

MULTIELEMENTAL CHARACTERIZATION OF SEDIMENTS FROM RIVERS AND RESERVOIRS OF A SEDIMENT QUALITY MONITORING NETWORK OF SÃO PAULO STATE, BRAZIL

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ABSTRACT

The Environment Company of the State of São Paulo (CETESB) by means of its quality monitoring network does, systematically, the assessment of water and sediment quality in rivers and reservoirs in the São Paulo state. The quality evaluation is done by means 50 parameters in water and 63 for sediment that are considered the more representative for CETESB monitoring. In 2011 the network monitoring analyzed 420 points being 24 in sediments. In the present study the multielemental characterization (total concentration) of 13 sediment samples from 24 rivers and reservoirs belonging to the CETESB monitoring network were analyzed by instrumental neutron activation analysis (INAA). The analytical validation according to precision and accuracy was checked through certified reference materials analyzes BEN (Basalt-IWG-GIT), SL-1 (Lake Sediment – IAEA) and Soil-5 (IAEA), that presents certified concentration values for all elements analyzed. The results obtained for multielemental characterization were compared to NASC values (North American Shale Composite) and the enrichment factor (EF) by using Sc as a normalizer element was calculated. The results showed higher enrichment values for As, Br, Cr, Hf, Ta, Th, U and Zn and rare earth elements (REE) Ce, Eu, La, Nd, Sm, Tb and Yb in many of the tested sediment samples indicating that there may be an anthropogenic contribution for these elements. The multielemental results were also compared to the granulometric composition of the sediment samples. Factorial and Cluster Analysis were applied and indicated that the elements distribution is controlled, mainly by the granulometric fractions of the sediments.

1. INTRODUCTION

The Environmental Company of the State of São Paulo (CETESB) has performed the assessment of the quality of the waters of the rivers and reservoirs in the state by means of its Network for Monitoring the Quality of Inland Waters of the State of São Paulo, since 1974. This program has as main objectives, perform diagnostic and evaluate the temporal evolution of the quality of surface waters, assess the compliance with environmental legislation; identify priority areas for the control of pollution; subsidize the diagnosis and control of the quality of water used for public supply, among others. In 2002 with the aim of complementing the diagnostic quality of aquatic ecosystems, the assessment of sediment was incorporated into the Monitoring Network [1,2].

To assess the quality and control of the pollution of the waters and sediments of rivers and reservoirs in their Monitoring Network CETESB uses quality standards to define the concentration limits of each substance. For the definition of these standards CETESB determines approximately 50 water quality and 63 sediment quality variables (physical, chemical, microbiological, and ecotoxicological) considered most representative [1,2,3].

State Law no 9,034 of 1994 - State Water Resources Plan proposed the division of the state of São Paulo in 22 Water Resources Management Units (UGRHI's), classifying them by vocations into four large groups: Agribusiness, Conservation, under Industrialization and Industrial. Figure 1 presents the 22 UGRHI's and the classification [2].

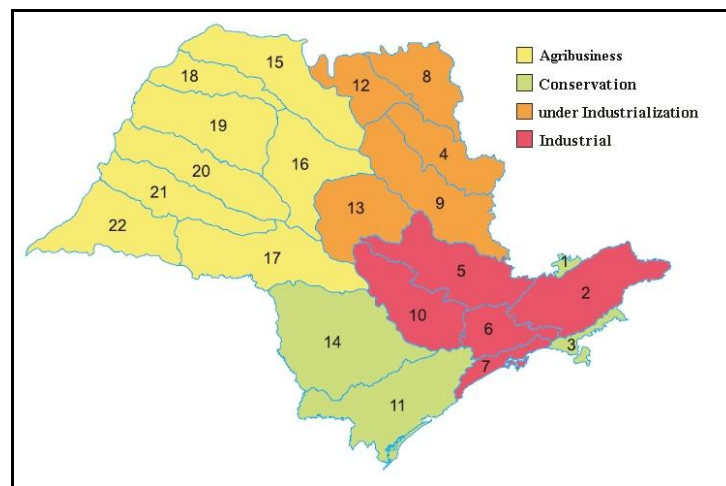


Figure 1. UGRHI's classification [2]

In 1974, at the start of the operation of the network, it had 47 points for water sampling. Already in 2011 the Monitoring Network operated with 420 sampling points, in 22 UGRHI's being 24 belonging to the Network of Sediment, distributed in 13 UGRHIs in rivers and reservoirs in the state [2].

As a criterion for the evaluation of the quality of the sediments, CETESB adopted the values TEL and PEL limit values, established by the Canadian Council of the Ministry of the Environment (CCME) 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. Occasionally effects are expected in the range between TEL and PEL values. Table 1 presents the values of TEL and PEL for arsenic and heavy metals [4].

An important characteristic of sediments to be studied is the granulometry, because the finer particles have a greater capacity to retain chemical substances, due to greater surface area, which provides large capacity of interaction with several ions and molecules [5]. According to the particle size, the sediment can be classified according to the Granulometric Scale of Wentworth (1922) cited by CONAMA [6]. The characterization of sediments should be performed in the total fraction (particle size < 2 mm). [3]

Table 1. CCME oriented values for arsenic and heavy metals to freshwater

Variable	TEL (mg kg⁻¹)	PEL (mg kg⁻¹)	Variável	TEL (mg kg⁻¹)	PEL (mg kg⁻¹)
Arsenic	5.9	17	Chromium	37.3	90
Cadmium	0.6	3.5	Mercury	0.17	0.486
Lead	35	91.3	Nickel	18	35.9
Copper	35.7	197	Zinc	123	315

Obs.: values expressed in dry weight of sediment

The determination of metal and trace elements in sediments may be performed by either destructive or non-destructive analytical techniques. Nuclear and related analytical techniques are used. Gamma-ray spectrometry is used for the determination of natural and/or artificial, radionuclides while instrumental neutron activation analysis (INAA) and X-ray fluorescence (XRF), are used for multielemental characterization. Other non-destructive techniques used are: ion beam analysis (IBA) which includes technical PIXE (Particle Emission Induced by X-rays) and "Rutherford Backscattering spectrometry (RBS). [7]

The INAA technique is being widely used for the analysis of soils and sediments [8,9], and in Brazil it has been used in various studies and regions by the group of researchers from the Neutron Activation Analysis Laboratory (LAN) of IPEN/CNEN - SP [10-18].

Within this context the purpose of the present study was to complement the data obtained by CETESB in their Monitoring Network of sediments by using quality standards, with the NAA technique. Thus with this analytical technique some major (Ca, Fe, K and Na), trace (As, Ba, Br, Co, Cr, Cs, Hf, Rb, Sb, Sc, Ta, Th, U and Zn) and rare earth elements (REE) (La, Ce, Nd, Sm, Lu, Tb and Yb) were evaluated.

The assessment of heavy metals and As concentrations in sediments is performed routinely by CETESB in their Monitoring Network and as such it was not the purpose of this study to perform this type of analysis.

In order to obtain more information about the quality of the sediments evaluated, the present work performed multielemental characterization of sediments from 13 of the 24 rivers and reservoirs belonging to the CETESB Sediment Monitoring Network, by using INAA technique.

2. MATERIAL AND METHODS

2.1. Sampling locations

In this study 13 of the 24 points of the Sediment Monitoring Network from rivers and reservoirs of CETESB were sampled. These points are distributed in UGRHI's belonging to four groups (conservation, agriculture, under industrialization and industrial). Table 2 described the sampling points, location, geographical coordinates and collection dates.

Table 2. Description of sampling points, location and dates of collection

	Point code	UGRHI	Water body	Location	Lat S Long W	Collection dates
Rivers	LENS3900	13	Rio Lençóis	1 km from the mouth of Tiete river	22 30 15 48 30 15	30/08/2011
	PARD2590	4	Rio Pardo	2 Km upstream of the bridge of the highway that connects Pontal to Cândia	20 58 41 48 00 56	25/08/2011
	PRET2600	15	Rio Preto	Upstream of the bridge of the road that connects the district of Ibioporanga (Tanabi) to Palestina, in Boa Sorte farm	20 26 36 49 32 36	24/08/2011
	RIBE2650	11	Rio Ribeira	Near the ferryboat to the neighborhood of Pilões, at Poço Grande	24 32 47 48 29 58	27/09/2011
	RIJU2800	3	Rio Juqueriquerê	Upstream from ETE of Sabesp	23 41 16 45 27 18	14/09/2011
	SAGU2150	1	Rio Sapucaí Guaçú	Near the bridge Descansopolis neighborhood	22 41 56 45 31 32	13/09/2011
	SJDO2150	18	Rio São José dos Dourados	Next to the dirt road bridge of Duas Pontes, downstream of Monte Aprazível ETE	20 43 02 49 46 00	24/08/2011
	TBIR3400	20	Rio Tibiriçá	Near the bridge of the Rosalia district, in Marília	21 56 42 49 57 10	31/08/2011
Reservoirs	ATSG2800	5	Reservatório Salto Grande	In the main body, in front of Praia Azul	22 43 30 47 13 49	01/06/2011
	BILL2100	6	Reservatório Billings	In the middle of the central body, towards the Borore tributary	23 47 11 46 38 49	06/07/2011
	JARI0800	5	Reservatório Jaguari	In the main body, in front of the island	22 55 40 46 25 27	28/07/2011
	MOCA2300	9	Reservatório Cachoeira de Cima	Approximately 1.5 km upstream of the dam, in the middle of reservoir	22 22 44 46 53 42	18/08/2011
	RGDE2900	6	Reservatório Rio Grande	In the main body, 2 km from the dam, in front of the Banespa club	23 46 40 46 30 42	27/07/2011

2.2. Sampling and sample preparation

Sampling was carried out by the CETESB Sampling Sector, following the internal procedures of the sector, which are also described in the national collection and preservation of samples: water, sediment, aquatic communities and liquid effluents, edited by CETESB and by ANA (Agencia Nacional de Águas) [19]. The samples were collected using a van Veen sampler, transferred to a polyethylene tray, homogenized with polyethylene spoon and stored in polyethylene bottles, under-cooling.

For multielemental characterization by INAA it is necessary to carry out the drying, maceration and screening of samples for removal of any coarse material (> 2 mm), usually composed of pebbles, leaves, carcasses and other materials that are not part of the sediment

constitution. In this way, all the material that passes through the opening of 2 mm is considered as the total fraction sediment [20]. The samples, after homogenization, were dried in a ventilated oven at 40°C until constant mass, and then macerated in an agate mortar and sieved in a 200 mesh. After sieved, the samples were stored in polyethylene bottles, ready for analysis.

2.3. Metal and trace element determinations

Multielemental characterization in the sediment samples was performed using Instrumental Neutron Activation Analysis (INAA) technique. Some metals (Cr, Zn), major (Ca, Fe, K, Na), trace elements (As, Ba, Br, Co, Cr, Cs, Hf, Rb, Sb, Sc, Se, Ta, Th, U, Zn) and rare earth elements (La, Ce, Eu, Nd, Sm, Lu, Tb, Yb) were determined.

Activation methods are based on radioactivity measurements of that have been induced in samples by irradiation commonly with neutrons [21]. NAA is a sensitive analytical technique useful for performing both qualitative and quantitative multi-element analysis of major, minor and trace elements in samples from almost every conceivable field of scientific or technical interest. The application of purely instrumental procedures is commonly called Instrumental Neutron Activation Analysis (INAA). When a neutron interacts with a nucleus via non-elastic collision, a compound nucleus forms in an excited state. The compound nucleus will almost instantaneously de-excite into a more stable configuration through emissions of one or more characteristic prompt gamma rays. About 70% of the elements have properties suitable for measurement by NAA [22]. Care is taken to be sure the samples and standards are exposed to the same neutron flux. The time of irradiation is dependent upon a variety of factors and often is determined empirically; generally this varies from several minutes to several hours. Often these procedures are nondestructive and for this reason are applied to the analysis of art objects, coins, forensic and environmental samples, and archaeological specimens [21].

For the multielemental 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 by pipetting adequate aliquots of standard solutions (SPEX CERTIPREP) onto small sheets of Whatman No.41 filter paper. Sediment samples, reference materials and synthetic standards 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. Gamma spectrometry was performed using a Canberra gamma X hyperpure Ge detector and associated electronics, with a resolution of 0.88 keV and 1.90 keV for ⁵⁷Co and ⁶⁰Co, 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 done 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 errors propagation. The methodology validation was verified by measuring the reference materials Lake Sediment (SL-1, IAEA), Soil 5 (IAEA) and BEN (Basalt –IWG-GIT). Details of the analytical methodology are described at Larizzatti et al [18].

For checking precision and accuracy of the methodology the certified reference materials (CRMs) BEN, SL-1 and Soil-5 were analyzed, which have certified values for almost all elements analyzed. For validation of the results obtained by INAA, Z-score criterion is frequently used. [23] The calculation of the standardized difference, or Z value, of an analytical result is given by equation 1:

$$Z = \frac{C_i - C_{ref}}{\sqrt{\sigma_i^2 + \sigma_{ref}^2}} \quad (1)$$

where:

C_i : concentration of element i in the CRM analysis,

C_{ref} : certified value of concentration or consensus for element I,

σ_i : uncertainty of the concentration of element i in the CRM analysis;

σ_{ref} : uncertainty of the consensus value for element i.

According to BODE [23], the use of Z value for approval of results considers that if $|Z| \leq 3$, the result of concentration of an individual element in the reference material that is being analyzed must be within 99% of the confidence interval of the expected value.

2.4 Enrichment Factor (EF)

The Enrichment factor (**EF**), defined as a double ratio normalized to a reference element (**RE**), is an index used as a tool to evaluate the extent of metal and trace element pollution [24]:

$$EF = ([M]/[RE]_{sed}) / ([M]/[RE]_{ref}) \quad (2)$$

Fe, Al and Sc are generally used as reference elements for normalization purposes [25]. In the present study Sc was chosen as a reference element and NASC (North American Shale) values as reference values for sediments [26]. According to Zhang and Liu [27], if $0.5 < EF < 1.5$, the elemental concentration is probably entirely due to crustal or natural weathering origins; values above 1.5 indicate anthropogenic contributions. The higher the EF value, the more severe the anthropogenic contribution.

2.5 Multivariate Statistical Analysis

Cluster and Factorial Analysis were applied to the chemical data. The Statistica 7.0 software (STATSOFT) was used. Cluster analysis consists in the classification of these objects through similarity. For a better interpretation in this study, the results obtained were divided into two groups, i.e., the cluster analysis was made considering the concentration of elements analyzed and the sampling points.

Factorial analysis is one of the techniques most commonly used of what is conventionally called multivariate analysis. When we employ this type of analysis we are often interested in the behavior of a variable or group of variables in covariance with others. In fact, the factorial analysis refers not to a single statistical technique, but to a variety of related techniques to make the observed data more easily (and directly) interpreted.

2.6. Granulometric Analysis

The granulometric analysis of the sediment samples was performed by CETESB (Limeira) according to CETESB standard L6.160 [28]. This analysis is based on the principles of sieving and sedimentation guided by the Wentworth scale, that it based on the average speeds of the particles in an aqueous medium. The larger the particles, the greater its sedimentation speed. The granulometric classification was based on the following criteria: silt (particles from 0.004 to 0.063mm), clay (< 0.004 mm) and sand (> 0.063mm).

3. RESULTS AND DISCUSSION

The results obtained for the granulometric analysis for the sediments are presented in Table 3.

Table 3. Results for the granulometric analysis in the sediment samples

	Samples	Sand (%)	Clay (%)	Silt (%)	Textural classification
Rivers	LENS3900	79.18	9.57	11.24	Very sandy
	PARD2590	19.62	50.00	30.38	Silty Clay
	PRET2600	79.67	13.13	7.19	Very sandy
	RIBE2650	67.01	17.81	15.18	Sand-clay-silt
	RIJU2800	72.13	6.78	21.08	Very sandy
	SAGU2150	91.54	1.95	6.51	Very sandy
	SJDO2150	55.06	25.02	19.92	Clayey Sand
	TBIR3400	87.83	4.05	8.11	Very sandy
Reservoirs	ATSG2800	0.19	76.50	23.30	Very clayey
	BILL2100	3.14	71.40	25.40	Very clayey
	JARI0800	5.10	72.50	22.49	Very clayey
	MOCA2300	1.89	66.82	31.29	Silty Clay
	RGDE2900	2.66	52.60	44.73	Very clayey

Points ATSG2800, BILL2100, JARI0800, GIRL2300 and RGDE2900, located in reservoirs and PARD2590, in river, showed high concentration of fine (silt and clay) (above 80 %) and low proportion of sand (< 20 %), characterizing environments of clayey texture, where, due to the large surface area, the adsorption capacity of both organic matter and metals is greater. [5,29] Points LENS3900, PRET2600, RIBE2650, RIJU2800, SAGO2150 and TBIR3400, all

in rivers, presented a composition with a higher proportion of sand (> 60 %) and smaller proportion of silt and clay. Point SJDO2150 presented a composition of 55% sand and the remainder in silt and clay (44 %).

3.2 Multielemental characterization of sediments by INAA

3.2.1 Validation of the methodology

For checking precision and accuracy of the method CRMs that have certified values for almost all elements were analyzed. Figure 2 shows the Z-score values for all elements determined in the CRMs. In this study all the results showed values within the interval $|Z| \leq 3$, proving the precision and accuracy of the INAA analytical technique.

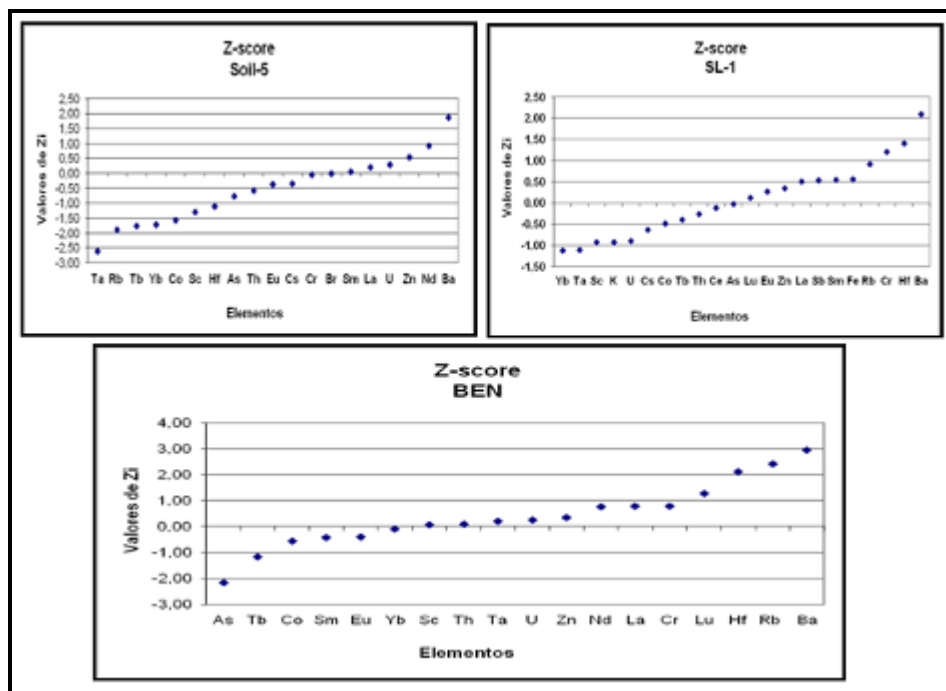


Figure 2. Z-score values obtained for the CRMs analyzed by INAA

3.2.2. Multielemental concentration results for the sediment samples

Table 6 presents the means and standard deviations of the results obtained by INAA in the sediment samples, in mg kg^{-1} , in addition to the reference values of the NASC (North American Shale Composite) [26] and TEL (threshold effect level) and PEL (probable effect level) oriented values from CCME (Canadian Council of Minister of the Environment) [4]. The values are presented in dry weight and correspond to the total concentration of the elements present in the sample.

When the results of **As** were compared to the TEL and PEL values, point RIBE2650 showed concentration between these values. In this way, occasionally adverse effect to aquatic biota is expected. However, points RGDE2900 and Bill2100 showed concentrations above the PEL

value. In this case, adverse effects to aquatic biota is expected. The remaining points showed concentrations below TEL.

In relation to **Cr**, ATSG2800, RIBE2650, MOCA2300, PARD2590, JARI0800, RIJU2800 and SAGO2150 exhibited concentrations between TEL and PEL values. In this way, on these points adverse effects to aquatic biota is occasionally expected. In points LENS3900, PRET2600, SJDO2150, TBIR3400, RGDE2900 and Bill2100 concentrations were above PEL level and adverse effects to aquatic biota is expected.

Regarding **Zn**, the points ATSG2800, RIBE2650, LENS3900, MOCA2300, PARD2590, RGDE2900, and SAGO2150 exhibited concentrations between TEL and PEL values and thus, occasionally adverse effects to aquatic biota is expected. At point Bill2100 the concentration found was above PEL value, indicating that adverse effects to aquatic biota can occur. Points PRET2600, SJDO2150, TBIR3400, JARI0800 and RIJU2800 showed concentrations below TEL values.

3.3. Enrichment Factor

From the results obtained (Table 6) the enrichment factor for the sediment samples was calculated using Sc as a normalizing element. According to Zhang and Liu [27], if $0.5 < EF < 1.5$, the elemental concentration is probably due entirely to crustal or natural weathering origins; values above 1.5 indicate anthropogenic contributions. The higher the EF value, the more severe the anthropogenic contribution. The EF calculated are presented in Table 7.

$EF > 1.5$ selected in Table 7 indicate the more enriched elements Br, Cr, Hf, Ta, Th, U and Zn and the rare earth elements (REE) Ce, Eu, La, Nd, Sm, Tb and Yb. In this case, it appears that an anthropogenic contribution for these elements is occurring and needs to be more closely investigated.

The highest values for EF were found for As, Br and Hf, especially in points TBIR3400, RGE3900, RIJU2800 and SAGU2100. The highest values for the REE were also found, mainly at these points. The other values found are distributed between $EF < 0.5$ and $0.5 < EF < 1.5$ indicating no enrichment is occurring, i.e., crustal contribution.

Table 7. Enrichment Factor (EF) for the sediment samples

	LENS 3900	PARD 2590	PRET 2600	RIBE 2650	RIJU 2800	SAGU 2150	SJDO 2150	TBIR 3400	ATSG 2800	BILL 2100	JARI 0800	MOCA 2600	RGDE 2900
As	0.63	1.00	1.62	5.19	0.38	0.46	0.79	2.62	1.54	7.78	1.02	0.71	7.64
Ba	0.11	0.47	0.41	1.33	1.30	1.10	0.68	1.73	0.62	0.53	0.72	0.80	0.58
Br	2.21	3.62	3.36	9.23	17.59	11.30	2.48	4.75	7.60	46.54	8.75	5.30	24.56
Ca	2.06	1.08	1.32	0.93	0.67	0.57	0.88	1.79	0.12	0.47	0.41	0.38	0.42
Ce	0.48	1.19	2.27	1.93	2.77	3.21	1.54	3.17	1.48	1.58	2.51	2.06	0.77
Co	0.87	0.64	0.39	0.74	0.42	0.56	0.61	0.79	0.55	0.48	0.38	0.50	0.24
Cr	0.50	0.35	2.70	0.64	0.34	0.69	2.19	3.60	0.52	1.51	0.34	0.53	0.65
Cs	0.07	0.20	0.26	0.72	1.05	0.53	0.29	0.63	0.85	0.77	0.47	0.67	1.19
Eu	0.67	1.35	1.96	1.55	1.51	1.42	2.47	2.13	1.46	0.84	2.07	1.53	0.47
Fe	1.74	1.40	0.91	1.37	1.09	1.29	1.07	1.29	1.27	1.63	1.22	1.07	1.45
Hf	2.53	1.39	2.14	4.28	7.48	10.38	2.31	19.64	0.44	0.58	0.87	0.50	0.77
La	0.47	1.28	4.68	2.19	2.86	3.50	3.24	3.26	2.12	1.62	2.78	2.17	0.59
Lu	0.61	0.63	0.79	1.01	2.75	1.85	1.01	4.38	0.77	0.69	0.53	0.63	0.68
Na	0.04	0.09	0.05	0.94	1.24	0.27	0.07	0.29	0.07	0.09	0.03	0.10	0.10
Nd	0.67	1.15	5.16	1.94	2.85	2.67	2.80	4.41	2.03	1.21	3.14	2.06	0.66
Rb	N.D.	0.20	0.13	0.62	1.23	0.70	0.33	0.77	0.53	0.31	0.31	0.56	0.52
Sb	0.07	0.10	0.23	0.39	0.07	0.24	0.13	0.48	0.28	2.13	0.05	0.11	0.37
Sc	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Sm	0.49	1.13	2.97	1.70	2.84	2.48	2.25	3.16	1.58	0.78	1.78	1.70	0.41
Ta	2.31	1.32	4.72	1.83	3.10	1.95	4.35	4.85	0.99	1.80	0.75	1.19	1.47
Tb	0.31	1.02	0.79	1.08	2.62	1.73	1.61	3.65	1.04	1.25	0.94	1.59	0.75
Th	0.34	0.62	1.27	1.33	3.77	3.46	1.47	2.96	1.30	1.53	1.34	1.41	1.25
U	0.52	0.60	1.73	1.45	4.45	3.11	1.08	3.67	1.30	1.72	0.80	1.00	1.43
Yb	0.54	0.60	1.64	0.99	2.61	1.76	0.99	3.83	0.68	0.58	0.51	0.70	0.57
Zn	0.99	1.07	0.68	1.84	1.27	1.75	0.39	1.41	1.49	5.79	0.87	1.24	1.09

3.4. Multivariate Statistical Analysis

Factorial Analysis with extraction of Principal Components and Varimax Rotation normalized was performed, using the results obtained by INAA technique and also the particle size data. The values $> /0.6/$ were selected and in the extraction of Principal Components 4 factors could be extracted, responding by 79.2% of the total variance observed. Factor 1 explained 31.2% of the total variance; Factor 2 is responsible for 22.2 %; Factor 3 for 16.3% and Factor 4, for 9.4% of the variance observed.

Factor 1: comprises the elements Cr, Eu, La, Nd, Sm and Ta. Factor 2 comprises Ba and Th that have a negative correlation with the elements Ca, Co, Fe, Sc and Ta. Factor 3 shows a positive correlation for Hf, Lu, U, Yb and sand and a negative correlation with the content of silt+clay. Factor 4 shows a negative correlation for the elements As, Br, Sb and Zn.

Table 6. Results for the elements determined by INAA (mg kg⁻¹): mean (duplicate) (dry basis), standard deviation, NASC, TEL and PEL values

	LENS 3900	PARD 2590	PRET 2600	RIBE 2650	RIJU 2800	SAGU 2150	SJDO 2150	TBIR 3400	ATSG 2800	BILL 2100	JARI 0800	MOCA 2600	RGDE 2900	NASC	TEL	PEL
As	2.9 ± 0.2	3.6 ± 0.1	3.5 ± 0.4	10.4 ± 0.5	0.7 ± 0.2	0.9 ± 0.2	2.5 ± 0.2	2.1 ± 0.2	3.8 ± 0.7	18.4 ± 0.6	2.6 ± 0.3	1.9 ± 0.2	21.7 ± 1.0	2.0	5.9	17.0
Ba	161 ± 23	538 ± 21	283 ± 24	847 ± 36	795 ± 35	706 ± 32	700 ± 29	457 ± 24	491 ± 81	401 ± 21	576 ± 31	663 ± 37	523 ± 30	636		
Br	3.5 ± 0.4	4.5 ± 0.2	2.5 ± 0.5	6.4 ± 0.7	11.6 ± 1.2	7.8 ± 0.8	2.8 ± 0.2	1.4 ± 0.2	6.5 ± 0.3	38.0 ± 1.7	7.6 ± 0.8	4.8 ± 0.3	24.0 ± 2.5	0.69		
Ca(%)	12.3 ± 0.2	5.1 ± 0.1	3.7 ± 0.1	2.4 ± 0.1	1.67 ± 0.04	1.47 ± 0.04	3.7 ± 0.1	1.9 ± 0.1	0.40 ± 0.03	1.4 ± 0.1	1.32 ± 0.04	1.3 ± 0.1	1.53 ± 0.04	2.59		
Ce	81.2 ± 1.7	158 ± 6	179 ± 5	141 ± 5	194 ± 8	235 ± 9.3	181 ± 10	96.1 ± 4.5	135 ± 17	137 ± 5	230 ± 8	196 ± 8	79.2 ± 1.7	73		
Co	56.0 ± 1.0	32.4 ± 0.5	11.7 ± 0.3	20.8 ± 0.4	11.2 ± 0.2	15.7 ± 0.3	27.5 ± 0.5	9.2 ± 0.1	19.1 ± 0.6	15.8 ± 0.3	13.4 ± 0.24	18.2 ± 0.3	9.4 ± 0.2	28		
Cr	144 ± 5	79.7 ± 3.2	365 ± 18	79.8 ± 0.4	40.7 ± 1.4	86.9 ± 2.9	441 ± 14.0	187 ± 4.9	81.1 ± 9.8	224 ± 7	53.2 ± 1.9	85.6 ± 2.2	115 ± 4	125	37.3	90.0
Cs	0.82 ± 0.22	1.9 ± 0.2	1.4 ± 0.2	3.7 ± 0.2	5.2 ± 0.3	2.8 ± 0.2	2.4 ± 0.2	1.4 ± 0.1	5.5 ± 0.2	4.7 ± 0.3	3.1 ± 0.2	4.5 ± 0.2	8.8 ± 0.5	5.2		
Eu	1.9 ± 0.1	3.0 ± 0.1	2.6 ± 0.2	1.9 ± 0.1	1.8 ± 0.1	1.8 ± 0.1	4.9 ± 0.2	1.1 ± 0.1	2.26 ± 0.03	1.2 ± 0.1	3.2 ± 0.2	2.5 ± 0.1	0.82 ± 0.02	1.24		
Fe(%)	16.1 ± 0.1	10.2 ± 0.1	3.9 ± 0.1	5.5 ± 0.1	4.16 ± 0.04	5.2 ± 0.1	6.9 ± 0.1	2.14 ± 0.02	6.3 ± 0.2	7.7 ± 0.1	6.1 ± 0.1	5.6 ± 0.1	8.2 ± 0.1	4		
Hf	36.9 ± 1.0	15.9 ± 0.3	14.6 ± 0.5	27.0 ± 0.9	45.2 ± 1.5	65.7 ± 2.1	23.5 ± 0.4	51.3 ± 1.0	3.4 ± 0.2	4.4 ± 0.1	6.9 ± 0.2	4.1 ± 0.1	6.9 ± 0.2	6.3		
La	34.7 ± 0.5	74.2 ± 0.8	162 ± 2	70.1 ± 1.0	87.7 ± 1.2	113 ± 2	167 ± 2	43.3 ± 0.6	84.8 ± 2.4	61.2 ± 0.7	112 ± 1.5	90.5 ± 1.3	27.0 ± 0.4	32		
Lu	0.68 ± 0.06	0.55 ± 0.03	0.41 ± 0.05	0.49 ± 0.04	1.3 ± 0.1	0.89 ± 0.07	0.78 ± 0.05	0.87 ± 0.06	0.46 ± 0.03	0.39 ± 0.02	0.32 ± 0.03	0.40 ± 0.03	0.46 ± 0.04	0.48		
Na	670 ± 15	1166 ± 19	378 ± 18	7054 ± 43	8928 ± 80	2053 ± 44	888 ± 16	902 ± 20	696 ± 24	817 ± 13	267 ± 10	937 ± 20	1062 ± 23	7500		
Nd	42.3 ± 2.9	57.3 ± 3.1	153 ± 8	53.3 ± 2.6	75.0 ± 4.9	73.6 ± 2.8	124 ± 7	50.1 ± 2.7	69.4 ± 9.0	39.2 ± 2.4	108 ± 6	73.7 ± 3.2	25.7 ± 1.8	27.4		

Rb	N. D.	45.4 ± 3.1	18.0 ± 1.9	77.2 ± 3.5	146 ± 6	88.3 ± 3.8	67.1 ± 3.9	39.8 ± 1.8	82.1 ± 4.9	46.2 ± 3.0	49.1 ± 2.8	90.7 ± 3.5	92.4 ± 4.9	125		
Sb	0.33 ± 0.03	0.36 ± 0.04	0.51 ± 0.05	0.81 ± 0.22	0.14 ± 0.03	0.50 ± 0.05	0.43 ± 0.05	0.42 ± 0.03	0.72 ± 0.04	5.3 ± 0.6	0.13 ± 0.03	0.29 ± 0.03	1.1 ± 0.3	2.09		
Sc	34.7 ± 0.9	27.2 ± 0.7	16.2 ± 0.6	15.0 ± 0.4	14.4 ± 0.4	15.1 ± 0.4	24.2 ± 0.6	6.2 ± 0.2	18.7 ± 1.1	17.8 ± 0.4	18.8 ± 0.5	19.5 ± 0.4	21.3 ± 0.5	15		
Sm	6.4 ± 0.1	11.7 ± 0.2	18.3 ± 0.4	9.7 ± 0.3	15.5 ± 0.5	14.2 ± 0.5	20.7 ± 0.4	7.5 ± 0.2	11.2 ± 0.1	5.3 ± 0.6	12.7 ± 0.3	12.7 ± 0.2	3.3 ± 0.1	5.7		
Ta	6.0 ± 0.4	2.7 ± 0.2	5.7 ± 0.5	2.1 ± 0.2	3.3 ± 0.3	2.2 ± 0.2	7.9 ± 0.2	2.3 ± 0.1	1.4 ± 0.1	2.4 ± 0.3	1.1 ± 0.1	1.7 ± 0.1	2.3 ± 0.2	1.1		
Tb	0.61 ± 0.12	1.6 ± 0.2	0.72 ± 0.11	0.92 ± 0.09	2.1 ± 0.2	1.5 ± 0.1	2.2 ± 0.2	1.3 ± 0.2	1.1 ± 0.2	1.3 ± 0.2	1.0 ± 0.1	1.8 ± 0.2	0.9 ± 0.2	0.85		
Th	9.3 ± 0.3	13.4 ± 0.3	16.5 ± 0.7	16.0 ± 0.5	43.4 ± 1.2	41.8 ± 1.2	28.4 ± 0.6	14.7 ± 0.4	19.4 ± 1.5	21.8 ± 0.5	20.2 ± 0.6	22.1 ± 0.5	21.3 ± 0.6	12		
U	3.3 ± 0.2	2.9 ± 0.2	5.1 ± 0.4	3.9 ± 0.2	11.5 ± 0.7	8.4 ± 0.5	4.7 ± 0.2	4.1 ± 0.2	4.4 ± 0.2	5.5 ± 0.2	2.7 ± 0.2	3.5 ± 0.2	5.5 ± 0.4	2.7		
Yb	3.9 ± 0.2	3.4 ± 0.2	5.5 ± 0.3	3.1 ± 0.2	7.7 ± 0.4	5.5 ± 0.3	5.0 ± 0.2	4.9 ± 0.2	2.6 ± 0.2	2.1 ± 0.1	2.0 ± 0.1	2.8 ± 0.1	2.5 ± 0.2	3.1		
Zn	194 ± 8	166 ± 6	62.5 ± 3.6	156 ± 6	104 ± 4.2	150 ± 6	53.8 ± 2.8	49.9 ± 2.0	157 ± 6	583 ± 21	93.2 ± 3.9	137 ± 5	131 ± 5	85	123	315

N. D. – not determined

Using the same data base of Factors Analysis the Cluster Analysis was applied, using the Ward's method and Euclidean distances. The objective of this analysis was to verify possible similarities between the sampling points (Figure 3) and among the elements analyzed and the other parameters (Figure 4).

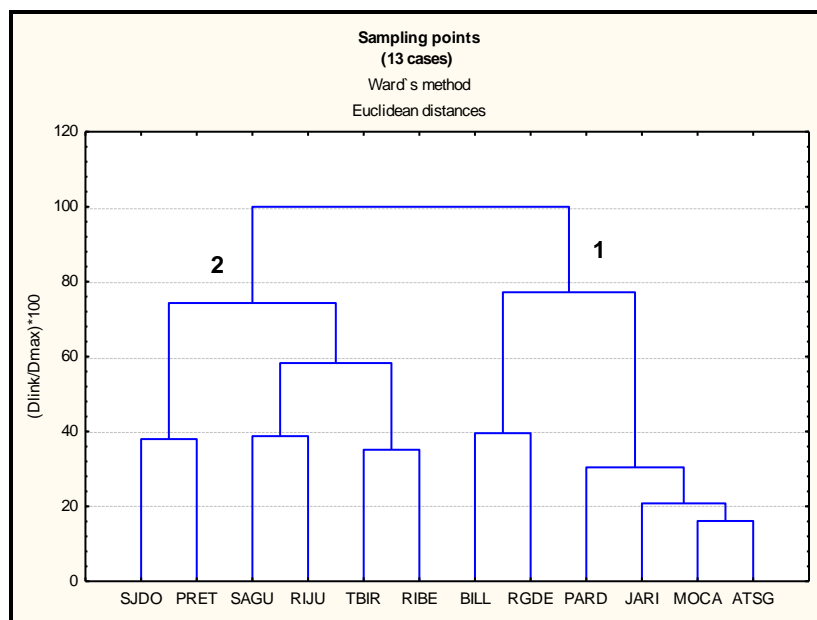


Figure 3. Dendrogram resulting from the Cluster Analysis, variables: sampling points

Figure 3 presents the formation of the 2 groups. Group 1 was formed by points, Bill, RGDE) PARD, JARI, DAMSEL and ATSG. Points Bill and RGDE presented the highest concentrations for the elements As, Br and Zn and also high levels for Cs, Fe and silt + clay. Another factor to be considered in group 1, formed by reservoirs and the Pardo river, was probably the high levels of silt + clay fraction presented in this group.

Group 2 was composed of 2 sub-groups. The sub-group 1, formed by points SJDO, PRET and LENS showed, in general, similar levels of sand and silt + clay fractions and SJDO and PRET, high concentrations of Cr, I, La, Nd, Sc, Sm, Ta, Th and U. Sub-group 2, formed by points SAGU, RIJU, TBIR and RIBE, showed the highest sand fraction levels. These points showed, in general, high levels of Ba, Hf and Na (SAGU, RIJU and RIBE) and some rare-earth elements (Ce, La, Lu). Point TBIR presented high levels of Ce, Lu and Yb.

When the same data base was run through the same program considering the parameters analyzed as variables, two groups were also formed (Figure 4). Group 1 was composed of 2 sub-groups: one formed by elements Fe, Sc, Co and Ca and the second, by the fraction silt + clay, Cs, Zn, Sb, Br and As.

Group 2 was also formed by 2 sub-groups. Sub-group 1, formed by elements Ta, Cr, Sm, Nd, La, Eu, Ce and sub-group 2, consisting of Yb, Lu, Sand, Hf, U, Th, Tb, and Ba. This result indicates that the distribution of elements is controlled mainly by the granulometric fractions.

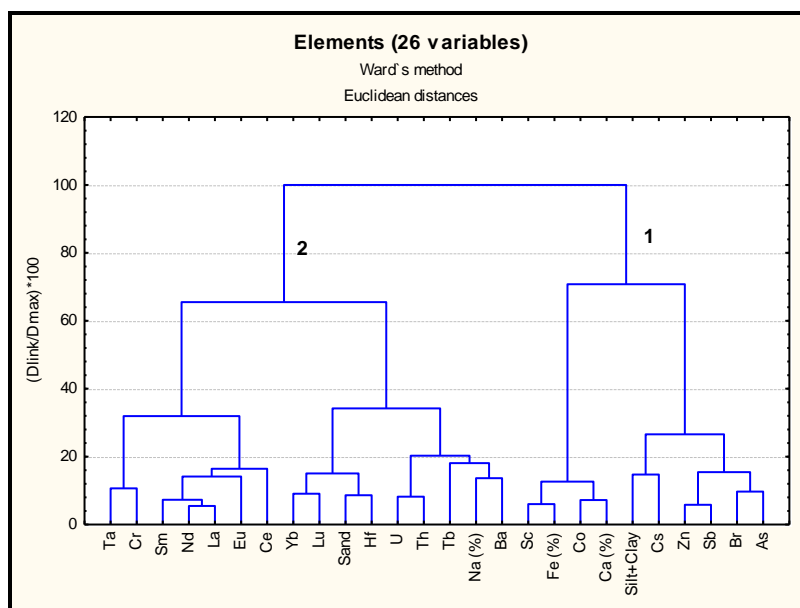


Figure4. Dendrogram resulting from the Cluster Analysis, variables: elements and granulometry

4. CONCLUSIONS

The determination of metals and trace elements by way of Instrumental Neutron Activation Analysis (INAA) proved to be highly appropriate and can be an extremely important tool for sediment characterization as its sensitivity, precision and accuracy are highly reliable.

The multielemental characterization of the sediment samples studied as well as the calculation of enrichment factor (EF) allowed higher EF values to be found for the elements, Br, Cr, Hf, Ta, Th, U and Zn and the rare-earth elements (REE) Ce, Eu, La, Nd, Sm, Tb and Yb in many of the samples analyzed indicating that there may be an anthropogenic contribution for these elements. This contribution could be the focus of further studies.

Statistical analysis seems to indicate that element distribution in the sediments studied is mainly due to granulometric fraction composition.

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