COMPARISON OF TOTAL Hg RESULTS IN SEDIMENT SAMPLES FROM RIO GRANDE RESERVOIR DETERMINED BY NAA AND CV AAS

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ABSTRACT

The Rio Grande reservoir is located in the Metropolitan area of São Paulo and it is used for recreation purposes and as source water for drinking water production. During the last decades has been detected mercury contamination in the sediments of this reservoir, mainly in the eastern part, near the main affluent of the reservoir, in the Rio Grande da Serra and Ribeirão Pires counties. In the present study bottom sediment samples were collected in four different sites into four sampling campaigns during the period of September 2008 to January 2010. The samples were dried at room temperature, ground and passed through a 2 mm sieve. Total Hg determination in the sediment samples was carried out by two different analytical techniques: neutron activation analysis (NAA) and cold vapor atomic absorption spectrometry (CV AAS). The methodology validation, in terms of precision and accuracy, was performed by reference materials, and presented a recovery of 83 to 108%. The total Hg results obtained by both analytical techniques ranged from 3 to 71 mg kg^{-1} and were considered similar by statistical analysis, even though NAA technique furnishes the total concentration while CV AAS using the 3015 digestion procedure characterizes only the bioavailable Hg. These results confirm that both analytical techniques were suitable to detect the Hg concentration levels in the Rio Grande sediments studied. The Hg levels in the sediment of the Rio Grande reservoir confirm the anthropogenic origin for this element in this ecosystem.

1. INTRODUCTION.

The Rio Grande Reservoir is located in the Metropolitan Region of Sao Paulo (RMSP) and plays a very important socio-economic role supplying both water and leisure for approximately 1.6 million people [1]. Fish consumption from the reservoir is also a common practice.

In 1982, the Rio Grande Reservoir was separated from the already highly polluted Billings Reservoir in an attempt to preserve its water quality. This separation eliminated the entrance of polluted waters from São Paulo city. However, domestic and industrial sewage from the Rio Grande da Serra and Ribeirao Pires counties continued to be thrown directly into the reservoir [1,2].

Initially, the reservoir was a branch of the Billings reservoir. In the early 40s, some of the water from the Rio Tiete and Pinheiros Rivers and their tributaries were diverted to the Billings reservoir in order to increase the flow of the dam and consequently expand the capacity of power generation, for which the reservoir was initially built. This operation increase the production of electricity, also proved useful for flood control and the removal of industrial effluents and sewage generated by the growing city [2].

The water pumped from the Tietê River to the Billings, however, began to have serious environmental consequences. The growth of the city of São Paulo and the lack of sewage collection and treatment led to increased pollution of the Tietê River and its tributaries, which in turn, began to compromise the water quality of Billings reservoir. Furthermore, the large amount of resulting sewage led to a serious increase of blue-green algae. Thus, there was a need for a total interception of the Rio Grande branch. This action took place in 1982 which the construction of the Anchieta dam, to ensure water supply for ABC region, in 1958 [2,3].

Over the last decades, Hg has been detected in the Rio Grande reservoir sediments originating from anthropogenic contributions, mainly in the east, near the Rio Grande da Serra and Ribeirão Pires counties [4-8].

Sediments are environmental compartments with high accumulation potential for natural and anthropogenic materials. Due to this characteristic, sediments act as an excellent register, for seasonal and spatial environmental information. This characteristic differentiates it from a simple quality water evaluation [9]. The finer the sediment, the greater its capacity to retain chemicals due to greater surface area as in the case of clay and silt which are able to interact with ions and diverse molecules.

In the present study, sediment samples from Rio Grande reservoir were collected and analyzed by two different analytical techniques for total Hg quantification, CV AAS and NAA. The CV AAS determines the Hg available after a digestion according to 3051A US EPA procedure while NAA furnishes the total Hg in the samples. The results obtained for the two analytical techniques were compared and discussed.

2. MATERIAL AND METHODS

2.1 Sampling and sample preparation

Four points were chosen at the Rio Grande reservoir, being two in the proximities of Rio Grande da Serra and Ribeirão Pires counties, one in the middle of the reservoir and the fourth near the catchment point of the water supply (Figure 1). The sampling campaign, four, took place from September 2008 to January 2010. These sampling points have already been characterized by Franklin et al [10].

The sediment samples were collected by using a Van Veen sampler and were kept in polyethylene recipients. The samples were homogenized and an aliquot was removed and dried at room temperature. After drying, the samples were ground in a mortar, passed through a 2.00 mm sieve and then homogenized before analysis.
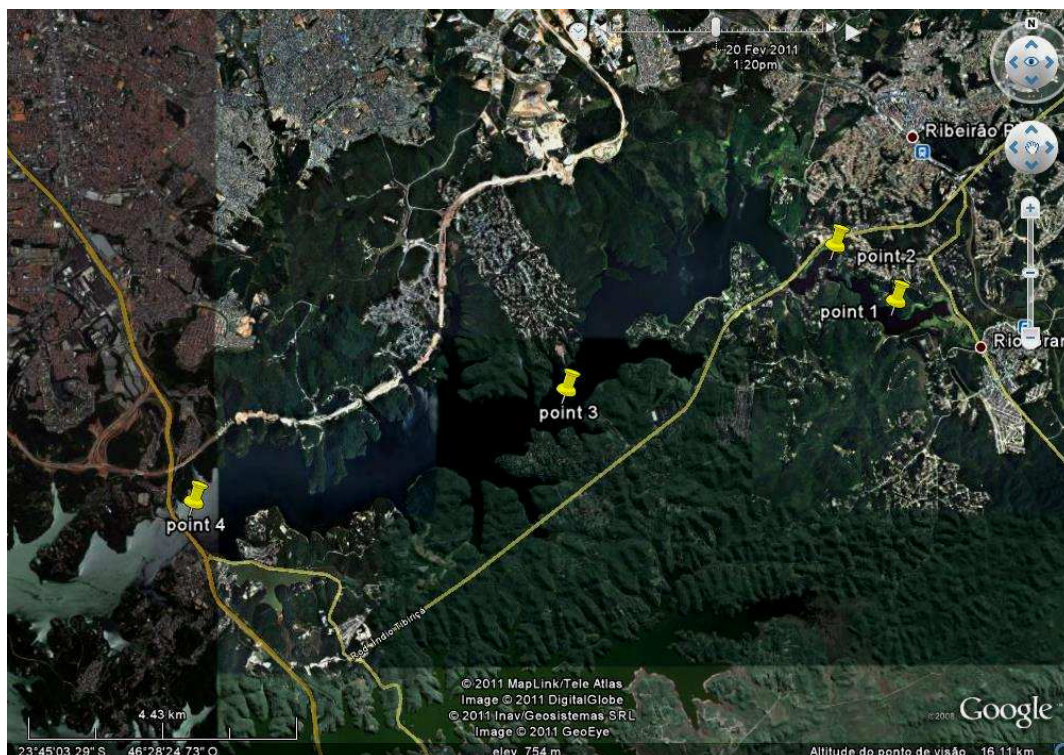
Figure 1 – Sampling point location.

2.2 Total Hg determination by CV AAS

Total Hg determination in the sediment samples was carried out by CV AAS (cold vapor atomic absorption spectrometry). The samples were previously digested in acid media according to 3051A US EPA methodology [11], where only the available metals (not complete digestion) are quantified. About 0.5 g of the dried sediment sample was digested with 10 mL HNO_{3conc} in the experimental conditions recommended by the US EPA methodology. After digestion the sample was transferred to a 50 mL volumetric flask and the volume completed with Milli-Q water. When needed an aliquot of 1.0 mL was diluted to 100 mL volumetric flask. The sediment samples were quantified by measuring total Hg in a FIMS 100 (Flow Mercury System – from Perkin Elmer) by means of Hg^{+2} reduction with $SnCl_2$ and comparison with a calibration curve made with Hg standard from Accustandard and traced to a NIST (National Institute of Standard) standard. A Hg lamp wavelength of 253.7 nm was used. The measurement uncertainty was calculated according to Franklin et al description [12].

2.3 Total Hg determination by NAA

This procedure quantifies total Hg in the sediment samples with a high Hg content because the detection limit is high (DL= 1.0 mg kg^{-1}).

The synthetic Hg standard was prepared by pippeting 100 µL of 10 mg mL^{-1} thioacetamide solution onto small sheets of a Nº 41 Whatman filter paper and after half an hour, 50 µL of a 90.0 mg mL^{-1} Hg standard solution. In these conditions Hg^{+2} remain immobilized on the filter paper due to complex formation with thyoacetamide avoiding the Hg loss by volatilization during irradiation.[13,14]

About 100 mg of the sediment sample and reference materials were weighed in pre-cleaned polyethylene bags. Samples, Hg synthetic standard and reference materials were irradiated for 1 hour under a thermal neutron flux of $5E10^{12}$ n cm^{-2} s^{-1} (2 MW Power) in the IEA-R1 nuclear research reactor at IPEN/CNEN-SP. After a cooling time of 48 hours sample and standards were measured using a CANBERRA HPGe detector detector and associated electronics, with a resolution of 0.88 keV and 1.90 keV for ^{57}Co and ^{60}Co respectively. Samples and standards must be counted under identical geometrical conditions. The uncertainties measurements were calculated for error propagation.

^{197}Hg radioisotope was used for total Hg quantification by measuring the activity of the photo peak 77.3 keV and comparison with the activities in the synthetic Hg standard and reference materials. The validation of methodology according to precision and accuracy was performed by means of reference materials analyzes with certified values for Hg concentration: IAEA 405, trace elements and methylmercury in estuarine sediment; IRMM BCR 145R, Sewage Sludge; NIST SRM 2711, Montana Soil; CRM 049, Sandy Clay Soil and IRMM BCR 580, Trace elements in estuarine sediment.

3. RESULTS AND DISCUSSION

Reference material results (with uncertainty) by using CV AAS and NAA analytical techniques are shown in Table 1.

All the reference materials analyzed by CV AAS presented chemical recoveries varying from 83 to 108%, proving the accuracy of the analytical methodology. The reference material SRM 2711 was not analyzed by CV AAS and IAEA 405 by NAA due to the fact that Hg concentration was in the same level of the detection limit of NAA technique. The relative standard deviation varied from 2.9 to 22.0% and relative errors from 0.74 to 16.7%, proving the precision and accuracy of the NAA technique for total Hg determination. It should be noted that the higher values for RSD were found for the lowest Hg concentration in the reference materials and near the DL of the NAA technique. For the CV AAS technique the relative standard deviation varied from 4.7 to 12.0% and relative errors from 3.7 to 12.8%, proving the precision and accuracy of this technique for total Hg determination.

Table 2 presents the results (with uncertainty and n=2) obtained for the sediment samples collected at the Rio Grande reservoir by CV AAS and NAA analytical techniques in the four sampling points and 4 sampling campaigns.

Table 1. Results of reference material analyses (mg kg⁻¹) by CV AAS and NAA (± uncertainty)

Reference material (n=2)	Certified values	Results by CV AAS	Recovery (%)	Results by NAA	Recovery (%)
IAEA 405	0.81 ± 0.04	0.78 ± 0.08	96	< DL	----
BCR 145	2.01 ± 0.22	1.75 ± 0.21	87	1.68 ± 0.37	84
SRM 2711	6.25 ± 0.19	NA	---	5.2 ± 0.5	83
CRM 050	13.5 ± 0.4	14.6 ± 0.9	108	13.6 ± 0.4	99
BCR 580	132 ± 6	127 ± 6	96	135 ± 5	102
DL		0.01		1.0	

NA – Not analyzed; DL – Detection Limit; n= number of determinations

Table 2. Results (mg kg⁻¹) of the sediment samples by CV AAS and NAA in the four sampling campaigns (± uncertainty and n=2)

	Point 1		Point 2		Point 3		Point 4	
	CVAAS	NAA	CVAAS	NAA	CVAAS	NAA	CVAAS	NAA
Sep/08	45.7 ± 1.0	52.5 ± 2.0	71.3 ± 1.2	68.6 ± 2.4	1.9 ± 0.4	3.0 ± 0.5	NA	NA
Feb/09	68.3 ± 0.9	65.2 ± 2.2	61.5 ± 0.9	59.7 ± 1.9	4.5 ± 0.3	3.6 ± 0.5	1.0 ± 0.1	ND
Jul/09	25.9 ± 1.0	29.7 ± 1.2	68.1 ± 0.9	69.8 ± 2.6	2.2 ± 0.1	2.6 ± 0.4	1.8 ± 0.1	ND
Jan/10	43.4 ± 1.5	38.0 ± 1.5	57.6 ± 0.8	47.8 ± 1.6	3.7 ± 0.3	5.7 ± 0.7	1.5 ± 0.1	ND

NA – Not analyzed; ND – Not detected

The Student´s test was applied to the results obtained for comparison of the two analytical techniques used in order to verify the similarity between them. This method is based on the mean differences obtained individually for each sample and for each one of the analytical techniques[15,16] by using equation 1:

$$t_{n-1} = \frac{\mu_d \sqrt[2]{n}}{s_d}$$

(1)

where;

μ_d – mean sample of the differences
S_d – standard deviation of the differences
n – Number of observations

This test attempts to verify the hypothesis (H_0) that the mean of the results between the two analytical methodologies is zero. The other hypotheses (H_1 and H_2) assume that the

mean differences are greater or less than zero. In this case it has to be assumed the normality of the variables in order that μd has a normal distribution.

Pairing the results obtained by both analytical methods presented in Table 2, we have a total of 12 pairs. These pairs which have a sample mean difference of 0.650 and a standard deviation of differences of 4.372. Dixon test was applied and no outliers were found. Equation 1 resulted in a value of 0.515. The tabulated value for Student's t with 95% confidence level is 2.179. This means that the hypothesis H_0 for equality of means cannot be excluded [15,16].

In general, the results obtained for both analytical techniques were considered statistically similar for Hg quantification in the sediment samples analyzed even taking into account that Hg determination by CV AAS used a 3051A (digestion procedure from US EPA where only the available metals are quantified. In the NAA technique Hg concentration corresponds to the total Hg in the sample as this technique does not required the digestion step. NAA is a non-destructive analytical technique. The results obtained for point 4 were not possible to compare for both analytical techniques.

The results obtained were quite similar being the greater difference (20%) found for point 2 (Jan 2010), 57.6 mg kg^{-1} for CV AAS and 47.8 mg kg^{-1} for NAA. Regarding point 3 samples, the absolute value difference were lower, but at these concentration interval (2 to 5 mg kg^{-1}) for Hg determination by NAA the uncertainty measurements are high and near the quantification limit, and justifying the difference between the results.

As can be observed for points 1 and 2 the results for both analytical methodologies were quite similar being the greater difference (20%) found for point 2 (Jan 2010), 57.6 mg kg^{-1} for CV AAS and 47.8 mg kg^{-1} for NAA. Regarding point 3 samples, the absolute value difference were lower, but at these concentration interval (2 to 5 mg kg^{-1}) for Hg determination by NAA the uncertainty measurements are high and near the quantification limit, and justifying the difference between the results. At sampling point 4 there were no Hg concentration values by NAA since they were at the same level of detection limits (LD) of the technique. Two technical aspects should be pointed out for these findings. The first is related to the Hg concentration at points 1 and 2, much lower than points 3 and 4. NAA is not adequate for lower Hg levels since the detection limit is about 1 mg kg^{-1} in sediment samples and in the experimental conditions used in the present study. Besides that the uncertainties values are much higher at this concentration level. The second aspect is related to the difference between the analytical techniques: the NAA technique furnishes the total concentration while CV AAS using the 3051A digestion procedure characterizes only the bioavailable Hg present in the sample.

4. CONCLUSIONS

Both analytical techniques CV AAS and NAA used in the present study showed good precision and accuracy for Hg determination in sediment samples. The total Hg results obtained by both analytical techniques ranged from 3 to 71 mg kg^{-1} and were considered statistically similar. The results confirm that both analytical techniques were suitable to detect the Hg concentration levels in the Rio Grande sediments studied.

The Hg levels in the sediment of the Rio Grande reservoir confirm the anthropogenic origin for this element in this ecosystem, mainly at points 1 and 2.

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