LUMEN ET VIRTUS
ISSN: 2177-2789

EVALUATION OF THE REUSED WATER OF THE PINHEIROS SUBWAY STATION IN THE CITY OF SÃO PAULO (BRAZIL) FOR THE PRESENCE OF METALS BY THE TECHNIQUE OF X-RAY FLUORESCENCE WITH SYNCHROTRON RADIATION

https://doi.org/10.56238/levv15n41-096

Submitted on: 09/25/2024 **Publication date:** 10/25/2024

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ABSTRACT
Ensuring the conservation of water reserves is a challenge for all humanity, which makes it essential to continuously study new forms of treatment and use of water sources on the planet. One of the focuses of water conservation and sustainability is the reuse of water sources in order to ensure the continuity of the main reserves of drinking water for watering and food production activities. The present research aimed to investigate the quality of the water used for reuse in the Pinheiros subway station in the city of São Paulo (Brazil) in order to evaluate the degree of presence of heavy metals and other chemical elements by the X-ray fluorescence technique by synchrotron radiation of the National Synchrotron Light Laboratory (LNLS). The data collection for a sample collected in the summer and analyzed revealed a pH of 6.8 and the presence of 19 chemical elements by the technique with concentrations in the order of $^{ng.mL^{-1}}$, with emphasis on the presence of lead (Pb).

Keywords: Water. Reuse. Sustainability. Water Economy.

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INTRODUCTION

Water resources are an important constituent for the existence of life. The survival of all living beings and their supply in quantity and quality is vital for the maintenance of humanity.

The reflection of the importance of drinking water sources can be noticed by the presence and development of ancient civilizations such as Egyptian, Babylonian and Greco-Roman. Since these peoples only prospered and developed thanks to nearby drinking water reserves in their territories.

According to Shiklomanov (1997), in quantitative terms, the total volume of water on Earth is constant and only 2.5% of it is made up of fresh water. However, of the 2.5% portion of fresh water, only 0.3% constitutes the surface portion of water present in rivers and lakes, which are subject to exploitation and use by humans.

Shiklomanov (1997) explained that when analyzed in qualitative terms, water is a molecule composed of hydrogen and oxygen capable of transporting biotic and abiotic substances and molecules from the earth's surface to rivers, lakes, oceans and aquifers, making them a point of concentration of the materials carried, such a characteristic gives water the title of universal solvent.

The vertiginous growth of the human population and the great upsurge of the industrial and technological sector led to an increasingly accelerated and massive demand for sources of clean water for public supply and as raw material for the primary and secondary sectors.

Due to the fact that surface reserves are constant and the great environmental impact generated by the misuse of water sources, which causes major environmental disasters with the rampant pollution of water bodies, it is important to study technologies and methodologies that aim to preserve drinking sources and consequently preserve life on the planet.

According to projections by the United Nations (UN) indicate that, if the trend of consumption and pollution persists, in 2050 more than 45% of the world's population will be living in countries that will not be able to guarantee the minimum daily quota of 50 liters of water per person (MELO JÚNIOR *et al.*, 2019).

OBJECTIVE

The purpose of the research was to evaluate the relationship of heavy metals and other chemical elements present in the reused water from the rainwater source, captured and stored in a well for use in general activities at the Pinheiros subway station in the city of

São Paulo, Brazil. Remembering that the use used in the place is varied, with the exception of potability.

For this study, the high-standard technology for synchrotron radiation was used thanks to the support of the National Synchrotron Light Laboratory (LNLS).

LITERATURE REVIEW

WATER RESOURCES IN BRAZIL

According to Lima (1999), due to the territorial dimension of Brazil, it presents great variations related to climate, geology, relief, vegetation and also water resources, economic and social development and population distribution.

Based on the distribution of surface waters, the Brazilian territory holds 13.7% of the fresh water of the globe. It should be noted that the surface reserves of fresh water on the planet are only 0.3% (MARTINS, 2003).

Most of Brazil's surface freshwater reserves are 73% (of the 13.7% in global reserve) in the northern region of the Amazon basin, which is inhabited by less than 5% of the Brazilian population (LIMA, 1999).

On the other hand, only 27% of Brazilian surface water resources are available to the other regions, where 95% of the country's population resides (LIMA, 1999).

Poor water distribution causes problems and possible supply crises in the centers of greatest demand, and the problems are greater in hydrographic basins where water withdrawals exceed water availability, which forces the population to seek alternative sources of water. In this context, the basins close to large urban centers are the most affected, in addition to having the aggravating factor of compromising water quality due to uncontrolled urbanization, which causes an increase in treatment costs and restricts water use (ANA, 2005).

In rural areas, the main interferences with water resources are the destruction of permanent vegetation areas, the indiscriminate use of pesticides and fertilizers, and the poor disposal of animal and human waste. All these contaminants are carried by the water with soil particles or are deposited directly in surface water sources (GONÇALVES, 2003).

According to Gonçalves (2003), one of the great limitations of crop productivity is the supply of water. Thus, the use of technologies aimed at crop irrigation increases more and more and with it comes greater water consumption, an increase in the number of dams, reservoirs, river exploration and even groundwater. In addition, in agriculture, water waste is very large, especially in crop irrigation, when furrow or flood systems are used. In this way, in quantitative terms, agriculture becomes the great user of water resources.

According to Shiklomanov (1997), on average, the agricultural sector uses 70% of the total fresh water consumed, followed by industrial (20%) and water for supply (10%).

Concomitantly, the acquisition of inputs such as fertilizers and pesticides has increased significantly, which are considered essential products to obtain high productivity ceilings. However, the massive use of these inputs can have serious consequences for the environment and for man himself, and can cause the contamination of both terrestrial and aquatic resources (LIMA, 1999).

Thus, according to Von Sperling (2000), agriculture has become a major source of diffuse pollution of surface waters, due to the use of the soil without respecting its capacity to support and simplify production, through the adoption of technological packages.

ADVANCES IN ENVIRONMENTAL LEGISLATION

In Brazil, in 1930, the Head of the Provisional Government of the Republic of the United States of Brazil, using the powers conferred on him by Decree No. 19,398, of 11/11/1930, and, on July 10, 1943, through Decree No. 24,643, establishes the Water Code. Among the formulations of the legislation, there is the Treaty on Environmental Education for Sustainable Societies and Global Responsibility, presenting 16 principles, among which principle 16 stands out, described below: Principle 16 - Environmental education should help develop an ethical awareness of all forms of life with which we share this planet, respect their life cycles and impose limits on the exploitation of these forms of life by human beings. By signing this Treaty, the organizations set out to program twenty-two essential guidelines, and agreed, among other things, to disseminate and promote in all countries the Treaty on Environmental Education for Sustainable Societies and Global Responsibility through individual and collective campaigns, promoted by NGOs, social movements and others (MARTINS, 2003).

In Brazil, Law No. 9,433/97, known as the Water Law, completes 22 years in 2019 and brought advances in the field of national water resources management, such as the preparation of the National Water Resources Plan (PNRH), approved in 2006 (MARTINS, 2003).

WATER REUSE

As reported by Cetesb (2023), the reuse or reuse of water or the use of wastewater is not a new concept and has been practiced around the world for many years. There are reports of its practice in Ancient Greece, with the disposal of sewage and its use in irrigation. However, the growing demand for water has made the planned reuse of water a current and important topic.

In this sense, water reuse should be considered as part of a broader activity that is the rational or efficient use of water, which also includes the control of losses and waste, and the minimization of effluent production and water consumption (CETESB, 2023). Within this perspective, treated sewage plays a fundamental role in the planning and sustainable management of water resources as a substitute for the use of water for agricultural and irrigation purposes, among others.

Types of Reuse

According to CETESB itself (2023), water reuse can be direct or indirect, resulting from actions planned or not by the responsible sector. It is important to differentiate each type of reuse water.

Unplanned indirect water reuse

This process occurs when water, used in some human activity, is discharged into the environment and used again downstream, in its diluted form, in an unintentional and uncontrolled manner. Walking to the point of capture for the new user, it is subject to the natural actions of the hydrological cycle (dilution, self-purification).

Planned Indirect Water Reuse

This type of reuse occurs when the effluents, after being treated, are discharged in a planned manner into surface or groundwater bodies, to be used downstream, in a controlled manner, to meet some beneficial use. The planned indirect reuse of water presupposes that there is also control over any new effluent discharges along the way, thus ensuring that the treated effluent will only be subject to mixtures with other effluents that also meet the quality requirement of the targeted reuse (CETESB, 2023).

Planned direct reuse of water

In this type of reuse, its use process occurs when the effluents, after being treated, are sent directly from their point of discharge to the place of reuse, not being discharged into the environment. It is the case with the highest occurrence, intended for use in industry or irrigation (CETESB, 2023).

X-RAY FLUORESCENCE

Kneip and Laurer (1972) describe the advantages of energy-dispersive X-ray fluorescence over wavelength scattering. Initially, quantitative analysis with XRF required many standards, for the construction of system calibration curves or for calculations of the so-called alpha coefficients.

The alpha coefficients are constant correction factors and at least **n-1** standards are required ; where **n** is the number of elements present in the sample (KNEIP and LAURER, 1972)

This method is based on corrections that are made 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 the intensity of fluorescent radiation in terms of fundamental physical parameters and instrumental parameters. The method is simple and does not require a large number of patterns, making it currently one of the most used and widespread methods in terms of XRF.

Fluorescence of synchrotron radiation by total reflection (TXRF)

Yap *et al.* (1989), used total reflection X-ray fluorescence for the analysis of fine samples of mineral sand.

The total reflection X-ray fluorescence method was tested with certified rock samples (JB-3J). They evaluated that the method has some advantages, namely: multi-elementary; with simplified sample preparation; contribution of scattered radiation and the need for small amounts of digested samples, about 2 ml, for the analysis.

Chen *et al.* (1990), showed that synchrotron radiation sources have important characteristics for the analysis of materials, mainly due to 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.

Salvador (2003) 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 element concentrations 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 an 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 to be able to establish the ideal experimental conditions that lead to complete agreement between TXRF and PIXE.

METHODOLOGY

CASE STUDY

The research was based on analyzing the reused water of the Pinheiros subway station located in the city of São Paulo, Brazil.

Figure 1 shows a visualization of the station's location.

Figure 1: Overview of the Pinheiros subway station.

The region covered by figure 1 (above) has the fundamental characteristic of being a region of great importance and mass circulation of people. The Pinheiros station has an average flow of 60 thousand passengers per day. It is also an important transport exchanger, with access to the Metro and the Companhia Paulista de Transporte Metropolitano (CPTM).

Line 4 (see figure 1) that corresponds to the study line, called the yellow line, has about 13 km of route with 11 stations allocated along the route.

The station has the process of capturing the local rainwater network in order to use rainwater for general activities within its facility, that is, the use of a rainwater reuse system in order to minimize costs and allow a process of local sustainability.

Thus, the research aimed to verify the quality of the water in relation to the levels of heavy metals and other chemical elements present by the synchrotron radiation technique.

An aliquot of 500 mL of reused water from the location of interest of study was taken for analysis in scientific research. The sample was collected in the Brazilian summer period and frozen for its multielemental analysis and acidity/alkalinity degree.

SYNCHROTRON RADIATION ANALYSIS BY TOTAL REFLECTION

The research project included an analysis of the elemental chemical concentration present in a sample of reused water from rainfall in the location of interest of the study (figure 1).

The sample aliquot was 500 mL, and it was previously frozen at -50C to preserve its initial characteristics.

The technique adopted was carried out at the National Synchrotron Light Laboratory (LNLS), in Campinas, by the process of total reflection using synchrotron radiation, which allows a multi-element analysis of the chemical compounds present in bottled rainwater, without the need to destroy the samples by acid action. Such a process allows a clearer and more concise analysis of the concentration and a wider spectral range of analysis by the adopted radiation beam.

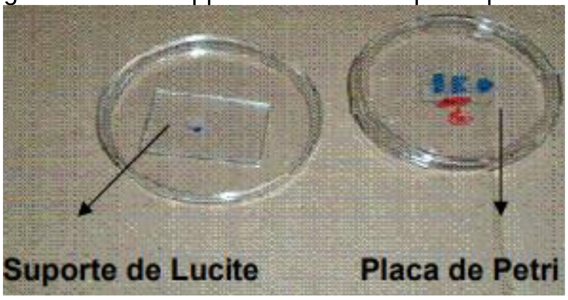
Synchrotron Radiation with Total Reflection Metal Detection Tool

In the total reflection analysis, an aliquot of 1 mL of reused water (from the 500 mL bottle) was removed from the study and a 100 μL Gallium standard (102.5 mg. L-1) used as the internal standard, resulting in a concentration of 9.32 mg. L-1 in sample.

The internal pattern was used to eliminate the non-uniformity of the aliquot on the substrate, because the thin film formed on the substrate does not have a regular geometry. Thus, the intensity of the X-rays obtained in the irradiation of the sample depends on the position in which it was placed on the support, as reported by Melo Júnior (2007). With the addition of the internal standard, the result obtained will always be in relation to this standard, regardless of the position of the sample (MELO JÚNIOR, 2007).

At the end of the preparation, 5.0 μL of the resulting solution was then pipetted under a lucite plate and dried with the aid of an infrared lamp the sample, as shown in figure 2.

Figure 2: Lucic support used for sample deposition.



Synchrotron Radiation Line Installations – Total Reflection Technique

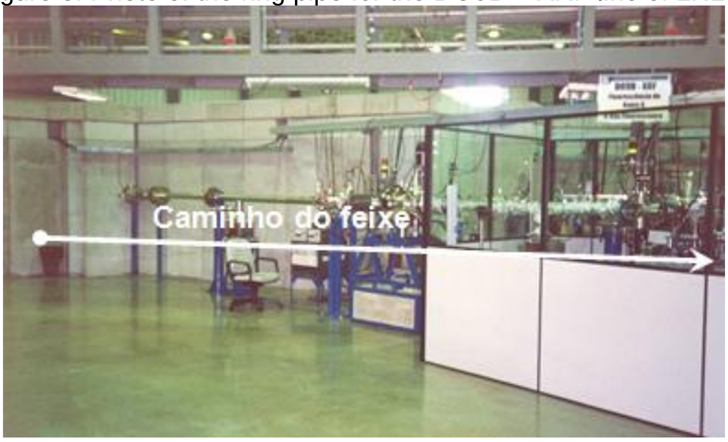
The synchrotron radiation line for total reflection is intended for the analysis of multielemental chemical composition (Z ≥ 13) in scientific applications of trace element determination in environmental, biological and material sciences, thin film chemical depth profiling and chemical mapping. It operates with a beam from 4 to 23 KeV, in table 1 other characteristics of the line can be seen (MELO JÚNIOR, 2007).

Table 1 - General Characteristics. Source: National Synchrotron Light Laboratory. www.lnls.br (2023).

Source	Deflector magnet D09B(15º), σy = 0.222 mm, in-sample flux: 4 x 109 photons/s at 8 keV.
Monochromator	Channel-cut *monochromator.*
Crystals	Si (111) (2d=6.217 Aº): 4-14 keV (E/ΔE=2800); Si (220) (2d=3.84 Aº): 5-23 keV (E/ΔE=15000).
Detectors	Solid-state detectors of hyperpure Ge (150 eV resolution) and Si(Li) (165 eV resolution); photodiodes and ionization cameras.
Optics	Capillary optics with 20 μm spatial resolution.
Sample handling	Vacuum chamber (2-10 mbar) with conventional excitation geometry (45º - 45º). Stations for grazing incidence and 2D mapping experiments, both with full control of sample positioning.

Figure 3 shows the pipe of the DO9B – XRF line, used in the experiment, through which the synchrotron light beam passes from the ring to the fluorescence experimental station located at LNLS.

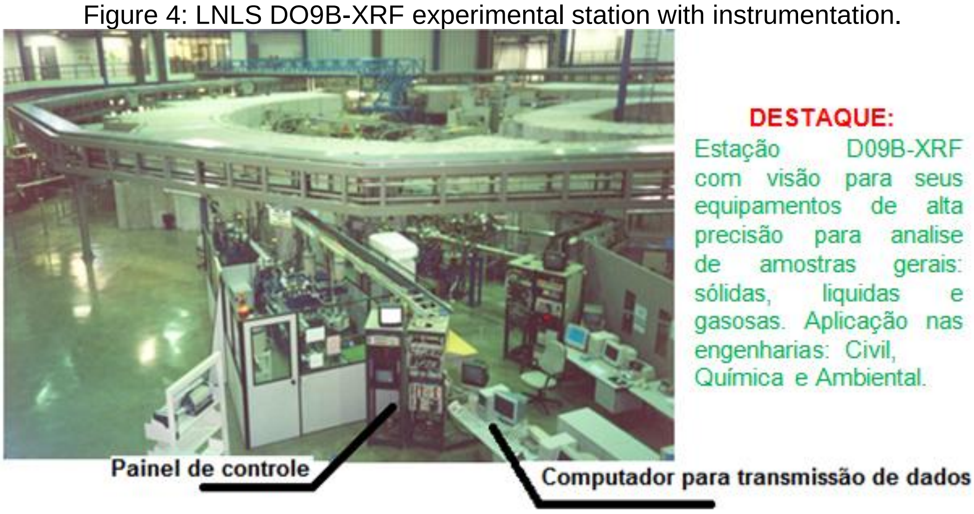
Figure 3: Photo of the ring pipe for the DO9B – XRF line of LNLS.



In the X-ray fluorescence experimental station (figure 3), a hyperpure Ge semiconductor detector with an 8 m thick beryllium windowμ, an active area of 30 mm2, coupled to an amplifier module and a multichannel analyzer board, inserted in a microcomputer, was used for the detection of X-rays.

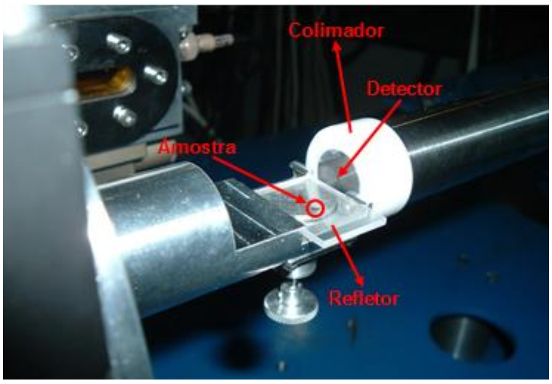
Figure 4 shows station D09B-XRF and a partial view of the radiation ring.

Figure 4: LNLS DO9B-XRF experimental station with 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 to the rectangular lucite plate (*Perspex*) fixed in the sample holder, allowing the measurement of the chemical elements contained in the sample. Figure 5 shows in detail the rainwater sample (reuse) deposited on the reflector and the detector with the collimator. It is important to highlight that for statistical purposes, triplicates were made from the same sample for a better accuracy of the data captured by the technique.

Figure 5: Experimental arrangement of the SR-TXRF.



PH ANALYSIS

Care was taken to analyze the degree of acidity/alkalinity of the sample that was the focus of the research.

For this purpose, a conventional pH meter was used, and the PH-127 Digital model from Conteck was adopted.

This meter is widely used in swimming pools and due to its practicality and low cost, it was chosen for use in Unicamp's partner laboratories with LNLS.

RESULTS

MULTI-ELEMENT ANALYSIS

Analysis by the Synchrotron Radiation Technique – Validation

To ensure that the detected values are reliable, a characteristic curve with defined patterns was constructed. Thus, a degree of reliability was obtained to later evaluate the samples collected.

The elemental sensitivity was calculated using five standard solutions with known elements and in different concentrations, plus the element gallium (Ga) used as the internal standard. For this purpose, the range for this pattern curve is called the K series.

The determined values of the experimental sensitivity for the elements contained in the solutions and the results obtained are presented in Table 2, below.

Table 2 - Experimental sensitivity for the K series.

Atomic number	Chemical element	Sensitivity
19	K	0,083270
20	Ca	0,086387
22	Thee	0,199891
24	Cr	0,393820
26	Fe	0,593576
28	Nu	0,796228
30	Zn	0,897568

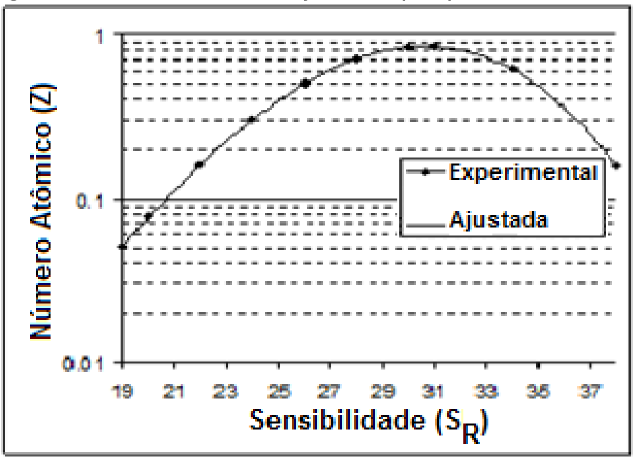
31	Ga	0,975819
34	If	0,809614
38	Mr	0,306673

Reliability Curve

Using the data obtained from table 2, the reliability degree curve was raised from a characteristic graphic curve, called the relative sensitivity curve for series K. Figure 6 (below) shows the characteristic reliability curve for the elements in the range of interest of the study.

Such a curve is important to align the error deviation and reflect on the accuracy of the analyses and ensure the reliability of the analyzed data.

Figure 6: Relative sensitivity curve (SRi) for the K series.



The sensitivity curve presented in figure 6 initially allowed the use of certified samples with known values. This made it possible that when using the same energy beam in the sensitivity curve for the certified samples, the values were close to the pre-defined ones, thus allowing the collected and analyzed samples to have their values really within reality without detection errors.

Default Adjustment by NIST

The adjustment was made to a standard certified by the *National Institute of Standards and Technology* (NIST).

Table 3 shows the samples certified by NIST for the standard called Drinking *Water Pollutants*, with the values measured at LNLS and those certified by NIST, respectively.

Table 3 - Comparison of the values measured in LNLS and certified by NIST.

Element	Measured Value and Confidence Interval (mg. L-1)	Certified Value and Confidence Interval (mg. L-1)
Cr	8.91 ± 0.18	8.89 ± 0.45
The	8.66 ± 0.17	8.77 ± 0.45
If	4.87 ± 0.07	4.69 ± 0.23
CD	4.55 ± 0.64	4.54 ± 0.23
Ba	89.99 ± 0.76	91.89 ± 4.55
Pb	10.03 ± 1.01	10.09 ± 0.45

Results surveyed from the rainfall sample

Only after this validation of the system was the dry rainwater sample used in the lucite plate, in which the average concentrations of the measured chemical elements can be evaluated by table 4.

Table 4 - Average concentration ($^{ng.mL-1}$) of the elements present in the rainfall sample.

Chemical Element Symbol	Concentration ng.mL-1
Al	126,40
S	140,00
Cl	372,70
K	16,80
Ca	738,50
Thee	1,60
Cr	19,60
Mn	13,00
Fe	118,50
Co	0,60
Nu	0,80
Ass	29,95
Zn	679,60
The	2,20
If	0,70
Br	1,30
Mr	2,32
Hg	10,50
Pb	35,90

The values found of the elements in table 4 make it possible to verify the degree of water quality. It can be noted that the presence of concentrations of lead (Pb), chromium (Cr) and mercury (Hg) among the others reflects the study locality that has a high level of hydrocarbon combustion motor vehicles that emit these compounds into the air, being "washed" from the local air by rain and stored in reuse water.

PH ANALYSIS

Thanks to the use of Conteck's PH-127 Digital pH meter. It was possible to measure the average pH value of the collected rainwater, which revealed an average pH of 6.8. This showed a slight acidity of the stormwater studied in question.

The values found in table 4 (above), as well as the pH values, showed an acceptable reuse water quality value for general activities that do not involve: human thirst, bathing or use in fruit and vegetable foods; since there is no data on the presence and concentration, for example, of fecal coliforms from rainwater that is stored in a rainwater reserve containment tank at the Pinheiros station.

It should also be taken into account that the sample was a one-off collection, which does not reflect the quality of the water over a longer temporal amplitude.

CONCLUSION

The research had an important focus because it further disseminated the use of a refined and high-tech technique used in the scientific field. However, the fact of using only one rainwater collection cannot be generalized and ensure that the water quality is the same throughout the year.

As implications, there is the fact of the need for collections on more days of the week, as well as during the climatic seasons, especially in the summer and winter, which has the lowest distribution of rain and consequently a greater accumulation of contaminant levels in the winter period in dissonance with the Brazilian summer. This implication is due to the high concentrations of compounds from automotive combustion in the atmosphere, which are more prominent in winter.

If there were collections in this period of winter, it would be very interesting to verify the dissolved levels in the reused water at the time of "washing" the elements dispersed in the atmosphere.

But the research had the merit of the concern in researching and studying the quality of reused water that is of great importance, showing a significant evolution in the environmental concern of the São Paulo government sector and a clear evolution of the goals of the United Nations (UN) for 2050 in relation to water preservation.

Another fact that can be raised is the continuous need to change the energy matrix, especially the terrestrial network represented by the vehicle sector, with the adoption of new practices that minimize the automotive concentration in regions such as the one studied, which reflects the presence of toxic and harmful chemical elements to humans, especially lead (Pb) and mercury (Hg) detected.

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