Presence and quantification of the microplastics and bisphenol-A in sediments along the Guanabara Bay, Brazil

Presença e quantificação de microplásticos e bisfenol-A em sedimentos ao longo da Baía de Guanabara, Brasil

Ana Dalva de Oliveira Santos[1]*
Diego Gomes de Carvalho[1]
Marilia Teresa Lima do Nascimento[1]
Alex da Silva de Freitas[1]
Rachel Ann Hauser-Davis[3]
Danieli Lima da Cunha[1]
Estefan Monteiro da Fonseca[1]
Daniele Maia Bila[2]
José Antonio Baptista Neto[1]

[1] Universidade Federal Fluminense
Instituto de Geociências
Departamento de Geologia
Avenida General Milton Tavares de Souza, s/nº
Boa Viagem
Niterói RJ Brasil.
CEP 24210-340

[2] Universidade do Estado do Rio de Janeiro
Departamento de Engenharia Sanitária e Ambiental
Avenida Marechal Rondon, n. 381
São Francisco Xavier
Rio de Janeiro RJ Brasil.
CEP 20550- 900

[3]Fundação Oswaldo Cruz
Instituto Oswaldo Cruz
Avenida Brasil, n. 4.365
Manguinhos
Rio de Janeiro RJ Brasil
CEP 21040-360

* Corresponding author:
santosanadalva@gmail.com

DOI:10.21715/GB2358-2812.202337001

ABSTRACT

Microplastics (MP) and endocrine disruptors, such as bisphenol-A (BPA) have both become significant environmental concerns worldwide, although assessments in estuarine environments are still scarce. In this regard, Guanabara Bay is one of the most important Brazilian estuarine systems, displaying significant economic and environmental relevance, although it has suffered increasing anthropogenic effects for decades. Thus, this study aimed to assess the occurrence of both MP and BPA in the sediments of this estuarine system though stereomicroscope identification and high-performance liquid chromatography. Both pollutants were detected in all sediment samples. A total of 3 to 11 MP particles (<5 mm) per 50 cm^2 were detected, higher than in other studies worldwide. MPs were categorized as fibers and fragments, mostly green, possibly from fisher rope and net degradation. BPA ranged from 0.36 to 19.75 ng g^{-1}, higher near Governador Island and the Rio de Janeiro harbor. Potential correlations between MPs and BPA, however, could not be determined. Both MP and BPA represent significant environmental concerns in the already highly impacted Guanabara Bay estuarine system, and further assessments are paramount to understand potential ecotoxicological hazards associated to these pollutants.

Keywords: Marine pollution, Sediments, Microplastics, Bisphenol-A, Endocrine disruptors.

RESUMO

Microplásticos (MP) e desreguladores endócrinos, como o bisfenol-A (BPA), tornaram-se preocupações ambientais significativas ao redor do mundo, embora as avaliações em ambientes estuarinos ainda sejam escassas. Nesse sentido, a Baía de Guanabara é um dos mais importantes sistemas estuarinos brasileiros, apresentando significativa relevância econômica e ambiental, embora tenha sofrido crescentes efeitos antrópicos por décadas. Assim, este estudo teve como objetivo avaliar a ocorrência de MP e BPA nos sedimentos desse sistema estuarino por meio de identificação em estereomicroscópio e cromatografia líquida de alta eficiência. Ambos os poluentes foram detectados em todas as amostras de sedimentos. Um total de 3 a 11 partículas de MP (<5 mm) por 50 cm^2 foram detectadas, mais altas que em outros estudos mundiais. Os MP foram categorizados como fibras e fragmentos, principalmente verdes, possivelmente devido à degradação de cordas e redes de pescadores. As concentrações de BPA variaram de 0,36 a 19,75 ng g^{-1}, mais altas próximos à Ilha do Governador e ao porto do Rio de Janeiro. Correlações potenciais entre MPs e BPA, no entanto, não puderam ser determinadas. Tanto os MP quanto o BPA representam preocupações ambientais significativas no sistema estuarino da Baía de Guanabara, já altamente impactado, e avaliações adicionais são fundamentais para entender os perigos ecotoxicológicos potencialmente associados a estes poluentes.

Palavras-chave: Poluição marinha, Sedimentos, Microplásticos, Bisfenol-A, Desreguladores endócrinos.

1. INTRODUCTION

Environmental degradation has increased exponentially due to anthropogenic activities, mainly boosted by industrial and urban development, leading to significant and chronic pollution in different environmental matrices (SOLAUN *et al*., 2021). In this regard, aquatic ecosystem contamination is of significant concern, directly affecting both exposed biota and human populations (BOGER *et al*., 2015; OMAR *et al*., 2016; ZHONG *et al*., 2021). This

is extremely concerning especially in coastal areas, where lack of sanitation efforts and inadequate waste disposal associated with the intense exploration of local water bodies and increasing solid waste disposal has compromised water resources, especially near large industrial centers (HIRATA, 2001; CARVALHO; BAPTISTA NETO, 2016; MARTÍN-LARA *et al.*, 2021; WAYMANA; NIEMANN, 2021).

Concerning solid waste, plastic pollution has become a worldwide issue (USEPA, 2016), with about 6.4 million tons are dumped into seas and oceans each year, 80% of which is marine waste (MARTÍN-LARA *et al*., 2021). Due to their buoyant and persistent properties, plastics can become widely dispersed via hydrodynamic processes, reaching distant sites from their initial input area (HOLMES *et al*., 2012). A clear example of this comprises, the floating garbage patches that form ocean plastic patches (UNEP 2005; HOLMES *et al*., 2012; KINSLEY, 2017; LEAL-FILHO *et al*., 2021).

Microplastics (MPs) comprise small plastics ranging from 0.1 to 5.000 μm, categorized as primary when originally manufactured in that size, while secondary microplastics originate from the fragmentation of larger plastics (COLE *et al*., 2011; GESAMP, 2015). Fragmentation processes can consist in both physical and chemical degradation, such as abrasive forces, oxidation, hydrolysi and the effect of UV light, or biodegradation, caused by fungi, bacteria or algae (KLEIN *et al*., 2018). Once in the ocean, MPs can undergo further changes in density, resulting in increased mass that is then deposited on beaches and in bottom sediments (VAN CAUWENBERGHE *et al*., 2015).

Marine MP contamination drastically affects the many organisms (*e.g.*, bivalves, fishes, turtles, cetaceans) that ingest these particles daily (DERRAIK, 2002; CARSON *et al*., 2011; THOMPSON, 2015). Several studies concerning MP exposure in different aquatic species under laboratory conditions have indicated significant physiological effects, as depicted in Table 1.

Table 1. Some Microplastic exposure effects in different aquatic species determined under laboratory conditions.

Study aims	Results	Reference
Evaluate the influence of MP ingestion on the energy reserves of marine worms	Decreased lipid and energy reserves, which may compromise maintenance, growth and reproduction	WRIGHT *et al.* (2013)
Evaluate the uptake and biodistribution of polystyrene in zebrafish embryos	Systemic organ distribution (intestines, epidermis, eye)	VAN POMEREN *et al.* (2017)
Evaluate the uptake, distribution, and toxicity of polystyrene in developing zebrafish	Decreased heart rate, altered swimming behavior	PITT *et al*. (2018)
Evaluate the effects of polyethylene ingestion in the mussels and lugworms	Inflammatory response and granulocytomas were observed after the intake of particles up to 80 μm	VAN CAUWENBERGHE *et al.* (2015)
Evaluate the effects of 30 nm polystyrene particle ingestion (0, 0.1, 0.2, and 0.3 g L^{-1}) in mussels	Filtering activity was reduced in presence of polystyrene. When exposed to 0.1 gL^{-1}, polystyrene was recognized as a low nutritional food by mussels	MOOS *et al.* (2012)
Evaluate the ingestion, translocation, and accumulation of MPs debris (3.0 or 9.6 μm) in the mussels	MP accumulation was observed in the gut and MP translocation from the gut to the circulatory system	WEGNER *et al*., 2012
Evaluate the presence of MPs in soft mussel tissues	0.36 ± 0.07 particles per gram in mussel soft tissues	BROWNE *et al*., 2008
Evaluation of the effects of microscopic unplasticised polyvinylchloride (UPVC)	Energy reserve depletion corresponding to 5% of sediment weight was observed after chronic exposure to UPVC. Accumulation of UPVC in the long gut and inflammation with enhanced phagocytic response was detected after chronic exposure	BESSELING *et al*., 2013

In addition, MPs contain chemicals additives and can adsorb several other contaminants, both organic and inorganic, also representing ecotoxicological risks, as both the MPs and their leached chemicals can bioaccumulate and biomagnify throughout the trophic chain (HOLMES *et al*., 2012; AUTA, 2017; ANBUMANI *et al*., 2018; WANG, *et al*., 2020). The main plastic additives found in the environment are phthalates, bisphenol-A (BPA), polybrominateddiphenyl ethers (PBDEs), nonylphenols (NP), andalkylphenol-ethoxylates (APEs) (USEPA, 2016; HERMABESSIERE *et al*., 2017). These compounds are considered endocrine disruptors, altering endocrine system functions in both animals and humans, affecting their growth and reproduction while also leading to several diseases, such as cancer, fertility disorders, and abnormal sexual development (BILA; DEZOTTI, 2006; CUNHA, *et al*., 2016). BPA exposure, for example, leads to both development and reproduction effects, even at low concentrations, *i.e.*, decreasing levels of male hormones, reduced sperm density and motility, testicular cell death, and inhibition of egg production and spermatogenesis (KANG *et al*., 2007; CANESI; FABBRI, 2015; ENCARNAÇÃO *et al*., 2019; WU; SEEBACHER, 2020). BPA may also respond differently depending on organismal life stage and physiological state, making it difficult to trace its possible mechanisms of action (CANESI; FABBRI, 2015).

Studies on microplastics associated to endocrine disruptor concentrations in estuarine environments are, however, still scarce worldwide. Therefore, this study aimed to investigate MP distribution and the presence of BPA in the coastal sediments of one of the most important water systems on the Brazilian coast, Guanabara Bay, with significant ecological and socio-economic relevance (ZHANGA, *et al*., 2016; CAJARAVILLE *et al*., 2016), even though it is subject to intense contamination from several polluting sources, leading to extremely high aquatic biota risks due to exposure to numerous contaminants with toxic potential (SINGARE, 2016).

2. MATERIAL AND METHODS

2.1 STUDY AREA

Guanabara Bay, located in the state of Rio de Janeiro, Southeastern Brazil (22º40'S and 23º00'S latitude and 043º00'- 043º18'W longitude), is one of the largest Brazilian coastline bays, comprising about 384 km^2 (Figure 1). It is surrounded by the highly urbanized cities of Rio de Janeiro, Duque de Caxias, Niterói and São Gonçalo, as well as three other municipalities (AMADOR, 2012; SOARES-GOMES *et al*., 2016). Its connection with the open sea is through a narrow entrance only 1.6 km wide, which directly influences the bay's hydrodynamics (CARVALHO; BAPTISTA NETO, 2016). Its maximum depth is of 58 m in the central region, becoming shallower to the north, near Ponte Rio-Niterói, with an average depth of 5.7 m (KJERFVE *et al*., 1997; MELO *et al*., 2015). This depth change is due to high sedimentation rates originating from human activities in surrounding areas (CARVALHO; BAPTISTA NETO, 2016).

The Guanabara Bay drainage basin extends 4080 km^2 consisting of 91 rivers and channels, encompassing the Rio de Janeiro, Nova Iguaçu, Belford Roxo, Duque de Caxias, Magé, Petrópolis, Itaboraí, São Gonçalo, Niterói, Rio Bonito, Teresópolis and Cachoeiras de Macacu municipalities, with a population concentration equivalent to 80% of the population of the entire state of Rio de Janeiro. Many of these rivers, mainly in the metropolitan area, are highly polluted. In addition, this estuarine system receives drainage from two harbors, refineries, and over 12,000 industries which account for 25% of all organic pollution released into the bay (KJERFVE *et al*., 1997; BAPTISTA NETO *et al*., 2006), as well as industrial and domestic sewage effluents, urban and agricultural runoff, as well as atmospheric fallout (COSTA, 2018). However, although this is a well-studied area, there is still much to investigate about its contamination levels (BAPTISTA NETO *et al*. (2006).

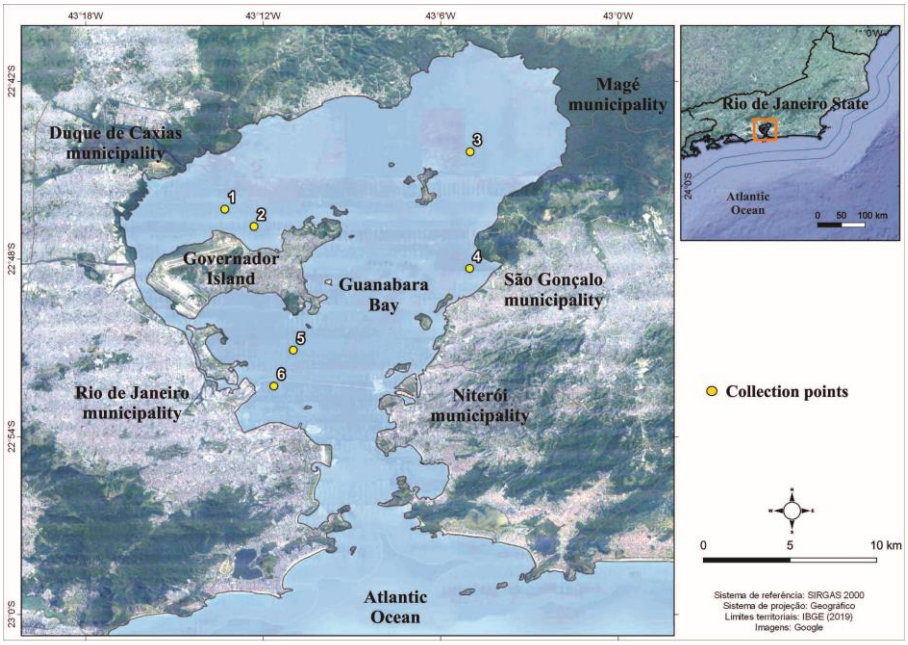

Figure 1. Map indicating the study area comprising Guanabara Bay, Brazil. Sediment sampling sites are displayed in yellow.

2.2 SAMPLING

Sediment samplings were carried out in December 2014, at six sampling points using a Van Veen grab sampler (KC Denmark AS) and a spatula (both stainless steel). For the MPs analysis, 50 cm² of the surface sediment layer about 1 cm deep were obtained according to CAUWENBERGHE *et al*. (2013), and surface sediment aliquots were separated for the BPA analyses. The depth of the sampling stations ranged from 2.8 to 5.9 m. The sediment samples were then transferred to previously decontaminated amber glass bottles and stored at 4 °C until further analyses. Figure 1 and Table 2 depict the location and basic information of each sampling station.

Table 2. Sediment sampling stations located within Guanabara Bay, Rio de Janeiro, Brazil.

Station	Location	Depth (m)	GPS coordinates
1	Governador Island	2.8	22º46'19"S 43º13'17.9"W
2	Governador Island - Southwest	2.9	22º46'53.9"S 43º12'18.6"W
3	Paquetá Island	4.4	22º44'22.7"S 43º5'00.1"W
4	São Gonçalo city	2.4	22º48'19.0"S 43º5'1.2"W
5	Fundão Island	4.1	22º51'4.6"S 43º10'59.0"W
6	Rio de Janeiro Harbor	5.9	22º52'17.3"S 43º11'38.4"W

2.3 LABORATORY ANALYSES

All materials and glassware used for sample collection and preparation were thoroughly decontaminated with a 10 % nitric acid solution to avoid interference from potential contaminants.

Concerning the MP analysis, sediment samples were prepared according to THOMPSON *et al*. (2004) and MASURA *et al*. (2015). Flotation was used to separate less dense MP particles from the sediments following 30% hydrogen peroxide (H_2O_2) addition to remove organic matter, as the samples were muddy, containing high organic matter concentrations and impairing MPs separation. Briefly, sediment aliquots were mixed with a hypersaline solution (140 g L^{-1} NaCl) at 1.5- to 2- fold the sediment volume in a beaker, stirred for four minutes and left to rest it was until sediment decantation and MP floating. The supernatants were filtered employng a vacuum filtration system using filter paper (47 mm) and oven-dried at 60 °C. The paper filters were then stored in Petri dishes until the analysis. The obtained MPs were separated and manually identified under a Zeiss STEMI 2000 C stereomicroscope for size class determinations and categorization according to their appearance, characteristics, and origin

(such as from fishing activities, fibers, fragments, Styrofoam, or pre-production pellets).

For the BPA determinations, 10 g aliquots of the dried sediment were extracted using 10 mL of methanol in an ultrasonic bath for 5 min. The samples were subsequently centrifuged at 2,500 g for 5 min and the supernatants were transferred to a 200 mL volumetric flask. This procedure was repeated three times. The sample volume was then made up to 200 mL with ultrapure water and acidified to pH 2.0. Subsequently, BPA was extracted by solid-phase extraction using StrataX cartridges (500 mg per 6 mL, Phenomenex®) and a manifold (Agilent Technologies®). The cartridges were preconditioned with 3 x 2 mL hexane, 1 mL acetone, 3 x 2 mL methanol and 5 x 2 mL ultrapure water at pH 3.0. The samples were then percolated under vacuum at about a 10 mL min^{-1} flow and maintained under vacuum for 30 minutes after extraction. Analyte elution was then performed using 4 mL of acetone. The extracts were finally evaporated under a nitrogen flow to dryness and resuspended with 500 µL of acetonitrile.

The BPA sediment determination methodology was previously validated according to guidelines reported by Silva *et al.* (2016), based on Brazil's National Institute of Metrology, Standardization and Industrial Quality (INMETRO, 2010) method. This method employs a high-performance liquid chromatography and a fluorescence detector (HPLC/FLU) (Waters Corporation®) using a 60% acetonitrile and 40% ultrapure water mobile phase, a 20 µL injection volume and three replicates for each sample. The eluent flow rate was set at 1 mL min^{-1}, with emission wavelength set at 300 nm and excitation wavelength set at 223 nm. The stationary phase comprised a Novapak PAH chromatographic column (4.6 x 250 mm, 5 microns) maintained at 40 °C ± 1 throughout 8 min runs in isocratic mode. The BPA concentrations were identified by comparing peak retention times with corresponding standard solution peaks. Analytical curve correlation coefficient (R^2) values were always > 0.99. The limit of detection was 1.899 µg L^{-1} and the limit of quantification was 62.5 µg L^{-1}, with recoveries ranging from 97 to 106%.

3. RESULTS AND DISCUSSION

The presence of MP particles was observed in all sediments sampled from Guanabara Bay (Figure 2), categorized mainly as microplastics and fibers.

The detected MPs ranged from 3 to 11 particles per 50 cm^2 (Figure 3 and Table 3). Most of the identified MPs originated from local sources such as effluents, fishing, and port activities. MP migration from the water column to the sediment is probable, as indicated in a study conducted in the northeastern Atlantic Ocean, that detected MPs in 23 of 30 samples collected from bottom sediment (THOMPSON *et al*., 2004).

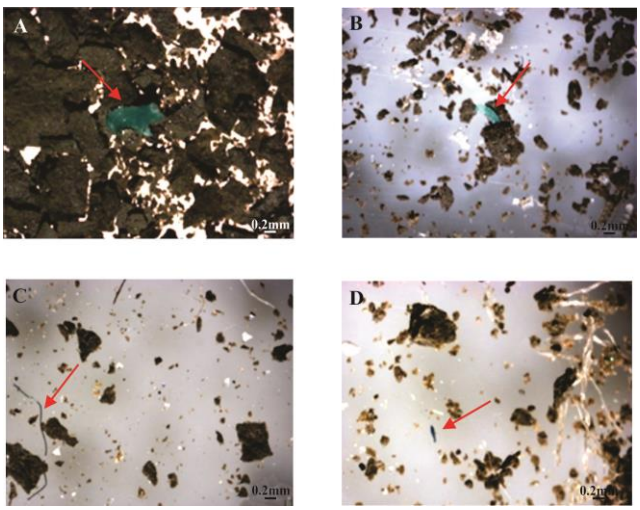

Figure 2. Microplastics detected in sediment samples from Guanabara Bay, southeastern Brazil observed under a Zeiss STEMI 2000 C stereomicroscope. The red arrows indicate A and B - microplastic fragments; C and D - fibers.

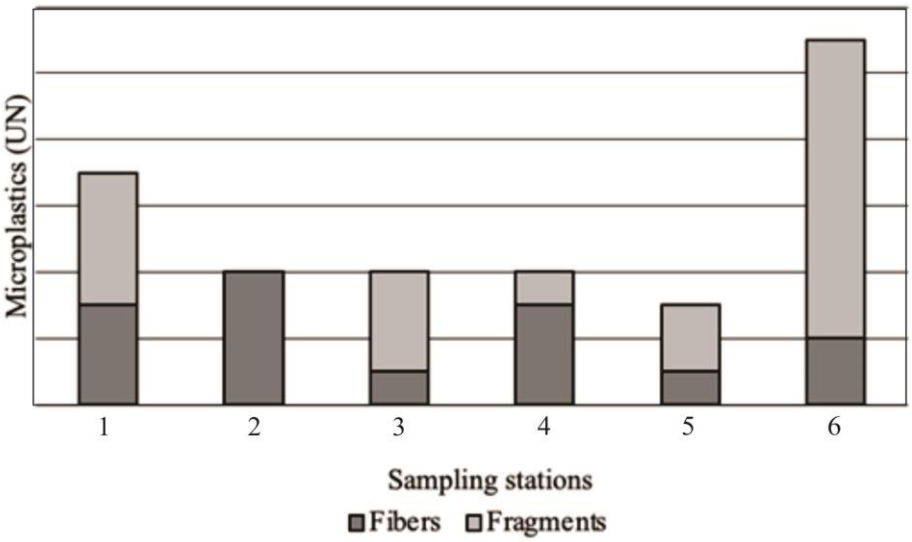

Figure 3. Microplastic particles (< 5 mm) detected in sediment samples in Guanabara Bay, southeastern Brazil. UN=Unit

Table 3. Microplastic particles (< 5 mm) in sediment samples in Guanabara Bay.

Sampling Stations	Fibers (UN)	Fragments (Unit)
1	3	4
2	4	0
3	1	3
4	3	1
5	1	2
6	2	9

Guanabara Bay MP fragment concentrations are higher than in other studies conducted worldwide, which report an average abundance of 1 MP per 50 cm^2 (CAUWENBERGHEET *et al*., 2013), demonstrating that this coastal marine area suffers from higher MP concentrations due to intense anthropogenic activities. Sampling station 6 near the Rio de Janeiro harbor, a significantly impacted area, presented the highest MP concentration, of 11 particles per 50 cm^2. In the present study, most of the detected MPs were green, indicating they may originate from the degradation of fisher ropes and nets, which are mostly this color.

High MP abundances have been previously reported at Guanabara Bay, for example, by ALVES and FIGUEIREDO (2019), who reported from 160 to 1,000 items kg^{-1} or 4,367 to 25,794 items m^2 in all sediment samples analyzed in their study, with translucent polyester microfibers being the most frequent MPs. In another assessment, CASTRO *et al*. (2020) evaluated the distribution of plastic items in different matrices (surface waters and bottom and beach sediments) and presenting different hydrodynamic properties, from Jurujuba and Itaipu Coves, both located within Guanabara Bay. The samples were composed of MPs (83%), mesoplastics (13%), and macroplastics (4%), with sizes ranging from 100 μm to 170,000 μm (17 cm), with bottom sediments containing mostly fibers/lines and MP fragments. Another investigation conducted by CARVALHO and BAPTISTA NETO (2016) analyzed microparticles on 35 surrounding Guanabara Bay beaches, reporting concentrations ranging. from 12 to 1300 per m^2, comprising mostly MP fragments (56%). followed by Styrofoam fragments (26.7%), pellets (9.9%), and fibers (7.2%). OLIVATTO *et al*. (2019) determined the presence of MPs and identified plastic residues in all surface water Guanabara Bay samples analyzed in their study, with average concentrations of 1.40 to 21.3 particles per m^3. In another assessment, BAPTISTA-NETO *et al*. (2019) detected the presence of MPs in 100 % of analyzed sediment samples from the inner continental shelf of Rio de Janeiro, close to the Guanabara Bay estuary system, composed mainly of secondary MPs,

with almost 50% categorized as fibers, followed by plastic films, plastic fragments, and pellets. Studies have also been carried out in Guanabara Bay aiming to assess the impact of MPs on aquatic organisms and potential trophic chain effect, mainly through ingestion as the ingestion of MPs, which is an important pathway for these particles to enter the trophic chain. In this regard, CASTRO *et al*, (2016) and more recently BIRNSTIEL *et al*., (2019), analyzed MPs in a mussel farming area in Guanabara Bay (Jurujuba Cove), both reporting high MP concentrations in these bivalves.

Concerning BPA, this compound was detected in all sediment samples ranging from 0.40 to 20 ng g^{-1} (Figure 4). The highest concentrations were observed in sediments from sampling stations 2 (20 ng g^{-1}) and 6 (19 ng g^{-1}), located near Governador Island and the Rio de Janeiro harbor, respectively. BPA concentrations have been reported worldwide for different matrices such as surface water (rivers, lakes, and lagoons), suspended particulate matter, and sediments (CUNHA, *et al*., 2021; WEN *et al*., 2018). For example, BPA concentrations in sediment samples from the Daliao River ranged from 3.7 to 25.3 ng g^{-1} (CALDWELL *et al*., 2012) and in the Yangtze River, from 1.2 to 6.5 ng g^{-1} (SHI; ZHANG, 2012), both in China, while samples from the Bay of Biscay, in Spain, ranged from 0.01 to 0.04 ng g^{-1} (PUY-AZURMENDI *et al*., 2013). In Brazil, NASCIMENTO (2016) analyzed two important tributaries of Guanabara Bay and nine points within Guanabara Bay, comprising both surface and deep waters, detecting BPA concentrations from 22.33 to 1325.16 ng L^{-1} at Mangue Channel and Maracanã River, both Guanabara Bay tributaries, and at Guanabara Bay itself, from 14.06 to 298.55 ng L^{-1} to surface water and from 51.24 to 465.55 ngL^{-1} in deep water. In the state of São Paulo, also in Southeastern Brazil, BPA concentrations in surface waters in the city of Campinas BPA ranged from 0.005 to 1.760 µg L^{-1} (SODRÉ *et al*.; 2007, 2010), while samples from the state of Minas Gerais ranged from 8.6 to 168.3 ng L^{-1}, with an applied risk analysis indicating toxic BPA (MOREIRA *et al*., 2011).

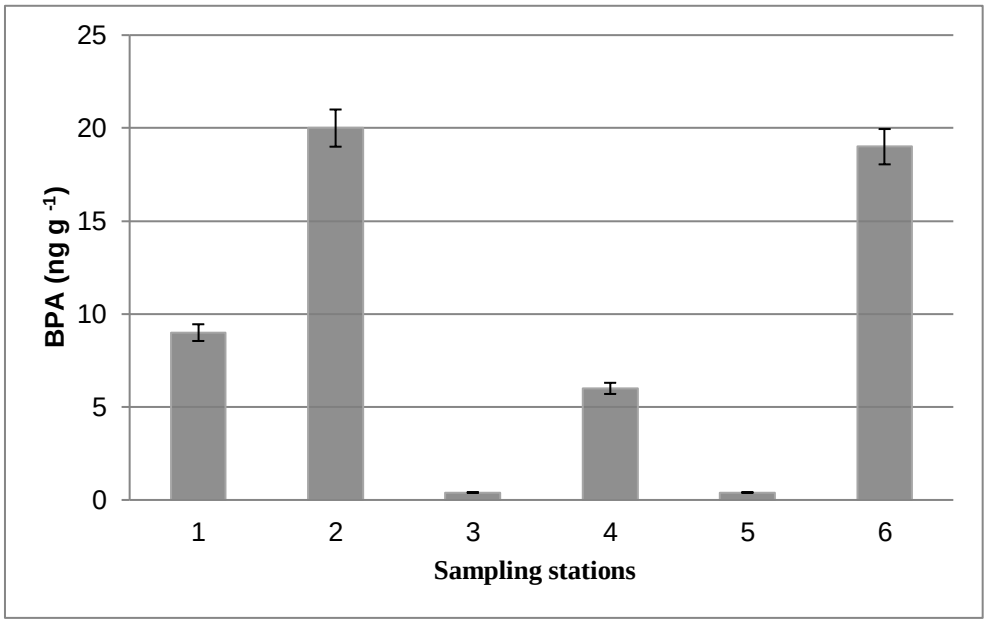

Figure 4. Bisphenol A concentrations (ng g^{-1}) in sediments sampled from Guanabara Bay, Southeastern Brazil.

Associations between MP and BPA, as well as with other pollutants, have been reported previously as leading to combined toxic effects (Pittura et al., 2018; Sun et al., 2021; Tang et al., 2020), directly affecting physiological processes in aquatic species (Aarab et al., 2006; Juhel et al., 2017). Furthermore, BPA has been proven to significantly adsorb to MPs and, consequently by aquatic species, suggesting that both pollutants interact in organisms (Chen et al., 2017). These associations, however, could not be determined herein, due to the need for expensive and time-consuming chemical MP analyses. Thus, further research is required in this regard at Guanabara Bay, to determine the toxic potential of BPA associated to MP.

4. CONCLUSION

Both MPs and BPA were detected in all sediment samples obtained along the Guanabara Bay. Guanabara Bay MP fragment concentrations were higher than in other studies conducted worldwide, especially near the Rio de Janeiro harbor, which presented the highest MP concentrations. Most of the detected MPs were green, possibly from fisher rope and net degradation. BPA concentrations were higher near Governador Island and the Rio de Janeiro harbor, both highly impacted areas. Although potential correlations between MPs and BPA could not be determined herein, both represent significant environmental concerns in this already highly impacted estuarine system, and further assessments in this regard are paramount.

5. ACKNOWLEDGEMENTS

This study was supported in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001, the Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ), and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq).

6. REFERENCES

AARAB, N., LEMAIRE-GONY, S., UNRUH, E., HANSEN, P. D., LARSEN, B. K., ANDERSEN, O. K.,; NARBONNE, J. F. Preliminary study of responses in mussel (Mytilus edilus) exposed to bisphenol A, diallyl phthalate and tetrabromodiphenyl ether. **Aquatic Toxicology**, 78, S86-S92, 2006.

ALVES, V. E. N.; FIGUEIREDO, G. M. Microplastic in the sediments of a highly eutrophic tropical estuary.**Mar. Pollut. Bull**. 146:326–335, 2019. https://doi.org/10.1016/j.marpolbul.2019.06.042

AMADOR, E. D. S. Bacia Da Baía De Guanabara: Características geoambientais, formação e ecossistemas. Interciência, Rio De Janeiro, 2012.

ANBUMANI, S.; KAKKAR, P. Ecotoxicological effectsofmicroplasticson biota: a review. **Environ SciPollut Res Int**. 25(15): 14373-14396, 2018. https://doi.org/10.1007/s11356-018-1999-x

AUTA, H. S.; EMENIKE, C. U.; FAUZIAH, S. H. Distribution and importance of microplastics in the marine environment: A review of the sources, fate, effects, and potential solutions. **Environ. Int**. 102:165-176, 2017. https://doi.org/10.1016/j.envint.2017.02.013

BAPTISTA NETO, J. A.; GINGELE, F. X.; LEIPE, T., BREHME I. Spatial distribution of heavy metals in superficial sediments from Guanabara Bay: Rio de Janeiro, Brazil. **J. Environ. Geol**. 49:1051-1063, 2006. https://doi.org/10.1007/s00254-005-0149-1

BAPTISTA NETO, J. A; CARVALHO, D. G.; MEDEIROS, K.; DRABINSKI, T. L.; MELO, G. V.; SILVA, R. C. O.; SILVA, D. C. P.; BATISTA, L. S.; MACEDO DIAS, G. T. M.; FONSECA, E. M.; SANTOS FILHO, J. R. The impact of sediment dumping sites on the concentrations of microplastic in the inner continental shelf of Rio de Janeiro/Brazil.**Mar. Pollut. Bull**. 149:110558, 2019. https://doi.org/10.1016/j.marpolbul.2019.110558

BESSELING, E.; WEGNER, A.; FOEKEMA, E. M.; MARTINE, J.; HEUVEL-GREVE, V. D.; KOELMANS A. A. Effects of microplastic on fitness and PCB bioaccumulation by the lugworm Arenicola marina (L.).**Environ. Sci. Technol**. 2:593-600, 2013. https://doi.org/10.1021/es302763x

BILA, D. M; DEZOTTI, M. Desreguladores endócrinos no meio ambiente: efeitos e conseqüências. **Quím.Nova**. 30:651-66, 2007. https://doi.org/10.1590/S0100-40422007000300027

BIRNSTIEL, S.; SOARES-GOMES, A.; GAMA, B. A. P. Depuration reduces microplastic content in wild and farmed mussels. **Mar Pollut Bull**. 140:241-247, 2019. https://doi.org/110.1016/j.marpolbul.2019.01.044

BOGER, B.; TONIN, F. S.; ZAMORA, P. G. P.; WAGNAR, R.; GOMES, E. C. Micro-poluentes emergentes de origem farmacêutica em matrizes aquosas do Brasil: uma revisão sistemática. **Ciência&Natura**. 37(3):725-739, 2015. https://doi.org/10.5902/2179460X18174

BROWNE, M. A.; DISSANAYAKE, A.; GALLOWAY, T. S.; LOWE, D. M.; THOMPSON, R. C. Ingested microscopic plastic translocates to the circulatory system of the mussel *Mytilusedulis* (L.). **Environ. Sci. Technol**. 42:5026–5031, 2008. https://doi.org/10.1021/es800249a

CAJARAVILLE, M. P.; ORIVE, E.; VILLATE, F.; LAZA MARTINEZ, A.; URIARTE, I.; GARMENDIA, L.; ORTIZ-ZARRAGOITIA, M.; SEOANE, S.; IRIARTE, A.; MARIGÓMEZ, I. Health status of the Bilbao estuary: A review of data from a

multidisciplinary approach. **Estuar.Coast. Shelf Sci**. 179:1-11, 2016. https://doi.org/10.1016/j.ecss.2016.01.013

CALDWELL, J. T.; MELKANI, G. C.; HUXFORD, T. BERNSTEIN, S. I. Transgenic expression and purification of myosin isoforms using the Drosophila melanogaster indirect flight muscle system.**Methods**. 56(1):25-32, 2012. https://doi.org/10.1016/j.ymeth.2011.12.002

CANESI, L.; FABBRI, E. Environmental Effects of BPA: Focus on Aquatic Species. **Dose-Response: An International Journal**. 1-15, 2015.https://doi.org/10.1177/1559325815598304CARSON, H. S.; COLBERT, S. L.; KAYLOR, M. J.; MC DERMID, K. J. Small plastic debris changes water movement and heat transfer through beach sediments. **Mar Pollut Bull**. 62:1708-1713, 2011. https://doi.org/10.1016/j.marpolbul.2011.05.032

CARVALHO, D.; BAPTISTA NETO, J. A. Microplastic pollution of the beaches of Guanabara Bay, Southeast Brazil. **Ocean Coast. Manag**. 128:10-17, 2016. https://doi.org/10.1016/j.ocecoaman.2016.04.009

CASTRO, R. O.; SILVA, M. L.; MARQUES, M. R. C.; ARAÚJO, F. V. Evaluation of microplastics in Jurujuba Cove, Niterói, RJ, Brazil, an area of mussels farming. **Mar. Pollut. Bull**. 110(1):555-558, 2016. https://doi.org/10.1016/j.marpolbul.2016.05.037

CAUWENBERGHE, V. L.; VANREUSEL, A.; MEES, J.; JANSSEN, C. R. Microplastic pollution in deep-sea sediments. **Environ. Pollut**. 182:495–499, 2013. https://doi.org/10.1016/j.envpol.2013.08.013

CHEN, Q., YIN, D., JIA, Y., SCHIWY, S., LEGRADI, J., YANG, S.,; HOLLERT, H. Enhanced uptake of BPA in the presence of nanoplastics can lead to neurotoxic effects in adult zebrafish. **Science of the Total Environment**, 609, 1312-1321, 2017.

COLE, M.; LINDEQUE, P.; HALSBAND, C.; GALLOWAY, T. S. Microplastics as contaminants in the marine environment: a review. **Mar. Pollut. Bull**. 62(12):2588-2597, 2011. https://doi.org/10.1016/j.marpolbul.2011.09.025

COSTA, L. A. A.; PESSOA, D. M. M.; CARREIRA, R. S. Chemical and biological indicators of sewage river input to an urban tropical estuary (Guanabara Bay, Brazil). **Ecol. Indic.** 90:513-518, 2018. https://doi.org/10.1016/J.ECOHYD.2020.12.003

CUNHA, D. L.; MUYLAERT, S.; NASCIMENTO, M. T. L.; SILVA, G. G. M.; FONSECA, E. M.; BILA, D. M.; SARCINELLI, P. N.; LARENTIS, A. L. Atividade estrogênica de desreguladores endócrinos em águas superficiais do município de Santa Maria Madalena, Sudeste do Brasil. **Eng. Sanit. e Ambient**. 26(1):21-28, 2021. https://doi.org/10.1590/s1413-415220180133

CUNHA, D. L.; SILVA, S. M. C.; BILA, D. M.; OLIVEIRA, J. L. M.; SARCINELLI, P. N.; LARENTIS, A. L. Regulation of the synthetic estrogen 17aethinylestradiol in water bodies in Europe, the United States, and Brazil. **Cad.deSaudePublica**. 32(3):1-13, 2016. https://doi.org/10.1590/0102-311X00056715

DERRAIK, J. G. B. The pollution of the marine environment by plastic debris: a review. **Mar. Pollut. Bull**. 44:842-852, 2002. https://doi.org/10.1016/S0025-326X(02)00220-5

ENCARNAÇÃO, T.; PAIS, A. A.; CAMPOS, M. G.; BURROWS, H. D. Endocrine disrupting chemicals: Impact on human health, wildlife and the environment. **Sci. Prog**. 102(1):3-42, 2019. https://doi.org/10.1177/0036850419826802

ALVES, V. E. N.; FIGUEIREDO, G. M. Microplastic in the sediments of a highly eutrophic tropical estuary. **Mar Pollut Bull**. 146:326-335, 2019. https://doi.org/10.1016/j.marpolbul.2019.06.042

GESAMP. Sources, fate and effects of microplastics in the marine environment: a global assessment (Kershaw, P. J., ed.). (IMO/FAO/UNESCO-IOC/UNIDO/WMO/IAEA/UN/UNEP/UNDP Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection). Rep. Stud. GESAMP No. 90, 96 p, 2015.

HAN, Y., SHI, W., TANG, Y., ZHOU, W., SUN, H., ZHANG, J., LIU, G. (2022). Microplastics and bisphenol A hamper gonadal development of whiteleg shrimp (Litopenaeus vannamei) by interfering with metabolism and disrupting hormone regulation. **Science of The Total Environment**, 810, 152354, 2022.

HERMABESSIERE, L.; DEHAUT, A.; PAUL-PONT, I.; LACROIX, C.; JEZEQUEL, R.; SOUDANT, P.; DUFLOS, G. Occurrence and effects of plastic additives on marine environments and organisms: A review. **Chemosphere**. 182:781-793, 2017. https://doi.org/10.1016/j.chemosphere.2017.05.096

HIRATA, R. Recursos Hídricos. In: Teixeira, W; Toledo, M.C. M; Fairfield, T. R; Taioli, F. (2001)(Org). Decifrando a Terra. São Paulo: Oficina de Textos, p. 421-444, 2001.

HOLMES, L.; TURNER, A.; THOMPSON, R. Adsorption of trace metals to plastic resin pellets in the marine environment.**Environ. Pollut**. 160:42-48, 2012. https://doi.org/10.1016/j.envpol.2011.08.052

INMETRO - Instituto Nacional de Metrologia, Qualidade e Tecnologia. **Orientation about analytical methody validation, overal coordination of accreditation**.20 p. 2010.

JUHEL, G., BAYEN, S., GOH, C., LEE, W. K.,; KELLY, B. C. Use of a suite of biomarkers to assess the effects of carbamazepine, bisphenol A, atrazine, and their mixtures on green mussels, Perna viridis. **Environmental Toxicology and Chemistry,** 36(2), 429-441, 2017.

KANG, J. H.; AASI, D.; KATAYAMA, Y. Bisphenol A in the Aquatic Environment and Its Endocrine-Disruptive Effects on Aquatic Organisms, **Crit. Rev. Toxicol**. 37(7):607-625. 2007.https://10.1080/10408440701493103

KLEIN, S.; DIMZON, I. K.; EUBELER, J.; KNEPPER, T. P.; WAGNER, M.; LAMBERT, S. Freshwater Microplastics.The Handbook of Environmental Chemistry. vol 58, Springer, Cham (2018). https://10.1007/978-3-319-61615-5_3KINSLEY, A. Synthetic Seas: The Great Pacific Garbage Patch. HOHONU. 15:1-3, 2017. Disponivel em https://hilo.hawaii.edu/campuscenter/hohonu/volumes/documents/SyntheticSeasTheGreatPacificGarbagePatch.pdf

KJERFVE, B. C. H. A.; RIBEIRO, G. T. M.; DIAS, A. M.; FILIPPO, V. S. Q. Oceanographic characteristics of an impacted coastal bay: Baía de Guanabara, Rio de Janeiro, Brazil. **Cont. Shelf. Res**. 17(13):1609-1643, 1997. https://doi.org/10.1016/S0278-4343(97)00028-9

LEAL FILHO, W.; HUNT, J.; KOVALEVA M. Garbage Patches and Their Environmental Implications in a Plastisphere. **J. Mar. Sci. Eng**. 9(1289):1-6, 2021. https://doi.org/10.3390/jmse9111289

MARTÍN-LARA, M. A.; GODOV, L.; QUESADA, L.; LOZANO E. J.; CALERO, M.Environmental status of marine plastic pollution in Spain. **Mar. Pollut. Bull**. 170:1-20, 2021 https://doi.org/10.1016/j.marpolbul.2021.112677

MASURA, J.; BAKER, J.; FOSTER, G.; ARTHUR, C. Laboratory methods for the analysis of microplastics in the marine environment: recommendations for quantifying synthetic particles in waters and sediments. NOAA Technical Memorandum NOS-OR&R-48. 2015.

MELO, G. V.; BAPTISTA NETO, J. A.; MALM, O.; FERNANDEZ, M. A. S.; PATCHINEELAM, S. M. Composition and behaviour of heavy metals in suspended sediments in a tropical estuarine system. **Environ. Earth Sci**. 73:1331-1344, 2015. https://doi.org/10.1007/s12665-014-3491-3

MOOS, N.; BURKHARDT-HOLM, V.; KÖHLER, A. P. Uptake and effects of microplastics on cells and tissue of the blue mussel *Mytilusedulis* L. after an experimental exposure.**Environ. Sci. Technol**. 46:11327-11335, 2012. https://doi.org/10.1021/es302332w

PITT, J. A.; KOZAL, J. S.; JAYASUNDARA, N.; MASSARSKY, A.; TREVISAN, R.; GEITNER, N. Uptake, tissue distribution, and toxicity of polystyrene nanoparticles in developing zebrafish (*Daniorerio*). **Aquat. Toxicol**. 194:185-194, 2018. https://doi.org/10.1016/j. aquatox.2017.11.017

PITTURA, L., FOGLIA, A., AKYOL, Ç., CIPOLLETTA, G., BENEDETTI, M., REGOLI, F., FATONE, F. Microplastics in real wastewater treatment schemes: Comparative assessment and relevant inhibition effects on anaerobic processes. **Chemosphere**, 262, 128415, 2021.

PUY-AZURMENDI, E.; ORTIZ-ZARRAGOITIA, M.; VILLAGRASA, M., KUSTER, M.; ARAGON, P.; ATIENZA, J.; PUCHADES, R.; MAQUIEIRA, A.; DOMÍNGUEZ, C.; ALDA, M. L.; FERNANDES, D.; PORTE, C.; BAYONA, J. M.; BARCELÓ, D.; CAJARAVILLE, M. P. Aragon. Endocrine disruption in thick lip grey mullet (Chelonlabrosus) from the Urdaibai Biosphere Reserve (Bay of Biscay, Southwestern Europe). **Sci. Total Environ**. 443:233-244, 2013.https://doi.org/10.1016/j.scitotenv.2012.10.078

SILVA, L. L. S.; SALES, J. C. S.; FONSECA, F. V.; CAMPOS, J. C.; BILA, D. M. Advanced oxidative processes and membrane separation for micropollutant removal from biotreated domestic wastewater. **Environ. Sci. Pollut. Res. Int**. 16:1-10, 2016. https://doi.org/10.1007/s11356-016-7312-y

SINGARE, P. U. Distribution and risk of suspected endocrine-disrupting pesticides in creek water of Mumbai, India. **Mar. Pollut. Bull**. 102(1):72-83, 2016. https://doi.org/10.1016/j.marpolbul.2015.11.055

SOARES-GOMES, A.; DA GAMA, B.A.P.; BAPTISTA NETO, J.A.; FREIRE, D.G.; CORDEIRO, R.C.; MACHADO, W.; BERNARDES, M.C.; COUTINHO, R.; THOMPSON, F.L.; PEREIRA, R.C. Anenvironmental overview of Guanabara Bay, Rio de Janeiro. **Reg. Stud. Mar**. 8:319-330, 2016. https://doi.org/10.1016/ j.rsma.2016.01.009

SOLAUN, O.; RODRÍGUEZ, J.G.; MENCHACA, I.; LÓPEZ-GARCÍA, E.; MARTÍNEZ, E.; ZONJA, B.; LARRETA, J. Contaminants of emerging concern in the Basque coast (N Spain): Occurrence and risk assessment for a better monitoring and management decisions. **Sci. Total Environ**. 765:142765, 2021. https://doi.org/10.1016/j.scitotenv.2020.142765

SUN, P., LIU, X., ZHANG, M., LI, Z., CAO, C., SHI, H., ZHAO, Y. Sorption and leaching behaviors between aged MPs and BPA in water: the role of BPA binding modes within plastic matrix. **Water Research**, 195, 116956, 2021.

TANG, Y., ZHOU, W., SUN, S., DU, X., HAN, Y., SHI, W.,; LIU, G. Immunotoxicity and neurotoxicity of bisphenol A and microplastics alone or in combination to a bivalve species, Tegillarca granosa. **Environmental Pollution**, 265, 115115, 2020.

TEUTEN, E. L.; ROWLAND, S. J.; GALLOWAY, T. S.; THOMPSON, R. C. Potential for plastics to transport hydrophobic contaminants. **Environ. Sci. Technol**. 41:7759–7764, 2007. https://doi.org/10.1021/es071737s

THOMPSON, R. C.; OLSEN, Y.; MITCHELL. R. P.; DAVIS, A.; ROWLAND, S. J.; JOHN, A. W. G.; MCGONIGLE, D.; RUSSELL, A. E. Lost at

sea: where is all the plastic? **Science**. 304(5672):838, 2004. https://doi.org/10.1126/science.1094559

THOMPSON, R. C. Microplastics in the Marine Environment: Sources, Consequences and Solutions. In: Bergmann M., Gutow L., Klages M. (eds) Marine Anthropogenic Litter. Springer, Cham. 2015. https://doi.org/10.1007/978-3-319-16510-3_7

WANG, T,; HU, M. H.; XU, G.G.; SHI, H. H.; LEUNG, J.Y.S.; WANG, Y. J. Microplastic accumulation via trophic transfer: can a predatory crab counter the adverse effects of microplastics by body defence? **Sci. Total Environ**. 754:142099, 2020. https://doi.org/10.1016/j.scitotenv.2020.142099

UNEP 2005 ***Marine litter, an analytical overview***. Nairobi, Kenya: United Nations Environment Programme.

USEPA - United States Environmental Protection Agency. EPA-822-R-16-009. State of the Science White Paper: A Summary of Literature on the Chemical Toxicity of Plastics Pollution to Aquatic Life and Aquatic-Dependent Wildlife. 2016. 50p. Disponivel em: https://www.epa.gov/sites/default/files/2016-12/documents/plastics-aquatic-life-report.pdf

VAN CAUWENBERGHE, L.; CLAESSENS, M.; VANDEGEHUCHTE, M, B.; JANSSEN, C. R.Microplastics are taken up by mussels (*Mytilusedulis*) and lugworms (*Arenicola marina*) living in natural habitats. **Environ. Pollut**. 199:10-17, 2015. https://doi.org/10.1016/j.envpol.2015.01.008

VAN POMEREN, M.; BRUN, N.; PEIJNENBURG, W.; VIJVER, M. J. A. T. Exploring uptake and biodistribution of polystyrene (nano) particles in zebrafish embryos at different developmental stages. **Aquat.Toxicol**. 190:40-45, 2017. https://doi.org/10.1016/j.aquatox.2017.06.017

WEGNER, A.; BESSELING, E.; FOEKEMA, E. M.; KAMERMANS, P.; KOELMANS, A. A. Effects of nanopolystyrene on the feeding behaveior of the blue mussel (*Mytilusedulis* L.). **Environ. Toxicol.and Chem**. 31:2490-2497, 2012. https://doi.org/10.1002/etc.1984

WEN, Z.; HUANG, X.; GAO, D.; LIU, G.; FANG, C.; SHANG, Y.; DU, J.; ZHAO, Y.; LV,L.; SONG, K. Phthalate esters in surface water of Songhua River watershedassociated with land use types, Northeast China. **Environ. Sci. Pollut. Res**. 25(8):7688-7698, 2018. https://doi.org/10.1007/s11356-017-1119-3

WU, N. C.; SEEBACHER, F. Effect of the plastic pollutant bisphenol A on the biology of aquatic organisms: A meta-analysis. **Glob. Chang. Biol**. 26(7):3821-3833, 2020. https://doi.org/10.1111/gcb.15127

WAYMANA, C.; NIEMANN, H.The fate of plastic in the ocean environment – a minireview. **Environ. Sci.: Processes Impacts**. 23(2):1-16, 2021. https://doi.org/10.1039/d0em00446d

WRIGHT, S. L.; RICHARD, D. R,; THOMPSON, C.; GALLOWAY, T. S. Microplastic ingestion decreases energy reserves in marine worms. **Curr. Biol**. 23:1031-1033. 2013.https://doi.org/10.1016/j.cub.2013.10.068

ZHANGA, I.; DONGB, S.; WANGH, H.; TAOA, S.; KIYAMAC, R. Biological impact of environmental polycyclic aromatic hydrocarbons (PAHs) as endocrine disruptors. **Environ. Pollut.**213:809-824, 2016. https://doi.org/10.1016/j.envpol.2016.03.050

ZHONG, R.; ZOU, H.; GAO, J.; WANG, T.; BU, Q.; WANG, Z. L.; WANG, Z.A critical review on the distribution and ecological risk assessment of steroid hormones in the environment in China.**Science of the Total Environment**. 786:147452, 2021. https://doi.org/10.1016/j.scitotenv.2021.147452