Chemical characterization and recent sedimentation rates in sediment cores from Rio Grande reservoir, SP, Brazil

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The Rio Grande reservoir lies southeast of the Metropolitan Area of São Paulo. In order to evaluate if the sediments contain a historical registration of anthropogenic activity, four sediment cores were sampled from the reservoir. In these cores the Hg concentration was determined by the CV AAS technique, major and trace elements by instrumental neutron activation analysis and the sedimentation rates by the ^{210}Pb method. The results obtained for Hg are much higher than expected, showing an anthropogenic contribution. As a general trend, the elemental concentration decreases with depth, indicating recent contamination.

Introduction

The Metropolitan Area of São Paulo, MASP is the most extensive and populous urban agglomerate of South America and one of the largest industrial complexes of the world. This region has problems of high demographic density and lack of water resources that are typical of great urban centers. The population suffers from environmental impacts, such as residue disposal, insufficient water availability, air and soil pollution, etc. These problems can easily be observed in reservoirs that supply water for cities because they receive a large amount of sediments as a consequence of the soil degradation.[1]

In the last years, a project was established in one of the most important reservoirs of São Paulo city, Rio Grande reservoir, located in the Southeast portion of the MASP, to study and identify these kinds of problems and characterize areas of sediment production, as well as the corresponding silt deposition.

The Rio Grande reservoir is responsible for the water supply of four counties (São Bernardo do Campo, São Caetano do Sul, Santo André and Diadema), with approximately 1.7 million inhabitants. This reservoir has been seriously affected by urban expansion, due to chaotic urban occupation, with irregular use of the land. This region presents extensive degraded areas caused not only by erosion, but also by pollution of diffuse loads, as recent sedimentary deposits. An expressive amount of sediments has been loading the reservoir since the beginning of its operation in 1935.[2]

Due to the utilization of the Rio Grande for public water supply, the reservoir was separated (end of the 80's) from the Billings Dam. Since then a considerable improvement was observed in the water quality.

The main sources of pollution come from Grande and Ribeirão Pires rivers.

Bottom sediments are a sink, as well as, a source of contaminants in an aquatic environment.[3] In order to evaluate if the sediments contain an historical registration of anthropogenic activity, four sediment cores were sampled from the reservoir. In these cores the Hg concentration was determined by cold vapor atomic absorption spectrometry (CV AAS) and major and trace elements by instrumental neutron activation analysis. The sedimentation rates and age of the sediments were determined using the ^{210}Pb dating method.

Experimental

Sampling and sample preparation

Four sediment cores, Core 01, 52.5 cm long, Core 02, 128 cm long, Core 03, 57 cm long and Core 04, 80.5 cm long were collected in January 1998, using a piston corer in the reservoir. Figure 1 shows the Rio Grande Reservoir and the location of the sampling sites: Core 01 – near the catchment point of the water supply; Core 02 – in the middle of the reservoir, and Cores 03 and 04 – at the mouth of the Grande and Ribeirão Pires Rivers, respectively, (discharge of contaminants).

Grain-size analysis of sediment samples showed that the grain sizes are dominantly silt and clay, which indicate the prevalence of settling processes. Sediment organic matter contents in the first centimeters of the four cores are very high and decrease with depth.

These cores were collected in different geographical positions (Fig. 1) and sliced in different thickness as well. For Cores 03 and 04, the first slice corresponds to 5 cm, the second corresponds to 4 cm. The following

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slices correspond to 2 or 3 cm. Cores 01 and 02 were sliced at every 2 or 3 cm. In the laboratory all samples were previously dried at 60 °C in a ventilated oven, passed through a 0.065 mm sieve and homogenized in a glass mortar prior to analyses.

Analytical methods

^{210}Pb methodology: The measurement of the ^{226}Ra and ^{210}Pb radionuclides was used to determine the dates and sedimentation rates. These radionuclides were determined in each slice of the cores. More details are presented in a previous study.[4]

Fig. 1. Sampling sites at Rio Grande Reservoir, Billings dam, São Paulo, Brazil

Total mercury determination methodology: For total mercury determination the sediment samples were analyzed by CV AAS technique in a Perkin Elmer Flow Injection Mercury System (FIMS). Samples were digested by a mixture of concentrated HNO_3, H_2SO_4 and 30% H_2O_2 in Teflon vials. The vials were closed and left overnight at room temperature. The following day, the vials were put into an aluminum block at 90 °C and left there for 3 hours. The vials were cooled to room temperature and diluted to the mark of 50 ml with Milli-Q water. At the end, the vials were shaken and left to rest until the non-digested fraction sedimented. Hg standard solution (stock solution) was prepared from metallic mercury from Merck P.A. (purity 99.9995%) dissolved in concentrated HNO_3. Calibration was performed using synthetic standards prepared from stock solution in the same acid mixture as the digested samples. All the analytical steps performed on the samples were used for the calibration standards. All calibration solutions were prepared in the day of the experiment. Methodology validation was performed by analysis of certified reference materials showing different total Hg concentrations: Montana Soil (NIST SRM 2710),[5] Buffalo River Sediment (NIST SRM 2704),[6] Lake Sediment (BCR CRM 280)[7] and Estuarine Sediment (NIST SRM 1646a).[8]

Detection and calculation of quantification limits: Five Hg standard solutions in the same concentration range of the analyzed samples were prepared and measured. The linear coefficient obtained from the regression curve (absorbance at zero concentration) was taken and multiplied by three times the standard deviation obtained for ten measurements of the blank solution. This was taken as the detection limit absorbance (LD), which was then transformed into concentration units by means of the regression equation. The limit of quantification (LQ) was defined as ten times the detection limit.[9]

Instrumental neutron activation analysis technique (INAA)

For the multielemental analyses approximately 150 mg of the sediment (duplicate samples) and reference materials were accurately weighed and sealed in pre-cleaned double polyethylene bags. Single and multielement synthetic standards were prepared by pipetting convenient 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 16 hours, under a thermal neutron flux of 10^{12} n·cm^{-2}·s^{-1} in the IEA-R1 Nuclear Research Reactor at IPEN – Instituto de Pesquisas Energéticas e Nucleares, São Paulo, Brazil.[10] Methodology validation was verified by measuring Buffalo River Sediment (NIST SRM 2704),[6] Soil 7 (IAEA)[11] and BEN (Basalt-IWG-GIT)[12] reference materials.

Results and discussion

The sediment cores were dated by the ^{210}Pb method. Core 01 yielded a mean sedimentation rate of 0.63 cm·y^{-1} (level 52.5 cm, year 1919); Core 02, a mean sedimentation rate of 0.97 cm·y^{-1} (level 59.5 cm, year 1939); the Core 03, a mean sedimentation rate of 0.61 cm·y^{-1} (level 54 cm, year 1910); and finally Core 04, a mean sedimentation rate of 1.22 cm·y^{-1} (level 80.5 cm, year 1932). Lower rates were related to the period prior to the water dam operation, when the loading of the sediments was less significant. Higher rates were related to rainy seasons and the urban expansion of the reservoir surroundings (Figs 2a, b).

In Fig. 2b, Cores 3 and 4, showed two important pulses on the sedimentation rates, the first one during the 40's and 50's and the second, during the 70's, 80's and 90's, where the highest depositions took place. During the 40's and 50's, Core 03 presented the impact caused by fast growth of the Ribeirão Pires county. In Core 04, located before Core 03, this was not observed probably due to the silt composition of the erosion material that was accumulated around point 03.[13]

In the 70's and 90's new urbanization pulses occurred in this county, reflecting, with more intensity in the Ribeirão Pires river mouth region and presented sedimentation rates of 3 cm·year^{-1} at point 04 and 2 cm·year^{-1} at point 3. These sedimentation rates were much higher than that estimated by PETRI and FÚLFARO[14] of 1 cm·year^{-1}, value found for the first 30 years of this reservoir.[13]

The CV AAS methodology for total mercury determination was validated by reference materials analysis. The results obtained showed the precision, expressed in terms of relative standard deviation of at least 4 independent determinations, from 1.2 to 4.1%. The accuracy, expressed in terms of relative error varied from 0.6 to 2.1%. The agreement with certified values is good for all reference materials analyzed (Table 1). The limit of detection (LD) was estimated to be about 0.5 ng·ml^{-1} and the LQ, 5 ng·ml^{-1}.
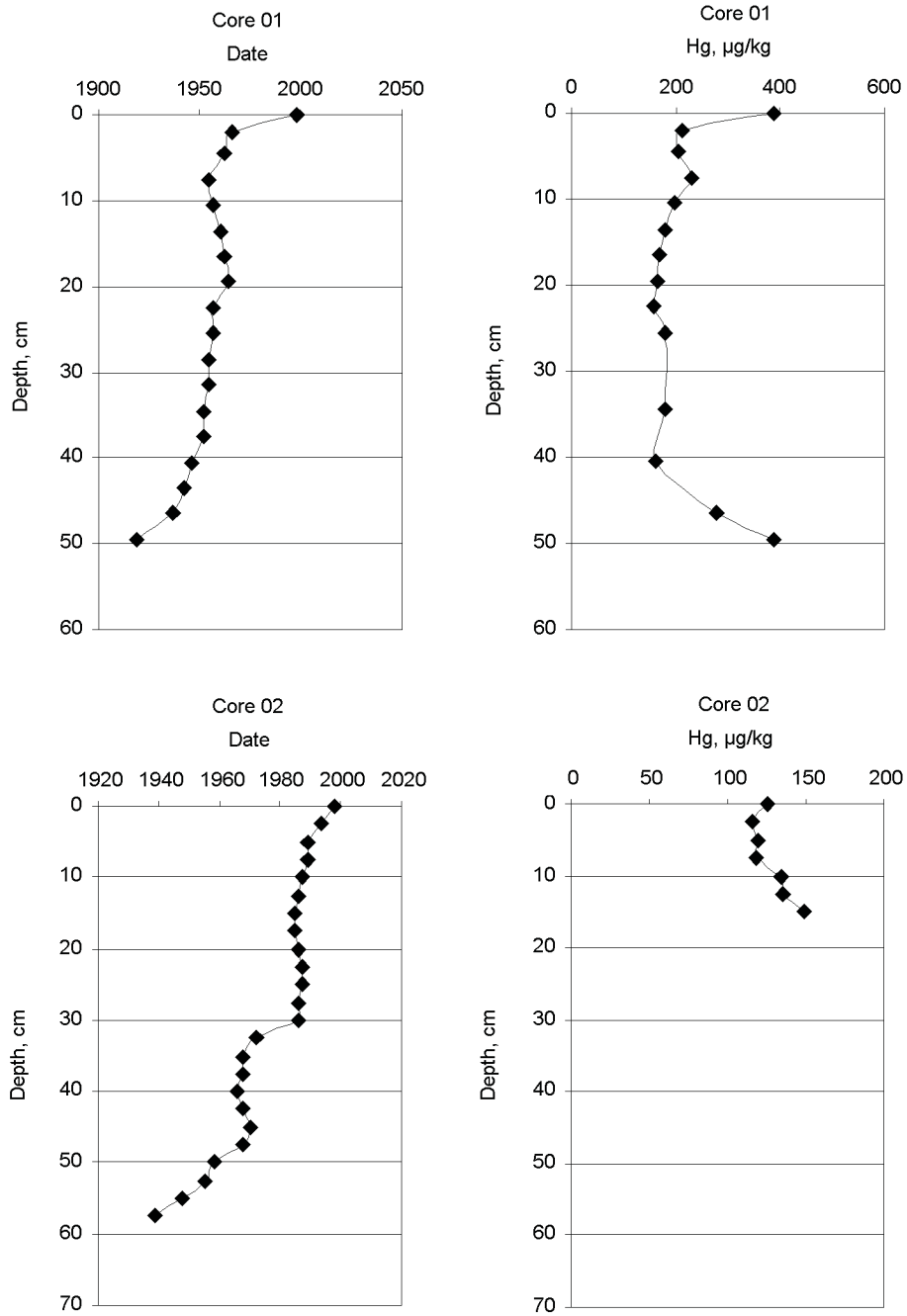
Fig. 2a. Age–depth and Hg concentration–depth relationship for Cores 01 and 02
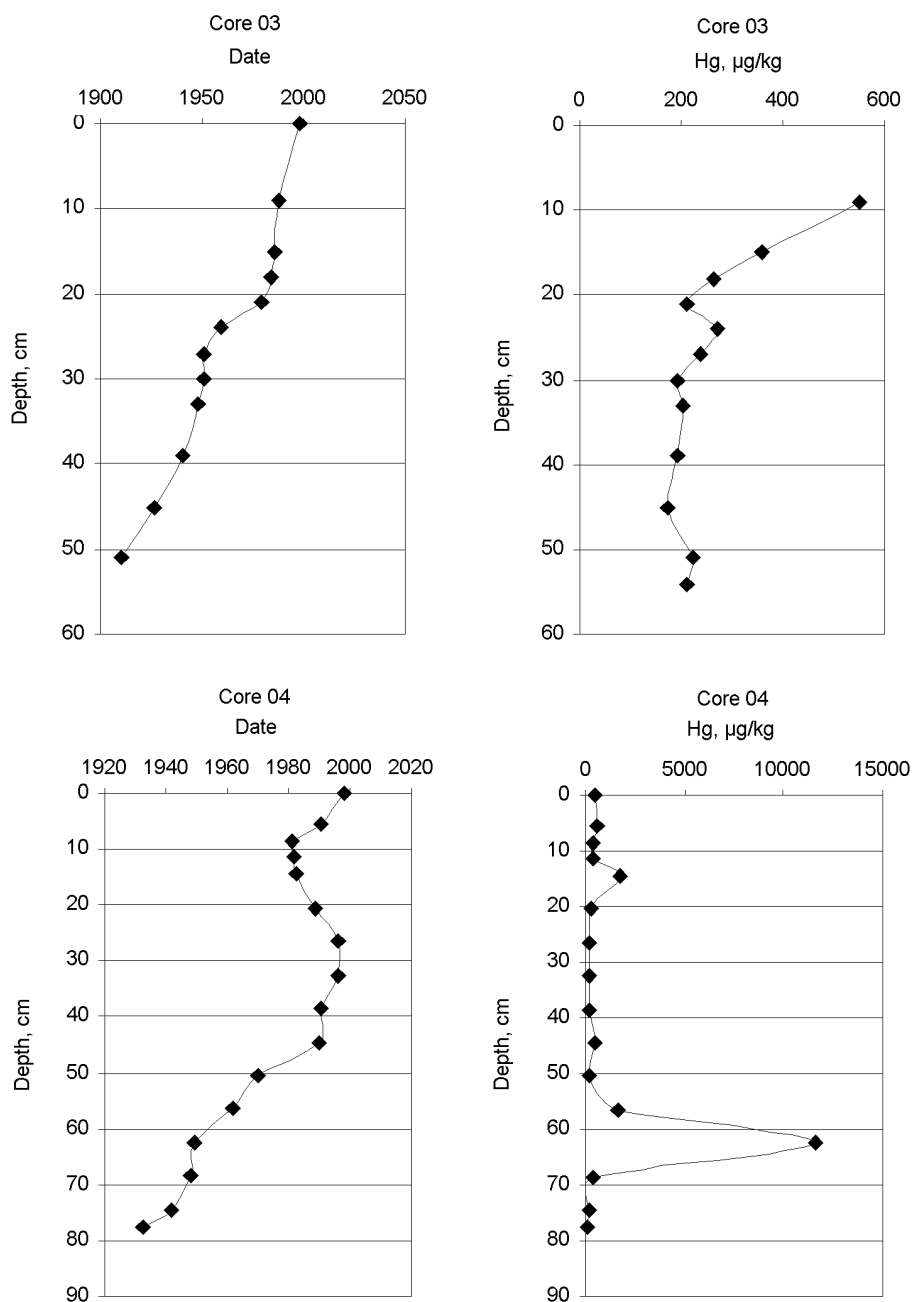
Fig. 2b. Age–depth and Hg concentration–depth relationship for Cores 03 and 04

Table 1. Results obtained for total mercury concentration (in µg·kg^{-1})
in reference material analysis by CV AAS

Reference material	Certified value	Found value	RSD, %	Relative error, %
Estuarine Sediment (NIST SRM 1646[a])[8]	40	41.5 ± 1.7	4.1	
Lake Sediment (BCR CRM 280)[7]	670 ± 19	681 ± 20	2.9	1.6
Buffalo River Sediment (NIST SRM 2704)[6]	1470 ± 70	1501 ± 29	1.9	2.1
Montana Soil (NIST SRM 2710),[5] (mg·kg^{-1})	32.6 ± 1.8	32.8 ± 0.4	1.2	0.6

Total mercury concentration was evaluated in all sediment samples. When comparing Hg levels to the age of the sediments (Figs 2a, b), the following was observed: Core 01 – in the first 4 cm (1998 to 1962) Hg levels varied from 387 to 206 $\mu g \cdot kg^{-1}$. In the rest of the sediment column [1962 (4.5 cm) to 1919 (52.5 cm)] a mean concentration value of 180 μg Hg·kg^{-1} was observed. In the latter 6 cm of the core, Hg level reached values of 386 $\mu g \cdot kg^{-1}$. Core 02 – in this core only 7 sediment samples were evaluated showing a mean concentration value of 128 μg Hg·kg^{-1}, corresponding to the age of 1998 to 1985 (0 to 15 cm deep). Core 04 – during 1998 to 1983 (0 to 14.5 cm deep) Hg values ranged from 474 to 1718 $\mu g \cdot kg^{-1}$. A peak of 11586 μg Hg·kg^{-1} occurred in 1949 (62.5 cm deep). At the end of the core (1932 – 80.5 cm deep), the values found were about 145 μg Hg·kg^{-1}. Core 03 – in the first 5 cm of the core (1998 to 1993) a high value of 165 mg Hg·kg^{-1} was found. From 1993 to 1910 (5 to 54 cm deep), the Hg concentration values decreased until reaching a mean value of 211 μg Hg·kg^{-1}.

The average Hg concentrations in the cores, excluding the points with concentrations higher than 1 mg·kg^{-1}, are shown in Table 2.

Comparing these values with the threshold effects level (TEL) from Canadian Sediment Quality Guidelines for Protection of Aquatic Life,[15] we can observe that only in Core 02 we have Hg mean value lower than the TEL value. For the other Cores (01, 03 and 04), the mean values are between TEL and the probable effects level (PEL) values. In Brazil there is still no legislation concerning sediment quality guidelines and, therefore, the values adopted for the Environmental Technology Company from São Paulo State (CETESB) are those from Environment Canada.[15]

Cores 03 and 04 clearly show an anthropogenic influence in the mercury concentration probably due to the discharges of the chlor-alkali industry, which is located near Core 03.This industry has been operating at the Rio Grande Reservoir since 1948. The influence is also apparent in Cores 01 and 02 located downstream (Fig. 3).

Considering a silting volume of around 7 million cubic meters[7] and the mean value of 0.227 mg Hg·kg^{-1} in the reservoir, it can be estimated that about 6.5 tons of Hg were released during the last 50 years. The limit adopted by the Environmental Technology Company of São Paulo State (CETESB), based on Canadian legislation, is 0.13 mg·kg^{-1}. 95% of the sediment samples from the Rio Grande Reservoir had levels higher than this limit and which could be transferred to the aquatic life environment. It should be emphasized, however, that the superficial contamination at Core 03 was not taken into account in the above estimation.

Table 3 shows the results obtained for multi-elemental analysis in the certified reference materials by INAA. The precision achieved, expressed in terms of relative standard deviation of at least 3 independent determinations, varied from 0.8 to 16.3%. The accuracy, expressed in terms of relative error varied from 0.8 to 14.9%. The agreement with the certified values is good for all reference materials analyzed (Table 3).

Table 4 shows the mean, standard deviation, minimum and maximum concentration values obtained for major and trace elements by INAA in the 4 sediment cores analyzed. In general, we verified a great difference in concentration for the elements analyzed in the four cores according to depth.

Comparing the mean values obtained in the present study with the average continental crust content,[16] we can observe that, in general: (1) highly enriched elements (enrichment factor EF>2): As, Br, Cs, Hf, Lu, Sb, Ta, Th, U, Yb and Zr; (2) slightly enriched elements (1.1<EF<2): Ce, La, Nd, Sc, Sm, Tb and Zn; (3) non-enriched elements (0.9<EF<1.1): Ba; Eu; Rb; and (4) depleted elements (EF<0.9): Co, Cr, Fe, K and Na.

Figure 4 shows the average concentration obtained for the elements As, Cr, Hg and Zn in the 4 cores and TEL and PEL values.[15] For As, with the exception of Core 03, all the values exceed the TEL value (5.9 mg·kg^{-1}). For Cr, the mean value in the four cores exceeded the TEL value (37.3 mg·kg^{-1}). For Zn, only the mean values in Cores 03 and 01 were lower than the TEL value (123 mg·kg^{-1}).

Figure 5 shows the cluster analysis of the chemical data (major and trace elements), where two main groups were identified. The first one comprises elements related to the iron group Cr, Ce, Fe, Na, Sc, Th and Zn. The second group, comprises rare earth elements, Hf, Rb, Ba, Sb, As, K and Cs. These last two elements are related to the grain size variations.

Figure 6 shows the concentration variation of some elements according to depth in the four cores. A decrease in concentration according to depth was observed, for the following elements:

Core 04: As, Br, Cr, Sc and Zn;
Core 03: As, Br, Ce, Cr, Co, Th and Zn;
Core 02: Co, Cr, Cs, Nd, Sm and Th;
Core 01: Br, Co, Ce, Cr, La, Th and Zn

and an increase according to depth for:

Core 03: Cs and Rb;
Core 02: Zn;
Core 01: Hf and Rb.

Table 2. Average Hg concentrations

Core	Hg, mg·kg^{-1}	TEL,* mg·kg^{-1}	PEL,* mg·kg^{-1}
01	0.22 ± 0.08	0.17	0.486
02	0.13 ± 0.01		
03	0.26 ± 0.10		
04	0.30 ± 0.15		

* See the text.

Table 3. Results obtained (in µg·kg⁻¹) in reference materials analyzed by INAA

Element	Soil 7 (IAEA)[11]				Buffalo River Sediment (NIST SRM 2704)[6]				BEN-Basalt-IWG-GIT[12]			
	Certified value	Found value	RSD, %	RE, %	Certified value	Found value	RSD, %	RE, %	Certified value	Found value	RSD, %	RE, %
As	13.4 ± 0.84	13.6 ± 0.8	5.9	−1.5	23.4 ± 0.8	22.6 ± 0.7	3.1	3.4	1.8 ± 0.3	1.95 ± 0.04	2.1	−8.3
Ba	159	173 ± 13	7.5		414 ± 12	439 ± 23	5.2	−6.0	1025 ± 30	1142 ± 126	11.0	−11.4
Br	7	7.8 ± 0.3	4.3		7	5.43 ± 0.2	3.7					
Ce	61 ± 7	58.3 ± 0.7	1.1	4.4	72	59.0 ± 0.9	1.5		152 ± 4	140 ± 6	4.3	7.9
Co	8.9 ± 0.9	9.1 ± 0.6	6.6	−1.7	14.0 ± 0.6	12.6 ± 0.2	1.6	10.0	60 ± 2	53 ± 3	5.7	11.7
Cr	60 ± 13	65.5 ± 1.6	2.4	−9.1	135 ± 5	131 ± 3	2.3	3.0	360 ± 12	341 ± 18	5.3	5.3
Cs	5.4 ± 0.7	4.7 ± 0.4	8.5	13.0	6	5.2 ± 0.3	5.8		0.8 ± 0.1	0.71 ± 0.06	8.5	11.3
Eu	1.0 ± 0.2	1.0 ± 0.1	6.6	3.5	1.3	1.29 ± 0.07	5.4		3.6 ± 0.18	3.1 ± 0.4	12.9	13.9
Fe (%)	2.57	2.48 ± 0.02	0.8		4.11 ± 0.10	4.0 ± 0.1	2.5	2.7	5.24 ± 0.08	5.28 ± 0.04	0.8	−0.8
K (%)	1.21	1.35 ± 0.22	16.3		2.00 ± 0.04				1.15 ± 0.02	1.20 ± 0.06	5.0	−4.3
La	28 ± 1	26.5 ± 0.4	1.6	5.4	29	30.4 ± 0.6	2.0		82 ± 1.5	79 ± 3	3.8	3.7
Lu	0.3	0.33 ± 0.02	6.5		0.6	0.53 ± 0.05	9.4		0.24 ± 0.03	0.21 ± 0.02	9.5	12.5
Na (%)	0.24	0.26 ± 0.03	11.5		0.547 ± 0.014	5368 ± 435	8.1	1.9	2.36 ± 0.04	2.40 ± 0.05	2.1	−1.7
Nd	30 ± 6	25.0 ± 1.3	5.0	10.0					67 ± 1.5	58 ± 9	15.5	13.4
Rb	51 ± 4.5	49 ± 6	12.6	3.0	100	98 ± 8	8.2		47 ± 2	40 ± 4	10.0	14.9
Sb	1.7 ± 0.2	1.6 ± 0.1	6.1	4.1	3.8 ± 0.2							
Sc	8.3 ± 0.1	8.0 ± 0.1	1.8	3.3	12.0	11.2 ± 0.5	4.5		22 ± 1.5	21.4 ± 0.7	3.3	2.7
Se	0.4				1.1 ± 0.1							
Sm	5.1 ± 0.3	4.9 ± 0.4	8.2	3.9	6.7	6.1 ± 0.1	1.6		12.2 ± 0.3	11.8 ± 0.5	4.2	3.3
Tb	0.6 ± 0.2	0.63 ± 0.04	5.7	−4.2					1.3 ± 0.1	1.2 ± 0.1	8.3	7.7
Th	8.2 ± 1.1	7.5 ± 0.3	4.3	8.0	9.2	8.6 ± 0.2	2.3		10.4 ± 0.7	9.5 ± 0.6	6.3	8.7
U	2.6 ± 0.5	2.7 ± 0.2	5.7	−2.6	3.1 ± 0.1	3.2 ± 0.3	9.4	−2.2	2.4 ± 0.18	2.6 ± 0.2	7.7	−8.3
Yb	2.4 ± 0.4	2.1 ± 0.1	6.7	12.5	2.8	2.9 ± 0.1	3.4		1.8 ± 0.2	1.7 ± 0.2	11.8	5.6
Zn	104 ± 6	110 ± 8	7.3	−5.5	438 ± 12	433 ± 14	3.2	1.1	120 ± 13	127 ± 11	8.7	−5.8

RSD: Relative standard deviation.
RE: Relative error.

457

Table 4. Mean, standard deviation, minimum and maximum concentration for the elements analyzed by INAA (in mg·kg⁻¹) and Hg (in µg·kg⁻¹)(CV AAS), for the 4 sediment cores analyzed, and comparison with continental crust values[16]

Core		As	Ba	Br	Ce	Co	Cr	Cs	Eu	Fe, %	Hf	K, (%	La	Lu	Na	Nd	Rb	Sb	Sc	Se	Sm	Ta	Tb	Th	U	Yb	Zn	Zr
C-04	mean	9.6	516	5.8	125	9.2	88	5.7	1.28	6.24	10.8	1.68	40.7	0.82	1402	42	82	0.69	22.4	1.8	8.1	2.9	1.0	25.2	7.8	5.0	199	355
	sd	3.0	77	2.8	17	1.2	16	2.0	0.37	2.14	6.8	0.26	9.2	0.34	294	11	12	0.24	3.0	0.6	2.0	0.5	0.3	3.1	1.2	2.0	82	197
	min	2.1	333	3.0	87	7.8	56	3.6	0.96	1.55	3.0	0.96	26.9	0.38	708	24	48	0.31	16.2	1.1	2.9	2.2	0.4	18.6	5.0	2.3	56	121
	max	12.7	685	16.2	156	12.7	120	11.5	2.94	8.69	26.4	2.09	60.2	1.59	1999	58	108	1.38	26.9	3.6	12.5	4.1	1.7	28.8	9.6	8.9	384	848
C-03	mean	5.3	642	4.5	74	6.6	71	12.7	1.23	2.28	11.6	1.84	44.5	0.70	1050	40	98	0.53	18.8	n.d.	6.7	3.5	1.0	14.5	7.0	4.2	102	291
	sd	1.6	82	1.7	11	0.7	14	1.6	0.09	0.86	2.1	0.27	3.2	0.08	104	6	13	0.27	0.8	n.d.	0.5	0.5	0.2	1.9	0.9	0.4	42	44
	min	2.9	489	2.4	66	5.8	60	7.5	1.09	1.68	7.2	1.40	41.0	0.50	839	27	63	0.11	17.3	n.d.	5.9	2.4	0.7	12.0	4.9	3.1	65	231
	max	9.6	805	9.8	111	8.5	124	14.7	1.50	5.25	13.9	2.20	52.0	0.80	1195	50	110	1.10	20.0	n.d.	7.6	4.1	1.4	21.3	9.2	4.6	252	405
C-02	mean	7.8	930	3.6	115	18.4	97	18.7	1.78	3.09	12.6	n.d.	50.3	0.94	1002	56	108	0.70	21.9	2.1	9.3	3.2	1.2	22.0	9.3	4.8	149	697
	sd	1.3	138	0.6	22	3.8	7	1.0	0.29	0.77	1.3	n.d.	5.3	0.26	92	8	9	0.02	0.9	0.5	1.4	0.8	0.1	1.4	0.9	0.5	16	444
	min	6.2	790	1.3	76	12.3	84	16.5	1.26	2.06	10.5	n.d.	42.9	0.70	887	40	100	0.69	20.1	1.7	6.6	2.4	1.1	19.1	7.2	4.0	131	383
	max	9.7	1125	3.2	135	23.3	104	19.7	2.04	4.20	14.1	n.d.	57.0	1.50	1154	64	128	0.75	22.8	3.2	10.6	4.7	1.4	23.4	9.8	5.3	173	1394
C-01	mean	8.3	636	6.9	96	8.7	77	19.2	1.46	1.86	15.1	1.63	52.6	0.90	994	46	100	0.70	18.7	3.5	10.7	3.1	1.2	18.2	7.7	5.3	92	451
	sd	1.8	93	2.8	19	1.9	9	3.9	0.34	0.38	4.7	0.56	8.3	0.21	140	6	13	0.10	1.1	1.1	5.4	0.4	0.3	2.1	0.8	1.1	13	128
	min	6.6	493	4.3	72	6.1	64	13.8	1.10	1.33	8.4	0.96	41.1	0.55	795	35	78	0.53	16.6	1.1	5.5	2.4	0.8	13.8	6.3	3.3	70	268
	max	14.4	845	12.4	136	12.1	93	25.6	2.12	2.64	20.9	2.29	69.6	1.21	1241	56	124	0.89	20.1	5.1	28.6	3.8	1.7	21.4	9.3	7.0	119	624
Continental crust		1.7	584	1.0	60	24	126	3.4	1.3	4.32	4.9	2.14	30	0.35	2.36	27	78	0.3	16	0.12	5.3	1.1	0.65	8.5	1.7	2.0	65	203
												(%)			(%)													

n.d.: Not determined.

More recent contamination
(80's and 90's), showing high
Hg levels, indicating two
different events of discharge
and contamination reaching
the point of water supply
system

Older contamination (50's),
presenting high Hg values at
Point 04 (Core 04), indicating
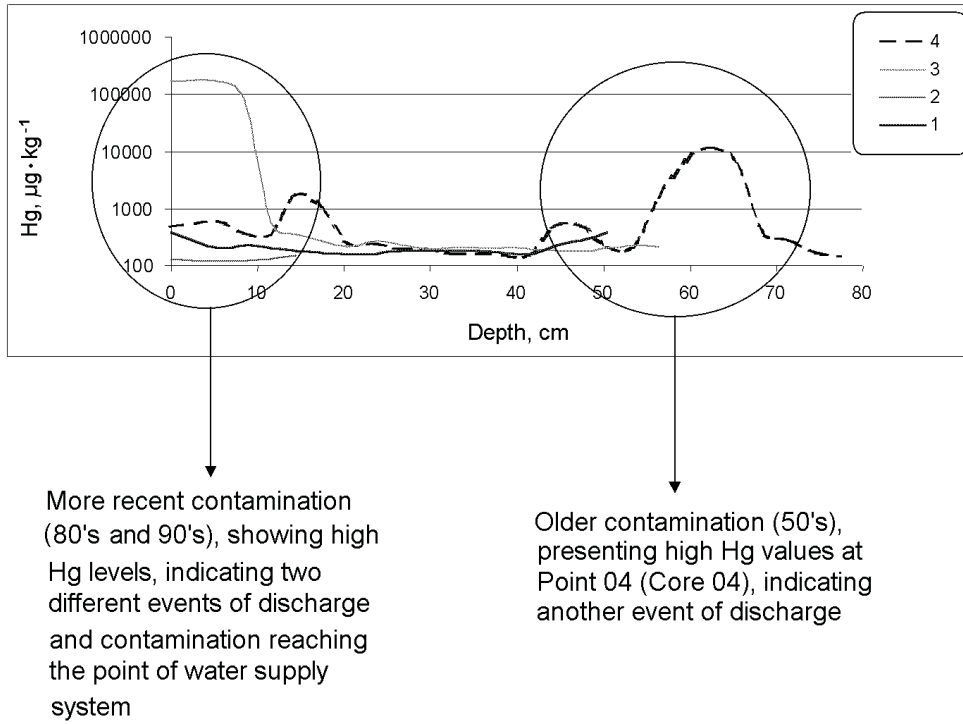another event of discharge

Fig. 3. Hg distribution in the points analyzed according to depth
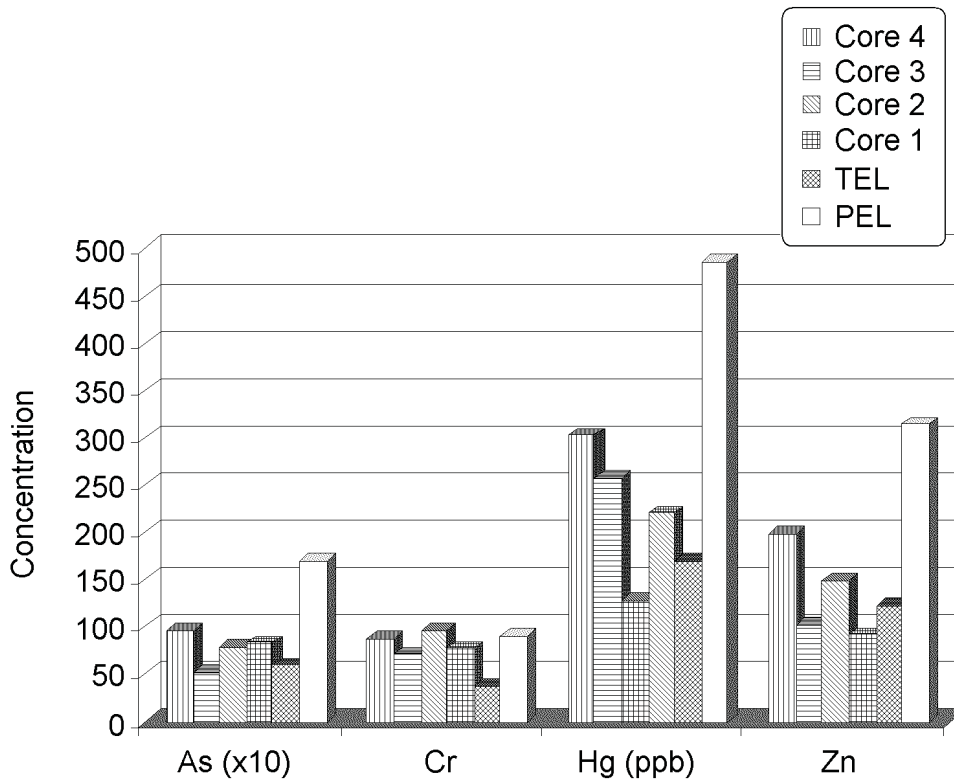
Fig. 4. Average concentration for As, Cr, Hg and Zn in the cores and TEL and PEL values[15]

Tree diagram for 25 variables
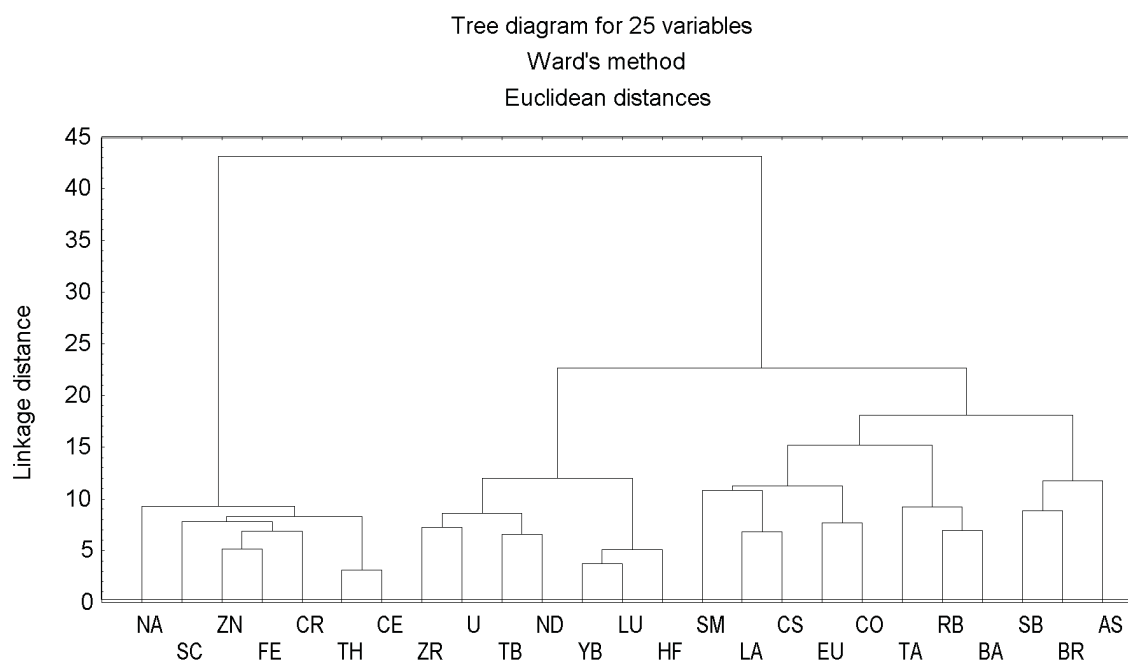Ward's method
Euclidean distances

Fig. 5. Cluster analysis for the chemical data in the sediment samples

Table 5. Factorial analysis for chemical data obtained by the VARIMAX method

Element	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
As	0.01	−0.07	−0.05	0.03	**0.67**
Ba	−0.21	0.08	0.31	**−0.82**	0.03
Br	−0.05	−0.20	0.28	**0.84**	0.17
Ce	**0.80**	0.20	0.39	0.23	0.14
Co	0.37	0.00	**0.71**	−0.34	0.23
Cr	**0.72**	−0.29	0.43	0.05	0.27
Cs	**−0.72**	0.01	0.49	−0.25	0.25
Eu	0.02	0.00	**0.88**	0.02	0.01
Fe	**0.93**	−0.21	−0.18	0.14	0.08
Hf	−0.37	**0.86**	−0.08	−0.18	−0.13
La	−0.47	0.32	**0.71**	0.18	−0.01
Lu	0.04	**0.92**	0.01	−0.15	−0.03
Na	**0.76**	0.16	−0.24	0.00	−0.22
Nd	−0.01	0.48	**0.73**	−0.09	−0.18
Rb	−0.44	0.17	0.05	**−0.69**	−0.14
Sb	0.28	−0.09	0.30	0.30	0.29
Sc	**0.74**	−0.16	−0.03	−0.15	0.16
Sm	−0.08	0.46	0.20	0.02	0.35
Ta	−0.47	0.04	−0.03	−0.23	**−0.62**
Tb	−0.20	**0.66**	0.53	0.07	−0.14
Th	**0.90**	0.11	0.18	0.16	0.17
U	0.26	**0.61**	0.38	−0.39	−0.25
Yb	0.00	**0.97**	−0.04	−0.01	−0.08
Zn	**0.84**	−0.17	0.02	0.14	0.01
Zr	−0.03	**0.63**	0.34	−0.42	0.14

Concentration x depth - Core 04

Concentration x depth - Core 04

Concentration x depth - Core 03

Concentration x depth - Core 03

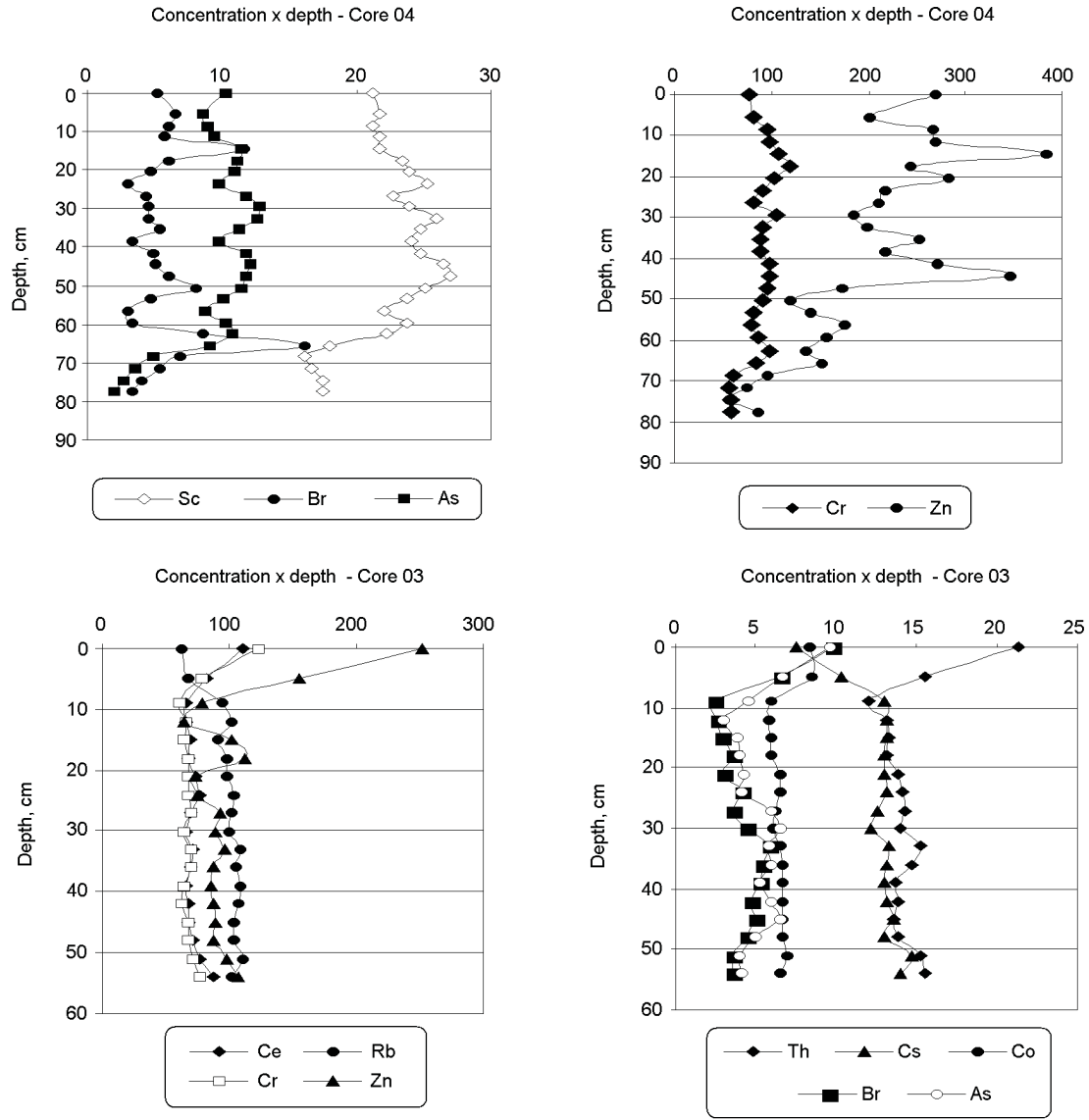*Fig. 6.* Concentration variation with depth in the cores 01, 02, 03 and 04, for some elements

Concentration x depth - Core 02

Concentration x depth - Core 02

Concentration x depth - Core 01

Concentration x depth - Core 01
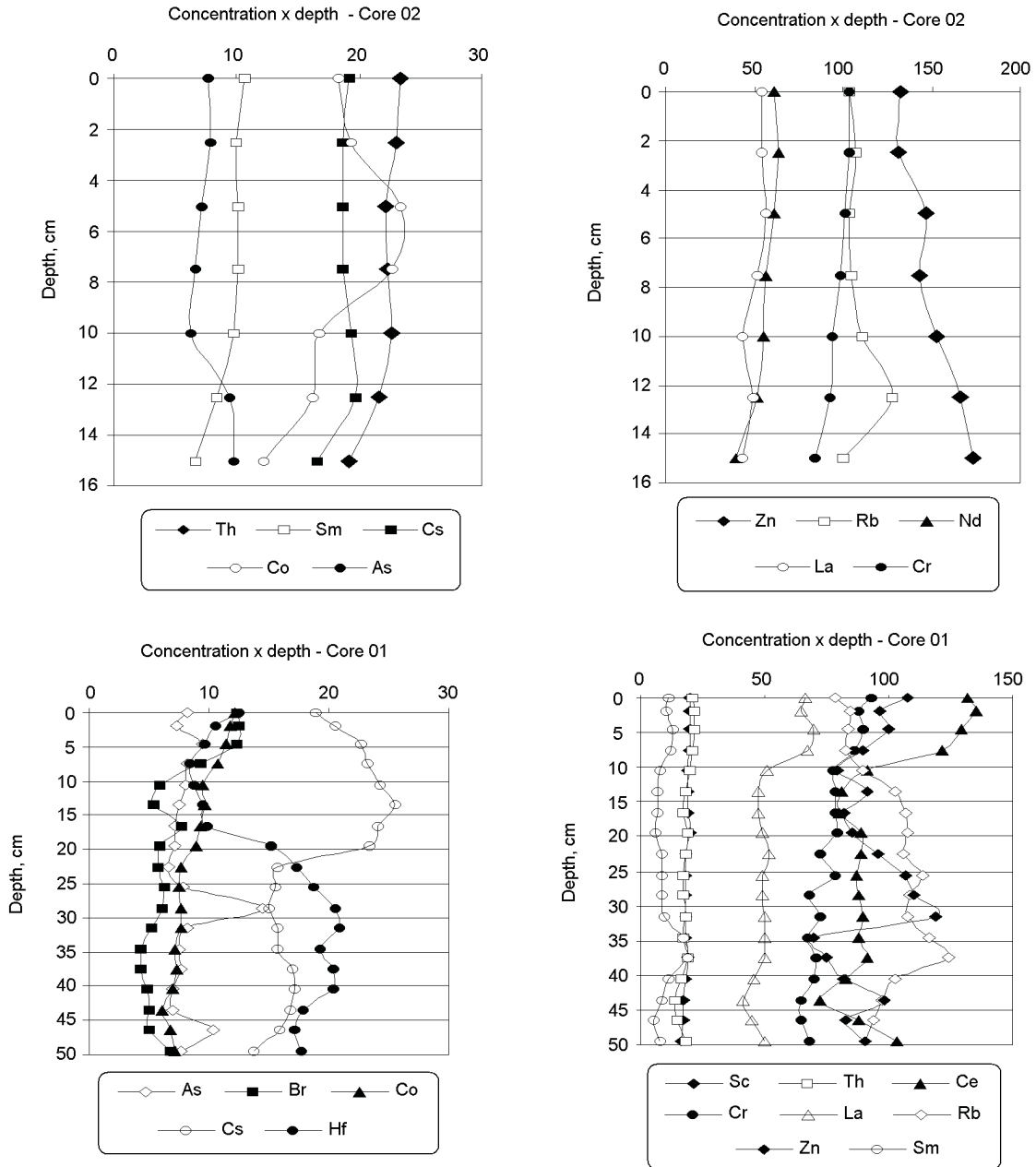
Fig. 6. Concentration variation with depth in the cores 01, 02, 03 and 04, for some elements

In order to investigate the association among the elements in sediments, *R*-mode factor analysis was performed with the chemical data obtained for the four cores (Table 5). By the Varimax method, five factors were extracted. Results can be interpreted as follows:

F1: (29.83% of the total variance) – load >0.70: points to the association of Ce, Cr, Cs, Fe, Na, Sc, Th and Zn;

F2: (50.99% of the total variance) has high loading on Hf, Lu, Tb, U, Yb and Zr;

F3: (63.36% of the total variance) has high loading on Co, Eu, La and Nd;

F4: (71.87% of the total variance): Ba, Br and Rb;

F5: (76.52% of the total variance): As and Ta

Conclusions

The sedimentation rates observed, mainly at Cores 04 and 03, showed that the reservoir is affected by surrounding urban expansion, which is the main source of silting in rivers or reservoirs. The evolution of the sediment deposit is usually related to the historic evolution of land use. These rates show the tolerance of the erosive process in a basin and are characteristic of geological substratum, geomorphology, types of soils and land use. Furthermore, these rates can be taken as reliable environment geoindicators to measure the effectiveness of preventive and corrective measures adopted in the hydrological basins to mitigate soil degradation.

Concerning the contamination, it can be concluded that the levels of Hg in the reservoir are much higher than expected, showing a strong anthropogenic contribution. This contamination varied with depth, the first discharge being observed in the beginning of the 50's and the more severe during the 80's and 90's. As for the elemental composition, the following elements, As, Cr and Zn, presented several results above TEL. As a general trend the elemental concentration decreases with depth, indicating recent contamination. Sampling location of Core 01 deserves more investigation since it is close to the distribution point of the water supply system.

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