DETERMINATION OF METALS IN WATER FROM BILLINGS DAM, SAO PAULO

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ABSTRACT

The Billings reservoir, located in Sao Paulo, Brazil, is used for several purposes such as: water supply, electric generation, fishing and leisure. Although considered an area of environmental protection, in recent years the dam has suffered diverse environmental aggressions including the release of toxic metals. This study presents a recent evaluation of metal contents along the Dam. Samples were collected every three months during the period of winter 2009 to summer 2010. Samples were collected in thirteen points along of the dam, as follows: Rio dos Porcos (Point 1), Summit Control (Point 2), Ilha do Biguá (Point 3), Casa Caída (Point 4), Barragem (Point 5), Foz de Taquacetuba (Point 6), Braço Bororé (Point 7), Foz de Bororé (Point 8), Alvarenga (Point 9), Pedreira (Point 10), Bororé´s Margin (Point 11), Capivari I´s Margin (Point 12) and Capivari II´s Margin (Point 13). The determination of Al, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn was performed by using high resolution inductively coupled plasma mass spectrometer (HR-ICP-MS). The methodology has been validated using certified reference material Riverine Water Reference Material for Trace Metals provided by National Research Council Canada (NRCC). The sampling points located in the Pedreira, Bororé´s Margin, Alvarenga, Barragem Taquacetuba, Casa Caída e Ilha do Biguá presented the highest concentrations. The level for Fe, Cu and Ni were higher than the ones reported in the literature and above the limit set by CONAMA 2914/2011.

1. INTRODUCTION

Nowadays one of the main concerns of the humanity consists of water pollution. Water is crucial for all terrestrial ecosystem. For human being, in particular, is directly related to fundamental activities such as public supply and industrial sanitation, agricultural irrigation, electricity production, transportation, leisure, among others [1].

Billings reservoir is extremely important due to the fact that it is the largest water reservoirs in South America's. Dam is located within the Metropolitan Region of Sao Paulo – RMSP, Brazil, and occupies an area of approximately 582.8 km2. The reservoir produces 12 m³/s of the water that supplies the Great ABC (Santo André, Sao Bernardo do Campo and Sao Caetano do Sul), part of Sao Paulo and the Santos region [2; 3].

In spite of that, since the beginning of its flooding, several environmental aggressions were observed such as deforestation, an uncontrolled increase of urbanization in its margins, illegal settlements, discharge of domestic sewage and solid residues, among other. Besides, the Dam is also used to control the Pinheiros river's floods receiving contaminated waters from this river mainly during rainfalls [4].

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This frequent input of contaminants in the dam becomes worrisome, considering that, in its surroundings, there are different kinds of settlements, among them families of fishermen, who use these waters without conventional treatments for domestic consumption and artisanal fishing for livelihood [4; 5-15 and 16].

Preliminary studies in the region detected higher levels of metals in Foz de Taquacetuba, Alvarenga and Pedreira sites [17].

Besides, during the period of 2001 - 2012 the Environmental Agency of the State of São Paulo - Cetesb monitored the region and also detected elevated concentration of Al, Cd, Pb, Cr, Mn, Hg Ni and Zn in the water column [5-15].

This study reports the recent results on the concentrations of potentially toxics metals present in water from Billings Reservoir in thirteen different points around the dam.

2. MATERIAL AND METHODS

2.1. Site Description

The reservoir is an artificial lake located in the metropolitan region of Sao Paulo, Fig. 1, 23° 42' and 23° 45' S and 46° 26' and 46° 42' W at an altitude of 760 m, 10 m depth and covers a total of 127 km² (FURLAN, 2011). Make the reservoir boundary with the municipalities: Sao Paulo, Sao Bernardo do Campo, Diadema, Ribeirão Pires, St. Andre and Rio Grande da Serra as can be showed in Fig. 1 [18; 19].

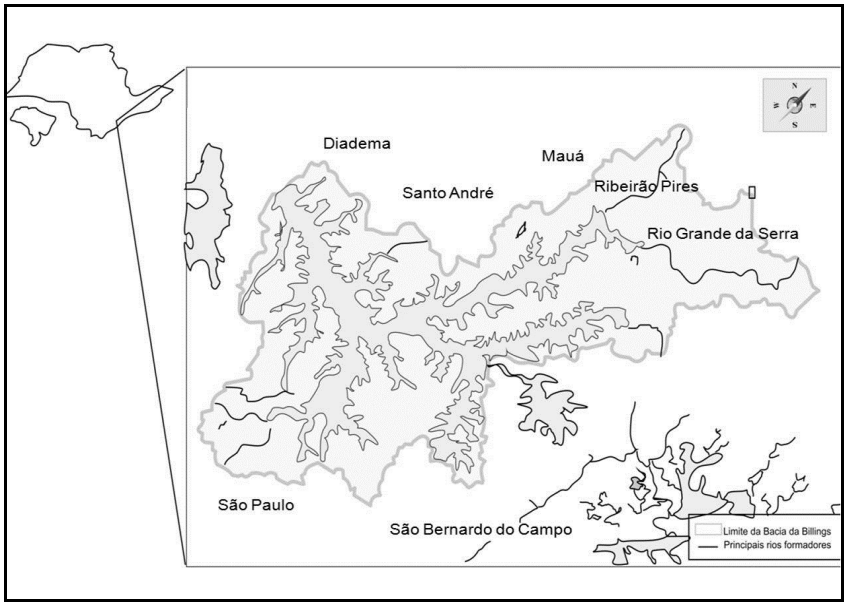

Figure 1: Map showing the Billings Reservoir and Metropolitan Region of Sao Paulo – RMSP. (Adapted of the http://www.mananciais.org.br/slideshow/albuns/ 1165258 798/ ma pa3_RiosForm.gif)

2.1 Sample collection

Water samples were collected during each quarter, from June/2009 to May/2010. They were collected in two depths (superficial (S) and deep (D)). Thirteen points in the Billings dam were selected for this study: Rio dos Porcos – P1 (23° 52' S / 46° 33' W), Summit Control – P2 (23° 48' S / 46° 32' W), Ilha do Biguá – P3 (23° 48' S / 46° 31' W), Casa Caída – P4 (23° 46' S / 46° 35' W), Barragem – P5 (23° 49' S / 46° 38' W), Foz de Taquacetuba – P6 (23° 48' S / 46° 37' W), Braço do Bororé – P7 (23° 48' S / 46° 40' W), Foz do Bororé – P8 (23° 47' S / 46° 39' W), Alvarenga – P9 (23° 46' S / 46° 37' W), Pedreira – P10 (23° 42' S and 46° 39' W), Bororé Margin – P11 (23° 48' S / 46° 41' W), Capivari 1 Margin – P12 (23° 48' S / 46° 32' W), Capivari 2 Margin – P13 (23° 48' S / 46° 32' W), which are represent the main environments impacted by industrial activities and increasing disorderly process of urbanization, besides the points are the used for the inhabitants of the region to collected waters and their use without conventional treatments for domestic consumption [4; 16; and 20]. The position of the points are shown in Fig. 2.

Water samples were collected at two depths: surface (S) and bottom (F). We analyzed the same analytes accompanied by Cetesb found in higher concentrations in fish, these correspond Al, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn were determined and quantified using the technique HR-ICPMS.

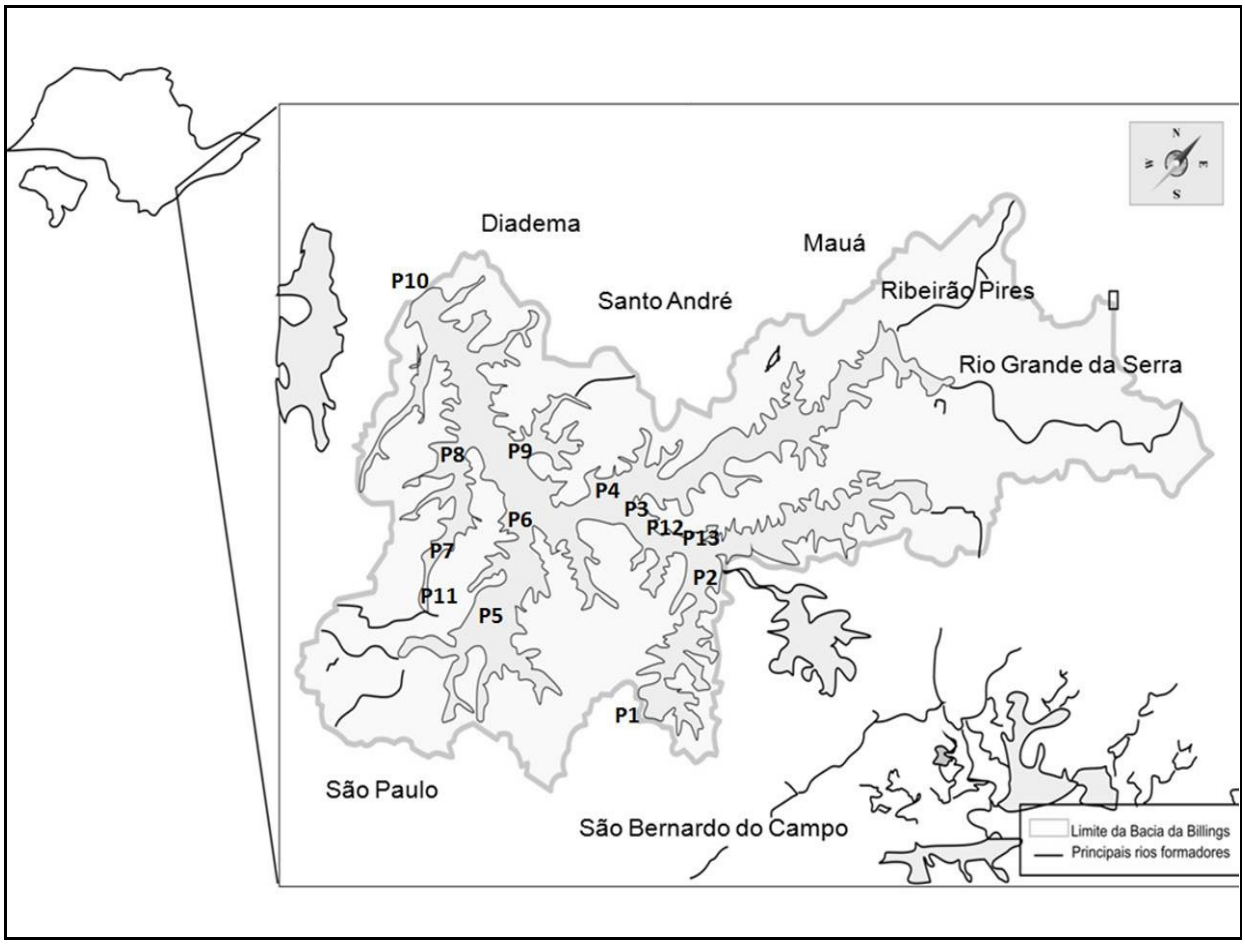

Figure 2. Sampling points in the Billings reservoir

All procedures for collection, storage and chemical analyzes of the samples were performed in accordance with the methods 1638 and 200.8 of United States Environmental Agency - USEPA

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[21-22], the Protocol of 3000 American Public Health Association - APHA [23] and studies conducted by Milani and Vicente-Martorell [1; 24].

Immediately after collection, the samples were acidified to 5% V/V with nitric acid, filtered and stored refrigerated until the time of analysis. A total of 86 samples were analyzed. During the samples analysis, and in order to avoid cross concentration, Milli-Q water samples were analyzed every 10 samples.

2.2 Analysis of metals Al, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn

Figure 3 represents the main steps of the analytical methodology. All procedure were performed by weight. Then, 1g of solution of In (Spex) 10 ug kg^{-1}, was added to 9 g of each sample.

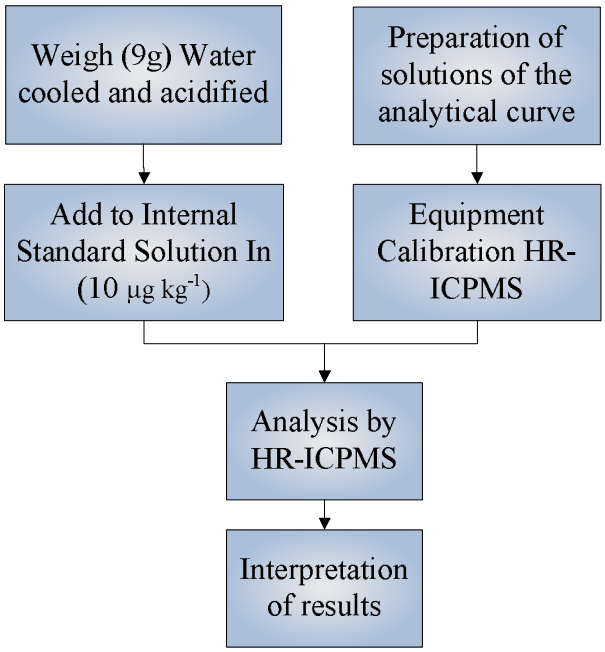

Figure 3. Representation of the process for analysis of metals by HR-ICP-MS

The validation of analytical methodology was carried out analyzing a certified reference material (MRC) *Riverine Water Reference Material for Trace Metals* provided by the National Research Council Canada - NRCC, which is certified for Al, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn.

2.2.1 Equipment

The analysis were performed using a high resolution inductively coupled plasma mass spectrometer (HR-ICP-MS) Element Finnigan MAT - Bremen, Germany in 1996. This equipment has a double focusing analyzer system of ions with reverse geometry (Nier-Johnson), one magnetic analyzer followed by an electrostatic analyzer.

3. RESULTS AND DISCUSSION

The results obtained with reference material are presented in Table 1.

Table 1. The certified values and result obtained with their respective expanded uncertainties from Riverine Water MRC

Elements	*Riverine Water* *Expanded uncertainty certified* ($\mu g\ ml^{-1} \pm \mu g\ ml^{-1}$)	*Riverine Water* *Obtained result* ($\mu g\ ml^{-1} \pm \mu g\ ml^{-1}$)
Al	31 ± 3	29 ± 5
Cd	0.013 ± 0.002	0.011 ± 0.009
Cr	0.3 ± 0.004	0.27 ± 0.01
Cu	1.35 ± 0.07	1.30 ± 0.1
Fe	100 ± 2	97 ± 6
Mg	1.6 ± 0.2	1.2 ± 0.5
Mn	3.9 ± 0.3	3.6 ± 0.25
Ni	0.83 ± 0.08	0.8 ± 0.1
Pb	0.068 ± 0.007	0.065 ± 0.01
Zn	1.04 ± 0.09	1.0 ± 0.1

The recovery for each element is present in the figure 4.

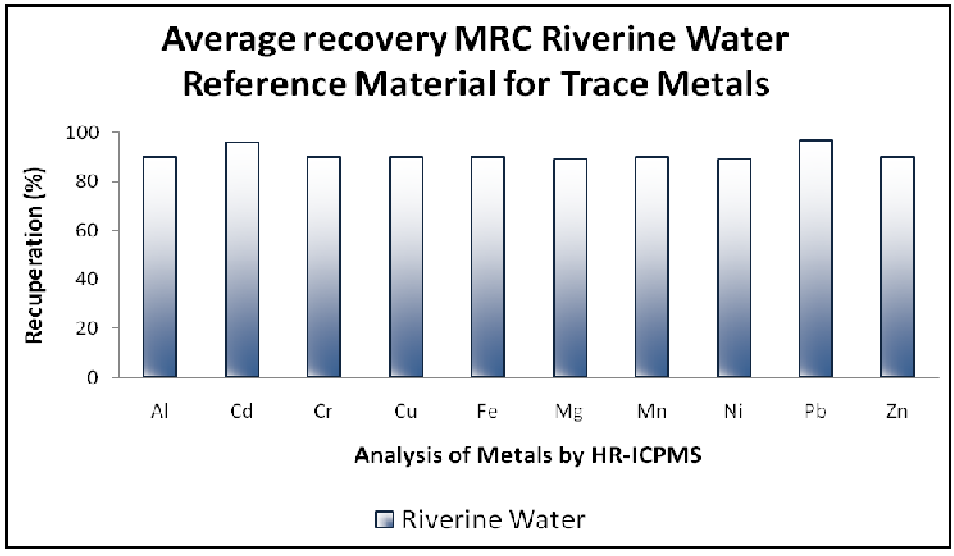

Figure 4. Average recovery MRC Riverine Water

As it can be observed all analyzed elements presented a recovery higher than to 85% (Fig. 4).

The results obtained with the real samples are presented in Table 2.

In general, it was observed an increase in the values in comparison with the ones detected by Cetesb and Sampaio [5-15; 17].

The most contaminated area were: Pedreira, Bororé Margin, Alvarenga, Casa Caída and Ilha do Biguá

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Table 2. Average concentration of metals present in water form Billings dam, Sao Paulo.

Sampling points	Depth	Al (mg L^{-1})	Cd (µg L^{-1})	Cr (µg L^{-1})	Cu (µg L^{-1})	Fe (mg L^{-1})	Mg (mg L^{-1})	Mn (mg L^{-1})	Ni (µg L^{-1})	Pb (µg L^{-1})	Zn (µg L^{-1})
P1	S	6	0.759	20.36	98	36	2.8	0.41	57.3	4.93	86
	B	29	2	22.05	125	93	6.5	1.06	67.9	5.62	97
P2	S	5	0.609	20.37	103	30	3.9	0.96	60.6	4.87	123
	B	19	1	21.44	130	65	7.7	2.83	70.5	4.99	156
P3	S	6	4	20.60	110	54	4.0	1.30	63.0	4.91	80
	B	13	7	21.69	132	77	8.4	2.58	71.4	4.98	87
P4	S	6	0.684	19.07	102	25	3.5	1.96	57.7	4.87	74
	B	26	5	21.66	143	68	8.6	3.45	73.6	4.85	102
P5	S	16	0.650	20.25	105	25	5.6	0.94	64.9	4.38	88
	B	27	0.784	23.71	125	60	10	1.44	74.1	4.97	106
P6	S	11	0.529	20.80	105	41	4.5	0.97	64.5	5.14	91
	B	30	5	22.64	129	91	10.5	4.09	78.6	5.35	114
P7	S	14	1	21.12	111	69	4.7	1.41	60.8	5.01	94
	B	31	1	23.83	132	118	9.1	2.17	75.7	5.42	95
P8	S	13	0.704	20.54	106	47	4.5	1.86	65.9	4.94	90
	B	29	1	21.48	121	85	6.5	2.49	71.8	4.90	92
P9	S	12	0.707	20.56	109	51	4.2	1.36	64.5	4.67	75
	B	18	0.955	21.20	123	71	9.8	3.88	73.6	5.06	90
P10	S	18	2	20.85	156	194	3.0	2.62	67.4	4.68	65
	B	21	2	24.62	218	324	3.9	3.48	89.6	6.29	100
P11	M	23	1	23.95	145	74	8.3	1.70	87.6	5.21	257
P12	M	15	2	21.33	120	65	5.6	1.43	65.5	5.93	111
P13	M	15	3	21.63	109	67	5.2	1.12	64.2	5.38	95
Expanded uncertainty (%)		17	71	4	8	6	40	7	13	15	10
Portaria 2914/11		**0.2**	**5**	**50**	**2000**	**0.3**	**----**	**0.1**	**70**	**10**	**5000**

Legend: S: Surface / B: bottom / M: Margin

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Circa of 13% of the samples presented values for Cd above the limits established by CONAMA, Portaria 2914/2011 [25], and in all analysed samples the values obtained for Al, Fe and Mn were also above these limits.

The higher levels of Cd in the water from Bororé can be attributed to small battery factory present in the region.

The higher presence of Al and Fe is probably due use of aluminum sulfate and ferric chloride as coagulant during the flotation process in Pinheiros River.

The levels of Cr, Cu, Pb and Zn were within the limits stipulated by CONAMA. There is no previous data in the literature and values defined for the analyte Mg.

Different values were observed between the concentrations obtained in the surface and bottom from Billings reservoir.

4. CONCLUSION

The samples showed values of Al, Cd, Fe, Mn and Ni above the limits established by law. Sampling sites located in the regions of Pedreira, Margem do Bororé, Alvarenga, Barragem Taquacetuba, Casa Caída e Ilha do Biguá were the most contaminated with values for Cd, Fe, Mn and Ni above the limits defined by CONAMA. The values found for Cr and Pb are lower than those of historical data dam.

All samples showed levels concentrations of Fe, Cu and Ni higher than those reported in the literature and above the limit established by CONAMA.

The results presented in this work demonstrated the necessity to establish a continuous monitoring program in the region as well as to identify the origin the main pollutants ensuring the quality of the water and, as consequence, the health of the inhabitants of the region.

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