ASSESSMENT OF METAL, TRACE AND RARE EARTH ELEMENT CONCENTRATIONS IN A SEDIMENTARY PROFILE FROM PONTE NOVA RESERVOIR, SÃO PAULO STATE, BRAZIL, BY NAA

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ABSTRACT

Ponte Nova reservoir, located in the upper basin of the Tietê River in the southern region of São Paulo State, covers an area of 25.7 km^2 and drains an area of 320 km^2. It was built in 1972 to control the rivers flow in the Metropolitan Region of São Paulo (MRSP) and water supply. A 30 cm sediment core was collected in the dam in August 2014, sliced at every 2.5 cm. Instrumental neutron activation analysis (INAA) was applied to the sediment samples to determine some major (Fe, K and Na), trace (As, Ba, Br, Co, Cr, Cs, Hf, Rb, Sb, Sc, Ta, Tb, Th, U and Zn) and rare earth (Ce, Eu, La, Lu, Nd, Sm, Tb and Yb) elements. The enrichment factor (EF) and *Igeo* were applied to the results by using NASC (North American Shale Composite) as reference values for sediment contamination index assessment. An EF>1.5 was obtained for As, Hf, Rb, Ta, Th, U, and rare earths Ce, Eu, La, Nd and Sm when NASC values were used, but only for Br, when the last layer concentration values were used as reference values. Similar results were obtained for the *Igeo* index. For semi-metal As and metals Cr and Zn concentration values were compared to oriented values from Environmental Canada (TEL and PEL) only Cr exceeded TEL value in some slices of the profile. These results may indicate that there is no anthropogenic contribution for the elements analyzed in this reservoir. Multivariate statistical analysis was applied to the results.

1. INTRODUCTION

The Tiete River drains an area composed of six sub-basins (Alto Tiete, Sorocaba/Médio Tiete, Piracicaba-Capivari-Jundiai, Tiete/Batalha, Tiete/Jacaré and Baixo Tiete). The Alto Tietê region comprehends Tietê River from Salesópolis (headwaters) to Rasgão' Dam. This area accounts for 5 reservoirs of water but occupation is seriously affecting the water quality. The general uses for water of this region are: public and industrial activities, irrigation, and generation of energy and dilution of pollutants [1]. According to the Water and Energy Department, DAEE, Ponte Nova Reservoir, located at Salesópolis, supplies 3.4 thousand liters per second of water. Close to this reservoir, there are industrial cities: Mogi das Cruzes and Suzano with heavy negative environmental interferences and effluents as well. Mogi das Cruzes has no sewage treatment station and the sewage from this city is partially treated at the Suzano Waste Water Treatment Plant [2]. Ponte Nova reservoir is the only reservoir before MRSP. Its surroundings are characterized by pasture and agricultural areas and remnants of the Atlantic Forest [3].

Because of long time residence for contaminant in sediment, the study of sediments plays and important role in proof of contamination, especially metals contamination [4]. It is reported that metals concentration in sediments may be several orders of magnitude

higher than in the overlying water. Nowadays sediment monitoring and studies are often recommended since sediment provides habitat for many aquatic organisms and is a major repository for many persistent chemicals introduced to this system [5].

Reservoirs are effective traps for the incoming sediment loads. Because of this trapping ability, reservoirs have the unique capacity for recording variations in sediment loadings and sediment-associated water parameters within the drainage basin. These sediments impoundments have proven to be important environmental "archives" of changes in watershed land use, sediment and water quality, and pollutant and nutrient loadings [6].

Several studies [7-14] have been developed in reservoirs at this region of the Tietê River assessing mainly the content and distribution of heavy metal in sediments.

Silva et al. [7] studied three reservoirs located in the surroundings of the Metropolitan Area of São Paulo (MASP) city that has a population of over 17 million people, at the Billings, Pirapora and Rasgão reservoirs. The metals Al, Fe, Mn, Ca, Cu, Pb, Cd, Zn, Ni and Cr in sediments were analyzed in order to assess the mobility and to establish the possible forms or phases in which heavy metals are associated with the sediments.

Alegre et al. [8] evaluated sediment samples from 5 sampling points at the Tietê River, in 4 sampling campaigns, from Salesópolis (P_0) until Suzano (P_4) and surrounding municipalities, being P_0 at the Ponte Nova reservoir. The study included toxicity evaluation (sediment, elutriate and pore-water). The worst effects were obtained at Mogi das Cruzes and Suzano counties (sampling stations P_3 and P_4), the most polluted points.

Favaro et al. [9] using the same sediment samples of Alegre et al. [8], did an evaluation of sediment samples by means of INAA and also the content of toxic metals Cd, Hg and Pb. The ecological assays with *H. asteca* were also assessed in the same sampling stations. The results showed that the assessment of trace and toxic metals in sediments together with ecotoxicological assays with *H. asteca* organism allowed a more complete contamination evaluation of the Tietê River.

Mortatti et al. [10] evaluated the concentration and distribution of heavy metals in bottom sediments in the upper basin of the Tietê River. In another study [11], the authors evaluated the origin and distribution of heavy metals in bottom sediments along the Tietê River basin, showing the geochemical aspects of successive standardization in sediment profiles from Salesópolis (headwaters) until its mouth (Paraná River). And finally, the authors studied the fractionation of heavy metals in sediments along the Tietê River basin, investigating a four-step sequential extraction procedure in order to determine the concentration and distribution of Cu, Co, Cr, Cd, Ni, Pb and Zn related to the potential mobility of geochemical phases[12].

A Nascimento and Mozeto [13] study proposed by the first time, to establish regional reference concentrations of metals and metalloids in bottom sediments of freshwater. The Tietê River Basin was selected for this purpose. The reference concentrations determined showed significant deviations from the assumed global geological reference for some elements and for the same element from different regions of the basin.

Favaro et al. [14] studied several sampling sites at Tietê River, from Salesópolis until Porto Feliz counties, assessing some major, trace and metal concentrations in bottom

sediments by means of INAA. Enrichment Factor, Geoaccumulation index, TEL and PEL criteria used to assess contamination levels allowed to classify the river as: less polluted (site 1 - headwaters), more polluted (sites 2A to 3C – after crossing São Paulo county) and moderately polluted (sites 4, 5, 6 and 7 – far from São Paulo city).

The present study takes part of the research project entitled: "Evaluation of the Extension and Pollution History by Metals and Trace Elements in River Sediments - Case Study, Tietê River, State of Sao Paulo". The aim of this study is to evaluate the concentration of metal, major and trace elements in surface and sediment core samples, in several points from its headwaters in Salesopolis until the end, Parana River. The present study presents major, trace and metal concentration in a sediment profile collected at Ponte Nova reservoir, Salesópolis County. The enrichment factor (EF) and geoaccumulation index (*Igeo*), geochemical tools to assess the presence of anthropogenic pollution sources, were used. In addition, the REE distribution and ratios in the sediment profile were assessed. From the toxicological point of view the quantification of the metals Cd, Cr, Cu, Hg, Ni, Zn and the semi metal As in sediments are of great interest and present oriented values for legal limits. In this study, considering the toxic metals only those that can be determined by INAA such as As, Cr and Zn will presented and discussed.

MATERIAL AND METHODS

Study area

Ponte Nova reservoir is located in the upper basin of the Tietê River in the southern region of São Paulo State, between the cities of Salesópolis and Biritiba-Mirim. It covers an area of 25.7 km^2 and drains an area of 320 km^2. It was the first reservoir built in the Tietê River with a medium depth of 9 m. Its construction was completed in 1972, with the purpose of controlling the river flow in the São Paulo Metropolitan Region (MRSP), flood control and public water supply. It is partially inserted into the headwaters ecological park of the Tietê River. Like most Brazilian reservoirs, no trees were cut when the reservoir was filled. This, in turn, affected water quality of the reservoir. The climate in the region is classified as mesothermal, with rainy summers and dry winters (Cwb type in Koppen classification) and temperature of 17.5^{0}C [3]. Its drained area is inserted in lithological sequences of the province Mantiqueira (Upper Proterozoic), especially in the context of Coastal Complex consisting of metamorphic rocks of the quartzite types, calcium-silicatic rocks, schists, paragnaisses (derived from sedimentary rocks), orthogneisses (derived from igneous rocks) and calcium-alkali. Igneous rocks of the calcium-alkali granite type occur in smaller proportions in the reservoir area [15].

Sampling and sample preparation

A sediment core from Ponte Nova reservoir was collected by using a core sampler on August 12th, 2014 by the Setores de Amostragem (ELCA) e Comunidades Aquáticas (ELHC) from CETESB (Companhia Ambiental do Estado de São Paulo). This point is located in the central region of the reservoir (23º34'325" S; 45º56'533" O) at 14 m depth. Figure 1 shows the Ponte Nova reservoir location. The sediment core (30 cm long) was sliced at every 2.5 cm *in situ* giving a total of 12 sediment samples.

Sediment samples were dried at 40ºC in a ventilated oven until constant weight. Sediment samples were passed through a 2 mm sieve, ground in a mortar, and passed again through a 125 mesh sieve to be homogenized before analysis. The total fraction (< 2 mm) of the sediment was analyzed.

Figure 1: Ponte Nova reservoir location at the Tietê River.

Instrumental Neutron Activation Analysis (INAA)

For multielemental determination about 150 mg of sediment (duplicate samples) and reference materials were accurately weighed and sealed in pre-cleaned double polyethylene bags, for irradiation. Sediment samples and reference materials were irradiated for 8 hours, under a thermal neutron flux of 10^{12} n cm^{-2} s^{-1} in the IEA-R1 nuclear reactor at IPEN. Two series of counting were made: the first, after one week decay and the second, after 15-20 days. The measurements of the induced gamma-ray activity were carried out in a gamma-ray spectrometer with a GX20190 hyperpure Ge detector (Canberra) and associated electronics, with a resolution of 0.88 keV and 1.90 keV for ^{57}Co and ^{60}Co, respectively. The elements analyzed 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. The analysis of the data was made by using in-house gamma ray software, VISPECT program to identify the gamma-ray peaks and by an ESPECTRO program to calculate the concentrations. The uncertainties of the results were calculated by error propagation. The methodology validation was verified by measuring the reference materials Lake Sediment (IAEA SL1), Soil 5 (IAEA) and BEN (Basalt –IWG-GIT). The results showed good accuracy (relative errors to certified values < 5%) and good precision (relative standard deviations < 10%). Details of the analytical methodology is given at Favaro *et al.* [9].

2. RESULTS AND DISCUSSION

2.1   Results obtained for the INAA technique

Table 1 shows the results obtained for the element analyzed by INAA. In general, there are three groups of elements with different behaviors (concentration x depth) those being:
   a) Higher concentrations in the top layers of the sediment profile: As, Br, Co, Cr, Fe, Sc, Th and Zn;
   b) Higher concentrations in the deeper layers: Ba, Hf, K, Na and Rb;
   c) Without or small variation along the profile: Cs, Sb, Ta and U.

Some elements showed an accentuated decrease and/or increase in the last layer of the profile: As, Ba, Cr, Fe, Hf, Na, Rb, Sc, Th and Zn.

When the results of the present study were compared to the results obtained by Favaro et al. [9] in another study in bottom sediments from Ponte Nova reservoir, it could observed that the results showed higher concentration values for Br, Co, Cs, Fe, Rb, Sc and Zn; lower for As, Hf, Sb, Ta and Th and the same order of magnitude for Ba and U, in the 2 first layers of the sediment profile (Table 1).

The results obtained in the present study were also compared to those presented in another study in the same region [14] using the same analytical technique for bottom sediment samples (sites 1A and 1B). The elements that showed a higher concentration at Ponta Nova reservoir (0-5 cm) were: As, Br, Co, Cr, Sb, Sc and Zn; elements that showed a smaller concentration were: Ba, Hf, Rb and Th and the same order of magnitude: Cs, Ta and U compared to Rocha et al. results [14] (Table 1).

The average values found for the Upper Tietê region in a Nascimento & Mozeto study [13], for bottom sediments were: As, 23 ± 17 ; Co, 19 ± 3; Cr, 36 ± 7; Th, 24 ± 8; U, 12 ± 5 and Zn, 82 ± 14 mg kg^{-1}. All these values were much higher than the values obtained in the present study, except for Cr. In the Nascimento & Mozeto study, the Upper Tietê region included Salesópolis, Biritiba Mirim, Cotia, São Paulo, and Pirapora do Bom Jesus Counties. The fact that this study included MRSP could explain the higher contents compared to the Ponte Nova study results, situated at Salesópolis County, near the river's headwaters.

As a criterion for the evaluation of the quality of the sediments, CETESB (Companhia Ambiental do Estado de São Paulo) adopted the values TEL and PEL limit values, established by the Canadian Council of the Ministry of the Environment (CCME) [17] for the total concentration of arsenic, metals and organic compounds, in order to assess possible deleterious effects on the biota. TEL (Threshold Effect-Level) indicates the concentration below which there is a rare occurrence of adverse effects to biota and Probable Effect Level (PEL) indicates the concentration above which there is frequent occurrence of adverse effects to biota. When the results for As, Cr and Zn were compared to TEL and PEL oriented values, none of the results for **As** surpassed the TEL value (5.9 mg kg^{-1}). For **Cr**, in general, most layers surpassed or were similar to TEL value (37.3 mg kg^{-1}), except for the last three deeper layers with lower values. For **Zn** all the results were much lower than TEL value (123 mg kg^{-1}), mainly the deeper layers.

2.2   Enrichment Factor (EF)

The Enrichment factor (**EF**), is defined as a double ratio normalized to a reference element (**RE**). It is an index used as a tool to evaluate the extension of metal pollution [18,19]:

$$EF = ([M]/[RE]_{sed})/ ([M]/[RE]_{ref}) \qquad (1)$$

Fe, Al and Sc are commonly used as elements for normalization purposes [19]. In the present study Sc was chosen as a normalizer element and NASC values as reference values for sediments [17]. According to Zhang and Liu [20], if $0.5<EF<1.5$, the elemental concentration is probably due entirely to crustal or natural weathering origins; values above 1.5 are indicative of anthropogenic contributions. The higher the EF value, the more severe the anthropogenic contribution.

Figure 2a presents the EF values using NASC as reference values [16] for the elements As, Hf, Rb, Ta, Th and U that showed EF >1.5, and Figure 2b, the same for the REE, an indication of anthropogenic influence. For the other elements analyzed, $0<EF<1.5$ was found.

Figure 2c shows the EF calculated by using the concentration values for the elements analyzed in the last layer of the sediment profile. As can be seen, $EF < 1.5$ was found for all elements (major, trace and REE), indicative of no anthropogenic contribution in the sediment profile, or that there is a natural contribution for these elements.

2.3   Geoaccumulation Index (*Igeo)*

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

The Geoaccumulation Index (*Igeo*) is a geochemical tool used to assess the contamination of a given location. The *Igeo* can be applied to organic and inorganic substances to evaluate contamination by comparing values of samples of pre-industrial locations or locations with no impact of the substances of interest. This index has been used for, at least, 30 years and is calculated using Eq. (2).

$$Igeo = \log_2 (C_n/1.5 \text{ x } B_n) \qquad (2)$$

Where:
C_n element concentration at the evaluated location,
B_n element concentration in the reference values used (background).

A factor of 1.5 for B_n, according to several authors [18-22], is applied to correct small fluctuations of lithogenic origin or even minor anthropogenic influences, in relation to background values. In the same manner as EF, the B_n variable represents the reference values (background) that should be used to represent element basal concentrations. The same considerations for EF are used for this calculation. Several authors use NASC

reference values and others even prefer local values, believing that these could be more representative. The *Igeo* index is associated with a qualitative pollution intensity scale, such as: *Igeo* < 0, not contaminated; 0 < Igeo< 1, not contaminated or moderately contaminated; 1 < Igeo< 2, moderately contaminated; 2 < Igeo< 3, moderately to highly contaminated; 3 < Igeo< 4, highly contaminated; 4 < Igeo< 5, highly to very highly contaminated and Igeo > 5, very highly contaminated.

The *Igeo* results obtained in the present study showed *Igeo <0 for* the elements analyzed, except for Br in the first two layers of the profile (0-2.5 cm, 1.7 and 2.5-5.0 cm, 1.3) indicating that there is no anthropogenic contribution for these elements.

Even though the sewage discharge are not common only for some small proprieties situated around the Ponte Nova reservoir, its waters are enriched by nutrients that sometimes provoke excessive algae proliferation. Soil use around the reservoir is mainly due to agricultural activities, natural pasturing and farming in the rural areas of the Mogi das Cruzes, Suzano and Itaquaquecetuba municipalities. This area shows high demographic occupation and mineral extraction mainly sand [23].
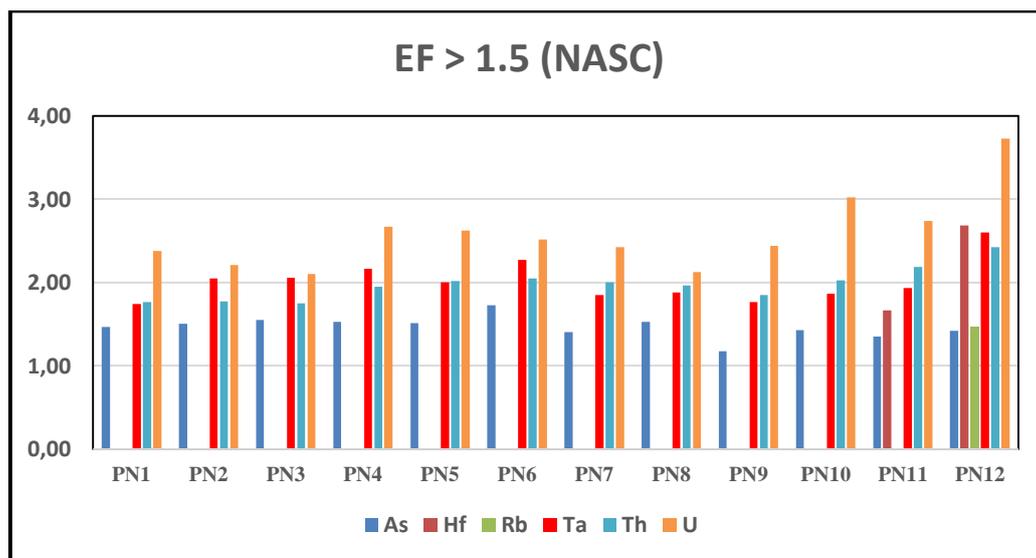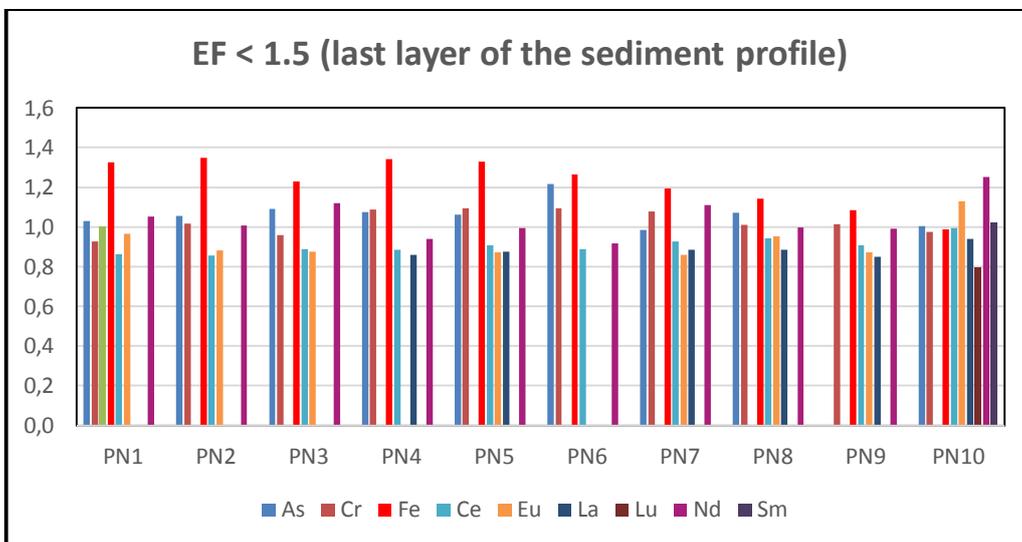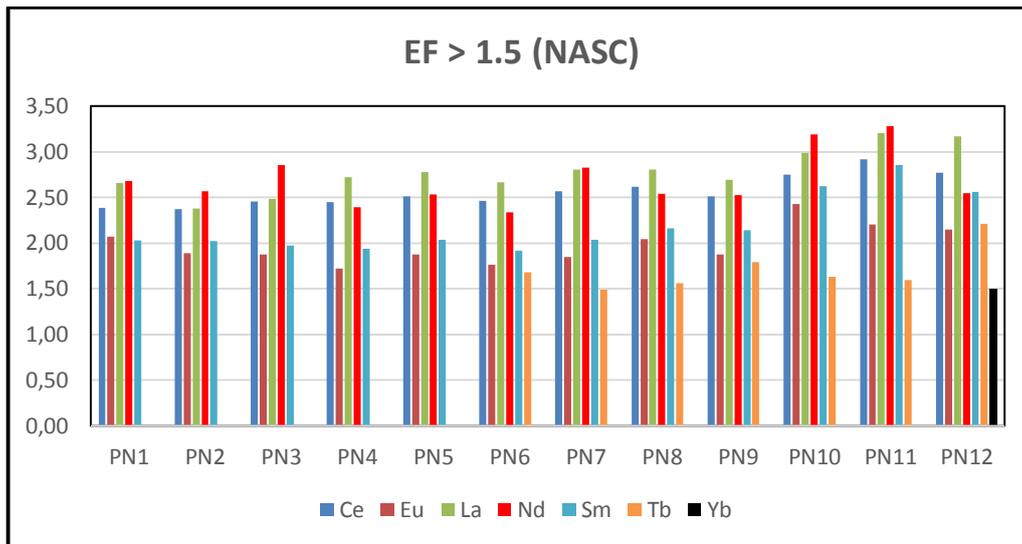
Figure 2: EF > 1.5 obtained for the elements analyzed by INAA: a) major and trace elements; b) for REE and c) for all elements analyzed (EF<1.5).

Figure 3 shows the REE Chondrite normalized patterns calculated to the REE results obtained in the present study. The signature or pattern of the REE is usually described by normalizing the individual RRE concentrations of a sample to those of the crustal abundance of the earth. An average REE composition of shale is used for this normalization [16,4]. In spite of their name, rare earth elements are more naturally abundant in sediments than many of the trace metals commonly studied by geochemists and environmental chemists [25].

The normalization of REE concentrations with respect to a geological "reference" value is a useful tool to obtain a comparison among information from "contamination" sources. The results obtained and the NASC reference levels were normalized in relation to chondrite values [26] as reference values (Figure 3). An enrichment of the light REE (LREE) (La to Sm) and for the middle REE (MREE) (Eu and Tb) just as in the NASC values, and depletion for Yb and Lu (heavy –HREE) were observed.

Normalized REE show that REE distribution is related to natural background. The REE distribution patterns may be related to the sedimentary rocks of the Tertiary Basin of São Paulo, which are the main parent material of São Paulo soils [27].
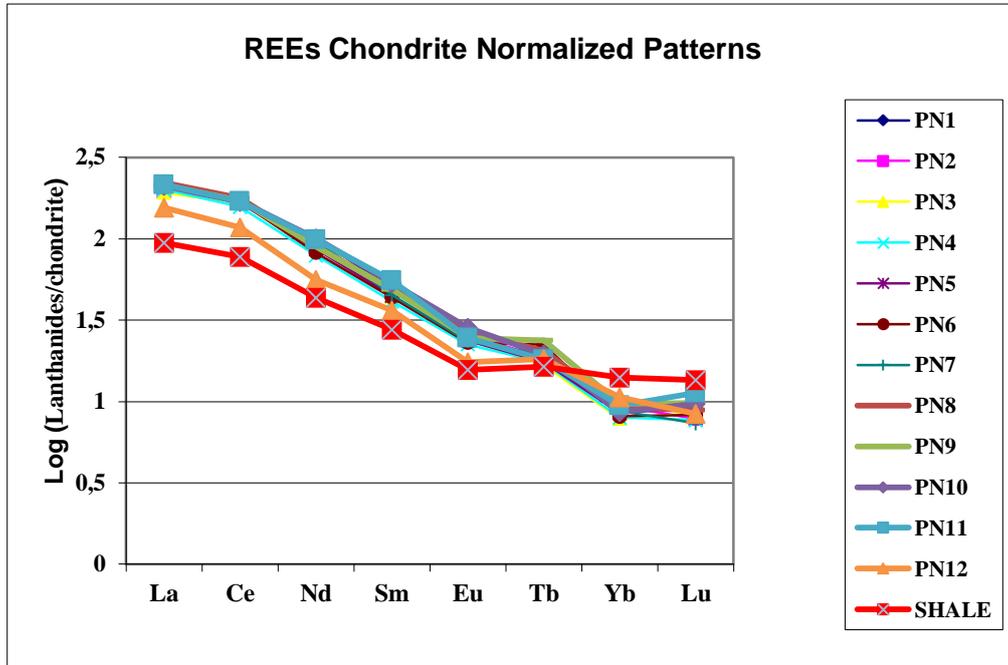

Figure 3: Chondrite-normalized curves showing the distribution patterns of REEs in sediments.

2.4 Multivariate Statistical Analysis

Factor analysis with principal component extraction and Varimax normalized rotation were performed in order to observe better data distribution as the relevance of the factors by component. Values > /0.7/ were marked and the extraction of principal components are presented in Table 2. Component 1 concentrated the samples 1, 2, 3, 10, 11 and 12 by the influence of As, Co, Cr, Fe, Hf, Na, Rb and Sc factors. Component 2 concentrated information about samples 3, 4, 5, 6, 12 influenced by Cs and Ba. Figure 4a shows the PCA for the elements analyzed and Figure 4b, for the core samples.

Using the same database of Factor Analysis, Cluster Analysis was performed using Ward´s method and Euclidian distances (Figure 5). The purpose of this analysis was to verify possible similarities between elements (Figure 5a) and core samples (Figure 5b). Two groups were identified (Figure 5):

Group 1, formed by 2 sub-groups:
- sub-group A: samples 1, 2, 4, 5 and 6, grouped by As, Ta, Co, Fe, Cr, Sc, Br;
- sub-group B: samples 3, 7, 9 and 8, grouped by Cs, Zn, Sb, Th and U

Group 2, formed by 2 sub-groups:
- sub-group A: samples 10 and 11, separated by Ba;

- sub-group B: sample 12, separated by Hf, Na and Rb.

From the Cluster Analysis results, we could observe that they confirm the Factorial Analysis results and were more complete, allowing the separation of the all core samples.

Table 2: Correlation between each element (major and trace elements) and significant PC

|	Factor Loadings (Varimax raw) Extraction: Principal components (Marked loadings are > 0.70)	
	Factor 1	**Factor 2**
As	0.784567	0.473571
Ba	-0.415572	-0.832023
Br	0.697567	0.105437
Co	0.855565	0.397045
Cr	0.737241	0.641647
Cs	0.329263	0.734228
Fe (%)	0.886303	0.394139
Hf	-0.906914	-0.304440
Na	-0.876617	-0.375403
Rb	-0.821792	-0.013249
Sb	0.485223	0.674805
Sc	0.880579	0.369238
Ta	0.641285	0.456116
Th	0.413805	0.776264
U	-0.275075	0.585078
Zn	0.425276	0.803076
Expl.Var	7.560467	4.814800
Prp.Totl	0.472529	0.300925
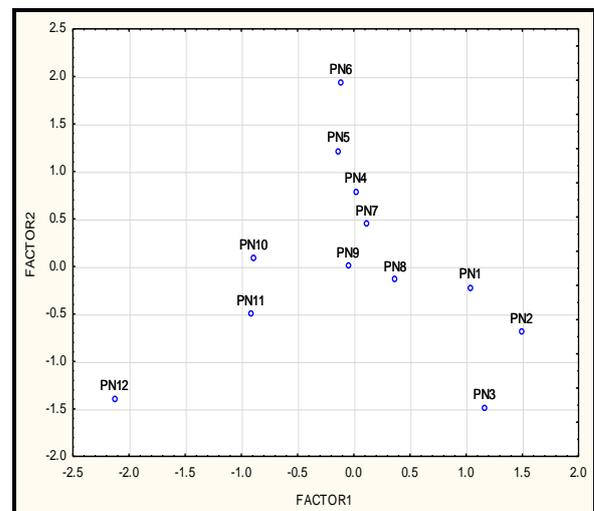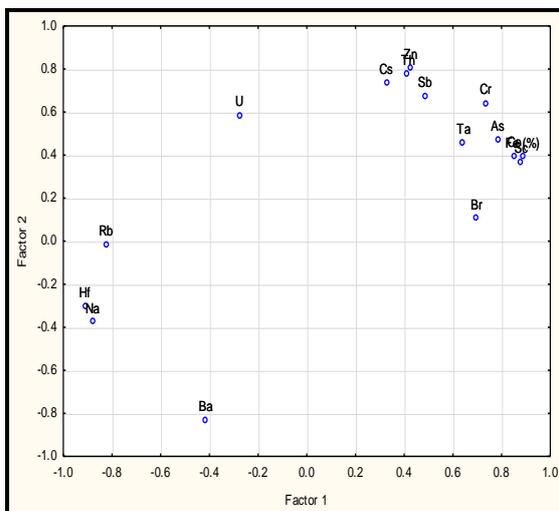
Figure 4: Principal Component Analysis (PCA) of all chemical data: a) elements; b) core samples.
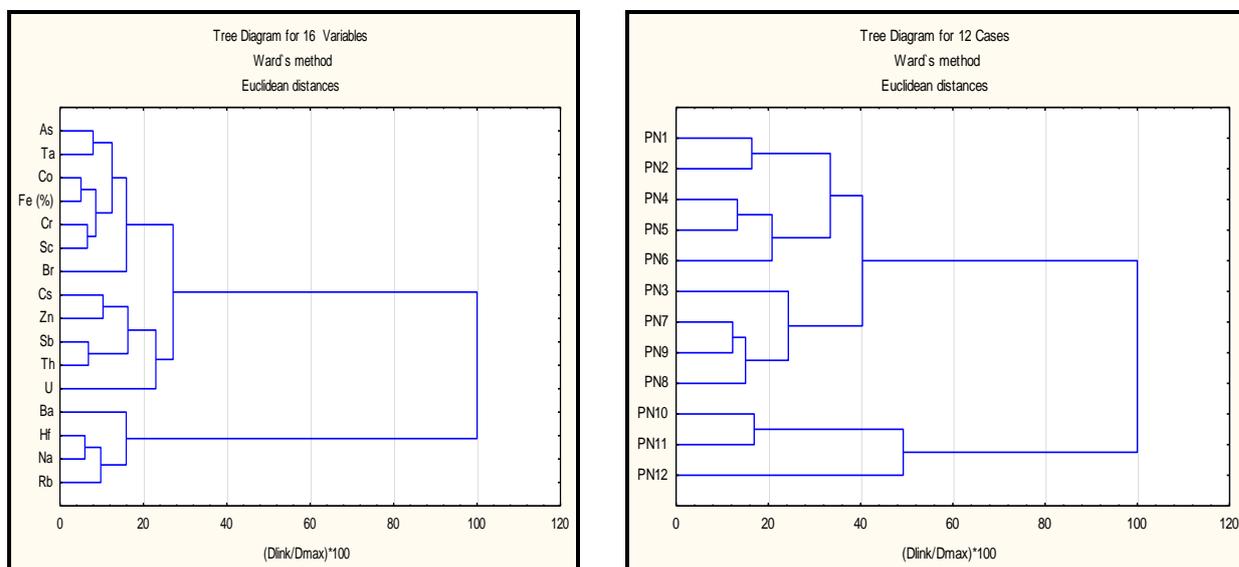

Figure 5: Cluster Analysis for the chemical data: a) elements; b) core samples.

The same statistical treatment was performed for the REE results in order to observe better data distribution as the relevance of the factors by component. Values > /0.7/ were marked and the extraction of principal components are presented in Table 3. Component 1 concentrated samples 1, 10, 11 and 12 by the influence of Ce, Eu, La, Nd and Sm factors. Component 2 concentrated information of samples 3, 4, 9, 11 and 12 influenced by Tb and Yb factors. Figure 3a shows the PCA for the core samples and Figure 3b, for the REE.

Table 3: Correlation between each element (rare earth elements - REE) and significant PC

	Factor Loadings (Varimax raw) Extraction: Principal components (Marked loadings are > 0.70)	
	Factor 1	**Factor 2**
Ce	0.951308	-0.118100
Eu	0.906604	0.111935
La	0.910216	-0.002526
Lu	0.420556	0.620735
Nd	0.929306	-0.137208
Sm	0.879646	0.351304
Tb	0.216786	0.728829
Yb	-0.313511	0.849744
Expl.Var	4.514952	1.807292
Prp.Totl	0.564369	0.225911
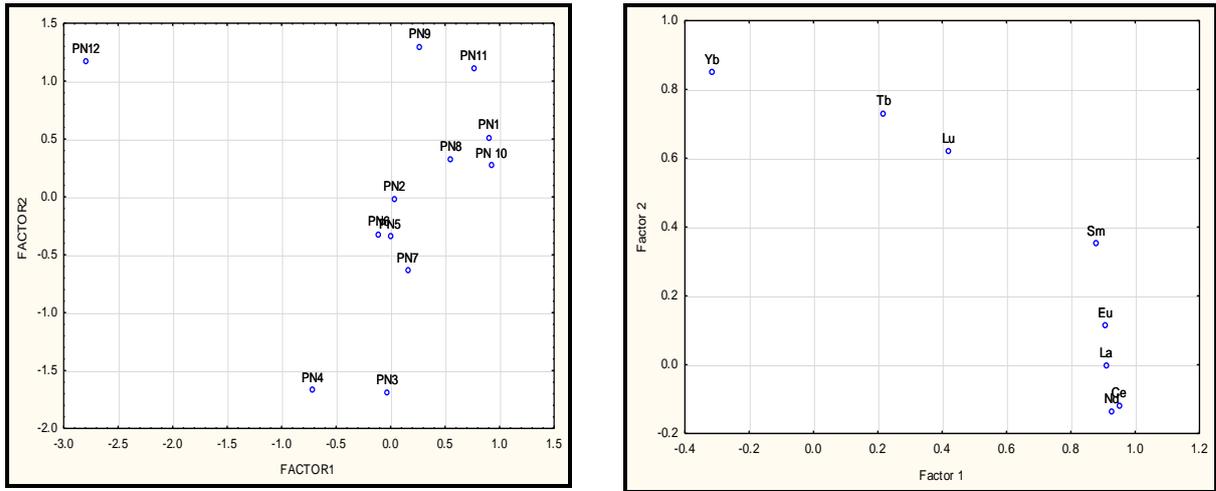
**Figure 6: Principal Component Analysis (PCA) of the REEs data:
a) core samples; b) REE**.

In order to confirm the Factorial Analysis results, Cluster Analysis was performed using Ward´s method and Euclidian distances (Figure 7). The purpose of this analysis was to verify possible similarities between elements (Figure 7a) and core samples (Figure 7b). Two main groups were again identified (Figure 7a and b): Group 1 formed by two sub-groups:

Group 1, formed by 2 sub-groups:
- sub-group A: samples 1, 8, 9, 10, 11 separated by Ce and La;
- sub-group B: samples 2, 3, 4, 5, 6, 7 separated by Eu, Nd and Sm

Group 2, formed by sample 12, separated by Tb, Yb and Lu (heavy RRE)

Once again, the data obtained by Cluster Analysis confirmed those obtained by Factorial Analysis and were more complete, separating all core samples.
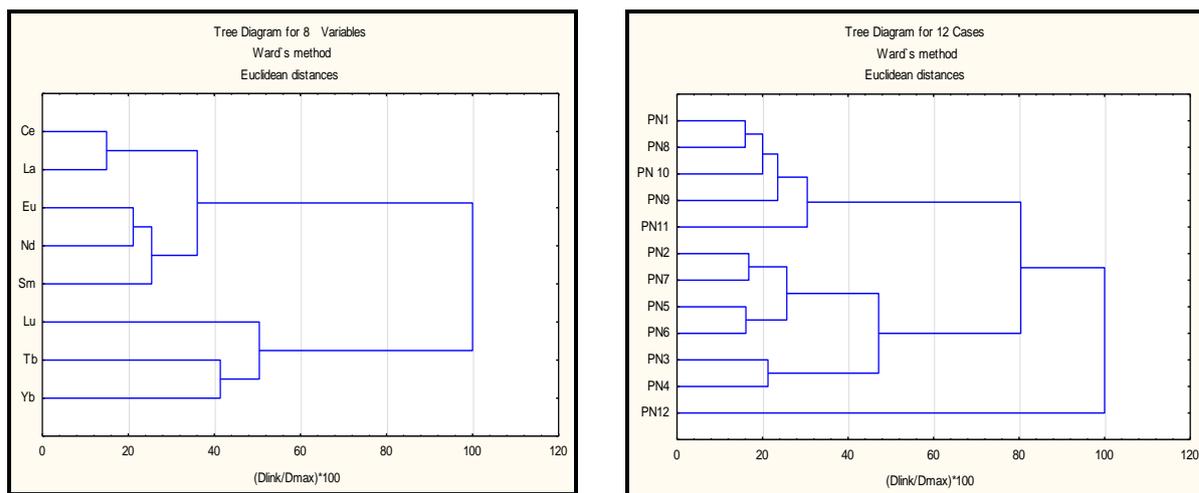
Figure 7: Cluster Analysis for the REE: a) elements; b) core samples.

3. CONCLUSIONS

The INAA technique showed good precision, accuracy and enough sensitivity to determine some major, trace and REE elements in sediment samples.

The results obtained showed that some elements (As, Br, Co, Cr, Fe, Sc, Th and Zn) showed a higher concentration and others (Ba, Hf, K, Na and Rb) a lower concentration in the top layers of the sediment profile. Some elements (Cs, Sb, Ta and U) presented no or small variation along the profile.

When EF and *Igeo* were applied to the results by using NASC (North American Shale Composite) as reference values for sediment contamination index assessment an EF>1.5 was obtained for As, Hf, Rb, Ta, Th, U, and rare earths Ce, Eu, La, Nd and Sm, but only for Br, when the last layer concentration values were used as reference values. Similar results were obtained for the *Igeo* index. The results are indicative of no anthropogenic contribution in the sediment profile, or that there is a natural contribution for these elements.

When the results of As, Cr and Zn of the present study were compared to the oriented values from Environmental Canada (TEL and PEL), none of the results for **As** surpassed the TEL value (5.9 mg kg^{-1}). For **Cr**, in general, most of layers surpassed or were similar to TEL values (37.3 mg kg^{-1}), except for the last three deeper layers with lower values. For **Zn** all the results were much lower than TEL value (123 mg kg^{-1}), mainly the deeper layers.

As a conclusion of the present study, all these results may indicate that there is no anthropogenic contribution for the elements analyzed in the sediment profile from this reservoir.

REFERENCES

1. Companhia de Saneamento Básico do Estado de São Paulo - SABESP. Estação de Tratamento de Esgotos de Suzano, ETE SUZANO (Folheto descritivo), s/ data.
2. G.F. Alegre, Sueli Borrely, T. M. Nascimento, D.I.T Favaro. Assessment of Sediments from Tietê River – Toxicity, and Trace Elements - from Salesópolis to Suzano Counties, São Paulo, Brazil. *Proceedings of the International Atlantic Nuclear Conference (INAC)*, Rio de Janeiro, September 26 - October 02, Cd Rom, (2009).
3. P.A.Z. Pamplin, O. Rocha. "Temporal and bathymetric distribution of benthic macroinvertebrates in the Ponte Nova Reservoir", Tietê River (São Paulo, Brazil). *Acta Limnol. Bras.* **Vol.** 19 (4), p. 438-452 (2007)
4. G.L. Yuan, C. Liu, L. Chen, Z. Yang. "Imputting history of heavy metals into the inland lake recorded in sediment profiles: Poyanf Lake in China." *J. Hazardous Materials*, **Vol.** 185, p. 336-345 (2011).
5. C.G. Ingersoll. "Sediment tests". In: Fundamentals of aquatic toxicology: effects, environmental fate, and risk assessment, G.M. RAND (ed), Taylor & Francis, Washington. (1995).
6. S.J. Bennet and F.E. Rhoton. "Reservoir Sedimentation and Environmental Degradation: assessing trends in sediment-associated trace elements in Grenada Lake, Mississippi." *Journal of Environmental Quality*, **Vol.** 36, p. 815-825 (2007).
7. I.S. Silva, G. Abate, J. Lichtig, J.C. Masini. "Heavy metal distribution in recente sediments of the Tietê-Pinheiros River System in São Paulo State, Brazil." *Applied Geochemistry*, **Vol.** 17, p. 105–116 (2002).
8. G.F. Alegre. "Avaliação toxicológica de sedimentos do Rio Tietê entre os municípios de Salesópolis e Suzano". Master of Sciences. IPEN–USP São Paulo, Brazil p. 97, (2009).
9. D.I.T. Favaro, G.F. Alegre, S.I. Borrely, W. Vukan, A.S. Vieira, S.M.B. Oliveira. "Major and trace element assessment of Tietê River sediments", São Paulo, Brazil. *J Radioanal Nucl Chem.*, **Vol.** 299(1) p.797-805 (2014).
10. J. Mortatti, C. Hissler, J.L. Probst. "Distribuição de metais pesados nos sedimentos de fundo ao longo da Bacia do Rio Tietê". *Revista Instituto de Geociências*, Série cient., **Vol.** 10(2), p. 3-11 (2010).
11. J. Mortatti J, G.M. Moraes, C.H. Kiang. "Distribuição e possível origem de metais pesados nos sedimentos de fundo ao longo da Bacia do Alto Rio Tietê: aplicação da normalização geoquímica sucessiva". *Geociências*, UNESP, São Paulo, **Vol.** 31(2), p. 175-184 (2012).
12. J. Mortatti, H. Oliveira, G.M. Moraes, D. Vendramini, A.M. Fernandes. "Distribution of heavy metals in the geochemical phases of sediments from the Tietê River", Brazil. *Chemical Speciation and Bioavailability*, **Vol.** 25(3) p.194-200 (2013).
13. M.R.L Nascimento, A.A. Mozeto. "Reference values for metals and metalloids concentrations in bottom sediments of Tietê River Basin, Southeast of Brazil." *Soil & Sediment Contamination*, **Vol.** 17, p. 269–278 (2008).

14. F.R. Rocha, P.S.C. Silva, L.M. Castro, I.C.C.L. Bordon, S.M.B. Oliveira, D.I.T. Fávaro. "NAA and XRF Technique Bottom Sediment Assessment for Major and Trace Elements – Tietê River", São Paulo State, Brazil**. *J Radioanal Nucl Chem.*, DOI: 10.1007/s10967-015-4261-8 (2015)

15. CPRM – Serviço Geológico do Brasil. 2006. *Mapa Geológico do Estado de São Paulo.* Disponível em http://geobank.sa.cprm.gov.br/ acesso em 08 de junho de 2015.

16. S.R. Taylor, S.Mc Lennan. "The continental crust: its composition and evolution." *Blackwell Scientific*, Palo Alto, Ca. pp. 25-27 (1985).

17. CCME, Canadian Environmental Quality Guidelines - Summary Tables, http://www.ec,gc,ca/ceqg-rcqe/English/ceqg/sediment/default,cfm, accessed in May 2015.

18. F.C. Gomes, J.M. Godoy, M.L.D.P. Godoy, Z.L. Carvalho, R.T. Lopes, J.A. Sanchez-Cabeza, L.D. Lacerda, J.C. Wasserman, Metal concentrations, fluxes, inventories and chronologies in sediments from Sepetiba and Ribeira Bays: A comparative study". *Marine Pollution Bulletin,* **Vol.** 59. pp. 123-133 (2009).

19. S. Audry, J. Schaefer, G. Blanc, U. J-M. Jousnnea, "Fifty-year sedimentary record of heavy metal pollution (Cd, Zn, Cu, Pb) in the Lot River reservoirs (France)." *Environ. Pollut*., **Vol.** 132, pp. 413-426 (2004).

20. J. Zhang, C.L. Liu, "Riverine composition and Estuarine Geochemistry of Particulate Metals in China – Weathering Features, Anthropogenic Impact and Chemical Fluxes". *Estuarine, Coastal and Shelf Science,* **Vol.** 54(6), pp. 1051–1070 (2002).

21. K. Loska, J. Cebula, J. Pelczar, D. Wiechula, J. Kwapulinski. "Use of Enrichment , and Contamination Factors together with Geoaccumulation indexes to evaluate the content of Cd, Cu, and Ni in the Rybnik Water Reservoir in Poland". *Water, Air and Soil Pollution,* **Vol.** 93, p. 347-365, 1997.

22. K .Loska, D. Wiechula, I. Korus. "Metal Contamination of farming soils affected by industry." *Environ Inter,* **Vol**.30, p.159-165(2004)

23. M.C. Carvalho. "Comunidade Fitoplanctônica como instrumento de biomonitoramento de reservatórios no Estado de São Paulo". Tese de Doutorado. Faculdade de Saúde Pública – USP, 130p., (2003).

24. P. Henderson. In Rare Earth Element Geochemistry; Henderson P. Ed; Elsevier: Amsterdam, 1984, p. 1-32.

25. I. Olmez, E.R. Sholkovitz, D. Hermann, R.P. Eganhouse. "Rare Earth Elements in Sediments of Southern California: a New Anthropogenic Indicator." *Environ. Sci. Technol.*, **Vol.** 25, p. 310-316 (1991)

26. A. Masuda. "Regularities in variation of relative abundances of lanthanide elements and an attempt to analyze separation-index patterns of some minerals." *J.Earth Sci. Nagoya Univ.,* **Vol.**10, p.173-187 (1962).

27. A.M.G. Figueiredo, S.P. Camargo, J.B. Sígolo. "Determination of REE in Urban Park Soils from São Paulo City for Fingerprint of Traffic Emission Contamination." *Proceedings of the International Atlantic Nuclear Conference (INAC)*, Rio de Janeiro, September 26 - October 02, Cd Rom, (2009).

Table 1: Results for the elements determined by INAA (mg kg^{-1}): mean (duplicate) (dry basis), standard deviation, minimum, maximum, NASC [16], TEL and PEL oriented values [17]

Depth (cm)		As	Ba	Br	Co	Cr	Cs	Fe(%)	Hf	K(%)	Na	Rb	Sb	Sc	Ta	Th	U	Zn
0- 2.5	PN01	2.6±0.2	207±16	67.4±6.8	6.3±0.1	36.6±1.3	2.8±0.2	3.80±0.04	4.7±0.1	0.7±0.1	283±7	34.5±1.8	0.25±0.02	13.1±0.3	1.7±0.1	18.5±0.5	5.6±0.3	65±2
2.5-5.0	PN02	2.5±0.2	223±16	53.1±5.4	7.4±0.1	38.8±1.3	3.0±0.2	3.73±0.03	3.9±0.1	0.8±0.1	356±8	35.5±2.7	0.26±0.02	12.7±0.3	1.9±0.1	17.9±0.5	5.0±0.3	56±2
5.0 -7.5	PN03	2.5±0.2	257±18	26.4±2.7	6.2±0.1	34.6±1.2	2.6±0.1	3.21±0.03	4.6±0.1	0.7±0.1	400±9	35.8±1.9	0.25±0.02	11.9±0.3	1.8±0.1	16.7±0.5	4.5±0.2	51±2
7.5–10.0	PN04	2.3±0.2	139±19	31.9±3.3	6.2±0.1	37.4±1.5	3.1±0.3	3.35±0.03	4.7±0.1	0.6±0.1	472±10	50.1±4.4	0.26±0.02	11.4±0.3	1.8±0.1	17.8±0.5	5.5±0.4	77±4
10.0–12.5	PN05	2.4±0.2	207±33	31.2±3.3	6.3±0.1	38.7±1.5	3.4±0.3	3.42±0.03	5.2±0.1	0.7±0.1	549±12	49.1±4.5	0.38±0.03	11.8±0.3	1.8±0.1	19.0±0.5	5.6±0.3	79±3
12.5-15.0	PN06	2.8±0.2	114±26	33.8±3.6	6.8±0.1	40.2±1.6	3.5±0.3	3.37±0.03	5.2±0.2	1.0±0.1	540±12	64.6±6.1	0.37±0.03	12.2±0.3	2.1±0.1	20.0±0.6	5.5±0.3	74±4
15.0–17.5	PN07	2.2±0.1	160±11	24.4±2.5	6.1±0.1	38.6±1.3	3.4±0.2	3.10±0.03	4.9±0.1	0.7±0.2	494±11	37.2±1.8	0.25±0.02	11.9±0.3	1.6±0.1	19.0±0.5	5.2±0.3	59±2
17.5-20.0	PN08	2.5±0.2	220±13	20.8±2.1	6.1±0.1	36.9±1.2	3.2±0.3	3.03±0.03	5.9±0.2	1.1±0.3	533±12	39.7±1.9	0.30±0.03	12.1±0.3	1.7±0.1	19.0±0.5	4.6±0.3	56±2
20.0–22.5	PN09	1.9±0.2	239±18	18.4±1.9	5.9±0.1	37.2±1.3	3.1±0.2	2.89±0.02	5.4±0.1	0.7±0.3	606±16	36.6±1.8	0.26±0.02	12.2±0.3	1.6±0.1	18.1±0.5	5.3±0.4	56±2
22.5-25.0	PN10	2.1±0.1	216±12	17.4±1.8	5.0±0.1	32.1±1.1	2.5±0.2	2.37±0.02	6.3±0.2	1.2±0.1	758±16	48.9±1.9	0.23±0.04	10.9±0.3	1.5±0.1	17.7±0.5	6.0±0.5	45±2
25.0-27.5	PN11	1.9±0.2	263±12	15.4±1.6	4.5±0.1	29.3±1.0	2.3±0.2	2.18±0.02	7.3±0.2	1.3±0.1	952±20	51.3±2.0	0.31±0.04	10.4±0.3	1.5±0.1	18.2±0.5	5.1±0.4	44±2
27.5-30.0	PN12	1.4±0.1	357±15	14.3±1.5	4.2±0.1	22.8±0.8	2.5±0.2	1.66±0.01	8.5±0.2	1.6±0.1	1958±40	92.5±3.7	n.d.	7.6±0.2	1.5±0.2	14.7±0.4	5.1±0.4	35±2
Mean		**2.3**	**217**	**30**	**5.9**	**35.3**	**2.9**	**3.0**	**5.6**	**0.9**	**658**	**48**	**0.28**	**11.5**	**1.7**	**18**	**5.3**	**58**
Std Dev		**0.4**	**63**	**16**	**0.9**	**5.0**	**0.4**	**0.6**	**1.3**	**0.3**	**446**	**17**	**0.05**	**1.4**	**0.2**	**1**	**0.4**	**14**
Min		**1.4**	**114**	**14**	**4.2**	**22.8**	**2.3**	**1.7**	**3.9**	**0.6**	**283**	**34**	**0.23**	**7.6**	**1.5**	**15**	**4.5**	**35**
Max		**2.8**	**357**	**67**	**7.4**	**40.2**	**3.5**	**3.8**	**8.5**	**1.6**	**1958**	**92**	**0.38**	**13.1**	**2.1**	**20**	**6.0**	**79**
TEL		**5.9**				**37.3**												**123**
PEL		**17**				**90**												**315**
NASC		**2.0**	**636**	**0.69**	**28**	**125**	**5.2**	**4.00**	**6.3**	**3.29**	**7500**	**125**	**2.09**	**15.0**	**1.1**	**12**	**2.7**	**85**
Nasc&Mozeto [13]		23± 17			19± 3	36± 17										24± 8	12± 5	82± 14
Favaro et al [9]		7.0± 0.1	180± 12	5.5± 0.1	2.27± 0.05	34± 2	1.9± 0.1	3.37± 0.02	28± 1	n.d.	n.d.	11± 1	0.43± 0.03	10.1± 0.2	2.6± 0.2	24.9± 0.8	5.4± 0.3	35± 1

n.d. – not determined

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