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Ions and Metals in Polystyrene Samples by X-Ray Fluorescence Technique

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1. Introduction

Nowadays, marine pollution caused by several sources of plastic polymers is a significant issue, primarily due to inadequate disposal of urban waste. Pollution from disposable and other types of plastic has become a major environmental concern in aquatic environments. The lack of effective disposal management raises serious concerns about the ecosystem's quality on a global scale. Plastics are now one of the most common and persistent pollutants in ocean waters and beaches worldwide, causing significant harmful effects on marine biota [1]. The composition of these plastics mainly includes polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS), polyvinyl, and metals (associated pigments color). The marine environment is impacted in various ways, including increased costs for water treatment, fish mortality, and changes in food chains. In extreme cases, diseases can emerge among seafood-consuming inhabitants due to contaminants accumulating on the surface of plastics, such as persistent organic pollutants, or due to toxic additives in the plastic composition that provide characteristics like color, thermal resistance, and flexibility [2]. This study focuses on characterizing plastics in the marine environment. The objective is to analyze ions and metals in polystyrene samples exposed in the Jurujuba region (Baía de Guanabara, Rio de Janeiro) for different periods (4, 8, and 12 weeks) using the Energy Dispersive X-Ray Fluorescence (EDXRF) analytical technique. This analysis will help identify toxic metals present in the polymer composition as well as metals adsorbed on the plastic surface, contributing to defining measures to address this issue.

2. Methodology

The samples of polystyrene (PS), acquired commercially, were exposed in the Jurujuba (Baia de Guanabara, RJ), a region with many fishing boats, forming a eutrophic environment. The polystyrene samples (in triplicate) were divided into three groups:

I. Standard (sample available commercially)
II. Control (sample exposed only to ultra-pure water, in the dark with a controlled temperature of 25 degrees)
III. Exposed samples in Jurujuba (Baía de Guanabara, RJ)

The Energy Dispersive X-Ray Fluorescence (EDXRF) [3] measurements were performed using a compact X-Ray spectrometer (X-123SDD X-ray Spectrometer, Amptek®) constituted by a Silicon Drift Detector (25 mm^2 x 500 µm, with Be window of 12.5 µm) coupled a mini X-ray tube (Ag). The X-ray characteristics intensities (K_α lines) measured with 30 kV and 5 µA excitation using a counting time of 300 s. The analysis was carried out using software provided by Amptek ® [4].

3. Results and Discussion

The data for the Polystyrene standard (available commercially) are presented in Table 1 and the data for the exposed samples (4, 8, and 12 weeks) in Jurujuba (Baía de Guanabara, RJ) are presented in Table 3 and 4, respectively. The control data were included in tables 2, 3 and 4 for comparison. All the results are expressed by mean value (MV) and standard deviation (±1SD).

Table I. Concentrations results in polystyrene samples by EDXRF.

Polystyrene standard	
Elements	MV ± 1SD, mg/g
P	5.06 ±0.25
S	3.66 ± 0.26
Cl	9.48 ± 0.38
Ca	9.05 ± 0.45
Cr	1.40 ± 0.28
Fe	2.65 ± 0.27

Table II. Concentrations results in polystyrene samples by EDXRF for exposition time of 4 weeks.

Polystyrene	**Control - 4W**	**BG - 4W**
Elements	MV ± 1SD, mg/g	
P	1.22 ± 0.06	3.37 ± 0.17
S	2.22 ± 0.16	3.11 ± 0.22
Cl	20.4 ± 0.8	8.27 ± 0.33
Ca	3.62 ± 0.18	7.40 ± 0.37
Ti	0.89 ± 0.07	2.59± 0.21
Cr	0.76 ± 0.15	1.72 ± 0.34
Mn	nd	1.51 ±0.23
Fe	1.52 ± 0.15	3.33 ± 0.33
Br	0.67 ±0.11	nd

nd: not determined.
BG: Baía de Guanabara

Table III. Concentrations results in polystyrene samples by EDXRF for exposition time of 8 weeks.

Polystyrene	**Control - 8W**	**BG - 8W**
Elements	MV ± 1SD, mg/g	
P	1.59 ± 0.08	nd
S	2.21 ± 0.15	0.24 ± 0.02
Cl	16.7 ± 0.7	3.47 ± 0.14
Ca	4.21 ± 0.21	7.40 ± 0.37
Ti	1.10 ± 0.09	0.19 ± 0.02
Cr	1.01 ± 0.20	3.18 ± 0.64
Mn	0.59 ± 0.09	1.19 ± 0.18
Fe	2.34 ± 0.23	23.1 ± 2.3
Br	1.58 ± 0.25	nd

nd: not determined
BG: Baía de Guanabara

Table IV. Concentrations results in polystyrene samples by EDXRF for exposition time of 12 weeks.

Polystyrene	**Control - 12W**	**BG - 12W**
Elements	MV ± 1SD, mg/g	
P	3.15 ± 0.16	0.37 ± 0.03
S	2.08 ± 0.17	1.16 ± 0.52
Cl	9.35 ± 0.47	7.48 ± 0.30
Ca	6.95 ± 0.35	2.18 ± 0.11
Ti	0.83 ± 0.22	0.18 ± 0.03
Cr	0.95 ± 0.05	0.31 ± 0.03
Mn	0.61 ± 0.22	6.09 ± 0.91
Fe	3.80 ± 0.19	11.8 ± 1.2
Zn	nd	0.11 ± 0.05
Br	3.45 ± 0.17	1.64 ± 0.26

nd: not determined
BG: Baía de Guanabara

The presented results highlight important points in the composition of the polystyrene polymer, where the presence of chromium was found. Chromium is potentially toxic to organisms, affecting ion homeostasis, causing oxidative damage, inhibiting reproduction, and possibly bioaccumulating in marine organisms. These results increase the risks of bioconcentration and bioaccumulation along the food chain, affecting heavily top predators. In relation to algae, chromium can inhibit photosynthesis and growth. In invertebrates, it can affect larval development, reproduction, and the survival of crustaceans and marine mollusks. In fish, it can cause damage to the respiratory system, liver, kidneys, and affect behavior and reproduction. In marine mammals, it can accumulate and cause reproductive, neurological, and developmental problems [5]. We observed in the results of polymers exposed to environmental conditions in Baía de Guanabara changes in concentration not only of chromium but also of other potentially toxic metals, such as iron and manganese. Chromium and Iron both presented a higher concentration at 4W in comparison with 8W, this can be attributed to temporary or punctual contamination, increasing the concentrations of these metals at a certain moment, or by the desorption of these metals due to changes in the physicochemical parameters of the water.

Both iron and manganese are essential micronutrients for marine life, playing a crucial role in photosynthesis, cellular respiration, and other physiological processes. However, an excess of these elements can be harmful to marine organisms in various ways. The toxicity of these elements may be even greater in reducing conditions of high salinity and temperature and low oxygen, conditions commonly found in Baía de Guanabara.

4. Conclusion

These data constituted the first qualitative-quantitative estimate of the polystyrene samples. They were able to introduce improvements in the investigation of marine pollution, mainly with regard to toxicity, in the region of Jurujuba (Baía de Guanabara, Rio de Janeiro). These findings suggested that polymeric plastics, under environmental conditions, could act as vectors, accumulating pollutants from the most polluted ecosystems to other ecosystems or bioaccumulating in animals that could actively or passively ingest this material.

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