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MAJOR AND TRACE ELEMENTS ASSESSMENT IN SEDIMENT FROM ITUPARARANGA RESERVOIR, BY ACTIVATION ANALYSIS AND ICP OES

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ABSTRACT

The Itupararanga reservoir was built to generate electric power by the LIGHT Company and started its operation in 1912. It is fed by the Una, Sorocamirim and Sorocabuçu rivers. This reservoir supplies water to a population of 600.000. This water system is affected by irregular soil occupation and urban development which has caught CETESB's (Environmental Company of São Paulo State) attention. In this study four geo-referenced sampling points were used and bottom sediment samples were collected. The sediment samples were dried at 40^0C, ground in an agate mortar, sieved (200 mesh) and again homogenized. The instrumental neutron activation analysis was applied to the sediment samples in order to determine some major elements (Fe, K and Na), trace (As, Ba, Br, Co, Cr, Cs, Hf, Rb, Sb, Sc, Ta, Tb, Th, U and Zn) and rare earth (Ce, Eu, La, Lu, Nd, Sm, Tb and Yb) elements. By using ICP OES metals determination for Cd, Cr, Cu, Pb and Ni was undertaken after digestion procedure according to the 3051 method from US EPA. The methodology validation for precision and accuracy was carried out by reference material analyses. For metals Cd, Cr, Cu, Pb and Ni the concentration values were compared to the oriented values from Environmental Canada (TEL and PEL). The Enrichment Factor (EF) was calculated for sediment contamination assessment.

1. INTRODUCTION

The basin of the Itupararanga reservoir suffers strong environmental pressures, especially when considering that a part of the drainage area of Itupararanga dam belongs to the Metropolitan Region of Sao Paulo (RMSP). Furthermore, the rivers that form the basin of the Upper Sorocaba also suffer severe environmental impacts throughout their course due to diffuse pollution from agricultural production and organic load, when crossing small villages and cities [1]. The waters from the Itupararanga dam are used for multiple purposes, such as water supply for more than half of the region's population, power generation, regulation of

water flow of the Sorocaba River Basin and recreation activities for nearby cities. Despite having an excellent spring, the dam is suffering serious environmental risks due to use and occupation.

The sedimentary column of aquatic environments, especially their organic fraction, trade nutrients with the overlying water column. In general, sediments are not just a warehouse for products that are found in the water column, but represent a recycling compartment that some biological pathways involving compounds, physicochemical, chemical and transport process [2]. With the use of sediment analysis from these aquatic systems, it is possible to assess contamination by toxic metals [3], understand transport phenomena that occur in these complex systems and trace the history of pollution [4].

Instrumental neutron activation analysis (INAA) has been widely applied for soil and sediment analysis at LAN [5-6], allowing the determination of several elements such as Zn, As, Ba, Br, Ca, Co, Cr, Cs, Fe, Hf, Sb, Se, Ta, Th, U, W, Zr and rare earth elements (REE). By using ICP OES metals determination mainly for Cd, Cr, Cu, Hg, Pb and Ni are commonly used for soil, sediments and environmental samples.

The objective of this study was to assess the concentration of some heavy metals and trace elements in sediment samples from the Itupararanga reservoir by instrumental neutron activation analysis (INAA) and ICP OES, and thus, evaluate the pollution conditions of its aquatic system. For metals Cd, Cr, Cu, Pb and Ni the concentration values were compared to the oriented values from Environmental Canada (TEL and PEL). The Enrichment Factor (EF) was assessed for sediment contamination index with the results obtained by INAA.

2. MATERIAL AND METHODS

2.1. Sampling and sample preparation

Four bottom sediment samples were collected in the Itupararanga reservoir. The geographical positions of the sampling points are presented in Table 1. Sediment samples were previously dried at 40^{o}C in a ventilated oven until constant weight. After this step, sediment samples were passed through a 2 mm sieve, ground in a mortar, once again passed through a 200 mesh sieve and then homogenized before analysis. The total fraction (< 2 mm) was analyzed. Sampling stations are presented in Figure 1.

Table 1: Sampling point location in the Itupararanga reservoir

Samplings Points	Location	Geographical Position (GPS)	Depth (m)
P-01	Upstream from Sorocaba River	S 23º37'17.80'' W 047º13'525''	6.5
P-02	Near village stream	S 23º37'14.10'' W 047º18'313''	14
P-03	Dowstream from Village	S 23º36'5.50'' W 047º20'188''	16
P-04	2 Km from the dam	S 23º37'56,8'' W 047º23'105''	17

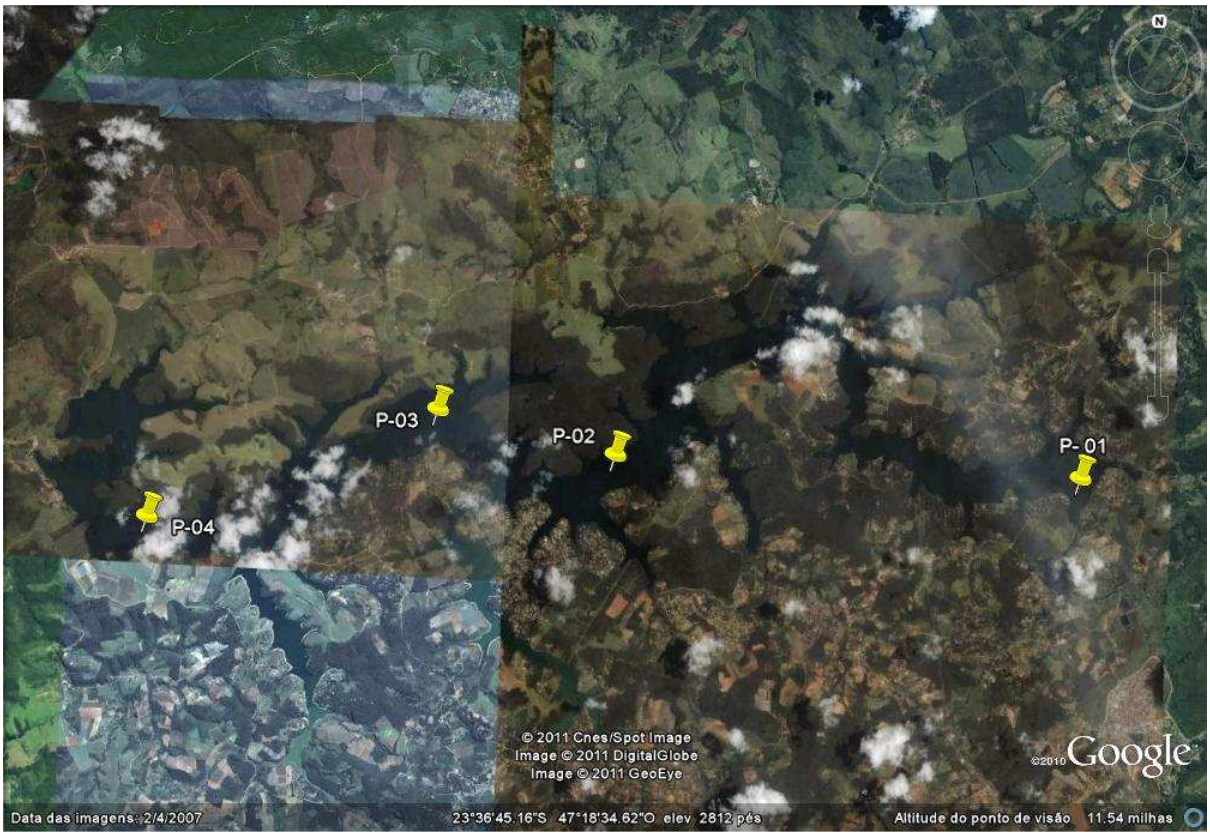

Figure 1. Sampling point locations in the Itupararanga reservoir

2.2 Multielemental determination by Instrumental Neutron Activation Analysis (INAA)

2.2.1 INAA

Activation methods are based on radioactivity measurements of that have been induced in samples by irradiation with neutrons [7]. Neutron Activation Analysis is (NAA) is a sensitive analytical technique useful for performing both qualitative and quantitative multi-element analysis of major, minor and trace elements in samples from almost every conceivable field of scientific or technical interest. For many elements and applications, NAA offers

sensitivities that are superior to those attainable by other methods, on the order of parts per billion or better. The application of purely instrumental procedures is commonly called Instrumental Neutron Activation Analysis (INAA). When a neutron interacts with a nucleus via non-elastic collision, a compound nucleus forms in an excited state. The compound nucleus will almost instantaneously de-excite into a more stable configuration trough emission of one or more characteristic gamma rays. About 70% of the elements have properties suitable for measurement by NAA [8]. Using the comparative technique, sample plus one or more standards are irradiated simultaneously with thermal neutrons (with energy about 0.04 eV). The samples may be solid, liquid or gases, and the standards should approximate the samples as closely as possible both physically and chemically. Care is taken to be sure the samples and standards are exposed to the same neutron flux. The time of irradiation is dependent upon a variety of factors and often is determined empirically; generally vary from several minutes to several hours. Often these procedures are nondestructive and for this reason are applied to the analysis of art objects, coins, forensic and environmental samples, and archaeological specimens [8].

2.2.2 Experimental Procedure

For the multielemental analysis, approximately 150 mg of sediment (duplicate samples) and reference materials were accurately weighed and sealed in pre-cleaned double polyethylene bags, for irradiation. Single and multi-element synthetic standards were prepared by pipetting convenient aliquots of standard solutions (SPEX CERTIPREP) onto small sheets of Whatman $N^{o}41$ filter paper. Sediment samples, reference materials and synthetic standards were irradiated for 8 hours, under a thermal neutron flux of 1 to $5x10^{12}$ n cm^{-2} s^{-1} at the IEA-R1 nuclear research reactor at IPEN. Two series of counting were made: the first, after one week decay and the second, after 15-20 days. Gamma spectrometry was performed using a Canberra gamma X hyperpure Ge detector and associated electronics, with a resolution of 0.88 keV and 1.90 keV for ^{57}Co and ^{60}Co, respectively.

The elements analyzed by using this methodology were As, Ba, Br, Co, Cr, Cs, Fe, Hf, Na, Rb, Sb, Sc, Ta, Th, U, Zn and the rare earths Ce, Eu, La, Lu, Nd, Sm, Tb and Yb. The analysis of the data was undertaken by using an in-house gamma ray software, VISPECT program to identify the gamma-ray peaks and by an ESPECTRO program to calculate the concentrations. The uncertainties of the results were calculated by error propagation. The methodology validation was verified by measuring reference material Soil 7 (IAEA), Lake Sediment SL1 (IAEA) and BEN Basalt-IWG-GIT. Details of the analytical methodology is described at Larizzatti et al [5].

2.3 Multielemental determination by ICP OES

2.3.1 Inductively coupled plasma atomic emission spectroscopy (ICP OES) [7]

It is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample.

The ICP OES is composed of two parts: the ICP and the optical spectrometer. The ICP torch consists of 3 concentric quartz glass tubes. The output or "work" coil of the radio frequency (RF) generator surrounds part of this quartz torch. Argon gas is typically used to create the plasma. When the torch is turned on, an intense electromagnetic field is created within the coil by the high power radio frequency signal flowing in the coil. This RF signal is created by the RF generator which is, effectively, a high power radio transmitter driving the "work coil" the same way a typical radio transmitter drives a transmitting antenna. The argon gas flowing through the torch is ignited with a Tesla unit that creates a brief discharge arc through the argon flow to initiate the ionization process. Once the plasma is "ignited", the Tesla unit is turned off.

The argon gas is ionized in the intense electromagnetic field and flows in a particular rotationally symmetrical pattern towards the magnetic field of the RF coil. Stable, high temperature plasma of about 7000 K is then generated as the result of the inelastic collisions created between the neutral argon atoms and the charged particles.

A peristaltic pump delivers an aqueous or organic sample into a nebulizer where it is transformed into a mist and introduced directly inside the plasma flame. The sample immediately collides with the electrons and charged ions in the plasma and is itself broken down into charged ions. The various molecules break up into their respective atoms which then lose electrons and recombine repeatedly in the plasma, giving off radiation at the characteristic wavelengths of the elements involved.

In the optical chamber(s), after the light is separated into its different wavelengths (colors), the light intensity is measured with a photomultiplier tube or tubes positioned to "view" the specific wavelength(s) for each element line involved. In more modern units, the separated colors fall upon an array of semiconductor photo detectors such as charge coupled devices (CCDs). In units using these detector arrays, the intensities of all wavelengths (within the system's range) can be measured simultaneously, allowing the instrument to analyze for every element to which the unit is sensitive all at once. Thus, samples can be analyzed very quickly.

The intensity of each line is then compared to previously measured intensities of known concentrations of the elements, and their concentrations are then computed by interpolation along the calibration lines. In addition, special software generally corrects for interferences caused by the presence of different elements within a given sample matrix

The ICP OES technique is applicable to a wide range of metals, particularly the so-called refractory ones that form stable oxides and not break down easily with the flame temperatures. The high temperatures generated in this technique provide excellent sensitivities for many refractory elements, eliminating chemical interferences.

2.3.2 Experimental Procedure for ICP OES

For metal determination in sediment by using ICP OES analytical technique a previous digestion of the samples is needed. In this study sample digestion was performed by a microwave-assisted method following the SW-846-3051 – US EPA for sediments [9]. About 500 mg of sediment sample (duplicate) and 500 mg of the WQB-3 and 1646[a] reference materials were weighed directly in Teflon tubes and 10 mL of conc HNO_3 was added. After

the digestion procedure the sample was filtered and transferred to a volumetric flask and the final volume was completed to 50 mL. The measurements were carried out using the ICP OES SPECTRO FLAME MODULAS, CETESB (Companhia de Tecnologia de Saneamento Ambiental) equipment. Methodology validation in terms of precision and accuracy was verified by means of reference materials analyses (WQB-3 (NRCC, Canada) and Estuarine Sediment (NIST SRM 1646[a]). These materials present certified/information values for the concentration of the elements analyzed by using the digestion procedure 3051 from US EPA.

3. RESULTS AND DISCUSSION

Table 2 presents the results obtained by ICP OES in the reference materials WQB-3 and 1646[a]. The relative standard deviation (RSD) ranged from 2.7 to 12.5 % for WQB-3 reference material. For the 1646a reference material the RSD ranged from 2.8 to 7.9 % and relative error from 6.1 to 15.4% for 1646[a] reference material, proving the precision and accuracy, respectively of the ICP OES analytical technique for these elements.

Table 2. Reference materials analyses results by ICP OES (n= 2)

WQB-3				
Element	**Information value**	**Found value**	**RSD (%)**	
Cr	105	88 ± 7	8.0	
Cd	4.70	4.0 ± 0.5	12.5	
Pb	242	212 ± 10	4.7	
Zn	1407	1320 ± 102	7.7	
Cu	81.0	78.6 ± 2.1	2.7	
Ni	53.8	48.7 ± 2.0	4.1	

1646[a] Estuarine Sediment				
Element	**Certified value**	**Found value**	**RSD (%)**	**RE (%)**
Cd	0.100 ± 0.007	< 0.2		
Pb	11.7 ± 1.2	9.9 ± 0.7	7.1	15.4
Zn	48.9 ± 1.6	45.9 ± 1.3	2.8	6.1
Cu	10.01 ± 0.34	8.9 ± 0.7	7.9	11.1
Ni	23*	20.1 ± 1.4	7.0	

n = number of determinations, * oriented value

Table 3 presents the results obtained for the metals Cd, Pb, Ni, Zn, Cu, Cr analyzed by ICP OES in the sediments from four sampling points and the oriented values TEL and PEL from CCME (Canadian Council of Minister of the Environment) [10] and adopted by CETESB for

sediment quality monitoring program. TEL (Threshold Effect Level) is the limit below which no adverse effects on the biological community is observed and PEL, the probable level of occurrence of adverse effects on the biological community [10].

The results for Cr were below or at the same level of TEL (37.3 mg kg^{-1}) at points 1 and 4. For point 3 the value was between TEL and PEL and at point 2, the concentration value exceeded the PEL value (90 mg kg^{-1}).

For Cd the concentration levels in the 4 sampling points were below the quantification limit of the analytical technique (QL = 0.20 mg kg^{-1}). For Pb and Cu, all the results were below the TEL limit (35 mg kg^{-1} and 35.7 mg kg^{-1}, respectively). For Ni, only point 2 exceeded the TEL value (18 mg kg^{-1}).

Table 3: **Results for the elements analyzed by ICP OES (mg kg^{-1}): mean (duplicate) (dry basis), standard deviation, TEL and PEL values [10]**

	Sampling Points				TEL	PEL
Elements	**P-1**	**P-2**	**P-3**	**P-4**		
Cr	34.5 ± 2.5	148 ± 8	49.5 ± 4.8	37.5 ± 1.4	37.3	90
Cd	--	--	--	--	0.6	3.5
Pb	0.135±0.14	33.3±14.3	20.1±10.3	12.6±1.9	35	91.3
Cu	0.900±0.007	18.6±1.0	20.5±0.2	26.7±0.4	35.7	197
Ni	0.13±0.01	20.1±1.0	17.4±0.3	15.6±0.8	18	35.9

-- : not determined (< QL)

Point 1, 2, 3 and 4 presented concentration values for all metals analyzed below the TEL values, except for Cr at points 2 and 3 and Ni at point 2. However, points 2, 3 and 4 showed the highest concentration values for these metals.

The precision and accuracy of the INAA analytical methodology were verified by reference material analysis and Z value calculation was made according to Bode [11]. If $|Z| < 3$, the individual result of the control sample (reference material) lies on the 99% confidence interval of the target value. For the reference materials analyzed in the present study all the results were in the interval range of $|Z| < 3$, indicating good precision and accuracy of the INAA technique.

Table 4 shows the results obtained by INAA, mean (duplicate) and standard deviation, Enrichment Factor (**EF**), and Upper Continental Crust values [12].

Table 4: Results (mg kg^{-1}) for the elements analyzed by INAA, EF and UCC values

Element	P-1	EF	P-2	EF	P-3	EF	P-4	EF	UCC
As	2.1 ± 0.3	0.49	6.0 ± 0.4	1.34	7.7 ± 0.2	1.64	5.40 ± 0.3	1.80	**2**
Ba	3047± 371	2.14	320±26	0.22	464±32	0.30	246±19	0.24	**668**
Br	4.9 ±0.2	1.45	10.4±0.3	2.93	15.4±0.2	4.12	6.6±0.1	2.72	**1.6**
Ca (%)	2.0 ± 0.1	0.32	1.0±0.1	0.15	1.3±0.1	0.19	1.6±0.1	0.36	**2.945**
Ce	224 ± 14	1.61	171±10	1.17	161±6	1.05	57±4	0.57	**65.7**
Co	12.2 ± 0.5	0.49	12.7±0.5	0.49	13.0±0.3	0.48	3.5±0.2	0.2	**11.6**
Cr	70.9± 2.7	0.95	73.3±2.7	0.94	68.2±4.3	0.83	54.0±4.4	1.01	**35**
Cs	7.0±0.7	0.57	7.0±0.7	0.54	5.3±0.4	0.39	14.2±1.0	1.61	**5.8**
Eu	2.64±0.24	1.31	1.56±0.20	0.74	1.33±0.05	0.60	0.77±0.07	0.54	**0.95**
Fe(%)	3.25±0.03	0.49	5.49±0.03	0.80	6.86±0.04	0.95	1.82±0.01	0.39	**3.089**
Hf	39.7±1.6	3.22	3.7±0.2	0.29	4.5±0.1	0.33	13.8±0.6	1.57	**5.8**
K(%)	1.8±0.2	0.30	0.6±0.1	0.09	0.8±0.1	0.11	1.1±0.2	0.25	**2.865**
La	113.0±1.7	1.64	67.1±1.0	0.93	55.4±0.5	0.73	34.7±0.8	0.71	**32.3**
Lu	0.74±0.05	1.29	0.29±0.02	0.48	0.28±0.02	0.44	0.46±0.04	1.13	**0.27**
Na (%)	0.119±0.031	0.02	0.040±0.013	0.01	0.039±0.005	0.01	0.346±0.012	0.01	**2.57**
Nd	76±7	1.38	44±4	0.76	35±2	0.58	27±3	0.69	**25.9**
Rb	91±7	0.39	n.d.		63±5	0.24	72±4	0.43	**110**
Sb	0.29±0.06	0.44	0.39±0.06	0.57	0.45±0.04	0.62	0.80±0.07	1.71	**0.31**
Sc	14.9±0.5	1.00	15.6±0.5	1.00	16.4±0.4	1.00	10.6±0.2	1.00	**7**
Sm	9.7±0.4	0.97	10.3±0.3	0.99	6.8±0.2	0.62	4.2±0.2	0.65	**4.7**
Ta	3.2±0.4	1.00	1.7±0.2	0.52	1.6±0.1	0.44	1.9±0.3	0.85	**1.5**
Tb	2.1±0.4	2.00	0.9±0.2	0.84	0.7±0.0	0.61	0.9±0.2	1.23	**0.5**
Th	30.5±1.7	1.39	22.1±1.7	0.96	21.3±0.8	0.88	14.9±0.8	0.95	**10.3**
U	7.4±1.0	1.39	3.8±0.3	0.68	4.1±0.3	0.71	3.9±0.4	1.03	**2.5**
Yb	5.4±0.5	1.69	2.2±0.2	0.66	1.8±0.1	0.52	3.4±0.2	1.50	**1.5**
Zn	102±7	0.92	91±6	0.79	57±3	0.46	79±4	1.01	**52**

Enrichment Factor (**EF**), is an index used as a tool to evaluate the extent of metal pollution [13,14] and is defined as a double ratio normalized to a reference element (RE) and calculated by the equation:

$$\mathbf{EF = ([M]/[RE]_{sed})/ ([M]/[RE]_{ref})} \quad \mathbf{(1)}$$

Fe, Al and Sc are generally used as reference elements for normalization purposes [13]. In the present study Sc was chosen as a reference element and UCC values as reference values for sediments [14]. There is still no regional reference value for comparison in Brazil and and as such the UCC is commonly used. According to Zhang and Liu [15], by convention if $0.5<EF<1.5$, is taken an indication that trace metals is entirely provided from crustal contribution (e.g. weathering product); values above 1.5 are considered to indicate that an important proportion of trace metals is delivered from non-crustal materials, for example,

anthropogenic contributions. The higher the EF value, the more severe the anthropogenic contribution.

From Table 4 it can be observed that sediment from point 1 showed EF > 1.5 for the elements Ba, Ce, Hf, La, Tb and Yb, being the higher EF value found for Hf (3.2). Point 2 presented a value of 2.9 for Br; point 3, for As (1.6) and Br (4.1) and point 4, for the elements As, Br, Cs, Hf and Sb, being the higher value for Br (2.7). It appears that for these elements an anthropogenic contribution is occurring in the Itupararanga reservoir. For most elements analyzed by INAA the EF was <0.5< EF< 1.5 indicating that the elemental concentrations are probably due to crustal or natural weathering origins.

3. CONCLUSIONS

The determination of some metals and trace elements by Instrumental Neutron Activation Analysis (INAA) and ICP OES analytical techniques proved to be highly appropriate and can thus be important tools for sediment monitoring as their sensitivity, precision and accuracy are extremely reliable.

From the results for toxic metal concentrations points 1, 2, 3 and 4 presented concentration values below the TEL values, except for Cr at points 2 and 3 and Ni at point 2. Cr at point 2 exceeded the PEL oriented value. However, points 2, 3 and 4 showed the highest concentration values for these metals. It is important to emphasize that point 4 is near the catchment point of water supply in this reservoir.

From the results obtained by INAA it can be observed that sediment from point 1 showed EF > 1.5 for the elements Ba, Ce, Hf, La, Tb and Yb, being the higher EF value found for Hf (3.2). Point 2 presented a value of 2.9 for Br; point 3, 1.6 for As and 4.1for Br. Point 4 presented EF> 1.5 for the elements As, Br, Cs, Hf and Sb, being the higher value 2.7 for Br. For these elements it seems that an anthropogenic contribution is occurring in the Itupararanga reservoir. For most elements analyzed by INAA the EF was <0.5< EF< 1.5 indicating that the elemental concentrations are probably due to crustal or natural weathering origins.

These are preliminary results and other sampling campaigns must be undertaken in order to obtain further data for a better evaluation of the sediment monitoring quality from the Itupararanga reservoir. Also a core sample will be collected in order to know the history of pollution in this reservoir.

4. ACKNOWLEDGMENTS

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