River Deltas as hotspots of microplastic accumulation: the case study of the Ebro River (NW Mediterranean)

Laura Simon-Sánchez[1], Michaël Grelaud[1], Jordi Garcia-Orellana[1, 2], Patrizia Ziveri[1, 3]

[1] Institute of Environmental Science and Technology (ICTA-UAB), Universitat Autònoma de Barcelona, 08193 Cerdanyola del Vallès, Barcelona, Spain

[2] Departament de Física, Universitat Autònoma de Barcelona, Autonomous University of Barcelona (UAB), Bellaterra 08193, Spain

[3] Catalan Institution for Research and Advanced Studies (ICREA), Pg. Lluís Companys 23, Barcelona 08010, Spain

Highlights

- Occurrence of microplastic pollution in the Ebro Delta, Spain
- Microplastic abundances were investigated in three different environmental matrices
- Microplastics, predominantly fibers, were found in all the samples
- Riverbed benthic sediments were identified as sink areas for microplastics
- Salt-wedge estuaries dynamics may facilitate the sinking of microplastics

Abstract

Microplastics (MPs) are considered pollutants that are ubiquitously distributed in aquatic environments. One of the key hotspot areas to understand fluxes of MPs entering into the oceans are transitional systems, between fresh and marine waters, where river estuaries in particular play an important role. In this study we analyzed MPs occurrence in the Ebro River Delta, Northeastern Iberian Peninsula, one of the largest wetland areas in the NW

Mediterranean Basin. Microplastic profile, abundance, distribution, and characteristics were screened across different environmental matrices. MPs were collected in sandy beaches on the northern edge of the delta, in estuarine benthic sediments, and in surface waters of the Ebro River, with a mean abundance of 422 ± 119 MPs·kg^{-1} DW, 2052 ± 746 MPs·kg^{-1} DW and 3.5 ± 1.4 MPs·m^{-3}, respectively. Fibers were found to be the largest class (70 ± 22 %) of the three different environmental matrices investigated. We estimated that the Ebro surface water represents an input of 2.14 x 10^{9} MPs·yr^{-1} to the Mediterranean Sea. The main contribution of this study is a new insight on the distribution of MPs across different environmental matrices in river estuaries, where estuarine benthic sediments were identified as a potential important sink for MPs.

Keywords

Microplastics, Estuarine sediments, Surface waters, Beach

1. Introduction

The first evidence of micro-sized plastic particles in the marine environment goes back to the 1970s, when huge amounts of synthetic fibers (Buchanan, 1971) and plastic particles (Carpenter and Smith, 1972) were detected offshore the north-eastern coasts of England and in the North Atlantic Ocean, respectively. The term “microplastic” (MPs) was introduced in 2004 (Thompson et al., 2004), and despite the fact that there is still no standardized definition of the size range of MPs, it is commonly accepted that MPs are those plastic particles smaller than 5 mm (Arthur et al., 2009; Gray et al., 2018; Hidalgo-Ruz et al., 2012; Hurley et al., 2018; Peng et al., 2017; Rodrigues et al., 2018; Vermeiren et al., 2016; Yan et al., 2019). Since then, MPs pollution has raised specific concern due to their worldwide widespread. Their presence has been reported in different aquatic environments such as fresh water systems, including lakes (Eriksen et al., 2013; Faure et al., 2013; Free et al., 2014), rivers (Castañeda et al., 2014; Moore et al., 2011; Wagner et al., 2014; Williams and Simmons, 1996) or estuaries (Sadri and Thompson, 2014; Wessel et al., 2016); as well as in marine environment such as shorelines (Browne et al., 2011; Ivar Do Sul

and Costa, 2014), surface waters (Cole et al., 2011; Collignon et al., 2012; Cozar et al., 2014; Eriksson et al., 2013; Zhao et al., 2014) and even pristine deep marine sediments (Bergmann et al., 2017; Van Cauwenberghe et al., 2013). However, despite the abundance and occurrence of MPs in the aquatic environment, the fate (Ivar Do Sul and Costa, 2014) and impacts on living organisms (de Sá et al., 2018) remain complex and poorly understood. For example, one of the greatest concerns about MPs is their potential toxicity that can adversely affect freshwater and marine organisms, (e.g.: de Sá et al., 2018; Eerkes-Medrano et al., 2015) the food web and, by extension, human health (GESAMP, 2015). MPs under natural conditions can adsorb persistent organic pollutants (POPs) and act as carrier for these toxic compounds (Tsang et al., 2017; Wang et al., 2016). Besides, the MPs toxicity is related to the presence of inherent toxic monomers and additives used during the plastic manufacturing process to improve specific properties (Oehlmann et al., 2009.; Teuten et al., 2009; Tsang et al., 2017).

Microplastics are separated into two classes: Primary and Secondary. Primary MPs are those manufactured and used at MP size range and can include, among other, raw material used to create plastic products (such as pellets; EPA, 1992), small particles used for cosmetics purposes (Zitko and Hanlon, 1991) (i.e.: microbeads/spheres), beads used for industrial abrasive blasting media (Sundt et al., 2014), or fibers used for textiles purposes (Browne et al., 2011) (Brown et al., 2011). Secondary MPs originate from the degradation of larger plastic items when exposed to different physical, chemical and biological processes in the natural environment which break down to form smaller fragments (Barnes et al., 2009; Wang et al., 2016). Secondary MPs will probably play an important role in the near future as plastic items already present in the natural environment may remain there for decades and their fragmentation will produce huge amounts of MPs, even if plastic pollution is stopped right away (Barnes et al., 2009; Eerkes-Medrano et al., 2015).

The sources of MPs into aquatic environments are numerous (e.g.: Duis and Coors., 2016; Windsor et al., 2019). On land, municipal run-off and wastewater treatment plants are considered as a critical entrance, mainly for microbeads and synthetic fibers to the aquatic environment (Horton et al., 2017; Murphy et al., 2016). Atmospheric inputs could also represent a non-negligible source of MPs (mainly synthetic fibers, Dris et al., 2016, 2015) along with agriculture activity (Nizzetto et al., 2016) through the spreading of sewage sludge as fertilizer or plastic mulching (Steinmetz et al., 2016). The main inputs of plastic to the marine environment come from industrialized and densely populated coastal areas (Andrady, 2011; Derraik, 2002; Jambeck et al., 2015). In addition, plastic can enter into the marine environment through insufficient plastic waste management, illegal dumping, unintentional or accidental releases from vessels, and litter left on beaches (Crawford and Quinn, 2017; Duis and Coors, 2016). The studies of MP pollution are mainly focused on marine systems (Avio et al., 2017; Cole et al., 2011; Ivar do Sul and Costa, 2007; UNEP, 2011). Until now, rivers have received less attention despite the fact that they contribute 1.1-2.4 million tons of plastic to the marine environment annually (Lebreton et al., 2017) and are considered the main pathway for plastic litter to reach oceans. Few ongoing research activities have recently focused their attention on plastic pollution in freshwater ecosystems, seeking to close the knowledge gap about the occurrence, sources and fate of MPs in rivers (Besseling et al., 2017; Lagarde et al., 2016; Leslie et al., 2017; Wagner et al., 2014; Wang et al., 2017; Zhang et al., 2016). Further to this, emerging studies highlight the need to understand the distribution of MP fluxes between the MPs retained within river catchments and MPs exported to the open oceans (Windsor et al., 2019; Xiong et al., 2019). In particular, estuaries, transitional areas between freshwater and marine systems, are recognized as important accumulation areas for several anthropogenic pollutants (Foufoula-Georgiou et al., 2011; Vörösmarty et al., 2009), making them critical zones to understand the accumulation and export fluxes of MPs to the oceans.

This study represents the first evaluation of MPs pollution in the Ebro River Delta, one of the largest wetland areas in the western Mediterranean region, a sea characterized by high accumulation of plastic debris (Cózar et al., 2015; de Haan et al., 2019). Thus, understanding the role of estuarine systems, such as Ebro River, as source and sink for MP pollutants will aid in the struggle of estimating the number of MPs reaching the world's oceans using rivers as corridors. The aims of this study were to investigate the occurrence of MPs pollutants in the Ebro Delta in NE Iberian Peninsula in order: 1) to determine the fluxes of MPs across different deltaic environmental matrices, 2) to determine the characteristics of the particles (type, size and colour) and 3) to explore the potential sources of MPs in the area. We assess MP abundance in three different environmental matrices: river surface water, sandy beaches and estuarine benthic sediments ("benthic sediments" from here onwards).We hypothesized that estuarine systems would act as accumulation areas for MPs pollutants, and MPs abundances were expected to be higher in the riverine benthic sediments.

2. Material and methods

2.1. *Study site*

The Ebro Delta is located in Northwestern Mediterranean, in Catalonia, Spain (Figure 1). It drains one of the main contributors of the Mediterranean Sea, the Ebro River, with a catchment area of 85,569 km^2 and annual mean discharge of 464 $m^3 \cdot s^{-1}$ (Gobierno de España, 2015). The estuarine section is one of the main major delta systems present in the Mediterranean basin. The total subaerial area is of about 320 km^2 and its coastlines length of approximately 50 km. The coastal zone is microtidal (<0.3 m) and characterized by sandy beaches and dunes accumulations (Palanques and Guillén, 1998). According to the classification of Hansen and Rattray (1966), the Ebro River shape is a Type 4- salt wedge estuary (Ibañez et al., 1997), which extends along the last 32 km of the river, with an average width of 250 m and an average depth of 7 m (Nebra et al., 2016). The climatology of the Ebro Delta is characterized by low thermal

oscillation, high humidity and prevailing NW winds. The annual mean temperature is 17˚C and the annual mean precipitation of 548 mm, even though there is a high interannual variability (Gobierno de España, 2015).

The population density in the Ebro Delta is 78.1 inhab·km^2 (IDESCAT, 2018), which is relatively low considering that combined, the world's deltas host an average population density about ten time higher than the world average (Ericson et al., 2006; Foufoula-Georgiou et al., 2011). Nevertheless, the Ebro Delta is facing the challenge of finding balance between the anthropogenic activities and the conservation of the ecosystem. The ecological richness and vulnerability of the area lead to the declaration of specific zones of the Ebro Delta (77 km^2) as Natural Parks by the Catalonia Regional government in 1983. It is a Special Birds Protection Area (SPA) and is considered one of the Wetlands of International Importance under the Ramsar Convention. The main human transformations in the area are related to the economic activities: the agricultural use covers more than half of the surface of the delta and is mainly devoted to rice crops followed by vegetables and fruit trees production (Fatorić and Chelleri, 2012). Fishing is another notable activity in the area: the harbour of Sant Carles de la Ràpita, one of the largest fishing ports in Catalonia, concentrates the commercial fishing, while fish farming production is present through 13 facilities in the area (Agència Catalana de l'Aigua). The main infrastructures in the Ebro Delta are the extensive irrigation and drainage channels and 6 wastewater treatment plants (WWTP) discharging directly or indirectly into the Ebro river (Figure 1, Agència Catalana de l'Aigua).

Finally, an important feature of the lower part of the Ebro River is the reduction in the flow of sediment and water as a result of river management during the 20th century, based on the construction of dams. Specifically, the dams of the Mequinenza and Ribaroja are considered responsible for strongly regulating the river flow dynamics in the lower Ebro River (Nebra et al., 2016).

2.2. *Sampling*

The microplastic contamination of the Ebro River Delta system was assessed in three different environmental matrices: in sandy beaches on the northern edge of the delta, in benthic sediments and in surface waters of the river. The sampling surveys were conducted in winter 2017 (see Table S1 for more details). Ten stations were selected to investigate the concentration and characteristic of MPs (Figure 1). In order to evaluate the riverine influence of the presence of MPs on the seashore, four sites were selected along the northern beaches of the delta (S1-S4- Figure 1). Sampling stations S1, S2, S3 and S4 were located at 0.6, 2.3, 3.4 and 6.9 km from the mouth of the river. A fifth station (S5) was selected out of the geographical boundaries of the delta system, 23 km to the north of Ebro River's mouth. Three riverbed sampling stations (GS1-GS3) were selected along the last 17 km of the Ebro River, from the river mouth (GS1) to the first towns: Sant Jaume d'Enveja and Deltebre (GS3). The surface waters were sampled at two sites: WS1 at Deltebre, the most urbanized area in the delta, and WS2 at the nautical club of Riumar, about 3 km upstream of the river mouth.

For the beach samples about 1 L of sand was collected at the upper limit of the last high watermark, using a 20x20 cm quadrant and scraping the first 2.5 cm of sand with a stainless-steel spoon. Riverbed samples were collected close to the sediment deposition margin of the river with all stations depth ranging from 4 - 7 m (Nebra et al., 2016), see Table 1. Samples were collected using a van Veen grab sampler (0.046 m^2) deployed from a small boat. Once the grab sampler was loaded on board, from the top window of the sampler, the first 10 cm of surface benthic sediments were collected. Surface water sampling was performed with a 15 cm diameter round neuston net of 5 µm mesh. The net was deployed at the river surface against the water current flow during thirty minutes at the first station (WS1), where two replicates were collected, and during one hour at the second station (WS2) (Figure 1). To transfer the sample and to collect those particles that might remain on the mesh of the net, after each

sampling, the net was rinsed and the material collected was concentrated with water from Elix purification system. All samples were stored in unused, clean labelled glass containers and transferred to the laboratory where they were further processed. River flow data were retrieved from Confederación Hidrográfica del Ebro (CHE) (station A027- Tortosa).

2.3. *Microplastic extraction*

The most common method to extract MPs from sediment samples is based on density separation using the saturated NaCl solution (Quinn et al., 2017). This solution, which has a density of 1.2 $g \cdot cm^{-3}$, might fail to separate polymers with higher densities such as polyvinyl chloride (PVC, ρ=1.38 $g \cdot cm^{-3}$) or polyethylene terephthalate (PET, ρ=1.39 $g \cdot cm^{-3}$). However, it has been shown from previous studies that denser polymers can be separated with this brine solution, what is particularly true for fibers (Quinn et al., 2017; Sanchez-Vidal et al., 2018). In the present study, the extraction of MPs from the sand beach samples followed a slightly modified methodology developed by Thompson et al. (2004). For a given sample, about 150 g (wet weight) of sediments and 250 mL of concentrated NaCl solution were added into a pre-rinsed 2 L glass beaker. The mixture was stirred for 20 min at 200 rpm. The solution was left to settle for two hours. The supernatant solution was piped out into a clean glass beaker and vacuum filtered using a glass-fiber filter (GF/F; 47 mm ø, 0.7 µm pore size). The walls of the funnel attached to the vacuum system were rinsed twice with ultrapure water (MilliQ®) in order to remove those particles that might remain attached. The glass-fiber filters were stored in Petri dishes and dried at 40 °C overnight. The extraction was performed during five consecutive times to test the efficiency of the methodology used. After every extraction, the beaker containing the sample was rinsed with concentrated NaCl solution, again to avoid the lost and underestimation of some particles that might remain attached to the beaker walls. Finally, the residual solids were washed with MilliQ®, drained and dried at 40 °C to record the dry weight.

For benthic sediments, grain size distribution was determined by wet sieving for gravel (ø>2 mm), sand (ø>63µm) and mud (ø<63µm). MP extraction analysis consisted in repeated density separations using Wet Peroxide Oxidation (WPO) to remove the presence of organic matter. For each sample, three different replicates of approximately 10-20 g of sediments were added to three separated clean glass beakers with 200 mL of concentrated NaCl solution and 20 mL of 30% hydrogen peroxide (H_2O_2). The mix was heated at 50 °C, stirred for 20 min at 200 rpm and left to settle first for an hour at 50 °C and then one additional hour at laboratory temperature. The foam from the reaction was transferred to a clean glass beaker, mixed with 50 mL of concentrated NaCl solution and 20 mL of H_2O_2 (30%). After the heating, mixing and settling, the supernatant was collected and vacuum filtered (GF/F; 47 mm ø, 0.7 µm). In the meantime, 20 mL of H_2O_2 (30%) was added to the rest of the WPO solution and sediments. The mixture was again processed using the same aforementioned steps of heating, mixing and settling. The supernatant was then collected and transferred to a clean glass beaker. This mixture was again oxidized, heated, mixed and left to settle. Finally, the supernatant was collected and vacuum filtered (GF/F; 47 mm ø, 0.7 µm). For each replicate, the two filters were stored in Petri dishes and dried at 40 °C overnight. All the settled solids were collected, washed with MilliQ®, dried and weighed to record the dry weight.

To validate our extraction methodology, microplastics (n=40-80) were added to a benthic sediment sample (12.3 g DW) and to a sand sample (99.2 g DW). Acrylic, nylon, polyester and polyethylene fibers were added into the samples. Respectively, the MPs were gathered from cutting a line of acrylic pink wool, a transparent fishing line, a 100% polyester orange garment and a black backpack's strip. The spiked samples followed the same extraction treatment as the rest of the samples.

Surface water river samples were directly vacuum filtered (GF/F; 47 mm ø, 0.7 µm) in the laboratory. In order to remove particles that might remain attached to the walls of the glass

container, they were rinsed twice with a squirt bottle containing MilliQ®, and also filtered as part of the sample. The glass-fiber filters were dried at 40°C overnight and stored in Petri dishes.

2.4. *Microplastics identification and characterization*

The filters were processed under a stereomicroscope (Leica Z16 APO, magnification 7.1x – 115x). The entire filter surface was examined from the top left to the bottom right to avoid double-counting. For accurate MPs identification, the criteria indicated by Hidalgo-Ruz et al. (2012) were followed, such as ensuring that there was no presence of organic or cellular structures, and, that there was a consistent thickness of the fiber across its length with the consideration that some colored fibers presented split ends (Marine and Environmental Research Institute, n.d.). Similarly, for the criteria of homogeneous color throughout the entire particle, some exceptions were considered such as bleaching, embrittlement, biofouling and plastic design which can affect this characteristic of the particles (Lusher et al., 2017). Thus, those particles identified as MPs were quantified, photographed and classified under type, size and color categories. The categories of MPs types considered were: microbead, fragment, foam, fiber, film/foil and fiber aggregations. For size, the maximum particle length was measured using the software ImageJ (Schneider et al., 2012) and grouped under eight size classes (<50; 50-100; 100-200; 200-500; 500-1000; 1000-2000; 2000-3000; >3000 µm) (adapted from Song et al., 2015). Finally, particles were sorted under color properties considering four categories: transparency (transparent and translucent), black, white and color (light blue, dark blue, red, yellow, purple, grey, etc.).

In this study, a subsample of 25 particles were randomly selected for polymer identification by micro Fourier Transform Infrared Spectroscopy (µFT-IR; Micro FTIR Agilent Cary 610, optical bench Agilent Cary 680) operating in Attenuated Total Reflectance (ATR) mode. MP particles were directly measured on the glass-fiber filters. Analysis were performed with a variable size aperture, depending on the type and size of the particle, in the range of 600-4000 cm^{-1}, with 128 scans at a resolution of 2 cm^{-1}. Identification was based on the comparison of each FT-IR

absorbance spectrum against the presence of specific absorption frequencies in accordance with the literature (Cincinelli et al., 2017; Jung et al., 2018).

2.5. *Quality assurance*

All analyses were performed inside a laminar flow cabinet in order to reduce contamination from airborne particles. Researchers wore cotton lab coats. Glass materials or stainless-steel materials were used when possible and all materials were rinsed twice with MilliQ® before being covered or used or stored. Finally, concerning the possible contamination, blanks (GF/F; 47 mm ø, 0.7 µm) were placed inside the laminar flow and then analyzed on the microscope to identify and quantify potential background contamination. Airborne MPs such as fibers and fragments were observed in the procedural blanks (n=15) with an average of 0.5 ± 0.8 MPs·filter (ranging from 0-3 MPs·filter). Due to the relative low concentration of particles detected in the procedural blanks, no correction factor was used for the final concentrations of MPs reported in this study. Similarly, for the results reported in this study, no correction was applied following the recovery rate test nor was applied after the FT-IR analysis.

2.6. *Data analysis*

Microplastic concentrations were standardized and reported as particles·kg^{-1} D.W. for sandy and benthic sediments samples and as particles·m^{-3} for the river surface water samples. Overall, MPs abundances were reported as mean ± standard deviation. Statistical analyses were conducted using the statistical software RStudio (Version 1.1.453) with a significance level set at $\alpha \leq 0.05$. Non-parametric tests were chosen due to the small sample size per environmental matrix and the restrictive replication between samples. Differences in MPs abundance among stations within each environmental matrix were investigated using Kruskall-Wallis. Similarly, the presence of distributional differences between MPs size and environmental matrix were tested using Kruskall-Wallis test. Where significant differences were found, a post-hoc Dunn's test was used to reveal significant differences between groups.

3. Results

3.1. *Microplastic extraction efficiency from sand samples*

The spiked samples tested to assess the recovery rate of the extraction methods showed a recovery rate of 77.5% after five density separations in the sand samples, and a recovery rate of 70 % in the benthic sediments. The lowest recovery rate was obtained for the transparent nylon fibers (13 out of 20 fibers) in sand beach samples and orange polyester fibers (5 out of 10 fibers) in the benthic sediments.

As mentioned, five sequential density separations were performed to increase the recovery rate of MPs from each of the sand beach samples. Results showed a negative exponential trend on the recovery of particles (Figure 2). The validation of the method proved that not all the particles were recovered after the fifth density separation. The recovery rate in the first extraction represented only an average of 39 ± 8% compared to the total number obtained after five separations. From the consecutives extractions, the recovery rate increased to 63.4% in the second extraction, to 79.4% in the third and 91.0% in the fourth extraction. These results correlate well with previous studies showing that 93.3% were recovered after fourth density separations (Besley et al., 2017).

3.2. *Microplastics identification using µFT-IR*

From the 25 particles investigated for chemical composition using µFT-IR, a total of 76 % were identified as MPs. From the interpretation of the spectra, three particles could not be identified because the IR signal of the particle was not distinguishable from the background; three particles were identified as non-synthetic particles (cotton, vegetal fiber and coal) and from 19 particles the polymer type was identified. The polymer distribution was dominant by polyamide (24%), followed by polyethylene (16%), poly(methyl methacrylate) (acrylic, 12%), polyester (12%), polypropylene (8%) and polyacrylate (4%).

3.3. *Microplastic concentrations in the Ebro River Delta*

MPs were found in all analyzed samples. In the three environments studied, MPs were dominated by fibers, followed by plastic fragments and films. These three types of MPs categories were found at almost all sampling locations, except for the S2 sand beach sample where only fibers were detected (Figure 3).

The mean MPs concentration in sandy beaches samples were 422 ± 119 MPs·kg^{-1} of dry weight (DW) sediment (n=5) and 2052 ± 746 MPs·kg^{-1} of DW sediment in the riverbed (n=3). It is interesting to note that MPs concentrations were 4-fold higher in benthic sediments than in sandy beaches. Finally, the average concentration of MPs in surface waters of the Ebro River was 3.5 ± 1.4 MPs·m^{-3} (n=3).

Of the 5 sand samples collected from the beach, a total of 220 particles were extracted and analyzed. Fibers (89.5%) were the most common type of particles observed. Concentrations ranged from 283 MPs·kg^{-1} DW sediment in S3 to 557 MPs·kg^{-1} DW sediment in S5, there was not a significant difference in the MPs abundance between the stations (X_2 = 4, df = 4, p = 0.406). The highest concentration was found at the station located out of the delta system (S5), while within the delta there is a spatial variability with higher concentration of MPs in S1 (494 MPs·kg^{-1} DW sediment), closer to the mouth of the river and in S4 (461 MPs·kg^{-1} DW sediment), closer to the Desaigua del Pal (Figure 1). Reported concentrations are in the same order of magnitude to the concentration reported in other Mediterranean areas such as the littoral area of the Ombrone River, located in the Maremma Regional Park, Italy (166-318 MPs·kg^{-1}; winter; Guerranti et al., 2017), but lower in comparison to those concentrations reported close to the mouth of Albegna River, Italy (882-1069 MPs·kg^{-1} sediment; winter; Guerranti et al., 2017).

In benthic sediments samples, the highest concentration was found at the most distant station from the mouth of the river (GS3= 2899 ± 718 particles·kg^{-1} DW), located close to the urbanized areas of Sant Jaume d'Enveja and Deltebre (Figure 1). The MPs concentration decreases

downstream closer to the mouth of the river (GS2= 1766 ± 821 particles·kg^{-1} DW; GS1= 1491 ± 272 particles·kg^{-1} DW, but no significant difference was found between stations (X_2= 3.8222, df= 2, p= 0.1479).

The distribution of particles type in benthic sediments was led by high abundance of fibers (75.1%), followed by fragments (12.5%), film (10.5%) and the others categories (microbead, foam, and aggregation of fibers; 1.9%).

In river surface water samples, 634 particles were recovered. Fibers were the most predominant abundant type of MPs category (46.1%), but the proportion of fragments (39.4%) and films (13.5%) was relatively more abundant in water samples compared to the others two environmental matrices tested. The MPs abundance did not vary significantly between stations (X_2= 2, df= 2, p= 0.3679). The highest concentration was assessed at the upstream station (WS1: 4.3 ± 0.3 MPs·m^{-3}), in the urbanized areas, and lower at the downstream station (WS2: 1.95 MPs·m^{-3}), at the nautical club of Riumar.

3.4. *Size and colour of microplastics*

The size distribution of the particles varied significantly between the three environmental matrices (X_2= 137.83, df= 2, p< 2.2E-16*)*. Pairwise analysis identified significantly larger particles in the benthic sediments, compared with particles from both sandy beaches (p= 0.0005) and river surface waters (p< 0.0001). When MPs are organized by size, the distribution of MPs is unimodal for all samples (Figure 4). Most MPs were small microplastic particles sizing less than 1000 µm, the most frequent being particles ranging from 200 µm to 500 µm (29 ± 3%). Similar size distribution was reported, specifically for fibers, in the study conducted by Dris et al. (2016) in Paris. However, this size distribution is in contrast to studies using micro spectroscopy techniques for the identification of the particles (Simon et al., 2018; Vianello et al., 2013) that reported higher concentration of MPs as the size of the particles decreases.

The color distribution of MPs was investigated for the three different environments (Figure 5). The colored particles were the most abundant in the three environments, followed by black particles, with the exception of the river surface water samples that showed a higher concentration of white MPs (most of them being fragments; see Figure S1).

Fibers were the most common particles found in the three environments sampled. The size and color distribution of the fibers differed slightly between environmental matrices. Most of fibers detected were smaller than 1000 µm with the highest frequency in the 200-500 µm class, but it is worth mentioning that the highest concentrations of large fibers (>1000 µm) were found in the benthic sediments. Here, these large fibers (33.6% of all MPs in the benthic sediments) were predominantly colored (54.0%) and transparent (35.3%). In comparison, small fibers (<1000 µm, 41.8%) were predominantly colored (51.2%) and black (33.8%) in the benthic sediments as well as in the surface water samples (respectively 41.6% and 36.1%).

The second most abundant type of particles were fragments (Figure 3). They showed a higher frequency in size of 200-500 µm and were in general, the most abundant particles of less than 500 µm. Those fragments characterizing sand beach samples were colored (42.9%) and transparent (57.1%), while in benthic sediments, the colored category largely prevails (81.6%), and in surface waters the white (50.6%) and colored (38.2%) categories dominate. Films were the third most common type of particles found in the three environmental matrices sampled. Their presence was higher in surface water samples. Those films identified were mainly colored, followed by the transparent and black categories. The presence of microbeads was observed in river surface waters (n=4), and in benthic sediments (n=1). This type of particles was not found in sand beach samples.

4. Discussion

4.1. Microplastic occurrence in the Ebro Estuary

Estuaries are critical systems for the entrance of MPs to the open ocean. Emerging studies have reported the occurrence of MP in worldwide estuaries across different environmental matrices. MP pollution has been reported in the surface water of the Pearl Estuary (8902 particles·m^{-3}; Yan et al., 2019), in the sea surface microlayer of two South Carolina estuaries, USA (Charleston Harbor: 660 particles·m^{-3} and Winyah Bay: 3080 particles·m^{-3}; Gray et al., 2018) and in two estuarine systems of Southern U.K. (Hamble Estuary: 5380 particles·$m^{-3}$and Beaulieu estuary: 1050 particles·m^{-3};Anderson et al., 2018). These values are three orders of magnitude higher than the MP abundance reported for the Ebro Estuary (3.5 ± 1.4 particles·m^{-3}). In contrast, the concentration reported in the benthic sediments of Changjiang Estuary, China (121 ± 9 particles·kg^{-1} DW; Peng et al., 2017) is one order of magnitude lower than the concentration found in the river sediments of the Ebro Estuary (2052 ± 746 MPs·kg^{-1} DW). Albeit, the comparison of studies is difficult due to the different sampling, extraction/purification, identification methods and concentration units chosen by the researchers to characterize the occurrence of MPs in the natural environment. This first assessment of the MP occurrence in the Ebro Estuary suggests that MP pollution could be considered intermediate-low compared to the values reported in other estuaries. Nevertheless, few limitations of this study should be considered. For the extraction of MPs we used a NaCl solution, which might fail to recovered denser polymers such as PVC or PET. Our recovery test showed an efficiency of 77.5% and 70% for the extraction of MPs from sandy samples and benthic sediment samples, respectively. This indicates that the total concentration of MPs might have been underestimated in these two environmental matrices of the Ebro Estuary. Similarly, particles were identified visually using a stereomicroscope. In the study conducted by Song et al. (2015), the identification of the particles by FT-IR spectroscopy reported higher MP abundances in comparison to visual identification. It is due to stereomicroscope techniques might neglect smaller and/or transparent particles, especially MPs fragments (Song et al., 2015). Additionally, the visual identification technique does not allow one to distinguish between the synthetic and non-synthetic (natural or artificial)

fibers, even if criteria for visual identification are considered (Dris et al., 2015). This limitation of the technique has been reported to overestimate MPs fibers abundance (Frias et al., 2016; Hidalgo-Ruz et al., 2012; Song et al., 2015; Ziajahromi et al., 2017).In this study, a subsample of particles was selected for chemical characterization by μFT-IR spectroscopy to validate the visual characterization. The results of the analysis showed that a total of 76 % of the particles were correctly identified as MPs.

4.2. *Export and accumulation of microplastics in the Ebro river system*

The presence of MPs throughout the Ebro Delta, in benthic sediments, river surface waters and sandy beaches corroborates the ubiquitous presence of MPs in aquatic environments. Our results contribute to the understanding of the MPs distribution in river estuaries across the different environmental matrices. MPs concentrations found in the benthic sediments (2052 ± 746 particles·kg^{-1} DW) were higher than those observed in sandy beaches (422 ± 119 particles·kg^{-1} DW). This first observation were reported in other studies that also found high MPs concentration in riverine benthic sediments (Horton et al., 2017; Hurley et al., 2018; Xiong et al., 2019) supporting the hypothesis that estuarine benthic sediments might be an important accumulation pool for MP pollutants. Several factors might induce the sinking of MPs in freshwater environments: 1) the density of the water is lower than in the marine environment, 2) the properties of MPs (density, surface-volume ratio), and 3) the variability of the flow speed due to the geomorphology of the river and human activities (discharges, accumulation, drainage or transfers of water). In the case of the Ebro Delta system, it is important to consider the fact that the Ebro River estuary is highly stratified with two different water layers (Ibañez et al., 1997): a freshwater layer going from the surface to 1-3 m of water depth and a salt wedge right below. The salt wedge can extend up to ±30 km upstream from the river mouth when discharge is lower than ≈100 $m^3 \cdot s^{-1}$ and up to ±6 km when river discharges over ≈400 $m^3 \cdot s^{-1}$ (Ibañez et al., 1997), suggesting that the three benthic sediments samples were probably collected under the

influence of the salt wedge. There are few studies that focus on the influence of salt wedge on the distribution of MPs in estuaries. Vermeiren et al. (2016) pointed out the lack of data regarding the abundance of plastic debris ,-both micro- or macroplastics, accumulating within deltas in relation to the river catchment concentrations. Lima et al. (2015) also showed that the highest densities of MPs within the Goiana estuary (NE Brazil) were found at the bottom waters of the lower estuary during the late rainy season, when the highest river flow induces a flushing of MPs toward the sea. Another study focusing on macroplastics in sediments from Rio de la Plata estuary (Argentina), showed that their concentrations were higher within the salt wedge (Acha et al., 2003). This evidence suggests that the salt wedge could be a critical boundary within an estuary system where increased sinking of MPs is recorded (Vermeiren et al., 2016). In the Ebro estuary, the velocity profiles clearly show that within the salt wedge, the velocity of the flow is low (Table 1, Ibañez et al., 1997; Nebra et al., 2016) suggesting that once trapped within the salt wedge, MPs will settle and accumulate on the riverbed, simulating sediment deposition dynamics. We found three to six time higher concentrations of MPs in benthic sediments than on sandy beaches. While the fate of MPs in the aquatic and sedimentary systems still remains poorly understood, there are two recognized processes of MPs transportation, which are suspended load and wash load. By contrast, the process of MPs accumulation in benthic sediments of estuaries could be driven by a lower buoyancy that facilitates the entrance of MPs into the salt wedge, where with low flow velocity and longer hydraulic retention time, the sediment flocculation might facilitate the settling and accumulation of MPs on benthic sediments. In contrast to the potential of riverine sediments as storage for MPs, Hurley et al., (2018) reported significant reduction in the abundance of microplastics after severe flooding events, with approximately about the 70% of MP pollution accumulated in the river sediments cleansed from the catchments after a high flood event (Hurley et al., 2018). Hence, further data on the accumulation time of these pollutants is needed to understand the dynamic on the fluxes

of MPs to the oceans as well as to evaluate the level of exposure of benthic organisms to MPs pollutants.

The level of microplastic pollution in the surface waters of Ebro river (3.5 ± 1.4 MPs·m^{-3}) was below than other values reported in other studies, such as the Seine river (3-108 particles·m^{-3}; 80 µm mesh size) (Dris et al., 2015) or the Pearl River of China (379-7924 particles·m^{-3}; 20 µm mesh size) (Lin et al., 2018). The comparison of MPs abundance between areas is difficult and subject to uncertainty due to different sampling and analysis approaches. To some extent, the higher abundance of MPs could be expected in rivers located closer to urban areas under high anthropogenic pressure in contrast to the Ebro estuary, a high naturistic area with relatively low anthropogenic and demographic pressure (75.8 inhab·km^{-2}; IDESCAT, 2018). However, some additional factors such as the management of the Ebro River basin itself might influence the occurrence of MPs in the Ebro Delta area. Previous studies showed that the concentrations of MPs in surface water are usually higher upstream of a dam than downstream (Zhang et al., 2015). As was previously mentioned, the Ebro River contains one of the biggest dams of the Iberian Peninsula that affects the natural balance of water and sediments (Palanques and Guillén, 1998; Zografos, 2017). Thus, the dams of Mequinenza and Ribaroja when retaining water and also the underneath sediments can be a potential accumulation pools for MPs. However, further studies are needed to assess the role of dams in the fate of MPs, as these infrastructures might act as barriers retaining MPs and preventing them to reach the marine environment.

The distribution of MPs along the beaches of the northern delta suggests that once discharged by the river, the MPs are partially accumulated on the delta beach. If only stations S1 to S4 are considered (i.e., within the delta system), the highest concentrations were observed at S1 located near the mouth of the river (S1) and next to the Desaigua del Pal (S4) (Figures 1 and 3). Whilst for the station S2 and S3, the concentrations decrease as one moves away from the river

mouth. On the other hand, the highest concentration of MPs was measured at S5, a beach outside of the geographical boundaries of the Ebro Delta (Figure 3). Although this concentration was slightly higher than at the river mouth (+11%) or next to the Desaigua del Pal (+17%), it remains in the same order of magnitude. The proximity of urban areas such as Cap Roig and Perellò might influence the highest MPs concentration observed in S5. However, the interaction of multiple factors might contribute to the heterogeneous variability of the MPs abundance between the stations, such as prevailing winds, currents, proximity to a point-source of pollution, diffuse pollution, urbanization and socioeconomic activities (Gray et al., 2018).

The variability of MP distribution along the Ebro Delta clearly shows a decreasing gradient from the upstream stations (WS1 and GS3) next to the town of Deltebre toward the river mouth (WS2 and GS1, Figure 1 and 3).A similar pattern was observed in the surface waters of the Douro river estuary, Portugal (Rodrigues et al., 2019): higher MP occurrence was found in the middle part of the estuary close to urban areas and lower MP concentrations in the lower part of the estuary. This gradient suggests that the flux of MPs reaching the open sea is lower than the inputs to the river basin due to the retention factor of the catchment. Nevertheless, the MP concentration recorded at WS2 (1.95 MPs·m^{-3}) could represent about 2.14 x 10^{9} MPs·yr^{-1} reaching the Mediterranean Sea within the top layer (15 cm) of the Ebro River, considering the annual flow of the Ebro River 464 m^{3}·s^{-1} (stream gauge A027-Tortosa, CHE). However, the estimation of the net flux of MPs to the Mediterranean Sea from the Ebro River requires further understanding on the fluxes of accumulation and deposition of MPs in the littoral area of the Ebro Delta as well as studies on the vertical distribution of MPs in the water column in the estuarine area. Therefore, there is a need to present complete MP concentration profiles in the different compartments of estuaries, in order to provide more accurate estimation of the MP fluxes from rivers to the marine environment.

4.3. *Tracking potential sources of MPs in the Ebro Delta*

Here, we have discussed the potential sources of MPs considering the features and anthropogenic activities in the lower part of the Ebro River. The most common particles found in the collected samples were fibers (70 ± 22 %), as shown in previous studies that reported the presence of large amount of fibers in aquatic ecosystems (Claessens et al., 2011; Peng et al., 2017; Thompson et al., 2004). The presence of this type of MP in aquatic environments is mainly attributed to wastewater effluents (Magnusson and Norén, 2014; Talvitie et al., 2015), as consequence of clothes washing. Browne et al. (2011) concluded that up to 1900 fibers can be released washing a single garment of clothing. In the studied area, there are two main WWTP that discharge directly into the Ebro River, and possibly 2 others indirectly (Figure 1). The two WWTP that discharge directly into the river are located in the towns of Amposta and Deltebre, located 27 km and 14 km from the mouth of the Ebro River, respectively (Figure 1). Both use a secondary treatment (biological degradation), which is not able to remove all the textile fibers from domestic and commercial laundry (Ziajahromi et al., 2017). In particular, Browne et al. (2011) found that the predominant type of fibers were polyester, acrylic and polyamide at the effluents of WWTP. These polymers were also identified in the Ebro Delta. Albeit, it is difficult to track the origin of the fibers found in the three matrices, the main source of MPs pollution in the Ebro estuary could be related to the discharge of wastewater. Nevertheless, other sources cannot be disregarded as potential sources of fibers. Fishing and aquaculture activities, which have a relevant role in the study area, are other potential sources of MPs. Both use materials made of synthetic fibers and their degradation or direct disposal in the aquatic environment might lead to their degradation to the size of MP (Andrady, 2011). Finally, there might be contribution from the atmospheric compartment, which has not been thoroughly investigated. Fibers can be transported by wind and deposited in terrestrial and aquatic environments (Dris et al., 2016), especially in the vicinity of populated areas.

In contrast to fibers, the presence of secondary MPs (fragments, film, foams) were observed in the lower portion of the Ebro Delta (37%). The origin of these types of MPs lie in the breakdown

of larger plastics. One input of this type of MPs to the watercourse is related to the potential of rainfall run-off transporting plastic pieces already exposed to environmental factors (Horton et al., 2017). Recent studies showed that MP pollution in soils is as severe as in aquatic environments (He et al., 2018). Particularly in the Ebro Delta, agriculture practices might enhance the release of MPs accumulated in the soil matrix to the aquatic environment. Agriculture is the main economic activity in the study area where more than 65% of its surface is devoted to intensive rice production (Genua-Olmedo et al., 2016). Briefly, the rice crop production in the area involved practices such as ploughing, flooding, sowing, re-flooding, and draining the fields before the harvest. The practice of ploughing might help to release those MPs trapped in soils, while the practices of flooding and draining will act similar to rainfall run-off, dragging MPs to the aquatic environment. Thus, cultivation practices associated with the production of flooded crop should not be neglected as a potential source of MPs in the aquatic environment.

5. Conclusion

The present study contributed to the scientific understanding of the MP fluxes accumulating in estuaries and the MP fluxes flowing into the open ocean. The results showed the widespread distribution of these pollutants across the different environmental matrices investigated in the Ebro Delta. The MPs concentration reported suggest that rivers (1) act as direct corridors for MPs to reach the marine systems, (2) once MPs are in the sea, the currents and tidal dynamics are responsible for partially depositing some of these particles in the littoral area, and (3) estuarine sediments are important sink areas for MP pollutants. Particularly in salt wedge estuaries, hydrological and sediment transport dynamics might be responsible in facilitating the deposition of MPs onto bottom sediments. Considering that most of the world population is concentrated along rivers, estuaries and coastal areas, with the current plastic production, consumption and waste management system, the concentration of plastics and MPs in the

aquatic ecosystems is expected to increase. More extensive and regular monitoring of MPs is required across river catchments, especially estuaries, to fully illustrate the partitioning of MPs across different environmental matrices and therefore assessing the level of hazard and exposure of these pollutants to aquatic organisms and, by extension, to human health.

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Competing interests

The authors declare that they have no competing interests.

Appendix A. Supplementary data

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Table 1. *Benthic sediments site descriptions: distance to the mouth of the Ebro, sediment fractions, total organic matter (TOM), depth, salinity and velocity. Analysis on TOC and depth, salinity and velocity parameters (annual mean ± standard deviation; n=4) are published in Nebra et al. (2016).*

Sample	Lat N	Long E	Gravel (%) ø>2 mm	Sand (%) ø>63µm	Mud (%) ø<63µm	TOC* (%)	Depth* (m)	Mouth Distance (km)	Salinity* ($g \cdot l^{-1}$)	Velocity* ($m \cdot s^{-1}$)
GS1	40,7196	0,862288	2,4	28,43	71,57	4,8 ± 1,5	6,00 ± 0,5	11	32,0 ± 11,7	0,16 ± 0,14
GS2	40,69496	0,796825	0,44	64,92	35,08	3,6 ± 1,3	7,25 ± 0,5	7,7	35,3 ± 2,0	0,06 ± 0,01
GS3	40,70348	0,761786	0,1	39,75	60,25	4,9 ± 0,5	6,25 ± 0,5	1,5	34,8 ± 2,7	0,07 ± 0,11

Figure 1. Geographical location of the Ebro Delta indicating the sampling stations and microplastics concentration (sand and sediments: MPs·kg-1DW; surface water: MPs·m^{-3}) in the different environmental matrices. From the 13 sampling location: 5 beach sand station (S1-S5; ochre), 3 river bed sediments samples (GS1-GS3, green) and 2 river surface water samples (WS1-WS2; blue).

Figure 2. Number of microplastics recovered from sand beach samples, from a total of 5 NaCl consecutive extractions.

Figure 3. Concentration of particles at each sampling station: a) River surface water (MPs·m^{-3}), b) River bed sediments (MPs·kg^{-1} DW) and c) sand beach (MPs·kg^{-1} DW).

Figure 4. A comparison of the frequency of size class in the different environments sampled: sandy beaches (ochre), river bed sediments (green) and surface water river (blue).

Figure 5. A comparison of the frequency of colour class, Transparent, black, white and colour, in the different environmental matrices sampled: sand beach, river bed sediments and river surface water.

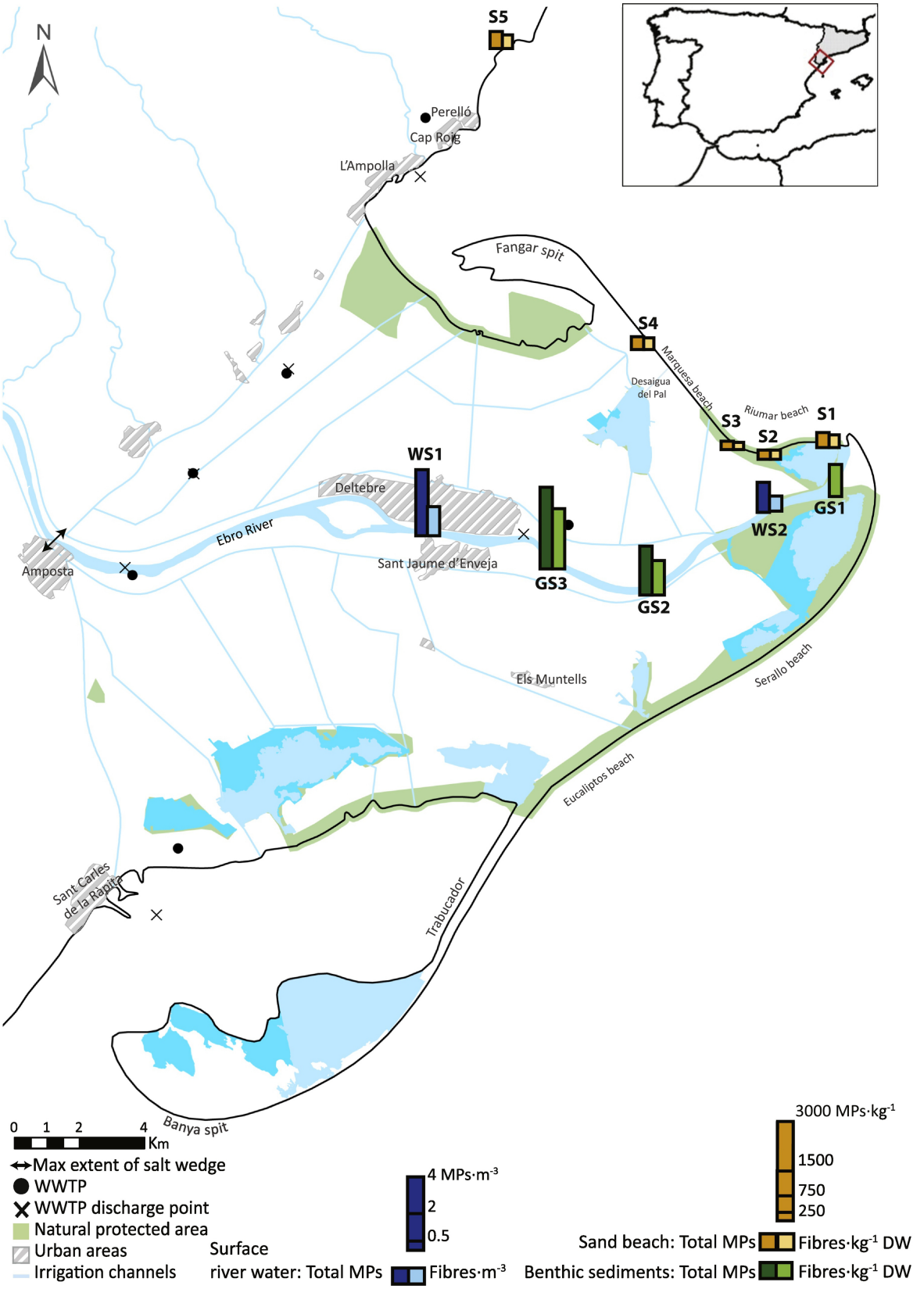
N
S5
Perelló
Cap Roig
L'Ampolla
Fangar spit
S4
Marquesa beach
Desaigua del Pal
Riumar beach
S3
S2
S1
WS1
Deltebre
Ebro River
Amposta
Sant Jaume d'Enveja
GS3
GS2
WS2
GS1
Els Muntells
Serallo beach
Eucaliptos beach
Trabucador
Sant Carles de la Rapita
Banya spit
0 1 2 4 Km
Max extent of salt wedge
WWTP
WWTP discharge point
Natural protected area
Urban areas
Irrigation channels
Surface river water: Total MPs
4 MPs·m-3
2
0.5
Fibres·m-3
3000 MPs·kg-1
1500
750
250
Sand beach: Total MPs
Fibres·kg-1 DW
Benthic sediments: Total MPs
Fibres·kg-1 DW

Figure 1

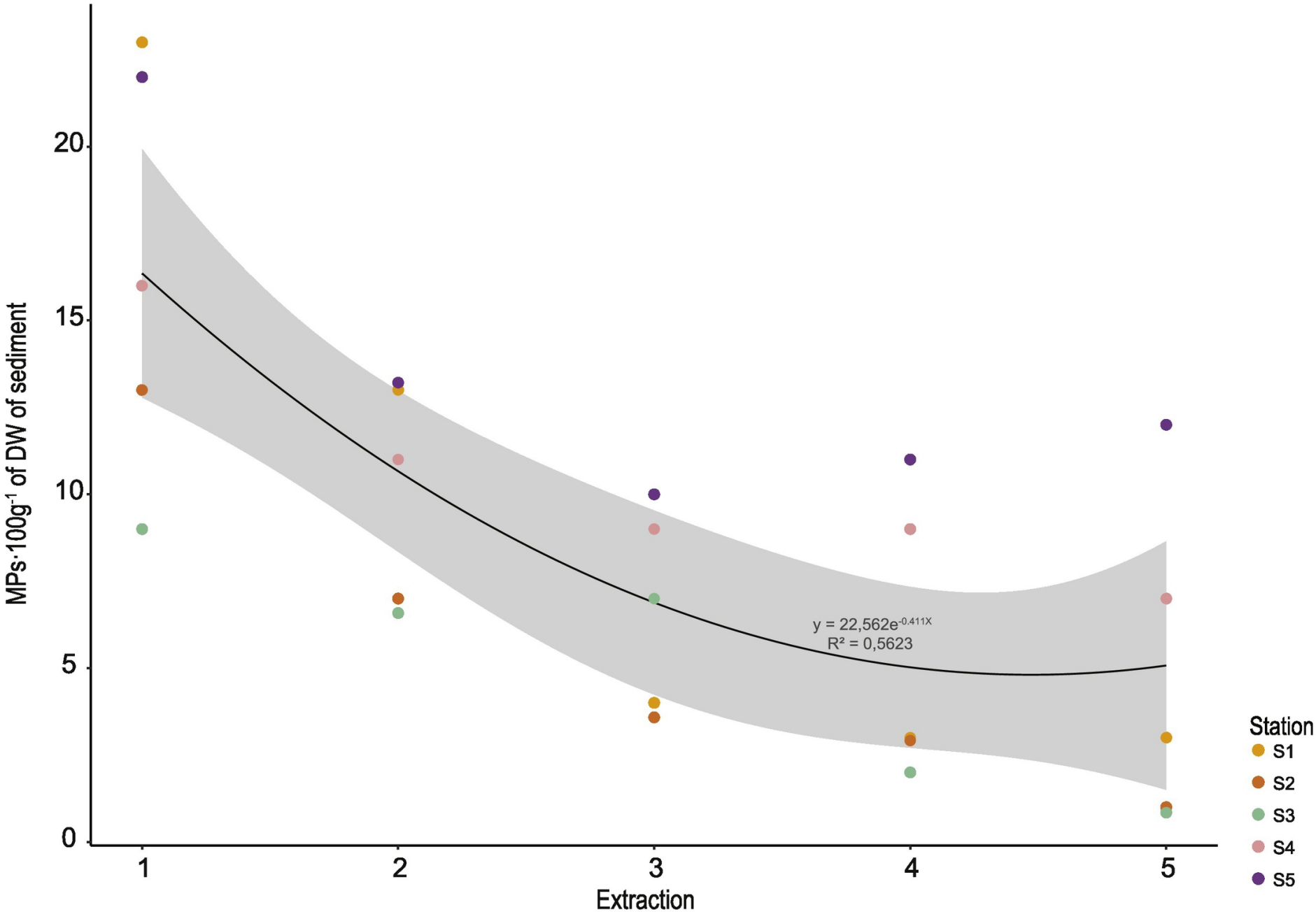
MPs·100g-1 of DW of sediment
20
15
10
5
0
1
2
3
4
5
Extraction
y = 22,562e-0.411X
R² = 0,5623
Station
S1
S2
S3
S4
S5

Figure 2

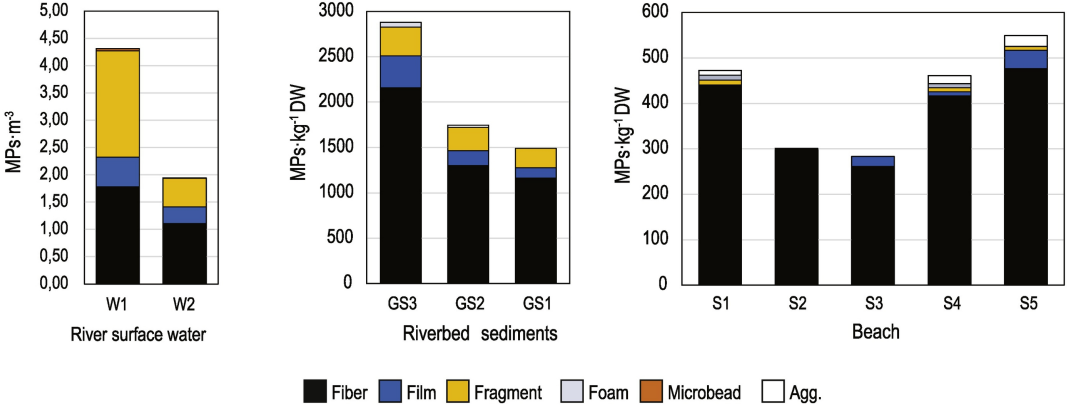
5,00
4,50
4,00
3,50
3,00
2,50
2,00
1,50
1,00
0,50
0,00
MPs·m-3
W1
W2
River surface water
3000
2500
2000
1500
1000
500
0
MPs·kg-1 DW
GS3
GS2
GS1
Riverbed sediments
600
500
400
300
200
100
0
MPs·kg-1 DW
S1
S2
S3
S4
S5
Beach
Fiber
Film
Fragment
Foam
Microbead
Agg.

Figure 3

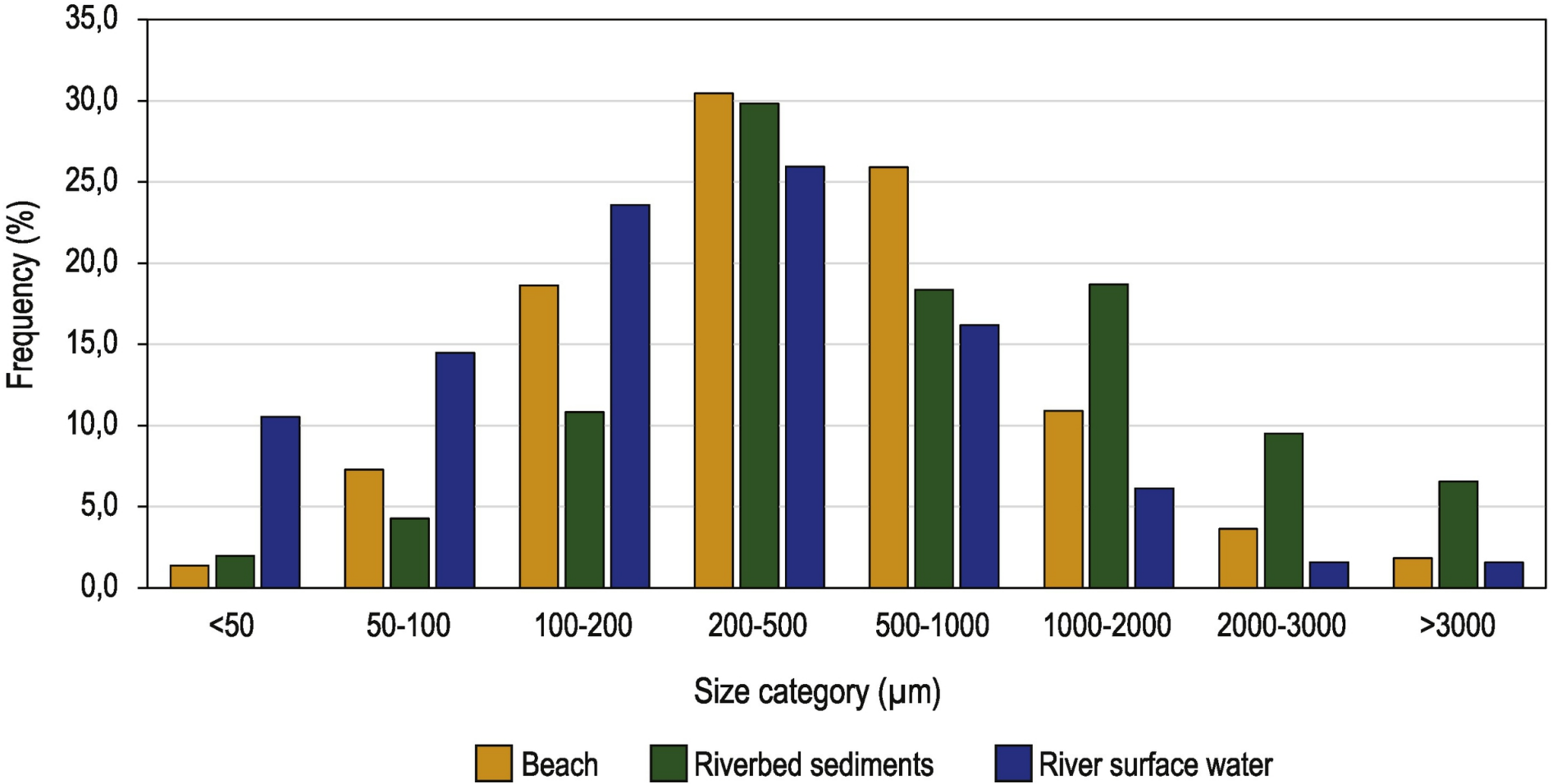
35,0
30,0
25,0
20,0
15,0
10,0
5,0
0,0
Frequency (%)
<50
50-100
100-200
200-500
500-1000
1000-2000
2000-3000
>3000
Size category (µm)
Beach
Riverbed sediments
River surface water

Figure 4

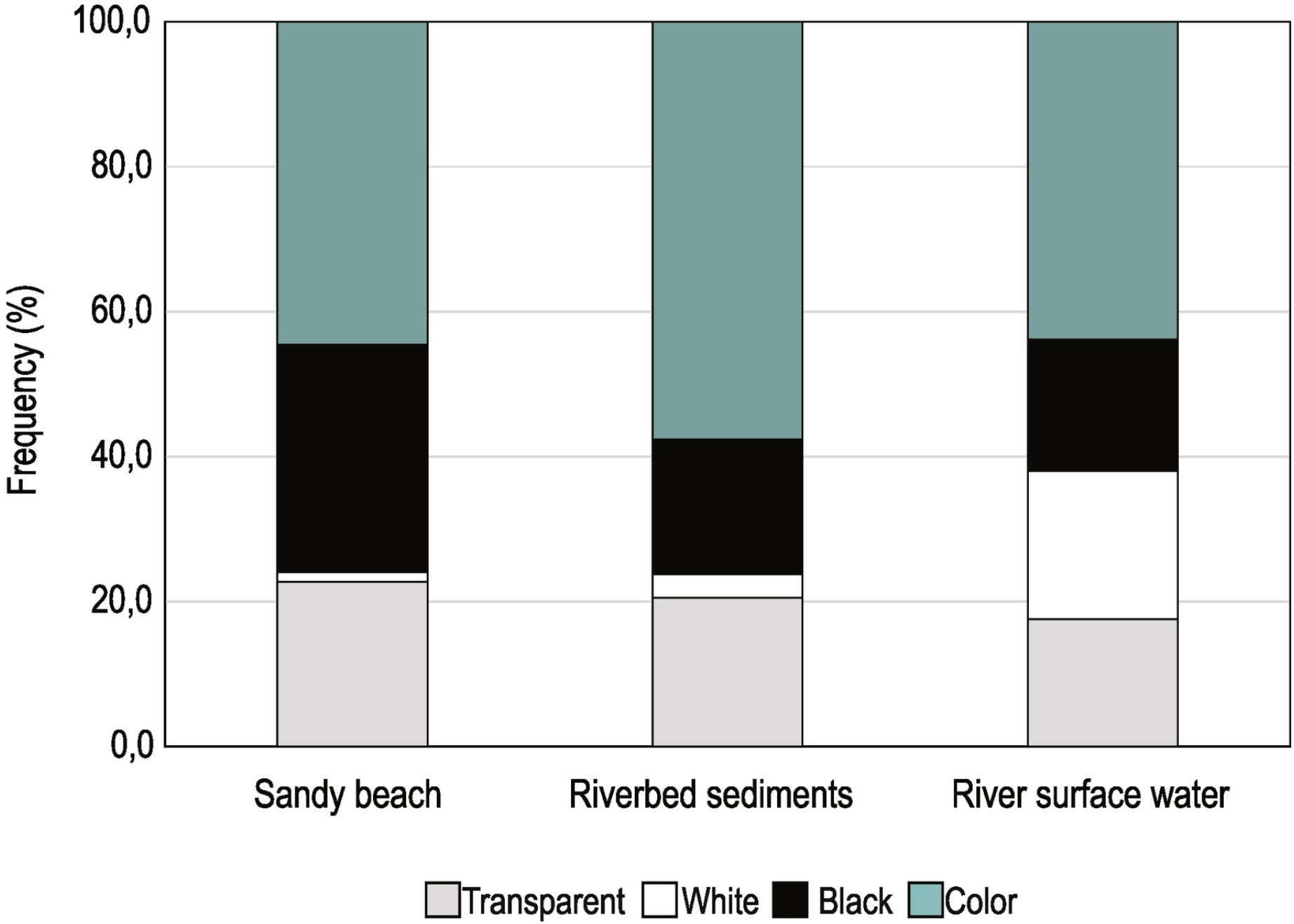
100,0
80,0
60,0
40,0
20,0
0,0
Frequency (%)
Sandy beach
Riverbed sediments
River surface water
Transparent
White
Black
Color

Figure 5