Toxic metal assessment in estuarine sediments from Cananeia, São Paulo, Brazil, determined by Atomic Absorption Spectrometry

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Resumo
Esse estudo apresenta resultados de distribuição dos metais tóxicos (Cd, Hg, Pb) em sedimentos coletados no complexo estuarino-lagunar de Cananéia-Iguape, verão e inverno/2005. Espectrometria de absorção atômica foi empregada para a determinação desses metais. Esses valores foram comparados aos valores orientadores (TEL e PEL) do Ministério do Meio Ambiente do Canadá. As amostras de sedimentos apresentaram valores bem abaixo dos valores orientadores TEL, mostrando que não há influência antrópica para esses metais.
Palavras-chave: sedimentos, metais tóxicos, AAS, Cananéia

Abstract
This study report results of toxic metals (Cd, Hg, Pb) distribution in bottom sediment samples collected in the Cananeia-Iguape estuarine-lagoon complex, in the summer and winter of 2005. Atomic Absorption Spectrometry was employed for total Hg, Cd and Pb determinations. These values were compared to the oriented values (TEL and PEL) from the Canadian Council of Minister of the Environment. Samples presented values far below the TEL values which showed no anthropogenic influence for these metals.
Keywords: sediment, toxic metals, AAS, Cananéia

1. Introduction

The Cananeia-Iguape estuarine-lagoon complex, located in the southern coastal region of Sao Paulo State, is part of the Biosphere Natural Reserve (UNESCO) due to its environmental-cultural importance. It is a region of overall low pollution impact in the southern part of the hydrological system (Cananeia estuary) and is an Environmental Protected Area (Bernardes, 2001). Some authors have studied the region to evaluate the levels of heavy metals. Saito et al (2001) and Mahiques *et al.* (2009) determined environmental changes in the lagoon system of Cananeia-Iguape.

The present study assessed the results for toxic metals Cd, Hg and Pb in the sediment samples from Cananéia estuary and compared the values with TEL and PEL oriented values from Canadian Council of Minister of the Environment (CCME).

2. Material and Methods

2.1 *Sampling and sample preparation*

By using a steel van Veen sampler, sediment samples were collected in two campaigns: summer and winter of 2005, on board the R/V Albacora of the Oceanographic Institute (USP). Twenty six sediment samples were collected in the south part of Cananeia-Iguape estuarine-lagoon complex at 13 points. Sampling was carried out in the “Mar de Cananéia” (stations 1 to 6 – **group 01**), Trapandé Bay (stations 7 to 9 – **group 02**) and “Mar de Cubatão” (stations

10 to 13 – **group 03**). Samples were previously dried at 50°C in a ventilated oven, passed through a 2 mm sieve and then homogenized before analysis. The total fraction (< 2 mm) was analyzed.

2.2 Total Hg determination (CV AAS)

Total mercury determinations were performed using CV AAS (Cold vapor atomic absorption spectrometry), FIMS (Perkin Elmer). The analytical procedure was that of Amorim et al (2007).

2.3 Cd and Pb determinations (GF AAS)

The sample digestion was performed by microwave-assisted method following the SW-846-3051 - USEPA (USEPA, 1994). The samples were analyzed in a Perkin Elmer Atomic Absorption Spectrometer AANALYST 800. Quality control was carried out by the results obtained for certified reference material WQB 3 (Lake Ontario Sediment Blended for Trace Elements - Environmental Canada) and San Joaquin soil (2709 NIST).

3. Results and Discussion

In relation to the methodology validation, the results for total Hg in Marine Sediment (IAEA 433), Estuarine Sediment (NIST SRM 1646[a]) and Buffalo River Sediment (NIST SRM 8704) reference materials, showed a relative standard deviation ranging from 1.3 to 2.3% and relative error from 1.4 to 3.6% showing good precision and accuracy. Cd and Pb determinations by GF AAS of the San Joaquin Soil and WQB-3 reference materials presented good agreement with the information values of both materials. All results were in agreement with the acceptance criteria adopted (uncertainty levels lower than 25%).

The results of Pb, Cd and Hg analysis in sediments samples collected in Cananeia estuary in the summer and winter of 2005 are presented in Table 1. The TEL values for the elements analyzed are: Cd (0.7 mg kg^{-1}), Pb (30.2 mg kg^{-1}), Hg (130 µg kg^{-1}). The PEL values are: Cd (4.21 mg kg^{-1}), Pb (112 mg kg^{-1}), Hg (700 µg kg^{-1}). According to the results obtained for the analyzed sediment samples (Table 1), Cd, Pb and Hg levels did not exceed TEL and PEL limits.

4. Conclusions

When the Cd, Hg and Pb concentration values in the sediment samples collected in Cananeia in 2005 were compared to TEL and PEL values from Canadian legislation and adopted by CETESB, no samples exceeded these limits, showing no anthropogenic influence for these metals. The trace metal concentration variation between sampling points is related to the granulometric properties and organic matter content which are associated with trace element retention. These trace metal concentrations were more significant than

seasonal variations. The results of this study point to a need for monitoring concentration levels at several points of this system, for example Hg at point 4.

Statistical tests applied to the results showed that in general there were no significant changes in the levels of Cd, Pb and Hg in summer and winter in groups 1, 2 and 3. The Pb results for group **01** indicated a statistically significant difference ($p<0.05$). Furthermore, Cd results showed a low correlation in group **01**, mainly due to the difference between the results obtained for sample 02 in the periods of summer (<LQ) and winter (0.174 mg kg^{-1}).

5. Acknowledgements

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Table 3 –- T-test for Cd in all groups analyzed

T-Test: paired two samples for means	Cd - Group 1		Cd - Group 2		Cd - Group 3	
	Winter	*Summer*	*Winter*	*Summer*	*Winter*	*Summer*
Average	0.018	0.047	0.020	0.026	0.016	0.015
Variance	0.00049	0.00425	0.00036	0.00056	0.00019	0.00013
Observations	6	6	3	3	4	4
Pearson Correlation	0.093		0.989		0.998	
Degrees of Freedom	5		2		3	
T Stat	-1.050		-1.867		1.481	
P (T <= t) one-caudal	0.171		0.101		0.118	
t critical one-caudal	2.015		2.920		2.353	
P (T <= t) two-caudal	0.342		0.203		0.235	
t Critical two-caudal	2.571		4.303		3.182	

6. References

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Table 1 – Concentrations of Cd (mg kg^{-1}), Pb (mg $kg^{-}1$) and Hg (µg $kg^{-}1$) in bottom sediments from Cananeia estuary – summer and winter of 2005.

T-Test: paired two samples for means	Hg - group 1		Hg - group 2		Hg - group 3		Pb - Group 1		Pb - Group 2		Pb - Group 3	
	Winter	*Summer*	*Winter*	*Summer*	*Winter*	*Summer*	*Winter*	*Summer*	*Winter*	*Summer*	*Winter*	*Summer*
Average	40.7	42.2	38.0	39.9	33.5	38.9	8.2	6.4	5.3	6.07	3.68	3.83
Variance	486	992	180	160	116	170	87.5	96.8	28.5	45.6	10.6	3.3
Observations	6	6	3	3	4	4	6	6	3	3	4	4
Pearson Correlation	0.973		0.930		0.833		0.984		0.999		0.843	
Degrees of Freedom	5		2		3		5		2		3	
T Stat	-0.312		-0.666		-1.500		2.501		-0.916		-0.152	
P (T <= t) one-caudal	0.384		0.287		0.115		0.027		0.228		0.445	
t critical one-caudal	2.015		2.920		2.353		2.015		2.920		2.353	
P (T <= t) two-caudal	0.768		0.574		0.231		0.054		0.457		0.889	
t Critical two-caudal	2.571		4.303		3.182		2.571		4.303		3.182	

Table 2 – T-test for Hg and Pb in all groups analyzed.

	CW0501	CW0502	CW0503	CW0504	CW0505	CW0506	CW0507	CW0508	CW0509	CW0510	CW0511	CW0512	CW0513
Cd	N.D.	N.D.	N.D.	0.063	N.D.	N.D.	N.D.	N.D.	0.042	N.D.	0.037	0.011	N.D.
Pb	0.9	5.7	5.3	26.0	10.1	1.2	0.8	3.9	11.2	1.9	8.5	2.7	1.6
Hg	23.3	31.6	33.2	84.3	40.7	31.3	28.3	32.4	53.3	31.4	48.7	30.8	23.2
	CS0501	**CS0502**	**CS0503**	**CS0504**	**CS0505**	**CS0506**	**CS0507**	**CS0508**	**CS0509**	**CS0510**	**CS0511**	**CS0512**	**CS0513**
Cd	0.012	0.174	0.011	0.059	0.015	N.D.	**0.009**	0.016	0.053	**0.009**	0.032	N.D.	N.D.
Pb	N.D.	0.5	3.9	25.5	8.0	N.D.	**0.1**	4.7	13.4	2.3	5.9	4.8	2.3
Hg	**20.9**	21.1	30.6	**101.0**	54.8	24.6	27.2	40.0	52.5	26.1	56.3	40.7	32.6

N.D. – Not detected (lower than Quantification Limits); CS05- samples collected in summer; CW05 – samples collected in winter