ASSESSMENT OF CR, CU, PB, NI AND ZN LEVELS IN SEDIMENT SAMPLES FROM RIO GRANDE RESERVOIR, SÃO PAULO, BRAZIL

1. INTRODUCTION

Bottom sediments are a sink as well as a source of contaminants in an aquatic environment (IAEA, 2003).

The Rio Grande Reservoir, in the São Paulo Metropolitan Area, which supplies water for four counties, has been seriously affected by chaotic urban expansion, occupation and improper use of the surrounding areas. To monitor the reservoir´s sediment contamination levels the concentration of Cr, Cu, Pb, Ni and Zn in theses samples were determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP OES) analytical technique.

2. EXPERIMENTAL

Sampling and sample preparation

Cores and bottom sediment samples were collected, by using a piston corer and Van Veen samplers, respectively, during the dry season (May to August, 2004). The Van Veen sampler collected 3 samples 50 cm from each other in a triangle around the point where the piston corer sample was collected. These 3 samples constituted a composed sample. Each of the four piston corer samples were sliced resulting in 4 samples each: 0-5, 5-10, 10-20 and 20-30 cm deep. Four sampling points were defined by using a GPS and are located at the mouth of Rio Grande and Ribeirão Pires Rivers (discharge of contaminants - point 4), in the middle of the reservoir (points of depuration – point 3 and 2) and near the catchment point of the water supply (point 1) (Figure 1). The samples were firstly homogenized, dried at 40 C in a ventilated oven until constant weight and sifted in 0.062 mm sieves.

Methodology for Cr, Cu, Pb, Ni and Zn determination in sediments

Samples were digested according to the SW-846-3051 method (USEPA), using microwave digestion system CEM MDS 2100. Determination of recoverable Cr, Cu, Ni, Pb and Zn levels in the samples was made by ICP OES analytical technique by "Spectroflame Modula S" from Spectro Analytical Instruments GmbH. Emission lines were: 220.351 nm for Pb, 324.745nm for Cu, 267.716 nm for Cr, 231.604 nm for Ni and 213.856nm for Zn.

10403

XIII INTERNATIONAL CONFERENCE ON HEAVY METALS IN THE ENVIRONMENT

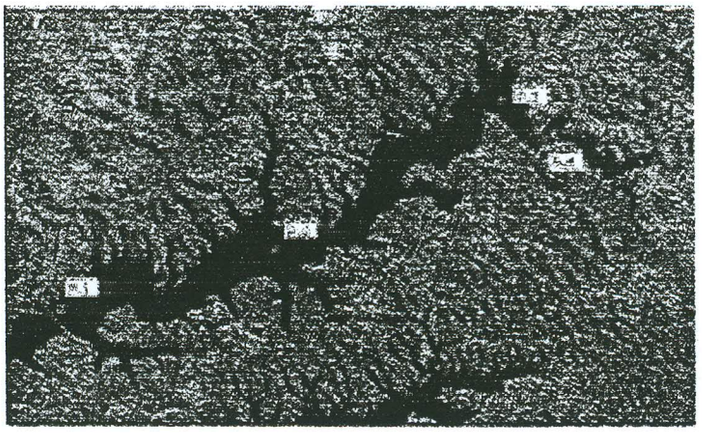

Figure 1- Sampling points.

3. RESULTS AND DISCUSSION

Methodology validation was carried out by means of the reference materials analyses NIST SRM 2782 (Industrial Sludge) and WQB-3 (Environmental Canada – Lake Ontario Blended Sediment). Results are presented in Table 1.The chemical yield ranged from 79% for Cr to 107% for Ni and the results showed good precision and accuracy.

Table 1 – Results (mg kg^{-1}) for metals determination by ICP OES in the reference materials

	WQB-3					SRM NIST 2782				
	Elements					Elements				
	Cr	Ni	Cu	Zn	Pb	Cr	Ni	Cu	Zn	Pb
Values found	83 ± 5	54 ± 4	73 ± 3	1440 ± 123	246 ± 14	63 ± 4	103 ± 7	2290 ± 103	1240 ± 106	482 ± 27
Recovery (%)	79	100	91	102	102	96	107	94	106	87
Stand. Dev (%)	2.3	0.5	2.2	0.8	0.7	2.3	0.5	1.0	1.1	1.1
Certified Value	105*	53.8*	80.8*	1410*	242*	66 ± 9	96 ± 5	2435 ± 47	1167 ± 57	554 ± 36
Certified Recorevy (%)	---	---	---	---	---	61	62	94	93	97

* Because reproducibility is strongly dependent on the digestion procedure, proportion of acids and extraction conditions, uncertainty intervals are not provided

Table 2 shows the results for samples collected at Rio Grande reservoir, for the metals Cr, Cu, Ni, Pb and Zn, at points 1 to 4. From point 4 to 1 mean concentration levels and coefficient variation (%) for the bottom sediment (composed samples) were: Cr, 60.7 mg kg^{-1} (28%); Cu, 1131 mg kg^{-1} (114%); Ni, 22.5 mg kg^{-1} (22%); Pb, 74.7 mg kg^{-1} (12.7%) and Zn, 218.5 mg kg^{-1} (69%). When we compared these values with ISQG and PEL from Environmental Canada (Canadian Sediment Quality Guidelines) we observed that Cr, Ni, Zn and Pb levels are below the PEL values (90.0, 35.9, 315 and 91.3 mg kg^{-1}, respectively). The mean value for Cu at points 1 and 2 (2740 and 1597 mg kg^{-1}) far exceeded the PEL value (197.0 mg kg^{-1}). This is probably due to the use of algaecide near the catchment point of the water supply.

As for the results obtained for these elements in the core samples, there was no significant concentration variation according to depth for the elements Cr, Zn and Pb.

Table 2 – Results for the elements Cr, Cu, Pb, Ni and Zn in sediment samples (mg kg^{-1})

Point	Sampler	depth (cm)	pH	Humidity(%)	Cr	Ni	Cu	Zn	Pb
P1	Piston core	0 - 5	6.81	77.5	44.6 ± 2.2	19.1 ± 1.0	4505 ± 225	98.4 ± 4.9	74.1± 3.7
		5 - 10	6.84	77.3	44.0 ± 2.2	19.9 ± 1.0	4654 ± 233	99.0 ± 5.0	68.4 ± 3.4
		10 - 20	6.75	73.3	46.4 ± 2.3	20.6 ± 1.0	6039 ± 302	102 ± 5.1	77.7 ± 3.9
		20 - 30	6.74	57.7	47.5 ± 2.4	20.6 ± 1.0	3198 ± 160	89.2 ± 4.5	68.4 ± 3.4
		mean	6.79	71.5	45.6 ± 2.3	20.0 ± 1.0	4599 ± 230	97.1 ± 4.9	72.2 ± 3.6
	Van Veen	—	6.79	69.5	49.2 ± 2.5	18.4 ± 0.9	2740 ± 137	88.16 ± 4.4	64.5 ± 3.2
P2	Piston core	0 - 5	6.72	83.7	49.0 ± 2.5	22.0 ± 1.1	2264 ± 113	133 ± 6.6	79.0 ± 4.0
		5 - 10	6.80	80.9	52.1 ± 2.6	23.4 ± 1.2	2095 ± 105	126 ± 6.3	77.3 ± 3.9
		10 - 20	6.69	73.8	55.3 ± 2.8	24.3 ± 1.2	2443 ± 122	127 ± 6.3	75.7 ± 3.8
		20 - 30	6.47	66.1	60.6 ± 3.0	36.5 ± 1.8	3494 ± 175	133 ± 6.6	82.8 ± 4.1
		mean	6.67	76.1	54.3 ± 2.7	26.5 ± 1.3	2574 ± 129	130 ± 6.5	78.7 ± 3.9
	Van Veen	—	6.58	81.7	59.5 ± 3.0	24.0 ± 1.2	1597 ± 79.9	122 ± 6.1	75.7 ± 3.8
P3	Piston core	0-5	6.75	78.9	52.1 ± 2.6	19.3 ± 1.0	148 ± 7.4	241 ± 12.0	69.4 ± 3.5
		5 - 10	6.73	76.0	44.1 ± 2.2	16.5 ± 0.8	104 ± 5.2	205 ± 10.2	59.8 ± 3.0
		10 - 20	6.49	80.8	45.0 ± 2.3	16.6 ± 0.8	107 ± 5.3	222 ± 11.1	61.7 ± 3.1
		20 - 30	6.49	61.1	43.2 ± 2.2	19.5 ± 1.0	56.9 ± 2.8	138 ± 6.9	60.7 ± 3.0
		mean	6.62	74.2	46.1 ± 2.3	18.0 ± 0.9	104 ± 5.2	201 ± 10.1	62.9 ± 3.1
	Van Veen	—	6.80	73.0	49.1 ± 2.5	16.6 ± 0.9	118 ± 5.9	240 ± 12.0	71.4 ± 3.6
P4	Piston core	0 - 5	6.80	82.5	60.1 ± 3.0	23.8 ± 1.2	96.3 ± 4.8	374 ± 18.7	75.2 ± 3.8
		5 - 10	6.80	80.8	77.2 ± 3.9	121 ± 6.0	49.3 ± 2.5	364 ± 18.2	92.4 ± 4.6
		10 - 20	6.70	77.9	64.3 ± 3.2	25.2 ± 1.3	53.0 ± 2.7	347 ± 17.4	79.7 ± 4.0
		20 - 30	6.70	72.1	68.3 ± 3.4	28.7 ± 1.4	57.5 ± 2.9	326 ± 16.3	87.7 ± 4.4
		mean	6.75	78.3	67.5 ± 3.4	49.6 ± 2.5	64.0 ± 3.2	353 ± 17.7	83.8 ± 4.2
	Van Veen	—	6.60	74.0	65.0 ± 3.3	28.9 ± 1.4	70.4 ± 3.5	424 ± 21.2	87.1 ± 4.4
Quality Guidelines				ISQG	37.3	18.0	35.7	123	35.0
				PEL	90.0	35.9	197	315	91.3

ISQG: Interim sediment quality guideline.
PEL: Probable effect level.
Quality Guidelines: ENVIRONMENTAL CANADA. Canadian Sediment Quality Guidelines for the Protection of Aquatic Life.

Ni was an exception at point 4, 5-10 cm deep, and showed a concentration level of 120.8 mg kg^{-1} (four times higher). Cu showed a strong concentration variation according to depth. In conclusion our study showed that pollutant levels for these elements decreased from point 4 to point 1, but are still above the acceptable levels (ISQG) for all elements analyzed, except Zn.

4. REFERENCES

Canadian Environmental Quality Guidelines - Summary Tables.- http://www.ec.gc.ca/ceqg-rcqe/English/ceqg/sediment/default.cfm

USEPA – United States Environmental Protection Agency – **Behavior of Metal in Soil** – EPA, Oklahoma, 1992.

International Atomic Energy Agency. **Collection and preparation of bottom sediment samples for analysis of radionuclides and trace elements**, IAEA-TEC-DOC 1360, July, 2003.

Authors Contact

BOSTELMANN, ELEINE[1]; FÁVARO, DÉBORAH I.T.[2]; FERREIRA, FRANCISCO J.[1]; BEVILACQUA, JOSÉ E.[3]

[1]LABORATÓRIO DE QUÍMICA INORGÂNICA E RADIOATIVIDADE - EAAI
CETESB - SÃO PAULO, BRAZIL
E-MAIL: ELEINEB@CETESB.SP.GOV.BR

[2]LABORATÓRIO DE ANÁLISE POR ATIVAÇÃO NEUTRÔNICA - LAN-CRPQ
IPEN/CNEN-SP, SÃO PAULO, BRAZIL
E-MAIL: DEFAVARO@CURIANGO.IPEN.BR

[3]DIVISÃO DE QUALIDADE DAS ÁGUAS - EEQ - CETESB - SÃO PAULO, BRAZIL