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Assessment of metal and trace element concentrations in the Cananéia estuary, Brazil, by neutron activation and atomic absorption techniques

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Twenty six bottom sediment samples were collected from the Cananéia estuary in summer and winter of 2005. Multielemental analysis was carried out by instrumental neutron activation analysis. Total mercury was determined by cold vapor atomic absorption. As, Cr, Hg and Zn concentrations were compared to the Canadian oriented values (TEL and PEL). Sample points 4 and 9 presented higher concentration for most elements and As and Cr exceeded the TEL values. Organic matter (>10%) associated with siltic and clay sediments was observed. Climatic conditions, hydrodynamic and biogeochemical processes promote differences in seasonal concentrations of elements at some points, which contribute to special distributions.

Introduction

The protected environmental area of Cananéia-Iguape estuarine-lagoon complex is composed of five water bodies and four islands[1] and received the UNESCO recognition of Natural Patrimony of Humanity in 1999. However, the Ribeira River Valley located in the North, suffered intense mining and refining activities up to 1996.

Mining and processing ceased operations in 1996 but the population still faces environmental contamination from Pb and As.[2] The presence of enormous mangroves contributes to an important input of organic matter with humic substance representation.

Sediments were collected from 13 points including two internal water bodies (the "Mar de Cananéia" and "Mar de Cubatão") and the Trapandé bay connected to the open sea. Tidal influences decreases from the Trapandé bay to the Mar the Cananéia and Mar the Cubatão, considering only the southern part of the system. The transport of particulate matter along the estuary and the resuspention processes are influenced by the tide movements contributing to the differences in the surface sediment composition other than those established by local inputs and biogeochemical processes.

This study discusses the distribution of some metals and other trace elements, the content of organic matter, P content (inorganic, organic and total) and granulometric fraction in the Cananéia sediments.

Experimental

Sampling and sample preparation

Twenty six sediment samples were collected at 13 points (Fig. 1) using a steel van Veen sampler in two campaigns: summer and winter of 2005, on board of the *R/V Albacora* of the Oceanographic Institute (USP). Sampling was carried out in the "Mar de Cananéia" (Stations 1 to 6), "Mar de Cubatão" (Stations 10 to 13) and Trapandé bay (Stations 7 to 9). The samples were dried at 50 °C in a ventilated oven, passed through a 2 mm sieve and then homogenized. The total fraction (<2 mm) was analyzed.

Instrumental neutron activation analysis (INAA)

Details of the methodology is described by LARIZZATTI et al.[3] Quality control was performed by analyzing the certified reference materials Buffalo River Sediment (NIST SRM 2704), Soil 7 (IAEA) and BEN (Basalt – IWG-GIT). The results agreed with the certified values presenting relative errors and relative standard deviations lower than 10%.

Cold vapor atomic absorption spectrometry (CV AAS)

Details of the methodology is described by FÁVARO et al.[4] Quality control was performed by analyzing the certified reference materials Buffalo River Sediment (NIST SRM 2704), Estuarine Sediment (NIST SRM 1646a) and Marine Sediment (IAEA 433). The results agreed with certified values presenting relative errors and relative standard deviations lower than 5%.

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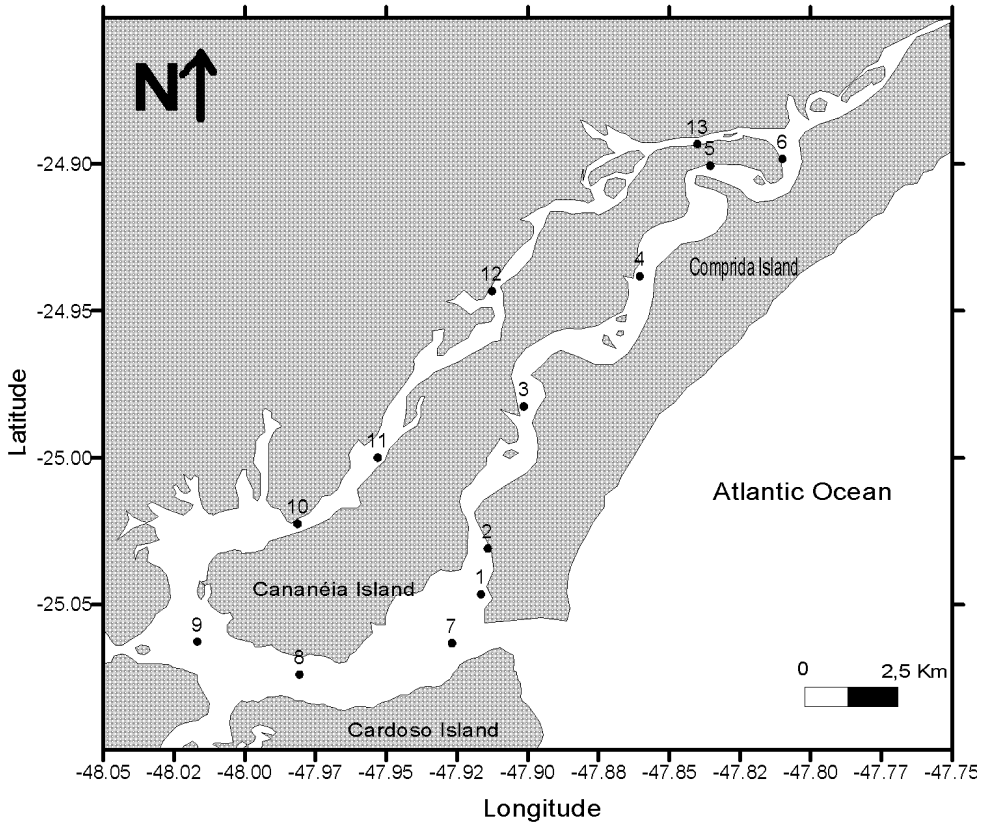

Fig. 1. Sampling point locations in the southern Cananéia-Iguape estuarine-lagoon complex

Granulometric fraction determination

The granulometric analysis was carried out according to SUGUIO.[5]

Organic matter (OM) determination

Organic matter determination was carried out according to BYERS' methodology.[6]

Phosphorus determination (inorganic, organic and total)

Organic phosphorus (P) determination was performed according to ASPILAS' procedure.[7]

Results and discussion

Table 1 presents the concentration values ($mg \cdot kg^{-1}$) for the elements determined by INAA and Table 2, for organic matter content (OM%), granulometric fractions, phosphorus concentrations (inorganic, organic and total) ($\mu mol \cdot g^{-1}$) and total Hg concentrations ($\mu g \cdot kg^{-1}$), for sediment samples, at each sampled point, in the two seasons. Stations 4, 9 and 11, showed a significant pelitic fraction (silt and clay) from 20.0 to 86.7%, corresponding to the high OM content as well as to the high organic P concentrations (2.5 to 9.4 $\mu mol \cdot g^{-1}$). Station 4 contains silt and clay content higher than 80% for the two sampling periods and a high inorganic P fraction (>20%). Naturally, OM and pelitic sediment fraction in the sediment participate in metal retention processes in the benthic compartment contributing to determine the risk areas in metal trace contamination. There was an important presence of inorganic P concentration at Station 4 due to a considerable terrestrial input and hydrodynamic contributions that influence the deposition process in the internal part of the system, in the northern direction, before the channel narrows near point 5. At point 9, the high organic P fraction means that at the internal part of the Trapandé bay, there is an OM input from the "Mar the Cubatão" and "Ararapira Chanel". A second group is formed by Stations 2, 3, 5 and 8, that show an important OM content, facilitating retention of metals and agrees with the results obtained for most elements (Table 1).

Station 2 presented higher seasonal variations in relation to the other Stations (3, 5 and 8) maybe in function of this point being close to anthropic activities of the Cananéia city. A third group is formed by the other Stations (1, 6, 7, 10, 12 and 13) with concentrations much lower than the average values due to the internal location and other parts, in function of more intense tidal influences.

Table 1. Results obtained for the elements determined by INAA (in $mg \cdot kg^{-1}$), mean, standard deviation, minimum, maximum and NASC values

Station	As		Ba		Br		Ce		Co		Cr		Cs		Eu		Fe, %		Hf		La		Lu	
	W	S	W	S	W	S	W	S	W	S	W	S	W	S	W	S	W	S	W	S	W	S	W	S
1	1.2	3.0	109	141	14	23	5	12	0.5	1.3	3	6	0.3	0.7	0.09	0.17	0.2	0.4	2.0	4.0	2.6	5.6	n.d.	0.1
2	6.1	2.2	210	n.d.	50	22	34	15	3.7	1.7	24	11	1.9	0.9	0.49	0.23	1.2	0.5	6.0	2.7	16.6	7.9	0.3	0.2
3	4.3	6.4	262	n.d.	37	42	27	39	3.4	4.1	19	31	1.8	1.8	0.43	0.53	1.2	1.3	6.6	6.7	14.0	17.2	0.3	n.d.
4	11.3	12.1	602	n.d.	74	91	95	91	12.2	11.7	76	71	6.3	6.3	1.37	1.40	4.7	4.5	3.7	4.5	42.8	41.0	0.5	n.d.
5	5.3	3.9	289	164	17	17	32	30	3.8	2.8	22	16	1.8	1.5	0.44	0.35	1.3	1.0	4.8	4.7	14.5	13.7	0.1	0.1
6	1.0	1.0	196	162	6	7	7	9	0.8	0.7	5	5	0.3	0.4	0.10	0.13	0.2	0.2	2.2	2.9	3.0	4.3	n.d.	0.1
7	2.1	2.5	152	216	12	21	7	17	1.0	1.8	3	9	0.4	0.9	0.13	0.29	0.3	0.5	1.2	2.6	3.7	7.8	0.0	0.1
8	5.6	5.3	232	339	35	42	31	32	4.2	4.3	19	24	1.5	1.7	0.53	0.46	1.2	1.3	3.4	3.5	13.5	14.1	0.1	0.1
9	15.4	15.8	149	n.d.	109	74	67	79	8.8	10.1	57	60	4.3	5.2	1.09	1.20	3.0	3.4	5.0	5.4	30.7	36.3	n.d.	0.4
10	2.6	2.6	n.d.	43	23	22	16	22	1.6	1.7	15	12	0.7	0.8	0.20	0.22	0.5	0.5	9.7	5.7	6.5	10.1	n.d.	0.3
11	6.3	9.4	133	95	60	42	40	40	4.1	4.6	31	41	2.7	2.6	0.58	0.62	1.6	1.5	4.7	4.6	18.1	19.6	0.2	0.2
12	2.0	2.8	171	167	17	26	16	37	2.9	2.7	21	29	0.9	1.3	0.24	0.40	0.9	0.9	16.1	11.9	7.2	16.7	0.4	0.4
13	1.7	1.3	188	167	11	14	15	11	1.1	1.2	4	12	0.6	0.5	0.15	0.16	0.3	0.3	2.7	5.3	7.6	5.0	n.d.	n.d.
Mean:	5.0	5.3	224	166	36	34	30	33	3.7	3.8	23	25	1.8	1.9	0.45	0.47	1.3	1.3	5.2	5.0	13.9	15.3	0.2	0.2
Std:	4.2	4.5	130	82	30	24	26	26	3.4	3.4	22	21	1.8	1.8	0.39	0.40	1.3	1.3	4.0	2.4	11.6	11.5	0.2	0.1
Min:	1.0	1.0	109	43	6	7	5	9	0.5	0.7	3	5	0.3	0.4	0.09	0.13	0.2	0.2	1.2	2.6	2.6	4.3	0.0	0.1
Max:	15.4	15.8	602	339	109	91	95	91	12.2	11.7	76	71	6.3	6.3	1.37	1.40	4.7	4.5	16.1	11.9	42.8	41.0	0.5	0.4
TEL.:	7.24										52.3													
PEL.:	41.6										160													

Station	Na, %		Nd		Rb		Sb		Sc		Sm		Ta		Tb		Th		U		Yb		Zn	
	W	S	W	S	W	S	W	S	W	S	W	S	W	S	W	S	W	S	W	S	W	S	W	S
1	0.2	0.4	1.0	5.3	16	23	0.09	0.15	0.4	1.3	0.4	0.9	0.1	0.2	0.03	0.08	0.9	1.7	0.4	0.5	0.2	0.4	1	12
2	0.7	0.4	10.8	7.5	42	22	0.24	0.14	4.0	1.8	2.6	1.3	0.5	0.3	0.30	0.13	3.7	2.4	2.2	0.5	1.0	0.5	25	14
3	0.7	0.7	17.0	15.6	44	n.d.	0.24	0.30	3.7	4.3	2.4	1.9	0.5	0.5	0.23	0.25	3.9	6.3	1.8	1.2	1.2	1.2	25	29
4	1.8	1.1	30.7	30.8	76	86	0.87	n.d.	14.8	14.1	7.6	6.5	1.0	0.9	1.03	1.02	13.1	12.0	3.7	3.3	2.1	1.8	94	96
5	0.6	0.4	15.1	12.8	27	24	0.48	0.32	4.1	3.0	2.5	2.2	0.4	0.4	0.32	0.16	8.1	3.9	1.6	1.0	0.8	0.7	28	29
6	0.2	0.2	2.7	3.3	11	14	0.07	0.10	0.6	0.7	0.5	0.7	0.2	0.2	0.09	0.08	0.9	1.3	0.5	0.5	0.3	0.3	3	8
7	0.4	0.4	5.0	7.9	21	22	0.10	0.14	0.6	1.5	0.6	1.2	0.1	0.2	0.04	0.28	0.9	2.0	0.3	0.5	0.3	0.5	7	13
8	0.8	0.9	16.2	17.2	40	46	0.34	0.29	3.5	3.9	2.0	2.2	0.3	0.4	0.27	0.23	3.3	3.7	1.3	1.3	0.9	0.9	33	35
9	1.9	1.6	35.1	24.8	75	77	0.47	0.61	9.7	11.2	5.0	6.2	0.7	0.6	0.75	0.90	8.6	10.4	3.2	2.9	1.7	2.0	70	62
10	0.4	0.4	6.8	8.3	13	10	0.21	0.26	1.6	1.8	1.2	1.6	0.4	0.3	0.34	0.21	2.3	3.4	2.0	1.9	1.5	1.6	19	14
11	1.1	0.8	20.0	20.1	40	22	0.38	0.40	5.5	5.4	3.0	3.2	0.5	0.4	0.26	0.78	5.3	5.5	2.1	4.8	1.1	0.9	32	29
12	0.3	0.5	8.3	14.4	34	17	0.25	0.24	2.8	1.7	1.6	3.1	0.9	0.6	0.09	0.73	5.3	6.3	2.8	2.5	2.0	1.8	16	19
13	0.3	0.3	8.3	5.6	28	8	0.11	0.15	0.8	1.0	1.2	0.6	0.2	0.4	0.10	0.16	3.2	1.5	0.6	0.8	0.4	0.5	11	1
Mean:	0.7	0.6	13.6	13.4	36	31	0.30	0.24	4.0	4.0	2.4	2.4	0.5	0.4	0.30	0.38	4.6	4.7	1.7	1.7	1.0	1.0	28	28
Std:	0.6	0.4	10.3	8.2	21	25	0.22	0.16	4.1	4.1	2.0	1.9	0.3	0.2	0.29	0.34	3.6	3.4	1.1	1.3	0.6	0.6	27	26
Min:	0.2	0.2	1.0	3.3	11	8	0.07	0.00	0.4	0.7	0.4	0.6	0.1	0.2	0.03	0.08	0.9	1.3	0.3	0.5	0.2	0.3	1	1
Max:	1.9	1.6	35.1	30.8	76	86	0.87	0.61	14.8	14.1	7.6	6.5	1.0	0.9	1.03	1.02	13.1	12.0	3.7	4.8	2.1	2.0	94	96
TEL.:																							124	
PEL.:																							271	

n.d.: Not determined.
TEL: Threshold effect level.
PEL: Probable effect level.[9]
w: Winter.
s: Summer.

Table 2. Values of OM, silt, clay and sand, P (in μmol·g^{-1}) and total Hg (in μg·kg^{-1}) in winter and summer in 2005

Point	OM,* %		Silt+clay, %		Sand,* %		$CaCO_3$*		P (inorg)		P (org)		P (total)		Hg (total)	
	W	S	W	S	W	S	W	S	W	S	W	S	W	S	W	S
1	3.1	1.0	0.7	0.4	99.3	99.6	2.1	2.7	1.0	1.3	0.0	0.9	1.0	2.2	23.3	20.9
2	3.0	1.3	0.7	1.7	99.3	98.3	2.0	1.9	2.2	1.2	2.4	0.9	4.6	2.1	31.6	21.1
3	2.2	8.3	4.1	3.1	95.9	96.9	3.0	2.9	3.7	3.0	0.9	2.3	4.5	5.3	33.2	30.6
4	11.8	15.4	85.5	86.7	14.5	13.3	7.1	9.8	26.1	26.4	6.4	6.7	32.5	33.1	84.3	101
5	3.5	3.7	12.6	17.2	87.5	82.8	2.6	2.6	2.9	2.1	1.6	1.3	4.5	3.4	40.7	54.8
6	0.5	0.5	0.0	0.0	100	100	0.0	0.4	1.3	1.3	0.2	0.2	1.5	1.5	31.3	24.6
7	0.7	2.2	3.5	0.0	96.5	100	4.1	1.2	1.5	2.0	0.6	0.8	2.0	2.7	28.3	27.2
8	3.2	3.1	18.8	8.4	81.2	91.7	3.4	4.7	3.7	3.2	2.9	2.6	6.6	5.8	32.4	40.0
9	11.7	10.5	49.5	63.9	50.5	36.1	8.7	9.2	7.8	7.5	9.4	7.6	17.2	15.0	53.3	52.5
10	2.1	2.7	0.6	0.1	99.4	99.9	1.6	1.7	1.4	1.3	1.6	1.3	3.0	2.6	31.4	26.1
11	11.2	10.1	20.4	39.6	79.6	60.2	2.9	3.8	4.2	2.8	4.1	2.5	8.3	5.3	48.7	56.3
12	3.1	5.8	11.5	1.3	88.5	98.7	1.9	4.0	1.2	1.7	2.2	1.5	3.4	3.2	30.8	40.7
13	0.7	0.6	0.1	0.1	99.9	99.9	1.0	0.9	2.6	1.8	1.5	0.6	4.1	2.4	23.2	32.6
Mean:	4.4	5.0	16.0	17.1	84.0	82.9	3.1	3.5	4.6	4.3	2.6	2.2	7.2	6.5	37.9	43.9
Std:	4.2	4.7	25.0	28.5	25.0	28.5	2.4	2.9	6.7	6.9	2.7	2.3	8.7	8.7	16.5	20.3
Min:	0.5	0.5	0.0	0.0	14.5	13.3	0.0	0.4	1.0	1.2	0.0	0.2	1.0	1.5	23.2	21.1
Max:	11.8	15.4	85.5	86.7	100	100	8.7	9.8	26.1	26.4	9.4	7.6	32.5	33.1	84.3	101

* Data from PERRETTI.[8]
w: Winter.
s: Summer.

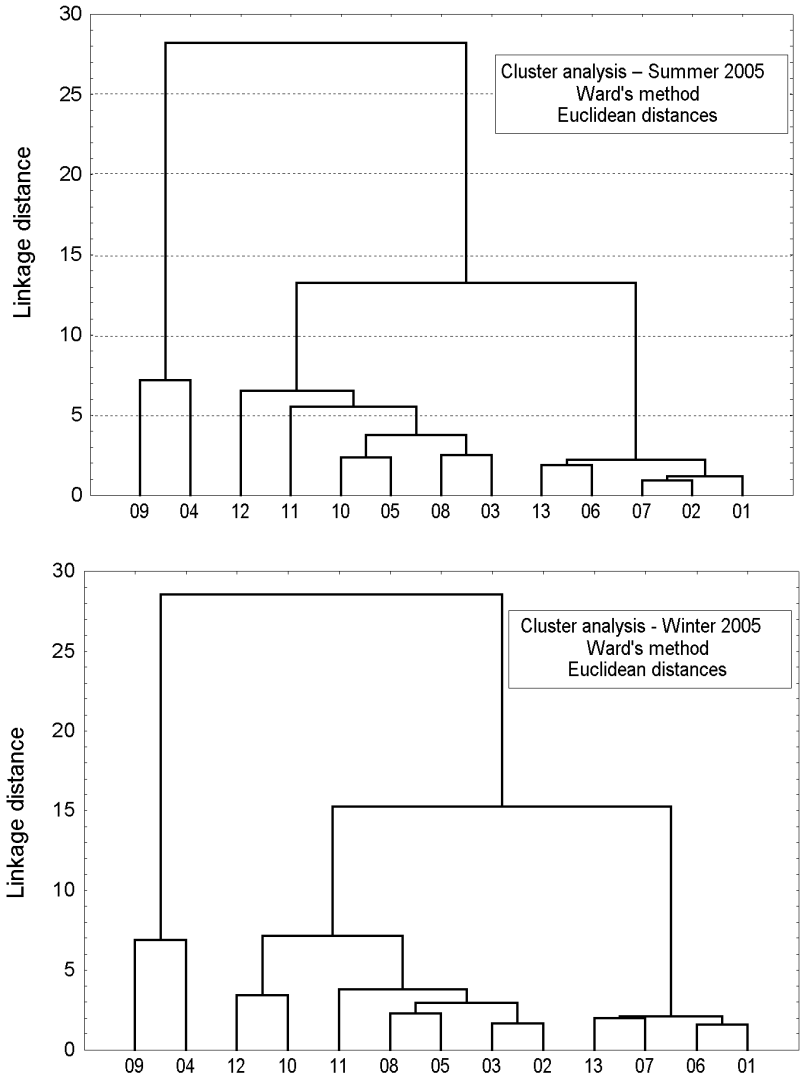

Fig. 2. Cluster analysis considering all chemical data for the sediment samples: summer and winter (2005)

Cluster analysis (Fig. 2) showed that Stations 4 and 9 formed a separate group, in both figures. Another representative group is formed by two important sub-groups: (1, 6, 7 and 13) and (2, 3, 5, 8, 10, 11, 12) Stations in the winter sampling. Two summer sampling sub-groups were formed: (i) points 3, 5, 8, 10, 11, 12 and (ii) points 1, 2, 6, 7 and 13. Cluster analysis for the winter sampling reflected better the observations made above, with regards to the group sample separation (1, 2 and 3). The high correlation between OM content, pelitic fraction and trace metals in this system under low anthropic impact was established. The volume of water is more important in the summer and the transport of particulate matter increases in this period. In the winter, the volume of water is lower and resuspention processes are possible in function of the storms and climatic changes associated to the winds and the hydrodynamics. The internal position of the points and the different seawater influences along the system, the OM production period, sinking transport and biogeochemical processes affect the final distribution on the surface sediments in this system.

Chemical contamination is classified by the limited values of the Canadian Council of Ministers of the Environment (CCME)[9] as As, heavy metals and organic compounds. Brazil still has no legislation for sediment quality guidelines for these contaminants. The Environmental Technology Company from São Paulo State (CETESB) responsible for environmental fiscalization for São Paulo State uses the Environmental Canada criteria.[9] The values for As, Cr, Hg and Zn were compared to the oriented values (TEL and PEL values) (Table 1). In general, most samples presented values for these elements lower than TEL values. Samples collected at points 4 and 9 presented higher concentrations for most elements and As and Cr exceeded TEL values (7.24 and 52.3 $mg \cdot kg^{-1}$, respectively).

Conclusions

Cananéia sediments are composed mainly by sand fraction. At some points, the pelitic fraction is important and retains metal and trace elements. Associated with the siltic and clay there was OM, with values >10%, with important content in total and organic P particularly at three points (4, 9 and 11). These points showed the most important values of pelitic sediments with the highest values in the summer period, due to: (i) its inner position to the estuary mouth, (ii) the high volume of water and suspended matter. The metals showed values positively associated with the organic matter contents and to the sediment pelitic fraction. The climatic conditions of this region, the sedimentation processes, hydrodynamic and biogeochemical processes can promote differences in the seasonal concentrations of elements at some points.

This study confirmed a high correlation between OM content, pelitic fraction and metals in the sediments as found in other estuaries in other parts of the world. The present low anthropic impact contributed to verify the distinct influence of the hydrodynamics along the estuary and the seasonal differences in this southern region. The OM and the pelitic fraction of the sediments marked a slight difference in the spatial distributions of the trace element concentrations and identified the main retention points in the southern part of the system.

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