

# Plastic pollution in freshwater ecosystems: macro-, meso-, and microplastic debris in a floodplain lake

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Abstract Plastic pollution is considered an important environmental problem by the United Nations Environment Programme, and it is identified, alongside climate change, as an emerging issue that might affect biological diversity and human health. However, despite research efforts investigating plastics in oceans, relatively little studies have focused on freshwater systems. The aim of this study was to estimate the spatial distribution, types, and characteristics of macro-, meso-, and microplastic fragments in shoreline sediments of a freshwater lake. Food wrappers (mainly polypropylene and polystyrene), bags (high- and low-density polyethylene), bottles (polyethylene terephthalate), and disposable Styrofoam food containers (expanded polystyrene) were the dominant macroplastics recorded in this study. Contrary to other studies, herein macroplastic item surveys would not serve as surrogates for microplastic items. This is disadvantageous since macroplastic surveys are relatively easier to conduct. Otherwise, an average of 25 mesoplastics (mainly expanded polystyrene) and 704 microplastic particles (diverse resins) were recorded per square meter in sandy sediments. Comparisons with other studies from freshwater and marine beaches

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indicated similar relevance of plastic contamination, demonstrating for the first time that plastic pollution is a serious problem in the Paraná floodplain lakes. This study is also valuable from a social/educational point of view, since plastic waste has been ignored in the Paraná catchment as a pollutant problem, and therefore, the outcome of the current study is a relevant contribution for decision makers.

Keywords Plastic pollution  $\cdot$  Macro-, meso-, and microplastic  $\cdot$  Floodplain lake  $\cdot$  Endanger environment  $\cdot$  FT-IR spectrophotometer

# Introduction

Plastics are already present in sufficient numbers to be considered as one of the most important types of "technofossil" that will form a permanent record of human presence on Earth (Zalasiewicz et al. 2016). For decades, humans have been disposing plastic waste in the sea and rivers, causing beach and water pollution (Faure et al. 2015a, b). At present, plastic pollution is considered a crucial environmental problem (UNEP 2014), and it is identified alongside climate change as an emerging issue that might affect human health and biological diversity in the near- to medium-term future (Sutherland et al. 2010).

Despite wide research efforts investigating plastics in oceans, little studies have focused on freshwater systems (Wagner et al. 2014). Thus, there is a relatively lack of knowledge on plastic waste occurrence in river water

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and sediment worldwide. Data on their presence, sources, and fate is still scarce (Thompson et al. 2009; Eerkes-Medrano et al. 2015). The same is true for their chemical burden and ecological/physiological effects.

However, in raising questions about the origin and risk posed by plastic litter in freshwater environments, some studies should be emphasized. Most of these researches have focused on lakes, for instance the Great Lakes (Eriksen et al. 2013), Victoria Lake (Biginagwa et al. 2016), and alpine lakes (Imhof et al. 2013). Other studies concentrated on river systems, e.g., the Danube (Lechner et al. 2014), Thames (Morritt et al. 2014), Tamar (Sadri and Thompson 2014), Los Angeles (Moore et al. 2011), Rhine and Main rivers (Klein et al. 2015).

As plastic breaks into smaller pieces (microplastics), it is more likely to infiltrate food webs (Browne et al. 2008). Studies have proved that freshwater invertebrates and fish can ingest plastic particles, causing injuries, stress, contaminant bioaccumulation, and tumor formation; immune response disrupting feeding; and altering metabolic function (e.g., Rosenkranz et al. 2009; Imhof et al. 2013; Sanchez et al. 2014; Biginagwa et al. 2016). As a result, estimations of particle composition (type of plastic conforming it) are a key point to determine potential risks to the environment since many plastics are chemically harmful, either because they are toxic or because they absorb other pollutants (Teuten et al. 2009; Rochman et al. 2013).

Most plastic pollution studies focused on micro-, meso-, or macroplastics. Very few of them reported all size ranges (e.g., Noik and Tuah 2015). Because there are no antecedents of plastic contamination in shore sediments of the Paraná River system, we included in this study the three size ranges.

Considering the above, the aim of this study was to estimate the spatial distribution, types (resin composition and origin), and characteristics (color, shape, size) of macro-, meso-, and microplastic fragments in shoreline sediments of a freshwater lake.

#### Methodology

## Study area

The Paraná is ranked ninth among the largest rivers of the world according to its mean annual discharge to the ocean (18,000 m<sup>3</sup> s<sup>-1</sup>; Latrubesse 2008), supporting 19

large cities (with a population greater than 100,000 inhabitants) and having a great ecological, cultural, and economic importance. This river has a large flood-plain area with thousands of permanent and semipermanent lakes and ponds, which support one of the most diverse biotic community in the world (Wong et al. 2007). The current study was performed in the Setúbal Lake, one of the larger floodplain lakes of the Paraná River (Fig. 1). This shallow lake has a surface area of 32 km<sup>2</sup>, an average depth about 2 m, and a water residence time of 0.002 year (Pecorari et al. 2006). Santa Fe City (653,000 inhabitants) extends along the western shore of the Setúbal Lake, with rubbish dumps and storm sewers directly discharging into the lake.

#### Sampling trip

Prior to conducting the sampling, some background information on the lake shores was documented such as morphological features and human interventions (i.e., concrete groynes), based on the NOAA Technical Memorandum (Lippiatt et al. 2013). Since the lake shores are used for recreational purposes during the summer season, the sampling was performed before starting it (December 2016). This was to avoid the sporadic and temporal influence of beachgoers during the summer season.

#### Macroplastic sampling

Many authors noted the difficulty in comparing data among plastic pollution studies (Ryan et al. 2009). This difficulty is largely owing to differences in sampling protocols. In order to make direct comparisons with other studies, we adopted the most widely used methods. Referring to the size ranges, the plastic debris was termed micro- ( $\leq$ 5 mm), meso- (5 mm to 2.5 cm), or macroplastic (> 2.5 cm), since they have been adopted by UNEP (Cheshire et al. 2009), MSFD Technical Subgroup on Marine Litter (2013), and NOAA (Lippiatt et al. 2013).

With the aim to obtain a reliable estimation of plastic litter, two transects of 50 m in length and 5 m wide were selected for the macroplastic survey (Noik and Tuah 2015). Transects were chosen on higher and lower polluted areas of the beach, based on a previous visual inspection (transects 1 and 2, respectively; Fig. 1), involving the most recent flotsam line and covering more than a 20% of the shoreline section, as recommended by



Fig. 1 Study area in the Paraná River floodplain and the specific sampling location on the shoreline of Setúbal Lake

Lippiatt et al. (2013). Macroplastic items were visually collected by hand and transferred to the laboratory for further analyses. The macrodebris item concentration (number of debris items  $m^{-2}$ ) per transect was calculated as follows (Lippiatt et al. 2013):

$$c = \frac{n}{(w \ l)}$$

- c concentration of debris items (no. of debris items  $m^{-2}$ ).
- *n* no. of macrodebris items observed.
- w transect width (m).
- *l* transect length (m).

The same equation was also used to estimate the weight, area, volume, and length of macroparticles (macroplastics were also referred to the no. of items per  $250 \text{ m}^2$ — $50 \times 5 \text{ m}$ —and even per  $100 \text{ m}^2$ ).

## Mesoplastic sampling

Mesoplastics were collected from triplicate samples  $(1 \text{ m}^2 \text{ quadrats})$  located in the line of the macroplastic transects (Lippiatt et al. 2013). Once the quadrat placement was selected, we collect the top 3 cm of sand sediments. Each sample was sieved in the field using a

stainless steel 5 mm mesh size, removing any pieces of mesoplastics. Mesodebris particles were transferred to the laboratory for further analyses.

The mesodebris item concentration (number of debris items  $m^{-2}$ ) was calculated as follows (modified from Lippiatt et al. 2013):

$$c = \frac{n}{a}$$

- c concentration of debris items (no. of debris items  $m^{-2}$ )
- *n* no. of debris items observed.
- a area sampled.

The same equation was also used to estimate weight, area, volume, and length of mesoparticles.

## Microplastic sampling

As in the case of mesoplastics, samples for microplastics were collected per triplicate from macroplastic transects employing the quadrat method ( $25 \times 25 \times 3$  cm; Klein et al. 2015).

Once the "microquadrat" placement was selected, we removed the top 3 cm of sand sediments using a small stainless steel shovel. Sediment samples were transferred to the laboratory for further analyses. Each sample was equivalent to 1.8 kg of dry sand, approximately.

The same equation as in the case of mesoplastics was also used to estimate the number of items, weight, area, volume, and length of microplastics.

## Processing samples

## Macroplastic identification

Collected macroplastic debris were washed, counted, measured, weighed, and classified in the laboratory (item by item). Macroitems were classified taking account their functional origin (e.g., food wrappers, beverage bottles, cups, shopping bags, etc.) according to the NOAA Technical Memorandum (Lippiatt et al. 2013) and type (hard plastic, foam, film, etc). Additionally, the ASTM (American Society for Testing and Materials International) International Resin Identification Coding System (RIC, Standard Practice for Coding Plastic Manufactured Articles for Resin Identification 2016) was used to identify the plastic resin used in manufactured macroarticles (Gasperi et al. 2014). The later procedure was not always possible since the ASTM code was not always visible. In these cases, we compiled information based on the product functionality and most commonly used resin (e.g., Driedger et al. 2015).

#### Mesoplastic identification

Mesoplastics were classified into hard plastic fragments, foam, films, and others (Gündoğdu and Çevik 2017). Furthermore, number of items, weight, area, volume, length, and color were recorded. Mesoplastic volume was estimated through the water displacement method (Archimedes' principle), using graduated cylinders and pipettes. As many plastics float, they were individually pricked and forced to sink using very thin needles of negligible volume.

#### Microplastic separation and identification

#### Drying, sieving, and density separation

Microplastic separation was performed according to Masura et al. (2015). In this regard, full samples were dried 60 °C per 24 h, weighed, and sieved through a stainless steel sieve with 350  $\mu$ m mesh size (45) using a

Retsch<sup>™</sup> sieve shaker. All material left above the sieve was transferred to a 1-L beaker for wet peroxide oxidation, and 30% hydrogen peroxide at 4:1 proportion was added to the sample. The mixture was placed on a hot plate set to 60 °C, and the reaction was allowed to continue until all organic material disappeared (Yonkos et al. 2014). Hydrogen peroxide was completely washed from the sampling through a 350-µm mesh size, using distilled water.

After the full dissolution of the organic matter, a concentrated saline NaCl solution  $(1.2 \text{ g cm}^{-3})$  was added and strongly stirred for about 1 min (Hidalgo-Ruz et al. 2012; Yonkos et al. 2014). Subsequently, the supernatant with the plastic particles was extracted and washed with distilled water for further processing. This step was repeated as many times as it was needed in order to ensure the absence of plastic particles between sand sediments.

#### Microscope examination

Careful visual sorting of residues was necessary to separate the plastics from other materials, such as shell, fish bones, and scale fragments, as well as other no natural particles (metal paint coatings, glass, aluminum foil, etc.). This procedure was performed under a Boeco<sup>TM</sup> zoom stereo microscope and a Nikon™ binocular microscope with a magnification range of ×10-40. Microscopic examinations were repeated three times, to be sure all plastic particles were properly identified. The criteria advanced by Norén (2007) were used to define a plastic particle: (i) no cellular or organic structures were visible in the plastic particle/fiber; (ii) if the particle was a fiber, it should be equally thick, not taper toward the ends, and have a three-dimensional bending (not entirely straight fibers which indicates a biological origin); and (iii) clear and homogeneously colored particles.

Microplastics were classified into hard plastic fragments, fibers, foams, and films (Gündoğdu and Çevik 2017). Subsequently, number of items, weight, area, volume, length, and color were recorded for each item category (Castañeda et al. 2014). Microparticles were weighed using a Mettler Toledo<sup>™</sup> analytical balance (readability of 0.1 mg).

### Fourier transform infrared (FT-IR) spectrophotometer

FT-IR Spectrophotometer Shimadzu IR Prestige  $21^{TM}$  was used to analyze the particles of doubtful origin in

order to confirm (or reject) their plastic composition. This is an optimal means of polymer identification (Song et al. 2015) and is widely used in plastic pollution studies (e.g., Frias et al. 2014; Li et al. 2016). Furthermore, the most abundant items of macro-, meso-, and microplastics were further identified by spectrophotometry. Spectra ranges were set at 4000–400 cm<sup>-1</sup>, using the IRsolution Agent software. The resulting spectra were directly compared with the reference library databases.

## Results

## Macroplastics

Based on the NOAA's classification (Lippiatt et al. 2013), a total of 24 categories of macroplastic debris were recorded in this study. They were bags (mainly shopping and garbage bags), food wrappers (cookies, powdered juices, etc), beverage bottles (mainly water and soft drinks), beverage bottle caps (and other product caps), label bottles, cleaning product containers, personal care product containers, paint pots, disposable cigarette lighters, pens, disposable tableware products, disposable hard food containers, disposable foam food containers (cups, etc), straws and stirrers, toys, strapping bands, personal care products (toothbrush and hairbrush, etc), medical products (blister packs, etc), household appliances pieces, plastic cards, rope pieces, fish line, and hose pieces. Subsequently, we summarized them into nine wider categories (Table 1).

According to Table 1, food wrappers, bags (plastic film), and disposable foam food containers (mainly packaging for clamshells, trays, and cups) were the dominant macroitems recorded in this study. An average of 217 macroitems were recorded per transect (i.e., 1.15 macroplastics m<sup>-2</sup>), with 91 of them being food wrappers. Beverage bottles were the heaviest group of macroplastics, totalizing about 600 g per transect, followed by bags (190 g). An average of 1.23 kg of plastic was collected from each transect (i.e., 4.9 g m<sup>-2</sup>). Otherwise, plastic films (bags and food wrappers) covered an average surface of 3.5 m<sup>2</sup> per transect. As expected, the highest volume was given by bottles (empty bottles), particularly water and soft drinks (Table 1).

Based on the ASTM RIC, Standard Practice for Coding Plastic Manufactured Articles for Resin Identification (2016) and the FT-IR spectrophotometer, polypropylene (PP) and polystyrene (PS) were the main resins used in food wrappers. PP was additionally present in bottle caps and closures. High-density polyethylene (HDPE) and low-density polyethylene (LDPE) were the main plastic resin out of which the bags were made. Otherwise, HDPE was widely found in other products like personal care products (toothbrushes, hairbrushes, combs, deodorants, and shampoos) and cleaning product containers (floor cleaners; Table 1).

Numerous macroitems made up of expanded polystyrene (EPS) were recorded, generally fragmented in several pieces. Styrofoam food containers were the dominant items composed of this resin, including foam bowls, lids, trays, cups, and clamshell boxes. Beverage bottles, cosmetic product containers, hard food containers, and even strapping bands were made up of polyethylene terephthalate (PET; Table 1).

Other resins were identified but at relatively low densities. The presence of polyvinyl chloride (PVC) was relatively irrelevant in terms of number of items and total weight. PVC was found in miscellaneous products, from fragments of hoses to blisters. Nylon (generic designation of dry polyamide) was found in little pieces of rope and fish lines. Pieces made up of polymethylmethacrylate (PMMA; also known as acrylic or acrylic glass) of unknown origin were identified. Finally, several disposable lighters manufactured of styrene acrylonitrile (SAN) were registered (Table 1). However, we do not exclude the presence of other plastic resins occurring at low densities.

#### Mesoplastics

Foam plastics (EPS) were the dominant mesoplastic category (17 items m<sup>-2</sup>, Table 2), while the heaviest ones were hard plastics (1.22 g m<sup>-2</sup>). The latter exhibited several colors, which is a proxy indicator of high variation in resin composition and origin. All mesoplastics combined totaled an average of 25 items m<sup>-2</sup> and 1.9 g m<sup>-2</sup>, covering a hypothetical area of 0.003 m<sup>2</sup>.

#### Microplastics

Microfragments of hard plastics and fibers were the dominant items recorded (Table 3). However, foam microparticles (EPS) represent the largest area

	Туре	No. of items	Weight (g)	Area (m <sup>2</sup> )	Volume (L)	Length (m)	Resin
Bags	Film	52.5	190.4	3.49	-	-	HDPE, LDPE
Food wrappers	Film	91	85.3	1.45	-	-	PP, PS
Hard food container/food service items	Hard	12	82.4	-	_	-	PS, PET
Foam food containers	Foam	29.5	17.4	-	_	-	EPS
Beverage bottles	Hard	9.5	597.1	-	21.88	-	PET
Personal care products	Hard	2.5	73.7	-	0.33	-	HDPE, PET
Cleaning product containers	Hard	3.5	68.6	-	2.04	-	HDPE, PET
Fish lines	Line	0.5	1.7	-	-	1.5	Nylon
Others	Others	16.5	116.5	-	-	1	PMMA, PVC, SAN
Total		217.5	1232.8	4.945	24.24	2.5	10

Table 1 Summary of the main macroplastic debris and their quantification per transect (transect area =  $250 \text{ m}^2$ ) according to number of items, weight, area, volume, and length

Resins are sorted by decreasing order of frequency. Dash (-) indicates negligible or absent values

HDPE: high-density polyethylene; LDPE: low-density polyethylene; PP: polypropylene; PS: polystyrene; PET: polyethylene terephthalate; EPS: expanded polystyrene; Nylon: dry polyamide; PVC: polyvinyl chloride; SAN: styrene acrylonitrile; PMMA: polymethylmethacrylate

 $(6.9 \text{ cm}^2)$ . In total, an average of 704 microplastic fragments (m<sup>2</sup>) was found in shoreline sediments.

#### Macro-, meso-, and microplastics

Figure 2 shows a large variety of plastic debris solely collected from transect 1. Note the diversity of manufacture origins (domestic rather than industrial), usages, consistencies, sizes, colors, shapes, etc.

Table 4 shows that film was clearly the dominant macroplastic category (in number of pieces), while foam was for mesoplastics, and hard and fiber were for microplastics. According to ANOVA results (Table 4), both transects for macroplastic collection were significantly different between each other, with T1 being the dominant one in number of items. However, sampling stations for mesoplastics located at T1 and T2 were not statistically different between each other (Table 4). Otherwise, significantly higher densities of microplastics were recorded in sampling stations located at T2.

Figure 3 shows results of the IR spectra of some selected plastic particles. The IR spectrum of HDPE (Fig. 3a) presents the characteristic vibrational bands of polyethylene: CH<sub>2</sub> stretching (2920 and 2850 cm<sup>-1</sup>), bending deformation (1473 and 1463 cm<sup>-1</sup>), CH<sub>3</sub> symmetric deformation (1377 cm<sup>-1</sup>), weak wagging deformation (1366, 1351, and 1173  $\text{cm}^{-1}$ ), weak twisting deformation (1306 cm<sup>-1</sup>), and rocking (730 and 720 cm<sup>-1</sup>). The IR spectrum shown in Fig. 3b is assigned to the LDPE. Even though the IR bands are the same as those of HDPE, the intensity of the CH<sub>3</sub> symmetric deformation mode at 1377  $\text{cm}^{-1}$  was well defined, indicating a higher concentration of methyl groups and, therefore, a considerable amount of side chains, which is distinctive of LDPE (Gulmine et al. 2002). The vibrational modes observed in Fig. 3c match with those of PS. This polymer, which contains aromatic rings, was identified by its group of bands around (i) 3090 and 2900 cm<sup>-1</sup> (aromatic and alkane C-H stretching), (ii) 1600 cm<sup>-1</sup> (ring breathing vibration and CH<sub>2</sub> deformation), and (iii) 1300 and

 Table 2
 Mesoplastic average recorded per square meter

	No. of items	Weight (g)	Area (cm <sup>2</sup> )	Volume (mL)	Length (cm)	Color
Films	1.7	0.0177	5.32	0.001	_	TRN, MTRN
Hard plastics	5.7	1.2248	10.3	1.4	_	RD, BL, LB, WHI, GRY
Foam plastics	17	0.6913	21.65	5.56	_	WHI, YEL
Others	0.7	0.01	_	0.0007	6.5	WHI
Total	25	1.9439	37.26	6.97	6.5	8 colors

TRN: transparent; MTRN: milky transparent; RD: red; BL: blue; LB: light blue; WHI: white; GRY: gray; YEL: yellow

 Table 3 Microplastic average recorded per square meter

	No. of items	Weight (g)	Area (cm <sup>2</sup> )	Length (cm)	Color
Films	36	0	1.69	0	WHI, YEL, OR, TRN
Hard plastics	288	0.073	1.292	0	WHI, GN, LB, OR, TRN, BL, BK, YEL
Foam plastics	116	0.001	6.894	0	WHI
Lines	24	0	0	66	WHI, GN, LB, TRN, BL
Fibers	140	0	0	76.4	WHI, BL
Total	704	0	9.876	142.4	9 colors

TRN: transparent; MTRN: milky transparent; BL: blue; LB: light blue; WHI: white; GRY: gray; YEL: yellow; GN: green; OR: orange; BK: black

700 cm<sup>-1</sup> (aromatic C–H deformation). The IR spectrum of Fig. 3d is consistent with that of PMMA, characterized by (i) C–H stretching bands in the region of 3010–2800 cm<sup>-1</sup>; (ii) CO<sub>2</sub> stretching at 2350 cm<sup>-1</sup>; (iii) n(CO) bands at 2200 and 2120 cm<sup>-1</sup>; (iv) carbonyl stretching band at 1750, 1752, 1711, and 1600 cm<sup>-1</sup>; (v) IR bands around 1485 and 1030 cm<sup>-1</sup>, due to de C–H and CH<sub>3</sub> deformation and C–C–O stretching modes; (vi) O–CH<sub>3</sub> and CH<sub>2</sub> rocking modes between 990 and 800 cm<sup>-1</sup>; and (vii) C–C stretching bands around 760 and 700 cm<sup>-1</sup> (Ennis and Kaiser 2010).

# Discussion

### Macroplastics

The number of macroplastics significantly differed per transect (p = 0.023; Table 4). This could be explained by T1's proximity to a concrete groyne (originating a depositional area slightly downstream). An average of 217 macroplastic items were recorded per transect (i.e., 115 items 100 m<sup>-2</sup>). In comparison, Sciacca and van Arkel (2015) reported an average of 51 macrodebris 100 m<sup>-2</sup>



Fig. 2 Examples of macro- (a), meso- (b), and microplastics (c-f) recorded in one transect (T1), one quadrat  $(1 \text{ m}^2)$ , and one microquadrat  $(0.0625 \text{ m}^2)$ , respectively. Microplastic images were

obtained under an optical microscope, where c is a piece of nylon, d piece of PET, e piece of EPS, and f milky transparent piece of PMMA

 
 Table 4
 Average of macro-, meso-, and microplastic items recorded per square meter

Per m <sup>2</sup>	Macroitems	Mesoitems	Microitems
Films	0.574	1.7	36
Hard plastics	0.11	5.7	288
Foam plastics	0.118	17	116
Lines	0.002	0	24
Fibers	0	0	140
Others	0.066	0.7	0
Total	0.87	25.1	704
ANOVA	T1 vs. T2	SS1 vs. SS2	SS1 vs. SS2
р	0.023	0.098	0.199
F	5.47	2.96	1.77
Total	1.26 vs. 0.47	46 vs. 4	504 vs. 904

ANOVA comparison between both T1 and T2 transects (macroplastics) and sampling stations for meso- and microplastic. ANOVA data was log<sub>(10)</sub> transformed

*T*: transect; *SS*: sampling station; *Total*: total number of items per transect and per sampling station

in Bermuda, 33 in Azores, and 26 in Easter Island beaches. While these beaches are located on the Atlantic Ocean, what should be considered is that the plastic input is conveyed by rivers and released into oceans, both environments being connected (Morritt et al. 2014).

A significant proportion of macroplastics consisted of food wrappers, bags, and disposable foam food containers (Table 1). Polypropylene was widely recorded in food wrapper/packaging and bottle labeling (Table 1). PP is liable to chain degradation from exposure to heat and UV radiation from sunlight in dry beach sediments, as it has been found herein. However, PP is extremely resistant to biodegradation (Nicholson 2006). In addition, the ability of PP to absorb persistent organic pollutants may cause further environmental problems. Little is known about the effects of PP in freshwater systems. However, Mato et al. (2001) documented 100,000 to 1 million times higher concentrations of polychlorinated biphenyls (PCBs) and dichlorodiphenyldichloroethylene (DDE) in PP pieces from the sea than in the surrounding water.

Williams and Simmons (1996) suggested photodegradation in river shorelines as the principal cause of sample deterioration for LDPE. These authors concluded that the longevity of such plastics is a major reason for their abundance and widespread distribution both on river banks and beaches. In line with this, we observed many LDPE macroitems (mainly grocery bags) between sediments at initial and advanced plastic breakdown process, and its relevance in number was evident (Table 1).

According to our results, plastic pollution was more associated to domestic solid wastes than to industrial ones. This statement is also supported by the fact that no meso- or microplastic pellets were recorded in this study (pellets are mainly used in plastic production; Klein et al. 2015). Partial coincident results were found by Gasperi et al. (2014), who recorded food wrappers/ containers and plastic cutlery as dominant floating debris in the Seine River.

Out of all the categories recorded, plastic bags (HDPE and LDPE) outnumbered the other categories in total surface and were the second most abundant and heaviest (Table 1). Contrary to this, Morritt et al. (2014) reported a relatively small amount of plastic bags (< 2%) along the Thames River. It is important to say that these authors intercepted submerged plastic items using eel fyke nets anchored to the river bed. To start with, this methodological disparity would be attributed to the design of this net which could exclude larger plastic bags (Morritt et al. 2014). Likewise, UK public policies encourage people not to use supermarket carrier bags, which could also contribute to explain this discrepancy. The monomers making up some plastic bags are thought to be relatively harmless. Yet, these materials can still become toxic by picking up other pollutants (Rochman et al. 2013).

On the other hand, beverage bottles (PET) were the heaviest group of macroplastics, totalizing about 600 g per transect (Table 1). From a 5-m wide transect at Merthyr Mawr beach, an estuarine beach of South Wales, Williams and Simmons (1996) found 96 plastic bottles per km. In the present study, we have recorded an equivalent to 190 bottles per km, almost twice that amount. From an ecological perspective, bottles could encourage the invasion of species that prefer hard surfaces, and as a result, indigenous species would be displaced (Derraik 2002). An example of this is the alien bivalve Limnoperna fortunei. This species attaches strongly to hard substrate like plastic bottles (Karatayev et al. 2010). During our sampling campaign, some aggregations of L. fortunei valves were observed attached to plastic bottles.



Fig. 3 Resulting FT-IR spectra for pieces of HDPE (a), LDPE (b), PS (c), and PMMA (d)

Metals are widely used in additive agents during plastic production, functioning as catalysts, pigments, and plastic stabilizers. For example, lead stearate enhances smoothness and stability of plastic products made from PVC polymer (Minagawa 1996). Nakashima et al. (2012) suggested that PVC products act as a transporting vector of toxic metals to beach environments. Propitious-ly, in this study, PVC (toys and hose pieces; see "Others" in Table 1) has been detected in low concentrations.

According to Table 1, the prevailing number of macroitems was made up of PS, followed by HDPE and EPS. In contrast, a dissimilar composition was reported by Gasperi et al. (2014) in floating macroplastics in the Seine River, where most items were composed of PP, PE, and to a lesser extent PET. At least from the beginning, this difference would be attributed to a potential disparity in consumer's behavior between France and Argentina.

#### Mesoplastics

Studies involving micro- and mesoplastic debris have proliferated in recent years (Collignon et al. 2014; Faure et al. 2015a, b; Young and Elliott 2016). Gündoğdu and Çevik (2017) found a proportion of mesoplastic items of 13% with respect to microplastics in pelagic areas of Turkish coasts. This ratio is similar to that reported by Eriksen et al. (2013) and Suaria et al. (2016). However, Jayasiri et al. (2013) reported mesoplastic debris as the dominant fractions by number in recreational beaches of India. In the present study, we found a ratio of 4% of mesoplastics with respect to microplastics. Establishing this percentage is important because one fraction could serve as surrogate of the other one, saving time and resources for future studies.

According to Table 2, 77.7% of the mesoplastic particles were white/transparent. This finding is in

agreement with other studies in beach sediments (Heo et al. 2013; Young and Elliott 2016). This result is of ecological relevance as it is described below. Styrofoam (EPS) was the dominant source of mesoplastic debris (Table 2). Given its low density, it is not surprising that Styrofoam has been the most common mesoplastic in the study area. A similar phenomenon was reported by Zbyszewski et al. (2014) and Driedger et al. (2015) in the Great Lakes surface waters and shorelines. Case studies around the world have reported serious pollution problems due to the presence of Styrofoam (Hinojosa and Thiel 2009; Heo et al. 2013; Lee et al. 2013).

### Microplastics

Mesh size of sieves and filters used during sampling survey and sample processing influences microplastic abundance estimations. However, at present, there is no universally adopted methodology or size definition (Hidalgo-Ruz et al. 2012), making direct comparisons difficult even when they are unavoidable. Klein et al. (2015) have reported an estimation of 1800-30,000 microparticles m<sup>-2</sup> in river shore sediments of the Rhine and Main rivers (Germany), which is by far above the average reported in the present study (704 particles  $m^{-2}$ ). However, it should be noted that these authors considered microplastics down to 63 µm. On the other hand, Imhof et al. (2013) found an average of 1108 microplastic particles m<sup>-2</sup> at the north shore of a subalpine lake (Garda, Italy) and only 108 microplastic particles  $m^{-2}$  at the south shore, considering microplastics down to 9 µm. Faure et al. 2015a, b) reported an average of 1300 microplastics per  $m^2$  (> 300 µm) in beach sediments of six Swiss lakes, occurring as follows: 2100 in Geneva, 320 in Constance, 700 in Neuchâtel, 1100 in Maggiore, 460 in Zurich, and 2500 microparticles m<sup>-2</sup> in Brienz lakes. The latter methodology and results are comparable and in accordance with this study, indicating a similar relevance of microplastic contamination (particularly with the Neuchâtel Lake).

Nevertheless, other studies reported the occurrence of microplastics in lake sediments but at very low densities. Thus, Zbyszewski and Corcoran (2011) accounted for 0–34 microplastic fragments ( $m^2$ ) on shorelines of Huron Lake (Canada). Extending their shoreline monitoring to the Lakes Erie and St. Clair, Zbyszewski et al. (2014) reported only 0.2–8 items m<sup>-2</sup>, which are notoriously lower concentrations than in the Setúbal Lake.

In the present study, 72.1% of the microplastics collected were white/transparent, a finding in agreement with other studies (Turner and Holmes 2011; Heo et al. 2013; Corcoran et al. 2015; Veerasingam et al. 2016; Young and Elliott 2016). Although filters, scrapers (grazers), and shredders indiscriminately ingest microplastics from the water column and sediments, Shaw and Day (1994) noted that some visual predatory planktivorous fish may mistakenly feed on microplastics that most closely resemble their zooplankton prey. Wright et al. (2013) suggested that prey item resemblance of microplastics as a result of color may contribute to the likelihood of ingestion. An examination of stomach contents in mesopelagic marine fish revealed microplastic color frequencies of 75% white/ transparent (Boerger et al. 2010). Greene (1985) suggests that microplastic ingestion due to food resemblance may also apply to pelagic invertebrate planktivores that are visual raptorial predators.

To date, relatively little is known about microplastic ingestion in freshwater environments. However, some studies have demonstrated that freshwater invertebrates and fish can ingest plastic particles, causing injuries, stress, contaminant bioaccumulation (chemicals inherent in plastic), and tumor formation; immune response disrupting feeding/swimming; and altering metabolic function (Rosenkranz et al. 2009; Imhof et al. 2013; Sanchez et al. 2014; Biginagwa et al. 2016). In this sense, we suggest a potential risk of microplastic ingestion (mainly white/transparent) by visual predator fish in the Setúbal Lake, particularly during flooding stages when microplastic debris from beaches are available for fish by flotation. However, further research is required to fully assess this potential impact.

According to Table 4, macroplastic item surveys would not serve as surrogates for microplastic items, as proposed by other authors (e.g., Lee et al. 2013). This would be disadvantageous since macroplastic surveys are more easily conducted by researchers (and even by volunteers; Sheavly 2007).

Finally, the current study demonstrates that plastic debris is a serious problem in Setúbal Lake and potentially in the Paraná system, since both environments are directly connected. However, we acknowledge that the present data represent a snapshot, and as such, it is difficult to estimate the extension of the problem in the Paraná system.

Results from this study are also important from a social/educational point of view, since plastic waste is

often ignored as a pollutant by the society in general (Faure et al. 2015a, b). In the current study, plastic food wrappers, bottles, and bags were a very visible sign of pollution, which is more easily understood by the general population than the "invisible" pollutants, like metals. Solving the visible problems will discourage disposal of all waste on riverbanks and floodplains and, hopefully, reduce overall pollution as noted by Heilmann and Whalley (2014).

#### Conclusions

- 1. An alarming number of macroplastics were recorded by comparison with other studies worldwide. Food wrappers (PP), bags (HDPE and LDPE), and beverage bottles (PET) were the dominant macroitems. The dominance of household waste over industrial ones showed the importance of implementing consumer awareness-raising strategies in the region.
- 2. Macroplastic surveys would not serve as surrogates for meso- or microplastic items, as proposed by other authors. This is disadvantageous since macroplastic surveys can be conducted by researchers as well as by nonspecialized staff, who have played crucial roles in debris monitoring programs.
- 3. Our results indicated a similar relevance of microplastic contamination regarding other studies, with a predominance of white/transparent microparticles. Both facts suggested that visual predatory planktivorous fish could be under threat, since they may mistakenly feed on microplastics that closely resemble their zooplankton prey. Further studies should confirm or reject this suggestion.
- 4. The large amounts of plastic observed endanger the lake ecosystem and suggest the need to improve the environmental policies and educational strategies.

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