Microplastics levels, size, morphology and composition in marine water, sediments and sand beaches. Case study of Tarragona coast (western Mediterranean).

Nora Expósito[1], Joaquim Rovira*[1,2], Jordi Sierra[1,3], Jaume Folch[4], Marta Schuhmacher[1].

[1] Environmental Engineering Laboratory, Departament d'Enginyeria Quimica, Universitat Rovira i Virgili, Av. Països Catalans 26, 43007 Tarragona, Catalonia, Spain

[2] Laboratory of Toxicology and Environmental Health, School of Medicine, IISPV, Universitat Rovira i Virgili, Sant Llorenç 21, 43201 Reus, Catalonia, Spain

[3] Laboratory of Soil Science, Faculty of Pharmacy, Universitat de Barcelona, Av. Joan XXIII s/n, 08028 Barcelona, Catalonia, Spain

[4] Departament de Bioquímica i Biotecnologia, Facultat de Medicina i Ciències de la Salut, Universitat Rovira i Virgili, Reus, Tarragona, Spain

***Corresponding author: J. Rovira: joaquim.rovira@urv.cat**

Abstract

Mediterranean Sea has been proposed as the sixth greatest accumulation zone for marine litter and the most affected regarding to microplastics (MPs). Tarragona (Catalonia, NE Spain) coastal region suffers high pressure due to urbanization, tourism, industrial harbour and petrochemical/plastic industries. In recent years, the conflict between the two main economic sectors in Tarragona region: petrochemical/plastic industry and tourism highlight the importance of MPs pollution in the region. The present study aims to quantify and characterize in size, morphology and composition the MPs present in sandy beaches, marine sediments, and surface seawaters of Tarragona coastal region. MPs mean abundance were 1.30 items/m^3 in surface seawater, 32.4 items/kg in marine sediments, and 10.7 items/kg in sandy beaches. Polyester fibres were dominant MPs in bottom sediments and seawater meanwhile polyethylene and polypropylene fragments were the main MPs in beaches. The fibres balls associated with bottom sediments, organic matter and plankton were abundant, masking the real quantity of fibres in each reservoir. The abundance by volume of seawater MPs was higher to those found in oceanic areas and similar to other areas of Mediterranean Sea, corroborating that Western Mediterranean Sea as a region of MPs accumulation. MPs composition and abundance suggested the input of numerous land-base-sources, WWTP effluents discharges, and emissaries as the most important. Marine MP pollution were studied from an integrative point of view, that includes superficial sea water, sand from beaches and sediments. The dynamics of MPs in Tarragona coast were characterized by seawater as the media that receive and facilitates dispersion and fragmentation. The shoreline acts as an intermediate reservoir with constant weathering and active exchange with seawater surface and the sediments acts as a significant sink for medium MPs sizes. It is necessary to develop protocols and guidelines for MPs analysis to obtain harmonized and comparable results.

Key words: Microplastics, plastic pollution, sea, sediment, sand beach.

1. Introduction

Microplastics (MPs) are defined as "any synthetic solid particle or polymeric matrix, with regular or irregular shape with a size ranging from 1 µm to 5 mm, of either primary (intentionally manufactured microbeads and fibres) or secondary origin (mesoplastics breakdown in fragments), which are insoluble in water" (Frias and Nash, 2019; Verschoor, 2015). MPs are persistent in the environment because the majority have half-lives between hundreds to thousands of years (Barnes et al., 2009; Gasperi et al., 2018; GESAMP, 2016; Ivleva et al., 2017). In addition, MPs are ubiquitous in almost all environment compartments such as; marine environment (Andrady, 2011; Barboza and Gimenez, 2015; Deforges et al., 2014; Shim et al., 2018; Wright et al., 2013), marine sediment, surface seawater and sand (Alomar et al., 2016; Cincinelli et al., 2019; Constant et al., 2019; de Haan et al., 2019; Zhou et al., 2018), water column (Baini et al., 2016), deep sea floor, aquatic organisms (Chae et al., 2017; Sanchez-Vidal et al., 2018), freshwater (Simón-Sanchez et al., 2018; Strungaru et al., 2019), atmosphere (Gasperi et al., 2018), and soil (Nizzeto et al., 2016).

In one hand, primary MPs in the environment are coming mainly from the direct release of MPs-containing products such as pre-production pellets (used to manufacture plastic products), plastic micro- and nano-beads as additive in personal care products and textile fibres entering the aquatic systems by wastewater treatment plants (WWTP) discharges (Sundt et al., 2014). It should take into account that, synthetic textiles release of MPs (as fibres) to the environment during washing are not completely removed by WWTP (Sun et al., 2019). Some authors (Allen et al., 2019; Dris et al., 2015; 2016; 2017) also pointed out the importance of the atmospheric deposition of fibres not only in urban areas but also in remote sites. On the other hand, secondary MPs are formed by weathering and fragmentation of mismanaged large plastics present in seawater (Carbery et al., 2018; GESAMP, 2015; Lebreton et al., 2017; Wu et al., 2019). Primary and secondary microplastics from continental origin enter to the ocean through stormwater, agricultural and urban runoff, WWTP discharges, flowing into watercourses or directly discharged into coastal waters due to industrial spillage or during pellets transportation (Cozar et al., 2014). These MPs due to their small size and similarity with marine plankton, can be ingested by invertebrates, bivalves, and fish entering in the food web (Wright et al., 2013). Human exposure to MPs comes mainly form the ingestion route, through contaminated food in the environment or during food preparation, packaging and drinking water although, air inhalation cannot be neglected (Chang et al., 2020; Gasperi et al., 2018, Oliveira et al., 2019). There is a lack of knowledge regarding the effects in humans (Yong et al., 2020), however, these MPs could act as carriers of marine pollution (heavy metals and hydrophobic organic compounds), chemical additives incorporated in manufacture, even pathogen microorganisms. MPs and associated compounds can bioaccumulate through the food web with possible risks to health due to the fast desorption rates found in experimental physiological gut tests (Ashton et al., 2010; Bakir et al., 2014; Carbery et al., 2018; GESAMP, 2015; Masó et al., 2003; Ogata et al., 2009; Picó and Barceló, 2019; Wright et al., 2013).

Mediterranean Sea has a high human pressure, both urban and industrial, and the fact that it is almost a close sea with 90-year renewal period and plastics persistence, for periods exceeding 100 years, aggravates the environmental impact or plastics pollution (Jambeck et al., 2015; Mack et al., 2019; Pinna et al., 2019). In addition, tourism increase human pressure in summer season by multiplying the population in coastal areas by several times. For these reasons, Mediterranean Sea currently has been proposed as the sixth greatest accumulation zone for marine litter and the most affected regarding to MPs with levels around 240,000 plastic pieces/km^2 being 82% of them MPs (Alomar et al., 2016; Constant et al., 2019; Cozar et al., 2015; de Lucia et al., 2014; Fossi et al., 2016; Suaria, et al., 2016). In a recent study (Liubartseva et al., 2018), MPs pollution was modelled in the Mediterranean Sea and found that one of the most contaminated area is the Catalan Sea, between Balearic Island and Catalonia (NE, Spain). Inside this area, Tarragona coastal region allocates an industrial harbour and petrochemical and plastic manufacturers industries. In addition, this highly urbanized costal area suffers a seasonal intense touristic pressure. In recent years, the increasing awareness of the population regarding plastic marine pollution and the conflict between the two main economic sectors in Tarragona region, industry and tourism, emphasise the importance of this topic for the region (Rovira et al., 2018).

The present study aims to quantify and characterize in size, morphology and composition the MPs present in intertidal zone of sandy beaches, marine sediments and surface seawaters of Tarragona coastal region (western Mediterranean). To our knowledge, this is the first attempt to study MPs marine pollution in an integrated way, considering water, sand beach and marine sediments in western Mediterranean Sea. Present study will contribute to global MPs report and will provide useful data regarding the distribution of MPs in marine environment for future ecological risk assessments. The contribution of MPs due to atmospheric transport from urban areas to seawater surface and sand was not taken into account in present study.

2. Materials and methods

2.1 Study area

Tarragona, a crossroads between the axis of the Mediterranean Sea and the Ebro river, is located around 100 km at south from Barcelona metropolitan area. The coasts of Tarragona are located, according to the FAO classification, in the Balearic sea of the western Mediterranean. Tarragona city has around 130,000 inhabitants and is the centre of 30 km radius area, with more than 580,000 residents. In the area, there is the most important petrochemical cluster in southern Europe. As confirmed by the Tarragona Chemical Business Association (AEQT), the total production of the Tarragona petrochemical sector in 2019 was 19,500,000 tones, the sixth highest total production in the last 15 years, supplying the most demanding sector as rubber and plastic transformation industry (14 %). Tarragona harbour is the fifth most important port in Spain and it is also an important stop for the transit of tourism cruise ships.

Tarragona Sea have surface current flows mainly from the northward most of the year. Inside the harbour there is the Francolí river mouth (838 km^2 watershed area) with a water flow of approximately 1.18 m^3/s (Figure 1). Twelve biological wastewater treatment plant (WWTP) effluents discharge in its watershed with flow between 100 to 7,200 m^3/day. Inside to Tarragona harbour exists an important discharge of a big WWTP with flow about 24,000

m^3/day and at 4 km to the south, in front of La Pineda beach, there is other WWTP effluents with a flow of 47,500 m^3/day.

2.2 Sampling

Sand, sediment and water samples were collected between September and October 2018. During this period, the geostrophic current was mostly from North to South and South to North with 50% and 33% of the time, respectively, and a current velocity ranged from 0 to 0.5 m/s. The wind velocity ranged from 0.92 to 9.1 m/s and the Beaufort scale from 1 (small waves without scum) to 3 (medium waves). Due to wind velocity values were not greater than 5 m/s, it was not necessary to correct experimental values do to turbulent downward fluxes (Reisser et al., 2015; de Haan et al., 2019). Transects for water sampling, sand and sediment sampling points are depicted at Figure 1 and Table S1.

2.2.1 Surface seawater

Four transects (T1 to T4) were done to collect seawater surface samples from Tarragona coast (from La Mora to Tarragona harbour) along shoreline. A neuston net with 80 µm mesh, with a diameter mouth of 24 cm, and 1 m long were used in horizontal transects between 746 and 1017 m at a speed of 1.5–2 knots. The transects were separated from shoreline between 500 and 924 m and in front of sand beach sampling points. Average volume filtered was 45.2 m^3.

2.2.2 Marine sediments

Seven sediment samples (S1 to S7) were collected approximately at the start and end of each transect of seawater samples. Two divers descended between 15 and 17 m depth and collected subsamples in an area of 25 m^2 of top 5 cm sediment layer with a metal spoon and glass bottle. Average weight collected was 600 g. The bottom was characterized by sandy patches next to *Posidonia oceanica* and *Cymodocea* seagrass meadows.

2.2.3 Beach sands

A total of 14 samples were collected in 6 different beaches (B1 to B6) selected according of anthropogenic activities conditions as industrial pressure, tourism, urbanism, runoff, river mouth and WWTP effluents discharges. The beaches located alongshore the 19 km of Tarragona city presented low to moderate slope (5– 45º) and fine sand (Figure 1). These beaches are from north to south: La Mora and Sabinosa, characterized by low tourism and urban pressure, Arrabasada and Llarga with tourism pressure and runoff influence, Miracle with tourism, urban pressure, and runoff influence and La Pineda with industrial, tourism, and urban pressure, river mouth, runoff and wastewater effluents discharges influences.

As the MSFD- Guidance on Monitoring of Marine Litter in European Seas guidance document (European Commission, 2013) and NOAA Marine Debris Program (Masura et al., 2015) recommends, samples were collected randomly in the intertidal zone. This zone is influenced by waves dynamic with interchangeable material between sand and seawater. At intertidal zone, at upper 5 cm, five subsamples were collected randomly into a square 40 cm x 40 cm (0.16 m^2 area) with Kubiena boxes of 125 cm^3 (fixed volume) and stored in aluminium boxes covered to avoid contamination. Average weight of sand beach collected was 1.5 kg. Due to supralittoral zone of beaches in Tarragona coast are plow during summer and cleaned periodically with sand renewal (especially in spring), only the intertidal area was considered as the most representative area for the study of the MPs transport from sand to water.

2.3 Sample treatment

Regarding MPs analysis methodology, until now there are not standardized protocols instead considerable efforts showed by scientific community (Besley et al., 2017; Coppock et al., 2017; Löder et al., 2017; Masura et al., 2015; Mai et al., 2018; Munno et al., 2018; Nuelle et al., 2014; Prata et al., 2019; Wagner et al., 2017). In present study, a fast and practicable methodology for MPs extraction were applied adapting the processes sequence and parameters developed to specific samples requirements improving processes for turbidity and organic matter removal with less usage of expensive reagents and plastic materials in order to obtain clear filters for accurate MPs identification.

2.3.1 Surface seawater

The seawater samples retained in the cod-end of the net were carefully rinsed. The residues content of the cod-end was finally transferred to a sample container, stored frozen, and kept in the dark until further analysis (Bergmann et al., 2015). Seawater samples were sieved through a column of clean sieves (4, 2, and 1 mm; and 500, 125, and 45 μm) inside a fume hood. The material present in the sieves above 500 μm (4, 2, and 1 mm) were cleaned with ultrapure water. The big particles and fibres of organic matter were removed with tweezer; the big possible plastic particles and fibers were placed it in a covered petri dish and the residue was filtered on Teflon filter (PTFE 5 μm pore size). The material retained in the sieves of 500, 125 and 45 μm residues were filtered on Teflon filter.

Particles and fibres ≥500 μm without organic matter were selected with the stereoscopy microscope from 4 to 62 X magnification (LEICA DMS 1000). The possible plastic particles were weathered fibres, fibres balls, granules with colour and homogeneous surface, coloured fragments without strips or striation, fragments that do not break by applying light pressure with tweezers, transparent fragments, films, pellets, and spheres. These particles were analysed individually for microplastic composition. Particles and fibres ≥500 μm that contained a large amount of organic matter were filtered on Teflon filter of 5 μm pore size. For organic matter removal, the PTFE of 5 μm pore size were treated as follows: Alkali digestion (KOH 2M) followed by a Fenton process (H_2O_2 and $FeSO_4$) at 40 ºC and enzymatic digestion (cellulase) with sonication and agitations (Karami et al., 2016; Löder et al., 2017; Mai et al., 2018; Munno et al., 2018; Prata et al., 2019; Shokri, 2018). Finally, plastic particles and fibres were counted using the stereoscopy microscope (LEICA DMS 1000).

2.3.2 Sand and Sediment

Sand beach and sediment samples were dried at 40 °C during 48 h and weighed; a small part was collected for granulometry analysis. Samples were sieved through a column of clean sieves (4, 2, 1 mm and 500 μm) placed in a mechanical shaker. Particles smaller than 500 μm were stored in well-capped aluminium containers for future analysis. Particles equal or bigger than 500 μm were analysed with visual sorting procedure: quantification and morphologic description under stereomicroscopic observation from 8 to 62 X magnification. The potential plastic particles from 4 to 0.5 mm were: fibres associated with sand or sediment, white and coloured fragments, film weathered without strips or striations, plastics that do not break to pressure and pellets or transparent fragments non-iridescent, non-crystalline. The buoyancy of these particles was checked testing on tree solutions: H_2O, saturated NaCl (density 1.2 g/L), and saturated $ZnCl_2$ (density 1.8 g/L). The criteria to reject or accept the particle as a plastic was based to individual plastic density and its buoyancy in each solution; they were grouped according the buoyancy solutions. The particle with non-buoyancy in none of solutions it was considered inorganic particle (Löder et al., 2017; Mai et al., 2018; Munno et al., 2018; Prata et al., 2019):

2.3.3 Quality control

To avoid sample contamination a closed and isolated site (fume hood) was established in the laboratory for samples processing, wearing laboratory cotton coats, using glass or steel materials and tools rinsed with 70% ethanol and after with ultrapure (MilliQ® water filtered on 0.45 μm pore size filter (GF/F Whatman, 47 mm diameter, nitrocellulose), and covered in aluminium foils. All reagents were made with ultrapure water, stored in glass bottle and filtered (<0.43 μm pore size) before their use. Samples and subsamples were covered with aluminium paper for plastic contamination minimization trough air deposition. For sand and sediment analysis two blanks were applied for each sample analysis: in sieving and visual sorting methodology. The workplace particles deposition rate was determined for two months with a value of 0.04 fibres/cm^2/day. This rate was applied for the total filter area filtered in a day by sample. One blank for morphology examination on stereoscopy and optical microscope was located as an open petri dish. One blank for sample in basic—enzymatic digestion procedure was established for each sample. The blanks values, for each method were subtracted from the total particle counting due to deposit particle and fibres from laboratory environment.

2.4 Microplastic characterization in size, morphology and polymeric composition

Microplastics morphology visually or microscopic classified as fibre (including filaments and fishing line), films (items with a two-dimensional shape), fragments (items with a three-dimensional shape), and pellets (solid spheres).

Particles with a size above 0.5 mm were analysed with a Thermo Scientific NICOLET ATR-FTIR spectrometer with OMNIC™ Paradigm Software, with an Attenuated Total Reflectance (ATR) adapter; the measurements were performed in reflection mode in the range of 400–3600 cm^{-1}, with 50 scans at a resolution of 10 cm^{-1}. Background was done before analysis and every 20 samples. By contrast, seawater particles between 0.08 and 0.5 mm, filtered on PTFE filter, were examined totally with spectroscope-microscope Raman Renishaw 20X, 50 X objective magnification microscope-, 785 nm edge, laser state 1%, 10%, 50% intensity, bands from 25 cm^{-1}, 1200l/mm. The spectra polymer obtained with Raman spectroscopic technique were performed with WIRE 5.3 Software, the spectra were corrected for baseline displacement. The fibres found in sand and sediment samples, due to their morphology (small ratio volumes/length) and fragments equal to 0.5 mm, were analysed with a microscope IR-(µFTIR) spectrometer following a mapping procedure with a Thermo Scientific NICOLET iN10 with OMNIC™ Specta, and MCT detector opening 25 µm, accumulations 1 scans, spectral resolutions 16 cm^{-1}, spectral range 4000-715 cm^{-1}, ultrafast mapping 4x4 mm. The spectra were not corrected for light-reflectance penetration and baseline displacement. Kubelka-Munk or Kramers-Kronig corrections were not applied (Figure S1).

The identification of each polymer spectra obtained with ATR-FTIR and µFTIR techniques were performed comparing the unknown spectra with OMIC software libraries database, only match spectra with major or equal than 75% of similarity with reference spectra were accepted, the rejected items were counted as the temporary unidentified category. The unidentified spectra were also identified comparing with BIO-RAD IR spectral databases, matches, major or equal than 75% of similarity, were accepted (Figure S2). For temporary unidentified spectra with libraries, other criteria for spectral analysis were applied: a) The identification of the IR spectra was supported by comparing spectra with a library of own elaboration taking into account weathered particles analysed, only the spectra whose peaks were 60-70% or more coincident with the peaks of the reference spectra were identified; b) The non-identified items in previous steps were analysed according their characteristics absorption band or vibration modes of each polymer chemical grouping bonds for frequencies ranging mostly from 3200-1250 cm^{-1}(Primpke et al., 2018): 1480-1430 cm^{-1} for C-C aromatic ring stretching, 1790-1700 $cm^{-1}$for double binding C-O stretching, 2980-2780 cm^{-1} for C-H stretching of aliphatic and 3150-3030 cm^{-1} of aromatics. For aliphatic organohalogen, natural and synthetic cellulose identification, additional frequencies from 1150 to 550 cm^{-1} and from 3600 to 3000 cm^{-1} were evaluated. Finally, the non-identified in previuos steps items were counted as the definitive unidentified category.

The Raman spectra polymer were identified comparing the spectra with WIRE 5.3 polymer libraries database. Only match spectra with major or equal than 75% of similarity with reference spectra were accepted, the rejected items were counted as the temporary unidentified category. The identification of the Raman temporary unidentified spectra was supported by comparing spectra with a library of our own elaboration taking into account the main plastics products on the market, only the spectra whose peaks were 60-70% or more coincident with the peaks of the reference spectra were identified. The rejected items were also analysed according their characteristics absorption band (Figure S3-S5).

In surface seawater, a total of 34 fibres and 90 particles (fragments, pellets, films) were confirmed their polymeric composition being a confirmation percentage of 25% and 100%, respectively. Regarding sand samples, a total of 14 fibres and 196 particles (fragments, pellets, films) were confirmed being a confirmation percentage of 39 % and 98%, respectively. For sediment, a total of 78 fibers and 46 particles (fragments, pellets, films) were confirmed being a confirmation percentage of 44 % and 100% respectively.

3. Results and discussion

3.1 Superficial seawater

Levels of MPs on surface seawater in Tarragona coastal area and their size and morphology characterization are summarized in Table 1. Microplastics (from 80 µm to 5 mm) were analysed in four transects in Tarragona coastal surface waters. Mean MP levels was 1.30 MPs/m^3 ranging from 0.4 to 3.0 MPs/m^3 in the transect T4, close to the Tarragona harbour, and in T3, between Arrabasada and Miracle beaches, respectively. Almost all MPs were below 2 mm constituted mainly by fibres, between 54% and 63%, or fragments, ranging from 29 to 46%.

All MPs found in surface seawater were below 2 mm, except in Transect 1 that three MPs sized from 4 to 5 mm were found. According morphology, there was a north (T1) to south (T4) decrease trend for fragments from 44 to 29%; by contrast, fibre proportion slightly increased from 56 to 63 %, in north to south direction. The Transect 4 presented the highest proportion of MPs size from 1 to 2 mm and fibres morphology, in addition, pellets were detected. Transect 2 between Llarga and Arrabasada presented the highest proportion of MPs size spanning 80 µm to 0.5 mm and a slightly higher proportion of fibres (54%) than fragments (46 %). Regarding the general composition of these MPs (Figure 2), most of the fragments, pellets and films were made of polyethylene (46%) and polypropylene (22%); moreover, other materials such as polyvinyl chlorine (1%), polystyrene (4%), polyurethane (4%), polyethylene terephthalate (8%), polycarbonate (1%), acrylonitrile-butadiene-styrene copolymer (1%), and polymethylmethacrylate (6%) were detected. Regrading fibres, almost all were made of polyester (polyethylene terephthalate) (53%) and polyurethane (spandex or elastane) (23%). Other fibres found were made of polyamide (3%) and polyethylene (3%). The composition of all (100%) fragments, pellets and films were analysed. By contrast, only 25% of fibres were analysed due to their identification difficulty. For particle groups as pellets, fragments and films, the non-identified MPs were very low (7%), and respect fibre group was 18%. From the 18% of non-identified fibres, all of them were synthetic but were not clearly identify as particular polymer.

The MPs abundance in seawater in Tarragona coastal area was not homogenous. There were high density zones alternated with areas of low abundance, focusing the high abundances near Tarragona harbour area. The accumulation effect of MPs was magnified by intersection of Port structure of southward littoral marine surface currents carrying MPs from seawater upstream. The general seawater MPs morphology was characterized by textile synthetic fibres (present in ordinary clothes, sport clothes, socks, swimsuits). The higher abundance was observed in Tarragona Port, that is influenced by WWTP discharges. It is well known that WWTP does not eliminate completely the fibres that come from washing textiles (Carr et al., 2016; Murphy et al., 2016). The contribution of fibres to seawater via surface runoff can be also considered (Dris et al., 2015). The release of fibres from polyester, polyester-cotton blend and acrylic fabrics are around 730,000 fibres for every 6 kg of laundry (Browne, 2011; Napper and Thompson, 2016). In general, the WWTPs with tertiary treatment processes had a lower MPs concentration (0-51 particle/L) in the effluent than those with only primary or secondary treatment processes ($9\cdot10^{-4}$-447 particle/L). However, studies also showed the tertiary treatment in some WWTPs did not further decrease the MPs concentration in the effluent (Mason et al., 2016). The total MPs discharges from WWTPs were still considerably high (even if there are low abundances), as most of these facilities process millions of litres of wastewater every day. The estimated average diary efflux (based on annual efflux and effluent concentration), was $2\cdot10^{6}$ particle/day, corresponding to $1.37\cdot10^{5}$ m^3/day; about 9-110 kg of micro-fibres are discharged in WWTPs effluent daily (Hartline et al., 2016; Sun et al., 2019). Based on these reported values, the study area of Tarragona coastal receive approximately $1.3\cdot10^{6}$ particle/day from WWTP effluents. This area is affected by three principals WWTP localized in the coastal zone: Tarragona, Vila-seca and Altafulla; the latter located upstream of the sampling area with indirect influence on it by northern current.

Respect to MPs composition, the main polymers found from fragments were low density polymers as polyethylene and polypropylene, followed by polyethylene terephthalate, polystyrene, polymethylmethacrylate and polyurethane, the same trend than more demanded thermoplastics by European countries mainly for packaging uses, construction and building materials, and others uses such as furniture and electrical apparatus (PlasticsEurope, 2013, 2017, 2019). These are in accordance with other studies in Western and Central Mediterranean regions (de Hann et al., 2019; Suaria et al., 2016). Polyethylene and polypropylene are high-demanded polymers and with low density, so they are frequently found as dominating floating polymers (Hidalgo-Ruz et al., 2012; Prata et al., 2018). High-density polymers detected such as polyvinylchloride, polymethylmethacrylate and polycarbonate, probably are related with local hydrodynamics processes (local upwelling) that keep those particles in buoyance. According to de Hann et al. (2019), the presence of high-density MPs floating in seawater surface is related with the aggregation with floating organic matter (phytoplankton, algae, inorganic suspended) keeping MPs in buoyancy (Figure 3A).

The lack of standardized procedures for sampling, separation, identification and size measurement complicates the comparison with other studies. Nonetheless, a comparison of the existing data on the abundance of floating MPs in the Mediterranean Sea, and other seas and oceans has been carried out (Table 2). Average abundance in Tarragona coast was 1.30±0.98 items/m^3. In comparison with Mediterranean regions, this value was higher than average results obtained for Western and Central Mediterranean regions but lower than, Eastern Mediterranean regions. These regions in Western and Central Mediterranean (Ligurian, Sardinian, Tyrrenean, and Sicily Sea, Po Rhone and Tet delta, and Cartagena coast) with lower values than Tarragona coast are characterized by river discharges, high industrial, touristic and urban activities, and Atlantic currents influence. Many of these areas showed high fibres proportion with polyester as dominant composition. Regarding the composition of fragments, these regions are also dominated by the most abundant polymers (polyethylene and polypropylene). It is important to highlight that the average MPs values on the Tarragona coast were greater than values from Otrasto Sea Strain in Central Mediterranean Sea (Adriatic Sea) and North Catalan Coast in Western Mediterranean Sea, both areas with industrial-urban pressure and high flow river discharges. The polymeric composition of fragments from the North Catalan Coast was similar to those found in Tarragona Coast, possibly due to similar consumption patterns, socio-economic status and waste management characteristics in Catalonia. It should be taken into account that Tarragona surface seawater MPs mean levels (sized from 0.5 to 5 mm) was 0.81±0.70, higher than values from some Western and Central Mediterranean regions (Table 2). Conversely, Tarragona coast average values were lower than values from others Mediterranean regions such as west Menorca, Israel and Lebanese coast. The East Mediterranean regions are characterized as large accumulations zones due to enclose morphology, the presence of Lagmuir circulation, Nile river discharges and high terrestrial runoff. Other areas with higher MPs abundances were in Pacific Ocean, the California inshore (river mouth) and offshore, and in the Atlantic Ocean, Tampa Bay. Moreover, only Tarragona harbour area values were up to seven-fold higher than North Pacific Gyre and Todos Santos Bay (Mexico) values. This means that despite considering the Pacific Ocean to be a hot spot for MPs, with a highest MPs abundance, there is high variability, possibly due to high energy waterflow patterns, dilution and dispersion phenomenon (MP abundances have been observed to decrease with depth). In this sense, the values are not constant, and it is possible strong variation in a temporal (from one season to another) and spatial scale.

According to Liubartseva et al. (2018), high inputs of plastics from rivers and population areas from Barcelona City and its vicinities ranked Catalan Sea as one of the most polluted areas by plastics in the Mediterranean Sea. However, de Haan et al. (2019), found relative low MPs abundance values. The big difference found between the Northern region of Catalonia and the coasts of Tarragona is that the transect of Northern Catalonia samples were collected 4 km away from the coast while in our study the collection was just up to 1 km. one characteristic of Tarragona coast is that there are directs inputs of numerous land-based sources and less influence of high energetic level of oceanographic processes, resulting in high MPs abundances. Meanwhile, North Catalonia MPs values is influenced by the main geostrophic northern current what occasionally meanders over the littoral favouring MP higher dispersion rates and transport away from the coast. Moreover, results are also influenced by MPs transported from Ligurian Sea and Lyon Gulf in northern current. Present results differ from those found by Baini et al. (2018) that reported very low values, up to 0.5 km from the coast of North Tyrrenean Sea in summer and winter. However, results are in agreement with Pedrotti et al. (2016). These authors observed that the relative abundance of small fragments (<2 mm) was greater within the 1 km coastal strip. That suggest there is not only a rapid fragmentation along the coast (probably related to weathering mesoplastics on the beaches and incorporate to seawater by waves action) but also a contribution of land-based small size MPs (runoff, outfalls and treated wastewater). Furthermore, it is important the contribution of macroplastics and mesoplastics by land-based source that can be potentially fragmented on the seawater surface.

We have observed that synthetic fibres ball associated with plankton and other MPs fragments mask the real values of MPs abundance. Due to the difficulty of quantifying the real number of fibres within the ball, we count it as a unit fibre. (Figure 3B). The nature of organic aggregates entrapping MPs favors decreasing sinking MPs rates with low efficiency in carbon export to the deep sea, leading MPs availability to fish and invertebrates confusing MPs-bearing aggregates with food sources (Long et al., 2015; Lusher et al., 2016).

Conversely, the MPs aggregates containing exo-polymers particles enhances the particle-MPs flocculation with higher sinking rate and later deposit to deeper sea levels (Passow, 2002).

3.2 Marine Sediments

Regarding subtidal sediments, levels of MPs sized from 0.5 to 5 mm ranged from 5.5 to 89 MPs/kg$_{dw}$ with a mean value of 32 MPs/kg$_{dw}$. The highest levels were found in the sediments samples collected around industrial harbour (S7) (89 MPs/kg$_{dw}$) followed by a nearby sampling area, Arrabasada-Miracle beaches (S4), (41 MPs/kg$_{dw}$) and La Mora (32 MPs/kg$_{dw}$) (S1). Samples S1, S3, S4, S6 and S7 shown the highest MPs levels (>20 MPs/kg$_{dw}$) and are located very close to emissaries for runoff watercourses and specially wastewater effluent discharges and Francolí river mouth in Port area (Figure 1). Taking into account all the samples the majority of MPs in sediments were between 1 mm and 0.5 mm (49%); from 2 to 1 mm (25%) and from 4 to 2 mm (25%) (Figure 4). Globally, most of the MPs were fibres (64%) followed by fragments (25%) and films (10%).

Regarding the composition, fragment, pellets and films were made of polyethylene (55%), polyvinyl (11%) and phenolic resins (9%). Other materials found were made of polystyrene (4%), polyethylene terephthalate (4%), and even chemical additives (2%) without polymeric composition recorded. Fibbers were made of polyester (61%), polyamide (29%), polyacrylonitrile (7%) and polypropylene (3%). All fragments, pellets and films found were analysed and 15% were synthetic but unable to define particular polymers composition. One-third (34%) of the fibres were identified as synthetic polymers.

To assess whether the abundances of MPs in subtidal sediments are related to their grain size, inorganic and organic composition, data from the local reports (DARP report, 2018) were consulted. All the stations studied were very fine grain (0.1-0.5 mm), with increasing the organic matter concentration (0.31-2.65%), sulphur (0.01-0.08%). Metals and metalloids, were below EPA sediment screening benchmarks (except for Hg and Pb), along the Tarragona coast from La Mora to Tarragona harbour, with highest abundances in harbour area. There was no clear trend between sediment grain size and MP abundance in Tarragona coastal sediments, however significant correlations were found between the amount of MPs and the total organic carbon (r= 0.91; p=0.002) , the Hg levels(r= 0.83; p=0.010) and Pb levels (r= 0.88; p=0.005) in analysed sediments.

All stations showed that fibres proportion was higher than other morphologies, excepting for Punta de la Mora where it was found higher fragments content than fibers. Compared with sweater samples, more synthetic fibres balls associated with sediments grains and organic matter (seagrass, calcareous and algae remains) has been observed. These synthetic fibres balls were abundant in areas with high MPs abundances with the disadvantage of masking real values of fibres and total MPs abundance due to in present study these fibres balls were counted as a single fibre item (Figure 3C).

A significant fraction, 51 of the 78 confirmed fibres, were identified as cellulose without differentiating whether they were synthetic or not due to unclear spectra resolution. The cellulosic fibres were excluded for total MP count. The average cellulose fibres abundances in Tarragona sediments approximately 14.4±6.90 fibres/kg$_{dw}$. In fragments, pellets and films, the dominating composition was low density polyethylene (0.91-0.94 g/cm^3), followed by higher density polymers (1.2-1.45 g/cm^3) polyvinyl > Phenolic resins > polyethylene terephthalate (Pilato, 2013). The proportion of high-density polymers in sediments was higher than in seawater. In case of fibres, the dominating composition was high proportion of higher density polymers (1.05-2.3 g/cm^3) as Polyester > polyamide > polyacrylonitrile.

It is important to highlight the presence of MPs fragments with signs of weathering as bioturbation, biofilm growth, abrasion, and bacterial colonization, degrading the plastic material and exposing chemical additives such as phthalate, an endocrine disruptor, toxic for aquatic life (Harris et al., 1997; Ye et al., 2014). The primary and secondary MPs exposure to environmental conditions or weathering will change their properties such as surface morphological size, crystallinity, colours (yellowing discoloration) and densities, which may influence their physical and chemical actions in environments (Guo and Wang, 2019; Zhou et al., 2018). The change of MPs characteristics and biological colonization/impact may influence on its aggregation capacity. The MPs and organic matter set in "aggregates" may provide a transport mechanism of fragments, films, pellets and fibres to the deep stratus in the sea more likely in photic sediments. Even the aggregation could be the main processes for fibres balls formation. Once on the bottom, MPs are expected to continue fragmenting by weathering (interaction with sediments, eventual currents in shallows deep, and benthic organism ingestion) processes until they reach to nano-size stage but in a slow time scale, due to an environment with a lower incidence of UV light, low abrasion action, and low mechanical wave interaction. Other probably mechanism to transport low density MPs from surface to bottom is through MPs ingestion by biota, faecal pellets expulsion, new aggregations formations, and finally deposition in the bottom (Cole et al., 2016). In summary, marine hetero-aggregations, biofouling, faecal deposition and local hydrodynamics are suggested to be the possible causes of the presence of low-density MPs and synthetic fibres balls in the bottom.

The abundances of MPs in this study are comparable to those observed worldwide despite the wide range of MP sizes analysed and the different existing techniques for sediment analysis (Table 3). Comparing same regions in Western Mediterranean–Balearic Sea, in entire Spanish coast, only two studies reported greater average MP abundances in deeper water (43-154 m), with similar sizes and composition than present study. The hots spot were observed in sediments samples close to densely populated areas i.e. Barcelona coast, conversely the lower values were found in Mallorca island. Probably the depth influences the MPs abundances. Alomar et al. (2016) in Mallorca shallow depths (8-10 m) found high levels (897 ± 103 MPs/kg$_{dw}$) in pristine areas, far away from densely populated areas. According mean values from shallow depth areas from Poland coast inshore and South Portugal, the results of present study were higher, however, compared with Central and Western Mediterranean regions as Telaščica bay (Croatia), Stromboli Island, Lipari Island, *Cymodocea* Bottoms and Amphioxus sand, results here presented were lower. The Tarragona coast MP abundance in sediments were lower than the Northwest Pacific regions including

South Yellow Sea –China, Tokyo Bay Channel and Central Mediterranean regions as Venice lagoon. These areas (with values higher than thousands) are characterized by high abundance of urbanized and industrialized activities. The values found close to Tarragona harbour area demonstrate that harbour areas, with commercial and industrial activities, are zones with high MPs abundances. The values observed in our study, although lower, agrees with Belgium harbour and South African Durban Bay Harbour values, 166.7±92.1 and 1600 items/kg_{dw}, respectively (Table 3). Considering other Ocean Atlantic areas, Tarragona Industrial harbour showed similar abundance values and composition (higher fibres proportion) as UK Coast (Plymouth).

3.3 Beach sand

Beaches intertidal zone presented a mean level of 10.7 MPs/kg_{dw} with range between 0.7 MPs/kg_{dw} in La Mora beach (B1) and 42 MPs/kg_{dw} in La Pineda beach (B7) (Table 1). As it was observed in sediments and superficial seawaters, the sand samples located close to the harbour presented the highest levels of MPs. Globally, the main size category was those comprised between 2 and 1 mm, although the dominant size varied depending on the sampling point. By contrast with the other matrices, sandy beach samples showed an important percentage of larger MPs ranging size from 4 to 2 mm. Fragments were the principal morphology (68%), especially in La Pineda beach, followed by pellet (15%) and fibres (13%). Compared with seawater and sediments, pellets were found in higher levels, especially in Pineda and Miracle beaches. Fragments, pellets and films were made of polyethylene (47%), polypropylene (36%), polystyrene (6%), polyethylene terephthalate (6%), and chemical additives (3%) without polymeric composition recorded (Figure 5). However, fibres were made of polyester (45%), polyamide (33%) and synthetic cellulose polymers (22%). All fragments, pellets and films found were analysed and only 2% could not be identified. Meanwhile, only one third (29%) of the fibres were identified as synthetic polymers and all of them identified (Figure 5).

Isobe et al. (2014) found that relatively large mesoplastics with greater buoyancy are likely to be carried onshore (by drift of stokes, currents and wind) faster than MPs. However, Liutbarkeva et al. (2018) found that stokes drift in the Catalan Sea is relatively low; therefore, the higher proportion of MPs spanning from 2 to 4 mm in the intertidal zone is due to the presence of mesoplastics on the Tarragona beaches carried to onshore due to wind induced waves and surface currents favoured by beach orientation. These mesoplastics could be fragmented in shoreline by the mechanical action of the waves and generate large number of MPs that can be incorporated back into the seawater.

The high touristic pressure in La Pineda beach, its location, nearby Francolí river discharges, runoff, numerous emissaries and wastewater effluents discharges combined with dominant southward littoral drift currents and local hydrodynamics, favour that high quantity MPs arrive to beach. This effect is intensified by the storm events accumulating large deposits of MPs and mesoplastics on hide tide line that can be fragmented and transported to intertidal zone due to touristic activity and rainfalls. The pellets, as primary MPs found on the beach, especially in La Pineda, possibly comes from accidental spillage into industrial drainage and discharged by emissaries to the sea or through accidental spillage by transportation due to the proximity to industrial activity and dispersed by terrestrial runoff. Despite observing lower fibres number compared with water and sediment, like-synthetic ball fibers were again found in El Miracle and Arrabasada. Fibres abundance in intertidal sand probably were underestimated by the presence of this type of aggregations (counted as a unit). These balls were usually mixed or associated with inorganic and organic material from the surrounding environment.

The composition of MPs in intertidal zone from Tarragona coast beaches was similar to subtidal sediments composition, with a higher proportion of the most common and low-density polymers (polyethylene and polypropylene) for fragments meanwhile, for fibres, most common polymer found were polyester and polyamide. Other polymers such as synthetic cellulose in fibres and silicone in fragments were also found. Fragments with signs of weathering exposing chemical additives such as Erucyl-Erucamide and Tris(2.4-diterbutyl-phenyl) phosphite were also observed. This demonstrate that MP in the intertidal zone can experiment weathering processes due to intense UV radiation, abrasive sand interaction, mechanical forces such as hydraulic shear forces, thermal oxidation and salinity (Figure 3D). Although the fragments composition from seawater and intertidal sand were similar, the fibres composition between seawater and sand were different due to the polyurethane fibres observed in seawater. A significant fraction (6 out 36 confirmed fibres), were identified as cellulose without differentiating whether it is synthetic or not due to unclear spectra resolution. In consequence, the cellulosic fibres were excluded for total MPs count. Synthetic cellulose was considered in this study as manufactured fibres from regenerated cellulose (cellulose chemically modified), with lower density than cellulose not chemically modified (natural fibre) 1.44 g/cm^3 and 1.50 g/cm^3, respectively (Rana et al., 2014; Sanchez-Vidal et al., 2018). Cellulose acetate is a regenerated as well as a modified cellulosic fibre unlike viscose and cuprammonium rayon which are pure regenerated cellulosic fibres (Rana et al., 2014). Because the chemical composition and properties of the natural cellulose is significantly modified during the manufacturing process for rayon, this type of fibres has been included in studies reporting man-made synthetic fibres. Environmental impact of these fibres has been assessed using lifecycle assessment (Rana et al., 2014). According this analysis rayon have different characteristics than natural cellulose, with more impacts in human toxicity and freshwater aquatic ecotoxicity despite Lyocell fibres is the only type of rayon completely biodegradable.

The spatial distribution of MPs at small scale on the beaches was heterogeneous changing also temporally from summer to autumn. Present study found different composition and abundance between intertidal sand sampled in June and in September. In June, (beginning touristic activities) the abundance was higher, dominated by fragments from 2-4 mm composite by five different polymers (polystyrene (32%), polyethylene (32%), polypropylene (26%), Poly(methylmethacrylate) (6%), PEVA (3%)), meanwhile fibres composite were polystyrene (20%) and synthetic cellulose (80%). Conversely in September (after touristic activities and heavy storms), the abundance was lower, with similar fragments and fibres proportion; fibre composition was dominated only by synthetic cellulose (100%) meanwhile fragments composition varied with high proportion polyethylene (57%) followed by similar proportion of Poly(methylmethacrylate) (14%), polypropylene (14%) and polystyrene (14%). The differences in abundance and composition according to the sampling period may be due to the characteristics of the tourist activity and weather in June (summer) and September (autumn). In summer, there are many people on the beach contributing with MPs inputs and their transport from supralitoral and high tide line to intertidal zone. According to this hypothesis, at beginning summer, MPs should fill the beaches intertidal zone. In autumn, it was not observed, probably by low touristic activity and seasonal storms causing a MP movement of polluted intertidal sand to supralittoral zone or to sea.

Comparing MPs abundances of sand beaches from Tarragona coast with values from other Mediterranean Sea regions and worldwide, it was observed that average Tarragona coast values were lower than most of studies shown in Table 4. Beaches abundance values of the Atlantic, Indian and Pacific Oceans and the others Mediterranean regions were much higher than those found in our study. Studies carried out exclusively in the intertidal zone of Belgium coast (Groenendijk, Koksijde-Bad, Knokke) and Slovenia coast (zones nearby harbour and touristic relevance), reported values also higher than the Tarragona coast (highlighting that the studies done in Belgium included a wide size range). The average Tarragona coast values were similar to values from Atlantic zones as UK coast (Plymouth), Belgium coastal line-De Panne (low tide), Belgium Coastal low tide line and Greece (Northern Crete) values. These zones are densely populated with high pressure by touristic activities. Tarragona sand beach levels values were only higher than Germany-Nordesney Island high and low tide line, Germany Rostock Coast intertidal zones considering only particles and Baltic sea, Russia (Vistula Spit) on high tide line. The Germany zones were characterized by low anthropogenic influence and Vistula Spit influenced by windy events combined with recreation, fishing, and navigation activities. Specifically, La Pineda MPs abundance values were similar to other oceanic beach zones as Netherlands Coast –Ijmuiden low tide line (near to urbanized zone), India Dhanushkodi low tide line (touristic and fishering activities), Hauts-de-France region from high, low and intertidal line (combination of protected area, low flow river discharges and industrialized zone). La Pineda beach values were higher than Belgium Coastal line mean including two tide lines (low and high tide line), Baltic sea, Russia (Cape Tarán) high tide line, all of these areas densely populated. Conversely, la Pineda values were lower than Atlantic beaches (high tide line) located in Lithuania-Klaipéda (Baltic Sea), France-Normandy, Portugal-Madeira; the first area characterized by being a harbour city with a lagoon outlet that receive river flows discharges with industrial and agricultural pollution and the last two areas by tourist activities. Regarding other studies with similar MP sizes focused on western Mediterranean regions made in high tide line and showed in Table 4, La Pineda MP abundances values were about four-fold lower than other densely populated and industrialized zones near Tarragona (as Barcelona), and other densely populated zones from Spanish coast as Denia. With respect to other studies carried out on beaches of the central and eastern Mediterranean Sea (at the high tide line), la Pineda values were from two to three-fold lower than those found in densely populated areas such as Israel -Tel Aviv, Turkey-Dikili, Italy-Sicily beaches and Lido di Dante zone (Italy). The MPs morphology in most of the studies mentioned above (Table 4), were mainly fibres, in agreement with composition found in Arrabasada and Savinosa beaches and contrary to the dominant morphology found in La Pineda beach where fragment was the dominant morphology. Regarding the composition of the MPs in these studies (Table

4), it was similar to than present study beaches being polypropylene, polyethylene, polystyrene and polyethylene terephthalate the most found composition of MPs.

3.4 General Discussion

The developed protocols for MPs analysis have drawbacks and advantages and it was necessary to adapting them for different environmental samples requirements. In visual sorting, MPs pre-selection based in buoyancy, guided and supported the spectroscopy analysis, changes of H_2O_2:$FeSO_4$ relation in Fenton procedures for organic matters and turbidity removal, avoid filter yellowish coloration were developed or addapted in present study.

In this study, MPs pollution in western Mediterranean coastal environments was determined. The results confirm that MPs pollution on the three environment components is ubiquitous. Sandy beaches, marine sediment and superficial seawater from Tarragona coast showed MPs of different sizes, morphology, composition and significant mean values differences in average MP density in each one compartment. Seawater near the coast <1km, were around 0.0013 items/kg (0.0013 items/L), in intertidal beach sands around 10.7 items/kg ($7\cdot10^3$ higher than seawater values) and in marine sediments around 32.4 items/kg ($2\cdot10^4$ higher than seawater values). Considering the MPs pollution dynamics in Tarragona coast, the seawater is the media that receive and facilitates MPs transport. The shoreline acts as an intermediate reservoir with constant weathering and active exchange with seawater. Sediments acts as a significant sink for MPs from seawater, with high residence times.

Despite the differences observed in abundance values for sand, sediment and water, three polymers were common in the three compartments: polyethylene, polystyrene, and polyethylene terephthalate. Microplastics fragment and fibres composition always was dominated by polyethylene and polyethylene terephthalate (polyester), respectively. Polypropylene polymer was identified in beaches and seawater, with higher proportion in beaches. However polyvinyl polymers were detected in water and marine sediments with higher proportion in this last compartment. As many authors have observed (Cozar et al., 2014; GESAMP, 2015; Wu et al., 2019), MPs after entry or formed (by fragmentation) into the seawater can be distributed in the marine media according to their densities alone, in hetero-aggregations or by suffering biofouling, and transported by main and superficial currents, wind (wave height) and by biota ingestion (invertebrates and fish). The growth of biofilms on MPs, increase its density and affects its sedimentation velocity through water column. The number of secondary MPs will increase exponentially as the size becomes smaller. In steady state, the abundance–size distribution should follow a power law, with a scaling exponent equal to the spatial dimension of the plastic objects (Cozar et al., 2014). According to this assumption, the size distribution of MPs in seawater samples with high proportion of fragments 1 to 2 mm and 0.08 to 0.5 mm maybe follow a continuous and very fast fragmentation from millimetric scale to micrometric scale.

On Tarragona coast, there is a high degree of spatial variability in the MPs abundance values for samples of seawater, sediments and sands. The proximity to urban and industrial areas, rivers discharges, wastewater discharges, runoff, watercourses discharges (emissaries) together with the geostrophic southward currents (typical of the Catalan coast), coastal drift, predominant winds, coastal shoreline morphology and the presence of anthropic structures (Port seawall) that modify the surface currents direction and change the normal hydrodynamics in the coastal zone, causes high MPs accumulation in harbor area and La Pineda beach. In turn, the variability of MPs abundances in seawater was influenced by circulation and mixing processes (thermohaline gradients) of superficial strata. Rivers receive MPs and mesoplastics from different sources (sewer overflows, wastewater effluents discharges, soil runoffs, air dusts, precipitation and touristic activity waste disposal) and carry them to the ocean. Only plastics particles with lower or equal density than freshwater density, arrive to the seas (Lots et al., 2017). In the case of the Francolí River, this can be an important land-based MP source to Tarragona coast together with small watercourses fluxes and runoffs, due to the large number of populated areas and wastewater discharges effluents located on its watershed.

Mansui et al. (2015) modelled the effects of circulation on plastic accumulation in the Mediterranean, which finding in the western basin some specific gyres could retain and export floating objects and redistribute them after a shift in the large-scale circulation considering this area as one the most energetic regions. Liutbarkeva et al. (2018) found high spatio-temporal variability in sea-surface plastic concentrations without any stable long-term accumulations, specifically in the Catalan Sea. The North Current tends to weaken, which could result in plastic debris being trapped in the vicinity of its origin with substantial accumulation of plastics on coastlines and the sea bottom. These authors concluded that plastic pollution in that area is caused primarily by its own terrestrial sources. The MP accumulation observed on a small scale on Tarragona coastline, is mainly due to the land-based sources of the city (densely populated), river mouths, wastewater treatment plants, runoff and outfalls of watercourses. Other factors influencing the accumulation of MPs on Tarragona coast is also related to direct inputs from sources to short distance from de coast. The quantity and type of MPs will depend mainly on the degree of waste management in Francolí watershed and Tarragona city, WWTP depuration efficiency and hydrodynamics conditions on the coast. Comparing MPs abundance in seawater (by volume filtered) with other studies, it has been observed higher values of MPs abundances on the coast of Tarragona than those found in oceanic areas, and similar abundances values to other areas of Mediterranean Sea with high accumulation of MPs. This corroborate that the entire Mediterranean Sea basin (despite the variability of circulation in the basin that alters its spatial distribution), as a large region of MPs accumulation.

Microplastics hetero aggregations have the potential to be ingested by a wide range of marine organisms, including zooplankton, invertebrates, and fish depending on its size and morphology, in seawater surface and bottom sediments. The immediate possible toxicological effects of MPs involve physical blockage, entanglement, abrasion, loss of mobility in energy expenditure, absent stimulus for feeding, fish respiratory system block. Other long-term effects observed in laboratory studies may involve alterations in the gene regulation, immune response, behavioral alterations and embryonic development of fishes, as well as, histological damage, alteration of cellular oxidative balance and abnormal larval development in mussels (Andrady, 2011; Besseling et al.,2013; Lehtiniemi et al., 2018; Limonta et al., 2019; Paul-Pont, et al., 2016, Ravit et al., 2017; Rist et al., 2018; Rist et al., 2019; Ross et al., 2015). These toxicological effects of MPs could have a possible synergistic interaction between MPs and absorbed micro-pollutants/microbial pathogens; pollutants adsorbed on MPs are polychlorinated biphenyls (PCBs), hexachlorocyclohexane (HCH) and many other compounds included into 78% of priority pollutants (Guo et al., 2019; Rochman et al., 2013). MPs also can act as a sink of pollutants, highlighting the high quantity and large surface-to-volume ratio in marine environment (Rodrigues et al., 2019). In Tarragona coast, weathering signals were found on sediments and sands MPs with their surface modified with pores and roughness evidenced by the growth of microorganisms. These MPs can induce its high affinity for persistent organic pollutants and heavy metals present in sediments or seawater, particularly in the Port area where high concentrations of lead and mercury were found. Other signs of MPs weathering and fragmentation were the polymers additives exposition and loss of MPs structures. All this was evidenced in our samples by the presence of specifically additives spectra in the identification of MPs with FTIR. At molecular level, several degradation mechanisms exist and the domination of one mechanism over the others often depends on the polymer type. Most important mechanisms are chain scission (breaking the chemical bonds of the polymer molecule or depolymerisation) and chain stripping (the side atoms/groups attached to polymer chain are released) (Lithner et al., 2011). The plastic additives found in the samples collected in the sand of La Pineda beach were Erucil-Erucamida and Tris (2,4-diterbutyl-phenyl) phosphite. Erucyl-Erucamide is a slip compound responsible for significantly reducing the surface coefficient of friction of a polymer, also used to enhance the polymer with antistatic properties, enable better mould release, reduced melt viscosity, and anti-sticking properties. Tris(2.4-diterbutyl-phenyl) phosphite delay the overall oxidative degradation of plastics when exposed to ultraviolet (UV) light (Bhunia et al., 2013). Some studies showed high migrations capacity of these additives in aqueous and oily solutions and drinking water at 40ºC after short-term storage (Cooper and Tice, 1995; Gao et al., 2011; Li et al; 2016). The only plastics additives found in sediment samples (Tarragona Port) were phthalates. They are plasticizers used for improving the flexibility, durability and stretch-ability of polymeric films, improvement impact resistance in the final plastic film (Bhunia et al., 2013). The ingestion of plastics containing these additives by marine organisms can be of great concern because some of them have the ability to accumulate. Even if plastics are not ingested, the additives contained in MPs are sources of exposure. Brominated diphenyl ethers (PBDE), phthalates, nonylphenols (NP), bisphenol A (BPA) and antioxidants are some of the most common plastic additives found in marine environments. Exposure studies based on leaching processes conducted on a wide range of polymers and target organisms confirmed toxicity of plastics additives. Leaching of additives by plastic ingestion was more relevant for species with longer gut retention times, such as fish, and was also occasionally be relevant for seas worms. (Koelmans et al., 2013; Koelmans et al.,2014; Hermabessiere et al., 2017; Rochman et al., 2013; Teuten et al.,2009). The risk of exposure to polymeric additives is due not only to migration or leakage into the surrounding environment and possible toxicity to aquatic organisms, but also because the affinity of other contaminants for MPs (enhanced by hydrophobic/polar groups of the exposed additives). To estimate the real risk associated to MPs effects of exposure to these particles it is important to collect environmental data with accurate MPs measures, and thus to obtain deeply knowledge about the negative impact of MPs on the local aquatic biota (GESAMP, 2015). To assess an accurate environmental risk it is necessary to collect data about: a) the number of particles, b) the size distribution, c) shape, d) surface properties, e) polymer composition (and its additives) and density of the particles. However, until now, the environmental risk assessment of MPs in the marine environment has been carried out based on assumptions from the data available in literature and extrapolations. The data obtained of integration on Tarragona coast environment might be very useful for a precisely environmental risk assessment by MPs in the area.

This study also provides background information on the occurrence of MPs in three integrated environmental components such as sand, superficial seawater and sediments on Tarragona coastal area. This information will be used for the implementation of the Marine Strategy Framework Directive in accordance with the European Union directive that commits the EU Member States to take action aimed to achieve the "Good Environmental status" (GES) of the EU's marine environment by 2020. In particular, descriptor 10 focuses on the emerging problem of marine litter and its effects on the marine environment and biota.

4. Conclusions

In present work, MP abundance, size, morphology and composition were determined in sandy beaches, sediments and superficial seawater in Tarragona costal area. Microplastics mean abundance were 1.30 MPs/m^3 in surface sea water, 32.4 MPs/kg$_{dw}$ marine sediments, and 10.7 MPs/kg$_{dw}$ in sand of beaches. The abundance by volume of seawater MPs was higher to those found in oceanic areas and similar to other areas of Mediterranean Sea with high MPs accumulation, corroborating the Western Mediterranean Sea basin as a region of MPs accumulation. Fibres were the dominant MPs morphology in bottom sediments and seawater while fragments were mainly dominant in beaches. Fibres probably comes from effluents from WWTP and emissaries' discharges. Fibres balls associated with bottom sediments with organic debris and plankton were abundant, masking the real amounts of fibres in each reservoir. Taking into account composition, the highly demanded polymers were the most abundant; these mean polyethylene and polypropylene for fragments and polyester (polyethylene terephthalate) for fibres. In order to harmonize results and address specific problems such as fibres balls, it is necessary to adapt protocols and guidelines developed for MPs analysis. It was necessary to adapting developed protocols and guidelines for MPs analysis in order to harmonize results and deal with specific problems such as fibres balls. The size range between 4 and 5 mm was the lowest proportion among the three environmental compartments; MPs sized from 2 to 4 mm were present only in bottom sediments and sandy beach. MPs sized between 1 to 2 mm were more present in sandy beaches and seawater. MPs ranging from 0.5 to 1 mm was most abundant in bottom sediments than seawater, suggesting a selective deposition to sediments. The level of MPs fragments size below 0.5 mm in seawater suggests active fragmentation on surface by weathering action (mechanical forces, photo-oxidation and temperature). The composition and abundance of the MPs observed, suggests that the main contribution comes from numerous land base-sources (trough streams, terrestrial runoff, watercourse emissaries, port activities and WWTP effluents discharges). Fisheries and marine transport were less important sources of MPs on Tarragona coast.

Microplastics fate analysis is of fundamental importance to determine the nature of pollution and effects on the coastal environment. Three-dimensional numerical simulations taking account the sinking and beaching dynamic processes, seawater density, velocity wind-driven currents and stokes drift will help us to understand the microplastic residence times and the fluxes between compartments. Future studies are needed to assess spatial and temporary trends in MPs abundance on Catalan coastal environment.

Acknowledgments

N. Expósito received funds through AGAUR 2018 FI_B 01029 fellowship cofound by Secretaria d'Universitats i Recerca del Departament d'Empresa i Coneixement de la Generalitat de Catalunya and European Union. J. Rovira received postdoctoral fellowship from "Juan de la Cierva-incorporación" program of the Spanish "Ministerio de Ciencia, Innovación y Universidades" (IJC 2018-035126-I). This study was supported by the Catalan Ministry of Agriculture, Livestock, Fisheries and Food (Resolution DARP/619/2018) and Corbel Project PID: 6362 - "Environmental risk assessment by microplastics pollution in Catalonia Coastal areas".

References

Aliabad, M.K., Nassiri, M., Kor, K. Microplastics in the surface seawaters of Chabahar Bay, Gulf of Oman (Makran Coasts) (2019) Marine Pollution Bulletin, 143: 125-133. DOI: 10.1016/j.marpolbul.2019.04.037

Alomar, C., Estarellas, F., Deudero, S., Microplastics in the Mediterranean Sea: Deposition in coastal shallow sediments, spatial variation and preferential grain size (2016) Marine Environmental Research 115: 1-10. DOI: 10.1016/j.marenvres.2016.01.005

Allen, S., Allen, D., Phoenix, V.R., Le Roux, G., Durántez Jiménez, P., Simonneau, A., Binet, S., Galop, D. Atmospheric transport and deposition of microplastics in a remote mountain catchment (2019) Nature Geoscience, 12: 339-344. DOI: 10.1038/s41561-019-0335-5

Andrady, A.L. Microplastics in the marine environment (2011) Marine Pollution Bulletin 62,1596–1605. DOI: 10.1016/j.marpolbul.2011.05.030

Ashton, K., Holmes, L. and Turner, A. Association of metals with plastic production pellets in the marine environment (2010) Marine Pollution Bulletin, 60: 2050–2055. DOI: 10.1016/j.marpolbul.2010.07.014

Baini, M., Fossi, M.C., Galli, M., Caliani, I., Campani, T., Finoia, M.G., Panti, C. Abundance and characterization of microplastics in the coastal waters of Tuscany (Italy): The application of the MSFD monitoring protocol in the Mediterranean Sea (2018) Marine Pollution Bulletin, 133: 543-552. DOI: 10.1016/j.marpolbul.2018.06.016

Bakir, A., Rowland, S.J., Thompson, R.C. Enhanced desorption of persistent organic pollutants from microplastics under simulated physiological conditions (2014). Environmental Pollution. 185, 16–23. DOI: 10.1016/j.envpol.2013.10.007

Barboza, L.G, Gimenez, B.C.,. Microplastics in the marine environment : Current trends and future perspectives (2015) Marine Pollution Bulletin 97, 5–12. DOI: 10.1016/j.marpolbul.2015.06.008

Barnes, D. K. A., Galgani, F., Thompson, R. C. and Barlaz, M. Accumulation and fragmentation of plastic debris in global environments (2009) Journal of Polymers and the Environment, 15: 1985–1998. DOI: 10.1098/rstb.2008.0205

Bayo, J., Rojo, D., Olmos, S. Abundance, morphology and chemical composition of microplastics in sand and sediments from a protected coastal area: The Mar Menor lagoon (SE Spain) (2019) Environmental Pollution, 252: 1357-1366. DOI: 10.1016/j.envpol.2019.06.024

Bergmann, M., Gutow, L., Klages, M. Marine anthropogenic litter (2015) Marine Anthropogenic Litter, pp. 1-447. DOI: 10.1007/978-3-319-16510-3

Besley, A., Vijver, M.G., Behrens, P., Bosker, T. A standardized method for sampling and extraction methods for quantifying microplastics in beach sand (2017) Marine Pollution Bulletin, 114: 77-83. DOI: 10.1016/j.marpolbul.2016.08.055

Besseling E, Wegner A, Foekema EM, van den Heuvel-Greve MJ, Koelmans AA. Effects of microplastic on fitness and PCB bioaccumulation by the lugworm Arenicola marina (L.). “Effects of microplastic on fitness and PCB bioaccumulation by the lugworm Arenicola marina (L.).” (2013) Environmental science & technology vol. 47,1 593-600. DOI:10.1021/es302763x.

Bhunia, K., Sablani, S.S., Tang, J. and Rasco, B. Migration of Chemical Compounds from Packaging Polymers during Microwave, Conventional Heat Treatment, and Storage (2013) Comprehensive Reviews Food Science and Food Safety, 12: 523-545. DOI:10.1111/1541-4337.12028

Blašković, A., Fastelli, P., Čižmek, H., Guerranti, C., Renzi, M. Plastic litter in sediments from the Croatian marine protected area of the natural park of TelašČica bay (Adriatic Sea) (2017) Marine Pollution Bulletin, 114 (1), pp. 583-586. DOI: 10.1016/j.marpolbul.2016.09.018

Browne, M.A., Crump, P., Niven, S.J., Teuten, E., Tonkin, A., Galloway, T.,Thompson, R.,. Accumulation of microplastic on shorelines woldwide: sources and sinks. Environ. 2011. Sci. Technol. 45 (21), 9175-9179. DOI: 10.1021/es201811s

Carbery, M., O’Connor, W., Palanisami, T. Trophic transfer of microplastics and mixed contaminants in the marine food web and implications for human health (2018) Environment International. 115, 400–409. DOI: 10.1016/j.envint.2018.03.007.

Carr, S.A., Liu, J., Tesoro, A.G. Transport and fate of microplastic particles in wastewater treatment plants (2016) Water Res. 91, 174-182. DOI: 10.1016/j.watres.2016.01.002

Chae Y, An YJ. Effects of micro- and nanoplastics on aquatic ecosystems: Current research trends and perspectives (2017) Marine Pollution Bulletin.;124(2):624-632. DOI:10.1016/j.marpolbul.2017.01.070

Chang, X., Xue, Y., Li, J., Zou, L., Tang, M. Potential health impact of environmental micro- and nanoplastics pollution (2020) Journal of Applied Toxicology, 40: 4-15. DOI: 10.1002/jat.3915

Cincinelli, A., Martellini, T., Guerranti, C., Scopetani, C, Chelazzi, D., Giarrizzo, T. A potpourri of microplastics in the sea surface and water column of the Mediterranean Sea (2019) Trends in Analytical Chemistry 110: 321-326. DOI: 10.1016/j.trac.2018.10.026

Claessens, M., Meester, S.D., Landuyt, L.V., Clerck, K.D., Janssen, C.R. Occurrence and distribution of microplastics in marine sediments along the Belgian coast (2011) Marine Pollution Bulletin, 62: 2199-2204. DOI: 10.1016/j.marpolbul.2011.06.030

Cole M, Lindeque PK, Fileman E, Clark J., Ceri, L.,Halsband C. and Tamara Galloway Microplastics alter the properties and sinking rates of zooplankton faecal pellets. (2016) Environmental Science & Technology 50 (6), 3239-3246 DOI: 10.1021/acs.est.5b05905

Constant, M., Kerhervé, P., Mino-Vercellio-Verollet, M., Dumontier, M., Sànchez Vidal, A., Canals, M., Heussner, S. Beached microplastics in the Northwestern Mediterranean Sea (2019) Marine Pollution Bulletin, 142: 263-273. DOI: 10.1016/j.marpolbul.2019.03.032

Constant, M., Philippe, K., Sola, J., Sanchez-Vidal, A., Canals, M., Heussner, S. Floating Microplastics in the Northwestern Mediterranean Sea: Temporal and Spatial Heterogeneities (2018) Proceedings of the International Conference on Microplastic Pollution in the Mediterranean Sea. Springer pp 9-15.

Cooper, I., & Tice, P. A. Migration studies on fatty acid amide slip additives from plastics into food simulants (1995) Food Additives and Contaminants, 12(2), 235–244. DOI: 10.1080/02652039509374298

Coppock, R.L., Cole, M., Lindeque, P.K., Queirós, A.M., Galloway, T.S. A small-scale, portable method for extracting microplastics from marine sediments (2017) Environmental Pollution, 230: 829-837. DOI: 10.1016/j.envpol.2017.07.017

Cózar, A., Sanz-Martín, M., Martí, E., González-Gordillo, J.I., Ubeda, B., Á. Gálvez, J.,Irigoien, X., Duarte, C.M.. Plastic accumulation in the Mediterranean sea (2015) PLoS One 10, 1–12. DOI: 10.1371/journal.pone.0121762

DARP, Caracterizació de les Biocenosis de Fanerógames marines al Municipi de Tarragona (2018) Resolució ARP/619/2019. TecnATox –Fundació URV-(FEMP) 79 pp.

de Haan, W.P., Sanchez-Vidal, A., Canals, M. Floating microplastics and aggregate formation in the Western Mediterranean Sea (2019) Marine Pollution Bulletin, 140: 523-535. DOI: 10.1016/j.marpolbul.2019.01.053

de Lucia, G.A., Vianello, A., Camedda, A., Vani, D., Tomassetti, P., Coppa, S., Palazzo, L., Amici, M., Romanelli, G., Zampetti, G., Cicero, A.M., Carpentieri, S., Di Vito, S., Matiddi, M. Sea water contamination in the Vicinity of the Italian minor islands caused by microplastic pollution (2018) Water (Switzerland), 10: 1108. DOI: 10.3390/w10081108

de Lucia, G.A., Caliani, I., Marra, S., Camedda, A., Coppa, S., Alcaro, L., Campani, T., Giannetti, M., Coppola, D., Cicero, A.M., Panti, C., Baini, M., Guerranti, C., Marsili, L., Massaro, G., Fossi, M.C., Matiddi, M. Amount and distribution of neustonic micro-plastic off the western Sardinian coast (Central-Western Mediterranean Sea)(2014) Marine Environmental Research, 100: 10-16. DOI: 10.1016/j.marenvres.2014.03.017

Dekiff, J.H., Remy, D., Klasmeier, J., Fries, E. Occurrence and spatial distribution of microplastics in sediments from Norderney (2014) Environmental Pollution, 186: 248-256. DOI: 10.1016/j.envpol.2013.11.019

Desforges J-PW, Galbraith M, Dangerfield N, Ross PS. Widespread distribution of microplastics in subsurface seawater in the NE Pacific Ocean (2014) Marine Pollution Bulletin 79:94–99. DOI. 10.1016/j.marpolbul.2013.12.035

Dris, R., Gasperi, J., Mirande, C., Mandin, C., Guerrouache, M., Langlois, V., Tassin, B. A first overview of textile fibers, including microplastics, in indoor and outdoor environaments (2017) Environmental Pollution, 221: 453-458. DOI: 10.1016/j.envpol.2016.12.013

Dris, R., Gasperi, J., Saad, M., Mirande, C., Tassin, B. Synthetic fibers in atmospheric fallout: A source of microplastics in the environment? (2016) Marine Pollution Bulletin, 104: 290-293. DOI: 10.1016/j.marpolbul.2016.01.006

Dris, R., Gasperi, J., Rocher, V., Saad, M., Renault, N., Tassin, B. Microplastic contamination in an urban area: A case study in Greater Paris (2015) Environmental Chemistry, 12: 592-599. DOI: 10.1071/EN14167

Doyen, P., Hermabessiere, L., Dehaut, A., Himber, C., Decodts, M., Degraeve, T., Delord, L., Gaboriaud, M., Moné, P., Sacco, J., Tavernier, E., Grard, T., Duflos, G. Occurrence and identification of microplastics in beach sediments from the Hauts-de-France region (2019) Environmental Science and Pollution Research, 26: 28010-28021. DOI: 10.1007/s11356-019-06027-8

Esiukova, E. Plastic pollution on the Baltic beaches of Kaliningrad region, Russia (2017) Marine Pollution Bulletin, 114: 1072-1080. DOI: 10.1016/j.marpolbul.2016.10.001

Fastelli, P., Blašković, A., Bernardi, G., Romeo, T., Čižmek, H., Andaloro, F., Russo, G.F., Guerranti, C., Renzi, M. Plastic litter in sediments from a marine area likely to become protected (Aeolian Archipelago's islands, Tyrrhenian sea) (2016) Marine Pollution Bulletin, 113: 526-529. DOI: 10.1016/j.marpolbul.2016.08.054

Fettweis, M., Du Four, I., Zeelmaekers, E., Baeteman, C., Francken, F., Houziaux, J.-S., Mathys, M., Nechad, B., Pison, V., Vandenberghe, N., Van den Eynde, D., Van Lancker, V., Wartel, S. Mud Origin, Characterisation and Human Activities (MOCHA). Final Scientific Report (2007) Belgian Science Policy Office, Brusels. 59pp

Filgueiras, A.V., Gago, J., Campillo, J.A., León, V.M. Microplastic distribution in surface sediments along the Spanish Mediterranean continental shelf (2019) Environmental Science and Pollution Research, 26: 21264-21273. DOI: 10.1007/s11356-019-05341-5

Fossi, M.C., Marsili, L., Baini, M., Giannetti, M., Coppola, D., Guerranti, C., Caliani, I., Minutoli, R., Lauriano, G., Finoia, M.G., Rubegni, F., Panigada, S., Bérubé, M., Urbán Ramírez, J., Panti, C. Fin whales and microplastics: The Mediterranean Sea and the Sea of Cortez scenarios (2016) Environmental Pollution, 209: 68-78. DOI: 10.1016/j.envpol.2015.11.022

Fossi, M.C., Panti, C., Guerranti, C., Coppola, D., Giannetti, M., Marsili, L., Minutoli, R. Are baleen whales exposed to the threat of microplastics? A case study of the Mediterranean fin whale (Balaenoptera physalus) (2012) Marine Pollution Bulletin, 64: 2374-2379. DOI: 10.1016/j.marpolbul.2012.08.013

Frias, J.P.G.L., Gago, J., Otero, V., Sobral, P. Microplastics in coastal sediments from Southern Portuguese shelf wàters (2016) Marine Environmental Research, 114: 24-30. DOI: 10.1016/j.marenvres.2015.12.006

Frias, J.P.G.L., Nash, R. Microplastics : Finding a consensus on the definition (2019) Marine Pollution Bulletin 138, 145–147. DOI: 10.1016/j.marpolbul.2018.11.022

Gao, Y., Gu, Y., & Wei, Y. Determination of polymer additives-antioxidants and ultraviolet (UV) absorbers by high-performance liquid chromatography coupled with UV photodiode array detection in food simulants (2011) Journal of Agricultural and Food Chemistry, 59(24), 12982–12989. DOI: 10.1021/jf203257b

Garcia, T.M., Campos, C.C., Mota, E.M.T., Santos, N.M.O., Campelo, R.P.D.S., Prado, L.C.G., Melo Junior, M., Soares, M.D.O. Microplastics in subsurface waters of the western equatorial Atlantic (Brazil) (2020) Marine Pollution Bulletin, 150: 110705. DOI: 10.1016/j.marpolbul.2019.110705

Gasperi, J., Wright, S.L., Dris, R., Collard, F., Mandin, C., Guerrouache, M., Langlois, V., Kelly, F.J., Tassin, B. Microplastics in air: Are we breathing it in? (2018) Current Opinion in Environmental Science and Health, 1: 1-5. DOI: 10.1016/j.coesh.2017.10.002

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

GESAMP. “Sources, fate and effects of microplastics in the marine environment: part two of a global assessment” (2016) (Kershaw, P.J., and Rochman, C.M., eds). (IMO/FAO/UNESCO-IOC/UNIDO/WMO/IAEA/UN/ UNEP/UNDP Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection). Rep. Stud. GESAMP No. 93, 220 p.

Geyer, R., Jambeck, J.R., Law, K.L. Production, use, and fate of all plastics ever made (2017) Science Advances, 3 (7), art. No. e1700782. DOI: 10.1126/sciadv.1700782

Goldstein, M.C., Rosenberg, M., Cheng, L. Increased oceanic microplastic debris enhances oviposition in an endemic pelagic insect (2012) Biology Letters, 8: 817-820. DOI: 10.1098/rsbl.2012.0298

Graca, B., Szewc, K., Zakrzewska, D., Dołęga, A., Szczerbowska-Boruchowska, M. Sources and fate of microplastics in marine and beach sediments of the Southern Baltic Sea—a preliminary study (2017) Environmental Science and Pollution Research, 24: 7650-7661. DOI: 10.1007/s11356-017-8419-5

Guo, X., Wang, J. The chemical behaviors of microplastics in marine environment: A review (2019) Marine Pollution Bulletin 142 :1-14. DOI: 10.1016/j.marpolbul.2019.03.019

Harris, C. A.; Henttu, P.; Parker, M. G.; Sumpter, J. P. The estrogenic potential of phthalate esters in vitro (1997) Environmental Health Perspectives, 105 (8), 802−811.

Hartline, N. L., Bruce, N. J., Karba, S. N., Ruff, E. O., Sonar, S. U., & Holden, P. A Microfiber Masses Recovered from Conventional Machine Washing of New or Aged Garments (2016) Environmental Science & Technology, 50(21), 11532-11538. DOI: 10.1021/acs.est.6b03045

Hermabessiere L, Dehaut A, Paul-Pont I. Occurrence and effects of plastic additives on marine environments and organisms: A review (2017) Chemosphere.;182:781-793. DOI: 10.1016/j.chemosphere.2017.05.096

Hidalgo-Ruz, V., Gutow, L., Thompson, R.C., Thiel, M. Microplastics in the marine environment: A review of the methods used for identification and quantification (2012) Environmental Science and Technology, 46: 3060-3075. DOI: 10.1021/es2031505

Paul-Pont, I., Lacroix, C., González Fernández, C., Hégaret, H., Lambert, C., Le Goïc, N., Frère, L., Cassone, A. L., Sussarellu, R., Fabioux, C., Guyomarch, J., Albentosa, M., Huvet, A., & Soudant, P. Exposure of marine mussels Mytilus spp. to polystyrene microplastics: Toxicity and influence on fluoranthene bioaccumulation (2016) Environmental pollution (Barking, Essex:1987) 216, 724–737. DOI: 10.1016/j.envpol.2016.06.039.

Ivar, J. A., Spengler, Â. and Costa, M. F. Here , there and everywhere . Small plastic fragments and pellets on beaches of Fernando de Noronha (Equatorial Western Atlantic) (2009) Marine Pollution Bulletin, 58: 1236–1238. DOI: 10.1016/j.marpolbul.2009.05.004

Ivleva, N.P., Wiesheu, A.C., Niessner, R. Microplastic in Aquatic Ecosystems (2017). Angewandte Chemie- Int. Ed. 56, 1720–1739. DOI: 10.1002/anie.201606957

Jambeck, J.R., Geyer, R., Wilcox, C., Siegler, T.R., Perryman, M., Andrady, A., Narayan,R., Law, K.L. Plastic waste inputs from land into the ocean (2015) Science (80) 347,768–771. DOI: 10.1126/science.1260352.

Karami, A., Golieskardi, A., Choo, C.K., Romano, N., Ho, Y.B., Salamatinia, B. A high-performance protocol for extraction of microplastics in fish (2016) Science of the Total Environment, 578: 485-494. DOI: 10.1016/j.scitotenv.2016.10.213

Karlsson, T.M., Vethaak, A.D., Almroth, B.C., Ariese, F., van Velzen, M., Hassellöv, M., Leslie, H.A. Screening for microplastics in sediment, water, marine invertebrates and fish: Method development and microplastic accumulation (2017) Marine Pollution Bulletin, 122: 403-408. DOI: 10.1016/j.marpolbul.2017.06.081

Kazour, M., Jemaa, S., Issa, C., Khalaf, G., Amara, R. Microplastics pollution along the Lebanese coast (Eastern Mediterranean Basin): Occurrence in surface water, sediments and biota samples (2019) Science of the Total Environment, 696: 133933. DOI: 10.1016/j.scitotenv.2019.133933

Koelmans AA, Besseling E, Wegner A, Foekema EM. Plastic as a carrier of POPs to aquatic organisms: a model analysis [published correction appears in Environmental Science Technology. 2013 Aug 6;47(15):8992-3]. 2013 Environmental Science & Technology.;47(14):7812-7820. DOI: 10.1021/es401169n

Koelmans AA, Besseling E, Foekema EM. Leaching of plastic additives to marine organisms (2014) Environmental Pollution.;187:49-54 . DOI: 10.1016/j.envpol.2013.12.013

Kukulka, T., Proskurowski, G., Morét-Ferguson, S., Meyer, D.W., Law, K.L. The effect of wind mixing on the vertical distribution of buoyant plastic debris (2012) Geophysical Research Letters, 39: L07601 DOI: 10.1029/2012GL051116

Lacerda, A.L.F., Rodrigues, L.S., van Sebille, E., Rodrigues, F.L., Ribeiro, L., Secchi, E.R., Kessler, F., Proietti, M.C. Plastics in sea surface waters around the Antarctic Peninsula (2019) Scientific Reports, 9: 3977. DOI: 10.1038/s41598-019-40311-4

Laglbauer, B.J.L., Franco-Santos, R.M., Andreu-Cazenave, M., Brunelli, L., Papadatou, M., Palatinus, A., Grego, M., Deprez, T. Macrodebris and microplastics from beaches in Slovenia (2014) Marine Pollution Bulletin, 89: 356-366. DOI: 10.1016/j.marpolbul.2014.09.036

Lebreton, L.C.M., Zwet, J. Van Der, Damsteeg, J., Slat, B., Andrady, A., Reisser, J.,. River plastic emissions to the world 's oceans (2017). Nature Communications. 8, 1–10. DOI: 10.1038/ncomms15611

Lehtiniemi, M., Hartikainen, S., Näkki, P., Engström-öst, J., Koistinen, A., & Setälä, O.. Size matters more than shape: Ingestion of primary and secondary microplastics by small predators (2018) Food Webs, 17. DOI: 10.1016/j.fooweb.2018.e00097

Limonta, G., Mancia, A., Benkhalqui, A., Bertolucci, C., Abelli, L., Fossi, M.C., Panti, C. Microplastics induce transcriptional changes, immune response and behavioral alterations in adult zebrafish (2019) Scientific Reports 9, 15775. DOI: 10.1038/s41598-019-52292-5

Lithner D, Larsson A, Dave G. Environmental and health hazard ranking and assessment of plastic polymers based on chemical composition. (2011) The Science of the Total Environment 409(18):3309-3324. DOI: 10.1016/j.scitotenv.2011.04.038.

Li, C., Xu, J., Chen, D., & Xiao, Y. Detection of phthalates migration from disposable tablewares to drinking water using hexafluoroisopropanol-induced catanionic surfactant coacervate extraction (2016) Journal of Pharmaceutical Analysis, 6(5), 292–299. DOI: 10.1016/j.jpha.2016.04.002

Liu, T., Zhao, Y., Zhu, M., Liang, J., Zheng, S., Sun, X. Seasonal variation of micro- and meso-plastics in the seawater of Jiaozhou Bay, the Yellow Sea (2020) Marine Pollution Bulletin, 152: 110922. DOI: 10.1016/j.marpolbul.2020.110922

Liubartseva, S., Coppini, G., Lecci, R., Clementi, E. Tracking plastics in the Mediterranean: 2D Lagrangian model (2018) Marine Pollution Bulletin, 129: 151-162. DOI: 10.1016/j.marpolbul.2018.02.019

Löder, M.G.J., Imhof, H.K., Ladehoff, M., Löschel, L.A., Lorenz, C., Mintenig, S., Piehl, S., Primpke, S., Schrank, I., Laforsch, C., Gerdts, G. Enzymatic Purification of Microplastics in Environmental Samples (2017) Environmental Science and Technology, 51: 14283-14292. DOI: 10.1021/acs.est.7b03055

Long, M., Moriceau, B., Gallinari, M., Lambert, C., Huvet, A., Raffray, J., et al. Interactions between microplastics and phytoplankton aggregates: impact on their respective fates (2015) Mar. Chem. 175, 39–46. DOI: 10.1016/j.marchem.2015.04.003.

Lots, F.A.E., Behrens, P., Vijver, M.G., Horton, A.A., Bosker, T. A large-scale investigation of microplastic contamination: Abundance and characteristics of microplastics in European beach sediment (2017) Marine Pollution Bulletin, 123: 219-226. DOI: 10.1016/j.marpolbul.2017.08.057

Lusher, A.L., Tirelli, V., O'Connor, I., Officer, R. Microplastics in Arctic polar waters: The first reported values of particles in surface and sub-surface samples (2015) Scientific Reports, 5: 14947. DOI: 10.1038/srep14947

Lusher, A.L., O'Donnell, C., Officer, R., O'Connor, I. Microplastic interactions with North Atlantic mesopelagic fish. ICES J. (2016) Mar. Sci. 73, 250–262. DOI: 10.1093/icesjms/fsv241.

Mack, L., Andersen, H.E., Beklioğlu, M., Bucak, T., Couture, R.-M., Cremona, F., Ferreira, M.T., Hutchins, M.G., Mischke, U., Molina-Navarro, E., Rankinen, K., Venohr, M., Birk, S. The future depends on what we do today – Projecting Europe's surface water quality into three different future scenarios (2019) Science of the Total Environment, 668: 470-484. DOI: 10.1016/j.scitotenv.2019.02.251

Mai, L., Bao, L.-J., Shi, L., Wong, C.S., Zeng, E.Y. A review of methods for measuring microplastics in aquatic environanments (2018) Environmental Science and Pollution Research, 25: 11319-11332. DOI: 10.1007/s11356-018-1692-0

Masó, M., Garcés, E., Pagès, F. and Camp, J. Drifting plastic debris as a potential vector for dispersing Harmful Algal Bloom (HAB) species (2003) Scientia Marina, 67: 107–111.

Mason, S.A., Garneau, D., Sutton, R., Chu, Y., Ehmann, K., Barnes, J., Fink, P., Papazissimos, D., Rogers, D.L. Microplastic pollution is widely detected in US municipal wastewater treatment plant effluent (2016) Environ. Pollut. 218,1045-1054. DOI: 10.1016/j.envpol.2016.08.056

Masura, J., Baker, J., Foster, G. and Courtney Arthur. Laboratory methods for the analysis of microplastics in the marine environment: recommendations for quantifying synthetic particles in waters and sediments (2015) NOAA Technical Memorandum NOS-OR&R-48.

Matsuguma, Y., Takada, H., Kumata, H., Kanke, H., Sakurai, S., Suzuki, T., Itoh, M., Okazaki, Y., Boonyatumanond, R., Zakaria, M.P., Weerts, S., Newman, B. Microplastics in Sediment Cores from Asia and Africa as Indicators of Temporal Trends in Plastic Pollution (2017) Archives of Environmental Contamination and Toxicology, 73: 230-239. DOI: 10.1007/s00244-017-0414-9

McEachern, K., Alegria, H., Kalagher, A.L., Hansen, C., Morrison, S., Hastings, D. Microplastics in Tampa Bay, Florida: Abundance and variability in estuarine waters and sediments (2019) Marine Pollution Bulletin, 148: 97-106. DOI: 10.1016/j.marpolbul.2019.07.068

Moore, C.J., Moore, S.L., Weisberg, S.B., Lattin, G.L., Zellers, A.F. A comparison of neustonic plastic and zooplankton abundance in southern California's coastal waters (2002) Marine Pollution Bulletin, 44: 1035-1038. DOI: 10.1016/S0025-326X(02)00150-9

Mu, J., Zhang, S., Qu, L., Jin, F., Fang, C., Ma, X., Zhang, W., Wang, J. Microplastics abundance and characteristics in surface waters from the Northwest Pacific, the Bering

Sea, and the Chukchi Sea (2019) Marine Pollution Bulletin, 143: 58-65. DOI: 10.1016/j.marpolbul.2019.04.023

Munno, K., Helm, P.A., Jackson, D.A., Rochman, C., Sims, A. Impacts of temperature and selected chemical digestion methods on microplastic particles (2018) Environmental Toxicology and Chemistry, 37: 91-98. DOI: 10.1002/etc.3935

Murphy, F., Ewins, C., Carbonnier, F., Quinn, B. Wastewater treatment works (WwTW) as a source of microplastics in the aquatic environment (2016) Environ. Sci.Technol. 50 (11), 5800-5808. DOI: 10.1021/acs.est.5b05416

Napper, I.E., Thompson, R.C. Release of synthetic microplastic plastic fibres from domestic washing machines: effects of fabric type and washing conditions (2016) Mar. Pollut. Bull. 112 (1), 39-45. DOI: 10.1016/j.marpolbul.2016.09.025

Nizzetto, L., Bussi, G., Futter, M.N., Butterfield, D., Whitehead, P.G.,. A theoretical assessment of microplastic transport in river catchments and their retention by soils and river sediments (2016) Environmental Science Processes & Impacts 1050–1059. DOI: 10.1039/c6em00206d

Nuelle, M.-T., Dekiff, J.H., Remy, D., Fries, E. A new analytical approach for monitoring microplastics in marine sediments (2014) Environmental Pollution, 184: 161-169. DOI: 10.1016/j.envpol.2013.07.027

Ogata, Y., Takada, H., Mizukawa, K., Hirai, H., Iwasa, S., Endo, S., Mato, Y., Saha, M., Okuda, K., Nakashima, A., Murakami, M., Zurcher, N., Booyatumanondo, R., Pauzi, M., Quang, L., Gordon, M., Miguez, C., Suzuki, S., Moore, C., Karapanagioti, H. K., Weerts, S., Mcclurg, T., Burres, E., Smith, W., Velkenburg, M. Van, Selby, J., Lang, R. C., Laursen, D., Danner, B., Stewardson, N. and Thompson, R. C. International Pellet Watch : Global monitoring of persistent organic pollutants (POPs) in coastal waters . 1 . Initial phase data on PCBs, DDTs, and HCHs (2009) Marine Pollution Bulletin, 58: 1437–1446. DOI: 10.1016/j.marpolbul.2009.06.014

Oliveira, M., Almeida, M., Miguel, I. A micro(nano)plastic boomerang tale: A never ending story? (2019) TrAC - Trends in Analytical Chemistry, 112: 196-200. DOI: 10.1016/j.trac.2019.01.005

Panti, C., Giannetti, M., Baini, M., Rubegni, F., Minutoli, R., Fossi, M.C. Occurrence, relative abundance and spatial distribution of microplastics and zooplankton NW of Sardinia in the Pelagos Sanctuary Protected Area, Mediterranean Sea (2015) Environmental Chemistry, 12: 618-626. DOI: 10.1071/EN14234

Passow, U. Transparent exopolymer particles (TEP) in aquatic environments (2002) Prog.Oceanogr. 55, 287–333. DOI: 10.1016/S0079-6611(02)00138-6

Pedrotti, M.L., Petit, S., Elineau, A., Bruzaud, S., Crebassa, J.C., Dumontet, B., Martí, E., Gorsky, G., Cózar, A. Changes in the floating plastic pollution of the mediterranean sea in relation to the distance to land (2016) PLoS One 11, 1–14. DOI: 10.1371/journal.pone.0161581

Picó, Y., Barceló, D. Analysis and prevention of microplastics pollution in water: Current perspectives and future directions (2019) ACS Omega, 4: 6709-6719. DOI: 10.1021/acsomega.9b00222

Pilato, L. Phenolic resins: 100 Years and still going strong (2013) Reactive & Functional Polymers 73 270–277

Pinna, M.S., Bacchetta, G., Cogoni, D., Fenu, G. Is vegetation an indicator for evaluating the impact of tourism on the conservation status of Mediterranean coastal dunes? (2019) Science of the Total Environment, 674: 255-263. DOI: 10.1016/j.scitotenv.2019.04.120

Piñon-Colin, T.D.J., Rodriguez-Jimenez, R., Pastrana-Corral, M.A., Rogel-Hernandez, E., Wakida, F.T. Microplastics on sandy beaches of the Baja California Peninsula, Mexico (2018) Marine Pollution Bulletin, 131: 63-71. DOI: 10.1016/j.marpolbul.2018.03.055

Piperagkas, O., Papageorgiou, N., Karakassis, I. Qualitative and quantitative assessment of microplastics in three sandy Mediterranean beaches, including different methodological approaches (2019) Estuarine, Coastal and Shelf Science, 219: 169-175. DOI: 10.1016/j.ecss.2019.02.016

PlasticsEurope. Plastics - The Facts 2013. An analysis of European plastics production, demand and waste data for 2012. Plastics Europe 2013: Association of Plastic Manufacturers, Brussels.

PlasticsEurope. Plastics - The Facts 2017. An analysis of European plastics production, demand and waste data for 2016. Plastics Europe 2017: Association of Plastic Manufacturers, Brussels.

PlasticsEurope. Plastics - The Facts 2019. An analysis of European plastics production, demand and waste data for 2018. Plastics Europe 2019: Association of Plastic Manufacturers, Brussels.

Prata, J.C., da Costa, J.P., Duarte, A.C., Rocha-Santos, T. Methods for sampling and detection of microplastics in water and sediment: A critical review (2019) TrAC - Trends in Analytical Chemistry, 110: 150-159. DOI: 10.1016/j.trac.2018.10.029

Primpke, S., Wirth, M., Lorenz, C., Gerdts, G. Reference database design for the automated analysis of microplastic samples based on Fourier transform infrared (FTIR) spectroscopy (2018) Analytical and Bioanalytical Chemistry, 410: 5131-5141. DOI: 10.1007/s00216-018-1156-x

Ramírez-Álvarez, N., Rios Mendoza, L.M., Macías-Zamora, J.V., Oregel-Vázquez, L., Alvarez-Aguilar, A., Hernández-Guzmán, F.A., Sánchez-Osorio, J.L., Moore, C.J., Silva-Jiménez, H., Navarro-Olache, L.F. Microplastics: Sources and distribution in surface waters and sediments of Todos Santos Bay, Mexico (2020) Science of the Total Environment, 703: 134838. DOI: 10.1016/j.scitotenv.2019.134838

Rana, S., Pichandi, S., Shama P and Raul Fangueiro Regenerated Cellulosic Fibers and Their Implications on Sustainability (2014) S. S. Muthu (ed.), Roadmap to Sustainable Textiles and Clothing, Textile Science and Clothing Technology, DOI: 10.1007/978-981-287-065-08, Springer Science Business Media Singapore

Ravit, K., Cooper , G., Moreno, B., Buckley, I., Yang, A., Deshpande, S., Meola, D., Jones and A. Hsieh. Microplastics in urban New Jersey freshwaters: distribution, chemical identification, and biological affects (2017) AIMS Environmental Science, 4(6): 809-826. DOI: 10.3934/environsci.2017.6.809

Reisser, J., Slat, B., Noble, K., Du Plessis, K., Epp, M., Proietti, M., De Sonneville, J., Becker, T., Pattiaratchi, C. The vertical distribution of buoyant plastics at sea: An observational study in the North Atlantic Gyre (2015) Biogeosciences, 12: 1249-1256. DOI: 10.5194/bg-12-1249-2015

Renzi, M., Blašković, A., Fastelli, P., Marcelli, M., Guerranti, C., Cannas, S., Barone, L., Massara, F. Is the microplastic selective according to the habitat? Records in amphioxus sands, Mäerl bed habitats and Cymodocea nodosa habitats (2018) Marine Pollution Bulletin, 130: 179-183. DOI: 10.1016/j.marpolbul.2018.03.019

Rist S., Bethanie Carney Almrothb, Nanna B. Hartmann, Therese M. Karlsson Critical perspective on early communications concerning human health aspects of microplastics (2018) Science of the Total Environment 626: 720–7262. DOI: 10.1016/j.scitotenv.2018.01.092

Rist, S., Baun, A.; Almeda, R.; Hartmann, N. B. Ingestion and effects of micro- and nanoplastics in blue mussel (Mytilus edulis) larvae (2019) Marine Pollution Bulletin 140: 423-430. DOI: 10.1016/j.marpolbul.2019.01.069

Rochman, C., Hoh, E., Kurobe, T & Swee J. Teh. Ingested plastic transfers hazardous chemicals to fish and induces hepatic stress (2013) Scientific Reports 3, 3263-DOI: 10.1038/srep.

Rodrigues, J.P., Duarte, A.C., Santos-Echeandía, J., Rocha-Santos, T. Significance of interactions between microplastics and POPs in the marine environment: A critical overview. (2019) TrAC - Trends in Analytical Chemistry, 11: 252-260. DOI: 10.1016/j.trac.2018.11.038

Ross, P.S & Morales-Caselles, C. Out of sight, but no longer out of mind: microplastics as a global pollutant. (2015). Integrated Environmental Assessment Management. 11(4), 719-728. DOI:10.1002/ieam.1681

Rovira, J., Schuhmacher, M., Nadal, M., Domingo, J.L. Contamination by Coal Dust in the Neighborhood of the Tarragona Harbor (Catalonia, Spain): A Preliminary Study (2018)

The Open Atmospheric Science Journal, 12: 14-20. DOI: 10.2174/1874282301812010014

Sanchez-Vidal, A., Thompson, R.C., Canals, M., Haan, W.P. De. The imprint of microfibres in southern European deep seas (2018) PloS One 13 (11) 1–12. DOI: 10.1371/journal.pone.0207033

Shokri, A. Application of Sono – photo Fenton process for degradation of phenol derivatives in petrochemical wastewater using full factorial design of experiment (2018), International Journal of Industrial Chemistry, 9: 295–303. DOI: 10.1007/s40090-018-0159-y.

Shim,W., J., Hong, S.H., Soeun Eo. Chapter 1 - Marine Microplastics: Abundance, Distribution, and Composition (2018) Microplastic Contamination in Aquatic Environments, Editor(s): Eddy Y. Zeng, Elsevier, Pages 1-26.

Simon-sánchez, L., Grelaud, M., Garcia-orellana, J., Ziveri, P. River Deltas as hotspots of microplastic accumulation : The case study of the Ebro River (NW Mediterranean) (2019) Science of the Total Environment 687, 1186–1196. DOI: 10.1016/j.scitotenv.2019.06.168

Stolte, A., Forster, S., Gerdts, G., Schubert, H. Microplastic abundances in beach sediments along the German Baltic coast (2015) Marine Pollution Bulletin, 99: 216-229. DOI: 10.1016/j.marpolbul.2015.07.022

Strungaru, S.-A., Jijie, R., Nicoara, M., Plavan, G., Faggio, C. Micro- (nano) plastics in freshwater ecosystems: abundance, toxicological impact and quantification methodology (2019) TrAC Trends in Analytical Chemistry. 110, 116–128. DOI: 10.1016/j.trac.2018.10.025.

Suaria, G., Avio, C.G., Mineo, A., Lattin, G.L., Magaldi, M.G., Belmonte, G., Moore, C.J., Regoli, F., Aliani, S. The Mediterranean Plastic Soup: Synthetic polymers in Mediterranean surface wàters (2016) Scientific Reports, 6: 37551. DOI: 10.1038/srep37551

Sun, J., Dai, X., Wang, Q., Loosdrecht, M. C. M. Van and Ni, B. Microplastics in wastewater treatment plants: Detection, occurrence and removal (2019) Water Research, 152: 21–37. DOI: 10.1016/j.watres.2018.12.050

Sundt, P, Schulze, P.E, Syversen, F. (2014) 'Sources of microplastic- pollution to the marine environment. Project report'. Norwegian Environment Agency, 108. Aviable from: https://www.miljodirektoratet.no/globalassets/publikasjoner/M321/M321.pdf. Last access: 01.04.2020

Teuten, E. L., Saquing, J. M., Knappe, D. R., Barlaz, M. A., Jonsson, S., Björn, A., Rowland, S. J., Thompson, R. C., Galloway, T. S., Yamashita, R., Ochi, D., Watanuki, Y., Moore, C., Viet, P. H., Tana, T. S., Prudente, M., Boonyatumanond, R., Zakaria, M. P., Akkhavong, K., Ogata, Y., … Takada, H. Transport and release of chemicals from plastics to the environment and to wildlife (2009). Philosophical transactions of the Royal Society of London. Series B, Biological sciences, 364(1526), 2027–2045. DOI: 10.1098/rstb.2008.0284

Tiwari, M., Rathod, T.D., Ajmal, P.Y., Bhangare, R.C., Sahu, S.K. Distribution and characterization of microplastics in beach sand from three different Indian coastal environaments (2019) Marine Pollution Bulletin, 140: 262-273. DOI: 10.1016/j.marpolbul.2019.01.055

Van Cauwenberghe, L., Claessens, M., Vandegehuchte, M.B., Mees, J., Janssen, C.R. Assessment of marine debris on the Belgian Continental Shelf (2013) Marine Pollution Bulletin, 73: 161-169. DOI: 10.1016/j.marpolbul.2013.05.026

Van der Hal, N., Ariel, A., Angel, D.L. Exceptionally high abundances of microplastics in the oligotrophic Israeli Mediterranean coastal waters (2017) Marine Pollution Bulletin, 116: 151-155. DOI: 10.1016/j.marpolbul.2016.12.052

Vianello, A., Boldrin, A., Guerriero, P., Moschino, V., Rella, R., Sturaro, A., Da Ros, L. Microplastic particles in sediments of Lagoon of Venice, Italy: First observations on occurrence, spatial patterns and identification (2013) Estuarine, Coastal and Shelf Science, 130: 54-61. DOI: 10.1016/j.ecss.2013.03.022

Verschoor, A.J. Towards a definition of microplastics considerations for the specification of physico-chemical properties RIVM Letter report (2015) National Institute for Public Health and the Environment**.** The Netherlands. 38 pp

Wagner, J., Wang, Z.-M., Ghosal, S., Rochman, C., Gassel, M., Wall, S. Novel method for the extraction and identification of microplastics in ocean trawl and fish gut matrices (2017) Analytical Methods, 9: 1479-1490. DOI: 10.1039/c6ay02396g

Wang, J., Wang, M., Ru, S., Liu, X. High levels of microplastic pollution in the sediments and benthic organisms of the South Yellow Sea, China (2019) Science of the Total Environment, 651: 1661-1669. DOI: 10.1016/j.scitotenv.2018.10.007

Wright, S. L., Thompson, R. C. and Galloway, T. S. The physical impacts of microplastics on marine organisms : A review (2013) Environmental Pollution, 178: 483–492. DOI: 10.1016/j.envpol.2013.02.031

Wu, P., Huang, J., Zheng, Y., Yang, Y., Zhang, Y., He, F., Chen, H., Quan, G., Yan, J., Li, T., Gao, B. Environmental occurrences , fate , and impacts of microplastics (2019) Ecotoxicology and Environmental Safety 184: 109612. DOI: 10.1016/j.ecoenv.2019.109612

Ye, T.; Kang, M.; Huang, Q.; Fang, C.; Chen, Y.; Shen, H.; Dong, S. Exposure to DEHP and MEHP from hatching to adulthood causes reproductive dysfunction and endocrine disruption in marine medaka (Oryzias melastigma) (2014) Aquatic. Toxicology., 146 , 115−126. DOI: 10.1016/j.aquatox.2013.10.025

Yong, C.Q.Y., Valiyaveetill, S., Tang, B.L. Toxicity of microplastics and nanoplastics in Mammalian Systems (2020) International Journal of Environmental Research and Public Health, 17: 1509. DOI: 10.3390/ijerph17051509

Yu, X., Peng, J., Wang, J., Wang, K., Bao, S. Occurrence of microplastics in the beach sand of the Chinese inner sea: The Bohai Sea (2016) Environmental Pollution, 214: 722-730. DOI: 10.1016/j.envpol.2016.04.080

Zhang, D., Liu, X., Huang, W., Li, J., Wang, C., Zhang, D., Zhang, C. Microplastic pollution in deep-sea sediments and organisms of the Western Pacific Ocean (2020) Environmental Pollution, 259: 113948. DOI: 10.1016/j.envpol.2020.113948

Zhou, Q., Zhang, H., Fu, C., Zhou, Y., Dai, Z., Li, Y., Tu, C., & Luo, Y. The distribution and morphology of microplastics in coastal soils adjacent to the Bohai Sea and the Yellow Sea. (2018) Geoderma, 322, 201-208. DOI: 10.1016/j.geoderma.2018.02.015

Table 1. Levels and characteristics (size and morphology) of MPs in Tarragona costal area.

			% Size category (mm)					% Morphology type			
	n	**Levels**	**5-4**	**4-2**	**2-1**	**1-0.5**	**0.5-0.08**	**Frg**	**Pel**	**Fil**	**Fib**
Surface water		items/m^3									
Transect 1	1	0.8	11	0	0	52	37	44	0	0	56
Transect 2	1	1.0	0	0	0	23	77	46	0	0	54
Transect 3	1	0.4	0	0	37	26	37	32	0	10	58
Transect 4	1	3.0	0	0	57	16	27	29	1	7	63
Sediment		items/kg									
Punta de la Mora	1	32	0	56	0	44	NA	56	0	0	44
Cala de Roca Plana	1	5.6	0	0	33	67	NA	0	0	0	100
Llarga Center	1	22	0	50	7	43	NA	36	0	0	64
Miracle-Arrabasada	1	41	0	12	38	50	NA	11	4	31	54
Miracle Center	1	5.5	25	0	0	75	NA	0	0	0	100
Harbour (marina)	1	32	0	17	55	28	NA	17	0	17	66
Harbour (industrial)	1	89	0	22	22	56	NA	24	0	4	72
Sand Beach		items/kg									
La Mora	1	0.7	0	0	100	0	NA	0	0	100	0
Savinosa	1	1.3	0	0	100	0	NA	0	0	0	100
Llarga	4	1.1±1.9 [0-3.9]	0	29	0	71	NA	43	0	14	43
Arrabasada	2	5.3±1.2 [4.4-6.1]	5	18	24	53	NA	29	0	12	59
Miracle (Sept.)	3	2.0±0.7 [1.4-2.7]	0	56	22	22	NA	22	34	22	22
Miracle (June)	4	6.9±8.1 [0-15]	0	59	41	0	NA	36	30	11	23
Pineda	3	42±19 [21-54]	2	13	59	26	NA	76	16	1	7

Microplastic levels (mean ± standard deviation) and [Range] in water expressed as in items/m^3; in sediments and sand beaches expressed as items/kg$_{dw}$. NA: Not analysed. Frg: Fragment. Pel: Pellet. Fil: Film. Fib: Fibres

Table 2. Microplastics levels in surface water of Mediterranean Sea and other oceans of the world.

Autor	Year	Region*	Ubication	Mps/m^3	Sampling	Size
Present study	2018	wM-B	La Mora-Llarga Tarragona City	0.80	Nn	80 µm-5 mm
			Llarga-Arrabasada-Tarragona city	1.03		
			Arrabasada -Miracle Tarragona city	0.41		
			Tarragona Harbour-Tarragona city	2.96		
			Tarragona Coast mean	1.30±0.98		
Fossi et al. 2012	2011	wM-S	Ligurian sea mean	0.94±2.55	SnWP2	200 µm-5 mm
		wM-S	Sardinian Sea mean	0.13±0.27		
Fossi et al. 2016	2013	wM-S	Ligurian sea mean	0.49±1.66	SnWP2	200 µm-5 mm
		wM-S	Sardinia Sea mean	0.24±0.43		
Panti et al. 2015	2012/13	wM-S	Norwest Sardinia sea mean	0.17±0.32	SnWP3	200 µm-5 mm
de Lucia 2014	2012/13	wM-S	Central west-Sardinia Sea mean	0.15±0.11	Mt	500 µm-5 mm
Van der Hal et al. 2017	2017	eM-L	Israel coast	7.68±2.38	Nn	300 µm-5 mm
Kazour et al. 2019	2018	eM-L	Lebanese coast	4.3±2.2	Mt	200 µm-5 mm
de lucia 2018	2017	wM-S	Italian minors islands -Elba	0.33±0.02	Mt	333µm-5mm
		wM-S	Italian minors islands -Ventotene	0.26±0.28		
		wM-S	Italian minors islands -Ischia	0.71±0.20		
		wM-S	Italian minors islands -Eolie	0.29±0.26		
		cM-A	Italian minors islands -Tremiti	0.13±0.04		
		cM-A	Po Delta	0.64±0.33		
		wM-S	Tevere Delta	0.57±0.22		
Constant et al. 2018	2016	wM-Ly	Rhone delta	0.19	Mt	300 µm-5 mm
		wM-Ly	Tet delta	0.18		
de hann et al. 2019	2015	wM-B	Northern Catalonia coast mean	0.73±0.77	Mt	335 µm-5 mm
		wM-B	Cartagena coast mean	0.27±0.17		
		wM-B	Campo Dalias Coast mean	0.31±0.40		
Baini et al. 2018	2013/14	wM-S	North Tyrrenean Sea (0.5 km) Winter	0.05±0.05	Mt	330 µm-5 mm
		wM-S	North Tyrrenean Sea (0.5 km) Spring	0.09±0.10		
		wM-S	North Tyrrenean Sea (0.5-20 km) Winter	0.29±0.46		
		wM-S	North Tyrrenean Sea (0.5-20 km) Spring	0.26±0.26		
Suaria et al. 2016	2013	wM-B	Menorca West Coast	2.85±3.26	Nn	700 µm-5 mm
		cM-A	Otrasto Sea Strain	0.74±1.75		
		wM-S	Sicily Sea West Coast	0.66±0.62		
		wM-S	Tunisia and Algeria coast	0.54±0.62		
Liu et al. 2020	2016	nwP	Jiaozhou Bay	0.095	Nn	500 µm-5 mm
Moore et al. (2002)	2000/01	ecP	California inshore (mouth of the San Gabriel River)	7.25	Mt	333 µm-5 mm
			California offshore	2.23		
Goldstein et al. (2012)	1999/10	ecP	North Pacific Gyre mean ten years record	0.43	Mt	333 µm-5 mm
Ramírez-Alvarez et al. 2020	2016/17	ecP	Todos Santos Bay (Mexico)	[0.01-0.70]	Mt	333 µm-5 mm
Mu et al. 2019	2017	nwP	North-western Pacific Ocean	0.03±0.02	Mt	333 µm-5 mm
		nwP	Bering Sea	0.09±0.09		
		Ar	Chukchi sea	0.23±0.07		
McEachern et al. 2019	2017	wcAt	Tampa Bay, Florida	4.5±2.3	Nn	330 µm-5 mm
Garcia et al. 2020	2010	swAt	Equatorial Brazilian coast	0.14 ± 0.11	Nn	120µm -5 mm
Lusher et al. 2015	2014	neat	Artic, south of Svalbard	0.34±0.31	Mt	333 µm-5 mm
Lacerda et al. 2019	2017	An-At	Antarctic peninsula	0.009±0.005	Mt	330 µm-5 mm
Aliabad et al. 2019	-	wIn	Chabahar Bay, Iran	0.49 ± 0.43	Nn	333 µm-5 mm

Mean standard ± deviation. [Range]. Nn: Neuston net; Mt: Manta trawl; SnWP2: Standart Vertical Plankton Net WP2; SnWP3: Standart net WP3; *Regions acoording FAO Major fishing areas. WM: west Mediterranean sea (subdividded in B: Balearic; S: Sardinia; and Ly: Lyon gulf); CM: Cental Mediterranenan sea (subdivided in A: adriatic and I: Ionian); EM: Eastern Mediterranean sea (subdivided in Ag: Aegean and L: Levant); BS: Black sea (subdivided in BS: Black sea; M: Marmara sea and Az: Azov sea);nwP: northwest Pacific; ecP: Estern cental Pacific; wcAT: west central Atlantic; swAt: south-west Atlantic; neAt: northeast Atlantic; An-At: Atlantic-Antarctic; wIn: Western Indian ocean

Table 3. Microplastics levels in marine sediments of Mediterranean sea and oceans of the world.

Autor	Year	Region	Ubication	Mps /kg dw	Deep (m)	Size
Present study	2017	wM-B	La Mora	31.7	13	0.5-5 mm
			Cala de Roca Plana	5.6	14.4	
			Llarga Centro	21.6	15.3	
			Miracle-Arrabasada	40.5	14	
			Miracle Center	5.5	15	
			Harbour (marina)	31.7	14	
			Harbour (industrial)	88.6	17	
			Tarragona Coast Mean	32.4±28.4	13-17	
Bayo et al. 2019	2017/18	wM-B	Mar menor	53.1±7.6	-	
Filgueiras et al. 2019	2014/15	wM-B	Spanish mediteranean coast	113±89	43-154	0.5-5 mm
Blaškovića et al 2017	2015	cM-A	Telaščica bay (Croatia)	194±117	3.0-15	0.063-5 mm
Vianello et al 2013	2013	cM-A	Venice Lagoon (Italy)	1445±458	<1±0.5	0.030-0.5 mm
Fastelli et al 2016	2015	wM-S.	Stromboli Island	151±34	3.0-15	0.063-5 mm
			Lipari Island	679±346		
Renzi et al 2018	2016	cM-A. Caorle coast	Cymodocea Bottoms	170±95	3.5	0.4-5 mm
			Amphioxus sand+ Mäerl Bottoms	199±115	14.8	
			Amphioxus sand Bottoms	233±133	17.5	
Claessens et al., 2011	2011	neAt	Belgium Harbour mean	167±92.1**	sumerged	0.038–1 mm
			Belgium Continental shelf	97.2±18.6**		
			Belgium coast mean	91.9±21.9**		
			Belgium offshore mean	105±9.9**		
Graca et al 2017	2014	neAt-Baltic Sea	Poland Coast. inshore	21.8±5.4	11.1-18	0.1–5.0 mm
			Poland Coast. offshore	1.5±2.1	70-106	
Frias et al 2016	2013	neAt	South Portugal. mean	8.2±9.2	18.7-19.4	>0.001-5 mm
Thompson et al., 2004	2004	neAt	UK coast (Plymouth)	86.0*	Subtidal	
Zhang et al. 2020	2018	nwP	Western Pacific Ocean	240±291	4601-5732	<1 mm
Matsuguma et al 2017	2012	nwP	Tokyo Bay Channel	1845	5	0.315-5 mm
		wIn	South Africa-Durban bay Harbour	1600	3	
Wang et al 2019	2017	nwP	South Yellow Sea -China	1765	< 20	0.05-5 mm
			South Yellow Sea -China	2135±1020	20-40	

Results expressed in Mean standard ± deviation of number of MP per kilogram of dry weight. * Original unit (# fibres/ 50 mL) converted using an average sediment density of 1600 kg /m^3 (Fettweis et al., 2007) and 1.25 as average wet sediment/dry sediment ratio.**not fibers included.*Regions according FAO Major fishing areas. wM: west Mediterranean sea (subdivided in B: Balearic; S: Sardinia; and Ly: Lyon gulf); cM: Central Mediterranean sea (subdivided in A: Adriatic and I: Ionian); eM: Eastern Mediterranean sea (subdivided in Ag: Aegean and L: Levant); BS: Black sea (subdivided in BS: Black sea; M: Marmara sea and Az: Azov sea);nwP: northwest Pacific; ecP: Eastern central Pacific; wcAT: west central Atlantic; swAt: south-west Atlantic; neAt: northeast Atlantic; An-At: Atlantic-Antarctic; wIn: Western Indian ocean

Table 4. Microplastics levels (items/kg$_{dw}$) in sand of beaches of Mediterranean sea and oceans of the world.

Author	Year	Region**	Ubication	Mps/kg$_{dw}$	Zone	Size
This study	2018	wM-B	Tarragona-La Mora	0.7	I	0.5-5 mm
			Tarragona-Savinosa	1.3		
			Tarragona-Llarga	1.1±1.9		
			Tarragona-Arrabasada	5.3±1.2		
			Tarragona-Miracle (September)	2.0±0.7		
			Tarragona-Miracle (June)	6.9±8.1		
			Tarragona-Pineda	42±19		
			Tarragona Mean	10.7±18		
Thompson et al 2004	2004	neAt	UK coast (Plymouth)	8.00*	H	
Claessens et al., 2011	2011	neAt	Belgium, Groenendijk	156.2	H	0.038-5 mm
				77.9	I	
			Belgium, Koksijde-Bad	95.9	H	
				103.1	I	
			Belgium , Knokke	124.2	H	
				100	I	
Van Cauwenberghe et al 2013	2010/11	neAt	Belgium coastal line-De Panne	20.4	H	<1 mm
				7.2	L	
			Belgium Coastal Line-Zwin	18.2	H	
				12	L	
			Belgium Coastal line mean	17.6	H	
				9.2	L	
Laglbauer et al 2014	2012	cM-A	Slovenia Coast	178±133	I	0.25-5 mm
Piñon-Colin, et al 2018	2015/16	ecP	California Gulf and Ocean mean	135±92	H	0.034-5mm
			California gulf Mean	76±12		
			Ocean pacific coastline mean	179±50		
Piperagkas et al., 2019	2015/16	eM-Ag	Greece- Northern Crete	22±11	Dry	0.042-5mm
				5.5±5.0	I	
Karlsson et al.2017	2014	neAt	Netherlands Coast -Ijmuiden	48±55	L	< 5 mm
Constant et al 2019	2016	wM-Ly	France-Têt river discharge. South	58±53	Dry, H, L	0.063-5mm
			France-Têt river discharg.e North	166±205		
Yu et al 2016	2015	nwP	Bohai Sea, China -Xingcheng	163.3	I	< 5 mm
Dekiff et al 2014	2011	neAt	Germany , Nordesney Island	1.7±0.4	H, I	< 1 mm
Stolte et al 2015	2014	neAt	Germany, Rostock Coast)	[42-532] (fibers)*	I	< 1 mm
				[3.8-5.5] (particles)*		
Esiukova, 2017	2015/16	neAt	Baltic sea, Russia (Vistula Spit)	2.1±1.6	H	0.5-5 mm
			Baltic sea, Russia (Cape Tarán)	36.2±58.6		
Tiwari et al 2019	2017	In	India-Mumbai	220±50	L	0.036-5 mm
			India-Tuticorin	181±60		
			India-Dhanushkodi	45 ±12		
Doyen et al 2019	2017	neAt	Hauts-de-France region	46.5±17.3	H, I, L	< 5mm
Lots et al 2017	2015/17	neAt	Lithuania -Klaipéda	700±296	H	0.3-3mm
		neAt	France-Normandy	156±29		
		neAt	Portugal-Madeira	92±15		
		cM-A	Bosnia	76±13		
		eM-L	Israel -Tel Aviv	168±16		
		cM-A	Italy -Lido di Dante,	1512±187		
		eM-Ag	Turkey-Dikili,	248±47		
		cM-I	Italy-Sicily	160±31		
		wM-B	Spain-Barcelona	148±23		
		wM-B	Spain-Denia	156±29		

Results expressed in Mean standard ± deviation or [Range] of number of MP per kilogram of dry weight. * Original unit (# fibres/ 50 mL) converted using an average sediment density of 1600 kg/m^3 (Fettweis et al., 2007) and 1.25 as average wet sediment/dry sediment ratio. **Regions acoording FAO Major fishing areas. wM: west Mediterranean sea (subdivided in B: Balearic; S: Sardinia; and Ly: Lyon gulf); cM: Central Mediterranean sea (subdivided in A: Adriatic and I: Ionian); eM: Eastern Mediterranean sea (subdivided in Ag: Aegean and L: Levant); BS: Black sea (subdivided in BS: Black sea; M: Marmara sea and Az: Azov sea);nwP: northwest Pacific; ecP: Eastern central Pacific; wcAT: west central Atlantic; swAt: south-west Atlantic; neAt: northeast Atlantic; An-At: Atlantic-Antarctic; In: Indian ocean

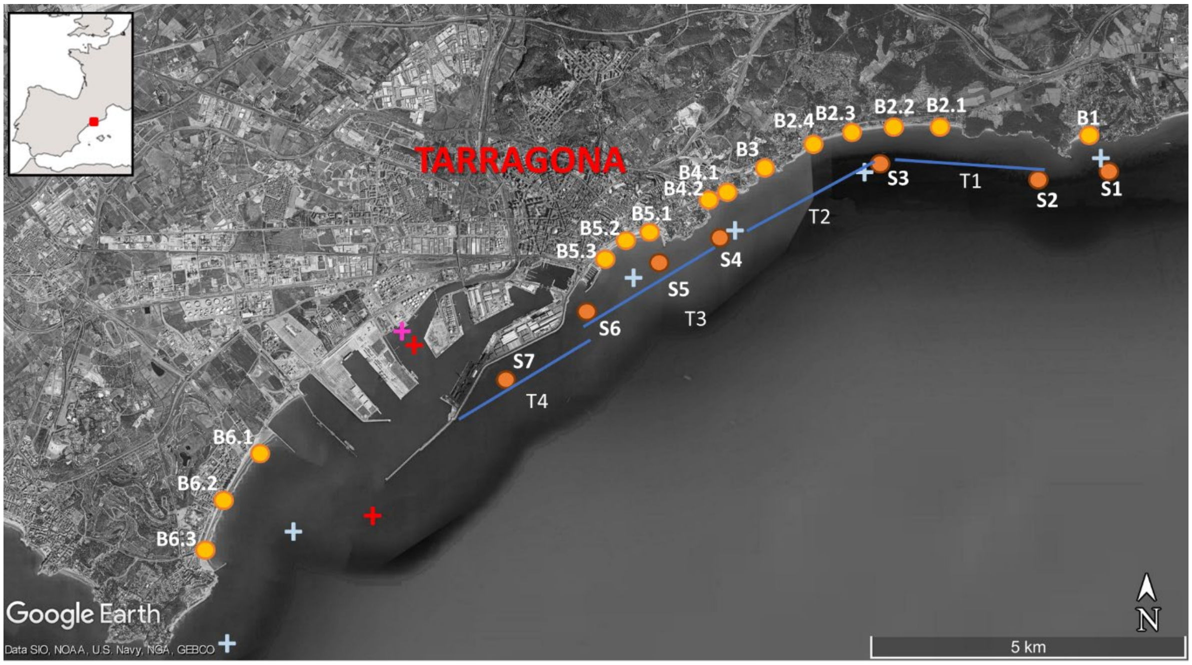


Figure 1. Sampling sites localization on Tarragona Coast (Catalonia, Spain). Sandy beaches in yellow (B); marine sediments marked in orange (S), Superficial marine water transects marked in blue (T). Red crosses are WWTP discharges, pink cross is Francolí river discharges and blue crosses are runoff discharges emissaries.

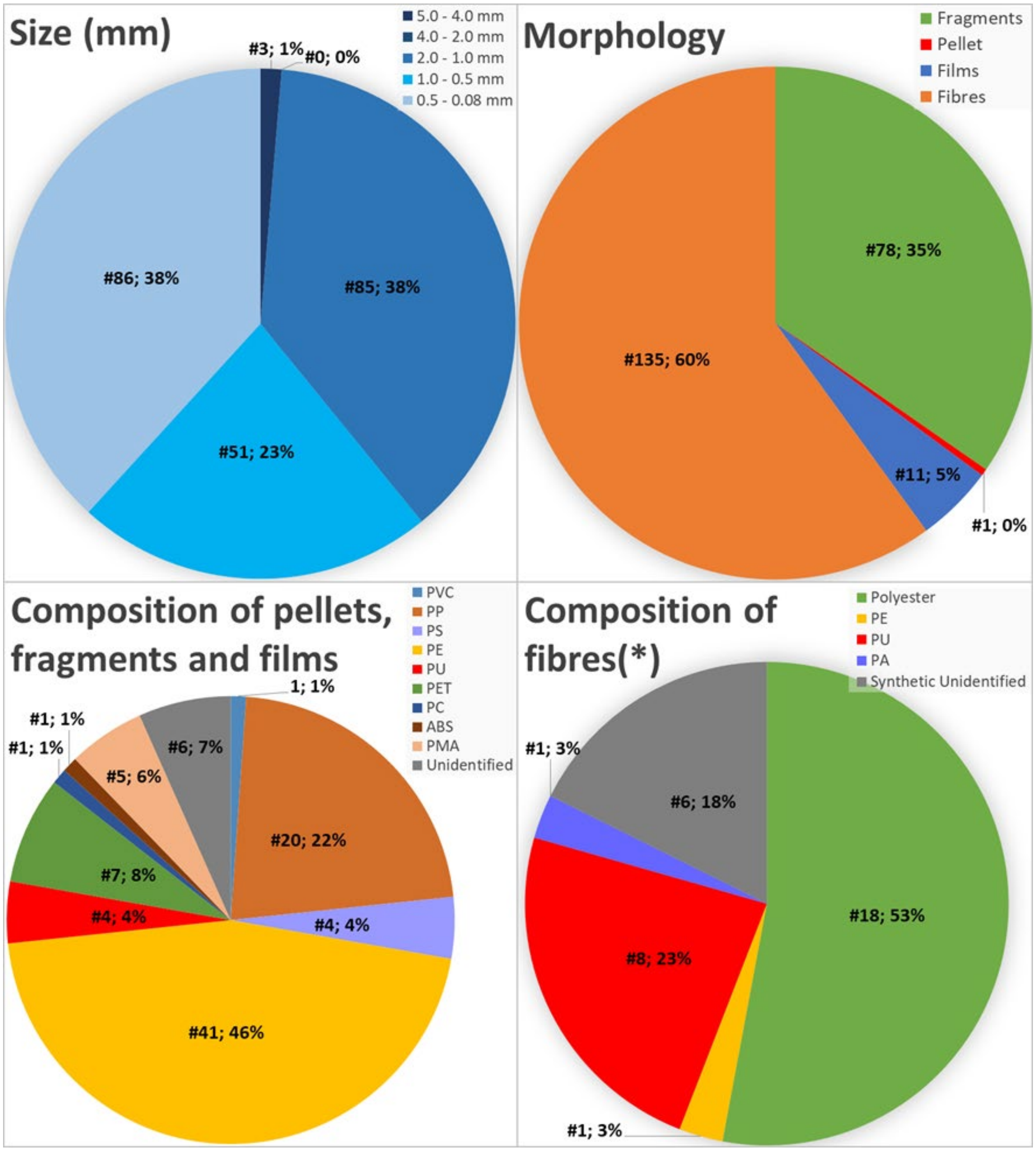


Figure 2. Size distribution (from 5 mm to 80 µm), morphology (fragments, pellets, films and fibres), and composition of MPs in surface seawaters in Mediterranean costal area of Tarragona. Result expressed as (#) number of MPs; percentage (%). *Composition analysed in the 25% of the fibres PVC: polyvinylchloride, PP: Polypropylene; PS: Polystyrene; PE: Polyethylene; PU: Polyurethane; PET: Poly(ethyleneterephthalate); PC: Polycarbonate: ABS: Acrylonitrile-butadiene-styrene copolymer; PMA: Poly(methylmethacrylate); and PA polyamide.

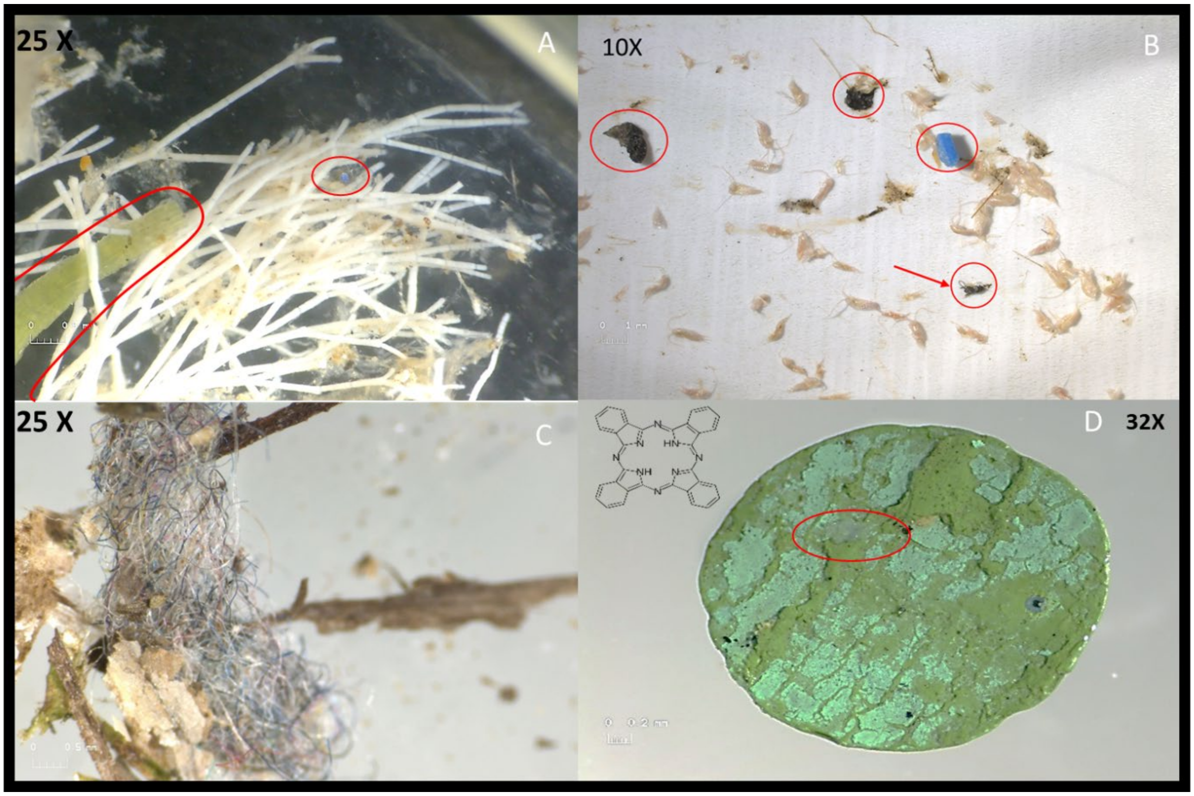


Figure 3. Microplastics associated to environmental samples. A: microplastics associated with algae aggregations. B: microplastics associated with plankton. C: fibres ball associated with marine sediments and algae organic remains. D: microplastic weathered with biofilm attached.

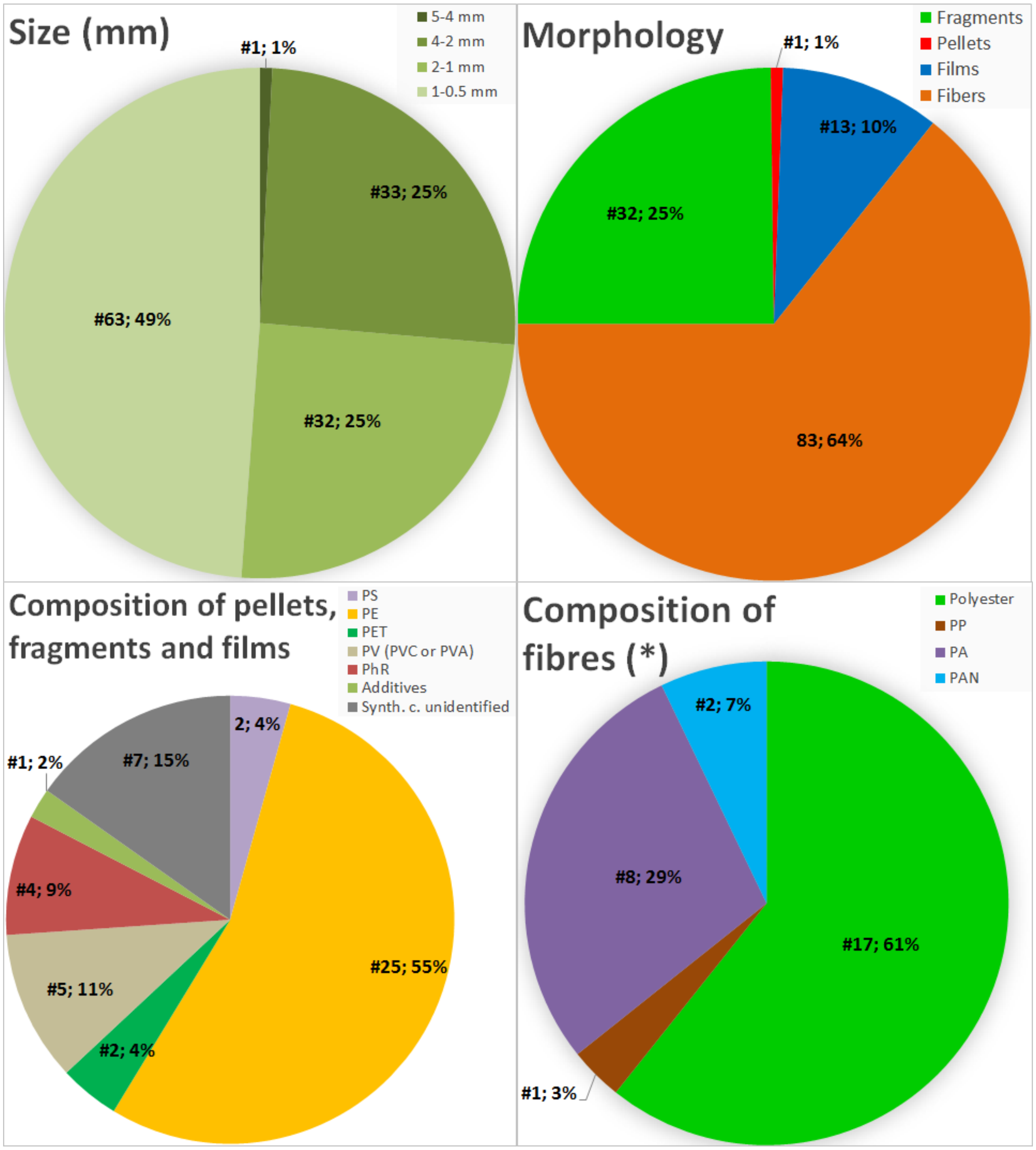


Figure 4. Size distribution (from 5 mm to 0.5 mm), morphology (fragments, pellets, films and fibres), and composition of MPs in marine sediments in Mediterranean costal area of Tarragona. Result expressed as (#) number of MPs; percentage (%). (*) Composition analysed in the 34% of the fibres considered as synthetics, excluding cellulose fibres. PP: Polypropylene; PS: Polystyrene; PE: Polyethylene; PET: Poly(ethyleneterephthalate); PV (PVC or PVA): Polyvinyl including Polyvinilchloride or polyvinyil alcohol; PhR: Phenolic resin; PC: Polycarbonate; PAN: Polyacryilonitile; Synth. c. unidentified: synthetic coloured unidentified; and PA polyamide.

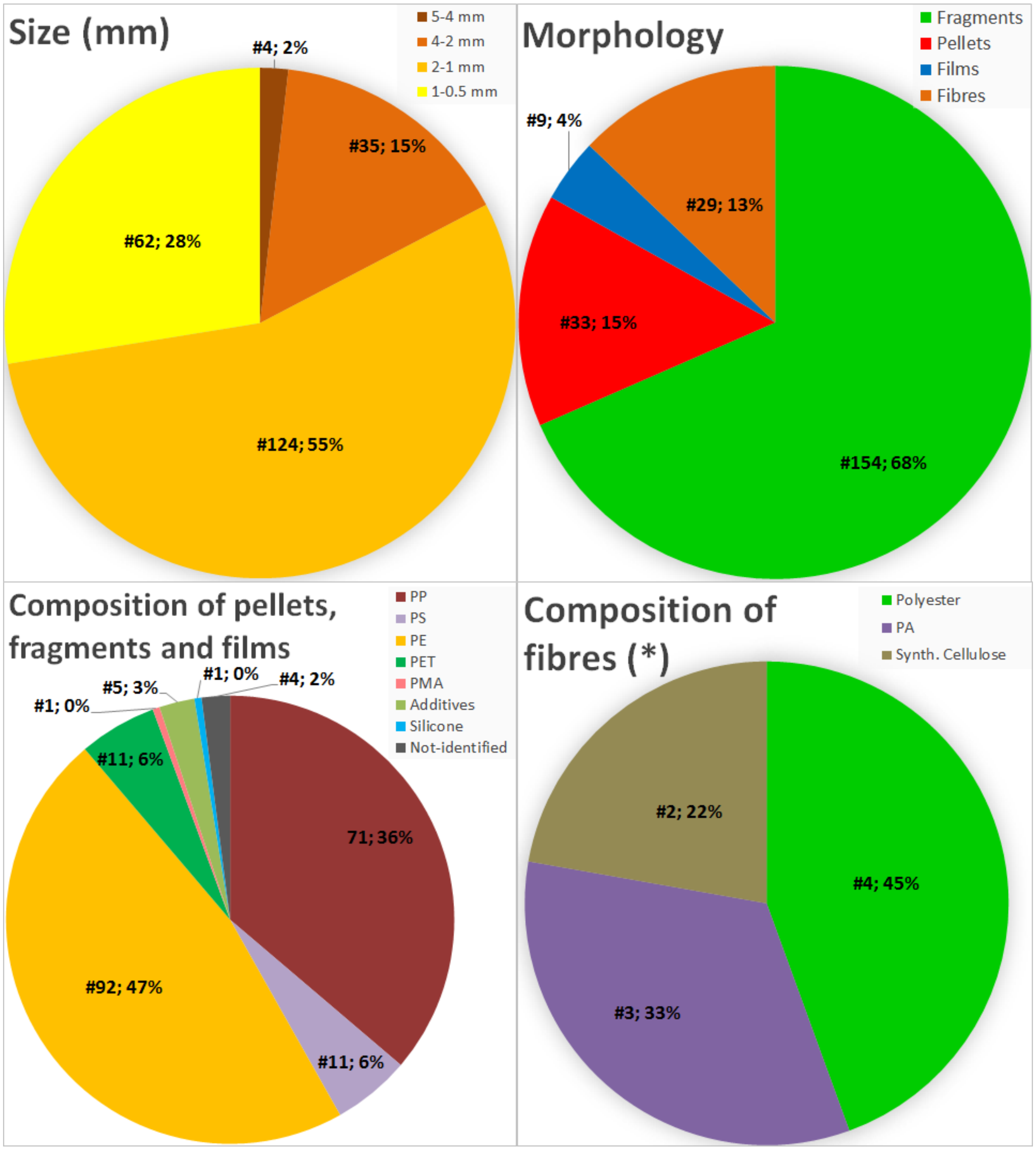
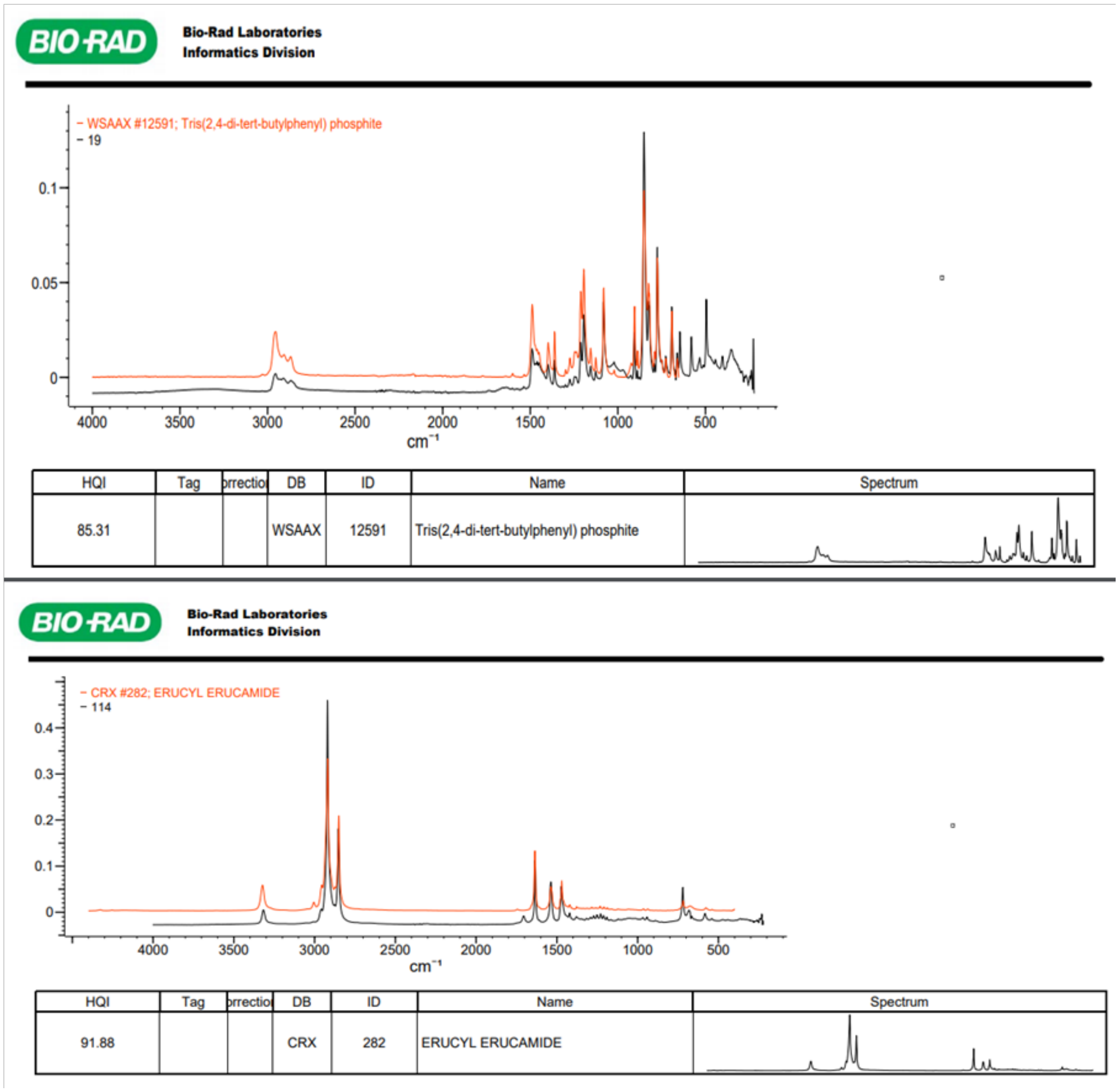


Figure 5. Size distribution (from 5 mm to 0.5 mm), morphology (fragments, pellets, films and fibres), and composition of MPs in sand beaches in Mediterranean costal area of Tarragona. Result expressed as (#) number of MPs; percentage (%). (*) Composition analysed in the 30% of the fibres considered as synthetics, excluding cellulose fibres. PP: Polypropylene; PS: Polystyrene; PE: Polyethylene; PET: Poly(ethyleneterephthalate); PC: Polycarbonate; PMA: Poly(methylmethacrylate); Synth. Cellulose: synthetic cellulose; and PA polyamide.

Supplementary information

Table S1: Location and characteristics of superficial seawater, sediments and sand beach sampling points.

	Surface waters			
	Coordinates of the transect	**Distance from shoreline (m)**	**Place**	
T1	From: N 41° 07’ 13’’; E 1° 20’ 19’’ To: N 41° 07’ 10’’; E 1° 19’ 49’’	924	La Mora-Llarga beach	
T2	From: N 41° 07’ 25’’; E 1° 18’ 23’’ To: N 41° 07’ 9’’; E 1° 17’ 50’’	765	Llarga-Arrabassada	
T3	From: N 41° 06’ 39’’; E 1° 16’ 19’’ To: N 41° 06’ 23’’; E 1° 15’ 43’’	702	Arrabassada -Miracle	
T4	From: N 41° 05’ 21’’; E 1° 13’ 47’’ To: N 41° 05’ 40’’; E 1° 14’ 22’’	500	Tarragona Harbour	
	Marine sediments			
	Coordinates	**Depth (m)**	**Place**	
S1	N41° 07´ 14´´; E1° 20´ 27´´	13	La Mora	
S2	N41° 07´ 15´´; E1° 20´ 13´´	14.4	Cala de Roca Plana	
S3	N41° 07´ 27´´; E1° 18´ 26´´	15.3	Llarga	
S4	N41° 06´ 40´´; E1° 16´ 19´´	14	Miracle-Arrabassada	
S4	N41° 06´ 34´´; E1° 16´ 02´´	15	Miracle	
S5	N41° 06´.03´´; E1° 14´ 53´´	14	Tarragona Harbour (Marina)	
S6	N41° 05´ 22´´; E1° 13´ 47´´	17	Tarragona Harbour (Industrial)	
	Beach sand			
	Coordinates	**Beach length (m)**	**Beach**	**Sub-samples**
B1	From: N 41° 07’ 40’’; E 1° 20’ 56’’ To: N 41° 07’ 36’’; E 1° 20’ 38’’	447	La Mora	1
B2	From: N 41° 07’ 23’’; E 1° 17’ 16’’ To: N 41° 07’ 20’’; E 1° 17’ 02’’	348	Savinosa	1
B3	From: N 41° 07’ 45’’; E 1° 19’ 22’’ To: N 41° 07’ 34’’; E 1° 17’ 34’’	2619	Llarga	4
B4	From: N 41° 07’ 13’’; E 1° 16’ 45’’ To: N 41° 07’ 03’’; E 1° 16’ 26’’	623	Arrabasada	2
B5.S	From: N 41° 06’ 52’’; E 1° 15’ 49’’	1074	Miracle (September)	3
B5.J	To: N 41° 06’ 36’’; E 1° 15’ 11’’		Miracle (June)	3
B6	From: N 41° 05’ 06’’; E 1° 11’ 27’’ To: N 41° 04’ 04’’; E 1° 10’ 46’’	2264	Pineda	3



Bio-Rad Laboratories
Informatics Division

HQI	Tag	orrectio	DB	ID	Name	Spectrum
85.31			WSAAX	12591	Tris(2,4-di-tert-butylphenyl) phosphite	

Bio-Rad Laboratories
Informatics Division

HQI	Tag	orrectio	DB	ID	Name	Spectrum
91.88			CRX	282	ERUCYL ERUCAMIDE	

Figure S2. Spectra Comparison with BIO-RAD database

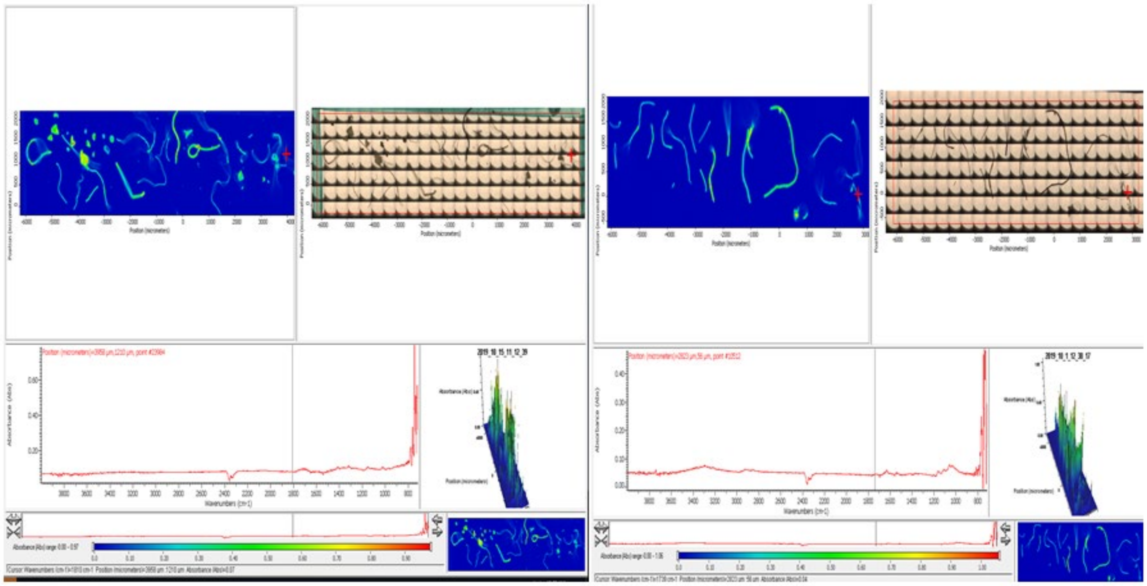


Figure S3. Fibres and small fragments identification with µFTIR technique.

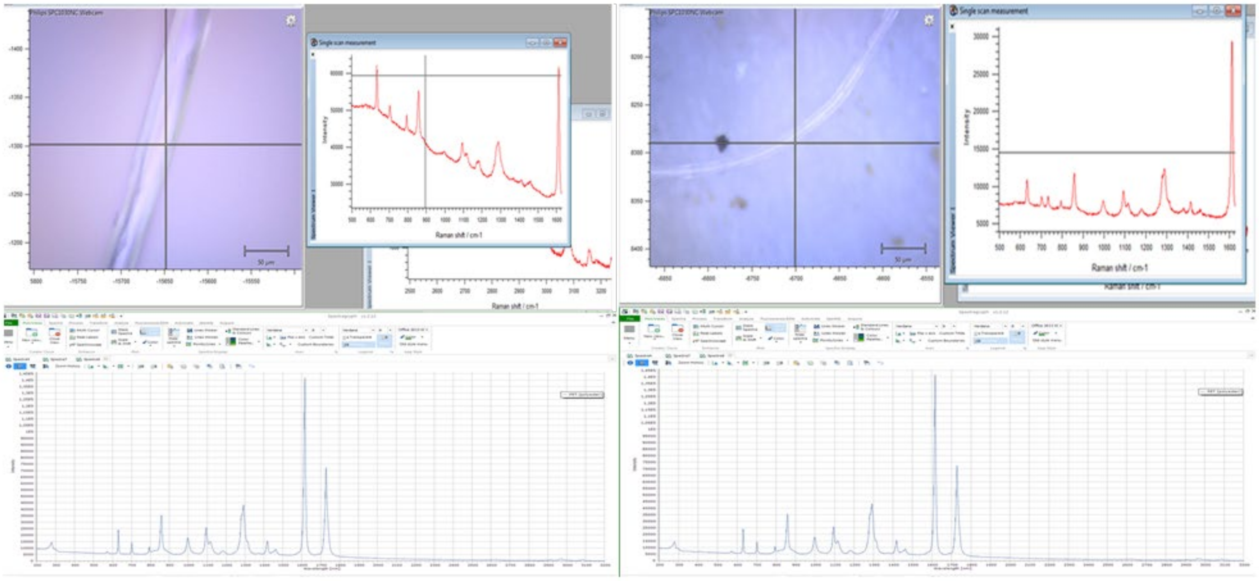


Figure S4. Raman spectra of fibres from seawater samples and comparison with spectra from libraries made with plastics found in the market.

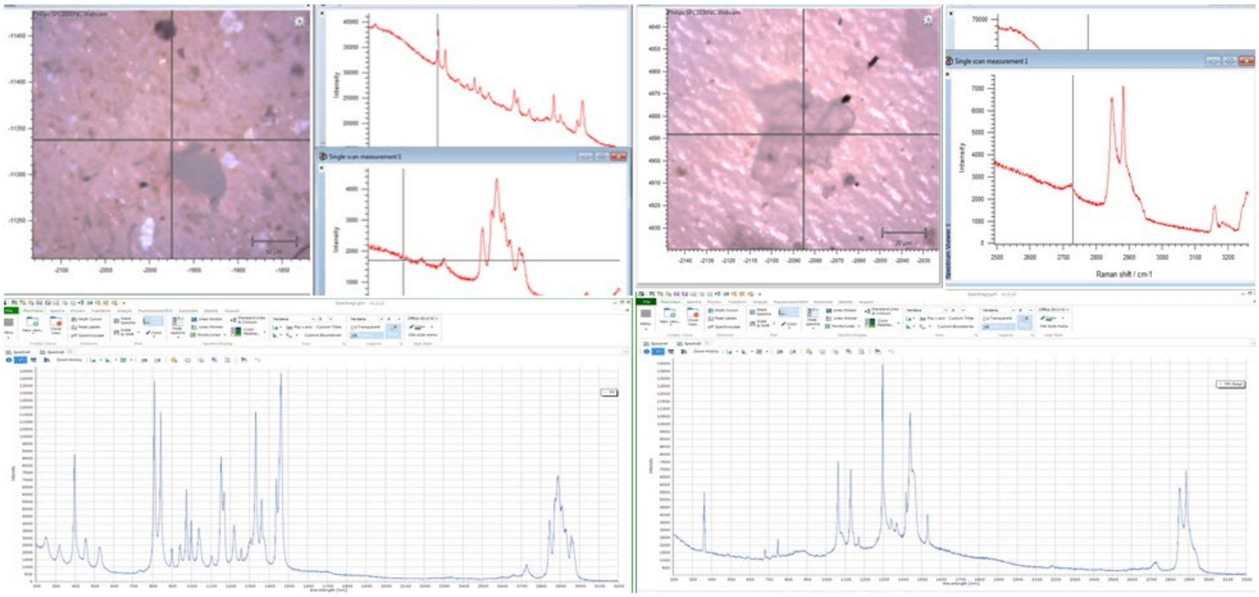


Figure S5. Raman spectra of small fragments from seawater samples and comparison with spectra from libraries made with plastics found in the market.