented low levels of contamination, but observing the results of I_{Geo}, 23 samples (48.9%) presented I_{Geo} class = 3, indicating sediments moderately polluted and 18 samples (38,3%) showed I_{Geo} class = 2, indicating sediments polluted to unpolluted. These results indicated that the Al has a moderate contamination and was spread in the reservoir.

Another weakness was the cobalt element, that has a relation G-2/G-1 = 2.49, an indication of association with anthropogenic sources. However, 46 samples (98%) showed I_{Geo} = 0 and I_{Geo} = 1, indicating levels of background and non-contaminated sediments.

Conclusions

In most sediment samples, the measured levels of metals were above TEL limits, indicating contamination according to the Canadian Sediment Quality Guidelines[6] and CONAMA criteria,[7] whereas below that no adverse effect in the biological community is observed. I_{Geo} can be used as complementary technique to detect and confirm the degree of metal contamination in sediments of the Billings Reservoir.

The highest I_{Geo} class average: 4 whit I_{Geo} range (3-4), indicative of sediments moderately to highly polluted by metal (Hg, Cu, Ni and Zn) concentration in sites P-10, P-2 and P-8. The metal pollution index showed the most critical areas concerning the total metal accumulation.

The results demonstrated that metal pollution is still a problem for the bent ecosystem of Billings Reservoir, although the metal levels in water presented concentrations below the CONAMA criteria,[4] according to some studies made by CETESB.[5]

The significance of the seasonal effect on metal concentration was evaluated by ANOVA and box plot. ANOVA results showed that there is no significant seasonal effect on metal concentration. Therefore, box plot demonstrated seasonal variations with slightly elevated mercury and lead levels during heavy rainy periods in January-2010 (3rd sampling campaigns).

The dendrogram showed for the relation G-2/G-1 that the metal concentration seemed to be associated with crustal material or natural weathering processes G-2/G-1 *ca.* 1 and the metals with G-2/G-1 among 2 and 3 seemed to be associated with anthropogenic sources. However, the dendrogram presented two deficiencies with Al and Co that were corrected by I_{Geo}.

These results justify a strong environmental policy to reduce the metal contamination in the Billings Reservoir and to implement the best control to the disposal of solid wastes and liquid effluents that present a greater degree of metal contamination. These strong efforts must be made to continue to allow safe recreation, fishing and other activities directly related to this reservoir.

Supplementary Information

Supplementary data (Tables S1-S4 and Figure S1) are available free of charge at http://jbcs.sbq.org.br as PDF file.

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