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Microplastic pollution in sublittoral coastal sediments of a North Atlantic island: The case of La Palma (Canary Islands, Spain)

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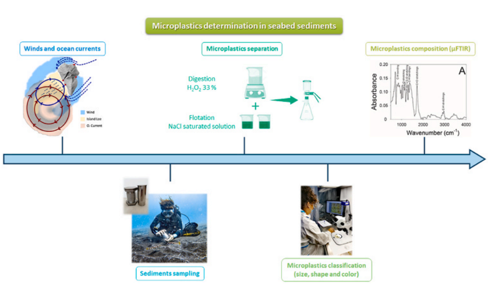
HIGHLIGHTS

- First evidence of the presence of microfibers in subtidal sediments (5–7 m) of the Canary Islands.
- An average concentration of 2682 ± 827 items per kg of dry weight was found.
- Microfibers were the most abundant (98.3%) which were mainly colorless and blue.
- µFTIR analysis of 13.9% of the items showed that most of the fibers were cellulosic.
- The winds and oceanic mesoscale dynamics in the area may explain their distribution pattern.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, the microplastic content of sediments collected in July 2020 between 5 and 7 m depth was studied in four locations of La Palma island (Canary Islands, Spain). At each sampling location, three samples were taken parallel to the shoreline. The microplastic content in each sampling corer was studied every 2.5 cm depth after

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digestion with a H_2O_2 solution followed by flotation in a saturated NaCl solution. Visualization of the final filtrates under a stereomicroscope revealed that all the sediment samples evaluated contained mostly microfibers (98.3%) which were mainly white/colorless (86.0%) and blue (9.8%), with an average length of 2423 ± 2235 (SD) mm and an average concentration of 2682 ± 827 items per kg of dry weight, being the total number of items found 1,019. Fourier Transform Infrared microscopy analysis of 13.9% (n = 139) of the microfibers also showed that they were mainly cellulosic (81.3%). No significant differences were found between the depths of the sediment. However, significant differences were found between the number of fibers from the sampling sites at the east and west of the island. Such variability could be driven by the winds and ocean mesoscale dynamics in the area. This study confirms the wide distribution of microfibers in sediments from an oceanic island like La Palma, providing their first report in marine sediments of the Canary Islands.

1. Introduction

Plastic pollution is nowadays one of the biggest problems that humans should face in the forthcoming years. The widespread presence of plastic materials, especially microplastics, in all environmental compartments (water, soil, air and biota) (Hashmi, 2022; Vighi et al., 2021), as well as their negative effects on living organisms, even potentially affecting human beings, clearly requires taking important and urgent actions in different directions and areas.

In the particular case of the marine environment, which is the environmental compartment in which microplastics have been most detected and, therefore, in which most studies have been developed (Harris, 2020; Pirsaheb et al., 2020), microfibers represent the largest percentage of anthropogenic-induced microparticles (Barrows et al., 2018; Gago et al., 2018; Reineccius et al., 2020). These fibers, which can be natural (i.e. cotton, wool), semi-synthetic (i.e. viscose, rayon) or synthetic (i.e. nylon, polypropylene, PP) are mainly released from textiles, especially during domestic laundry (Napper and Thompson, 2016), though they can also come from the fragmentation of fishing gears (Naji et al., 2017). Concerning the first case, a good number of studies have shown that thousands of microfibers are released during laundering (Gaylarde et al., 2021) and that their release through wastewater treatment plants or sludges constitutes an important source of their presence in the environment, although many studies clearly indicate that an extremely high percentage of microplastics is removed (Bayo et al., 2020; Salvador Cesa et al., 2017).

Research about the presence of microplastics in marine sediments, as well as in sediments from other aquatic systems (Irfan et al., 2020), has already been developed in different parts around the world, finding in most cases that microfibers are the most abundant form of microplastics found (Barrows et al., 2018; Harris, 2020). However, regarding the specific case of subtidal coastal sediments of less than 200 m depth (on average, the influence of coastal sediments reaches up to 200 m depth) the number of studies is much lower (Alomar et al., 2016; Bucol et al., 2020; Carretero et al., 2021; Filgueiras et al., 2019; Frias et al., 2016; Huang et al., 2020; Lorenz et al., 2019; Lourenço et al., 2017; Reed et al., 2018; Ronda et al., 2019; Zobkov and Esiukova, 2017). Some examples include the work by Reed et al., who determined microplastics in near-shore marine sediments close to Rothera Research Station, in Antarctica (Reed et al., 2018); that of Frias et al., who analyzed the coastal sediments of the Algarve in Portugal (Frias et al., 2016) or the work by Zobkov and Esiukova, in which sediments of the Baltic Sea near Russia were studied (Zobkov and Esiukova, 2017). In Spain, to the best of our knowledge, only the works by Alomar et al. (2016), who analyzed sediments down to 10 m depth in the Balearic Islands (Spain), Filgueira et al., who studied sediments of 43–154 m depth along the Spanish Mediterranean continental shelf (Filgueiras et al., 2019), as well as that of Carretero et al. (2021), who studied the microplastic content of sediments from Rías Baixas and Miño river shelf collected down to 17–375 m, have been published. Despite these few reports, it is also highly desirable to increase knowledge in this specific area in order to determine the current health of the seas and to take suitable and effective actions to decrease the presence and impact of microplastics in them.

Also concerning marine pollution, the European Union (EU) has implemented the Marine Strategy Framework Directive (MSFD) (*DIRECTIVE, 2008*/56/EC *Marine Strategy Framework Directive, 2008*) in an attempt to protect more effectively the marine environment across Europe and to achieve a Good Environmental Status (GES) of EU marine waters by 2020. For the first time, the amount of microplastics in the marine environment has been included as part of an environmental descriptor (Descriptor 10). In Spain, the MSFD was transposed by law 41/2010 (Boletín Oficial del Estado, 2010), in which the Spanish coasts were divided into 5 regions, being one of them the Canary Islands. Up to now, and to the best of our knowledge, microplastic pollution studies in the Canary Islands have only included the analysis of the digestive tracts of Atlantic chub mackerel (*Scomber colias*) (Herrera et al., 2019), of European sea bass (*Dicentrarchus labrax*) (Reinold et al., 2021) and the determination of microplastic occurrence in beaches of the islands of Lanzarote (Baztan et al., 2014; Herrera et al., 2018), La Graciosa (Baztan et al., 2014; Edo et al., 2019; Herrera et al., 2018), Fuerteventura (Baztan et al., 2014), Gran Canaria (Herrera et al., 2018; Rapp et al., 2020), Tenerife (Álvarez-Hernández et al., 2019; González-Hernández et al., 2020; Reinold et al., 2020) and El Hierro (Hernández-Sánchez et al., 2021). So far, no studies have reported their presence in the rest of the islands (La Palma and La Gomera), nor in subtidal sediments of any of the islands or in any other environmental compartment (i.e. soil or air). Concerning studies in the open ocean in the region, recently, Vega-Moreno et al., have evaluated the presence of fibers down to 1150 m depth (Vega-Moreno et al., 2021). All the previously mentioned studies have shown that the Canary Islands archipelago is especially vulnerable to microplastics contamination due to its geographical location. In fact, the Canary Islands are inside the Northeastern Atlantic Subtropical Gyre, an area also highly influenced by mesoscale processes which can generate transport and accumulation of microplastics due to eddies or similar processes with a horizontal scale from 10 to 100 km (Brach et al., 2018). However, little is known about such processes in the region, being necessary the implementation of a detailed study of the oceanic and wind dynamics and mesoscale oceanographic processes that could be present in the area at the time of sampling (Van Sebille et al., 2020).

This work aimed to study, for the first time, the presence of microplastics in sublittoral coastal sediments of the Canary Islands, in particular, in those of La Palma island, which has a population of 84,793 inhabitants (INE, 2019) and a very limited presence of industries, as well as to study their possible sources and the oceanic and wind dynamics of the region, including mesoscale oceanographic processes, that could influence their distribution and deposition. To the best of our knowledge, this work represents the first study of the presence of microplastics in sublittoral coastal sediments of the Canary Islands and one of the very few studies of this type carried out in Spain (see Table S1 of the Supplementary Material).

2. Materials and methods

2.1. Study area and field work

The study area included four locations on the island of La Palma (Canary Islands, Spain): Puerto Naos, Tazacorte, Puerto Espíndola and

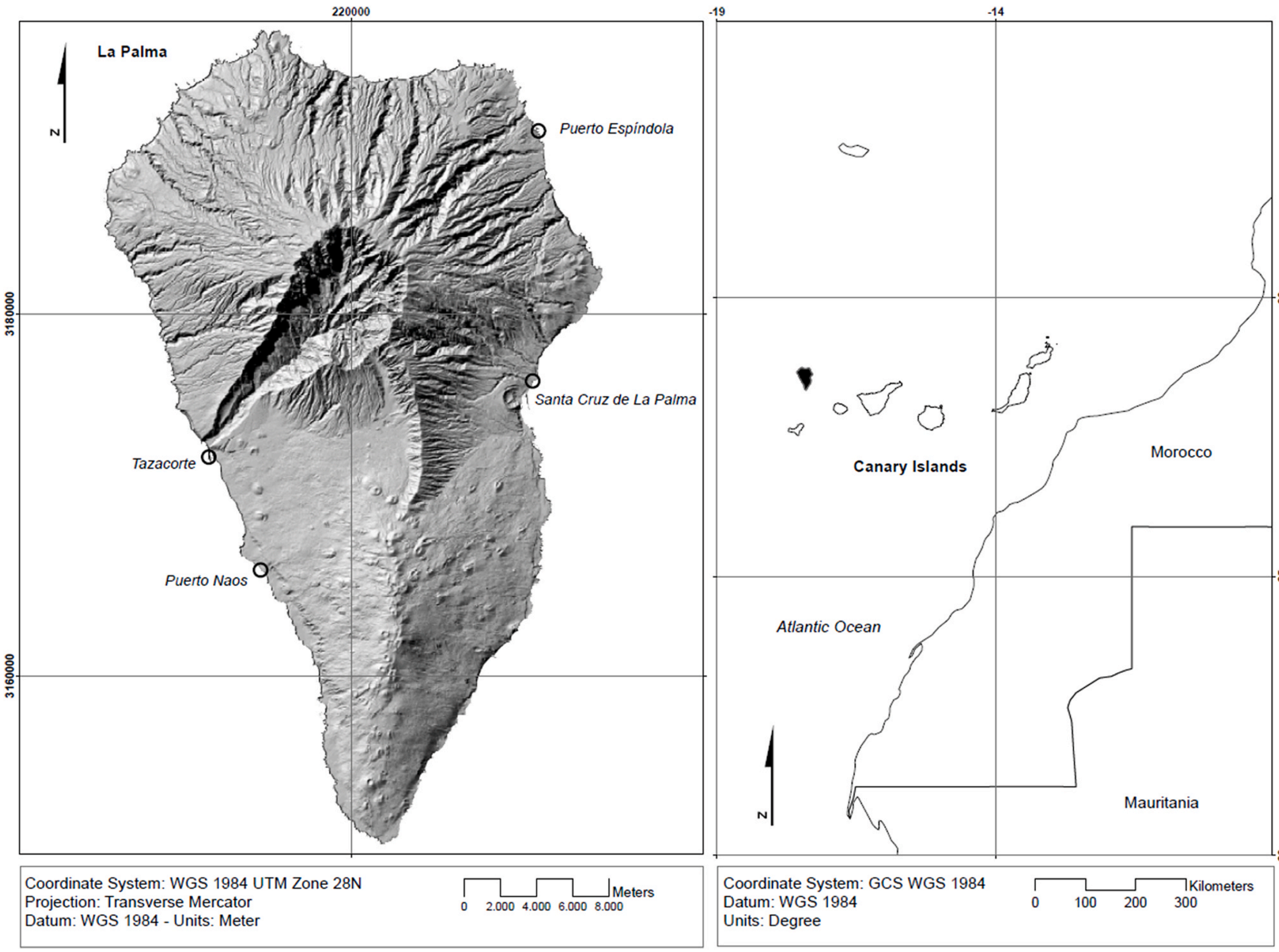

Fig. 1. Geographical location of the Canary Islands archipelago, La Palma island, and the four sampling locations (marked with cycles).

Table 1
Data of the sampling locations, sampling points and dates.

	Puerto Naos beach	Tazacorte beach	Puerto Espíndola	Santa Cruz de La Palma beach
Municipality	Los Llanos de Aridane	Tazacorte	San Andrés y Sauces	Santa Cruz de La Palma
Sampling date	07/22/2020	07/22/2020	07/23/2020	07/21/2020
Coordinates	28° 35′ 11″ N	28° 39′ 00″ N	28° 48′ 37″ N	28° 41′ 05″ N
	17° 54′ 41″ W	17° 56′ 49″ W	17° 45′ 47″ W	17° 45′ 36″ W
Depth	6.7–7.0 m	5.0–5.3 m	6.7–7.0 m	6.7–7.0 m
Orientation	Southwest	West	Northeast	East
Number of sampling points	3	3	3	3

Santa Cruz de La Palma (see Fig. 1 and Table 1 for sampling locations and sampling points characteristics, respectively). Sediment samples were collected by scuba divers during July 2020 at a depth between 5 and 10 m on a uniform sandy seabed (depth measurements were made using a dive computer from Cressi Leonardo). Samples were collected in triplicate parallel to the shoreline and separated 10 m from each other. Stainless-steel corers of 10 cm long and 5 cm diameter with stainless-steel nuts were used to collect the samples. The tube of the corer was carefully introduced into the seabed and then the upper nut was screwed on. Afterwards, the corer was slowly pulled out of the sand making small circles and, once it was out of the sand, the lower nut was immediately screwed on (see Fig. S1 of the Supplementary Material).

2.2. Sediment samples characterization

In order to determine the water content of the sediments, 10 g of wet sediment were accurately weighed in ceramic capsules using an analytical balance (Sartorius Entris 224I–1S with a maximum weighting capacity of 220 g and 0.1 mg of resolution) and placed in an oven at 105 °C for 24 h. The 10 g sediment subsample corresponded to a composite sample from the four different depths in each corer. Water content was determined in triplicate for each corer. After that time, the capsules were allowed to cool to room temperature in a desiccator and weighed again until constant weight. The water content was calculated by weight difference.

Determination of the organic carbon content was made by the weight loss-on-ignition method for marine sediments following the procedure of Wang et al. (2011). Approximately, 5 g of sediment were placed in a crucible and heated at 105 °C for 24 h to remove the moisture. The 5 g sediment subsample corresponded to a composite sample from the four different depths in each corer. The analysis was carried out in duplicate for each corer. The sample dry weight was first determined, and the same samples were placed in a programmable muffle furnace (Carbolite CWF 11/13) for 12 h at 550 °C. After calcination, samples were allowed to cool at room temperature in a desiccator and weighed until constant weight (Wang et al., 2011).

Particle size distribution was assessed by sieving (5 min at 8 rpm on a vibratory sieve shaker) about 100 g of the previously dry sediment (three samples per sampling location) through a standard series of ten sieves with the following mesh sizes: 16, 8, 4, 2, 1, 0.5, 0.25, 0.125, 0.063 and 0.030 mm. The 100 g sediment sample also corresponded to a composite sample from the four different depths in each corer. Textural group and sample statistics (median, mean, sorting) were calculated using the software GRADISTAT Version 9.1 following Blott and Pye (2001).

2.3. Sediment samples treatment for microplastics extraction

Once at the laboratory, the content of each corer was divided every 2.5 cm depth and deposited into a glass vessel and closed with a screw cap. Ten grammes of each 2.5 cm sediment fraction were accurately weighted in an analytical balance and digested during 2 h with 40 mL of 33% H_2O_2 in order to remove the organic matter (constant stirring at 300 rpm). Afterwards, 100 mL of a NaCl saturated solution (approximate density of 1.2 g·cm^{-3}) were added and after stirring for 1 min, the solution was left for an hour and filtrated under vacuum through a 50 μm stainless-steel filter previously washed with Milli-Q water obtained from a Milli-Q Gradient A10 system from Millipore (Burlington, MA, USA). The flotation procedure was repeated 8 times. The filters, which were immediately introduced in Petri dishes, were visualized under a trinocular light stereomicroscope with magnifications × 0.65 – × 5.5 (Euromex Nexius Zoom EVO, The Netherlands) and with an image analysis system (Levenhuk M1400 PLUS - 14 Mpx digital camera with the Levenhuk Lite software) to identify and classify plastic particles according to their size, color, and shape. The lower size limit of the particles studied was ~90 μm and the viewing time per filter was between 2 and 4 h. To visually establish if a particle is made of plastic, the criteria of Hidalgo-Ruz et al. was met (Hidalgo-Ruz et al., 2012; Marine & Environmental Research Institute, 2017), even though, a subset of samples was confirmed by microFourier Transform Infrared Spectroscopy (μFTIR).

2.4. Precautions to avoid sample contamination

All material used was plastic-free. Nonvolumetric glassware was cleaned by heating up to 550 °C for 4 h in a programmable muffle furnace (Carbolite CWF 11/13), while volumetric glassware was cleaned using a Nochromix® solution from Godax Laboratories (Cabin John, MD) in sulfuric acid (95% w/w, VWR International) for 24 h. Before their use, all laboratory materials were washed with Milli-Q water previously filtered through a 0.22 μm filter. Milli-Q water was also used to prepare the NaCl saturated solution. Both 33% H_2O_2 and NaCl saturated solutions were also filtered through a 0.22 μm filters. Laboratory blanks (full sample pretreatment without sediments) were also analyzed with every batch of samples in order to check that no laboratory contamination took place. Additionally, checks for contamination during processing were made by exposing filters to the air of the laboratory, whenever samples were open to the laboratory environment. In general, special care was taken to minimize laboratory contamination, which included the use of a glove box.

2.4.1. MicroFTIR analysis

The chemical composition of a randomly distributed subsample of microparticles (n = 139), which included fibers and fragments of each filter in each area, was analyzed by μFTIR using a Perkin-Elmer Spotlight™ 200 Spectrum Two instrument with a mercury cadmium telluride detector. Each microparticle was placed on KBr, which was used as a slide, and its spectrum was recorded in micro-transmission mode using the following parameters: spot 50 μm, 32 scans, and spectral range 550–4000 cm^{-1}. All spectra were compared with Omnic 9.1.26 (ThermoFisher Scientific Inc., Massachusetts, USA) database and with spectra from our own database. Microparticles were considered as plastics when the match confidence was >70%. Polyethylene terephthalate (PET) was classified as "polyester" since it is a thermoplastic polymer resin of the polyester. Natural (cotton and linen) and semi-synthetic fibers (rayon/viscose/cellophane, lyocell/Tencel) as well as both cotton and linen with non-natural colors that consists of cellulose, were classified as cellulosic since their spectra are practically identical and, therefore, they are difficult to differentiate especially in the case of the microparticles found in the environment due to weathering processes.

2.5. Statistical analysis

Statistical methods were implemented using Statistical Package for the Social Sciences (SPSS, Version 26.0). The level of significance for all tests was set to $p < 0.05$. Assumptions of normality (Kolmogorov–Smirnov test) and homogeneity of variance (Levene test) were met for each analysis. To detect differences in plastic debris (items per gram or items per cm^3) among all sampling locations and sediment depths, a general linear model (GLM) univariant analysis and *post hoc* Tukey's test were used. Same tests were applied to assess differences in percentages of plastic colors and length classes between sampling points. Differences in the amount of plastic debris extracted by sequential flotations (from 1 to 8 flotations), and differences in sediment water content, organic carbon content and particle size parameters (median, mean and sorting) among sampling locations were determined by using ANOVA and a *post hoc* Tukey's test.

2.6. Physical oceanographic environment

Ocean dynamics were analyzed with the daily outputs from the operational model Iberian Biscay Irish (IBI) Ocean Analysis and Forecast System from Copernicus Marine Service from July 2019 to July 2020. The model is based on an eddy-resolving NEMO-v3.6 model application driven by high frequency meteorological and oceanographic forcing that run at 1/36° (~3 km) with 50 vertical levels from the sea surface to 5500 m depth (product identifier IBI_ANALYSISFORECAST_PHY_005_001). On the other hand, altimetric observations at the surface were used as a validation of the previous dataset. This second database was also provided daily by Copernicus with a horizontal spatial resolution of some 14 km (product identifier SEALEVEL_EUR_PHY_L4_NRT_OBSERVATIONS_008_060).

With respect to wind data, the Spanish Meteorological Agency (AEMET) provides outputs from the HIRLAM-ALADIN Research on Mesoscale Operational NWP in Europe (HARMONIE). This weather prediction model has been designed for operational use at convective scale resolutions (2.5 km). The model is run four times per day over the Canary Islands with a forecast length of 48 h.

3. Results and discussion

3.1. Sampling and sample treatment

Subtidal coastal sediments were collected in triplicate (separation of 10 m between each stainless-steel corer) at four sampling locations of La Palma island in July 2020, in order to undertake a study of the potential contamination by microplastics of seabed sediments since, as indicated, no previous studies like this one have already been developed in this region.

Although some works have directly performed the flotation of the sediment samples without adding any oxidizing agent (Carretero et al., 2021; Filgueiras et al., 2019; Frias et al., 2016; Sanchez-Vidal et al., 2018), we decided to oxidize the organic matter because the high presence of organic matter and vegetable materials in the final filtrates made difficult the correct identification and quantification of the fibers.

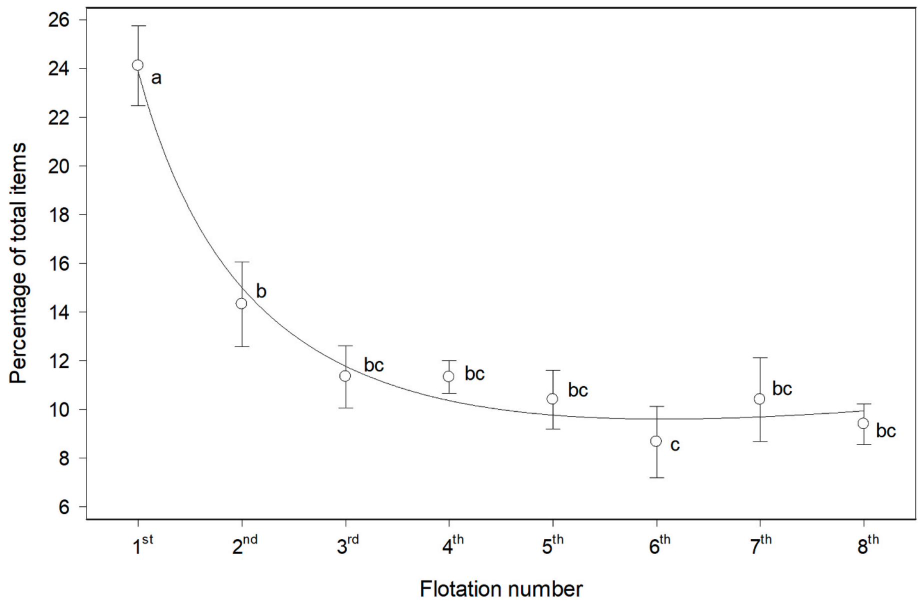

Fig. 2. Average percentage from the four sampling locations of total plastic debris extracted in each flotation; mean ± standard error; n = 4. Different letters denote significant differences ($p < 0.05$) among flotations.

In addition, due to a high microbiological growth, it required an immediate visualization of the samples in the following days after the extraction. Hydrogen peroxide oxidation provided extremely clear extracts that could be observed at any time at the stereomicroscope and also analyzed by μFTIR spectroscopy. Besides, H_2O_2 treatment at 60 °C is frequently used in the analysis of soil or sewage sludge samples (which have a much higher organic matter content). It has also demonstrated that it did not severely damage microplastics of different nature and that it is effective in the elimination of biofilms and, therefore, on the improvement of the visualization at the stereomicroscope (Hurley et al., 2018; Li et al., 2020). To complete the oxidation, as well as to apply a consistent and reproducible method, 2 h of digestion were established in all cases since it was found enough to eliminate the organic matter and to avoid the previously mentioned problems. Quite frequently, a fixed time has not even been set in a good number of works published in the literature.

Afterwards, up to eight flotations in a saturated NaCl solution were carried out. Since the density of the saturated NaCl solution is around 1.2 g·cm^{-3}, high-density fibers such as cellulosic-based fibers may not float. Even though, it was found that those fibers were efficiently extracted from the sediments as previously reported (Sanchez-Vidal et al., 2018).

After filtration, the filters were observed at the stereomicroscope. Microplastics were classified according to their shapes in fragments, fibers/lines, pellets, microbeads, foams and films, though, as it will be later indicated, most of them were fibers, but few fragments and microbeads were also found. Each particle was measured and photographed.

Since fibers are ubiquitous in everyday life, contamination control is an important issue that must be addressed in any laboratory devoted to their analysis since clothing may release them; for this reason, different precautions were taken to especially minimize this issue. In particular, procedural blanks were also analyzed in order to correct the results (see Experimental Section for more details).

Regarding the number of flotations, in this case, eight of them were carried out for each 2.5 cm fraction of each corer (48 subsamples) using a saturated NaCl solution, in order to study the effectivity of the extraction process. Fig. 2 shows the variation in the percentage of the total items identified in all the samples vs the number of flotations. As can be seen, in the first three flotations nearly 50% of the items were extracted, though the number of fibers in subsequent ones were still constant and probably a low number of them remained in the sediments. The reason might be the high density of the microfibers found (i.e. > 1.4 g·cm^{-3}), as it will be later shown. This pattern was found in all sampling points and fractions. In general, since there is not yet a stablished protocol for this step, there is still a certain controversy regarding the number of flotations to be applied for these specific studies since, from an experimental point of view, a high number of flotations is quite tedious on a daily basis. Even though, since the number of flotations carried out is relatively high compared to other works in the literature, it is clear that the results obtained are more realistic.

Table 2
Characteristics of sediment samples from the four sampling locations; mean ± standard error; n = 3; means with different letters denote significant differences ($p < 0.05$) between sampling locations.

Parameter/ location	Santa Cruz de La Palma beach	Puerto Espíndola	Puerto Naos beach	Tazacorte beach
Water content (%)	35.5 ± 9.0 a	13.9 ± 2.2 c	25.1 ± 0.8 b	18.7 ± 0.8 bc
Organic carbon (g·kg^{-1})	30.6 ± 5.2 a	9.7 ± 5.2 b	7.8 ± 9.9 b	6.1 ± 1.2 b
Textural group	Slightly gravelly sand	Gravelly sand	Sand	Sand
Median or D_{50} (μm)	197.5 ± 68.4 b	1143.6 ± 454.0 a	514.8 ± 494.5 ab	575.7 ± 16.9 ab
Geometric mean (μm)	203.7 ± 87.3 b	1207.0 ± 561.0 a	503.2 ± 461.3 ab	548.7 ± 9.9 ab
Sorting (σ)	2.0 ± 0.4 ab	2.2 ± 0.4 a	1.6 ± 0.0 b	1.6 ± 0.0 b

3.2. Sediment characterization

Several physicochemical characteristics of sediment samples are displayed in Table 2, while histograms with an average particle size distribution from the different locations are presented in Fig. S2 of the Supplementary Material. As can be seen in the table and figure, sediments from Santa Cruz de La Palma showed the highest water and organic carbon content while samples from Puerto Espíndola and Tazacorte had the lowest level of water and organic carbon, respectively. The locations in the eastern side of the island (Santa Cruz and Puerto Espíndola) exhibited poorly to moderately sorted sediments in

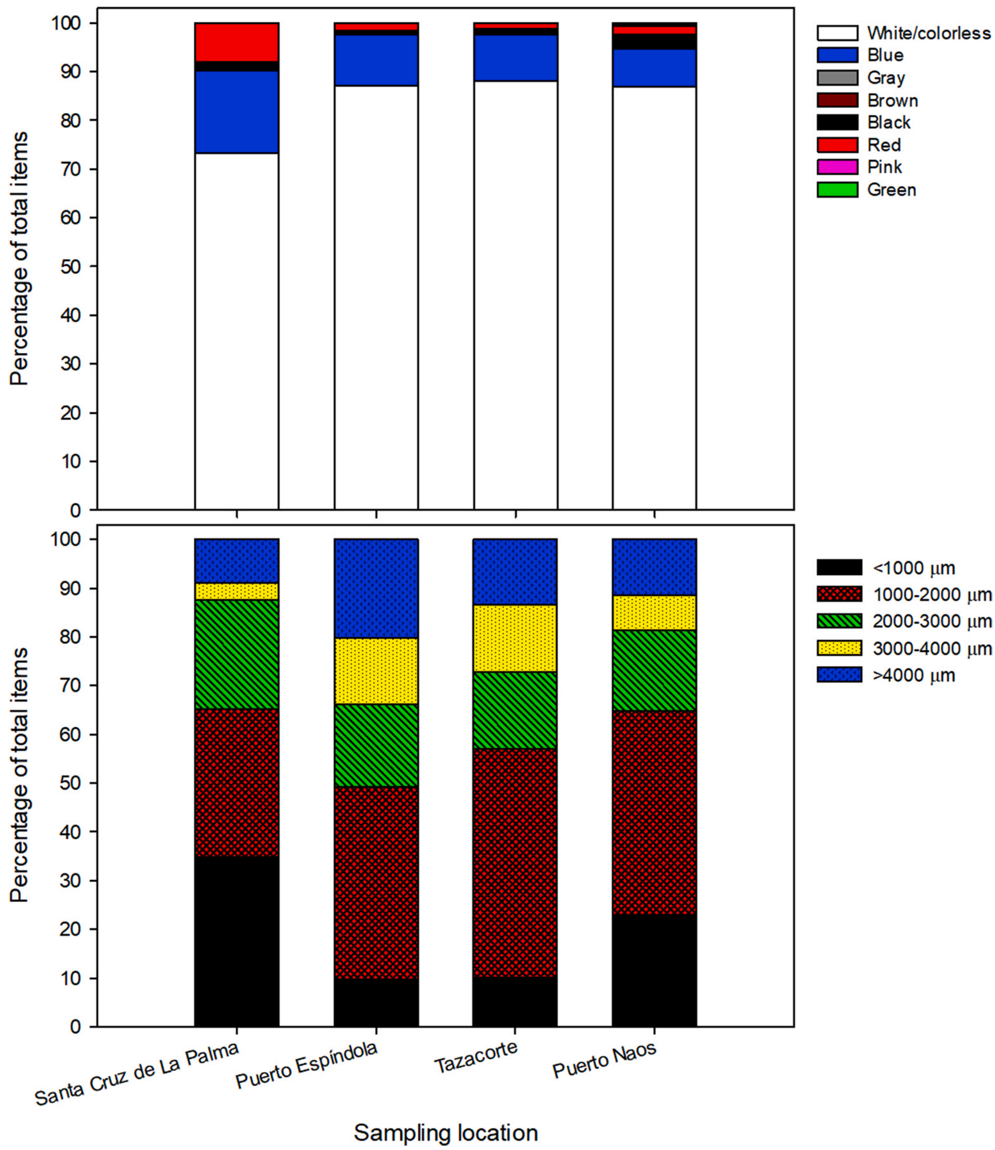

Fig. 3. Distribution of fiber colors and length from the four sampling locations (n = 3). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

contrast to the western side that were mostly moderately well sorted. The sediments from Puerto Espíndola showed the greatest gravel content, reaching up to 44.5% for some samples, while the sediments of Santa Cruz had the highest content of mud (e.g. silt and clay) up to 2.7%.

3.3. Microplastics occurrence

The visual examination of the filters through the binocular stereomicroscope showed that the vast majority of the particles found (1,019) were microfibers (98.3%). Nine particles were fragments, four of them were found in Puerto Naos (all of them had a blue color), three in Puerto Espíndola (two were red and one blue) and one was found in Santa Cruz de La Palma (red). Eight microbeads were also found, four of them in Puerto Naos (three were white and one was colorless) and the rest in Santa Cruz de La Palma (all of them white). Fig. S3 of the Supplementary Material shows the photographs of an example of a microfiber and a microbead found.

Fig. 3 shows the distribution of the microfiber colors at each location as well as the distribution of the length of the microfibers. As can be seen, in all cases, most of the fibers (between 73.2% for Santa Cruz de La Palma and 88.1% for Tazacorte) were white/colorless, followed by blue fibers (between 7.8% for Puerto Naos and 10.4% for Puerto Espíndola). Red, black, grey, green and brown fibers were also found, although in a lesser amount. Considering the total amount of fibers of the four sampling points, white/colorless fibers covered 86.0% of the total, blue fibers a 9.8%, red a 2.3% and black a 1.7%. Two of the previous works developed in Spain (Mediterranean continental shelf and Rías Baixas and Miño river) have also shown that the colorless fibers were the predominant ones found in sediments (Carretero et al., 2021; Filgueiras et al., 2019), although not in such high amounts, and, in certain cases, followed by blue fibers in abundance (Carretero et al., 2021; Filgueiras et al., 2021). However, this does not agree with those data reported by Alomar et al. in Balearic Islands (Alomar et al., 2016). Even though, as recently highlighted in several review articles (Gago et al., 2018; Kutralam-Muniasamy et al., 2020) most of the fibers found in the marine environment, in particular, in marine sediments, are blue and colorless, which is also coincident with our results.

As can also be seen in Fig. 3, in general, there is a quite homogenous distribution of the fiber length between the four sampling sites, being significantly most abundant those with sizes between 1 and 2 mm (~39% of total items). At Santa Cruz de La Palma, there is a higher number of fibers with a length below 1 mm, while at Puerto Espíndola,

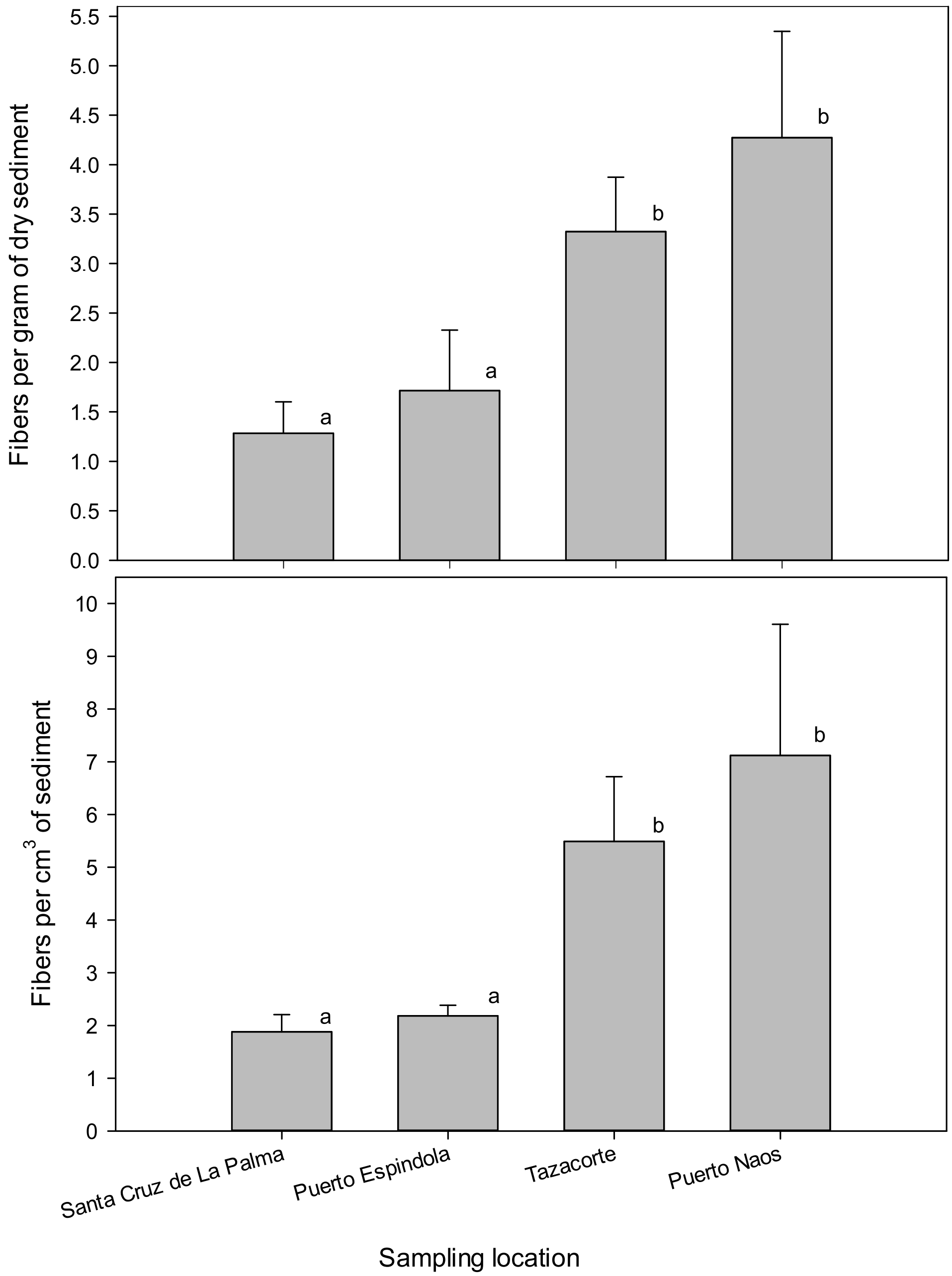

Fig. 4. Fibers content from the four sampling locations; bars represent mean ± standard error; n = 3; different letters denote significant differences ($p < 0.05$) among sampling points fiber content.

the highest number of fibers longer than 4 mm were found. Statistical analysis did not reveal significant differences ($p > 0.05$) in the percentage of fiber colors and length classes among sampling points.

Regarding the concentration of microfibers, an average of 2,682 ± 827 items per kg of dry weight was found. The concentration of each sampling location was as follows: 1,306 ± 543 items·kg^{-1} of dry weight in Santa Cruz de La Palma, 3,386 ± 839 items·kg^{-1} of dry weight in Tazacorte, 1,783 ± 1,024 items·kg^{-1} of dry weight in Puerto Espíndola and 4,254 ± 1,856 items·kg^{-1} of dry weight in Puerto Naos. Fig. 4 shows the distribution of the number of microfibers found in each sampling location, expressed as the number of fibers per gram of sediment dry weight and also per cm^3, while Fig. S4 of the Supplementary Material shows the variation of the number of fibers per sampling depth. As can be seen in Fig. 4, a significantly higher number of fibers ($p < 0.05$) was found in both, Tazacorte and Puerto Naos, located on the western side of the island, compared to the other two, Santa Cruz de La Palma and Puerto Espíndola, located in the eastern slope. This could suggest a possible difference in the accumulation pattern of microfibers in the sediments on each side of the island. In this sense, it should not be forgotten that regarding the granulometry of the sediments, those of the eastern side of the island were poorly to moderately sorted in contrast to the western side that were mostly moderately well sorted. Thus, it also provides a different microfiber sedimentation/retention pattern, though further studies should also be developed in this sense.

Table 1 of the Supplementary Material, compiles the information of several articles in which microplastics have been determined in seabed sediments < 200 m depth; the table also include the previous works developed in Spain. As can be seen, the average concentration of microfibers is higher than in previous works reported in the table. In the particular case of those works carried out in Spanish seabed sediments, the amount is also higher. Regarding microfibers length, it is also similar to that reported in other works.

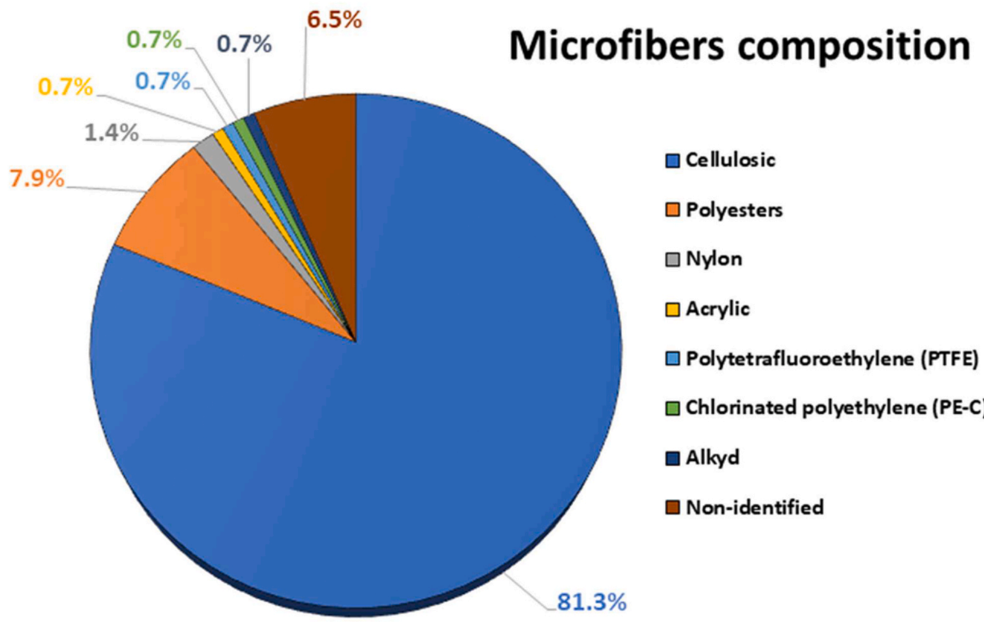

Fig. 5. Distribution of the composition of the microfibers found in the sediments of La Palma island during this study (n = 131).

Concerning the variation in the number of fibers per sampling depth (Fig. S4 of the Supplementary Material), a clear tendency cannot be observed (neither an increase nor a decrease) except for Puerto Naos, in which there is a slight increase in the number of fibers with the depth although not statistically significant ($p > 0.05$). On average, for the four locations, the percentage of total fibers found was 26.1, 21.9, 26.3 and 25.6 at 0–2.5, 2.5–5.0, 5.0–7.5 and 7.5–10.0 cm depth, respectively.

3.4. Microfibers composition

In order to identify the composition of the microfibers found in this study, 139 fibers (13.9% of the total) were analyzed by μFTIR spectroscopy. According to the Guidance of Marine Litter in European Seas of the European Commission, formal identification of the polymer composition is not so critical for larger particles (> 500 μm) while a proportion of 5–10% of all samples < 100 μm should be routinely checked. Despite most of the particles had a length higher than 500 μm, we have also considered such threshold of 10% as a reference (Galgani et al., 2013).

Figs. S5 and S6 of the Supplementary Material show the μFTIR spectra and photographs of some of the identified fibers, respectively, while Fig. 5, shows the complete distribution of the composition of the fibers that could be identified (n = 139). μFTIR analysis revealed that 113 of the 139 selected particles (81.3%) have a cellulosic composition. As indicated in the experimental section, natural fibers, like cotton, wool and linen, and semi-synthetic fibers, like rayon, viscose, cellophane, etc., consisting of cellulose, were all classified as cellulosic due to the high similarity of their FTIR spectra and the difficulty of classifying them as a result of potential weathering processes (Cai et al., 2019; Suaria et al., 2020). Even though, it is clear that they all have an anthropogenic origin since even natural fibers like cotton or wool are frequently dyed and released with wastewaters. In particular, natural and regenerated (semi-synthetic) cellulose fibers are used in clothing and apparel, industrial textiles such as mechanical rubber goods, and feminine hygiene products.

In a relevant number of works, it has been highlighted that most of the fibers that can be found in the marine environment, either in the water column or in the sediments are cellulosic (Sanchez-Vidal et al., 2018; Suaria et al., 2020) which are particles of higher density than that of seawater and, therefore, may sediment if appropriate conditions are achieved. Thus, the data obtained in this work agrees with previous ones.

Concerning the rest of the fibers, eleven were polyesters -widely used in any type of clothing-, two were nylon -a polyamine also used in clothing, home furnishing and fishing gears-, one was acrylic -also used in clothing and home furnishings-, one polytetrafluoroethylene (PTFE) -with an extremely wide variety of applications-, one chlorinated polyethylene -used to cover power cords, also as component of plastics mixtures- and one alkyd -used in paints and varnishes-, while nine of them (6.5%) could not be identified as a result of a low matching percentage (< 70%). All these microfibers have a density higher than sea water (1.02 $g \cdot cm^{-3}$) and, therefore, are more likely to sink, despite sedimentation of non-spherical particles such as fibers is still poorly understood. Regarding the percentage of polymeric fibers other than cellulosic, our data also agree with previously reported ones (Sanchez-Vidal et al., 2018; Suaria et al., 2020).

Concerning the possible sources of microfibers in such areas, Fig. S7 of the Supplementary Material shows the location of the nearest wastewater discharge points as well as that of the sampling points. Besides, Table S2 of the Supplementary Material, compiles the different characteristics of such water discharges points. Both data were taken from the official website of Grafcan (GRAFCAN, 2017). As can be seen in the maps, some of them are quite near and may also directly contribute to the presence of microfibers in the area, since some of them release non treated waters, basically from stormwater drainages, while the rest only receive secondary treatment from a wastewater treatment plants (WWTP).

Concerning the presence of other discharge points in rest of the island, it should be mentioned that they are limited, and only existent in the east of the island, below Santa Cruz de La Palma sampling point. Two of the discharges are present in Breña Baja and come from a WWTP (03LPBB) and a stormwater drainage (02LPBB) while another one also belongs to a swimming pool (04LPSC) from Santa Cruz de La Palma and two small industrial discharges, one from the cooling of engines (01LPBA) and another discharge from a hydrocarbon separator located at the airport (01LPVM) (GRAFCAN, 2017).

3.5. Environmental physical forcing

Finally, in order to uncover the physical forcing that might be

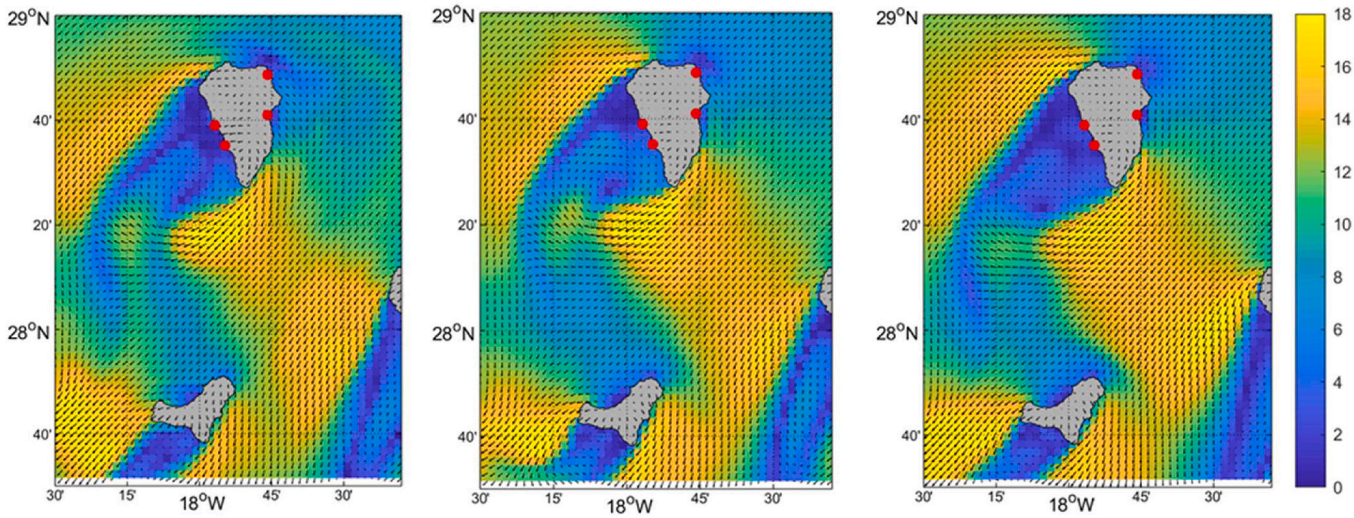

Fig. 6. Wind velocity and intensity (m·s^{-1}) at 10 m height during June 28th (left), July 10th (middle) and July 23rd of 2020 (right), as provided by the numerical model Harmonie.

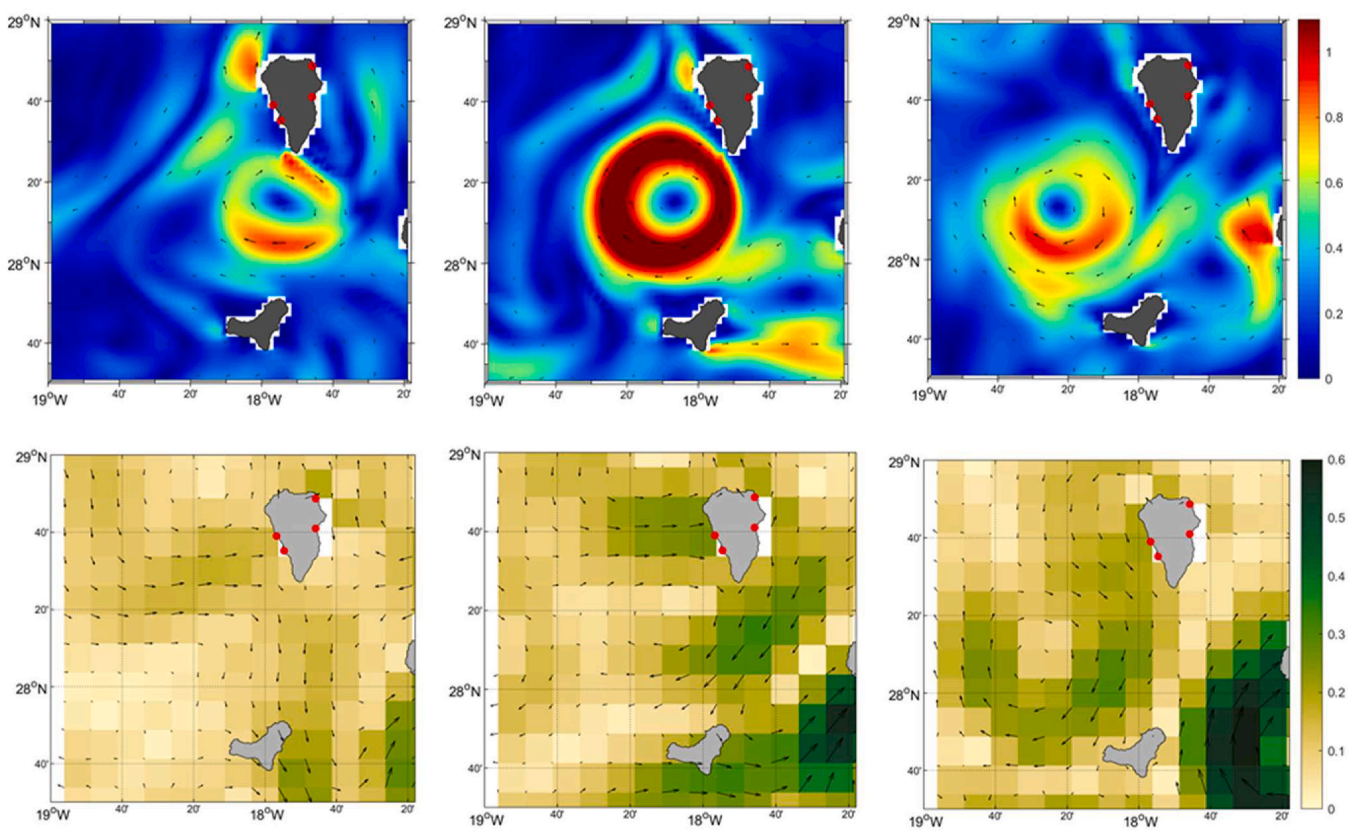

Fig. 7. Upper panels: Ocean velocity and intensity (m·s^{-1}) at the near surface during June 28th (left), July 10th (middle) and July 23rd of 2020 (right). Lower panels: Geostrophic velocity and intensity (m·s^{-1}) at surface obtained from altimetry observations during the same dates.

responsible for the previously mentioned microfibers spatial distribution of the region, the physical oceanographic environment was characterized by means of high spatial resolution databases. In particular, at the near surface microplastic spatial distribution responds to atmospheric and oceanic dynamics, so datasets from both environments should be considered (Van Sebille et al., 2020).

Physical forcing plays a main role in the spatial distribution of microplastics (Van Sebille et al., 2020). Here a plausible mechanism that combines the ocean and atmosphere dynamics is suggested to explain the variability observed in the microfibers distribution between the eastern and western sides of La Palma. In this context, microfiber deposition over the seabed is highly related to its residence time in the water column in a given domain, as shorter residence times would reduce the number of microfibers that would finally be part of the sediments. In turn, residence times are related to the wind speed and currents, as large speeds would drastically reduce microfibers residence times. Hence, low/high concentration of microfibers would be expected in places with high/low dynamics, respectively.

Three snapshots selected along the month before the in-situ sampling are taken to describe the temporal evolution in the environmental physical forcing. The wind field presented rather similar spatial distributions during the three dates selected. In all three cases, a uniform wind from the northeast (~ 8 m·s^{-1}) interacted with the island orography and accelerates to 16–18 m·s^{-1} at both the northwest and southeast of La Palma island (Fig. 6). A remarkable lee region develops in the western side of the island with an anticyclonic circulation and wind speeds below some 4 m·s^{-1}. It must be noticed that the orography of La Palma is characterized roughly by south to north ridge with heights well above 1,800 m, so a shelter effect in the lee region is indeed expected. In this respect, any microplastic close to the sea surface in the eastern side of La Palma would be shifted southwestward, with notable intensity at its southeast flank, a fact that would reduce their residence time in this eastern side of the island and their potential to sink over the sediments. Moreover, the steadiness in the pattern just described along the month before to the sampling would produce a significant amount of microplastics being driven from the east to the southwest of La Palma island. Then, the atmospheric anticyclonic circulation in the lee region would drift the microfibers to the coast with a relatively low speed (~ 4 m·s^{-1}), increasing their residence time and hence their potential to settle over the seabed.

On the oceanic side, an anticyclonic eddy started to develop south of La Palma by the end of June 2020, as revealed by the numerical model (Fig. 7). This mesoscale feature reaches its mature state by July 10th, and it detaches from La Palma by the end of July (see video of the Supplementary Material for its formation and evolution). The ocean currents at the surface (6 m depth) respond to the presence of this anticyclonic eddy, with northeastward velocity vectors pointing from the interior ocean to the western coast of the island. In addition, these northeastward velocity vectors occur precisely in the domain where the wind reduced its intensity because of the island shelter effect. This combined effect of atmospheric and ocean dynamics would allow microplastics to be driven northeastward by the surface currents within the lee region of the island and allowing a significant microfiber deposition over the seabed; even though, further studies/insights to clarify this issue would be necessary on a long-term basis.

Supplementary video related to this article can be found at https://doi.org/10.1016/j.chemosphere.2021.132530.

4. Conclusions

The analysis of subtidal sediments down to 5–7 m depth in four locations of La Palma island revealed the abundance of white/colorless microfibers of an anthropogenic origin, mainly cellulosic, between 1 and 2 mm long. Significant differences between sampling depths could not be observed; however, significant differences were evident between eastern and western sampling points suggesting a different microfiber deposition pattern, also reinforced by the difference in the granulometry of the sediments.

Atmospheric data also suggest that the wind field would be responsible for the microplastic wash out in the eastern side of La Palma, likely increasing their concentration southwest of the island. Subsequently, microfibers would be driven to the coast by the dynamics related to independent anticyclonic circulations developed south of the island in both the atmosphere and the ocean.

This study has confirmed the presence of microplastics in sediments of an oceanic island such as La Palma, providing the first report on microplastics in marine sediments of the Canary Islands region.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2021.132530.

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