

Evaluation of the presence of Bisphenol A and microplastics in the bottom sediments of Guanabara Bay.

Santos ADO^{1, 2}, Nascimento MTL^{1, 2}, Carvalho DG¹, Baptista Neto JA¹, Bila DM².

¹Departamento de Geologia/Instituto de Geociências da Universidade Federal Fluminense, Av. General Milton Tavares de Souza, Campus da Praia Vermelha, 24210346 Niterói, Rio de Janeiro, Brasil

²Department of Sanitary and Environment Engineering, State University of Rio de Janeiro, 524 São Francisco Xavier Street, room 5029-F, 20550-900 Rio de Janeiro, Brazil.

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Presenting author: danielbilauerj@gmail.com

Abstract

Environmental contamination is increasing and research on emerging contaminants becomes current and necessary. Research on potential risks of micropollutants in water bodies is relevant because of the wide use of the most varied substances, associated to factors such as the incorrect disposal of medicines; domestic and industrial sewage, agrochemicals, inefficiency of conventional treatment processes of sewage treatment plants, among others. In humans, the risks are associated with cancers, polycystic ovaries, reduction in sperm count. In animals the effects are masculinization, feminization, intersex conditions and until extinction of the species, even at low concentrations ($\mu\text{g/L}$ and ng/L) in the environment. The Guanabara Bay is one of the most important and polluted estuaries of the Brazilian coast. Thus, the objective of this study was to evaluate the occurrence of Bisphenol A and the incidence of microplastics in the bottom sediments of Guanabara Bay. The results indicated the occurrence of Bisphenol A in the range of 0.36 to 18.68 ng/g and 3 to 11 microplastic particles ($<5\text{ mm}$) per 50 cm^2 in the sediment samples.

Keywords: Bisphenol A, Microplastic, Endocrine disrupters, Guanabara Bay.

Introduction

Environmental degradation caused by human activities and intensified by industrial and urban development, resulted in high levels of pollution in the different environmental matrices. In this scenario, the contamination of water resources is directly affecting the quality of life of the population by exposure to various pollutants [1,2]. The inadequate waste disposal and sanitation associated with the intense exploration of water bodies has compromised its use especially in coastal areas near large industrial centers [3]. According to researchers, the deposition of waste in the seas has constituted a serious environmental hazard. [4].

Microplastics, due to their persistence in the environment and their migratory capacity, promote intense aquatic pollution. By the ocean currents, this contamination reaches sites much more distant of its initial point [5,6]. The use of plastic is great importance in modern society, because it is present in several products and used in human daily life.

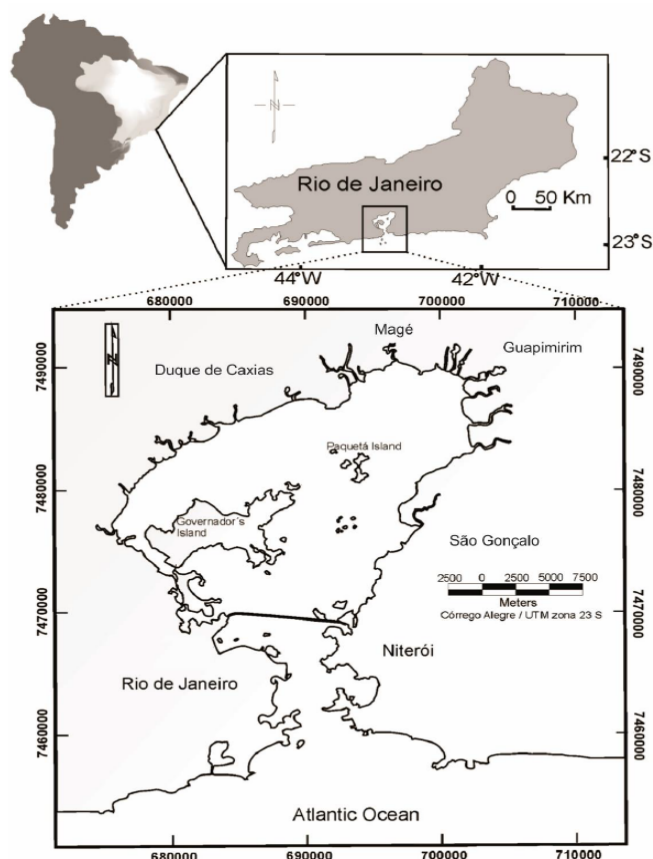
In addition, plastics contain chemical additives and absorb several organic pollutants, which could represent toxicological risks to marine organisms. The main plastic additives found in the environment are phthalates, bisphenol A (BPA), polybrominated diphenyl ethers (PBDEs), alkylphenol ethoxylates (APEs), these substances are considered as endocrine disrupters (EDC). Endocrine disrupter compounds (EDCs) are substances with capacity to alter the endocrine system's functions of humans and animal, affecting their growth and reproduction, as well as the evolution of diseases such as cancer, fertility disorders and abnormal sexual development. Despite the reported effects, the transport and fate of plastic additives leaching out from plastic debris in marine have been relatively few studied.

Contamination by microplastics in the marine environment drastically affects organisms. Especially small animals that ingest microplastics in their daily diet and can cause death [7]. Other animals that suffer from microplastic pollution are the mussels, since they are filtering organisms [8, 9]. Another important issue is the permeability of sand, which tends to increase in the presence of microplastics [9] influencing the size of the grains, which, when combined with other factors, can act negatively on the embryonic development of eggs of several organisms, such as crustaceans [11], molluscs [12], polychaetes [13] and fish [14].

Guanabara Bay is one of the most important estuaries of the Brazilian coast, known worldwide. It is inserted in the state of Rio de Janeiro, an area of great ecological and socio-economic relevance, which is subject to intense action of various pollution sources and numerous toxic pollutants. Currently, this estuary has been considered one of the most polluted environments of the Brazilian coast. This Bay receives large amounts of sanitary effluents, industrial, urban and agricultural waste, as well as leachate of municipal solid waste. Inserted in the center of the second Metropolitan Region of greater importance in Brazil, the Bay presents its water bodies quite deteriorated. Population growth associated with the extension of urban areas without adequate sanitary sewage has led to pollution by domestic sewage in the Bay, in addition to industrial effluents that discharge oil, heavy metals, toxic and organic substances in Guanabara Bay [15,16].

The aim of this study was to investigate the presence of BPA and distribution of microplastics in Guanabara Bay (Brazil) coastal sediments. Samples were collected from the bottom sediment of six sites of Guanabara Bay. Figure 1 displays the map of the study area.

Figure 1 Map of Guanabara Bay



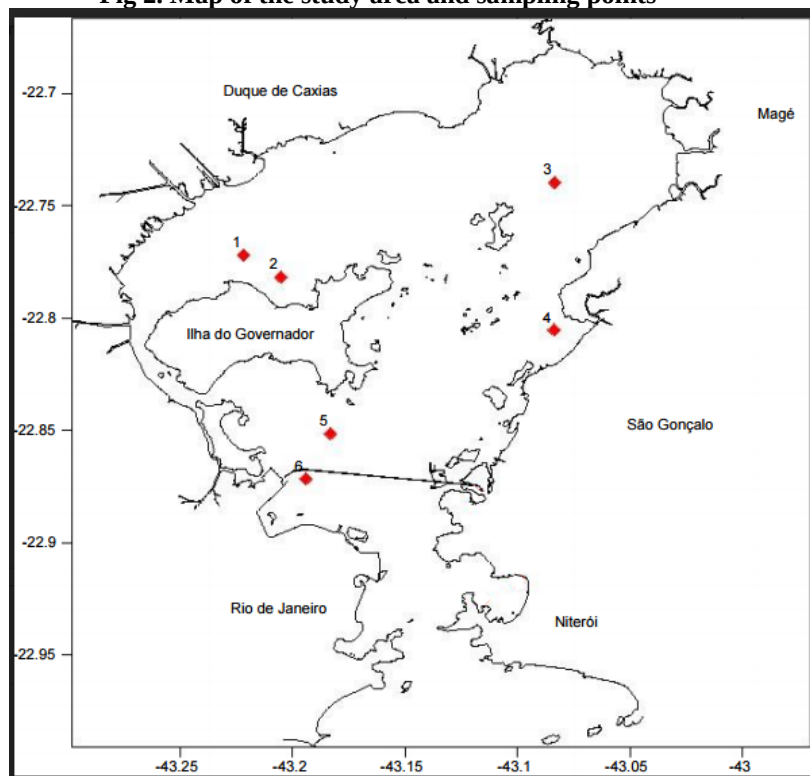
Materials and Methods

The sediment sample were collected with Van Veen dredge with capacity of 1 L, stored in an amber flask and kept at 4°C until the tests were carried out. Table 1 show the sampling sites characteristics.

Table 1. Sampling sites in the Guanabara Bay, Rio de Janeiro, Brazil

Station	Location	GPS coordinates
1	Ilha do Governador	22°46'19"S 43°13'17,9"W
2	Ilha do Governador – South West	22°46'53,9"S 43°12'18,6"W
3	Paqueta	22°44'22,7"S 43°5'00,1"W
4	São Gonçalo	22°48'19,0"S 43°5'1,2"W
5	Fundão	22°51'4,6"S 43°10'59,0"W
6	Portuária - Rio de Janeiro	22°52'17,3"S 43°11'38,4"W

Fig 2. Map of the study area and sampling points



For the determination of BPA, aliquots of 10g of dried sediment were extracted by 10mL of methanol in an ultrasonic bath for 5 min. To remove the supernatant, sample was subsequently centrifuged at 2500g for 5 min. This procedure was repeated 3 times, the supernatants were combined and extracted by solid phase extraction (SPE) using cartridges (StrataX, Phenomenex®). The extracts were acidified to pH 2 and percolated through the preconditioned cartridges. After elution, the extract was dried and resuspended in 500µL of acetonitrile and injected into the high-performance liquid chromatography using fluorescence detector (HPLC/FLU). HPLC analysis was performed on a Waters Breeze liquid chromatography system (Waters Corporation®), which comprises 1525 binary high-pressure pump and 2707 autosampler. A Waters 2475 multi-wavelength fluorescence detector was used for the quantitative detection. The BPA were analyzed by HPLC/FLU with mission wavelengths at 306nm and excitation at 280nm. The conditions of analysis were: 1mLmin⁻¹ mobile phase flow, gradient mode varying the percentage of acetonitrile (ACN) and ultrapure water, starting with 40% ACN, changing to 50%, 30% and 40% until the total running time of 8 minutes for analysis. The injected volume was 20µL with three replicates for each sample.

For the evaluation of the microplastics, 50cm² of the bottom surface of the Guanabara Bay was collected and the surface layer of approximately 1cm was removed for analysis. For quantification and qualification of the microplastics the sediment samples were prepared according to methodologies proposed by [17] and [18]. The supernatant was then collected and filtered using filter paper (47 mm) and

oven dried at 60°C. Samples were stored in petri dishes until analysis. For each sample, a volume of hypersaline solution (140g/L NaCl) 1.5-2-fold the sediment volume was added [17]. The contents were stirred for three to four minutes and remained at rest for sediment settling. After decantation of the sediment, the microplastics floated on the surface of the water and were collected. The sediment samples presented characteristics of a muddy sediment, with high concentration of organic matter, impairing the separation of the microplastics. Thus, 30% hydrogen peroxide (H₂O₂) was used for the removal of organic matter [18]. Subsequently, the supernatant was then collected and filtered using filter paper (47 mm) and dried at 60 °C. Microplastic particles were stored in petri dishes until quantification and qualification. The microplastics were divided according to their appearance, characteristics and possible origin in two categories: fiber and fragment. This process was performed manually using a stereomicroscope (Zeiss STEMI 2000 C) to perform the separation.

Results and discussion

Microplastic particles present in the bottom sediments collected at different stations of Guanabara Bay are shown in Table 2. Microplastics (<5mm) were found in all sediment samples. The depth of the collection sites ranged from 2.9 to 5.9 m. Microplastics concentrations in the sediment range of 3 to 11 particles per 50 cm².

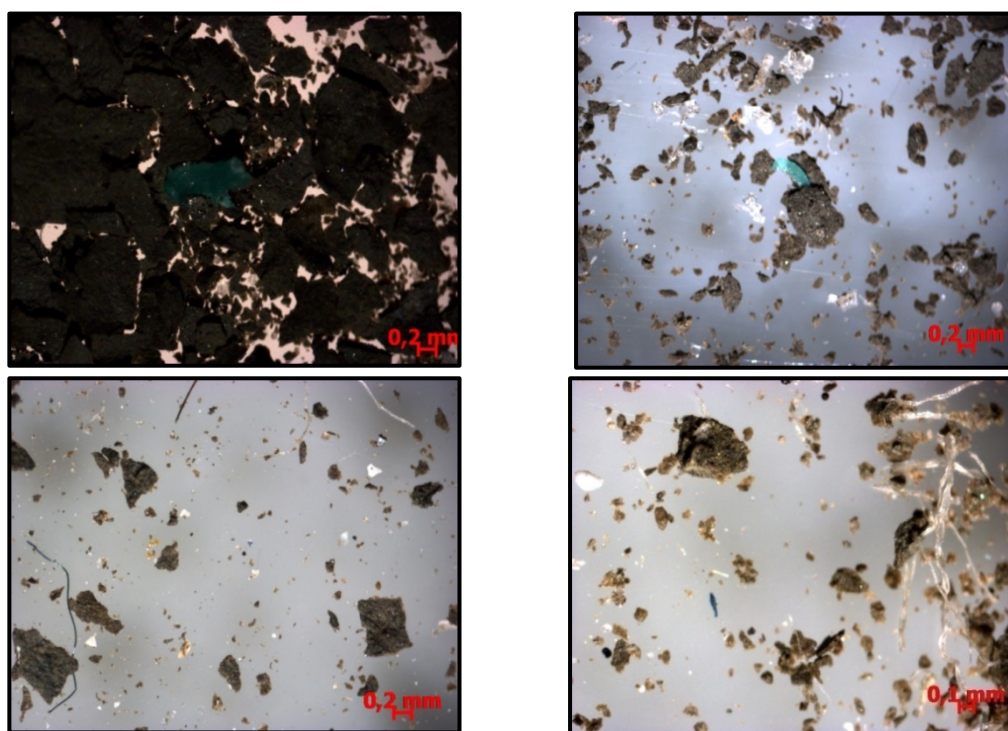
Table 2. Microplastic particles in sediment samples from Guanabara Bay

Station	Depth (m)	Microplastics	Fibers	Fragments
1	-	7	3	4
2	2,9	4	4	0
3	4,4	4	1	3
4	2,4	4	3	1
5	4,1	3	1	2
6	5,9	11	2	9

Microplastics particles were observed in fiber forms and fragments. In a study carried out with bottom sediments collected in several places of the world, an average abundance of 1 microplastic per 50 cm² was reported [20], demonstrating that in marine areas near the coast the concentration of microplastics is higher. The station 6 showed the highest concentration microplastic 11 microplastic particles per 50cm². This point is located near the Port Zone of Rio de Janeiro, a region impacted by effluents. In a study in the northeastern Atlantic Ocean, the microplastic particles and fibers were in 23 of the 30 samples collected from bottom sediment [17], indicating that the microplastics were transported from the water column to the sediments over the last decades.

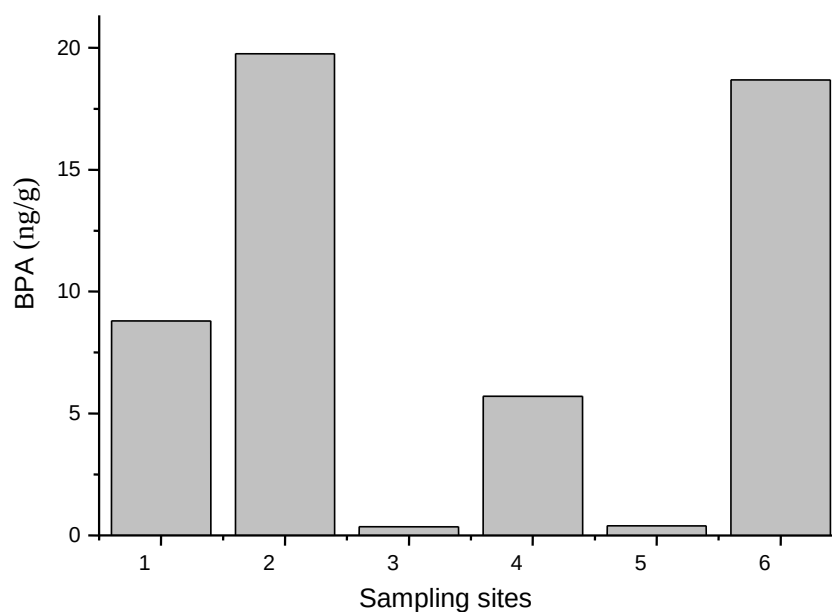
In the southern coast of Portugal, in the Algarve region, the presence of 31 microplastic particles was detected in a total of 27 sediment samples [21]. In the present study, all fragments of microplastics observed in the samples showed green coloration. From the areas at the bottom of the Guanabara Bay, close to the mangrove swamps, even in major areas such as Rio de Janeiro and Niterói. One hypothesis to explain the coloration of the fragments is that they originate from the degradation of the ropes and nets used by fishermen. In Algarve / Portugal, the microplastic fragments found were in the colors, blue and green [21]. Figure 3 shows photos of the microplastics present in the sediments collected in Guanabara Bay.

Figure 3. Microplastics collected in the sediments



The results showed the presence of BPA in all the sediment samples collected in Guanabara Bay, in the concentration range of 0.36 to 19.75 ng/g. The highest concentrations were observed in sediments collected at points BG2 and BG6 located near Ilha do Governador and port area of Rio de Janeiro, respectively. BPA concentrations were detected in sediment samples collected in the Daliao River in China in the range of 3.7 to 25.3 ng/g [22], in the Yangtze River sediments in the 1.2 to 6.5 ng/g range [23] and in the Bay of Biscay in Spain in the range of 0.01 to 0.04 ng/g [24]. Figure 4 shows the BPA concentrations in the bottom sediments collected in Guanabara Bay.

Figure 4. BPA concentration in bottom sediments



The deleterious effect of BPA on organisms in the marine environment may be higher than in freshwater due to the persistence of BPA in seawater (approximately 30 days) [25,26]. Large amounts of BPA containing material are continuously released into the environment, intensifying this persistence [27, 28, 29]. The microplastic concentration in the bottom sediments of Guanabara Bay is an alert about the contamination of this estuary. The potential for transport of toxic substances in microplastics, in addition to the chemical compounds present in the plastic, can be leached and affect marine organisms [30,31]. Table 3 summarizes studies that evaluated the effects of exposures of different species to microplastics, both in natural and laboratory conditions.

Table 3. Effects of exposures of different species to microplastics, both in natural and laboratory conditions.

Experiments	Goals	Results	References
Laboratorial exposure	Assess effects of polyethylene ingestion	After intake of particles with 0-80 µm, the effects observed: inflammatory response; granulocytomas	[32]
Laboratorial exposure	Assess the effects of 30 nm polystyrene particles (0, 0.1, 0.2, and 0.3 g/L)	Filtering activity was reduced in presence of polystyrene. When exposed to 0.1 g/L. The polystyrene was recognized as a low nutritional food by mussels.	[33]
Laboratorial exposure	Analyze of the Ingestion, translocation and accumulation of microplastics debris (3.0 or 9.6 µm	Microplastics accumulation in gut. Microplastics translocation from gut to circulatory system for 48 days.	[34]
Laboratorial exposure	Assess the presence of microplastics in soft tissues	0.36 ± 0.07 particles/g	[35]
Laboratorial exposure	Evaluation of the effects of microscopic unplastified polyvinylchloride (UPVC)	After a chronic exposure to a dose of UPVC, energy reserves depletion corresponding to 5% of sediment weight. Accumulation of UPVC in longer gut and inflammation with an enhanced phagocytic response after chronic exposure	[36]
Mediterranean Sea	Evaluation of phthalate levels	Presence of phthalates in bubbler (1.48 – 377.82 ng/g lipid basis).	[37]

Fonte: Adapted from [38]

According to Reis-Filho and Collaborators [39], the contaminants may be associated with certain particles becoming readily available to the ecosystem, undergo transformations leading to toxic forms, or migrate, via trophic chain, sediment for benthic organisms. Therefore, high levels of persistent contaminants in the sediment may have effects on the aquatic biota, depending on some factors that alter its bioavailability and toxicity [40].

Conclusion

The contamination by micropollutants and microplastics has caused concern, due to the damage cause to human health and the environment. BPA concentrations and microplastics detected in the bottom sediments of Guanabara Bay demonstrate that this estuary suffers with the release of pollutants. Most microplastics originate from chemical and mechanical fragmentation and plastics and larger debris. The smaller plastic fragments possibly originate from port activities, fishing, and local rivers.

This study showed the presence of BPA and microplastic particles in the bottom sediments collected in Guanabara Bay. The deleterious effects on animals are concern due to the concentration of

microplastics and their interaction with other chemical substances. Microplastics can absorb chemical pollutants and increase aquatic contamination.

The analyzes and methodologies were effective for the objective proposed in this study. For further studies it is suggested more sampling and other techniques of classification and characterization of microplastic particles, seasonal collections and other tests that provide different analysis parameters, specific methodologies, and more effective due to the complexity of evaluating marine bottom sediments.

Acknowledgments

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