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Occurrence and identification of microplastics along a beach in the Biosphere Reserve of Lanzarote

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ABSTRACT

This work studied the accumulation of plastic debris in a remote beach located in La Graciosa island (Chinijo archipelago, Canary Islands). Microplastics were sampled in the 1–5 mm mesh opening range. An average plastic density of 36.3 g/m^2 was obtained with a large variability along the 90 m of the beach (from 8.5 g/m^2 to 103.4 g/m^2). Microplastic particles preferentially accumulated in the part of the beach protected by rocks. A total number of 9149 plastic particles were collected, recorded and measured, 87% of which corresponded to fragments. Clear colours and microscopic evidence of weathering corresponded to aged plastics wind-driven by the surface Canary Current. The chemical composition of plastics particles corresponded to PE (63%), PP (32%) and PS (3%). Higher PE/PP ratios were recorded in the more protected parts of the beach, suggesting preferential accumulation of more aged fragments.

1. Introduction

The pollution of marine environment with microplastics is a global threat that poses one of the most serious environmental problems for aquatic ecosystems (Cole et al., 2011; Chae and An, 2017). Fragments lower than 5 mm are commonly defined as microplastics in line with the NOAA definition, which turned into an international standard (Gago et al., 2016). No lower size boundary is clearly defined despite its potential relevance (Gigault et al., 2018). The boundary between categories is commonly established based on the size opening of the sieves used for sampling or sorting. Accordingly, plastics with two dimensions smaller than mesh openings are eventually slip through the mesh and may get missed or counted in the category immediately lower. It has been argued that this phenomenon contributes to significant differences in mass and particle counts (Everaert et al., 2018). Concerning the chemical nature of plastic debris, the most used plastics are the most commonly found among sorted microplastics (Imhof et al., 2017). The higher occurrence corresponds to polyethylene (PE) and polypropylene (PP) together with polystyrene (PS), the latter probably over-represented in debris because of its major use as packaging material. Polyethylene terephthalate (PET), polyvinyl chloride (PVC), and other synthetic fibers are usually reported in lower amounts. The high-volume usage of PE together with its floatability makes it the material with higher likelihood of being recovered from marine litter (Hidalgo-Ruz et al., 2012).

Worldwide plastic production amounted to 348 million tonnes in 2017. In 2016, the more recent year available, the amount of plastic wastes collected through official schemes in the EU (plus Norway and Switzerland) amounted to 27.1 million tonnes, representing less than half of the total plastics production in the same countries (PlasticsEurope, 2018). The balance corresponds to goods still in use and non-collected waste, eventually ending up in the environment, particularly in oceans, which act as the final sink of most plastic debris. Accordingly, a high amount of plastics is being reported in seas and oceans as floating fragments. Eriksen et al. (2014) estimated a total number of 5.25 trillion (5.25×10^{12}) plastic particles in the world's oceans weighing one quarter million tonnes. Noteworthy, the observed amount of lower size microplastics is much lower than expected, which may imply the existence of efficient mechanisms that remove small plastic particles from the ocean surface (Eriksen et al., 2014). It has been suggested that coastal areas constitute a sink of plastics buried in beaches and marshes (Herrera et al., 2018). Another explanation is that

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deep-sea sediments accumulate microplastics (Woodall et al., 2014). Concerning environmental fate, the fragmentation to lower sizes is a well-known fact eventually making plastic debris undetectable to current sampling methods (Koelmans et al., 2015).

The obvious environmental risk associated to microplastics refers to the mechanical damage due to plastic ingested by marine organisms (Li et al., 2018). Large plastic debris, classified as mesoplastics or macroplastics, can produce damage to wildlife and fisheries (Kühn et al., 2015). Besides, their impact in touristic activities is apparent causing an important aesthetic issue, with economic losses due to the cost of cleaning and the reduction of visitors in touristic coastal areas (Jang et al., 2014). Other risk factor associated to plastic debris in the marine environment is the leaching of plastics additives. Plastic fragments may also pose a chemical risk due to the adsorption of hydrophobic pollutants on their surface (Avio et al., 2017). This issue is controversial as it has been argued that environmental concentrations are much lower than those required for plastics to behave as a vector of anthropogenic pollutants (Koelmans et al., 2016). Plastic debris exert biohazard due to its role in the spreading of microbial pathogens implicated in outbreaks for a variety of wildlife forms (Lamb et al., 2018). It has also been shown that microplastics in environments co-polluted with metals and antibiotics may develop co-selection of metal-driven antibiotic resistances, which is also an emerging threat to human health (Yang et al., 2019).

The Canary Islands are bathed by the Canary Current, which is a wind-driven surface current associated to the North Atlantic Gyre responsible for a high level of plastic pollution in the beaches of the Northern Islands (Baztan et al., 2014). Lanzarote and its Northern minor islands constituting the Chinijo Archipelago, are a highly protected area, declared Biosphere Reserve by UNESCO in 1993. Despite being a highly-protected area, their beaches are highly polluted by microplastics, with average mass surface concentration of 23.7 g/m^2 (annual maximum 125 g/m^2) and an average of 1656 pieces/m^2 (1 mm < size < 5 mm) (Herrera et al., 2018). In this work, the systematic quantification and characterization of plastic debris collected at several locations along Ámbar Beach in La Graciosa island is reported. The purpose was to perform a thorough particle size and chemical composition assessment to increase the knowledge about the plastic pollution that arrive at shorelines and evaluate its impact on a remote protected area.

2. Experimental section

2.1. Area of study

The sampling was carried out during the first week of September 2018 along the sandy beach Ámbar locally known as Lambra (Canary Islands, Spain). This beach is in the North of La Graciosa Island, the largest island of the Chinijo archipelago which, together with Lanzarote Island, constitute UNESCO Biosphere Reserve since 1993. Ámbar beach presents a total coastline length of 600 m, with intercalary stretches of white sand and black rocks along the shoreline (Fig. 1). Ámbar beach is oriented towards N-NE being one of the first locations in La Graciosa affected by the predominant winds and the ocean Canary Current, which runs in parallel to the African coast in SW direction until reaching the islands. La Graciosa (29 km^2) has a small population of < 800 people concentrated in two villages. Ámbar is an isolated beach characterized by low tourist pressure and limited waste accumulation not significantly increased by tourism or fishing activities. Nevertheless, there is evident deposition of plastic debris over the sand at different heights depending on tide levels, which tend to appear mixed up with wave-driven algae.

2.2. Sampling and sorting

Sampling was performed along the lowest high tide line due to the high amount of organic matter (mainly algae) deposited by waves along the highest tide line (Baztan et al., 2014). Sampling points A to D (Fig. 1) cover a linear extension of 90 m in the centre of the beach. All sampling points were located below the 5 m contour line and represented different hydrodynamic conditions. Whereas points A and B were open to the sea, C and D were protected from the waves by a line or rocks. A grade of 1.5–1.7 m existed between points C-D and the lowest point A due to the slope of the beach. Accordingly, points C and D were protected in a relatively quiet area even during high tides. Figs. S1 and S2 (Supplementary material, SM) show aerial images of Ámbar beach indicating sampling points and the directions of sea entry during high tides. Finally, according to the Spanish State Meteorological Agency (AEMET), the meteorological conditions during sampling and the period immediately before were stable with absence (< 2.5 mm) of precipitations and any abnormal winds.

The exact location of each sampling point was: A: 29°16′44.9″N 13°29′44.0″W, B: 29°16′45.6″N 13°29′44.8″W, C: 29°16′46.3″N 13°29′45.7″W and D: 29°16′46.7″N 13°29′46.3″W (Figs. 1, S1 and S2). Sampling was performed in 1 m × 2 m rectangles comprising free sandy and algae covered zones with a sampling depth of 1 cm (Baztan et al., 2014; Herrera et al., 2018). The sampling recommendations of the Technical Subgroup on Marine Litter (TSG-ML) were followed as exposed in the Guidance on Monitoring of Marine Litter in European Seas (Hanke et al., 2013). The samples, consisting of sand and debris, were sieved using a 5 mm opening sieve. Sieved samples were then separated by density in a stainless-steel bucket, using sea water. Plastic debris were then collected using a 1 mm opening size sieve. All collected microplastic debris was dried and preserved in glass bottles for further analysis.

Samples were carefully inspected with a stereo microscope Motic SMZ140 Series. All particles supposed to be microplastics were separated from tar balls and algal structures, counted and organized by type and colour. A selection based on colours and typologies wider than usual has been performed trying to gain a more detailed description (Hidalgo-Ruz et al., 2012). For all typologies and sampling points, the total amount of microplastics was weighed. After that, size measurement was performed by exhaustively photographing all plastic debris and processing images by means of the ImageJ software. Projected area, perimeter, length and width were recorded for every microplastic. Random subsamples from every colour and type were separated for polymer identification.

2.3. Analytical methods

The chemical composition of microplastics was assessed by means of Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) and Raman spectroscopy. ATR-FTIR spectra were obtained in a Thermo-Scientific Nicolet iS10 apparatus with a Smart iTR-Diamond ATR module. The associate software was OMNIC version 9.1.26 (Thermo Fisher Scientific Inc., Massachusetts, USA). Spectra were taken in the 4000–800 cm^{-1} range with a resolution of 4 cm^{-1} (data spacing of 0.483 cm^{-1}) using 32 scans. Between samples, the ATR-crystal was cleaned with isopropanol and background signal updated. Raman spectra were obtained using a Thermo Scientific DXR Raman Microscope with Omnic for dispersive Raman software version 8 (Thermo Fisher Scientific). Samples were observed using 10×, 20×, and 50× objectives. Measurements were performed using a 780 nm laser with a power range from 1 to 10 mW with a 400 lines mm^{-1} grating. The power was selected depending on the fluorescence produced by each particle (7–8 mW generally yielded good quality spectra). Spectral range selected was 3100 to 200 cm^{-1}, resolution 1.92 (spectral data spacing 0.964 cm^{-1}) and the number of repetitions and the duration of acquisition time was adjusted for every sample depending on signal-to-noise ratio and the quality of spectra. Both in FTIR and Raman studies, a minimum of three spectra were taken per particle in three random points. Polymer identification was performed by

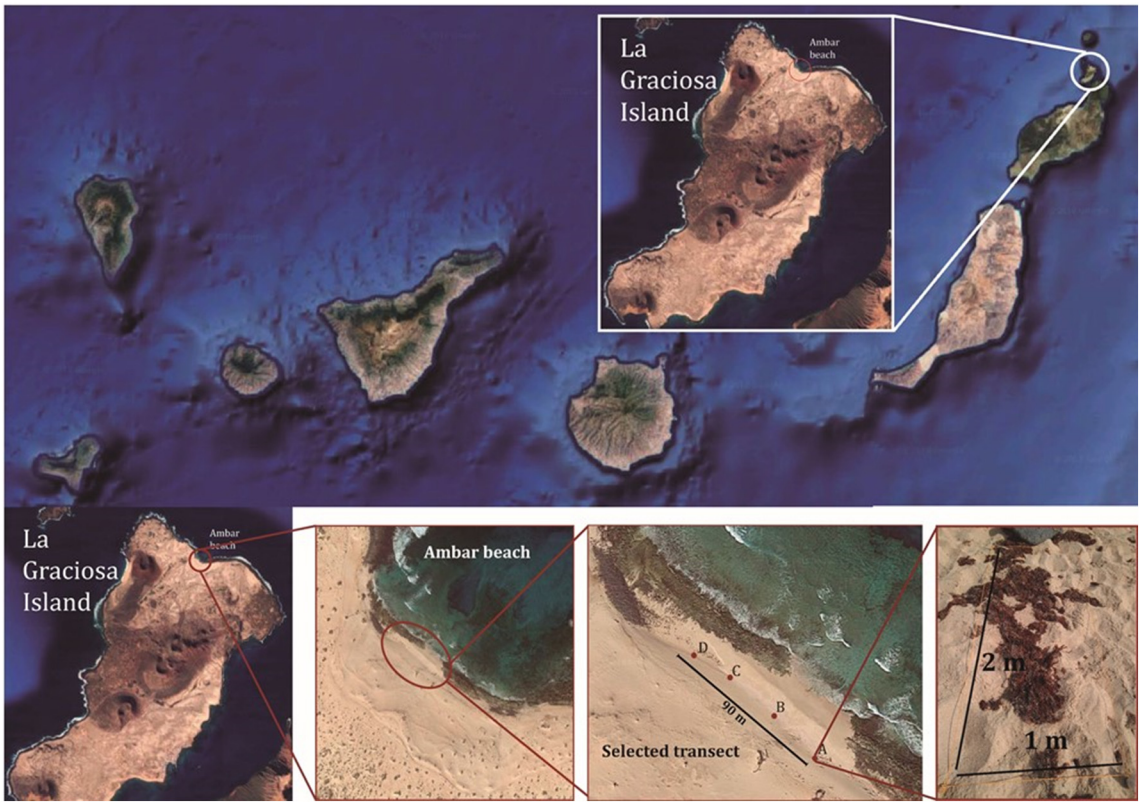

Fig. 1. Localization of the study area in La Graciosa island, in the North part of the Canary Islands (Spain).

statistically comparing (Pearson correlation) the obtained spectra with a library created with pure polymers acquired from Sigma-Aldrich and Goodfellow as well as using the spectral libraries included in Omnic Spectra software. The minimum matching for positive identification was set at 80% as recommended elsewhere (Rios-Mendoza et al., 2018). Scanning Electron Microscopy (SEM) was also used to visualize gold-covered plastic debris in a Philips XL30-FEG apparatus.

3. Results and discussion

In this work, the coastal line of Ámbar beach was sampled in four specific points (identified as A, B, C and D) as indicated before. The total weight of plastic particles collected was 290 g, which makes an average of 36.3 g/m^2 for the whole sampled surface, in line with results reported before (Baztan et al., 2014; Herrera et al., 2018). It is interesting to note the high variability observed along the beach. Moving from point A-B to D, the number of particles increased by almost a factor of 20 (Fig. 2A). The results for the four sampled points were, expressed in mass units: (A) 8.5 g/m^2, (B) 13.3 g/m^2, (C) 19.8 g/m^2, and (D) 103.4 g/m^2. The accumulation of plastic particles in point D clearly indicated their preferential deposition in the most protected area of the beach.

Microplastic particles, separated from sand and organic matter, were classified by shape into seven categories: Fragments, pellets, moulded particles, foams, filaments, microbeads and films. The categories were taken from the literature with the inclusion of "moulded particles" as a subcategory of plastic fragments that did not completely lose their original shape (Hidalgo-Ruz et al., 2012). Besides, and for every category, they were separated into twelve colours, namely, black, blue, brown, green, grey, orange, pink, purple, red, translucent, white and yellow. Figs. S3 and S4 (SM) show examples of the different colours and typologies. Shape distribution yielded 87% fragments, 9% pellets, 1.4% filaments and < 1% for the other categories (Fig. 2).

Most plastic particles were fragments or secondary microplastics

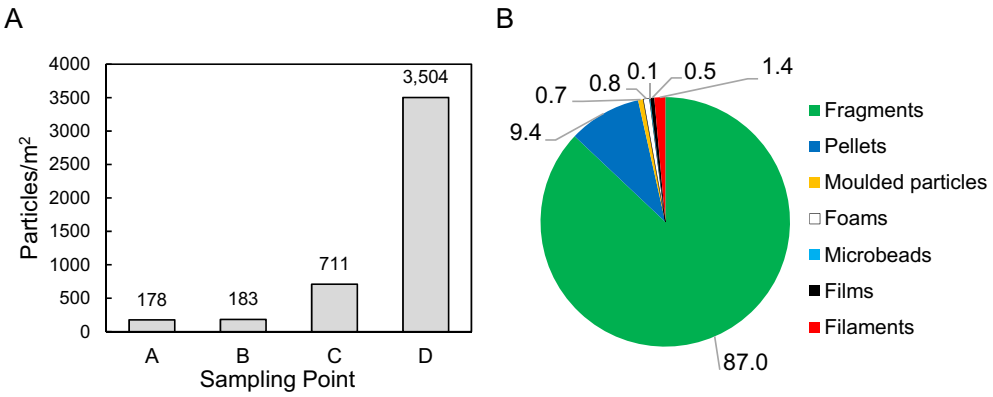

Fig. 2. Variability of plastic particles along the shoreline (A) and number percent global distribution among typologies (B).

product of the disaggregation of larger materials into smaller pieces (Bonanno and Orlando-Bonaca, 2018). On the contrary, Antunes et al., studied debris in Portuguese coasts and found that pellets were dominant (79%) with foams being also an important part of the sampled materials (Antunes et al., 2018). Plastic pellets are usually associated to industrial activity, which is far from the remote area sampled in this work (Domènech et al., 2019). The almost absence of foams in Ámbar beach could be explained because of the lower intensity of fishing activities. La Graciosa Island is almost uninhabited, and fishing is limited to traditional fishing according to its character of marine reserve. The Spanish Ministry of Environment attributed the contribution of fishing to no > 2% of the total marine pollution (MAGRAMA, 2018). The marine pollution in the Canary Islands has a diffuse origin and that from local sources can be preferentially attributed to tourism, which is the main economic activity of the region, but touristic pressure in the Chinijo reserve is very low. Another difference with other literature sources was the presence of fibers, which was very limited, amounting only to 0.2% in number. Whitmire et al. stated that fibers dominated in majority of sampling points in a study performed in USA, with beads being also frequent (Whitmire et al., 2017). Globally, our work shows the kind of diffuse pollution expected in remote areas far from the main sources of human activity and the capacity of microplastics to diffuse around the globe.

The dimensions of all particles were measured using ImageJ software. Our study recovered a total number of 9149 plastic particles between 1 mm and 5 mm opening size sieves. All of them were photographed, length, width, and perimeter measured, and projected area calculated. They were finally classified in the six size categories indicated in Fig. 3. It is interesting to note that 5 mm nominal mesh opening was compatible with the passing of a considerable number of particles with projected area diameter > 5 mm. In our case, 29.8% of the total number of particles passing through 5 mm sieves, therefore classified as microplastics, presented projected area diameter > 5 mm. Projected area diameter, defined as the diameter of a circle with the same projected area as the particle, was chosen as the most representative dimension for size classification. Clearly is an orientation-dependent measure that refers to the preferential stable orientation of the particle and its use can be controversial in case of highly anisometric particles. Fig. S5 (SM) compares particle width with projected area diameter for all the particles measured in this study.

Fig. 3 also shows that the abundance of particles decreased with decreasing size. The fraction ranging 4–5 mm was more abundant (23.1%) than the smaller categories: 3–4 mm (20.2%), 2–3 mm (17.9%), 1–2 mm (8.8%), and < 1 mm (0.2%). These results were compatible with the disaggregation of homogeneous particles producing smaller fragments without complete disaggregation of the parent particle. Similar results were previously reported for plastics from Famara beach in the neighbouring island of Lanzarote, Canary Islands (CEDEX, 2018). Our results showed the occurrence of many asymmetric

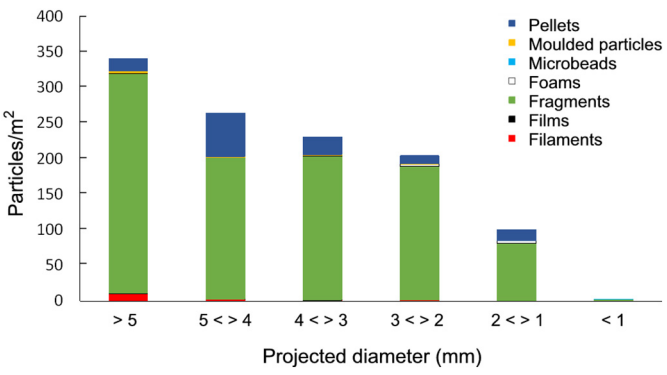

Fig. 3. Size frequency and typology of the different microplastic particles as an average of all sampling points.

particles, which are those falling below the parity line in the graph shown in Fig. S5 (SM). The plot shows that many particles had projected area diameter > 5 mm and could be considered as meso-debris according to their largest dimension. Conventionally, however, size cut-off is based on mesh size opening without explicitly considering the non-sphericity of plastic particles in line with the generally accepted definitions of TSG-ML and NOAA (Gago et al., 2016). The fraction < 1 mm was not sampled, but an important amount of particles < 1 mm was clearly observed in situ during sampling. Although discarded, this small fraction, consisting of fragments with size like sand grains may pose an important threat to the environment (Anderson et al., 2016). It is interesting to note that the asymmetry of sampled plastic particles increased when moving to points further to the sea entrance. Fig. S6 (SM) shows the tendency to lower projected circularity for fragments sampled in points C and D. This result may be explained by a preferential accumulation of more irregular fragments in the most protected part of the beach due to its specific hydrodynamic conditions.

Microplastics have also been sorted by colour (Fig. S7, SM). The analysis showed that both transparent and opaque particles were almost equally collected (about 50%). CEDEX sampling showed that amber, white and transparent particles were the most frequently found in debris collected from beaches (CEDEX, 2017, 2018). Colour distribution is influenced by the presence of pellets as they constitute most of the particles without specific colouration. However, a much higher proportion of clear colours was found (translucent, 50%; white 22%), which was not explained by the abundance of pellets (> 90% of which were translucent). A probable reason is that translucent fragments lost colour because of bleaching due to ageing. A relationship between colour and age was found before, indicating that opaque materials become translucent upon degradation (Fanini and Bozzeda, 2018). Turner and Holmes assessed the palette of colours for plastic pellets found in Maltese beaches (Turner and Holmes, 2011). They concluded that weathering and photooxidation resulted in the production of secondary quinoidal compounds that impart a yellowish colour. The fraction of yellowish plastics in our sampling was relatively small, probably meaning a further stage of ageing processes. Blue and green colours were the following most commonly found (10% and 5%, respectively) with other colours in lower frequencies. Colour characterization is important because some species of seabirds and some marine organisms select their preys depending on colour (Mattsson et al., 2015; Veiga et al., 2016).

A representative subsample was prepared with plastics from every sampling point and typology to perform chemical identification by Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) and Raman spectroscopy. They are vibrational spectroscopy techniques allowing non-destructive analysis in a fast and reliable way. Both techniques are generally applied to identify the chemical nature of microplastics in environmental samples. Their combination was necessary for the characterization of the smaller fractions and the coloured samples (Käppler et al., 2016; Strungaru et al., 2019). The number of plastic particles analysed was 711, representing 7.8% of the total number of particles recovered. Raman microscopy was used to identify the smaller sized particles and fragile particles, which showed tendency to break in smaller pieces. ATR-FTIR was used for larger particles or for particles with less tendency to break (Cabernard et al., 2018). Both techniques resulted in good quality spectra (Fig. 4), the use of Raman was more difficult because of its sensitivity to additives sometimes complicated the assessment of polymer characteristic bands. One example is shown in Fig. S8 (SM) in which cooper phthalocyanine, a blue colorant typically used in plastics, was identified (Caggiani et al., 2016; Ribeiro-Claro et al., 2017). The presence of additives is a subject topic of controversy as their leaking is a well-known cause for environmental concern (Koelmans et al., 2016; Whitmire et al., 2017).

The results of chemical analyses are summarized in Fig. 5. The most frequent polymer found in samples was PE, which corresponded to 63% (n = 445) of the particles. PP was the second representative with 32%

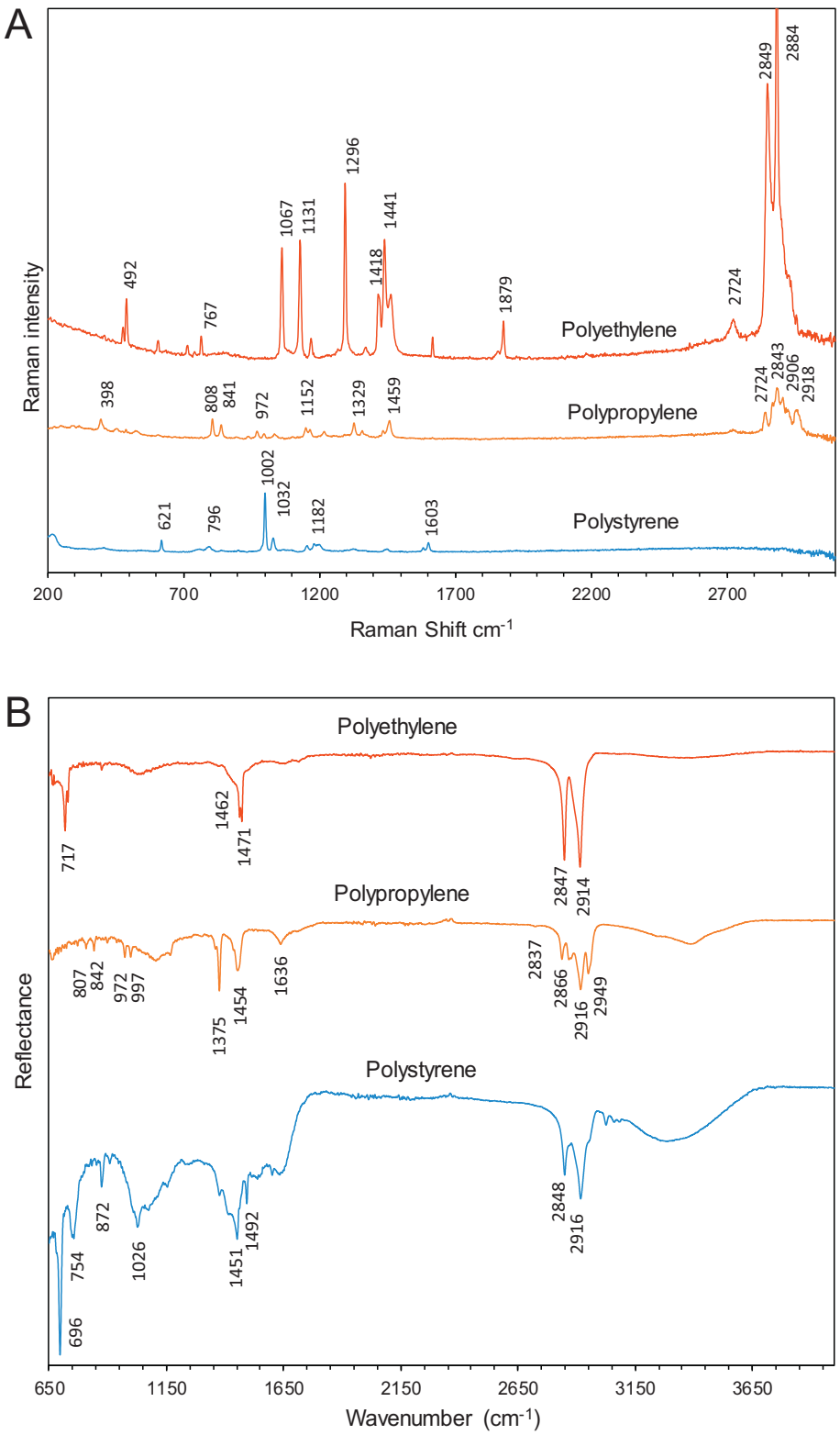

Fig. 4. Raman (A) and ATR-FTIR (B) representative spectra of different sampled microplastic fragments identified as PE, PP and PS.

(n = 226). PS minority occurred in only a 3% (n = 22) of the plastics. This result agreed with the fact that these three polymers account for roughly 90% of the 348 million tonnes of plastics produced annually (Mattsson et al., 2015; PlasticsEurope, 2018). PS was found mainly as forms of small size displaying the characteristic spongy structure of PS packaging material (Crawford and Quinn, 2017). Besides, PS appeared underrepresented in comparison with other sampling campaigns (Antunes et al., 2018; CEDEX, 2018; MAGRAMA, 2018). PE clearly dominated fragments and pellets, in coincidence with other's findings (Turner and Holmes, 2011). In our sampling 20% of pellets were PP. White particles preferentially consisted of PP (48% of white particles were PP), but translucent particles were dominated by PE (66%). PS was found mainly in white colour according to its main use. Concerning the 2% of remaining particles, polyurethane, methacrylate and some

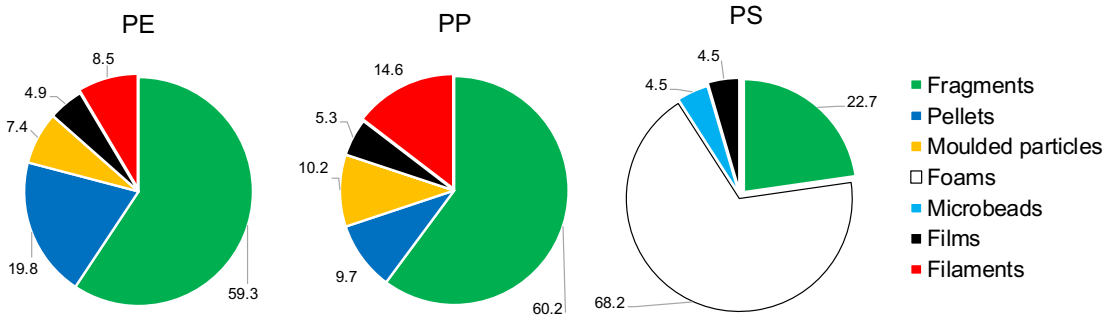

Fig. 5. Percent distribution of plastic typology by polymer nature.

copolymers (polyethylene-polypropylene, polypropylene-polyethylene and polyvinyl acetate-polyethylene) were identified. The characterization and significance of this minor fraction was a difficult task because of the chemical changes due to ageing and the scarcity of references.

It is a well-known fact that many organisms, including commercially important fish species, are exposed to buoyant, low-density plastics, which include PE, PP and PS (Cole et al., 2011). The main polymers detected in this work have a density ranging low enough to make them buoyant. Higher density polymers, usual in land-based wastes such as PET or PVC, were not represented in our samples suggesting sinking or association to biota before reaching the coast. The density of marine debris has been recognized as a major driver for their environmental fate (Rochman, 2018; Song et al., 2018). It is interesting to compare the ratio PE/PP obtained in our sampling with production figures. In 2017 the European (PlasticsEurope, EU28 + NO/CH) plastic demand by type was 29.8% for PE (high and low density) and 19.3% for PP, which corresponded to a PE/PP ratio of 1.54, lower than the ratio PE/PP 1.96 (in number) obtained in this work. The figures for 2006 (PlasticsEurope) were similar, 29% PE and 19% PP for PE/PP ratio 1.5. PE/PP production ratio was higher during the eighties and nineties (1.7–1.8) due to the increasing demand for PP (Geyer et al., 2017). Other studies found PE/PP ratios above production figures. Pan et al. reported PE/PP 1.61 in the Northwestern Pacific Ocean sampled using surface manta trawl with mesh size of ~330 μm. Modelling studies showed that plastic particles released to the marine environment may stay near coastal regions for years or decades (Lebreton et al., 2012). It may happen that certain conditions favour the preferential sampling of very old plastic particles, with historical PE/PP ratios, but the most probable cause for the bias in PE/PP ratio is that the hydrodynamic characteristics of the beach led to the accumulation of the more aged fragments in the more protected parts. The lower proportion of PP would be the consequence of its lower stability with respect to PE due to the presence of tertiary carbon atoms in the backbone, which are more prone to abiotic attack than the secondary carbons of PE (Gewert et al., 2015). Fig. 6 shows the ratio PE/PP for the four areas sampled in this work displaying a clear tendency towards higher PE/PP ratios for points C and D, which were those more distant from the opening in the rocks that connected the beach with the sea.

Sampled particles were clearly affected by environmental elements like photobleaching, and sand erosion. Visually, the samples obtained in this study could be described of soft consistence PE particles, while PP appeared more as brittle fragments, films and filaments. Fragments varied from pure smooth and flat surfaces to granulated or cracked surfaces. SEM images of aged particles show characteristic cracks, protrusions, and depositions covering their surface (Fig. 7). Detailed SEM images comparing samples of PE, PP and PS particles compared to new, pristine, pellets are shown in Fig. S9 (SM).

In this work, the characteristics defining microplastic (1 mm < > 5 mm) particles were established along a coastal line of an area of high biological importance and low human impact. The high amount of microplastic debris collected and measured, highlights the magnitude

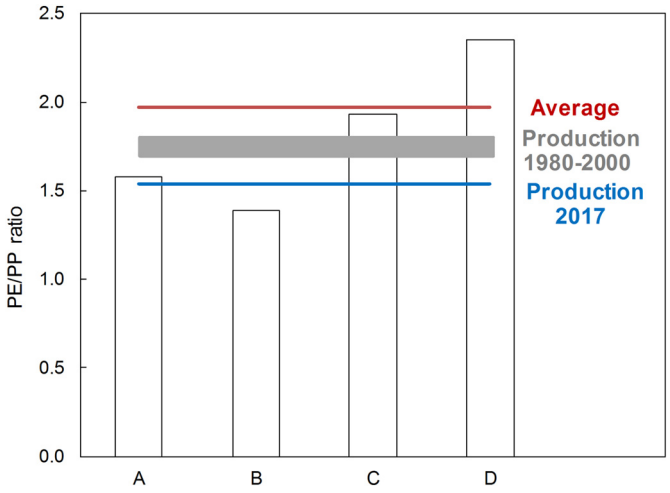

Fig. 6. Relative abundance of PE and PP in the points sampled in this work compared to production ratios.

of global plastic pollution. The relevance of having precise estimations of microplastics in beaches comes from the fact that coastal lines are one of the most important points of contact of anthropogenic heterogeneous materials with wildlife (Coppock et al., 2017). It is to be noticed that cleaning plastic litter on Ámbar beach is systematically performed since 2006 on a weekly basis, but only for macroplastics that can be manually collected. Volunteer groups do the best to recover minor fragments during extra Summer campaigns, but due to the difficulty of separating them from sand, microplastics are not collected and, once produced, remain unaffected by cleaning operations.

4. Conclusions

In this study, the sandy beach Ámbar was sampled. Ámbar beach is in a remote area in almost desertic island belonging to the Chinijo archipelago in the Canary Islands. An average density of 36.3 g/m^2 of microplastics in the 1–5 mm range was obtained, with a large variability along the 90 m of the beach sampled (from 8.5 g/m^2 to 103.4 g/m^2). No relationship was found between microplastics and local activities. The Canary Current, a wind-driven surface current part of the North Atlantic Gyre was deemed responsible of the high level of plastic pollution.

The total number of sampled plastic particles was 9149, in a distribution dominated by fragments (87%) and pellets (9%), with minor amounts of filaments, foams, moulded fragments and films. The average projected area diameter of sampled particles was 4.2 mm, explained by the large amount of microplastics with their larger dimension > 5 mm. Sampled plastics showed a high proportion of clear colours (translucent or white) that was not explained by the abundance of pellets, which was attributed to the bleaching of coloured plastics due to ageing.

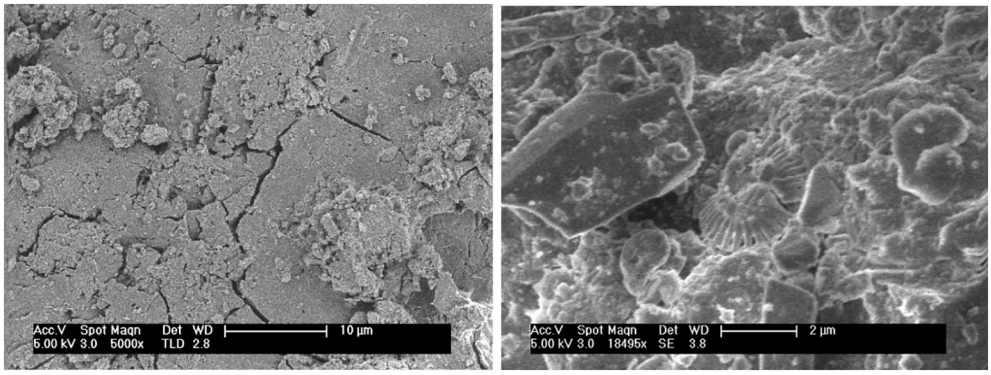

Fig. 7. SEM images of sampled PE fragments.

Raman and FTIR spectroscopy were used for the chemical identification of polymers. A total of 711 analyses showed that PE was the most frequently found polymer (63%) followed by PP (32%) and PS (3%). PE dominated most categories, particularly fragments and pellets, with high proportion of PP in moulded fragments, filaments and films. PS was found as white fragile foams according to its use as packaging material. We also measured a significant increase in the PE/PP ratio in the higher and more protected parts of the beach, suggesting the preferential accumulation of the more aged fragments in calmed parts of the beach.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2019.04.061.

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