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Microplastic occurrence and phthalate ester levels in neuston samples and skin biopsies of filter-feeding megafauna from La Paz Bay (Mexico)

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ABSTRACT

The impacts of microplastics on filter feeders megafauna have recently received increased attention. These organisms are potentially exposed to plastic ingestion and the release of added/sorbed contaminants during feeding activities. An assessment of microplastic abundance and the chemical impact of Phthalates esters (PAEs) were performed in neustonic samples and skin biopsies of *Balaenoptera physalus* and *Rhincodon typus* inhabiting the Gulf of California (Mexico). Sixty-eight percent of the net tows contained plastics with a maximum of 0.24 items/m^3 mainly composed of polyethylene fragments. PAE levels were detected both in environmental and skin biopsy samples, with the highest values in the fin whale specimens (5291 ng/g d.w). Plasticizer fingerprint showed a similar distribution pattern between neustonic samples and filter-feeding species, with DEHP and MBP having the highest concentrations. The detection of PAE levels confirmed their potential role as plastic tracers and give preliminary information about the toxicological status of these species feeding in La Paz Bay.

1. Introduction

The presence of plastic litter in the marine environment has been identified as a major concern alongside other key environmental issues in the last few years (Nash et al., 2017). In marine habitats, including beaches, sea surface, and seafloor, plastics are exposed to different environmental conditions that either accelerate or decelerate the fragmentation influencing their buoyancy, persistency, occurrence and distribution (Andrady, 2011; O'Brine and Thompson, 2010; Van Franeker, 2011). It has been demonstrated how plastics, according to their properties, could have deleterious impacts on marine organisms, representing physical (e.g., gastrointestinal blockage, starvation, and death) and chemical harm (Fossi et al., 2018; Kühn et al., 2020; Rochman, 2015; Werner et al., 2016). These impacts are well documented in various species such as fishes, seabirds and marine invertebrates; however, few studies focus on large filter feeders, resulting in a limited understanding of their pollution threats (Fossi et al., 2018, 2016, 2012; Germanov et al., 2018; Kühn et al., 2015; Kahane-Rapport et al., 2022). Many filter-feeding marine megafauna are charismatic and iconic species, with the potential to act as sentinels stimulating the awareness of scientific and local communities and encouraging actions to tackle microplastic pollution. Species such as mobulid rays, filter-feeding sharks, and baleen whales, characterized by a long life span and continued feeding activity are potentially chronically exposed to microplastic ingestion (Fossi et al., 2014, 2017a; Germanov et al., 2018). Recent estimates have reported an alarming theoretical number of ingested particles, ranging from 106 to 1505 items/day for the manta rays (Germanov et al., 2019), 547 to 3286 items/day for the whale shark (Fossi et al., 2017a; Germanov et al., 2019) and 2.99–9.96 × 10^6 items/day for the krill feeding whales (Kahane-Rapport et al., 2022), even though determining the exposure pathways (direct and/or trophic) tand the total particles amount have proven to be a challenging task (Zantis et al., 2021). The evaluation of the overlap of filter-feeding species habitat ranges with areas heavily impacted by plastic could be a useful tool to indirectly gain information on the pressure that this kind of pollution could exert on these species. The Mediterranean Sea (Fossi

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et al., 2017b; Galli et al., 2022), the Indian Ocean (Germanov et al., 2019; Argeswara et al., 2021), the Pacific Ocean and the Gulf of California (Fossi et al., 2017a; Kahane-Rapport et al., 2022) are some examples of areas where endangered species (i.e., manta rays, whale shark and whales) are affected by the presence of plastic and associated chemicals. According to that, plastic and MPs could contain potentially hazardous chemicals added during manufacture (e.g. plasticizers/additives and antimicrobials) or sorb to the surface from the surrounding ocean waters (e.g. persistent organic pollutants and metals) that could be released to organisms upon ingestion causing toxicological effects (Fossi et al., 2016; Hermabessiere et al., 2019; Paluselli et al., 2019). Among additives, Phthalate esters (PAEs) are widely used to make plastics more flexible and harder to break. Varying in alkyl chain length, branching, and molecular weight and not being chemically bound to plastics, they could be easily leached becoming bioavailable to marine animals (Baini et al., 2017; Fossi et al., 2014). PAEs can have various toxic harmful effects on organisms. In particular, they can act as endocrine disruptors (EDs) even at very low concentrations, interacting with hormone synthesis and altering reproduction or other physiological and metabolic functions (e.g., causing oxidative stress, and immunotoxicity) of organisms (Mathieu-Denoncourt et al., 2015; Talsness et al., 2009). With this background, this study aims to assess the presence and distribution of floating MPs in surface waters of one of the most biologically productive regions of the world, the Gulf of California and in particular the Bay of La Paz (Mexico). Plastic additive (PAEs) loads were evaluated in plankton samples and skin biopsies of fin whales (*Balaenoptera physalus*) and whale sharks (*Rhincodon typus*) to investigate the potential release of these toxic substances from plastic particles and the potential related chemical impacts on marine organisms.

2. Materials and methods

2.1. Study area

The Bay of La Paz is the largest coastal inner water body of the Gulf of California (Mexico) and it is composed of two main islands: San José, and Espiritu Santo located in the northern, central and southern sectors. The hydrodynamic features of the bay are influenced mainly by the tidal currents and winds. From winter until spring, north and northeast winds generate a relatively stable cyclonic eddy determining the upwelling of high fluxes of zooplankton, which deeply drops during the warm season (Reyes-Salinas et al., 2003). The related productivity generated favours the aggregations of different filter-feeders species such as whale sharks and fin whales. Globally classified as Vulnerable in the IUCN red list (Cooke, 2018), the fin whale inhabiting the Gulf of California constitutes a resident, genetically isolated population from that one living in the North Pacific Ocean (Bérubé et al., 2002). Their distribution in the Gulf is strictly connected with primary production bloom, determining the presence of cetaceans in the southern part during the cold season (December–June) and their migration to the northern Gulf of California in the warm season (July–October) (Fossi et al., 2016; Ladrón-de-Guevara et al., 2015; Jiménez-López et al., 2019). Aggregations of whale sharks, instead, are seasonally spotted to feed in Los Angeles Bay (Northern-central sector of the Gulf; Nelson and Eckert, 2007) from May to November (Ramírez-Macías et al., 2012) and La Paz Bay (Southern sector of the Gulf; Ketchum et al., 2013), from October to May (Ramírez-Macías et al., 2012) feeding on copepods, chaetognaths, and euphausiids (Whitehead et al., 2019). Listed as Endangered on the IUCN red list (Pierce and Norman, 2016), this shark species is protected under two national laws in Mexico (DOF, 2006, 2010).

The high primary productivity above describes, and the habitat heterogeneity deeply influenced the extraordinary biological diversity that characterized La Paz Bay and the Gulf of California in general (Cudney-Bueno et al., 2009; Enríquez-Andrade et al., 2005). Despite these areas being still considered pristine, the increasing human pressure in recent years is giving rise to chemical pollution from urban wastewater, heavy touristic fluxes, and agriculture and maritime activities (Páez-Osuna et al., 2017).

2.2. Neustonic samples collection and MPs characterization

A total of 25 neustonic samples were collected across the Bay of La Paz in different sampling stations (Cemex, Isla Ballena, Lobera, San Francisquito and San Juan de la Costa) during five survey campaigns carried out from May 2015 to June 2016 to evaluate floating MPs levels (Fig. 1).

Floating MPs were collected using a manta trawl (330 μm mesh size, 60 × 15 cm mouth opening), equipped with a flowmeter, and towed at 2–3 knots for 15 min. At the end of sampling, the net was thoroughly rinsed from the outside to ensure that both plankton and microparticles were washed into the end of the net. Samples were finally filtered through a 300 μm metal sieve to eliminate the remaining water in the cod-end bucket and stored in a 4 % formaldehyde-seawater buffered solution for subsequent analyses. Then, neustonic samples were filtered through a sieve (mesh size: 300 μm) and observed under an NBS stereo zoom microscope (Mod. NBS-STMDLX-T) equipped with an LED light and a micro metered eyepiece. The synthetic microparticles were manually isolated in a glass Petri dish and characterized according to different size classes (0.33–0.5 mm, 0.5–1 mm, 1–2.5 mm and 2.5–5 mm), shape (fragment, film, filament, and pellet) and colours (black, blue, white, transparent, red, green, and other) as described in Baini et al. (2018). All data obtained were corrected according to weather and sea conditions considering the possible "wind stress" effect as described by Kukulka et al. (2012). The chemical composition of the isolated MPs was evaluated using the Fourier-transformed infrared spectroscopy (FTIR) technique. Each particle was scanned 16 times using an Agilent Cary 630 spectrophotometer. To identify the polymers, the spectrum obtained was processed using Agilent Micro Lab FTIR software and compared to a database of reference spectra. Only results that showed >80 % overlap were accepted according to Baini et al. (2018). Simultaneously at the floating MPs monitoring, neustonic samples were collected to assess the levels of PAEs. Neuston tows were carried out using a WP2 plankton net (330 μm mesh size) in each sampling station during the five survey campaigns following the same methodological approach described above. Samples were on-board filtered through a 300 μm sieve and stored at −20 °C.

2.3. Prevention of contamination

To prevent contamination throughout the analytical process, all the materials used for sample collection, including the nets and jars, were accurately cleaned and rinsed before any tow with pre-filtered water (0.45 μm). During the laboratory procedures glassware was used and particular care was taken to prevent airborne contamination by performing sample analysis in a clean air flow cabinet and using two glass Petri dishes placed at each side of the stereomicroscope as blank control. Despite the adoption of contamination control procedures, fibres and paint chips were not considered due to the risk of external contamination during sampling activities. Any other synthetic particles (e.g., fragments, films, or filaments) were not detected in the control glass Petri dishes.

2.4. Skin biopsies collection

Skin biopsies were collected from two filter-feeder organisms inhabiting the Bay of La Paz (Supplementary material Table 1). Nine specimens of whale shark (*Rhincodon typus*) (8 males and 1 female) were sampled using a 200 cm pole with a stainless-steel biopsy tip (5 mm diameter) in December 2013 and January 2014 (authorizations No. SGPA/DGVS/03362/12 and SGPA/DGVS/03079/13 CITES permit MX 68569 and Nat. IT025IS, Int. CITES IT 007). Fin whale (*Balaenoptera physalus*) skin biopsies have been collected from 3 adult females,

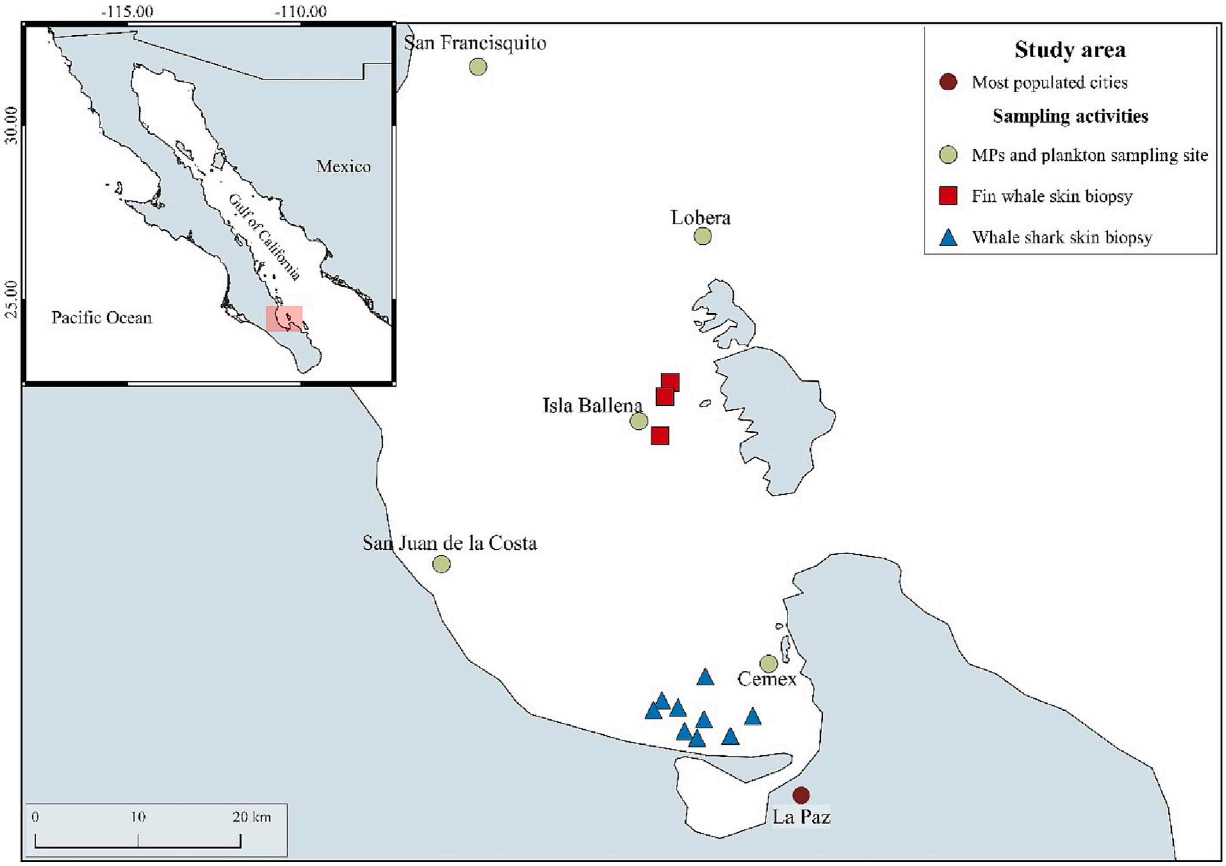

Fig. 1. MPs and neuston sampling sites, fin whale (*Balaenoptera physalus*) and whale shark (*Rhincodon typus*) skin biopsies collected in La Paz Bay (BCS, Mexico).

between April and August 2015, by remote sampling, using a modified dart with an aluminium tip (8 mm diameter) launched with a Panzer V crossbow. To avoid any possible infection, the tip was sterilised each time with alcohol before shooting. During the sampling process, attention was paid to taking the biopsy sample in the dorsal area close to the dorsal fin. Each biopsy (1–2 g of epidermal, dermal, and blubber tissue) was immediately stored in liquid nitrogen until the analysis.

2.5. PAEs extraction and evaluation

The presence of six different PAEs (Mono-benzyl phthalate -MBzP, Mono-butyl phthalate – MBP, Mono(2-Ethylhexyl) phthalate – MEPH, Di-n-hexyl phthalate – DNHP, Benzyl butyl phthalate – BBzP, Bis(2-Ethylhexyl) phthalate - DEPH) as tracers of plastic ingestion has been evaluated both in neuston samples and in skin biopsies of filter-feeding species. The synthetic particles were removed prior to the freeze-dried and extraction processes and only the plankton was analysed.

Samples were analysed following the methods proposed by Baini et al. (2017). Briefly, plankton and skin biopsy samples were freeze-dried for 48–96 h, their dry weight and fresh weight were measured and water content (%) was calculated. About 0.1 g of neuston biomass and 0.03 g of skin biopsies were homogenized and spiked with a 2.5 ng/μL standard solution of DEPH-d^4 and three times extracted with a mixture of dichloromethane:hexane (1:1 v/v) by ultrasound. The upper phase containing the extracted PAEs was collected after centrifugation. The extracts were cleaned up by acid washing with sulphuric acid (98 %, Sigma Aldrich), vortexed and stored for 48 h at +4 °C. The organic phase was collected, dry evaporated under a gentle stream of nitrogen and resuspended in hexane for chromatographic analysis. Each sample was analysed using a Hewlett-Packard (HP) 6890 gas chromatograph equipped with an HP-5MS column (30 m × 0.25 mm × 0.25 mm) and an HP 5973 mass spectrometer (GC–MS). The detection limits (LODs) for individual PAEs were: MBzP: 5 ng/g, MBP: 5 ng/g, MEHP: 10 ng/g, DNHP: 3 ng/g, BBzP: 9 ng/g, DEHP: 1 ng/g. Concentration values less than the LOD were labelled as below the detection limit (BDL) and a value of half of the BDL was used in statistical analysis.

2.6. Statistical analysis

Descriptive statistics and normality tests (Shapiro-Wilk normality test and Anderson-Darling test) were performed to determine whether parametric or non-parametric statistical analyses were appropriate. The Kruskal-Wallis test for multiple comparisons and post hoc Dunn's and Pairwise Wilcoxon rank sum tests were conducted to compare differences in the MP concentrations and PAE levels according to different sampling seasons and stations and biological matrices investigated, respectively. Spearman's rank correlation test was performed highlighting the potential relationship between MP abundances and PAE levels in neuston samples collected in the same sampling stations. A significance level ($p < 0.05$) was considered for all analyses performed using RStudio (R Core Team, 2017).

3. Results and discussion

3.1. MP abundance and characterization

Sixty-eight percent of the net tows (17 out of 25) contained MPs for a total of 67 plastic particles isolated and a concentration ranging from 0 to 0.24 items/m^3. The number of MPs found by this study resulted in the same order as that previously reported in the same area by Fossi et al. (2017a) varying between 0 and 0.14 items/m^3. On the other hand, it was lower than those found by Cardelli and coworkers in 2021 in Los Angeles Bay (northern Gulf of California) (0.47 items/m^3), and La Paz Bay (0.63 items/m^3), even if this study also considered the presence of textile fibres. Compared to the Mediterranean Sea and other ocean basins, the level of MPs contamination in the study area was considerably low (Cózar et al., 2014; Eriksen et al., 2014; Suaria et al., 2016).

No differences among sampling sites were highlighted by the statistical analysis with the highest mean concentration found floating in the facing waters of San Juan de la Costa (0.06 ± 0.10 items/m^3) (Table 1). This site is characterized by the presence of several tuna farms, and it is described as an area particularly affected by mining activities and heavy metals accumulation (Méndez-Rodríguez et al., 2021; Muciño-Márquez et al., 2018).

According to the sampling period, the highest particle abundance (0.08 ± 0.09 items/m^3) was found during the last survey carried out between December 2015 and January 2016, followed by the previous one performed in October 2015 (Table 1). More than 70 % of the total MPs were isolated during those two sampling campaigns accordingly to the findings shown by Cardelli et al. (2021) in the same area and sampling period. Conversely, the lowest MPs number has been collected between June and September (2nd and 3rd survey) with only four items identified.

Kruskal-Wallis test and post hoc analysis revealed a statistically higher concentration of MPs at the beginning of the dry season (December–January survey) compared to samples collected during the wet period (June–July survey) ($p = 0.012$). The role of heavy rain in generating run-off waters and facilitating the entry of land-based plastic debris into marine ecosystems through seasonal streams are well-known phenomena (Gündoğdu et al., 2018; Lebreton and Borrero, 2013; Lechner et al., 2014), described to deeply influence the MPs distribution also in a similar foraging area, the Banderas Bay, located along the western coast of Mexico (Pelamatti et al., 2019). However, our data seems not to be affected by the potential influence of the hurricane season insisting from June to October on the investigated area (Collins et al., 2016).

Comparable and low abundances of plastic particles (Table 1) were found in the Cemex and Isla Ballena sampling stations, described as preferential aggregated sites for the whale shark and fin whale, respectively. The proximity of the second most inhabited city of Baja California Sur (approx. 272.200 habitats recorded in 2015) and several tourist beaches (Piñon-Colin et al., 2018) located immediately close to the whale shark foraging sites in association with the strong north wind blowing during their aggregation season could potentially accelerate the influx of plastic debris from land and may be considered as potential sources of pollution.

The presence of beached plastic items potentially entering the sea has been reported by the study of Arreola-Alarcón et al. (2022) in the back and foreshore sediments facing the foraging area of the fin whale. The concentrations, generally ranging from 34 ± 15 to 75 ± 44 items/100 g sediment, showed the highest values during the October and December surveys (155 and 136 items/100 g sediment, respectively), confirming the intense plastic fluxes originating during the dry season.

Even if the assessment of the presence of synthetic particles in the feeding ground of investigated filtering species may not indicate direct ingestion of these pollutants, the adoption of this indirect approach could be considered a useful tool to assess the potential risk that MPs could represent for these poorly studied endangered species (Fossi et al., 2017b; Galli et al., 2022; Germanov et al., 2019). Scientific evidence of direct ingestion of plastic (mainly films, fragments, and lines) in the study area have been reported in faecal samples of three whale sharks by Cardelli et al. (2021) and of an adult fin whale (personal communication, data unpublished). Plastic and microplastic particle ingestion by these species has been recently demonstrated also in stranded organisms. Anthropogenic debris, specifically a cotton swab, fragments of packaging materials and bottle rings have been isolated from a whale shark specimen found dead along the coast of Brazil (Sampaio et al., 2018). Moreover, a mean of 2.8 items/g was found in scat collected in the Philippines from 2012 to 2019, already described as a particularly sensitive area for floating plastic accumulation (Germanov et al., 2019; Yong et al., 2021). MPs presence in fin whales was reported by two studies analysing respectively a stranded specimen found in east Asia (45 particles; Im et al., 2020) and the stomach content of 25 organisms sampled during a commercial operation off the Iceland coasts (57 ± 64 items/kg stomach content; Garcia-Garin et al., 2021). Despite these early data, more clear evidence was needed to better define the potential toxicological and pathogenic effects of MPs on these engendered species.

The most frequent plastic size category was 1–2.5 mm (Fig. 2A). According to previous studies reporting this plastic category as the most abundant, it is the same as that of most zooplankton organisms (Cózar et al., 2014; Doyle et al., 2011; Fossi et al., 2017b; Panti et al., 2015), potentially determining accidental ingestion of MPs mistaken for prey and an attendant risk for fin whale or other filter-feeders such as the whale shark, which spend many hours feeding at the surface. Plastic fragments (81 %) (Fig. 2B) were the majority of plastic items isolated, suggesting a possible fragmentation of large plastic manufactured objects. Moreover, deriving from the breakup of daily use products, they are likely to end up on local beaches and/or washed by currents into the coastline waters as suggested by the findings of Piñon-Colin et al. (2018). Filament was the second most abundant category (10 %), suggesting a potential impact derived from fisheries and aquaculture activities (Fig. 2B), generating over half a million metric tons of fish and seafood for human consumption (e.g. sharks, rays and shrimps) in the whole Gulf of California every year (Páez-Osuna et al., 2017). Differently from the study of Cardelli et al. (2021) where plastic films were described as the predominant shape in La Paz Bay (42 % of the total items), in this study, this category represented only 9 % of the MPs isolated. No spherical particles or pellets were found probably due to the low incidence of industrial activities. Polyethylene (PE) (52 %) and polypropylene (PP) (27 %) were the most detected plastic polymers. Due to the positive buoyancy, lower density and worldwide use, their presence as the main components of plastic litter is well-reported in all ocean basins (Fig. 2C) (Castillo et al., 2016; Pedrotti et al., 2016; Suaria et al., 2016; Wessel et al., 2016).

3.2. *PAE levels in neustonic and skin biopsies samples*

In the investigated area, the increasing tourist pressure has led local authorities to develop and promote management plans to guarantee the ecological and conservation status of the endangered species inhabiting

Table 1

MPs concentration (items/m^3) found in the different sampling stations during the five repeated surveys; Mean ± SD of the total MPs concentration in each survey.

Sampling station	May 2015 (items/m^3)	Jun.–Jul. 2015 (items/m^3)	Aug.–Sept. 2015 (items/m^3)	Oct. 2015 (items/m^3)	Dec. 2015–Jan. 2016 (items/m^3)	Site Mean ± SD
Cemex	0.07	–	–	0.02	0.03	**0.02 ± 0.03**
Isla Ballena	0.01	–	0.01	0.09	0.04	**0.03 ± 0.04**
Lobera	–	0.01	–	0.03	0.04	**0.02 ± 0.02**
San Francisquito	–	–	–	–	0.05	**0.01 ± 0.02**
San Juan de la Costa	–	–	0.02	0.02	0.24	**0.06 ± 0.10**
Season Mean ± SD	**0.02 ± 0.03**	**0.01**	**0.01 ± 0.01**	**0.03 ± 0.03**	**0.08 ± 0.09**	/

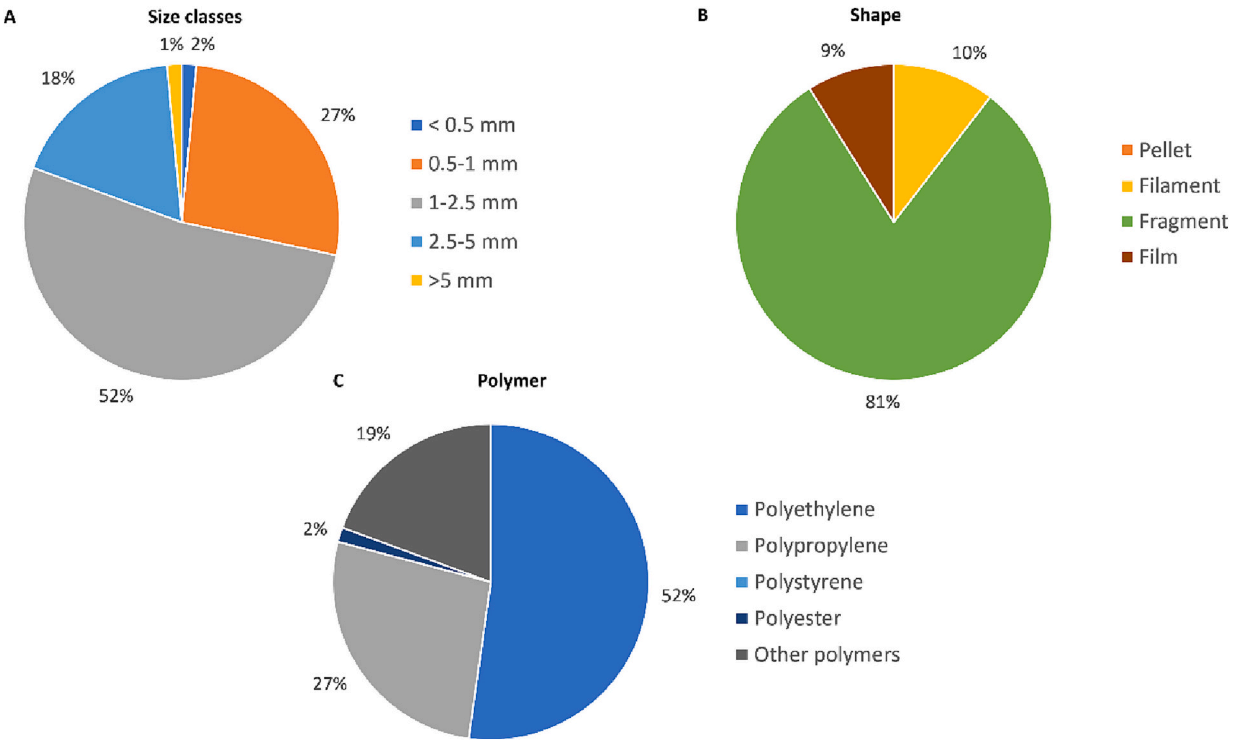

Fig. 2. Percentage of the different size classes (A), shapes (B) and polymers (C) of all MPs items collected in neustonic samples of La Paz Bay.

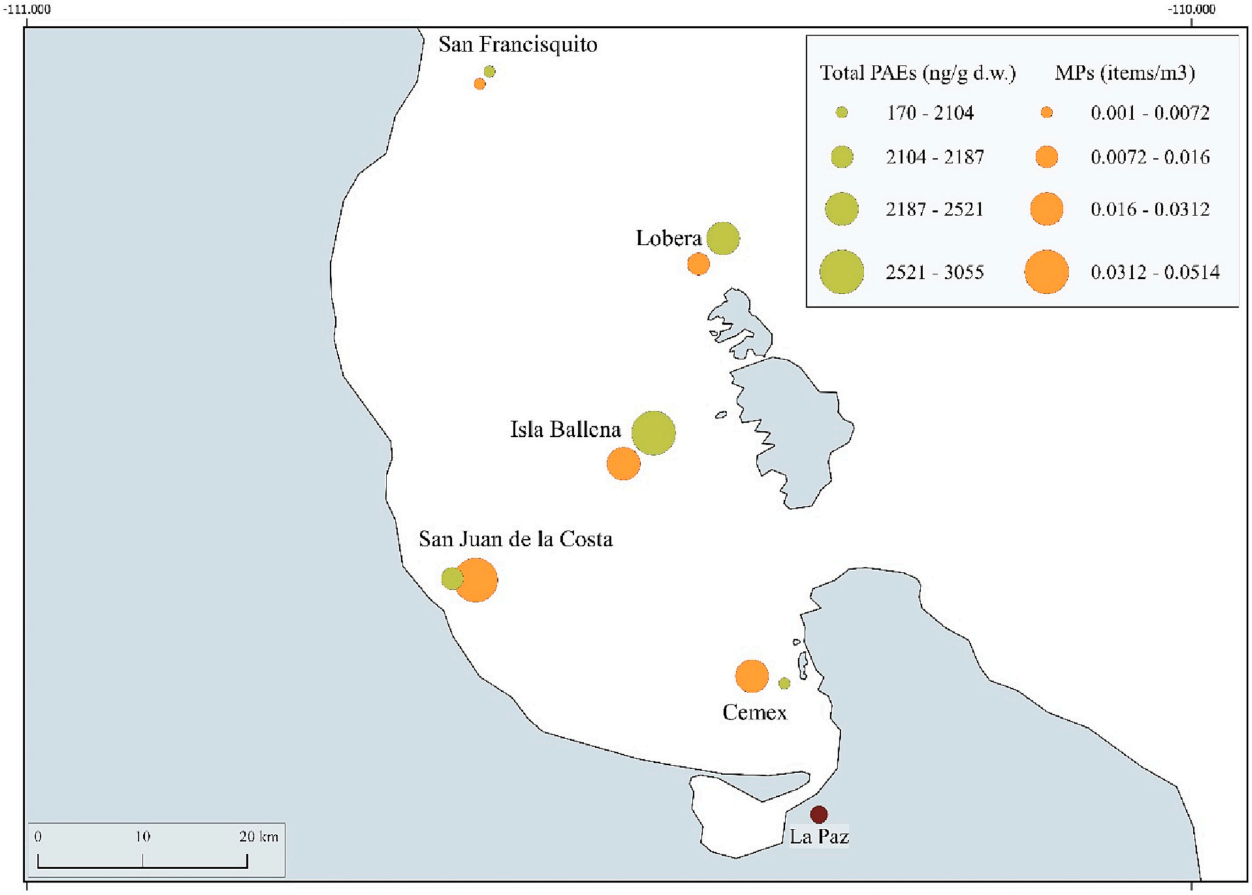

Fig. 3. Total PAE concentrations (green) and MPs abundance (orange) in neuston samples collected in the five sampling stations in La Paz Bay. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

this bay (SEMARNAT, 2017). Despite these measures, recent studies have shown that elasmobranchs and cetaceans from La Paz Bay are exposed to toxic substances as a result of continuous feeding activity on the sea surface near coastal urban areas. Heavy metals, such as selenium and mercury, have been detected in the skin biopsies of whale sharks (Pancaldi et al., 2019) as well as persistent organic compounds (Fossi et al., 2017a). In particular, mean concentration values of 8.42 ng/g w. w. for PCBs, 1.31 ng/g w.w. for DDTs, 0.294 ng/g w.w. for PBDEs and 0.192 ng/g w.w. for HCB were already detected and published (Fossi et al., 2017a) in sub-aliquots of whale shark skin biopsies analysed by this study to evaluate the levels of PAEs as tracers of plastic ingestion. All values of PAE compounds detected in the neuston and skin biopsies samples were reported in Supplementary material Table 2.

Among all PAEs detected in the neuston samples collected across the study area (mean: 2007.4 ng/g d.w), DEHP was the only compound found in each station, followed by its primary metabolite MEPH, MBP and MBzP (80 % frequency of occurrence). BBzP and DNHP were detected in two sampling stations (40 % frequency of occurrence), while in the other sites values were <BDL.

The highest phthalate ester levels have been measured in Isla Ballena (3055.2 ng/g d.w.) and Lobera sampling stations (2521.5 ng/g d.w.) (Fig. 3). These sites, characterized by the presence of all investigated compounds and located exactly in the feeding ground of the fin whale, were resulted also moderately polluted by MPs presence with an average of 0.02 items/m^3. According to the limited human impact, distance to the most populated city in La Paz Bay, and MP abundances, the lowest PAEs concentration (169.6 ng/g d.w.) represented exclusively by DEPH, has been detected in San Francisquito Island (Fig. 3).

Positive correlations between PAE levels and MP characteristics and abundance in the environment were previously found by Baini et al. (2017) concerning the size of synthetic particles and the detected compounds, and Borges Ramirez et al. (2019) and Zhang et al. (2019) about PAEs concentration and MPs presence in sediments and seawater, respectively. These data confirm the suitability to consider PAEs as a proxy of plastic pollution and potential tracers of plastic ingestion in marine organisms. Accordingly, to better investigate the potential relationship between the presence of plasticizers and their release by synthetic particles in the study area, a correlation analysis of the MPs abundance found in the five sampling stations and the levels of PAEs detected in neuston samples collected in the corresponding stations has been performed (Fig. 3). However, Spearman's rank correlation test did not show a clear relationship between the total phthalate loads and MP abundances ($R = 0.5$; $p > 0.05$). The PAE levels represent, indeed, an emerging concern in the area and their concentrations may depend on plastic pollution but also on the local hydrology (increased marine discharges and drainage in urban areas), and anthropogenic coastal activities which can be the direct contamination sources of these compounds as well as synthetic particle of different dimensions.

Plasticizer levels were detected in all the biological matrices investigated (Fig. 4), pointing out the effective exposure to this class of contaminants potentially affecting the marine food web of La Paz Bay.

Significant differences in the PAE levels among the different biological matrices investigated were revealed by the Kruskal-Wallis test and confirmed by the post-hoc Pairwise Wilcoxon sum rank analysis ($p = 0.041$). Plasticizer concentrations detected in the fin whales (5290.6 ng/g d.w.) were significantly higher than those found in neuston (2007.4 ng/g d.w.) and whale sharks samples (1808.1 ng/g d.w.) (Fig. 4). Differences in the total load of these compounds between the whale shark and fin whale can be linked to the excretory activity through the gills in sharks, which makes the PAE levels similar to those

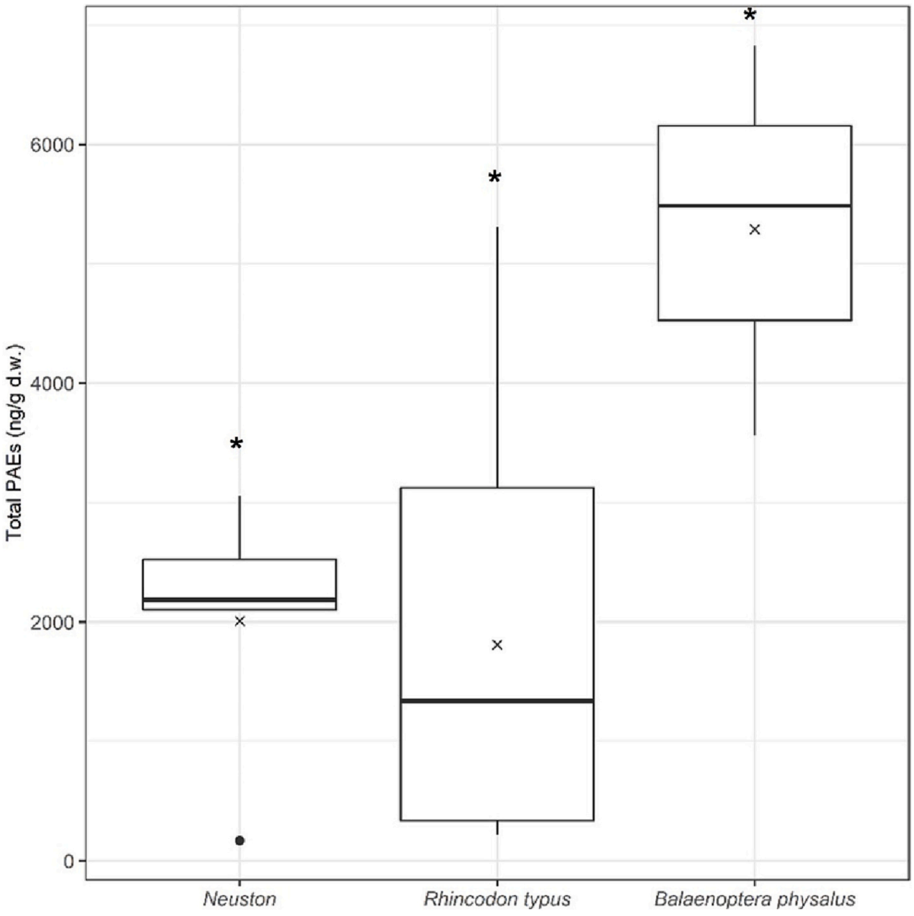

Fig. 4. PAE levels in neuston samples and skin biopsies of whale shark (*Rhincodon typus*) and fin whale (*Balaenoptera physalus*).

found in neuston. On the opposite, higher PAE levels in fin whales could be due to their accumulation in adipose tissue in cetaceans (Fossi et al., 2014). Moreover, the higher exposure risk of mysticete species may be also connected to chemical harm represented by microplastic ingestion, as recently reported by Kahane-Rapport et al. (2022). Differently to the whale shark species, well described as active surface feeders, whale lunges did not occur at the sea surface but recent evidence confirmed as fin whale feeding (92 %) took place deeper than 5 m up to 200 m (Savoca et al., 2021) where the higher concentrations of microplastics have been reported (Pabortsava and Lampitt, 2020; Choy et al., 2020). According to that, krill-feeding whales have been described to filter and potentially ingest a total amount of synthetic particles (2.99×10^6 to 1.74×10^7 MPs day^{-1}; Kahane-Rapport et al., 2022) >1 or 2 orders of magnitude compared to that predicted for the surface feeding whale shark (171 MPs day^{-1}) (Fossi et al., 2017a).

These differences in the behavioural ecology in association with plastic exposure surely influence the PAE uptake pathways in the investigated species, altering their accumulation and potentially explaining the levels detected in the specimens analysed. To date, only a few studies deal with the evaluation of plasticizers in free-ranging and stranded cetacean species and neustonic samples linking their detection with potential plastic ingestion. All these studies focused on the preliminary evaluation of DEHP and its primary metabolite MEHP concentration in neuston samples and blubber of stranded specimens of fin whales (Fossi et al., 2012, 2016). Despite that, data described by these studies cannot be compared with those here reported due to the different measurement units adopted (ng/g fresh weight vs ng/g dry weight). A more detailed study, published by Baini et al. (2017), evaluating the presence of seven PAE compounds in Mediterranean neuston samples and skin biopsies of four different cetacean species (one mysticete and three delphinid species) showed lower plasticizers levels (2935 ng/g d. w.) than those detected in specimens of La Paz Bay. Despite the different plastic pressure and potentially associated PAEs exposure that characterized the Mediterranean Sea (Cózar et al., 2014; Suaria et al., 2016), the data here reported, confirm the toxicological risk of organisms inhabiting La Paz Bay, already described as a polluted area, and highlight the urgent need to gain information on the relationship between plastic and associated chemicals, such as the phthalate ester compounds, involving the exposure pathways and the metabolic and accumulation processes potentially influencing their detection in biological tissues.

Analysis of PAE fingerprints shows a similar pattern of distribution between neuston samples and fin whale and whale shark skin biopsies. No statistical differences were highlighted between diester compound and monoester metabolite level ratios in the samples analysed, with DEPH (41 % of the total), MBP (27 % of the total) and MEHP (16 % of the total) showing the highest concentrations (Fig. 5). Nevertheless, slight differences in the level of both parent compounds (DNHP, BBzP, DEPH) and metabolites (MBP, MBzP, MEPH) in neuston, whale shark and fin whale suggest different metabolism of PAEs in these organisms, which is worth a deeper investigation on the fate and behaviour of these emerging compounds in biota. Globally used as a plasticizer in polymer products, characterized by a $\log K_{OW} = 7.73$ indicating the ability to accumulate into organisms and hydrophobicity due to the long carbon chain, the presence of DEHP in marine wildlife and marine mammals has been reported in several studies (Baini et al., 2017; Fossi et al., 2012, 2014; Net et al., 2015). Recently, moderate risk for this compound residuals in MPs has been assessed by Fauser et al. (2020), while its capacity to desorb from plastic has been widely confirmed in particular once ingested and exposed to gut conditions (Bakir et al., 2014; Kühn et al., 2020; Rani et al., 2014). Moreover, the relatively high

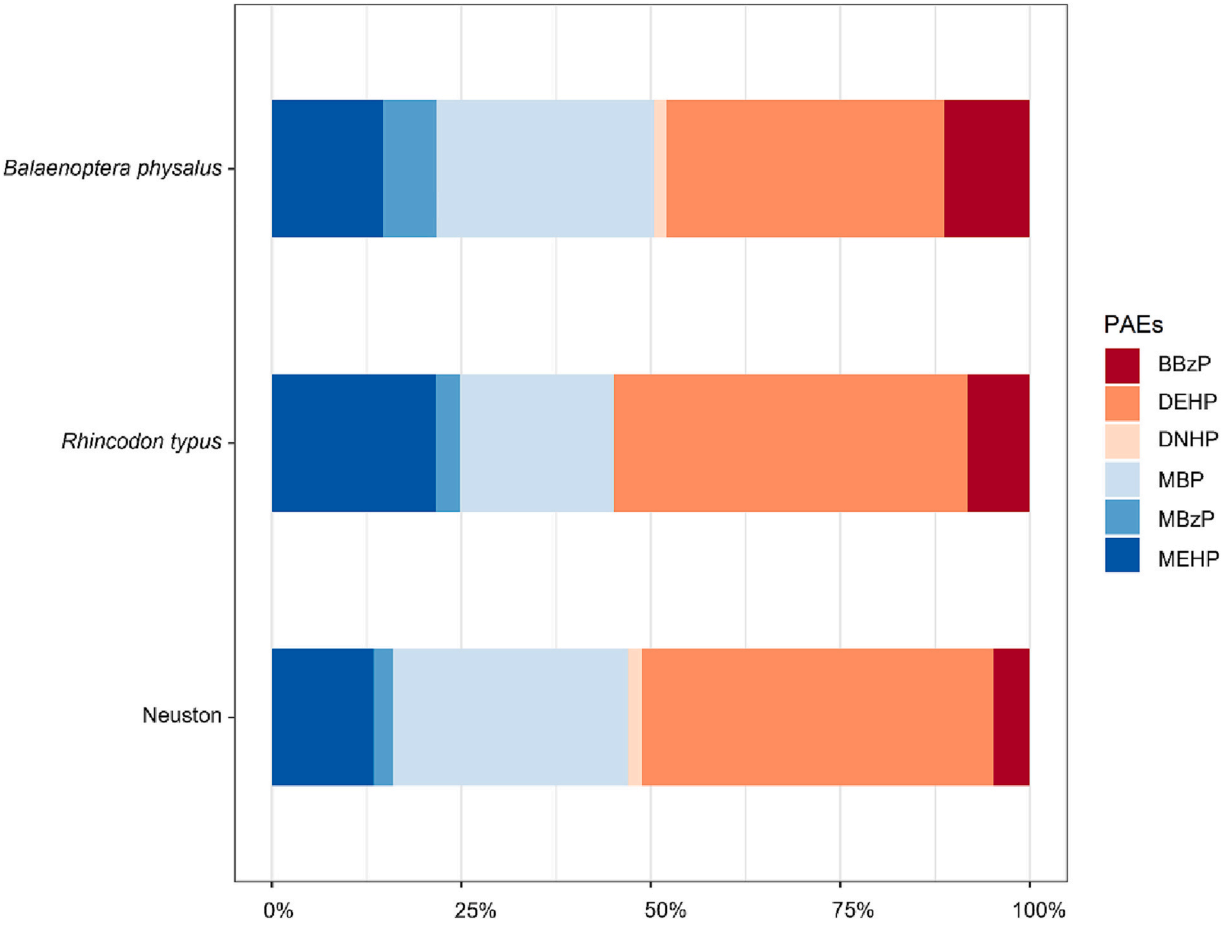

Fig. 5. PAEs fingerprint in neuston samples and skin biopsies of fin whales and whale sharks collected in La Paz Bay.

concentration of MEHP (270–776 ng/g d.w.), could be considered a marker for exposure to DEHP, as it is well known that this compound is rapidly metabolized to MEHP, its primary metabolite (Latini et al., 2004).

Little is known about Monobutyl phthalate (MBP). It is the principal metabolite of di(n-butyl) phthalate (plasticizer used in PE, PP and PS polymer) (Fries et al., 2013) and it is capable to act as an anti-androgenic compound by altering testosterone biosynthesis (Ema and Miyawaki, 2001). Its presence in marine environments has been highlighted only by the study carried out by Baini and colleagues in 2017.

4. Conclusions

The data achieved by this study clearly stated the urgency to better define plastic and its associated chemical pressure in an extremely biodiverse area, characterized by >850 endemic species and a growing anthropic pressure. Despite the low concentration of MPs detected in the five sampling stations, the evaluation of their accumulation and distribution according to seasonal variations is a prerequisite for a comprehensive study of their environmental impacts. Plastic presence in the fin whale and whale shark feeding grounds represents a serious threat to this species potentially exposed to the ingestion of heavy quantities of synthetic particles because of their feeding behaviour. Local policies that regulate the use of plastic items should be enforced especially in areas adjacent to feeding grounds of protected megafauna as well as monitoring activities to continuously assess their toxicological status. PAE levels evaluation and detection may be considered a useful indirect tool to evaluate the chemical impacts of plastic pollution although more consistent evidence is required to better define their association with ingested synthetic particles and the residual fraction dissolved in water. Moreover, other aspects such as phthalates sources (e.g., increasing industrialization, coastal resources exploitation, atmospheric and degradation processes), their mechanisms of dispersion and leaching and the chemical reactions occurring in the environment must be investigated and considered to perform a comprehensive assessment of the toxicological status of the ecological valuable areas, such as the La Paz Bay.

CRediT authorship contribution statement

Matteo Galli and Matteo Baini performed the microplastic and phthalates analysis, analysed the dataset and coordinated the writing, review and editing of the manuscript; Tabata Olavarrieta Garcia performed the sampling activities, microplastic and phthalates analysis, wrote, reviewed and edited the manuscript; Jorge Urbán R. designed and obtained funding for the sampling activity, performed the cetacean samples collection, reviewed the manuscript; Deni Ramírez-Macías obtained funding for the whale shark sampling, performed the samples collection, reviewed the manuscript; Lorena Viloria-Gómora contributed to design and perform cetacean and microplastic surveys, reviewed the manuscript; Cristina Panti contributed to the analysis of the data, wrote, reviewed and edited the manuscript; Tania Martellini and Alessandra Cincinelli supported the phthalate analysis and elaboration of the results, reviewed the manuscript; Maria Cristina Fossi conceived the study, participated to the sampling activities, obtained funding and coordinated laboratory analysis, wrote, reviewed and edited the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2023.115086.

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