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

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Abstract: Plastics are one of the most common and persistent pollutants in ocean waters and beaches worldwide, causing harmful effects on marine biota. The composition of these plastics mainly includes polyethylene (PE) and polystyrene (PS). The marine environment is impacted in various ways and, in extreme cases, diseases can emerge among seafood-consuming inhabitants due to contaminants (such as the toxic additives) in the plastic composition. Specifically, the objective of the present investigation is to analyze ions and metals in PE and PS samples exposed in the Jurujuba region (Baía de Guanabara, Rio de Janeiro, Brazil) for different periods using the Energy Dispersive X-Ray Fluorescence (EDXRF) analytical technique. This analysis will help identify toxic metals present in these polymer compositions as well as metals adsorbed on the plastic surface, contributing to defining measures to address this issue. 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 Celsius; III) Exposed samples in Jurujuba (Baía de Guanabara). This study is part of a larger research project "Strengthening capacities in Marine and Coastal Environments using nuclear and isotopic techniques" (IAEA/ARCAL: RLA7025). These results emphases the toxicity of marine pollution and show that PE and PS polymers can act as carriers of pollutants between ecosystems.

Keywords: microplastics, EDXRF, chemical elements, marine biota.

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Íons e Metais em amostras de Poliestireno pela Técnica de Fluorescência de Raios X

Resumo: Os plásticos são um dos poluentes mais comuns e persistentes nas águas oceânicas e nas praias de todo o mundo, causando efeitos nocivos na biota marinha. A composição destes plásticos inclui principalmente o polietileno (PE) e o poliestireno (PS). O ambiente marinho é afetado de várias formas e, em casos extremos, podem surgir doenças entre os seres vivos que consomem frutos do mar devido a contaminantes (como os aditivos tóxicos) presentes na composição do plástico. Especificamente, o objetivo da presente investigação é analisar íons e metais em amostras de PE e PS expostas na região de Jurujuba (Baía de Guanabara, Rio de Janeiro, Brasil) por diferentes períodos, utilizando a técnica analítica de Fluorescência de Raios X por Dispersão de Energia (FRXDE). Essa análise ajudará a identificar metais tóxicos presentes nessas composições poliméricas, bem como metais adsorvidos na superfície dos plásticos, contribuindo para a definição de medidas de combate a esse problema. As amostras (em triplicata) foram divididas em três grupos: I) Padrão: amostra disponível comercialmente; II) Controle: amostra exposta apenas à água ultrapura, no escuro com temperatura controlada de 25 graus Celsius; III) Amostras expostas em Jurujuba (Baía de Guanabara). Este estudo faz parte de um projeto de investigação mais vasto “Reforço das capacidades em ambientes marinhos e costeiros utilizando técnicas nucleares e isotópicas” (IAEA/ARCAL: RLA7025). Estes resultados enfatizam a toxicidade da poluição marinha, e mostram que os polímeros PE e PS podem atuar como transportadores de poluentes entre ecossistemas.

Palavras-chave: microplásticos, FRXDE, elementos químicos, vida marinha.

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 disposale and other types of plastic has become a major concern in aquatic environments. The lack of effective disposal management raises serious concerns about the ecossystem'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 resistante, 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 absorbed on the plastic surface, contribuiting to defining measures to address this issue.

2. MATERIALS AND METHODS

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

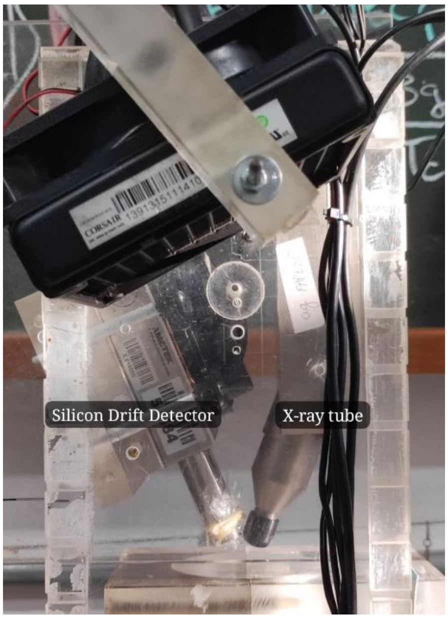
I. Standard (sample available commercially).

II. Control (sample exposed only to ultra-pure water, in the dark with a controlled temperature of 25 degrees Celsius).

III. Exposed samples in Jurujuba (Baía de Guanabara, RJ)

The Energy Dispersive X-Ray Fluorescence (EDXFR) [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) (Fig. 1). The X-ray characteristics intensities (Kα lines) measured with 30 kV and 5 µA excitation using a counting time of 200 s. The analysis was carried out using software provided by Amptek ® [4].

Figure 1: XRF Spectrometer



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3. RESULTS AND DISCUSSIONS

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 Tables, 2, 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 1 : 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 2 : Concentrations results in polystyrene samples by EDXRF for exposition time of 4 weeks (4W).

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	0.60 ± 0.11	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 3 : Concentrations results in polystyrene samples by EDXRF for exposition time of 8 weeks (8W).

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	nd
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 4: Concentrations results in polystyrene samples by EDXRF for exposition time of 12 weeks (12W).

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 (Cr) 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 (Figure 2) but also of other potentially toxic metals, such as iron and manganese (Figures 3 and 4, respectively). Chromium and iron both presented a higher concentration at 8W in comparison with 4W (Figures 2 and 3, respectively), 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.

Figure 2: Concentrations results in polystyrene samples for Cr. The control data were included for comparison.

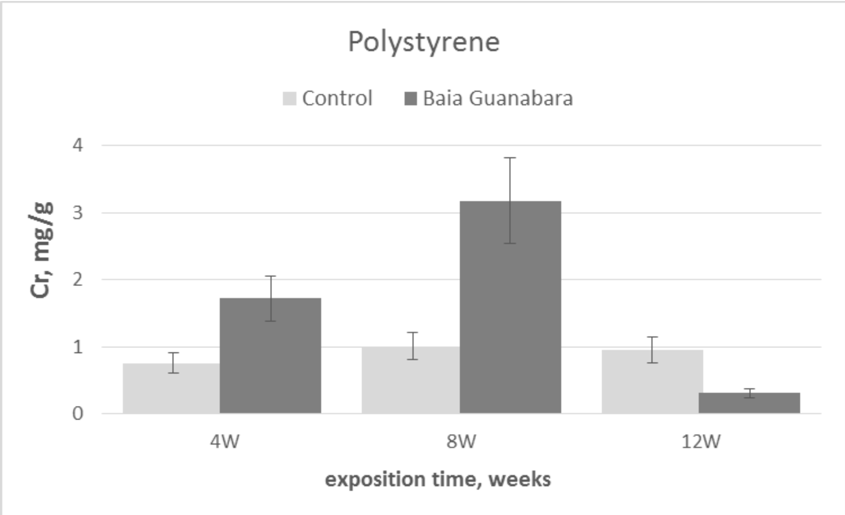


Figure 3: Concentrations results in polystyrene samples for Fe. The control data were included for comparison.

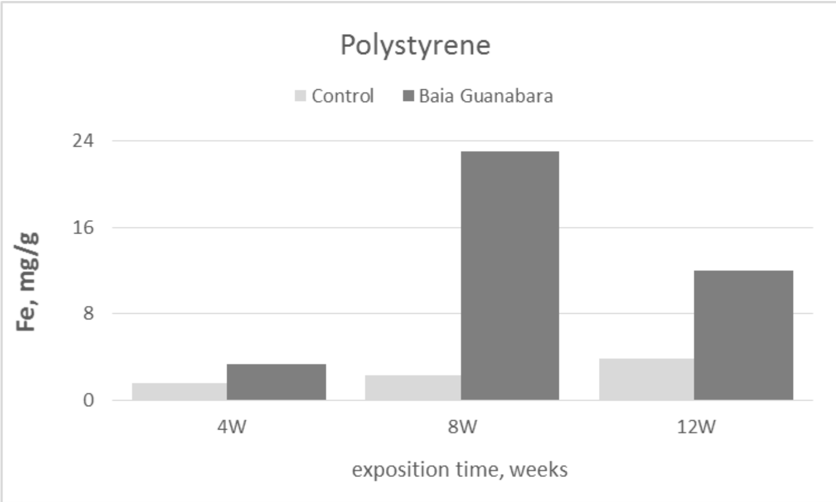
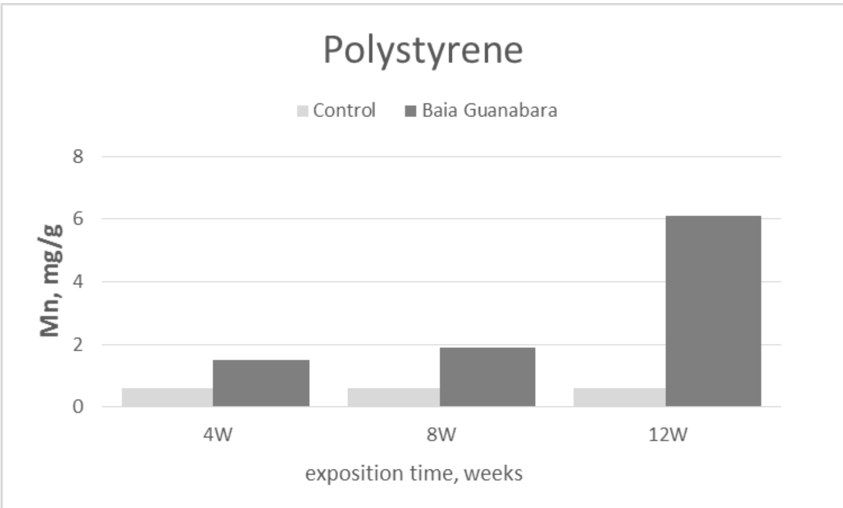


Figure 4: Concentrations results in polystyrene samples for Mn. The control data were included for comparison.



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. CONCLUSIONS

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 regarding toxicity, in the region of Jurujuba (Baía de Guanabara, Rio de Janeiro-Brazil). 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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CONFLICT OF INTEREST

All authors declare that they have no conflicts of interest.

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