

1           **Trace metal and rare earth elements in a sediment profile from the Rio Grande**  
2           **reservoir, São Paulo, Brazil – determination of anthropic contamination, dating and**  
3           **sedimentation rates**  
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24           **Abstract**

25  
26           The Rio Grande Reservoir, located in the southeast of the São Paulo Metropolitan Area, supplies water to  
27           four counties (about 1.8 million people). In this study, two sediment cores (0.36 and 0.40 m) were collected near  
28           the catchment point of the water supply. One was sliced every 2 cm for INAA (instrumental neutron activation  
29           analysis) and dating determinations and the other was sliced every 5 cm for grain size and Hg, Cd, Pb, Ni, Mn  
30           and Cu determinations by ICP OES (Inductively Coupled Plasma Optical Emission Spectrometry) and GF AAS  
31           (Graphite Furnace Atomic Absorption Spectrometry). By INAA, some major and trace elements (As, Ba, Ca,  
32           Co, Cr, Cs, Fe, Hf, Na, Rb, Sb, Sc, Ta, Th, U, Zn and the rare earths Ce, Eu, La, Lu, Nd, Sm, Tb and Yb) were  
33           determined. Sedimentation rates and sediment age of every layer of this core using the <sup>210</sup>Pb method were  
34           determined. The Enrichment Factor (EF) and the Geoaccumulation Index (*I*<sub>Geo</sub>) were calculated using the  
35           concentrations in the deeper layer of this profile as reference values and Sc as a normalizer element. Significant  
36           enrichment (2.0 < EF < 5.5) was found for Na, Mn, Ni, Pb, Sb and Zn in the upper layers. Extremely high  
37           enrichment was found for Hg and Cu (EF > 40) and Cd (EF > 20). From the data obtained in the present study it  
38           was possible to trace the history of pollution by some metals and trace elements in this reservoir over the last 90  
39           years.  
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42           **Keywords:** sediments, enrichment factor, geoaccumulation index, sedimentation rates, dating,

## 43 1 – INTRODUCTION

44 Sediment compartments have been increasingly used in quality evaluation studies in aquatic  
45 ecosystems as they record historic conditions of anthropic activity influences in these environments  
46 which are not always detectable in water compartments. The interaction between the sediment  
47 compartment and the water column can, in itself, be a source of contamination and the interaction can  
48 occur through the revolving sediment because of the increased flow due to rainfall or activity that  
49 interfere with the dynamics of the riverbed (CETESB 2011). The sediment, from the recycling of  
50 material and energy flow point of view, is one of the most important compartments of aquatic  
51 ecosystems. Biological, physical and/or chemical processes occurring therein, influencing the  
52 metabolism of the entire system, since the benthic organisms, through ichthyofauna and algae.

53 Metals of anthropic origin upon entering in an aquatic system can be predominantly in their  
54 dissolved form ( $M(aq)^{+x}$ ) and depending on their characteristics, can remain dissolved or form organic  
55 and/or inorganic complexes which, in turn can remain in a dissolved state, form colloids or be  
56 absorbed by suspended particles in the water body and be deposited in the sediment (Silvério 2003,  
57 Cánovas et al., 2012).

58 One of the big questions in environmental evaluations is how much an ecosystem is  
59 contaminated by a given metal. Many times the anthropic enrichment of a given element may cause  
60 great concern even though the high concentration may not result in toxic effects due to the fact this  
61 metal be in a form not readily available to the biota, either as sulfide or highly complexed with the  
62 organic matter. Another important aspect to take into consideration is if the internationally accepted  
63 sediment quality guide values used (for example, PEL, TEL or crust average) are adequate for tropical  
64 conditions (Quinágua 2012; Gomes et al. 2009), because if not, these can lead to interpretation errors  
65 of metal evaluations in aquatic bodies.

66 However, when dealing with artificial reservoirs this issue becomes a complex task, especially  
67 in function of their allochthonous characteristics. The sediments of reservoirs or dams operate as true  
68 deposits of particulate materials from the rivers that form them. Artificial reservoirs have high  
69 sediment rates when compared to those of the rivers that flow into them which are lotic system and the  
70 reservoirs lentic system. This difference influences the local sedimentation rates. Furthermore,  
71 depending on the location, the alterations that occur in the sediment may be characterized in relatively  
72 short periods of time, such as little as five years or less and a 10 cm layer of recent sediment. As a  
73 consequence, artificial reservoirs are little affected by diagenetic processes and provide a preserved  
74 historic record, from a lithological point of view, of the metal concentrations in their deeper sediment  
75 profiles (Audry et. al. 2004).

76 Metal evaluations in sediment profiles (Audry et al. 2004, Gomes et al. 2009) to obtain the basal  
77 levels of the sediments, mainly in tropical reservoirs where the dynamics of temperature and  
78 consequently weathering are greater (Albarede 2011) are a key point to ascertain whether or not an  
79 environment presents anthropic contamination or merely a lithological enrichment. In order to best

80 establish this difference both the Enrichment Factor (EF) and Geoaccumulation Index (Igeo) are used  
81 in the present study (Sutherland 2000, Audry et al. 2004, Luiz-Silva et al. 2008, Franklin et al. 2012a).

82 The Rio Grande Reservoir is located in the and covers the São Bernardo do Campo, Rio Grande  
83 da Serra, Santo André and Ribeirão Pires municipalities in the state of São Paulo in Brazil. This  
84 reservoir supplies water for around 1.8 million inhabitants. It is also used for leisure and recreation by  
85 the city's population and its fish is consumed by inhabitants of the surrounding regions.

86 This reservoir was built in the 1920's and initially was one of the branches of the Billings  
87 Reservoir. In 1982, the Rio Grande Reservoir was separated from the already highly polluted Billings  
88 Reservoir in an attempt to preserve its water quality. This separation eliminated the entrance of  
89 polluted waters from the city of São Paulo (Franklin et al. 2012a).

90 The objective of this study was to evaluate two sediment profiles from the Rio Grande  
91 Reservoir in order to determine basal values of some trace, metals and rare earth elements as well as to  
92 determine their level of anthropic pollution. The dates and sedimentation rates by  $^{210}\text{Pb}$  method in one  
93 of the sediment profiles were also determined.

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## 95 **2 – MATERIALS AND METHODS**

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97 Two sediment cores (0.40 and 0.36 m) were collected in November 2011 in front of the water  
98 catchment point of the reservoir for the public water system, coordinates S 23°46'18'' and  
99 W 46°31'35'', as showed in Figure 1. The first sediment profile was sliced every 5 cm, air dried at 20-  
100 25°C in a clean recipient, and separated in two aliquots: one for grain size determination and another  
101 for Hg and other metals by ICP-OES (Inductively Coupled Plasma – Optical Emission spectrometry)  
102 and GF AAS (Graphite Furnace Atomic Absorption Spectrometry). This aliquot was passed through a  
103 2.00 mm sieve, ground in a mortar and then homogenized before analysis. The second sediment  
104 profile was sliced every 2cm, air dried at 20-25°C in a clean recipient, passed through a 2.00 mm  
105 sieve, ground in a mortar and then homogenized before INAA and dating analysis.

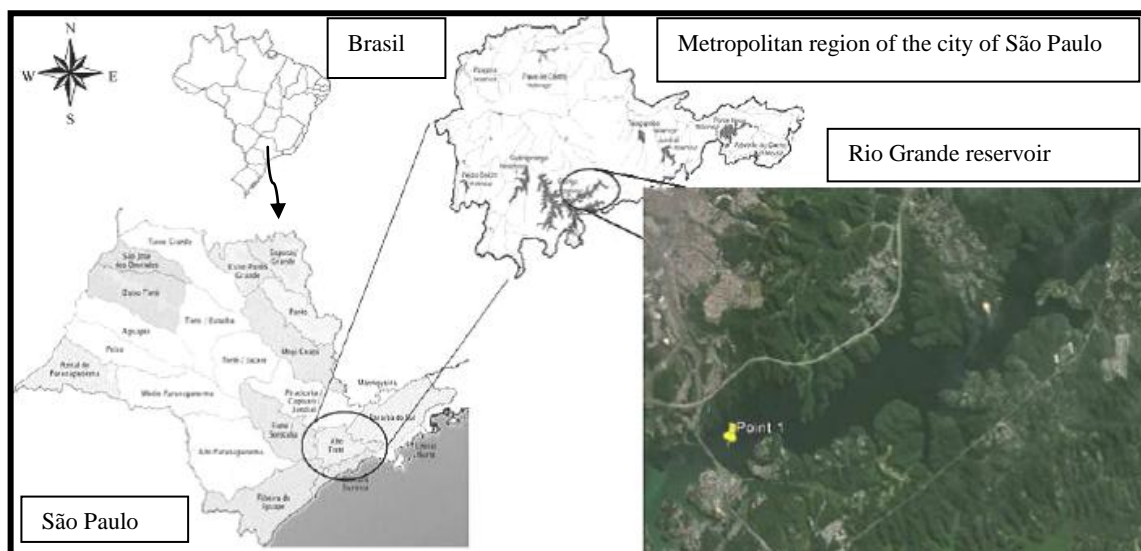


Figure 1 – Sampling Point Location

## 2.1 – Instrumental neutron activation analysis

Instrumental neutron activation analysis (INAA) has been extensively employed in geochemical studies due to the possibility of quantifying many elements at the same time with excellent precision and accuracy and without the need of previous digestion processes. The detection limits varied from 0.01 to 1 mg kg<sup>-1</sup> for most elements.

For the multi-elemental analysis, approximately 150 mg of sediment (duplicate samples) and reference materials were accurately weighed and sealed in pre-cleaned double polyethylene bags, for irradiation. Single and multi-element synthetic standards were prepared using pipettes with convenient aliquots of standard solutions onto small sheets of Whatman No. 41 filter paper. Sediment samples, reference materials and synthetic standards were irradiated for 8 h under a thermal neutron flux of 10<sup>12</sup> n cm<sup>-2</sup> s<sup>-1</sup> in the IEA-R1 nuclear research reactor at IPEN. Two series of counting were made: the first, after one week decay and the second, after 15-20 days. Gamma spectrometry was performed using a Canberra HPGe detector and associated electronics, with a resolution of 0.88 and 1.90 keV for <sup>57</sup>Co and <sup>60</sup>Co respectively. The elements determined by using this methodology were As, Ba, Br, Co, Cr, Cs, Fe, Hf, Na, Rb, Sb, Sc, Ta, Th, U, Zn and the rare earths Ce, Eu, La, Lu, Nd, Sm, Tb and Yb. For methodology validation regarding precision and accuracy reference materials SL-1 (Lake Sediment – IAEA), BEN-Basalt-IWG-GIT and Soil 5 (IAEA) were used.

## 2.2 – <sup>210</sup>Pb Dating Methodology

The dates and sedimentation rates were determined by <sup>210</sup>Pb method using the measurement of the radionuclides <sup>226</sup>Ra and <sup>210</sup>Pb in each slice of the core. The samples of sediments after drying at 20-25 °C were passed through a 2.00 mm sieve, ground in a mortar, homogenized and dissolved in mineral acids, (HNO<sub>3</sub> conc. and HF 40%), and H<sub>2</sub>O<sub>2</sub> 30% in microwave digester and submitted to the

133 radiochemistry procedure for the determination of Ra and Pb. This procedure consists in an initial  
134 precipitation of Ra and Pb with H<sub>2</sub>SO<sub>4</sub> 3M, dissolution of the precipitate with nitrilo-tri-acetic acid at  
135 basic pH, precipitation of Ba(<sup>226</sup>Ra)SO<sub>4</sub> with ammonium sulfate and precipitation of <sup>210</sup>PbCrO<sub>4</sub> with  
136 sodium chromate 30%. The <sup>226</sup>Ra concentration was determined by gross alpha counting of the  
137 precipitate of Ba(<sup>226</sup>Ra)SO<sub>4</sub> and the <sup>210</sup>Pb concentration through its decay product <sup>210</sup>Bi, by measuring  
138 the gross beta activity of the precipitate of <sup>210</sup>PbCrO<sub>4</sub>. The analyses were performed in duplicate and  
139 both radionuclides were determined in a low background gas flow proportional detector (Damatto  
140 2009).

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### 142 **2.3 – Metals determined by ICPOES, GF AAS and Direct Mercury Analyzer**

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144 The sediment samples were previously digested according EPA 3051 procedure (EPA 2007),  
145 with HNO<sub>3</sub> and HCl in microwave oven. The metals Cu, Ni, and Mn were determined by ICPOES and  
146 Cd and Pb, by GF AAS. Hg was determined by Direct Mercury Analyser. These analyses were  
147 performed at Inorganic Chemistry Laboratory of the Environmental Agency of São Paulo State  
148 (CETESB). The analyses were performed in duplicate.

149 Direct analysis of Hg has the advantage of dispensing steps of sample preparation and is  
150 applicable to virtually some matrix. This technique effectively determines the Total Mercury because  
151 it includes organic forms, not always possible to be destroyed in a HNO<sub>3</sub> digestion and reduced with  
152 stannous chloride. This technique includes determining species Hg volatilizable under the conditions  
153 of the method.

154 There are three sequential steps that comprise this analytical technique, thermal decomposition,  
155 in which the sample undergoes a drying process and combustion (approx. 650 °C) under constant flow  
156 of oxygen gas (O<sub>2</sub>). These combustion products are loaded by O<sub>2</sub> to a catalytic section which will  
157 retain possible interferences in the determination of Hg. In the amalgamation, the remaining gaseous  
158 species in the process of thermal decomposition are loaded to an amalgamator. After a retention time  
159 of Hg vapor, the amalgamator is heated to 850 °C to release the trapped Hg, which volatilizes to be  
160 loaded by the O<sub>2</sub> flow to the cell atomic absorption, where the transient Hg vapor will absorb the  
161 radiation from an Hg vapor lamp emitting a narrow band of wavelengths of 254 nm.

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### 163 **2.4 – Sediment Grain Size determination**

164 Sediment grain size determination was performed according to standard CETESB L6.160  
165 (CETESB 1995). This analysis is based on the principles of sieving and sedimentation guided by  
166 Wentworth scale, which is based on the average velocities of particles in an aqueous medium.  
167 According to this standard method, the sand fraction consists of particles with dimensions between 2.0  
168 and 0.063 mm, coarse sand being comprised between the diameters 1.0 to 2.0 mm. The silts are  
169 particles with size between 0.063 and 0.004 mm, clays with a diameter smaller than 0.004 mm.

### 170 **2.5 – EF and Igeo**

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172 The Enrichment Factor (EF) is a factor which allows the evaluation of the enrichment of a given  
173 element through the normalization of another element considered stable and fixed in the environment  
174 and then compared to reference concentrations taking into account a normalizing element. This tool  
175 was proposed in 1979 by Buat-Menard (Loska et al. (1997, 2003 e 2004), Szefer & Skwarzec 1988)  
176 and has been applied in several regions of the world to evaluate anthropic enrichment of certain  
177 elements. The formula used for this calculation follows (equation 1):

$$EF = \frac{(Me/X)_{loc}}{(Me/X)_{ref}} \quad (1)$$

178

179

Where

180

EF -enrichment factor

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Me - metal or element analyzed

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X -metal or element normalizer

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Loc -study location

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Ref -reference values

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Many elements can be used as normalizing elements such as Sc, Fe, Al, Ti, Y and Li (Loska et. al. 2003, Sutherland 2000, Lin et. al. 2008, Dias & Prudêncio 2008, Hernandez et al. 2003). The present study used Sc as the normalizing element.

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As an enrichment evaluation criteria, some authors accept values between  $0,5 \leq EF \leq 1.5$  as indicators that an element is not enriched, while values  $\geq 1.5$  indicate element enrichment (Zhang & Liu, 2002). However, for Hernandez et al. (2003), only when the  $EF > 2.0$  can be considered of anthropic origin. Sutherland (2000), after justifying the absence or lack of criteria to define a level of pollution for the EF, proposed five enrichment categories as shown in Table 1.

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**Table 1 -EF Categories (Sutherland 2000)**

Categories	Description
EF < 2	Depleted or low enrichment
EF between 2 and 5	Moderate enrichment
EF between 5 and 20	Significant enrichment
EF between 20 and 40	Very high enrichment
EF > 40	Extremely high enrichment

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The Geoaccumulation Index (*Igeo*) is a geochemical tool used to evaluate the contamination of a given location. The *Igeo* can be applied to organic and inorganic substances to evaluate

198 contamination by way of comparing values of samples of pre-industrial locations or locations with no  
 199 impact of the substances of interest. This index has been used for at least thirty years and is calculated  
 200 using equation 2.

$$201 \quad I_{geo} = \log_2 \left( \frac{C_n}{1,5 * B_n} \right) \quad (2)$$

202 Where;

203 Log2 -base 2 logarithms.

204  $C_n$  -element concentration at evaluated location

205  $B_n$  -element concentration in the reference values used(background)

206 A factor of 1.5 for  $B_n$  according to several authors (Audry et al. 2004, Cukrov et al. 2011,  
 207 Gomes et al. 2009, Loska et al.(1997, 2003 and 2004), Lin et al. 2008, Mortatti & Probst 2010; Rubio  
 208 et. al. 2000) is applied to correct small fluctuations of lithogenic origins or even small anthropic  
 209 influences in relation to background values. In the same manner of the EF, the  $B_n$  variable represents  
 210 the reference values (background) that should be used to represent element basal concentration. The  
 211 same considerations for EF are used for this calculation. Several authors use earth crust values and still  
 212 others prefer local values believing these to be more representative.

213 The *Igeo* Index is associated to a qualitative pollution intensity scale shown in Table 2.

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215 **Table 2 – Igeo Values and contamination intensity**

$I_{geo}$	Intensity (sediment quality)
< 0	Not contaminated
0-1	Not contaminated to moderately contaminated
1-2	Moderately contaminated
2-3	Moderately to highly contaminated
3-4	Highly contaminated
4-5	Highly to very highly contaminated
> 5	Very highly contaminated

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217 Both geochemical tools (EF and *IGeo*) for metal contamination studies are widely used by  
 218 various researchers using different sources as background references.

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### 220 **3 – RESULTS AND DISCUSSION**

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222 **3.1 – Granulometric composition of the sediments**

223 Table 3 shows the results for the grain size determination of the sediment slices.

224 **Table 3 – Grain size results for the sediment slices**

<b>Depth (cm)</b>	<b>Sand (%)</b>	<b>Silt (%)</b>	<b>Clay (%)</b>
<b>0 - 5</b>	1.1	50.0	48.9
<b>5 - 10</b>	1.0	50.2	48.8
<b>10 - 15</b>	0.9	54.4	44.7
<b>15 - 20</b>	1.3	44.5	54.2
<b>20 - 25</b>	2.5	46.7	50.8
<b>25 - 30</b>	0.8	66.2	33.0
<b>30 - 35</b>	2.3	63.4	34.3
<b>35 - 40</b>	3.6	50.4	46.0

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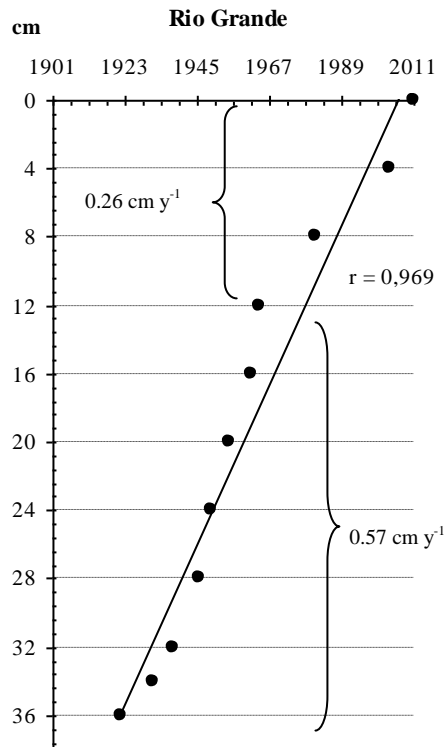
226 Particle size determination indicates that the sediment is predominantly silty-clayey throughout  
227 the profile, and characterized by a constant input of fine grained material.

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229 **3.2 – <sup>210</sup>Pb profile and sedimentation rates**

230 Isotopic ages for the core are presented in Figure 2. The <sup>210</sup>Pb profile depicts a linear trend  
231 ( $r=0.9687$ ) from level 0 cm (year 2011) to level 36 cm (year 1922), with a mean sedimentation rate of  
232 0.40 cm y<sup>-1</sup>. This <sup>210</sup>Pb profile can be divided in two trends: from level 0 cm (year 2011) to level 12cm  
233 (year 1964) indicating an average accumulation rate of 0.26 cm y<sup>-1</sup> and from level 12 cm to level 36 cm  
234 (year 1922) indicating an average accumulation rate of 0.57 cm y<sup>-1</sup>. Lower rates were related to the  
235 period prior to the water dam, when the loading of the sediments was stabilized. Higher rates were  
236 related to rainy seasons and urban expansion in the areas surrounding the reservoir. The values  
237 obtained at the latest slice were considered the background of the reservoir. This slice corresponded to  
238 sediment age of the 1920's.





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**Figure 2 - <sup>210</sup>Pb profile and sedimentation rates**

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### 3.3 – Multielemental determinations by INAA

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The precision and accuracy of the INAA analytical methodology was verified by reference materials analysis and  $Z$  value calculation was done according to Bode (1996). If  $|Z| < 3$ , the individual result of the control sample (reference material) lies on the 99% confidence interval of the target value. For the reference materials analyzed in the present study all the results were in the interval range of  $|Z| < 3$ , indicating good precision and accuracy of the INAA technique (Figure 3).

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Table 4 presents the results and respective uncertainties (calculated by error propagation) obtained by INAA. Tables 5 and 6 present EF and  $I_{geo}$  results, respectively.

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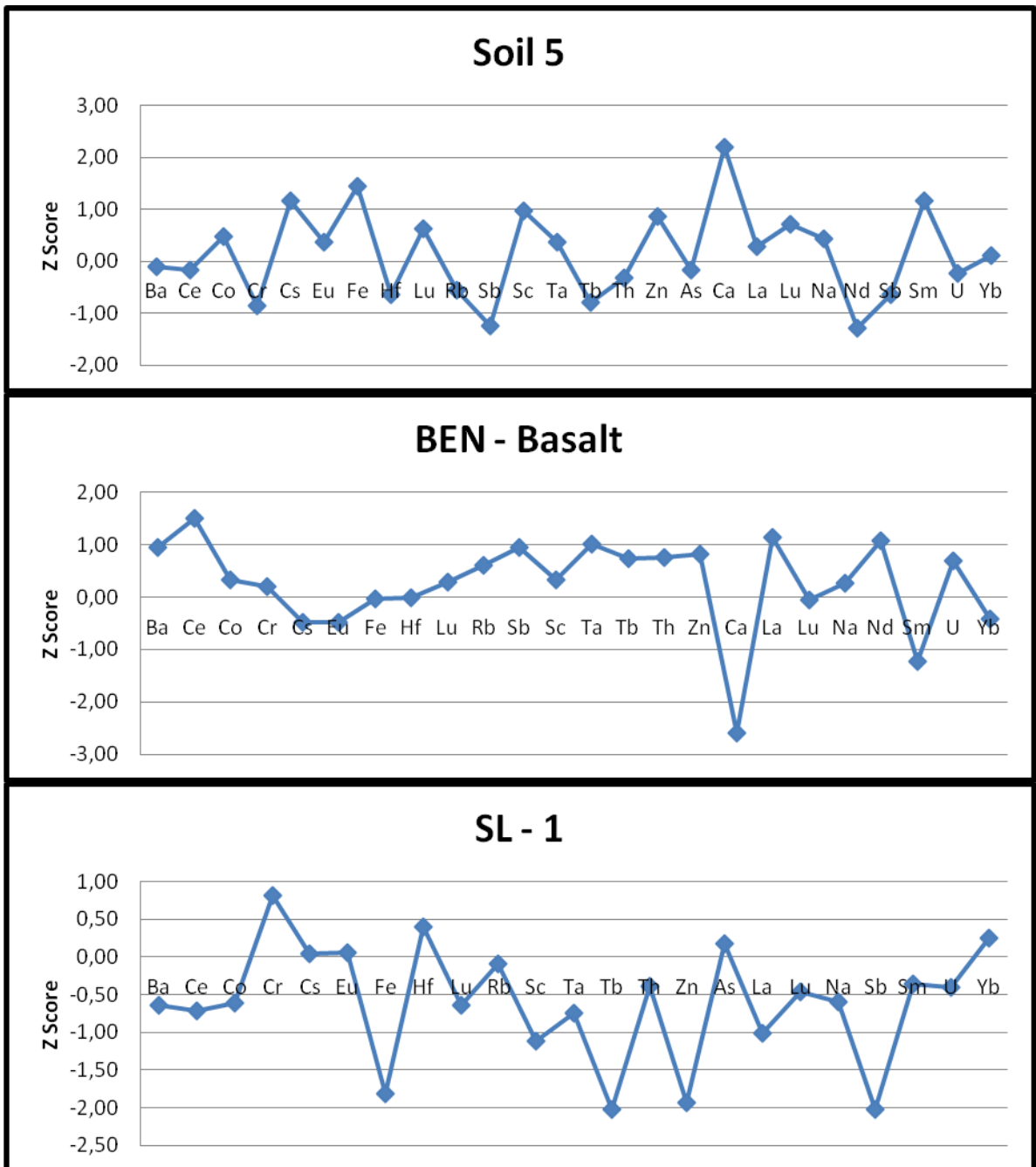
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EF was calculated using Sc as the normalizing element and the results obtained for the last layer of the 0.40 cm sampled profile as reference values (also used as reference values for  $I_{geo}$  calculations) that reflects the concentration of these elements during the 1920's when industrialization in the São Paulo metropolitan region was still incipient (Table 5).

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**Figure 3–Z-score values for the RM analysis**

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EF results indicated that most of the elements did not present enrichment as did *Igeo* results for the elements As, Ba, Ca, Cr, Co, Cs, Fe, Sm, Eu, Lu, Rb, Th, Nd and Ta which presented values always  $Igeo < 0.0$  and  $EF < 2.0$  for the entire profile evaluated (Tables 5 and 6). According to Sutherland (2000),  $EF < 2.0$  cannot be considered as anthropic enrichment.

Table 4 – Results obtained for the sediment samples by INAA along the profile (mg kg<sup>-1</sup>) and the Continental crust values (Wedepohl, 1995)

Depth	Year	As	Ba	Ca (%)	Ce	Co	Cr	Cs	Eu	Fe (%)	Hf	La	Lu
0 - 2	2011-2004	25.8 ± 2.9	522 ± 34	1.10 ± 0.04	97 ± 6	12.2 ± 0.3	82 ± 4	5.17 ± 0.48	0.75 ± 0.06	9.74 ± 0.12	5.04 ± 0.18	41.3 ± 0.8	0.37 ± 0.04
2 - 4	2004 - 1996	27.6 ± 3.1	500 ± 33	1.14 ± 0.04	98 ± 6	11.5 ± 0.3	88 ± 4	5.66 ± 0.52	0.69 ± 0.07	9.16 ± 0.11	5.36 ± 0.19	39.7 ± 0.8	0.43 ± 0.04
4 - 6	1996 - 1988	25.4 ± 2.9	541 ± 34	1.29 ± 0.04	92 ± 5	10.6 ± 0.3	92 ± 4	5.33 ± 0.49	0.80 ± 0.05	8.61 ± 0.11	5.23 ± 0.19	37.0 ± 0.7	0.37 ± 0.04
6 - 8	1988 - 1980	27.5 ± 3.1	478 ± 32	1.19 ± 0.04	94 ± 5	10.4 ± 0.3	92 ± 4	5.96 ± 0.55	0.77 ± 0.05	8.69 ± 0.11	4.83 ± 0.22	37.9 ± 0.7	0.35 ± 0.04
8 - 10	1980 - 1972	30.8 ± 3.6	562 ± 36	0.95 ± 0.04	92 ± 5	9.9 ± 0.2	96 ± 4	6.32 ± 0.58	0.67 ± 0.06	8.34 ± 0.10	4.82 ± 0.17	40.1 ± 0.8	0.36 ± 0.04
10 - 12	1972 - 1964	26.9 ± 3.1	464 ± 31	0.97 ± 0.04	90 ± 5	8.7 ± 0.2	94 ± 4	5.91 ± 0.55	0.70 ± 0.05	8.00 ± 0.10	5.11 ± 0.19	34.2 ± 0.7	0.35 ± 0.03
14 - 16	1964 - 1961	23.4 ± 2.6	487 ± 32	1.15 ± 0.04	92 ± 5	7.8 ± 0.2	98 ± 5	6.00 ± 0.55	0.74 ± 0.08	7.16 ± 0.09	5.17 ± 0.19	35.4 ± 0.7	0.41 ± 0.04
16 - 18	1961 - 1958	26.7 ± 1.8	579 ± 43	1.28 ± 0.04	101 ± 6	8.6 ± 0.2	121 ± 6	6.31 ± 0.51	0.84 ± 0.09	7.51 ± 0.09	5.94 ± 0.28	27.4 ± 0.6	0.33 ± 0.03
18 - 20	1958 - 1954	24.2 ± 1.6	501 ± 40	1.25 ± 0.04	110 ± 6	9.1 ± 0.2	113 ± 5	5.86 ± 0.49	0.77 ± 0.06	7.55 ± 0.09	5.63 ± 0.21	30.5 ± 0.6	0.40 ± 0.04
20 - 22	1954 - 1951	30.2 ± 2.1	490 ± 37	1.19 ± 0.04	114 ± 6	8.6 ± 0.2	115 ± 6	6.14 ± 0.92	0.85 ± 0.09	7.89 ± 0.10	5.86 ± 0.32	33.5 ± 0.7	0.40 ± 0.04
22 - 24	1951 - 1947	27.6 ± 1.9	536 ± 40	1.03 ± 0.04	109 ± 6	10.5 ± 0.3	104 ± 5	6.26 ± 0.93	0.85 ± 0.09	8.48 ± 0.10	6.33 ± 0.24	31.3 ± 0.6	0.40 ± 0.04
24 - 26	1947 - 1944	25.3 ± 1.7	467 ± 38	1.04 ± 0.04	109 ± 6	9.8 ± 0.2	91 ± 4	6.09 ± 0.51	0.73 ± 0.07	7.84 ± 0.10	6.23 ± 0.23	26.1 ± 0.5	0.46 ± 0.05
26 - 28	1944 - 1940	25.9 ± 1.8	525 ± 42	1.12 ± 0.04	135 ± 8	9.3 ± 0.2	80 ± 4	5.14 ± 0.44	0.68 ± 0.04	7.42 ± 0.09	5.88 ± 0.21	22.9 ± 0.5	0.45 ± 0.05
28 - 30	1940 - 1937	27.5 ± 1.9	571 ± 45	1.02 ± 0.03	158 ± 9	9.6 ± 0.2	85 ± 4	7.76 ± 0.40	0.75 ± 0.06	7.05 ± 0.06	5.96 ± 0.22	29.0 ± 0.6	0.48 ± 0.05
30 - 32	1937 - 1933	31.2 ± 2.2	592 ± 44	1.00 ± 0.04	162 ± 9	9.8 ± 0.2	82 ± 4	4.73 ± 0.69	0.80 ± 0.06	7.26 ± 0.09	6.11 ± 0.23	33.3 ± 0.7	0.44 ± 0.05
32 - 34	1933 - 1930	28.3 ± 1.9	542 ± 33	1.13 ± 0.04	146 ± 8	11.2 ± 0.3	83 ± 4	5.37 ± 0.40	0.83 ± 0.05	7.52 ± 0.09	7.15 ± 0.25	29.6 ± 0.6	0.48 ± 0.05
34 - 36	1930 - 1926	29.4 ± 2.0	523 ± 32	1.09 ± 0.04	123 ± 6	11.6 ± 0.3	83 ± 4	5.79 ± 0.48	0.77 ± 0.05	7.71 ± 0.09	7.87 ± 0.28	25.5 ± 0.5	0.52 ± 0.05
36 - 40	1926 - 1922	26.5 ± 1.9	550 ± 44	1.57 ± 0.04	83.0 ± 5	9.4 ± 0.2	91 ± 4	5.80 ± 0.47	0.66 ± 0.05	7.00 ± 0.08	7.17 ± 0.28	31.5 ± 0.6	0.53 ± 0.06
Continental Crust		2.0	668	2.95	65	11.6	35	5.8	0.95	3.09	5.8	32.3	0.27

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**Table 4 – Continuation – Results obtained for the sediment samples by INAA along the profile (mg kg<sup>-1</sup>) and dating of the sediment slices  
(continuation)**

Depth	Year	Na	Nd	Rb	Sb	Sc	Sm	Ta	Th	U	Yb	Zn
0 - 2	2011 - 2004	4490 ± 166	20.0 ± 2.7	79 ± 5	2.27 ± 0.22	17.9 ± 0.6	4.46 ± 0.15	1.45 ± 0.10	18.1 ± 0.7	4.99 ± 0.46	1.60 ± 0.11	164 ± 8
2 - 4	2004 - 1996	3854 ± 135	24.5 ± 2.5	96 ± 6	2.51 ± 0.25	19.2 ± 0.7	5.17 ± 0.21	1.52 ± 0.27	20.0 ± 0.8	4.79 ± 0.56	2.10 ± 0.15	146 ± 7
4 - 6	1996 - 1988	3422 ± 126	15.8 ± 2.6	89 ± 5	2.65 ± 0.26	19.1 ± 0.7	4.23 ± 0.14	1.71 ± 0.11	19.7 ± 0.8	5.14 ± 0.45	1.88 ± 0.15	134 ± 7
6 - 8	1988 - 1980	3126 ± 132	18.4 ± 2.6	89 ± 5	2.64 ± 0.26	19.8 ± 0.7	4.96 ± 0.20	1.76 ± 0.12	19.5 ± 0.8	5.08 ± 0.46	1.60 ± 0.11	123 ± 6
8 - 10	1980 - 1972	3113 ± 204	18.1 ± 1.6	94 ± 6	2.93 ± 0.29	19.8 ± 0.7	4.57 ± 0.18	1.70 ± 0.11	19.7 ± 0.8	5.34 ± 0.48	1.74 ± 0.14	119 ± 6
10 - 12	1972 - 1964	1490 ± 166	20.7 ± 1.5	88 ± 5	2.39 ± 0.24	20.4 ± 0.7	4.66 ± 0.18	1.83 ± 0.18	20.5 ± 0.8	3.47 ± 0.34	1.86 ± 0.15	120 ± 6
14 - 16	1964 - 1961	2624 ± 111	24.9 ± 1.7	95 ± 5	1.69 ± 0.17	20.1 ± 0.7	4.49 ± 0.18	1.69 ± 0.11	19.9 ± 0.8	5.10 ± 0.59	2.02 ± 0.14	113 ± 6
16 - 18	1961 - 1958	1033 ± 35	15.1 ± 1.7	93 ± 6	1.91 ± 0.17	20.0 ± 0.7	3.55 ± 0.11	1.77 ± 0.12	21.1 ± 0.8	5.39 ± 0.51	2.14 ± 0.18	123 ± 6
18 - 20	1958 - 1954	1080 ± 34	17.5 ± 2.3	109 ± 9	1.44 ± 0.14	20.5 ± 0.7	4.60 ± 0.14	1.95 ± 0.15	20.9 ± 0.8	6.10 ± 0.53	1.80 ± 0.14	149 ± 9
20 - 22	1954 - 1951	964 ± 34	24.7 ± 4.0	91 ± 6	1.49 ± 0.14	19.7 ± 0.7	3.86 ± 0.12	1.85 ± 0.11	21.6 ± 0.8	5.82 ± 0.42	2.37 ± 0.17	124 ± 6
22 - 24	1951 - 1947	978 ± 38	16.0 ± 3.0	87 ± 6	1.52 ± 0.14	19.8 ± 0.7	3.59 ± 0.11	1.86 ± 0.12	21.6 ± 0.9	5.07 ± 0.49	2.35 ± 0.17	131 ± 6
24 - 26	1947 - 1944	890 ± 29	20.0 ± 1.6	104 ± 8	1.23 ± 0.12	20.2 ± 0.7	3.88 ± 0.12	2.02 ± 0.16	21.3 ± 0.8	6.32 ± 0.71	2.42 ± 0.18	156 ± 9
26 - 28	1944 - 1940	896 ± 30	13.9 ± 1.2	134 ± 10	0.84 ± 0.16	22.1 ± 0.8	3.30 ± 0.10	1.84 ± 0.14	22.4 ± 0.9	6.87 ± 0.77	2.48 ± 0.20	104 ± 6
28 - 30	1940 - 1937	824 ± 28	22.9 ± 4.7	130 ± 8	0.53 ± 0.05	21.7 ± 0.8	3.77 ± 0.11	2.41 ± 0.30	22.8 ± 0.9	8.42 ± 0.60	2.56 ± 0.19	87 ± 4
30 - 32	1937 - 1933	581 ± 32	16.4 ± 1.6	135 ± 8	0.74 ± 0.05	21.5 ± 0.8	3.32 ± 0.10	1.76 ± 0.12	22.9 ± 0.9	7.63 ± 0.60	2.94 ± 0.23	70 ± 4
32 - 34	1933 - 1930	705 ± 25	20.1 ± 1.9	133 ± 10	0.70 ± 0.07	21.4 ± 0.7	3.43 ± 0.11	1.94 ± 0.14	24.2 ± 0.9	7.30 ± 0.78	3.05 ± 0.23	90 ± 6
34 - 36	1930 - 1926	938 ± 32	21.4 ± 3.0	117 ± 9	1.07 ± 0.10	20.9 ± 0.7	3.68 ± 0.12	2.12 ± 0.16	24.0 ± 0.9	4.98 ± 0.41	2.97 ± 0.24	95 ± 7
36 - 40	1926 - 1922	1048 ± 34	23.2 ± 4.0	96 ± 7	1.08 ± 0.10	21.1 ± 0.7	3.58 ± 0.11	2.07 ± 0.14	22.8 ± 0.9	4.81 ± 0.34	2.82 ± 0.20	77 ± 4
<b>Continental Crust</b>		<b>25670</b>	<b>25.9</b>	<b>110</b>	<b>0.31</b>	<b>7</b>	<b>4.7</b>	<b>1.5</b>	<b>10.3</b>	<b>2.5</b>	<b>1.5</b>	<b>52</b>

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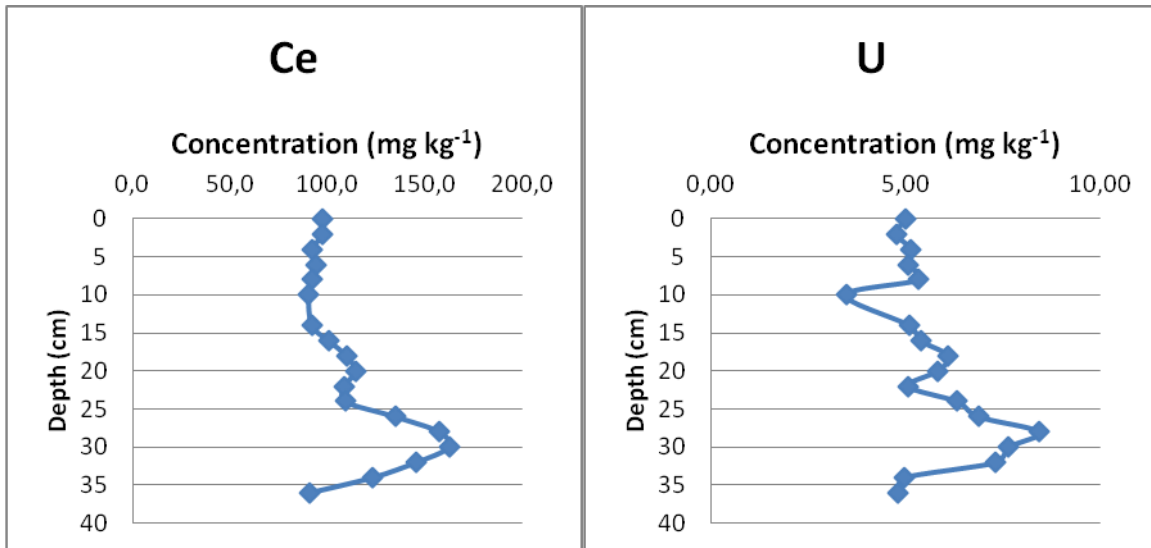
**Table 5 – Enrichment Factors (EF) results (Only elements which showed along profile EF >1.5 or EF <0.8)**

<b>Depth</b>	<b>Ca</b>	<b>Ce</b>	<b>Co</b>	<b>Fe</b>	<b>Hf</b>	<b>La</b>	<b>Lu</b>	<b>Na</b>	<b>Sb</b>	<b>Sm</b>	<b>U</b>	<b>Yb</b>	<b>Zn</b>
<b>0 - 2</b>	0.8	1.4	1.5	1.6	0.8	1.5	0.8	5.0	2.6	1.5	1.2	0.7	2.5
<b>2 - 4</b>	0.8	1.3	1.3	1.4	0.8	1.4	0.9	4.0	2.5	1.6	1.1	0.8	2.1
<b>4 - 6</b>	0.9	1.2	1.2	1.4	0.8	1.3	0.8	3.6	2.7	1.3	1.2	0.7	1.9
<b>6 - 8</b>	0.8	1.2	1.2	1.3	0.7	1.3	0.7	3.2	2.6	1.5	1.1	0.6	1.7
<b>8 - 10</b>	0.6	1.2	1.1	1.3	0.7	1.4	0.7	3.2	2.9	1.4	1.2	0.7	1.6
<b>10 - 12</b>	0.6	1.1	1.0	1.2	0.7	1.1	0.7	1.5	2.3	1.3	0.7	0.7	1.6
<b>14 - 16</b>	0.8	1.2	0.9	1.1	0.8	1.2	0.8	2.6	1.6	1.3	1.1	0.8	1.5
<b>16 - 18</b>	0.9	1.3	1.0	1.1	0.9	0.9	0.7	1.0	1.9	1.0	1.2	0.8	1.7
<b>18 - 20</b>	0.8	1.4	1.0	1.1	0.8	1.0	0.8	1.1	1.4	1.3	1.3	0.7	2.0
<b>20 - 22</b>	0.8	1.5	1.0	1.2	0.9	1.1	0.8	1.0	1.5	1.2	1.3	0.9	1.7
<b>22 - 24</b>	0.7	1.4	1.2	1.3	0.9	1.1	0.8	1.0	1.5	1.1	1.1	0.9	1.8
<b>24 - 26</b>	0.7	1.4	1.1	1.2	0.9	0.9	0.9	0.9	1.2	1.1	1.4	0.9	2.1
<b>26 - 28</b>	0.7	1.6	0.9	1.0	0.8	0.7	0.8	0.8	0.7	0.9	1.4	0.8	1.3
<b>28 - 30</b>	0.6	1.8	1.0	1.0	0.8	0.9	0.9	0.8	0.5	1.0	1.7	0.9	1.1
<b>30 - 32</b>	0.6	1.9	1.0	1.0	0.8	1.0	0.8	0.5	0.7	0.9	1.6	1.0	0.9
<b>32 - 34</b>	0.7	1.7	1.2	1.1	1.0	0.9	0.9	0.7	0.6	0.9	1.5	1.1	1.2
<b>34 - 36</b>	0.7	1.5	1.2	1.1	1.1	0.8	1.0	0.9	1.0	1.0	1.0	1.1	1.2
<b>36 - 40</b>	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

**Table 6 – Geoaccumulation Index (*IGeo*) results**

Depth	Ce	Na	Sb	U	Zn
0 - 2	< 0	1.5	0.5	< 0	0.5
2 - 4	< 0	1.3	0.6	< 0	0.3
4 - 6	< 0	1.1	0.7	< 0	0.2
6 - 8	< 0	1.0	0.7	< 0	0.1
8 - 10	< 0	1.0	0.8	< 0	0.0
10 - 12	< 0	< 0	0.6	< 0	0.1
14 - 16	< 0	0.7	0.1	< 0	< 0
16 - 18	< 0	< 0	0.2	< 0	0.1
18 - 20	< 0	< 0	< 0	< 0	0.4
20 - 22	< 0	< 0	< 0	< 0	0.1
22 - 24	< 0	< 0	< 0	< 0	0.2
24 - 26	< 0	< 0	< 0	< 0	0.4
26 - 28	0.1	< 0	< 0	< 0	< 0
28 - 30	0.3	< 0	< 0	0.2	< 0
30 - 32	0.4	< 0	< 0	0.1	< 0
32 - 34	0.2	< 0	< 0	0.1	< 0
34 - 36	< 0	< 0	< 0	< 0	< 0
36 - 40	< 0	< 0	< 0	< 0	< 0

280 Although *Igeo* results for Ce and U showed no indication of accumulation, the EF results  
 281 pointed to a discreet enrichment in the middle of the profile (Ce – 25-35 cm depth; U – 25-30 cm  
 282 depth) (Figure 4). This could be related to sources of pollution which existed in the past but today  
 283 either no longer exist or are under control. Figure 4 shows the behavior of these two elements along  
 284 the profile.



285

286 **Figure 4 – Behavior of Ce and U along the sediment profile**

287

288 In regards to the elements Na, Sb and Zn, EF results (> 2.0) at the top of the profile pointed to  
 289 an enrichment which can be considered as anthropic origin, according to Sutherland (2000) or Zhang  
 290 & Liu (2002) classification. The *Igeo* for these elements also presented values greater than zero. The  
 291 concentrations for Na at the top of the profile were considered moderately enriched by both criteria  
 292 (3.0 < EF < 5.0 and *Igeo* > 1.0), while 2.0 < EF < 3.0 and 0 < *Igeo* < 1.0 for Sb and Zn were  
 293 considered a light to moderate enrichment (Table 6).

294 It should be noted that the values obtained in this study for various elements, most notably As,  
 295 Cr, Ce, Fe, Zn, Sb, Th, Sc and U presented concentrations at the base of the profile (and in some cases  
 296 throughout the entire profile) well above those set by Wedepohl (1995) as continental crust values.  
 297 Concentrations obtained for Ba, Ca and Na at the reservoir were smaller than those established by  
 298 Wedepohl (1995) (Table 4).

299 It becomes clear that in this type of situation the use of local geochemical values for anthropic  
 300 enrichment or contamination assessment is crucial for correct environmental evaluations. If in this  
 301 study, the values set by Wedepohl (1995) had been taken as reference values, the conclusions would  
 302 have been much different. For example, As which presented a concentration between 23.4 and 31.2  
 303 mg kg<sup>-1</sup> throughout the entire profile would have been considered highly contaminated with *Igeo* > 3.0  
 304 and an EF > 12.0 as compared to the defined value for As in the continental crust of 2.0 mg kg<sup>-1</sup>. In this

305 study the  $EF < 1.5$  and  $I_{geo} < 0$  were obtained for As using the concentration of the base of the profile  
 306 as reference value.

307 Other studies developed at this reservoir with the purpose of metal concentration evaluations  
 308 were already published by Fávoro et al (2007), Bostelmann (2006) and Franklin et al (2012a). The  
 309 concentration values obtained by these authors for REE and As, Ba, Co, Fe, Rb, Sb and Zn were very  
 310 similar to the present study. These studies also concluded that the sediments from this reservoir,  
 311 collected in points near the point of this study, could be contaminated for some elements such as As,  
 312 Cs, Sb, Lu, Yb, Th, Hf and U due to the values obtained for the Enrichment Factors ( $EF > 2.0$ ) by  
 313 using the earth crust as reference values (Wedepohl, 1995). From this data it was possible to conclude  
 314 that the choice of the background geochemical values is fundamental for the correct interpretation of  
 315 the geochemical data as well as for the anthropic contamination evaluation. In the case of anthropic  
 316 contamination evaluation of sediments, the utilization of a sedimentary profile can offer an adequate  
 317 answer for this question.

318

#### 319 3.4 – Metals determination by ICPOES, GF AAS and Direct Mercury Analyzer(DMA)

320 The certified reference materials analyses for CRM050, SRM 8704, and SRM 2710 were done  
 321 under the same conditions of the samples and the results obtained are shown in Table 7. The Z-score  
 322 was calculated for all results and were in the range of interval  $|Z| < 3$  indicating good precision and  
 323 accuracy for all analytical methodologies applied.

324 Tables 8 to 10 show the results obtained (mean of replicates  $\pm$  uncertainty) and the enrichment  
 325 factor and  $I_{geo}$  for the elements analyzed, respectively. The uncertainty was calculated according to  
 326 Franklin et al. (2012 b).

327 **Table 7 – Results for the Certified Reference Materials analyses by ICP OES, GF AAS**  
 328 **and DMA ( $\text{mg kg}^{-1}$ )**

	Mn	Ni	Cu	Cd	Pb	Hg
<b>Certified Values</b>						
<b>CRM 050</b>	636 $\pm$ 21	344 $\pm$ 6	88.5 $\pm$ 1.7	80.0 $\pm$ 1.3	111 $\pm$ 2	13.5 $\pm$ 0.4
<b>SRM 8704</b>	544 $\pm$ 21	42.9 $\pm$ 3.7	-----	2.94 $\pm$ 0.29	150 $\pm$ 17	-----
<b>SRM 2710</b>	2140 $\pm$ 60	8 $\pm$ 1	3420 $\pm$ 50	12.3 $\pm$ 0.3	5520 $\pm$ 30	9.88 $\pm$ 0.21
<b>Obtained Values</b>						
<b>CRM 050</b>	593 $\pm$ 25	340 $\pm$ 9	89.1 $\pm$ 2.0	76.7 $\pm$ 2.2	110 $\pm$ 5	12.9 $\pm$ 1.1
<b>SRM 8704</b>	479 $\pm$ 12	37.6 $\pm$ 1.4	-----	3.45 $\pm$ 0.19	140 $\pm$ 6	-----
<b>SRM 2710</b>	1963 $\pm$ 80	7.21 $\pm$ 0.29	3355 $\pm$ 22	13.88 $\pm$ 0.57	-----	9.52 $\pm$ 0.44
<b>Z score</b>						
<b>CRM 050</b>	-1.32	-0.37	0.24	-1.29	-0.18	-0.51
<b>SRM 8704</b>	-2.69	-1.34	-----	1.47	-0.55	-----
<b>SRM 2710</b>	-1.77	-0.76	-1.19	2.45	-----	-0.74

329



330  
331

**Table 8 – Results obtained for elements determined by ICPOES, GF AAS and DMA (mg kg<sup>-1</sup>)**

Depth (cm)	Pb <sup>a</sup>	Hg <sup>b</sup>	Cd <sup>a</sup>	Cu <sup>c</sup>	Ni <sup>c</sup>	Mn <sup>c</sup>
0 - 5	52.9 ± 2.5	0.55 ± 0.08	1.02 ± 0.06	4867 ± 54	25.2 ± 2.1	907 ± 28
5 - 10	57.0 ± 2.4	0.68 ± 0.05	0.90 ± 0.07	5404 ± 62	26.4 ± 2.0	810 ± 21
10 - 15	69.7 ± 2.7	1.30 ± 0.10	0.69 ± 0.05	3774 ± 48	30.4 ± 2.1	599 ± 19
15 - 20	72.6 ± 2.9	2.69 ± 0.21	0.45 ± 0.03	1112 ± 27	33.9 ± 2.0	585 ± 22
20 - 25	60.0 ± 2.5	17.3 ± 1.1	0.30 ± 0.03	244 ± 10	22.9 ± 1.8	475 ± 16
25 - 30	42.4 ± 2.4	10.7 ± 0.9	0.06 ± 0.01	36.4 ± 1.9	14.9 ± 1.8	290 ± 13
30 - 35	38.6 ± 2.3	0.58 ± 0.06	0.05 ± 0.01	25.9 ± 1.1	13.3 ± 1.5	375 ± 15
35 - 40	29.0 ± 2.1	0.14 ± 0.03	0.04 ± 0.01	22.1 ± 1.0	10.9 ± 1.5	181 ± 12

332

a – GF AAS; b – DMA; c – ICP OES

333

334

**Table 9 – EF values obtained from metal results**

Enrichment Factor (EF)						
Depth (cm)	Pb	Hg	Cd	Cu	Ni	Mn
0 – 5	1.9	4.1	26.9	232	2.4	5.3
5 – 10	1.9	4.7	22.0	239	2.4	4.4
10 – 15	2.1	7.9	14.7	146	2.4	2.8
15 – 20	2.5	19.0	11.1	49.8	3.1	3.2
20 – 25	2.2	128	7.8	11.5	2.2	2.7
25 – 30	1.7	90.8	1.8	2.0	1.6	1.9
30 – 35	1.6	5.0	1.5	1.4	1.5	2.5
35 – 40	1.0	1.0	1.0	1.0	1.0	1.0

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336

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**Table 10 – *Igeo* values obtained from the metals results**

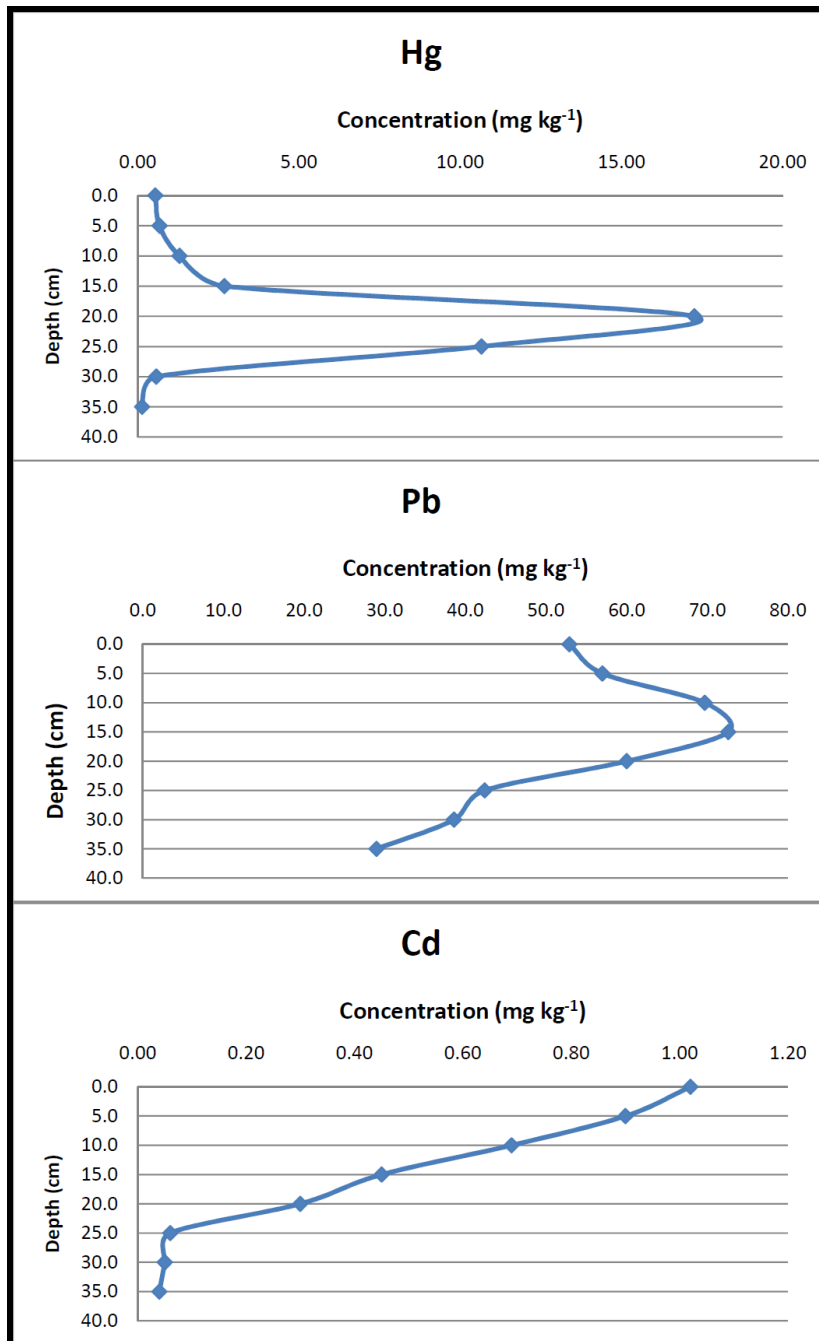
Geoaccumulation Index						
Depth (cm)	Pb	Hg	Cd	Cu	Ni	Mn
0 – 5	0.3	1.4	4.1	7.2	0.6	1.7
5 – 10	0.4	1.7	3.9	7.3	0.7	1.6
10 – 15	0.7	2.6	3.5	6.8	0.9	1.1
15 – 20	0.7	3.7	2.9	5.1	1.1	1.1
20 – 25	0.5	6.4	2.3	2.9	0.5	0.8
25 – 30	0.0	5.7	0.0	0.1	< 0	0.1
30 – 35	< 0	1.5	< 0	< 0	< 0	0.5
35 -40	< 0	< 0	< 0	< 0	< 0	< 0

338

339 It is clear that the great enrichment (EF) for Cd and Cu in the top of the profile, with values of  
340 26.9 and 232 respectively, confirmed by *Igeo* of 4.1 and 7.2 respectively, indicates extremely  
341 contaminated sediment (Tables 9 and 10). Such surface contamination for these elements indicates that  
342 the probable sources may still be active in the reservoir and may still be releasing such elements. In  
343 the case of Cu, this may be due to the use of their salts to prevent algae growth in the reservoir.  
344 Regarding Ni and Mn a moderate enrichment more significant on the surface of the profile could be  
345 observed. This moderate contamination was also confirmed by *Igeo*, with values between 0 and 1 for  
346 Ni and 1.1 and 1.7 for Mn (Table 10). In relation to Hg and Pb enrichment this is more significant in  
347 the middle of the profile, indicating that in the past there was a strong anthropic contribution of these  
348 elements, especially for Hg (EF from 91 to 128 and *Igeo* from 5.7 to 6.4). The current depletion of  
349 these concentrations in the surface is an indication that these sources are controlled or no longer exist.  
350 Figure 5 shows the behavior of Cd, Hg and Pb along the sediment profile.

351 Fávares et al. (2007) determined the multielemental concentrations of sediment cores from Rio  
352 Grande reservoir by INAA, Hg content by CV AAS and sedimentation rates by  $^{210}\text{Pb}$  method. For the  
353 sediment core located near the catchment point of the water supply (near the sediment profile collected  
354 in the present study), a peak of 11,586 mg Hg kg<sup>-1</sup> was found in 1949 and at the end of the core  
355 (1932), values about 0.145 mg Hg kg<sup>-1</sup> were found. In the present study a peak in the Hg content of  
356 17.3 mg kg<sup>-1</sup> was found around the 1950's (Figure 5) decreasing to 0.14 mg kg<sup>-1</sup> at the 35-40 cm depth  
357 (approximately 1920). The results obtained for Hg were very similar in both studies.

358



359  
360 **Figure 5 – Behavior of Pb, Hg and Cd along the sediment profile**  
361

362 **4 – CONCLUSION**

363 The <sup>210</sup>Pb profile showed an average accumulation rate of 0.26 cm y<sup>-1</sup> in the upper segments of  
364 the sediment profile (2011 to 1964 year) and average accumulation rate of 0.57 cm y<sup>-1</sup> (1964 to 1922  
365 year) in the lower section, clearly reflecting the different periods of sediment loading in this reservoir.

366 The Enrichment Factor and Geoaccumulation Index are excellent tools for environmental  
367 evaluations and in this study presented results aligned with the anthropic enrichment of some of the  
368 elements analyzed.

369 Most of the elements presented concentrations very similar over time in this reservoir. Cu and  
370 Cd have severe anthropic contributions in the reservoir, the same holding true for Hg. But for this  
371 element a peak in concentration in the middle of the profile was observed, indicating that there was a  
372 source in the past but nowadays appears to be under control, although the concentration in the surface  
373 is still considered high (0.55 mg kg<sup>-1</sup>). The reservoir still presents a discreet anthropic enrichment for  
374 Ni, Pb and Sb and a moderate enrichment for Na and Mn. All other elements and rare earth elements,  
375 in general, presented constant values throughout the sediment profile.

376 For this study background values for metals and trace elements in the sediments from the Rio  
377 Grande Reservoir were considered as the concentration present in the lowest slice of the profile  
378 corresponding to the age of 1920. At that time the industrialization of São Paulo was nearly non-  
379 existent and in its very early development stages. From the data of this study it can be seen that the  
380 choice of the local geochemical background values are fundamental for correct interpretations of  
381 anthropic contamination evaluation of sediments.

382

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