INTERNATIONAL SEVEN JOURNAL
OF MULTIDISCIPLINARY
ISSN: 2764-9547

Study of the chemical parameter relationship in the Guarapiranga, Mairiporã and Billings reservoir systems using the Synchrotron Radiation process

Estudo da relação do parâmetro químico no sistema das represas de Guarapiranga, Mairiporã e Billings utilizando o processo de Radiação Sincrotron

DOI: 10.56238/isevmjv2n4-017
Receipt of originals: 02/08/2023
Acceptance for publication: 23/08/2023

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ABSTRACT

The scarcity of water in the world makes it increasingly important to correctly manage water resources. Based on this dynamic, the work focused on the study of the chemical quality of three dams in the Region of the City of São Paulo. They are: Guarapiranga, Mairiporã and Billings. Where the analysis process was carried out by synchrotron radiation at the Brazilian Synchrotron Light Laboratory (LNLS). The results were promising, where 15 chemical elements were detected: Aluminum (Al), Silicon (Si), Phosphorus (P), Sulfur (S), Chlorine (Cl), Potassium (K), Calcium (Ca), Titanium (Ti), Manganese (Mn), Iron (Fe), Bromine (Br), Strontium (Sr), Tin (Sn), Barium (Ba) and Cerium (Ce). Their values were well below the limits called Maximum Permissible Values (VMP) for human consumption. All on the order of microliters (μl). Highlight for the Iron that had higher concentration for the dams, but without damage to human health.

Keywords: Water resources, Pollution, Environmental management, Sanitation and environment.

1 INTRODUCTION

The growing demands for new models of natural resource management, resulting from centuries of predatory activities against nature, have imposed greater responsibilities on the scientific community.

Water quality is currently a priority issue on the social, commercial, and political agendas of the governments of virtually all nations.

In this sense, the development of more precise techniques of physical and chemical analysis of water, is beyond obvious necessity, a constant challenge for the related sciences.

The study of water quality is a comprehensive and complex topic, since there are different approaches and there are many variables acting on the dynamics of water bodies.

Each research must necessarily delimit its exploration, relativize the concept of quality, that is, answer the question: Quality for what purpose?

In this way, we can establish different criteria to attest to quality. Some examples would be: potability, preservation of aquatic life, preservation of water sources, urban supply, specific industrial use and agricultural use. This question is fundamental since the establishment of quality criteria necessarily involves the definition of the term "quality".

Such criteria, in turn, should be established according to the specific characteristics of each environment or activity. In fact, the current guiding values for soil and groundwater in the State of São Paulo, approved by the Environmental Sanitation Technology Company-CETESB-SP on 11/23/2005, already bring specificities such as the differentiation of the Intervention Values (VI) by category of water use, in this case, agricultural, residential, and industrial.

The high consumption of metals in various industrial processes has implied the disposal of large amounts of these elements in the environment, especially in the riverbeds and tributaries of watersheds. Known deleterious effects of high concentrations of metals on the human body and biota constitute a source of constant concern, both relevant governmental bodies and of society in general.

The research proposal focused on identifying the possible heavy metals present and other chemical elements in the water from the dams of Guarapiranga, Mairiporã and Billings that feed the region of the great metropolis of São Paulo and adjacent areas by the synchrotron radiation technique.

2 LITERATURE REVIEW

2.1 WATER AND SEDIMENTARY RESOURCES

The distribution of water on land is approximately 97.57% saltwater and 2.43% freshwater. Of the fresh water, about 0.57% are in rivers and lakes, 24.97% in groundwater, 74.36% in the form of glaciers and icebergs in the polar regions and 0.1% in the biosphere and atmosphere (PEIXOTO and OORT, 1990).

These figures alone would justify an increase in attention to the availability of fresh water for the supply of cities and countryside since the world population increases every year. However, the greatest reason for apprehension stems from anthropogenic action, historically negligent in issues such as the control of deforestation, industrial and residential emissions, the disposal of garbage and land use and occupation.

One of the known consequences is the contamination of aquatic environments.

The pollution of rivers, lakes or reservoirs can occur by natural causes or by actions resulting from human activity.

The water characteristics of a reservoir are the result of the interaction of an intricate set of factors.

Two types stand out: Natural factors and human factors. Among the natural ones are: the geological aspect, the climatic cycle, and the ecological dynamics.

Human intervention can take place directly or indirectly. Direct actions concern the discharge of debris and various effluents directly into the aquatic environment.

2.2. METALS

2.2.1 Physico-chemical properties

The physical and chemical properties of metal solutions, such as temperature, pH, electrical conductivity and dissolved oxygen, are important for the careful evaluation of the concentrations of contaminant metals present.

In fact, different portions of the same water, at different temperatures, have different amounts of some metals. This is due to the favoring or inhibition of physicochemical processes that biomake available (more or less) elements in the solvent (NOGUEIRA and MATSUMURA, 1994).

Physicochemical changes in the environment can lead to variations in the concentration of SVA (acidification volatile sulfide).

A study conducted by the Institute of Technological Research - IPT (2005), in the reservoir of Rio Grande (Billings), reveals that in the first ten centimeters of sediment, practically all metal ions are weakly linked to their complexing phases, being susceptible to bioavailability, which evidences the importance of sulfide as a complexor of trace metals (MARIANI, 2006).

The chemical speciation of the metallic element is important to know its dynamics in the aqueous medium and its amplitude of impact on the environment.

In this work, the chemical elements studied originate from an aqueous medium, that is, from a solution. Chemically, a solution is defined as a homogeneous dispersion of two or more substances, so one must have at least one solute and one solvent. In this study the solvent will always be water and the solutes will be metals.

2.2.2 Biochemical properties and effects on man

Metals are absolutely essential for cellular life. The feeding of cells basically depends on the transport, through cell membranes, of organic nutrients such as glucose and amino acids, and of the metal ions Na+ (sodium) and K+ (potassium).

Ca2+ (calcium) and Mg2+ (magnesium) ions are also found inside and outside cells.

A complex protein called "sodium-potassium-adenosine-triphosphatase," or simply, "sodium pump," is responsible for the flow and counterflow of these ions through the cell wall.

All the vital actions of an organism are commanded by nerve and muscle cells.

3 X-RAY FLUORESCENCE

KNEIP and LAURER (1972) describe the advantages of X-ray fluorescence by energy dispersion over wavelength scattering. Initially, the quantitative analysis with XRF required many standards, for the construction of calibration curves of the system or for calculations of the so-called alpha coefficients. The alpha coefficients are constant correction factors and at least **n-1** patterns are required; where **n** is the number of elements present in the sample.

This method is based on corrections that are performed due to the interferences produced by an **element i1** in the intensity of the fluorescent radiation of an **element i2** present in the sample.

Another method, using the physical principles of X-ray fluorescence production, was developed by CRISS and BIRKS (1968). It is known as the Fundamental Parameters Method, this method is based on the analytical solution of theoretical equations that describe the dependence of fluorescent radiation intensity in terms of fundamental physical parameters and instrumental parameters. The method is simple and does not require a large number of standards, making it currently one of the most widely used and widespread methods in terms of XRF.

3.1. TOTAL REFLECTION X-RAY FLUORESCENCE (TXRF)

YAP *et al.* (1989), used X-ray fluorescence by total reflection for the analysis of fine samples of mineral sand. The method was tested with certified rock samples (JB-3J). They evaluated that the method has some advantages, being: multi-elementary; with simplified sample preparation; contribution of low scattered radiation and need for small amounts of digested samples, about 2 mL, for analysis.

CHEN *et al.* (1990), showed that synchrotron radiation sources have important characteristics for material analysis, mainly by the ability to determine the elemental composition and molecular structure. They reported that for microscopic analysis (micro characterization of materials), synchrotron radiation sources offer a spatial resolution of 10 μm with a detection limit between 10 and 100 ppb.

REUS (1991) used a total reflection X-ray fluorescence (TXRF) system to analyze samples of mineral and vegetable oils, using different sample preparation techniques. The direct preparation of dilute oil solutions showed good results for the concentrations of elements at trace levels higher than 1 μg.g-1.

LIENDO *et al*. (1999), described a comparative study between PIXE and TXRF for the analysis of Cl, K, Ca, Fe, Cu, Zn and Br in human amniotic fluid.

They found agreement in the measurements performed with the two techniques for the following elements: K (100%), Cl (60%), Fe (80%), Cu (50%) and Zn (50%). They reported the need for further studies in order to establish the ideal experimental conditions that lead to a complete agreement between the TXRF and the PIXE.

4 METHODOLOGY

The State of São Paulo is divided into 22 Water Resources Management Units (UGRHI), constituting a Hydrographic Basin of more than 5,900 km2, created with the purpose of favoring the planning and integrated use of the State's water resources seeking the resolution of conflicts such as the imbalance between demand and availability of water and the maintenance of good water quality according to the State Water Resources Plan of 1991 (COPOBIANCO, 2002).

According to the State Water Resources Plan, the UGRHI are based on the Hydrographic Basin. In addition, the division took into account the physical characteristics such as geomorphology and hydrogeology of the regions. Political and socioeconomic aspects were also considered, such as compatibility with the existing regional and administrative division, number of municipalities, physical areas of each unit, road distances and demographic aspects of the regions.

Figure 1 below shows the 22 UGRHI in the state of São Paulo.

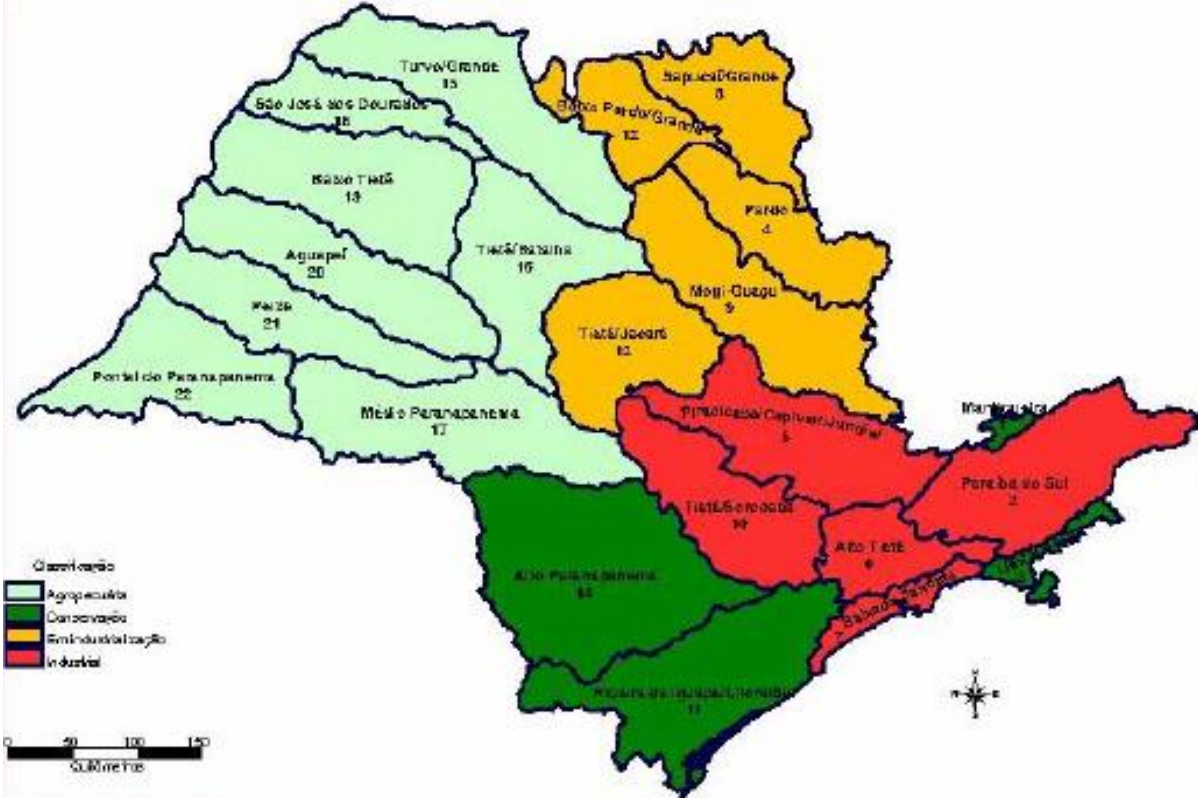


Figure 1 - Classification of the 22 UGRHI of the state of São Paulo. Source: CETESB (2005)

4.1 SAMPLE COLLECTION

Three samples of effluent from three large dams in the Metropolitan Region of São Paulo were collected: Guarapiranga; Mairiporã and Billings.

A point was chosen in the middle of the dams with the aid of a boat in order to raise observations about the quality and potability of the dams.

4.2 SAMPLE PREPARATION

The samples called R1 (Guarapiranga), R2 (Mairiporã) and R3 (Billings) to facilitate comprehension were filtered by a process with cellulose acetate membrane (0.45 μm porosity). After filtering, an aliquot of 1 mL was taken from each filtered sample and then 100 μL (102.5 mg. L-1) of a standard solution of Gallium (Ga), necessary for the analysis of metals by the technique used. An aliquot of 5.0 μ L of the resulting solution was placed in lucicite discs (Perspex), which were dried with the aid of infrared lamp. The samples were later packed in Petri dishes for protection and transport to the Brazilian Synchrotron Light Laboratory (LNLS) for further analysis by X-ray Fluorescence by Total Reflection with Synchrotron Radiation (SR-TXRF) for metal analysis.

The excitation of the samples by the SR-TXRF technique was for a time of 100 seconds while in the detection a hyperpure Ge semiconductor detector was employed, with a resolution of 150 eV at 5.9 keV.

In SR-TXRF there is no occurrence of the effect of absorption and reinforcement as in ED-XRF or WD-XRF, and it is not necessary to correct the matrix effect due to the very thin thickness of the sample (SIMABUCO, 1993).

Therefore, the quantitative analysis is done through equation 1.

Equation 1:

$$I_i = s_i \cdot C_i$$

Where:

Ii = Net X-ray intensity for element i (cps);

Ci = Concentration of element i (ppm or μg.mL^{-1}) and

$\boldsymbol{S_i}$ = Relative sensitivity for element i (cps/ppm or cps.mL. μg^{-1}).

4.3 PREPARATION OF SAMPLES FOR ANALYSIS BY SR-TXRF

In SR-TXRF analysis, the sample must be previously digested and deposited on a support. For full reflection to occur, the sample holder must be polished and flat.

Typically, quartz supports are used as a reflector. However, these have some disadvantages: the fluorescent radiation of the silicon present in the quartz makes a quantitative determination of silicon in the sample unfeasible. In addition, quartz supports are expensive ($ 50.00 each) and cleaning, both of new and used supports, must be done carefully, otherwise it can remain a contamination, mainly, by the main elements: Fe, Cu and Zn.

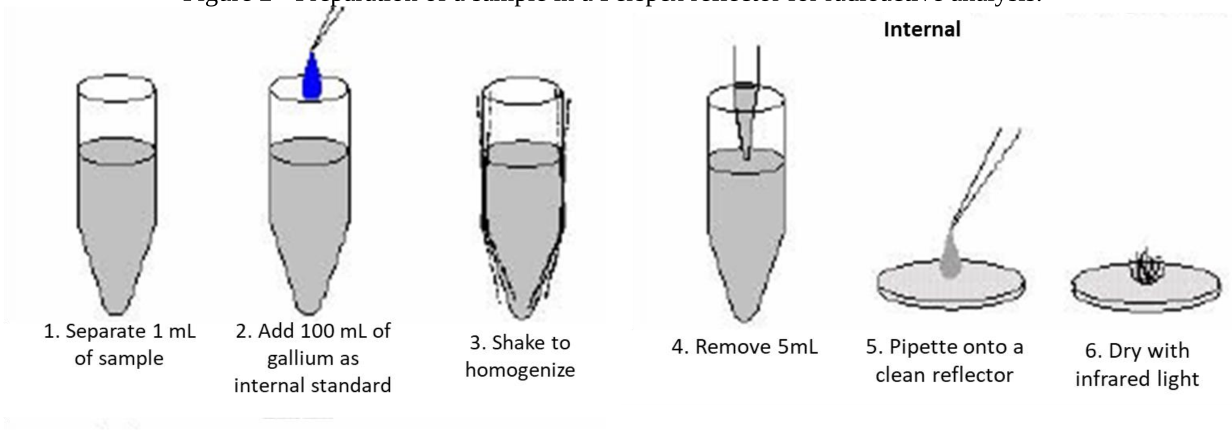
Lucite (Perspex) is a material that can be used without prior cleaning and as it is relatively inexpensive (R $ 2.50 each), it can be used only once and then discarded. It contains only the elements hydrogen, carbon and oxygen and is hardly contaminated by other elements.

The lucite reflector can be found in the form of rectangular plates, with very smooth surfaces that do not require polishing, this reduces the cost and the risk of contamination.

The surface of the lucite is protected with a thin plastic film to prevent scratches and contamination during handling. The lucite can be easily cut into the desired format and used immediately after the removal of the plastic film (SCHMITT *et al*., 1987).

Figure 2 below briefly shows a schematic of this procedure, already with the values effectively used in the laboratory preparation process. For each sample originated from R1, R2 and R3, triplicates were made and these were stored in Petri dishes for further analysis by synchrotron radiation.

Figure 2 - Preparation of a sample in a Perspex reflector for radioactive analysis.



4.4 SYNCHROTRON BEAMLINE

The beamline is the instrumentation that is coupled to the electron storage ring. In each beamline arrive the beams of photons (synchrotron light), generated by the electrons that circulate in the storage ring.

Figure 3 shows a general photo of the laboratory, where the storage ring is seen covered by a set of concrete plates (for shielding) of 30 cm thickness.

Figure 3 – Overview of the synchrotron light beam storage ring.

4.5 EXPERIMENTAL STATION - LINE DO9B – XRF X-RAY FLUORESCENCE

The XRF – X-ray Fluorescence line is intended for the analysis of multielemental chemical composition (Z≥13) in scientific applications of trace element determination in environmental, biological and materials sciences, chemical depth profile of thin films and chemical mapping.

Figure 4 shows a photo of the pipe of the DO9B – XRF line, through which the synchrotron light beam passes from the ring to the fluorescence experimental station.

Figure 4 - Photo of the ring pipe for the DO9B – XRF line of the Brazilian Synchrotron Light Laboratory, through which the synchrotron light beam passes.

4.6 INSTRUMENTATION OF THE LNLS D09B-XRF LINE

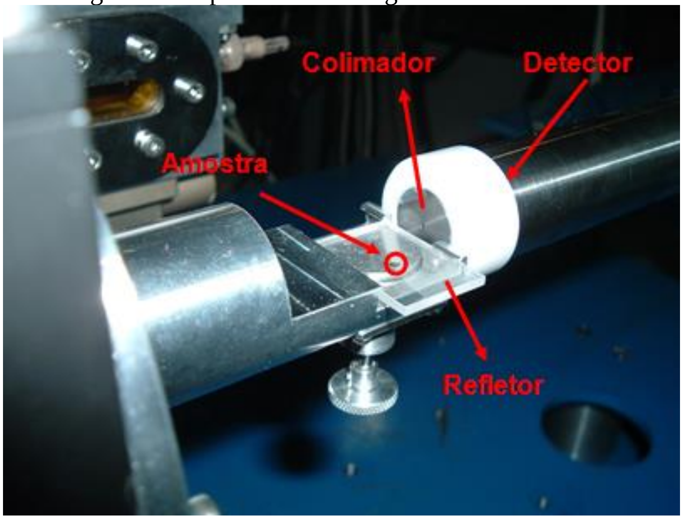
In the X-ray fluorescence experimental station, for the detection of X-rays, a hyperpure Ge semiconductor detector is used, with a beryllium window of 8 µm thick, an active area of 30 mm2, coupled to an amplifier module and multichannel analyzer board, inserted in a microcomputer (Figure 5).

Figure 5 - Overview of the experimental station DO9B-XRF of the Brazilian Synchrotron Light Laboratory with the instrumentation.

The experimental arrangement allows the rotation and translation of the sample in order to obtain the condition for the total reflection of the incident beam on the sample that is allocated in a rectangular plate of lucicite fixed in the sample holder, allowing the measurement of the elements contained in the sample.

Figure 6 shows in detail the sample deposited on the reflector and the detector with the collimator.

Figure 6 - Experimental arrangement of SR-TXRF.



The incidence of the synchrotron light beam allows the sample to reflect all wavelengths of the chemical elements present, which ensures the analysis of the compounds at the elemental level.

5. RESULTS

5.1 CERTIFICATION OF THE METHOD

To ensure that the samples are actually detecting the elements they claim to contain in the study samples, the method must be validated by the process of measuring samples certified to an international standard by the *National Institute of Standards and Technology* (NIST). This is a high-tech department responsible for the certification process in the areas of: engineering, chemistry, experimental physics and biology among others.

Elemental sensitivity was calculated using five standard solutions with known elements and at different concentrations, plus the element gallium (Ga) used as the internal standard.

The experimental sensitivity for the elements contained in the solutions was determined and the results obtained are presented in table 1.

Table 1- Experimental sensitivity for the K series.

Atomic number	Chemical element	Sensitivity
19	K	0,051170
20	Ca	0,076287
22	Ti	0,159690
24	Cr	0,301810
26	Fe	0,501466
28	Ni	0,713218
30	Zn	0,845466
31	Ga	0,852609
34	Se	0,618315
38	Sr	0,158471

With the data in table 1, the graph in Figure 7 was obtained, which represents the relative sensitivity for the elements in the range of interest of the study.

Figure 7 - Relative sensitivity curve (S_{Ri}) for K series using SR-TXRF.

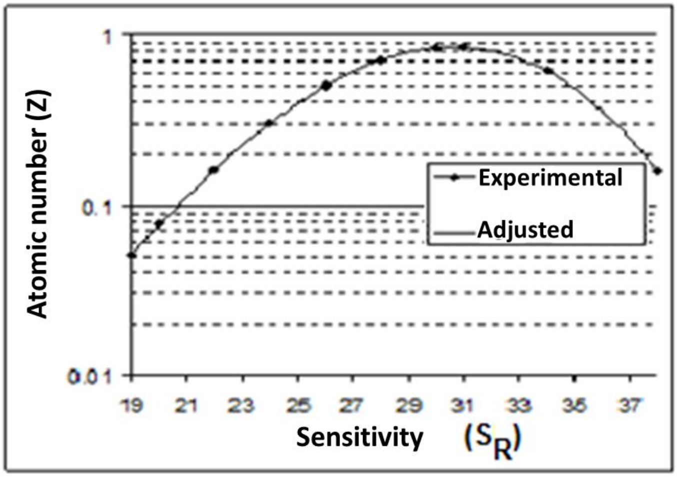


Figure 7 shows the difference between the experimental curve and the adjusted curve (obtained by the NIST certification), allowing the evaluation of the degree of standard deviation between both.

5.2 DAM CONCENTRATIONS

After obtaining the sensitivity curve, together with the data collected in the laboratory by SR-TXRF, the concentrations of the elements present in the samples R1, R2 and R3 were determined (Table 2).

Table 2- Elemental concentration (µg.L-1) of water samples from each dam.

Local	Chemical element														
	To the	Yes	P	S	Cl	Towards	Ca	In	Minutes	Faith	Br	Sr	His	Ba	That
Guarapiranga	987	484	565	3373	2023	8923	1261	484	257	13350	63	45	519	144	77
Mairiporã	1118	563	630	2977	2211	7589	1312	327	182	15272	77	29	403	129	68
Billings	943	500	612	1994	2450	8012	1282	448	195	14971	74	35	569	180	85

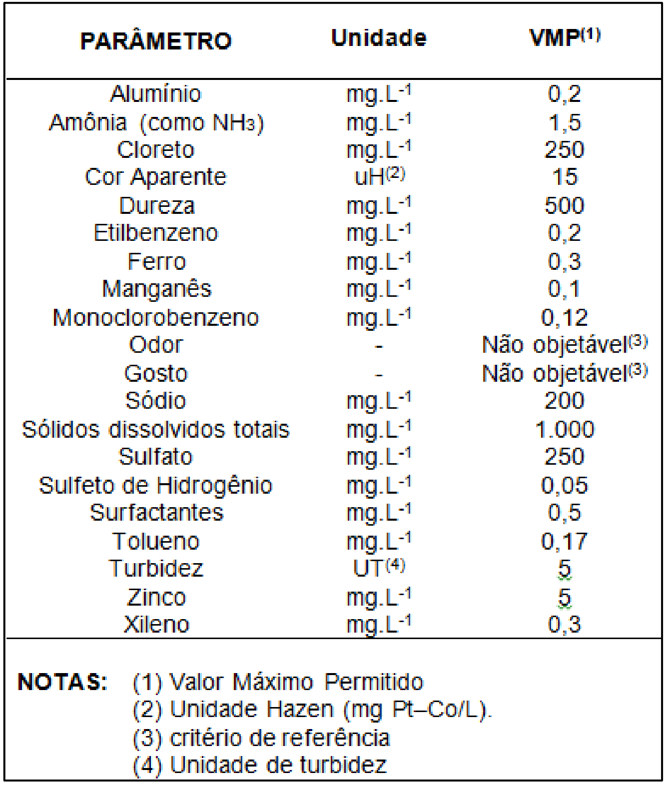
It should be analyzed that the evaluation of the quality of the environment is necessary.

According to CHAPMAN (1990), monitoring, in addition to providing important information about the extent of pollution, also evaluates the efficiency of mitigating actions, adopted with the purpose of reducing, controlling or even eliminating its origin.

The values detected by the process and presented in Table 2 show that the reservoirs of the dams: Guarapiranga (R1), Mairiporã (R2) and Billings (R3), are below the Maximum Allowed Values (VMP), which shows a good quality water.

This finding is observable when comparing some of the values detected with the considerable values satisfactory for human consumption, as shown in Table 3, below.

Table 3- Acceptance standard for human consumption (SABESP, 2022)



PARÂMETRO	Unidade	VMP(1)
Alumínio	$mg.L^{-1}$	0,2
Amônia (como NH_3)	$mg.L^{-1}$	1,5
Cloreto	$mg.L^{-1}$	250
Cor Aparente	uH(2)	15
Dureza	$mg.L^{-1}$	500
Etilbenzeno	$mg.L^{-1}$	0,2
Ferro	$mg.L^{-1}$	0,3
Manganês	$mg.L^{-1}$	0,1
Monoclorobenzeno	$mg.L^{-1}$	0,12
Odor	-	Não objetável(3)
Gosto	-	Não objetável(3)
Sódio	$mg.L^{-1}$	200
Sólidos dissolvidos totais	$mg.L^{-1}$	1.000
Sulfato	$mg.L^{-1}$	250
Sulfeto de Hidrogênio	$mg.L^{-1}$	0,05
Surfactantes	$mg.L^{-1}$	0,5
Tolueno	$mg.L^{-1}$	0,17
Turbidez	UT(4)	5
Zinco	$mg.L^{-1}$	5
Xileno	$mg.L^{-1}$	0,3

NOTAS: (1) Valor Máximo Permitido
(2) Unidade Hazen (mg Pt–Co/L).
(3) critério de referência
(4) Unidade de turbidez

6 CONCLUSION

The values detected by the technique showed an absolute value well below the VMP limits, which shows that the potability of the dams: Guarapiranga (R1), Mairiporã (R2) and Billings (R3) are with water of good origin and of adequate value for human needs.

We can notice that the values are a thousand times below the VMP values which does not lead to chronic problems in the long term.

The research had great scientific relevance for showing the technique and its precision in the chemical analysis of the elements present. Unfortunately, the research does not have a commercial aspect to disseminate, since by current standards it demands cost to use the National Synchrotron Light Laboratory (LNLS).

However, from the values found, it can be said that the water resources management plan administered by the São Paulo Public Supply Company (SABESP), together with the Environmental Sanitation Technology Engineering Company (CETESB) promoting the inspection are influencing the preservation of the water bodies of the three dams.

As a negative point that was raised was the fact that there was no time to collect sediment samples along the dams to evaluate the quality of these sites, remaining as a suggestion for future scientific research.

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