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Organic pollutants in marine plastic debris from Canary Islands beaches

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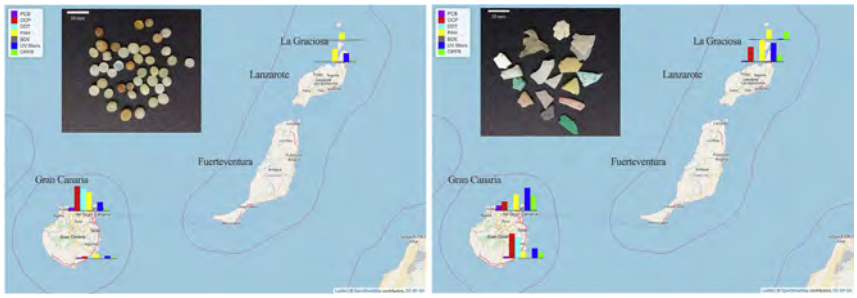
HIGHLIGHTS

- Pellets present higher contamination levels than plastic fragments
- High levels of DDT metabolites in the microplastic found in the coastal environment of the Canary Islands
- Higher levels of contamination were found in Gran Canaria, the most populated and industrialized island
- Part of the pollutant load in microplastic seem to be adsorbed from the coastal environment

GRAPHICAL ABSTRACT



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ABSTRACT

Given their capacity to adsorb chemical pollutants, microplastics represent a growing environmental concern in the oceans. The levels of 81 chemical compounds in two types of beached microplastic (pellets and fragments) were monitored across the Canary Islands (Spain). The highest concentrations were found for polycyclic aromatic hydrocarbons (PAH) (52.1–17,023.6 ng/g and 35.1–8725.8 ng/g for pooled pellets and fragments, respectively). The polychlorinated biphenyl (PCB) concentrations were 0.9–2285.8 and 1.6–772.5 ng/g for pooled pellets and fragments, respectively, whereas organochlorine pesticides (OCP) ranged from 0.4–13,488.7 and 0.4–3778.8 ng/g, respectively. The sum of polychlorinated biphenyls and diphenyl-dichloro-ethane (DDT) metabolites was significantly higher in beaches on Gran Canaria, which is the most populated and industrialized island. The sum of ultraviolet filters (UV-filters) was higher in those beaches more frequented by tourists (Famara and Las Canteras), than in occasionally or very rarely visited beaches (Cuervitos and Lambra), with values ranging from 0 to 37,740.3 ng/g and 3.7–2169.3 ng/g for pellets and fragments, respectively. Furthermore, the sum of brominated diphenyl ethers (BDE) (0–180.58 ng/g for pooled pellets and 0.06–3923.9 ng/g for pooled fragments) and organophosphorus flame retardants (OPFR) (20.0–378.0 ng/g for pooled pellets, and 22.6–7013.9 ng/g for pooled fragments) was significantly higher in an urban beach (Las Canteras) than in the rest of the studied beaches. Finally, the concentrations of the pesticide chlorpyrifos were much higher on Gran Canaria beaches than in the rest. In this research we provide further evidence of the important role of plastic debris in the adsorption of a wide range of marine pollutants. The regional pattern of chemical contamination of plastics reveals that the sorption of many compounds probably occurs in coastal waters. Further investigation is necessary to understand the relationship between plastic types and adsorption of different pollutants, especially for emerging pollutants.

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1. Introduction

Concern regarding the threat from plastics to the marine environment has grown in recent years. It has been estimated that between 4.8 and 12.7 million tonnes of plastic waste end up in the marine environment (Cozar et al., 2014; Jambeck et al., 2015), increasing its prevalence in the marine environment over the years. While macroplastics have been the main issue for some time due to their environmental consequences, more recently the so-called microplastics have gained relevance (Guzzetti et al., 2018). They are present in the environment as primary microplastic (virgin pellets coming from plastic manufacturing industries) or as a consequence of the degradation and fragmentation of larger plastic litter (secondary microplastic) (van Franeker and Law, 2015). The occurrence and distribution of microplastic in sediments worldwide have been the main focus of several studies, and most of the studies have been focused on sandy beaches because of their easy accessibility (Van Cauwenberghe et al., 2015).

Microplastic has become a major concern in the marine environment and biota because of its environmental persistence, its potentiality for trophic transfer and biomagnification in food chains, and the possible adverse consequences derived from its accumulation on biota (Lei et al., 2018a; Lei et al., 2018b; Wright et al., 2013). In fact, apart from the well-known negative impact of macroplastic ingestion in marine vertebrates and its physical effects (Derraik, 2002; Wright et al., 2013), smaller forms of litter plastic have been detected in marine biota (Tanaka et al., 2013). The adverse effects of microplastic on biota could be due to their own chemical composition, or through chemical compounds adsorbed onto their surface from the seawater (Teuten et al., 2009). It is known that hydrophobic pollutants are present in the seawater and can efficiently be adsorbed into microplastics (Bakir et al., 2014; Teuten et al., 2007; Teuten et al., 2009). In fact, the concentrations factors could reach ~10^6 relative to ambient seawater (Mato et al., 2001). By adsorbing hydrophobic chemical compounds, minute fragments of plastic debris become a source and sink of endocrine disrupting pollutants, which are efficiently absorbed from the digestive tract to the internal medium when the marine organisms ingest the microplastic (Slezakova et al., 2009). Thus, an increasing number of studies have monitored persistent organic pollutants (POPs) on microplastic samples as proxies for POP monitoring in marine environments (Heskett et al., 2012; Hirai et al., 2011; Le et al., 2016; Ogata et al., 2009; Taniguchi et al., 2016; Yeo et al., 2015).

Very few studies have reported either baseline data of microplastic in sediments (Baztan et al., 2017; Herrera et al., 2018), or the levels of pollutants associated with microplastics in the Canary Islands, Spain (Baztan et al., 2017; Heskett et al., 2012). Furthermore, according the literature, most of the previous studies monitoring chemical compounds in plastic debris have focused on the contamination of pre-production resin pellets rather than on small plastic fragments, foam, or macro-sized plastics (Hong et al., 2017). Therefore, the aim of this study was to monitor a wide suite of chemical compounds in stranded plastic debris (pellets and plastic fragments) from different beaches of the Canary Islands. We extracted and quantified the adsorbed persistent organic pollutants, such as organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), as well as semi-persistent contaminants such as polycyclic aromatic hydrocarbons (PAHs), and bromodiphenyl ethers (BDEs). In addition, we included a panel of selected emerging contaminants, such as organophosphorus flame retardants (OPFRs), chemical sunscreens (UV-filters), and the widely used pesticide chlorpyrifos. For this purpose, we collected samples from four beaches of three islands of the archipelago (Gran Canaria, Lanzarote, and La Graciosa), selected because of their different degrees of anthropogenic pressure (influence of tourism or vicinity of urban environments). All the selected beaches had a N or NE orientation attending to the prevalent marine current of this region. Data from both types of collected plastics and the four sampling sites were compared. To our knowledge, this is the first study reporting the adsorbed levels in plastic debris of some emerging pollutants such as UV-filters, OPFRs, as well as the widely employed organophosphate pesticide chlorpyrifos.

2. Material and methods

2.1. Sample collection and identification

All samples were collected between 2016 and 2017 in four beaches from the Canary Islands, Spain. The Canary Islands are an Atlantic archipelago comprised of eight islands that located south of 30°N, offshore of African. Fig. 1 shows the locations of the four beaches sampled from three different islands. In Gran Canaria island we sampled plastics from two beaches: an urban beach named "Las Canteras" which is located in the capital of the island (around 400,000 inhabitants) and an isolated beach named "Los Cuervitos" located on the east of the island, which is scarcely affected by tourism. On Lanzarote Island the samples were collected from "Famara" beach, a beach highly popular with tourists located in the north of the island, and finally, on La Graciosa Island we sampled plastic from a beach located in the northeast of the island - "Lambra" - which is recognized as a deserted, pristine beach.

Samples were collected at the high-tide line. Surface sand was collected with a metal spoon and placed in a 1 mm mesh bag. The bag was rinsed with distilled water until all the sand was removed so that only microplastics and organic matter larger than 1 mm were retained. The sample was dried at room temperature (approx. 25 °C) and finally, plastics were visually identified and separated with forceps from the organic material (Herrera et al., 2018). Two types of samples were differentiated: pre-production resin pellets and plastic fragments (Fig. 2). Plastic samples included in this study were separated into two classes, following the suggestion of plastic debris nomenclature based on size: large micro-debris (1–5 mm) consisting of pre-production plastic pellets, and meso-debris or mesoplastic (5–25 mm) consisting of plastic fragments. To perform the analysis of pollutants one gram from each type of plastic was randomly pooled in a glass tube, reaching a total of 133 samples of pooled pellets, and 119 samples of mesoplastic. This means that approximately 30 pools/beach of each type of plastic were obtained from the sampling campaigns carried out on the four beaches.

In order to obtain an idea of the polymer composition of the type of plastics collected, and in view of the impossibility of analyzing all the samples, a set of sub-samples, consisting on 20 pellets and 23 fragments were analyzed by Fourier transform infrared spectroscopy (FTIR) and calorimetry to determine their composition using an infrared spectrometer (Perkin-Elmer Spectrum BX from Perkin-Elmer Spain S.L., Madrid, Spain). 20 scans between 4000 and 600 cm^{-1} were performed with a resolution of 32 cm^{-1} in the reflection mode. Differential scanning calorimetry (DSC) was conducted in a Mettler-Toledo 821 calorimeter (Schwerzenbach, Switzerland) in air atmosphere, the heating program was from 30 to 300 °C at a heating rate of 10 °C min^{-1}.

2.2. Analytes of interest and chemical and reagents

All plastic samples (n = 252) were screened at the Laboratory of Toxicology of the University of Las Palmas de Gran Canaria (Spain), for the presence of the following anthropogenic contaminants: (a) 22 organochlorine pesticides (OCPs): aldrin, chlordane (cis- and trans-isomers), dicofol, dieldrin, p,p′-DDT and metabolites (p,p′ DDE and p,p′ DDD), o,p′ DDT and metabolites (o,p′ DDE and o,p′ DDD), endrin, endosulfan (α- and β-isomers), endosulfan-sulfate, hexachlorobenzene (HCB), the four isomers of hexachlorocyclohexane (α-, β-, γ-, δ-HCH), mirex, and methoxychlor; (b) 18 polychlorinated biphenyls (PCBs), including 6 congeners that are considered markers of environmental contamination (M-PCBs) and the 12 dioxin-like PCBs (DL-PCBs), which were numbered according to the International Union of Pure and Applied Chemistry (IUPAC): #28, 52, 77, 81, 101, 105, 114, 118, 123, 126, 138, 153, 156, 157, 167, 169, 180, 189; (c) the 16 polycyclic aromatic hydrocarbons (PAHs) in the USEPA priority list: acenaphthylene,

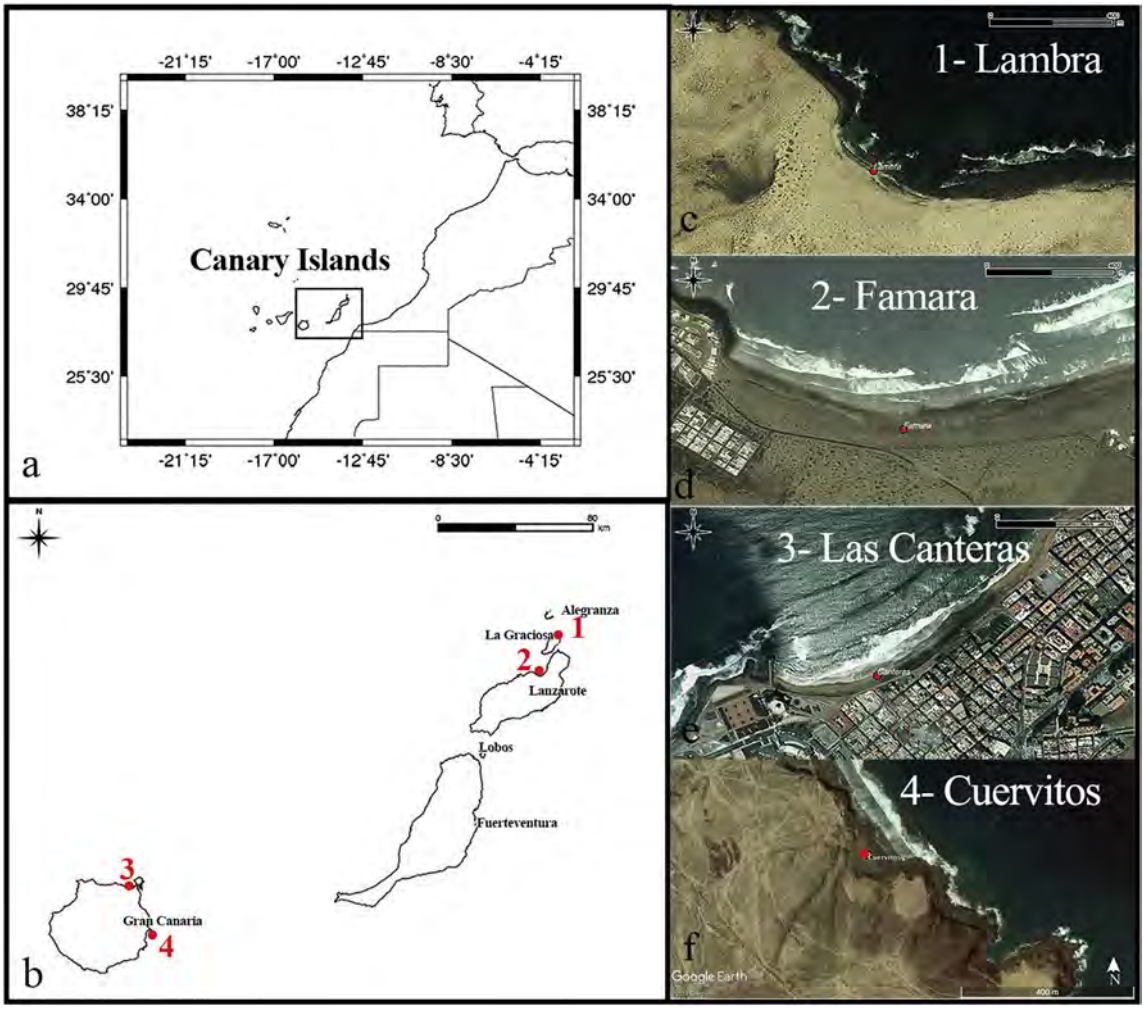

Fig. 1. Map of the Canary Islands, indicating the location of the four beaches sampled.

acenaphthene, anthracene, benzo[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*g,h,i*]perylene, benzo[*a*]pyrene, chrysene, dibenzo[*a,h*]anthracene, fluoranthene, fluorene, indeno[1,2,3,-c,d] pyrene, naphthalene, phenanthrene, and pyrene, of which carcinogenic PAHs were considered as a group as recommended (EFSA, 2008), and expressed as Σc-PAHs (the sum of benzo[*a*]pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*ghi*] perylene, dibenzo[*a,h*]anthracene, and indeno[1,2,3-*cd*]pyrene); (d) 8 polybrominated diphenylethers (PBDEs): congeners #28, 47, 85, 99, 100, 153, 154 and 183; (e) 11 organophosphate flame retardants (OPFRs): 2-ethylhexyldiphenyl phosphate, tri (2-ethylhexyl) phosphate, tributylphosphate, triethylphosphate, triisobutylphosphate, triphenylphosphate, tris ((2-chloro-1 chloromethyl)ethyl)phosphate, tris (2-butoxyethyl) phosphate, tris (2-chloroethyl) phosphate, tris (2-chloroisopropyl) phosphate, and tricresyl phosphate; (f) 5 ultraviolet filters (UVFs): 2-ethylhexyl 4-(dimethylamino)benzoate, 2-Ethylhexyl

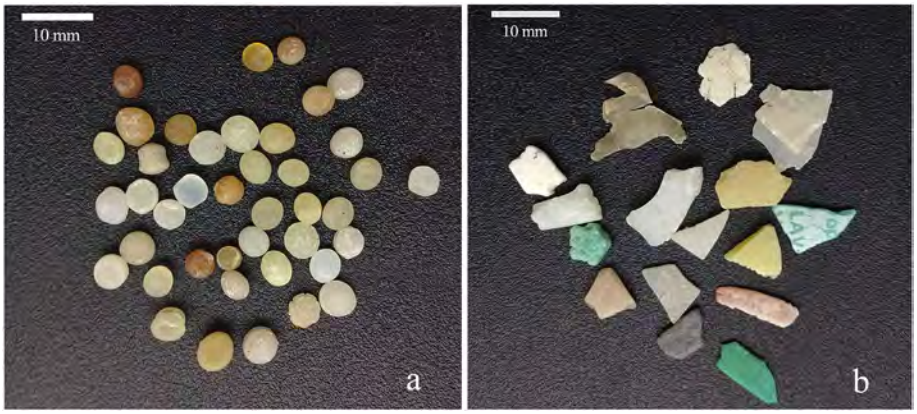

Fig. 2. Types of microplastic included in the study. (a) pre-production plastic pellets; (b) plastic fragments (mesoplastic).

p-methoxycinnamate, homosalate, 3-(4-methylbenzylidene) camphor, and 3-benzylidenecamphor; and (g) the widely employed organophosphate pesticide chlorpyrifos.

Stock solutions of each compound at 1 mg/ml were prepared in cyclohexane and stored at −20 °C. Diluted solutions from 0.1 ng/ml to 2000 ng/ml were used for calibration curves (10 points) in cyclohexane containing 1% olive oil as analyte protectant to help minimize the errors caused by matrix-induced signal enhancements, as described previously (Lynam and Smith, 2011). PCB 202, tetrachloro-m-xylene, p,p′ DDE-d8, heptachloro epoxide cis, diazinon-d10, and phenanthrene-d10 were employed as internal standards (ISs). All the standards were neat compounds, and were acquired from Dr. Ehrenstorfer Reference Materials (Augsburg, Germany). Cyclohexane (CHX) and ethyl acetate (AE) were of mass spectrometry grade (Merck, Darmstadt, Germany).

2.3. Extraction of chemical compounds from micro and macro-plastic and chemical analysis

A liquid-solid extraction was used for the extraction of target analytes. 5 ml of a mixture of CHX:AE (1:1) were added to each sample in amber glass vials, previously cleaned with CHX:AE (1:1). The vials were vigorously shaken and placed in an ultrasonic bath for 20 min. An orbital rotator was used over 24 h to allow the samples to soak in the solvent. The solvent was transferred to a new vial, and the extraction process was repeated two more times (24 h each). After 72 h we had recovered a total volume of 15 ml of CHX:ACE, which was considered to contain the entire quantity of chemical compounds adsorbed in plastic (previous experiments have demonstrated that further 24-h-extraction periods did not produce a significative increase in the recovery of chemical compounds; data not shown). The solvent was filtered through 0.45 μm using syringe disc filters and evaporated under a gentle N_2 stream and resuspended in 1 ml of CHX:ACE. The samples were considered ready for chromatographic analysis without any additional step of purification.

The determination of chemical was performed using a gas chromatography separation with a triple quadrupole mass spectrometer (QqQ; GC System 7890B and MSMS 7010 of Agilent Technologies, Palo Alto, CA, USA). Chromatographic separations were performed employing two 15-m capillary columns (Agilent J&WHP-5MS), which were connected in series using a Purged Ultimate Union (PUU, Agilent Technologies). The use of these two columns allowed employment of the back-flushing technique (constant flow rates of 1.2 ml/min of helium (99.999%) for column 2 and 1.0 ml/min for column 1). The temperatures of the GC oven were programmed as follows: a) initial temperature: 60 °C for 1 min; b) ramp 1: 40 °C/min to 170 °C; c) ramp 2: 10 °C/min to 310 °C; d) hold time: 3 min. Total run time was 20.75 min. Transfer line and injector were both set at 280 °C. Standards and samples were injected (1 μl) in the splitless mode.

Retention Time Locking (RTL) of the analytes with chlorpyrifos-methyl (Rt = 9.143 min) as the time reference was used. The QqQ mass spectrometer was operated under the previously described conditions (Henriquez-Hernandez et al., 2017). Nitrogen (99.999%) was used as the collision gas. Collision gas flow was set at 1.5 ml/min.

The quantification was based on peak areas, using 10-point calibration curves. These calibration curves were constructed using a least-squares linear regression from the injection of standard solutions (1% olive oil). The limits of quantification (LOQ) varied among compounds and ranged from 0.03 to 0.15 ng/g (Henriquez-Hernandez et al., 2017). The results of this study have been expressed in ng contaminant per gram of plastic (ng/g).

2.4. Quality assurance and quality control

In each batch of samples, three controls were included for every 18 vials: a reagent blank consisting of a vial containing only CHX (1% olive oil); a vial containing 2 ng/ml of each of the pollutants in CHX (1% olive oil); and an internal laboratory quality control sample (QC) consisting of CHX spiked at 10 ng/ml of each of the analytes, which was processed using the same method as the plastic samples of each series of solid-liquid extraction. The results were considered to be acceptable when the concentration of the analytes determined in the QC sample was within 15% deviation from the theoretical value.

2.5. Statistical analysis and calculations

Database management and statistical analysis were performed with PASW Statistics v 20.0 (SPSS Inc., Chicago, IL, USA). To ensure enough statistical power, only chemical pollutants detected in ≥50% of the series were included in the analyses, except when the sums of total analytes per group were considered. Because the data did not follow a normal distribution, the statistical analyses involved the use of non-parametric tests. The differences of contaminants between two independent groups were tested with the Mann–Whitney *U* test and Kruskal-Wallis test. P values of 0.05 (two-tailed) were considered statistically significant.

Given the large volume of data (81 pollutants in two types of microplastic from 4 sampling sites), only the summed concentrations of PCBs, OCPs, DDTs, PAHs, PBDEs, UV-filters, OPFRs and chlorpyrifos at each sampling site are shown in the main body of the manuscript. The concentrations of individual contaminants are provided as Supplementary material. To assess the level of contamination associated to microplastic on a regional scale (the Canary Islands archipelago), we also considered all the samples collected as a single group, which comprised of the data of 133 pools of pellets and 119 pools of mesoplastic.

3. Results and discussion

As far as we know, this research reports the largest series of pollutants associated with microplastics published to date (81 chemical compounds), covering with sampling the most developed island region of the Mid-Atlantic, the archipelago of the Canary Islands (Tables 1 to 3 and Supplementary Tables 1 to 5). Our sampling was intended to determine the contaminants in random pools of plastics found in the tidal line, which are those that will be available for ingestion by organisms, mainly seabirds. We were interested in studying pellets and fragments separately, since pellets, being virgin material, could have fewer additives than fragments of plastic objects, to which flame retardants and other additives may be added. The compositional analysis of a subset of samples indicated that most of the pellets analyzed (95%) were classified as polyethylene (PE) and 5% as polypropylene (PP); while the 78.3% of the fragments were classified as PE; 17.4% as PP and only 1 fragment (4.3%) as a thermoplastic elastomer.

In general terms we can say that this work presents four relevant findings: i) we find levels of contamination by POPs that are comparable to those of other highly polluted regions of the planet; ii) we report for the first time the levels of plastic contamination by several groups of emerging pollutants (such as OPFRs, ultraviolet filters, or the chlorpyrifos pesticide); iii) we find that contamination of mesoplastic is greater than that of pellets ($P < 0.001$); and iv) that the levels of pollutants associated with plastics found on much-visited beaches are much higher than those found on deserted beaches, which would indicate that there is a source of contamination in the beach itself (coastal waters) in addition to that produced in the open sea.

In the following sections, we present and discuss these findings in detail.

3.1. Profiles of the pollutants associated to microplastic from the Canary Islands

3.1.1. Persistent organic pollutants

In this study we included 38 chemical compounds that are usually classified as POPs, and 18 of them were detected in >50% of the samples.

Table 1
Concentrations of total PCBs, and OCPs (the DDTs are show separately) measured in plastic pellets and fragments from four sampling sites of the Canary Islands. The results are reported as nanograms of total pollutant type per gram of plastic particles (ng/g).

Type	Location		Compound [concentrations in ng/g]		
			∑PCBs	∑OCPs	∑DDTs
Pellets	Canteras	Range	28–2285	21–13,523	16–13,488
		Median	137.9	1059.3	993.5
		P_{90}	928.5	2240.4	2013.3
	Cuervitos	Range	29–329	40–3421	25–835
		Median	52.8	91.6	76.5
		P_{90}	147.7	1341.2	332.1
	Famara	Range	4–72	4–5786	0.4–5780
		Median	7.7	7.9	1.8
		P_{90}	25.3	775.8	738.3
	Lambra	Range	0.9–43	0.9–29	0.5–5
		Median	5.3	2.2	1.2
		P_{90}	11.5	7.9	3.6
Fragments	Canteras	Range	12–772	15–8444	6–2916
		Median	59.5	106.2	32.4
		P_{90}	306.6	6793.2	823.1
	Cuervitos	Range	7–318	25–40,275	24–3778
		Median	20.9	285.6	241.6
		P_{90}	102.5	3588.5	1115.5
	Famara	Range	1–118	0.7–17,725	0.4–524
		Median	12.3	172.7	6.4
		P_{90}	29.6	5616.1	491.5
	Lambra	Range	1.7–43	0.82–180	0.4–74
		Median	8.0	5.5	2.7
		P_{90}	28.1	54.7	24.4

Table 3
Concentrations of total UV Filters, and OPFRs measured in plastic pellets and fragments from four sampling sites of the Canary Islands. The results are reported as nanograms of total pollutant type per gram of plastic particles (ng/g).

Type	Location		∑UV-Filters	∑OPFRs
Pellets	Canteras	Range	70.1–1082.0	38.2–378.1
		Median	373.5	78.2
		P_{90}	704.2	335.3
	Cuervitos	Range	30.3–1154.1	20.1–141.2
		Median	117.0	52.3
		P_{90}	364.9	107.3
	Famara	Range	83.2–3740.1	29.2–123.1
		Median	369.5	57.9
		P_{90}	1449.9	98.7
	Lambra	Range	0.0 – 534.1	27.2–292.4
		Median	12.9	56.2
		P_{90}	29.3	102.7
Fragments	Canteras	Range	102.1–1517.2	56.1–5358.3
		Median	264.1	176.9
		P_{90}	869.9	814.1
	Cuervitos	Range	15.1–1106.2	39.2–900.3
		Median	115.5	68.5
		P_{90}	512.9	220.6
	Famara	Range	52.1–216.1	35.0–7013.2
		Median	217.6	73.3
		P_{90}	533.6	268.6
	Lambra	Range	3.7–48.1	22.2–2758.4
		Median	12.3	93.0
		P_{90}	28.6	658.5

Table 1 shows the results of ∑PCBs, ∑OCPs, and ∑DDTs per sampling site and microplastic type.

Regarding the group of PCBs, 11 compounds were frequently detected (>50% of samples; congeners #52, 77, 101, 105, 118, 138, 153, 156, 167 and 180). Fig. 3 shows the range of concentrations of the sum of these congeners according to sampling place and type of microplastic (see detailed graph in Supplementary Fig. 1 and the numerical data in Supplementary Table 1). Marker PCBs (#28, 52, 101, 138, 153, and 180) were detected in virtually 100% of samples (99.8%), while the dioxin-like PCBs (#77, 105, 118, 156, and 167) were detected in 85% of the pellets and 97.5% of plastic fragments studied. The PCB congeners that reached the highest concentrations in all beaches were #153 and #180 in both pellets and fragments. Our data are similar to those reported by other authors on plastic debris from industrialized areas all over the world (Antunes et al., 2013; Frias et al., 2010; Karapanagioti et al., 2011; Mizukawa et al., 2013; Taniguchi et al., 2016). However, other authors have reported a different pattern of contamination by the congeners of this chemical group (Hirai et al., 2011; Jayasiri et al., 2015; Rios et al., 2007). Nevertheless, the profiles reported in this study are consistent with those previously reported for marine biota from the same region (e.g., fish (Henriquez-Hernandez et al., 2017; Rodriguez-Hernandez et al., 2016), sea turtles (Camacho et al., 2013; Camacho et al., 2014), or dolphins (García-Álvarez et al., 2014a)), with a predominance of highly chlorinated congeners in all of them. The median values of the sum of PCBs by type of microplastic (without dividing by sample sites) were 28.15 ng/g and 17.23 ng/g for pellets and fragments, respectively. These values are consistent with those previously reported for African countries (Ogata et al., 2009) or Southeast Asian countries (Le et al., 2016; Ogata et al., 2009), but lower than those reported for Western European countries, such as The Netherlands, UK and Italy (Ogata et al., 2009) or Portugal (Antunes et al., 2013). On the contrary, our results were higher than those found for pellets and mesoplastic collected from beaches in California (Van et al., 2012). Like in previous reports, we found a large variability of ∑PCBs from sample to sample, in both pellets (0.9–2285.8 ng/g) and fragments (1.6–772.5 ng/g). Some authors have indicated probable reasons for this variability in plastic debris contamination, suggesting that the time of permanence in seawater and the transit through oceanic zones with different levels of pollution play a determining role (Endo et al., 2005). The adsorption of seawater contaminants to plastic, even with these chemicals being hydrophobic, takes up to 80 days to reach equilibrium (Karapanagioti and Klontza, 2008). That is why it is possible that fragments of microplastic that are dragged by the currents can pass through highly contaminated areas before they reach this equilibrium. Given that some plastic fragments can concentrate very high amounts of pollutants, some authors have suggested they might represent a very important source of exposure to pollutants for marine biota via ingestion (Endo et al., 2005).

Regarding organochlorine pesticides, we found that seven of them were present in >50% of the samples (p,p′-DDD, o,p′-DDE, p,p′-DDE,

Table 2
Concentrations of total PAHs, and PBDEs measured in plastic pellets and fragments from four sampling sites of the Canary Islands. The results are reported as nanograms of total pollutant type per gram of plastic particles (ng/g).

Type	Location		∑PAHs	∑BDEs
Pellets	Canteras	Range	135.2–7606.4	0.1–175.1
		Median	805.7	3.1
		P_{90}	1908.5	33.0
	Cuervitos	Range	52.0–17,068.7	0.4–6.2
		Median	203.8	1.4
		P_{90}	812.2	3.3
	Famara	Range	283–4020	1.0–180.2
		Median	568.4	3.0
		P_{90}	1148.8	16.6
	Lambra	Range	78.1–2667.4	0.0–7.1
		Median	312.8	0.5
		P_{90}	794.6	2.1
Fragments	Canteras	Range	83.2–1494.3	0.6–870.2
		Median	189.0	3.3
		P_{90}	562.2	100.8
	Cuervitos	Range	41.8–8725.3	0.3–34.1
		Median	77.9	1.3
		P_{90}	147.7	8.3
	Famara	Range	92.1–1032.5	0.4–3923.2
		Median	253.8	1.8
		P_{90}	759.2	80.1
	Lambra	Range	35.3–399.7	0.1–49.3
		Median	115.0	2.7
		P_{90}	292.2	20.6

HCB, heptachlor, dieldrin and mirex) (Supplementary Table 2). The compound present in the highest concentrations, not only of its chemical group but among all the POPs included in this study, was the p,p′-DDE, which reached median levels of 56.0 ng/g in the pellets collected in the urban beach "Las Canteras", in Gran Canaria. In fact, the DDT group and its metabolites generally showed high concentrations in the microplastics sampled in Gran Canaria (Table 1, Fig. 3, Supplementary Fig. 2 and Supplementary Table 2).

In fact, although high levels of these compounds have been reported in all types of samples from the Canary Islands before (Camacho et al., 2013; Diaz-Diaz and Loague, 2001; García-Álvarez et al., 2014b; Henriquez-Hernandez et al., 2016; Zumbado et al., 2005), it is surprising that these levels are still comparable to those described in countries where DDT continues to be used legally to combat malaria vectors (Hirai et al., 2011; Jayasiri et al., 2015; Ogata et al., 2009; Taniguchi et al., 2009). These levels are much higher than those generally reported for geographical areas where these compounds were banned decades ago, as is also the case with the Canary Islands (Frias et al., 2010; Heskett et al., 2012; Mato et al., 2001; Van et al., 2012), although there are reports of high levels in areas where these pesticides have not been used since the 1980s (Rios et al., 2007). Geographically, the Canary Islands are part of the African continent, and some publications have

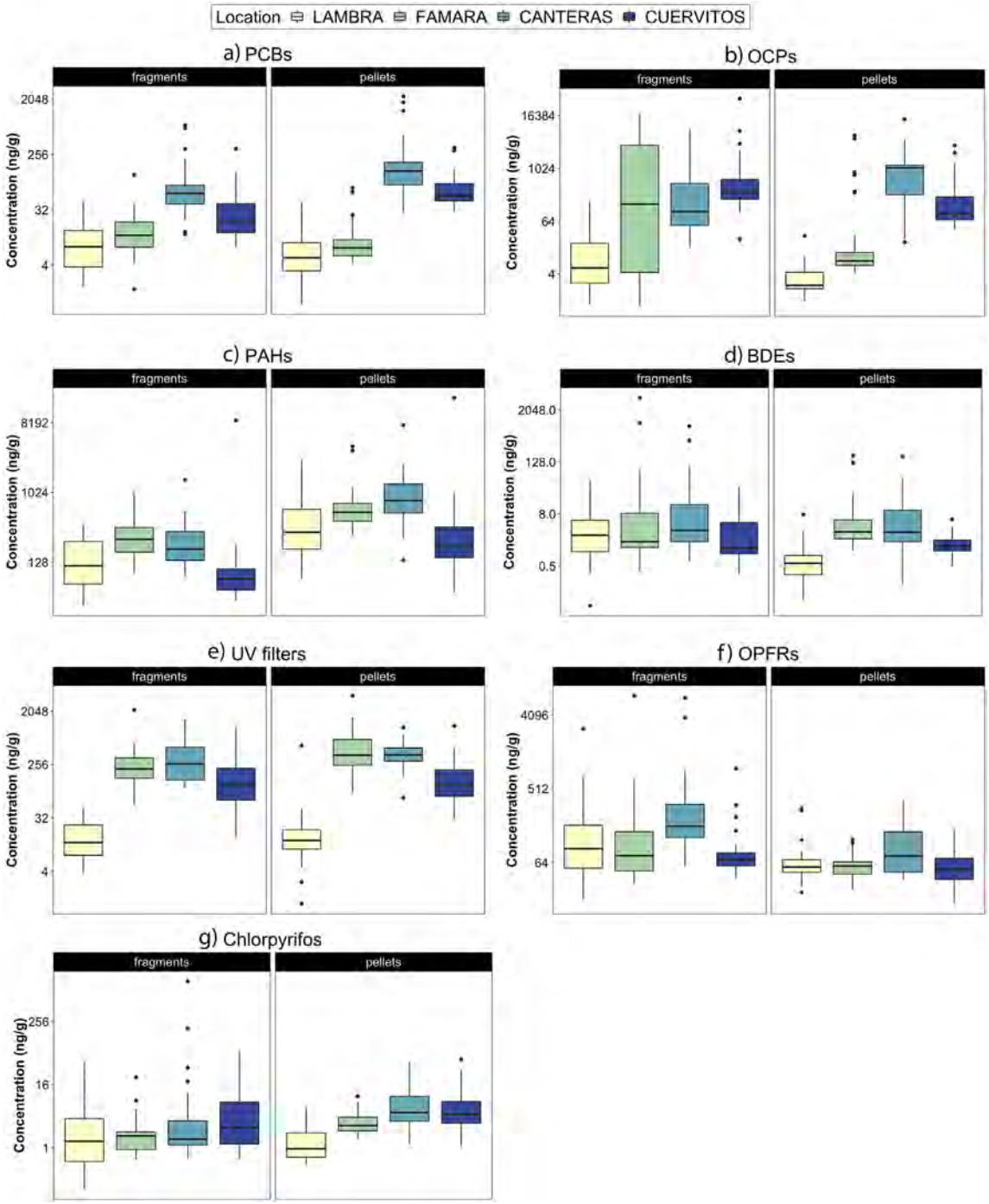

Fig. 3. Concentrations of the sum of chemical pollutants by chemical group in pre-production plastic pellets (a), and in plastic fragments (mesoplastic) (b). Y axis was $\log^2$ transformed in order to improve data visualization. The central thick line of each box designates the median, the box height shows the interquartile range, the extreme lines shows the highest and lowest value excluding outliers.

pointed to the proximity to countries such as Morocco being potentially responsible for the high levels of contamination of the archipelago by OCPs. However, a recent work of our group has shown how the levels of DDTs and other OCPs in the population of Morocco and the western coast of the Sahara are lower than those among the inhabitants of the Canary Islands (Henriquez-Hernandez et al., 2016). Therefore, it is plausible that these levels of contamination of the plastic - which are consistent with previous reports on samples of all kinds from this Atlantic archipelago - are due to the intensive use of these products in this region in the past (Diaz-Diaz and Loague, 2001; Zumbado et al., 2005), and that this may have occurred in the coastal environment of the islands, at least in part.

3.1.2. Semi-persistent organic pollutants

In the first place, it was remarkable that we found residues of the majority of PAHs in the USEPA list (EPA, 2001) in >50% of the microplastic samples (13 out of 16 compounds, including 4 carcinogenic chemical compounds) (Fig. 3, Table 2, Supplementary Table 3, and Supplementary Fig. 3). The median values for the complete series of samples were 528.3 ng/g for the pellets (range 52.1–17,023.6 ng/g) and significantly lower in the plastic fragments (147.5 ng/g, range 35.1–8725.79 ng/g; <0.001). Comparison with the literature does not clarify much about the source of pollution in the Canary Islands, since our values are consistent with those described by some authors who have sampled at different locations on the planet (Hirai et al., 2011), but are much higher than those reported in samples from Greece, Mexico, USA or China (Karapanagioti et al., 2011; Rios et al., 2007; Van et al., 2012; Zhang et al., 2015), though much lower than those reported from Brazil or Portugal (Antunes et al., 2013; Fisner et al., 2013). We find it interesting to highlight that the profile of contamination by PAHs of the pellets and fragments was not only quantitatively different but also compositionally. Thus, while the contamination of the pellets was dominated by high molecular weight compounds (tetra- to hexacyclic PAHs), the opposite happened in the plastic fragments, in which the low molecular weight compounds were predominant ($P < 0.001$). In any case, the phenanthrene/anthracene ratio was lower than 10 in the two types of samples, suggesting a contamination of pyrolytic origin rather than petrogenic origin (Budzinski et al., 1997). This could explain the fact that the highest levels of contamination by this group were found in the samples of the urban beach of "Las Canteras", since this beach is located within the area of influence of the port of Las Palmas de Gran Canaria, which occupies the 98th position among ports with the highest container traffic in the world. A very important source of contamination by PAHs of pyrolytic origin is the incomplete combustion of the fossil hydrocarbons derived from multiple port activities and refineries (Bayona et al., 1993). This would possibly indicate once again that a part of the contamination of the microplastics found on the beaches occurs either in situ or in the nearby coastal environment.

In relation to the group of BDEs, we detected congeners # 28, 47, 99 and 100 in >50% of the samples (Table 2, Supplementary Table 4, and Fig. 3). There are limited studies that have studied these compounds in oceanic microplastic (Hirai et al., 2011; Taniguchi et al., 2016), so it is difficult to contextualize our findings. In addition, among the available studies, Hirai et al. (2011) reported that the most frequently detected and concentrated compound was BDE 209. Unfortunately, due to a technical limitation, this congener was not included in our study. However, among the determined compounds in this group, BDE 47 was the most frequently detected and concentrated (Fig. 3, Supplementary Fig. 4, Supplementary Table 4), and this finding was consistent with that of Taniguchi et al. (2016), who also did not include BDE 209 in their study. For the total of the series, we found median levels of $\sum$BDEs of 1.9 ng/g in the pellets (range 0–180.6 ng/g), and 2.3 ng/g in the mesoplastic (0.1–3923.9 ng/g). The values reported so far in the literature range between 0.7 and 5.6 ng/g in Brazilian beaches (not including BDE 209) (Taniguchi et al., 2016), and between 0.3 and 9909 ng/g in microplastic collected in open sea and beaches (both deserted and urban), but including in this case BDE 209 (Hirai et al., 2011).

3.1.3. Emerging organic pollutants

There are >700 substances from 20 different chemical classes that have been identified in the aquatic environment. Many of them are classified as emerging pollutants (EPs). These are chemical compounds that are not commonly monitored but have the potential to enter the environment and cause adverse ecological and human health effects (Geissen et al., 2015). Among them, we have selected two chemical classes that have been identified by the European Union as of concern, the OPFRs (11 compounds) and UV-filters (5 compounds) (https://www.hbm4eu.eu/the-substances/). In addition, we have included the pesticide chlorpyrifos, of which >1200 tons a year are sold around the world (Saunders et al., 2012). As far as we know there is no previous study that has reported the levels of contamination in plastic by these chemical compounds. Surprisingly, we found that 13 of the 17 EPs were present in >50% of the samples (3 UV filters, 9 OPFRs, and chlorpyrifos).

Within the group of organic UV-filters, the most frequently detected and concentrated compounds were homosalate and 2-Ethylhexyl p-methoxycinnamate, but 3-benzylidenecamphor was also detected in >50% of the samples of both types of microplastic. The levels of the $\sum$UV-filters were higher in the pellets (median 231.7 ng/g, range from 0 to 3740.3 ng/g) than in the fragments (median 136.4 ng/g, range 3.7 to 2169.3 ng/g) ($P < 0.01$) (Fig. 3, Table 3, Supplementary Table 5, and Supplementary Fig. 5). These results are unsurprising. It is estimated that hundreds of tons of this type of chemical sunscreens are produced each year (Buser et al., 2006), and the Canarian archipelago, with >300 sunny days a year, is one of the main tourist beach destinations of the EU, receiving >13 million tourists annually. It is therefore expected that in the coastal environment of these islands there will be relatively high concentration of cosmetic products, and in particular sunscreens, which would be released directly into sea water, when this huge number of people bathe on the beaches. In fact, previous studies had already shown the presence of several of these compounds in the seawater of the beaches of these islands (Sanchez et al., 2015), as well as in their coastal fish (Henriquez-Hernandez et al., 2017). Some studies have indicated that UV filters pose a significant potential for estrogenic activity (Schlumpf et al., 2001). The growing concern about the accumulation of plastic debris and possible ingestion by marine organisms (and possibly by humans) makes the determination of these endocrine disruptors an important target of future studies.

Regarding other emerging pollutants of concern - the OPFRs - we found that the values were significantly higher in the plastic fragments (median 87.9 ng/g) than in the pellets (median 60.1 ng/g) ($P < 0.001$). We were struck by the enormous variability in concentrations among mesoplastic samples (22.6–7013.9 ng/g), which was much higher than that found among the pellets (20.1–378.1 ng/g) (Fig. 3, Table 3, Supplementary Table 6, and Supplementary Fig. 6). A possible explanation for this is that mesoplastic constitutes a highly heterogeneous type of sample. These fragments may come from a high variety of plastic types, and flame retardants, including OPFRs, are frequently employed to delay the spread of fire after the ignition of commercial products containing some plastic types (Hanari et al., 2017). Therefore, the fragments derived from these plastics would contain high concentrations of OPFRs as well. OPFRs have been reported previously in seawater (Hu et al., 2014), but in the parts-per-trillion range. However, the reported levels are much higher in marine biota (Henriquez-Hernandez et al., 2017). It is possible that the ingestion of contaminated plastic by these fish plays a relevant role in the trophic transfer of these pollutants. However, this hypothesis remains to be confirmed pollutant by pollutant, since some of these chemicals might have such a strong affinity that they do not desorb in the guts of organisms.

Finally, we also found the non-persistent pesticide chlorpyrifos bound to microplastic. This is a highly employed insecticide in the agriculture of the Canary Islands (i.e. banana production). In fact, this was the most frequently detected residue in bananas in a pesticide monitoring study conducted between 2014 and 16 in this archipelago (http://pervemac.itccanarias.org/resultados/). Its concentrations were higher in pellets (median 3.1 ng/g; range 0.5 to 48.4 ng/g) than in mesoplastic (median 1.6 ng/g; range 0.0 to 1508 ng/g). Again, the variability in fragments was much higher than in pre-production plastic pellets (Supplementary Fig. 7). As it occurs with the other emerging pollutants reported in this study, there are no data in the literature to compare with (for chorpyrifos in microplastic), although recent reports have indicated that chlorpyrifos has been detected at relatively high concentrations in coastal waters (Liu et al., 2018), in surface marine sediments (Moreno-Gonzalez and Leon, 2017), and in marine biota (Henriquez-Hernandez et al., 2017). However, further monitoring studies that include these emerging contaminants in plastic debris are needed.

3.2. Variability of the concentrations of pollutants in microplastic among beaches of the Canary Islands

As shown in Table 1, the pre-production resin pellets showed significantly higher values of ∑PCBs in three of the four beaches (Las Canteras Beach: MW, $P < 0.001$; Cuervito Beach: MW, $P < 0.001$; Famara Beach: MW, $P < 0.05$) than the values detected for plastic fragments. Examining differences among sampled beaches, all individual congeners show statistically differences among the beaches (Supplementary Table 1). Therefore, statistical differences were also observed among the four sampling sites and ∑PCBs levels (Kruskal-Wallis test; $P < 0.001$ for both types of plastics). We found the highest values of ∑PCBs in "Las Canteras" beach, reaching median values of 137.9 ng/g (pellets) and 59.48 ng/g (plastic fragments), followed by "Cuervitos" (52.8 and 20.91 ng/g for pellets and fragments, respectively). It is noteworthy that both beaches are located in Gran Canaria, which is the most populated and industrialized island of the archipelago. These values were several times higher than those in microplastic from beaches in much less populated and industrialized islands. This is consistent with previous reports, which have indicated that microplastic in beaches from industrialized areas (Endo et al., 2005; Jayasiri et al., 2015; Karapanagioti et al., 2011; Mato et al., 2001), as well as that found in urban beaches (Hirai et al., 2011), is more contaminated than that in remote beaches and the open sea. In previous publications relating to scarcely industrialized islands of this archipelago, such as Fuerteventura, the authors also reported much lower levels of ∑PCBs (Heskett et al., 2012). Nevertheless, according to the 1 to 5 classification of the level on PCB contamination of microplastic proposed by the International Pellet Watch global monitoring program (IPW; http://www.pelletwatch.org/), Gran Canaria beaches have a moderate pollution level (3) and the rest of the beaches sampled in this research could be categorized as categorized as slightly contaminated.

Something similar occurred with the other group of persistent pollutants -the OCPs - given that the urban beach of "Las Canteras" was the most polluted by far (up to 2 orders of magnitude higher than that in the rest of the beaches). Since this chemical group was clearly dominated by the DDTs group, these differences were reproduced for these pesticides as well (Table 1). In fact, we found a sample with an extreme value (13,488 ng/g of ∑DDTs) in "Las Canteras" beach, which is the highest value reported worldwide, at least among those recorded by the IPW. It is also remarkable that >50% of the microplastic sampled in "Las Canteras" beach presented levels of ∑DDTS >1000 ng/g, which can be considered very high in comparison with those reported in many other parts of the world. However, although the levels of the other beach of Gran Canaria - "Cuervitos" - may be considered high as well (Table 1, around 100 ng/g), those of the beaches of Lanzarote and La Graciosa are within the average levels worldwide, and consistent with those previously reported for the islands of Fuerteventura and Lanzarote (Heskett et al., 2012). As discussed above, it is very likely that the high level of microplastic contamination by OCPs found on the beaches of Gran Canaria has to do with the intensive use that was made of this pesticide in the island's agriculture in the past. Previous biomonitoring studies of the population of the archipelago already showed a positive correlation by islands between the current levels of contamination by DDT of the inhabitants and the total area devoted to intensive agriculture that employed these insecticides in the past (Zumbado et al., 2005).

With regard to the levels of semipersistent pollutants - PAHs and BDEs - it was again the case that the microplastic of "Las Canteras" beach presented the highest levels, although the statistically significant differences were much less striking than in the previous cases (Table 2 and Supplementary Tables 3 and 4). It is possible that the urban environment in which this beach is located can explain these differences, since other authors have reported higher levels of contamination in microplastics collected in areas of influence of anthropogenic activities, at least with respect to PAHs (Hirai et al., 2011).

With respect to EPs in microplastic, the highest concentration of UV-filters was found in beaches where the anthropogenic presence was greater (Las Canteras and Famara beach). Sanchez et al. (2015) had previously detected UV-filters in surface waters of six beaches from Gran Canaria with significant tourist pressure. These authors reported levels of 94.3 ng/L in waters from Las Canteras Beach (Sanchez et al., 2015). Finally, and in a manner consistent with what was described for the previous chemical groups, the microplastics collected at the beach of "Las Canteras" (or at the beaches of the island of Gran Canaria) were also the most contaminated by OPFRs and chlorpyrifos.

4. Conclusions

In this study of monitoring of pollutants associated with different types of microplastic, data from a little-studied geographical area are provided, and data from emerging pollutants from the seas and oceans in this material are also provided for the first time. In this paper, we describe quite high levels of organochlorine pesticides in the plastic found in the Canary Islands, among the highest reported in the world. This is consistent with previous studies that have indicated that this is a region heavily contaminated by these pesticides as a result of intensive past use. We also found that the beaches of the island of Gran Canaria, and in particular the urban beach of "Las Canteras" presented the most contaminated plastics by practically all the chemical groups included in this study, presenting levels similar to those found in highly industrialized regions and contaminated areas of the planet. It was a very striking fact that the UV filters in microplastic faithfully followed the pattern of tourist use of the beaches, being much higher in the plastics found on the beaches most frequented by bathers. These results seem to indicate that at least part of the microplastic contamination that appears on the beaches occurs locally, on the beach itself or in coastal areas. Consequently, the analysis of the pattern of contaminants associated with microplastic is important, not only because of the risk of exposure to this material for marine fauna, for ecosystems and for humans, but also because it would allow monitoring of contaminant levels of the region and the coastal areas in which they are found. In any case, future studies that evaluate such colour, size, type, and temporal variations will help to better understand the concentration and patterns that we currently observe.

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Competing financial interest declaration

There are no actual or potential conflicts of interest to declare for any author.

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