Organic pollutants in marine plastic debris from Canary Islands beaches

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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 35.1-8,725.8 ng/g for pooled pellets and fragments, respectively). The polychlorinated biphenyl (PCB) concentrations were 0.9-2,285.8 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 0.4-3,778.8 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 0-37,740.3 ng/g and 3.7-2,169.3 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 22.6-7,013.9 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.

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

72 hydrophobic pollutants are present in the seawater and can efficiently be adsorbed into
73 microplastics (Bakir et al., 2014; Teuten et al., 2007; Teuten et al., 2009). In fact, the
74 concentrations factors could reach ~ 10^6 relative to ambient seawater (Mato et al., 2001).
75 By adsorbing hydrophobic chemical compounds, minute fragments of plastic debris
76 become a source and sink of endocrine disrupting pollutants, which are efficiently
77 absorbed from the digestive tract to the internal medium when the marine organisms
78 ingest the microplastic (Slezakova et al., 2009). Thus, an increasing number of studies
79 have monitored persistent organic pollutants (POPs) on microplastic samples as proxies
80 for POP monitoring in marine environments (Heskett et al., 2012; Hirai et al., 2011; Le et
81 al., 2016; Ogata et al., 2009; Taniguchi et al., 2016; Yeo et al., 2015).
82
83 Very few studies have reported either baseline data of microplastic in sediments (Baztan
84 et al., 2017; Herrera et al., 2018), or the levels of pollutants associated with microplastics
85 in the Canary Islands, Spain (Baztan et al., 2017; Heskett et al., 2012). Furthermore,
86 according the literature, most of the previous studies monitoring chemical compounds in
87 plastic debris have focused on the contamination of pre-production resin pellets rather
88 than on small plastic fragments, foam, or macro-sized plastics (Hong et al., 2017).
89 Therefore, the aim of this study was to monitor a wide suite of chemical compounds in
90 stranded plastic debris (pellets and plastic fragments) from different beaches of the
91 Canary Islands. We extracted and quantified the adsorbed persistent organic pollutants,
92 such as organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), as well as
93 semi-persistent contaminants such as polycyclic aromatic hydrocarbons (PAHs), and
94 bromodiphenyl ethers (BDEs). In addition, we included a panel of selected emerging
95 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

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. Figure 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

119 plastic from a beach located in the northeast of the island - “Lambra” - which is
120 recognized as a deserted, pristine beach.
121
122 Samples were collected following the protocol previously published by Herrera et al.,
123 (2018). In the laboratory, plastic samples were manually separated with forceps from tar
124 and organic material. Two types of samples were differentiated: pre-production resin
125 pellets and plastic fragments (Figure 2). Plastic samples included in this study were
126 separated into two classes, following the suggestion of plastic debris nomenclature based
127 on size (MSFD GES Technical Subgroup on Marine Litter, 2013): large micro-debris (1–5
128 mm) consisting of pre-production plastic pellets, and meso-debris or mesoplastic (5–25
129 mm) consisting of plastic fragments. To perform the analysis of pollutants one gram from
130 each type of plastic was randomly pooled in a glass tube, reaching a total of 133 samples
131 of pooled pellets, and 119 samples of mesoplastic. This means that approximately 30
132 pools/beach of each type of plastic were obtained from the sampling campaigns carried
133 out on the four beaches.
134
135 2.2. Analytes of interest and chemical and reagents
136
137 All plastic samples (n = 252) were screened at the Laboratory of Toxicology of the
138 University of Las Palmas de Gran Canaria (Spain), for the presence of the following
139 anthropogenic contaminants: (a) 22 organochlorine pesticides (OCPs): aldrin, chlordane
140 (cis- and trans-isomers), dicofol, dieldrin, p,p′-DDT and metabolites (p,p’ DDE and p,p’
141 DDD), o,p’ DDT and metabolites (o,p′ DDE and o,p′ DDD), endrin, endosulfan (α- and β-
142 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, 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 p-methoxycinnamate, homosalate, 3-(4-methylbenzylidene) camphor, and 3-benzylidenecamphor; and (g) the widely employed organophosphate pesticide chlorpyrifos.

167 Stock solutions of each compound at 1 mg/ml were prepared in cyclohexane and stored
168 at −20 °C. Diluted solutions from 0.1 ng/ml to 2000 ng/ml were used for calibration curves
169 (10 points) in cyclohexane containing 1% olive oil as analyte protectant to help minimize
170 the errors caused by matrix-induced signal enhancements, as described previously
171 (Lynam and Smith, 2011). PCB 202, tetrachloro-m-xylene, p,p′ DDE-d8, heptachloro
172 epoxide cis, diazinon-d10, and phenanthrene-d10 were employed as internal standards
173 (ISs). All the standards were neat compounds, and were acquired from Dr. Ehrenstorfer
174 Reference Materials (Augsburg, Germany). Cyclohexane (CHX) and ethyl acetate (AE)
175 were of mass spectrometry grade (Merck, Darmstadt, Germany).
176
177 ## 2.3. Extraction of chemical compounds from micro and macro-plastic and chemical
178 ## analysis
179
180 A liquid-solid extraction was used for the extraction of target analytes. 5 mL of a mixture
181 of CHX:AE (1:1) were added to each sample in amber glass vials, previously cleaned with
182 CHX:AE (1:1). The vials were vigorously shaken and placed in an ultrasonic bath for 20
183 min. An orbital rotator was used over 24 hours to allow the samples to soak in the solvent.
184 The solvent was transferred to a new vial, and the extraction process was repeated two
185 more times (24 hours each). After 72 hours we had recovered a total volume of 15 mL of
186 CHX:ACE, which was considered to contain the entire quantity of chemical compounds
187 adsorbed in plastic (previous experiments have demonstrated that further 24-hr-
188 extraction periods did not produce a significative increase in the recovery of chemical
189 compounds; data not shown). The solvent was filtered through 0.45 µm using syringe disc
190 filters and evaporated under a gentle N_2 stream and resuspended in 1 ml of CHX:ACE. The

191 samples were considered ready for chromatographic analysis without any additional step
192 of purification.
193
194 The determination of chemical was performed using a gas chromatography separation
195 with a triple quadrupole mass spectrometer (QqQ; GC System 7890B and MSMS 7010 of
196 Agilent Technologies, Palo Alto, CA, USA). Chromatographic separations were performed
197 employing two 15-m capillary columns (Agilent J&WHP-5MS), which were connected in
198 series using a Purged Ultimate Union (PUU, Agilent Technologies). The use of these two
199 columns allowed employment of the back-flushing technique (constant flow rates of 1.2
200 ml/min of helium (99.999%) for column 2 and 1.0 ml/min for column 1). The
201 temperatures of the GC oven were programmed as follows: a) initial temperature: 60 °C
202 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
203 min. Total run time was 20.75 min. Transfer line and injector were both set at 280 °C.
204 Standards and samples were injected (1 µl) in the splitless mode.
205
206 Retention Time Locking (RTL) of the analytes with chlorpyrifos-methyl (Rt = 9.143 min) as
207 the time reference was used. The QqQ mass spectrometer was operated under the
208 previously described conditions (Henriquez-Hernandez et al., 2017). Nitrogen (99.999%)
209 was used as the collision gas. Collision gas flow was set at 1.5 ml/min.
210
211 The quantification was based on peak areas, using 10-point calibration curves. These
212 calibration curves were constructed using a least-squares linear regression from the
213 injection of standard solutions (1% olive oil). The limits of quantification (LOQ) varied
214 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). 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.

263

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

265

266 ## 3.1. Profiles of the pollutants associated to microplastic from the Canary Islands

267

268 ### *3.1.1. Persistent organic pollutants*

269

270 In this study we included 38 chemical compounds that are usually classified as POPs, and
271 18 of them were detected in >50% of the samples. Table 1 shows the results of ∑PCBs,
272 ∑OCPs, and ∑DDTs per sampling site and microplastic type.

273

274 Regarding the group of PCBs, 11 compounds were frequently detected (>50% of samples;
275 congeners #52, 77, 101, 105, 118, 138, 153, 156, 167 and 180). Figure 3 shows the range
276 of concentrations of the sum of these congeners according to sampling place and type of
277 microplastic (see detailed graph in Supplementary Figure 1 and the numerical data in
278 Supplementary Table 1). Marker PCBs (#28, 52, 101, 138, 153, and 180) were detected in
279 virtually 100% of samples (99.8%), while the dioxin-like PCBs (#77, 105, 118, 156, and
280 167) were detected in 85% of the pellets and 97.5% of plastic fragments studied. The PCB
281 congeners that reached the highest concentrations in all beaches were #153 and #180 in
282 both pellets and fragments. Our data are similar to those reported by other authors on
283 plastic debris from industrialized areas all over the world (Antunes et al., 2013; Frias et
284 al., 2010; Karapanagioti et al., 2011; Mizukawa et al., 2013; Taniguchi et al., 2016).
285 However, other authors have reported a different pattern of contamination by the
286 congeners of this chemical group (Hirai et al., 2011; Jayasiri et al., 2015; Rios et al., 2007).

287 Nevertheless, the profiles reported in this study are consistent with those previously
288 reported for marine biota from the same region (e.g., fish (Henriquez-Hernandez et al.,
289 2017; Rodriguez-Hernandez et al., 2016), sea turtles (Camacho et al., 2013; Camacho et
290 al., 2014), or dolphins (García-Álvarez et al., 2014a)), with a predominance of highly
291 chlorinated congeners in all of them. The median values of the sum of PCBs by type of
292 microplastic (without dividing by sample sites) were 28.15 ng/g and 17.23 ng/g for pellets
293 and fragments, respectively. These values are consistent with those previously reported
294 for African countries (Ogata et al., 2009) or Southeast Asian countries (Le et al., 2016;
295 Ogata et al., 2009), but lower than those reported for Western European countries, such
296 as The Netherlands, UK and Italy (Ogata et al., 2009) or Portugal (Antunes et al., 2013).
297 On the contrary, our results were higher than those found for pellets and mesoplastic
298 collected from beaches in California (Van et al., 2012). Like in previous reports, we found
299 a large variability of ∑PCBs from sample to sample, in both pellets (0.9 - 2285.8 ng/g) and
300 fragments (1.6 - 772.5 ng/g). Some authors have indicated probable reasons for this
301 variability in plastic debris contamination, suggesting that the time of permanence in
302 seawater and the transit through oceanic zones with different levels of pollution play a
303 determining role (Endo et al., 2005). The adsorption of seawater contaminants to plastic,
304 even with these chemicals being hydrophobic, takes up to 80 days to reach equilibrium
305 (Karapanagioti and Klontza, 2008). That is why it is possible that fragments of microplastic
306 that are dragged by the currents can pass through highly contaminated areas before they
307 reach this equilibrium. Given that some plastic fragments can concentrate very high
308 amounts of pollutants, some authors have suggested they might represent a very
309 important source of exposure to pollutants for marine biota via ingestion (Endo et al.,
310 2005).

311

312 Regarding organochlorine pesticides, we found that seven of them were present in more
313 than 50% of the samples (p,p'-DDD, o,p'-DDE, p,p'-DDE, HCB, heptachlor, dieldrin and
314 mirex) (Supplementary Table 2). The compound present in the highest concentrations,
315 not only of its chemical group but among all the POPs included in this study, was the *p,p*'-
316 DDE, which reached median levels of 56.0 ng/g in the pellets collected in the urban beach
317 "Las Canteras", in Gran Canaria. In fact, the DDT group and its metabolites generally
318 showed high concentrations in the microplastics sampled in Gran Canaria (Table 1, Figure
319 3, Supplementary Figure 2 and Supplementary Table 2).

320

321 In fact, although high levels of these compounds have been reported in all types of
322 samples from the Canary Islands before (Camacho et al., 2013; Diaz-Diaz and Loague,
323 2001; García-Álvarez et al., 2014b; Henriquez-Hernandez et al., 2016; Zumbado et al.,
324 2005), it is surprising that these levels are still comparable to those described in countries
325 where DDT continues to be used legally to combat malaria vectors (Hirai et al., 2011;
326 Jayasiri et al., 2015; Ogata et al., 2009; Taniguchi et al., 2009). These levels are much
327 higher than those generally reported for geographical areas where these compounds
328 were banned decades ago, as is also the case with the Canary Islands (Frias et al., 2010;
329 Heskett et al., 2012; Mato et al., 2001; Van et al., 2012), although there are reports of
330 high levels in areas where these pesticides have not been used since the 1980s (Rios et
331 al., 2007). Geographically, the Canary Islands are part of the African continent, and some
332 publications have pointed to the proximity to countries such as Morocco being potentially
333 responsible for the high levels of contamination of the archipelago by OCPs. However, a
334 recent work of our group has shown how the levels of DDTs and other OCPs in the

335 population of Morocco and the western coast of the Sahara are lower than those among
336 the inhabitants of the Canary Islands (Henriquez-Hernandez et al., 2016). Therefore, it is
337 plausible that these levels of contamination of the plastic - which are consistent with
338 previous reports on samples of all kinds from this Atlantic archipelago - are due to the
339 intensive use of these products in this region in the past (Diaz-Diaz and Loague, 2001;
340 Zumbado et al., 2005), and that this may have occurred in the coastal environment of the
341 islands, at least in part.
342
343 *3.1.2. Semi-persistent organic pollutants*
344
345 In the first place, it was remarkable that we found residues of the majority of PAHs in the
346 USEPA list (EPA, 2001) in >50% of the microplastic samples (13 out of 16 compounds,
347 including 4 carcinogenic chemical compounds) (Figure 3, Table 2, Supplementary Table
348 3, and Supplementary Figure 3). The median values for the complete series of samples
349 were 528.3 ng/g for the pellets (range 52.1 - 17023.6 ng/g) and significantly lower in the
350 plastic fragments (147.5 ng/g, range 35.1 - 8725.79 ng/g; <0.001). Comparison with the
351 literature does not clarify much about the source of pollution in the Canary Islands, since
352 our values are consistent with those described by some authors who have sampled at
353 different locations on the planet (Hirai et al., 2011), but are much higher than those
354 reported in samples from Greece, Mexico, USA or China (Karapanagioti et al., 2011; Rios
355 et al., 2007; Van et al., 2012; Zhang et al., 2015), though much lower than those reported
356 from Brazil or Portugal (Antunes et al., 2013; Fisner et al., 2013). We find it interesting to
357 highlight that the profile of contamination by PAHs of the pellets and fragments was not
358 only quantitatively different but also compositionally. Thus, while the contamination of

359 the pellets was dominated by high molecular weight compounds (tetra- to hexa-cyclic
360 PAHs), the opposite happened in the plastic fragments, in which the low molecular weight
361 compounds were predominant ($P < 0.001$). In any case, the phenanthrene/anthracene
362 ratio was lower than 10 in the two types of samples, suggesting a contamination of
363 pyrolytic origin rather than petrogenic origin (Budzinski et al., 1997). This could explain
364 the fact that the highest levels of contamination by this group were found in the samples
365 of the urban beach of "Las Canteras", since this beach is located within the area of
366 influence of the port of Las Palmas de Gran Canaria, which occupies the 98th position
367 among ports with the highest container traffic in the world. A very important source of
368 contamination by PAHs of pyrolytic origin is the incomplete combustion of the fossil
369 hydrocarbons derived from multiple port activities and refineries (Bayona et al., 1993).
370 This would possibly indicate once again that a part of the contamination of the
371 microplastics found on the beaches occurs either in situ or in the nearby coastal
372 environment.
373
374 In relation to the group of BDEs, we detected congeners # 28, 47, 99 and 100 in more
375 than 50% of the samples (Table 2, Supplementary Table 4, and Figure 6). There are limited
376 studies that have studied these compounds in oceanic microplastic (Hirai et al., 2011;
377 Taniguchi et al., 2016), so it is difficult to contextualize our findings. In addition, among
378 the available studies, Hirai et al. (2011) reported that the most frequently detected and
379 concentrated compound was BDE 209. Unfortunately, due to a technical limitation, this
380 congener was not included in our study. However, among the determined compounds in
381 this group, BDE 47 was the most frequently detected and concentrated (Figure 3,
382 Supplementary Figure 4, Supplementary Table 4), and this finding was consistent with

383 that of Taniguchi et al. (2016), who also did not include BDE 209 in their study. For the
384 total of the series, we found median levels of ∑BDEs of 1.9 ng/g in the pellets (range 0 -
385 180.6 ng / g), and 2.3 ng/g in the mesoplastic (0.1 - 3923.9 ng / g). The values reported
386 so far in the literature range between 0.7 to 5.6 ng/g in Brazilian beaches (not including
387 BDE 209) (Taniguchi et al., 2016), and between 0.3 and 9909 ng/g in microplastic
388 collected in open sea and beaches (both deserted and urban), but including in this case
389 BDE 209 (Hirai et al., 2011).
390
391 *3.1.3. Emerging organic pollutants*
392
393 There are more than 700 substances from 20 different chemical classes that have been
394 identified in the aquatic environment. Many of them are classified as emerging pollutants
395 (EPs). These are chemical compounds that are not commonly monitored but have the
396 potential to enter the environment and cause adverse ecological and human health
397 effects (Geissen et al., 2015). Among them, we have selected two chemical classes that
398 have been identified by the European Union as of concern, the OPFRs (11 compounds)
399 and UV-filters (5 compounds) (https://www.hbm4eu.eu/the-substances/). In addition,
400 we have included the pesticide chlorpyrifos, of which more than 1200 tons a year are
401 sold around the world (Saunders et al., 2012). As far as we know there is no previous
402 study that has reported the levels of contamination in plastic by these chemical
403 compounds. Surprisingly, we found that 13 of the 17 EPs were present in >50% of the
404 samples (3 UV filters, 9 OPFRs, and chlorpyrifos).
405

406 Within the group of organic UV-filters, the most frequently detected and concentrated
407 compounds were homosalate and 2-Ethylhexyl p-methoxycinnamate, but 3-
408 benzylidenecamphor was also detected in more than 50% of the samples of both types
409 of microplastic. The levels of the ∑UV-filters were higher in the pellets (median 231.7
410 ng/g, range from 0 to 3740.3 ng/g) than in the fragments (median 136.4 ng/g, range 3.7
411 to 2169.3 ng/g) ($P < 0.01$) (Figure 3, Table 3, Supplementary Table 5, and Supplementary
412 Figure 5). These results are unsurprising. It is estimated that hundreds of tons of this type
413 of chemical sunscreens are produced each year (Buser et al., 2006), and the Canarian
414 archipelago, with more than 300 sunny days a year, is one of the main tourist beach
415 destinations of the EU, receiving more than 13 million tourists annually. It is therefore
416 expected that in the coastal environment of these islands there will be relatively high
417 concentration of cosmetic products, and in particular sunscreens, which would be
418 released directly into sea water, when this huge number of people bathe on the beaches.
419 In fact, previous studies had already shown the presence of several of these compounds
420 in the seawater of the beaches of these islands (Sanchez et al., 2015), as well as in their
421 coastal fish (Henriquez-Hernandez et al., 2017). Some studies have indicated that UV
422 filters pose a significant potential for estrogenic activity (Schlumpf et al., 2001). The
423 growing concern about the accumulation of plastic debris and possible ingestion by
424 marine organisms (and possibly by humans) makes the determination of these endocrine
425 disruptors an important target of future studies.
426
427 Regarding other emerging pollutants of concern - the OPFRs - we found that the values
428 were significantly higher in the plastic fragments (median 87.9 ng/g) than in the pellets
429 (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) (Figure 3, Table 3, Supplementary Table 6, and Supplementary Figure 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 2014-16 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 Figure 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

454 in microplastic), although recent reports have indicated that chlorpyrifos has been
455 detected at relatively high concentrations in coastal waters (Liu et al., 2018), in surface
456 marine sediments (Moreno-Gonzalez and Leon, 2017), and in marine biota (Henriquez-
457 Hernandez et al., 2017). However, further monitoring studies that include these
458 emerging contaminants in plastic debris are needed.
459
460 3.2. Variability of the concentrations of pollutants in microplastic among beaches of the
461 Canary Islands
462
463 As shown in Table 1, the pre-production resin pellets showed significantly higher values
464 of ∑PCBs in three of the four beaches (Las Canteras Beach: MW, $p < 0.001$; Cuervito
465 Beach: MW, $p < 0.001$; Famara Beach: MW, $p < 0.05$) than the values detected for plastic
466 fragments. Examining differences among sampled beaches, all individual congeners show
467 statistically differences among the beaches (Supplementary Table 1). Therefore,
468 statistical differences were also observed among the four sampling sites and ∑PCBs levels
469 (Kruskal-Wallis test; $P < 0.001$ for both types of plastics). We found the highest values of
470 ∑PCBs in "Las Canteras" beach, reaching median values of 137.9 ng/g (pellets) and 59.48
471 ng/g (plastic fragments), followed by "Cuervitos" (52.8 and 20.91 ng/g for pellets and
472 fragments, respectively). It is noteworthy that both beaches are located in Gran Canaria,
473 which is the most populated and industrialized island of the archipelago. These values
474 were several times higher than those in microplastic from beaches in much less
475 populated and industrialized islands. This is consistent with previous reports, which have
476 indicated that microplastic in beaches from industrialized areas (Endo et al., 2005; Jayasiri
477 et al., 2015; Karapanagioti et al., 2011; Mato et al., 2001), as well as that found in urban

478 beaches (Hirai et al., 2011), is more contaminated than that in remote beaches and the
479 open sea. In previous publications relating to scarcely industrialized islands of this
480 archipelago, such as Fuerteventura, the authors also reported much lower levels of
481 ∑PCBs (Heskett et al., 2012). Nevertheless, according to the 1 to 5 classification of the
482 level on PCB contamination of microplastic proposed by the International Pellet Watch
483 global monitoring program (IPW; http://www.pelletwatch.org/), Gran Canaria beaches
484 have a moderate pollution level (3) and the rest of the beaches sampled in this research
485 could be categorized as categorized as sligthly contaminated.
486
487 Something similar occurred with the other group of persistent pollutants -the OCPs -
488 given that the urban beach of "Las Canteras" was the most polluted by far (up to 2 orders
489 of magnitude higher than that in the rest of the beaches). Since this chemical group was
490 clearly dominated by the DDTs group, these differences were reproduced for these
491 pesticides as well (Table 1). In fact, we found a sample with an extreme value (13488 ng/g
492 of ∑DDTs) in "Las Canteras" beach, which is the highest value reported worldwide, at least
493 among those recorded by the IPW. It is also remarkable that more than 50% of the
494 microplastic sampled in “Las Canteras” beach presented levels of ∑DDTS >1000 ng/g,
495 which can be considered very high in comparison with those reported in many other parts
496 of the world. However, although the levels of the other beach of Gran Canaria -
497 "Cuervitos" - may be considered high as well (Table 1, around 100 ng/g), those of the
498 beaches of Lanzarote and La Graciosa are within the average levels worldwide, and
499 consistent with those previously reported for the islands of Fuerteventura and Lanzarote
500 (Heskett et al., 2012). As discussed above, it is very likely that the high level of microplastic
501 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). Sánchez 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.

5. FIGURE LEGENDS

550

551 **Figure 1.** Map of the Canary Islands, indicating the location of the four beaches sampled

552

553 **Figure 2.** Types of microplastic included in the study. **(a)** pre-production plastic pellets;

554 **(b)** plastic fragments (mesoplastic).

555

556 **Figure 3.** Concentrations of the sum of chemical pollutants by chemical group in pre-

557 production plastic pellets **(a)**, and in plastic fragments (mesoplastic) **(b)**. Y axis was $\log^2$

558 transformed in order to improve data visualization. The central thick line of each box

559 designates the median, the box height shows the interquartile range, the extreme lines

560 shows the highest and lowest value excluding outliers.

561

562 **Supplementary Figure 1.** Concentrations of polychlorinated biphenyls (PCBs) in pre-

563 production platic pellets **(a)**, and in plastic fragments (mesoplastic) **(b)**. Y axis was $\log^2$

564 transformed in order to improve data visualization. The central thick line of each box

565 designates the median, the box height shows the interquartile range, the extreme lines

566 shows the highest and lowest value excluding outliers.

567

568 **Supplementary Figure 2.** Concentration of organochlorine pesticides (OCPs) in pre-

569 production plastic pellets **(a)**, and in plastic fragments (mesoplastic) **(b)**. Y axis was $\log^2$

570 transformed in order to improve data visualization. The central thick line of each box

571 designates the median, the box height shows the interquartile range, the extreme lines

572 shows the highest and lowest value excluding outliers.

573

574 **Supplementary Figure 3.** Concentrations of polycyclic aromatic hydrocarbons (PAHs) in
575 pre-production plastic pellets **(a)**, and in plastic fragments (mesoplastic) **(b)**. Y axis was
576 $\log^2$ transformed in order to improve data visualization. The central thick line of each box
577 designates the median, the box height shows the interquartile range, the extreme lines
578 shows the highest and lowest value excluding outliers.
579
580 **Supplementary Figure 4.** Concentrations of semi-persistent pollutants bromodiphenyl
581 ethers (BDEs) in pre-production plastic pellets (a), and in plastic fragments (mesoplastic)
582 (b). Y axis was $\log^2$ transformed in order to improve data visualization. The central thick
583 line of each box designates the median, the box height shows the interquartile range, the
584 extreme lines shows the highest and lowest value excluding outliers.
585
586 **Supplementary Figure 5.** Concentrations of emerging pollutants used in UV-filters in pre-
587 production plastic pellets (a), and in plastic fragments (mesoplastic) (b). Y axis was $\log^2$
588 transformed in order to improve data visualization. The central thick line of each box
589 designates the median, the box height shows the interquartile range, the extreme lines
590 shows the highest and lowest value excluding outliers.
591
592 **Supplementary Figure 6.** Concentration of organophosphate flame retardants (OPFRs) in
593 pre-production plastic pellets (a), and in plastic fragments (mesoplastic) (b). Y axis was
594 $\log^2$ transformed in order to improve data visualization. The central thick line of each box
595 designates the median, the box height shows the interquartile range, the extreme lines
596 shows the highest and lowest value excluding outliers.
597

598 Supplementary Figure 7. Concentrations of chlorpyrifos in pre-production plastic pellets
599 (a), and in plastic fragments (mesoplastic) (b). Y axis was $\log^2$ transformed in order to
600 improve data visualization. The central thick line of each box designates the median, the
601 box height shows the interquartile range, the extreme lines shows the highest and lowest
602 value excluding outliers.
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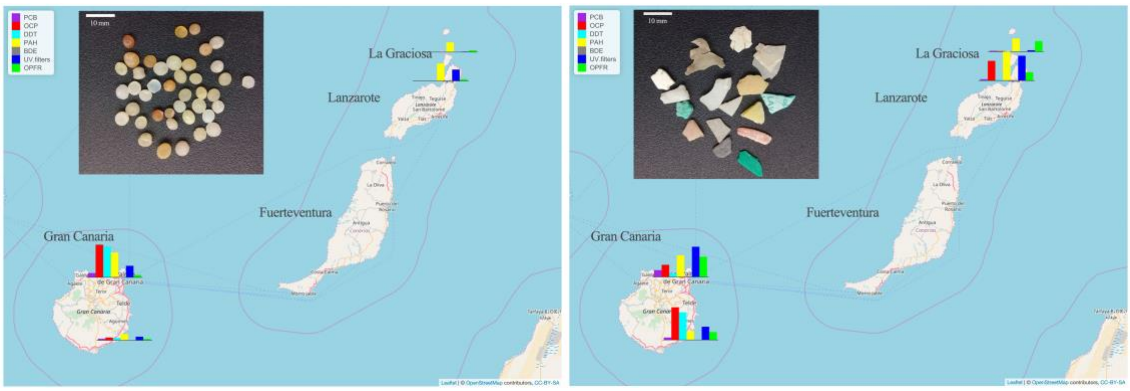
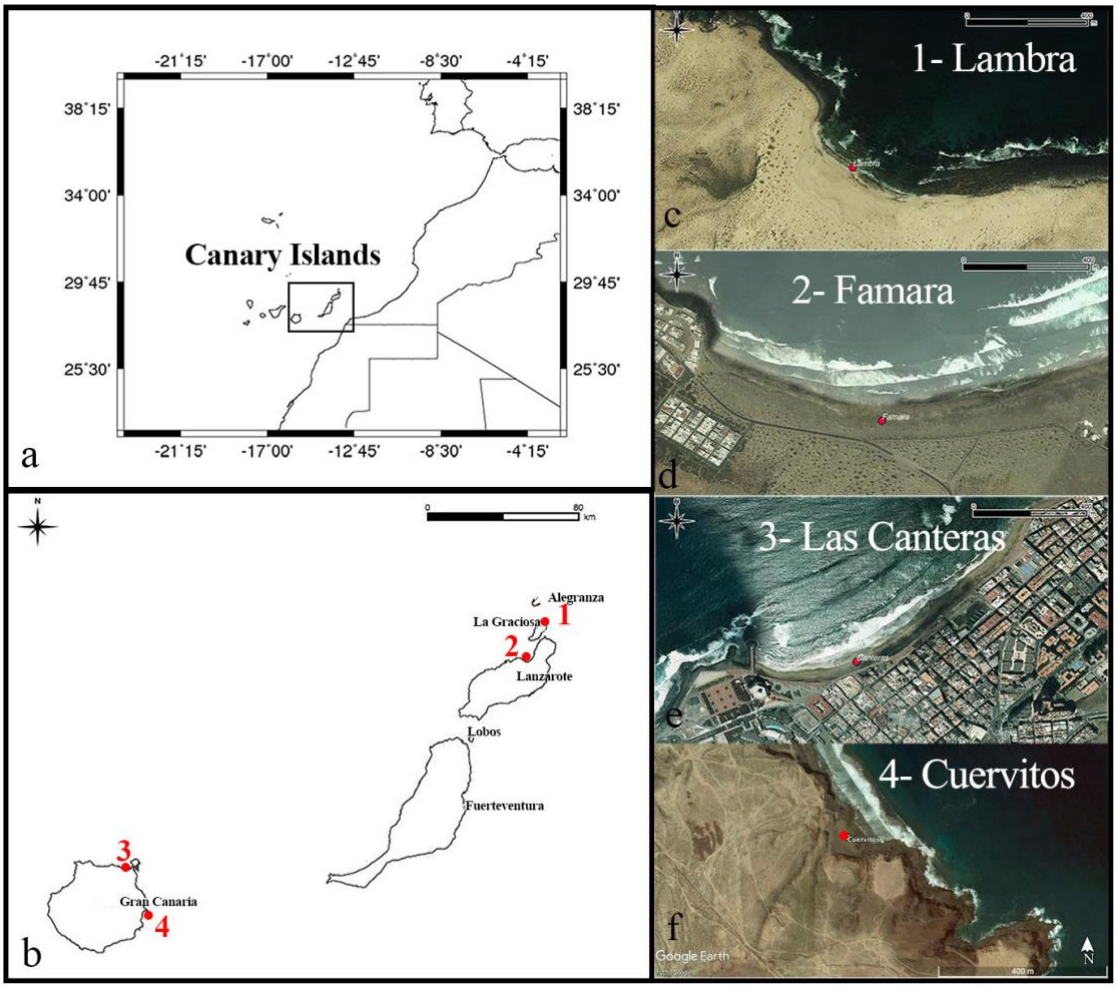
Graphical abstract

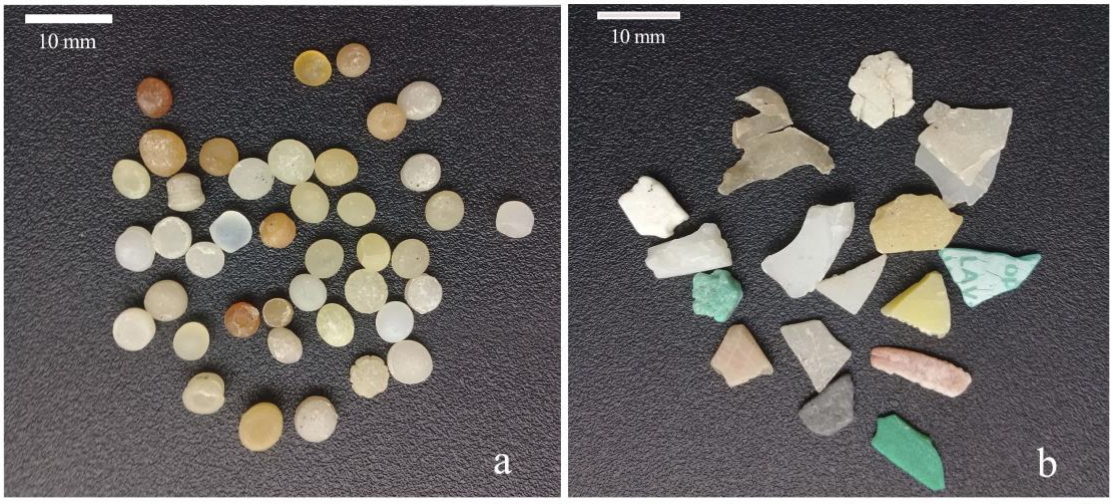


Figures



834

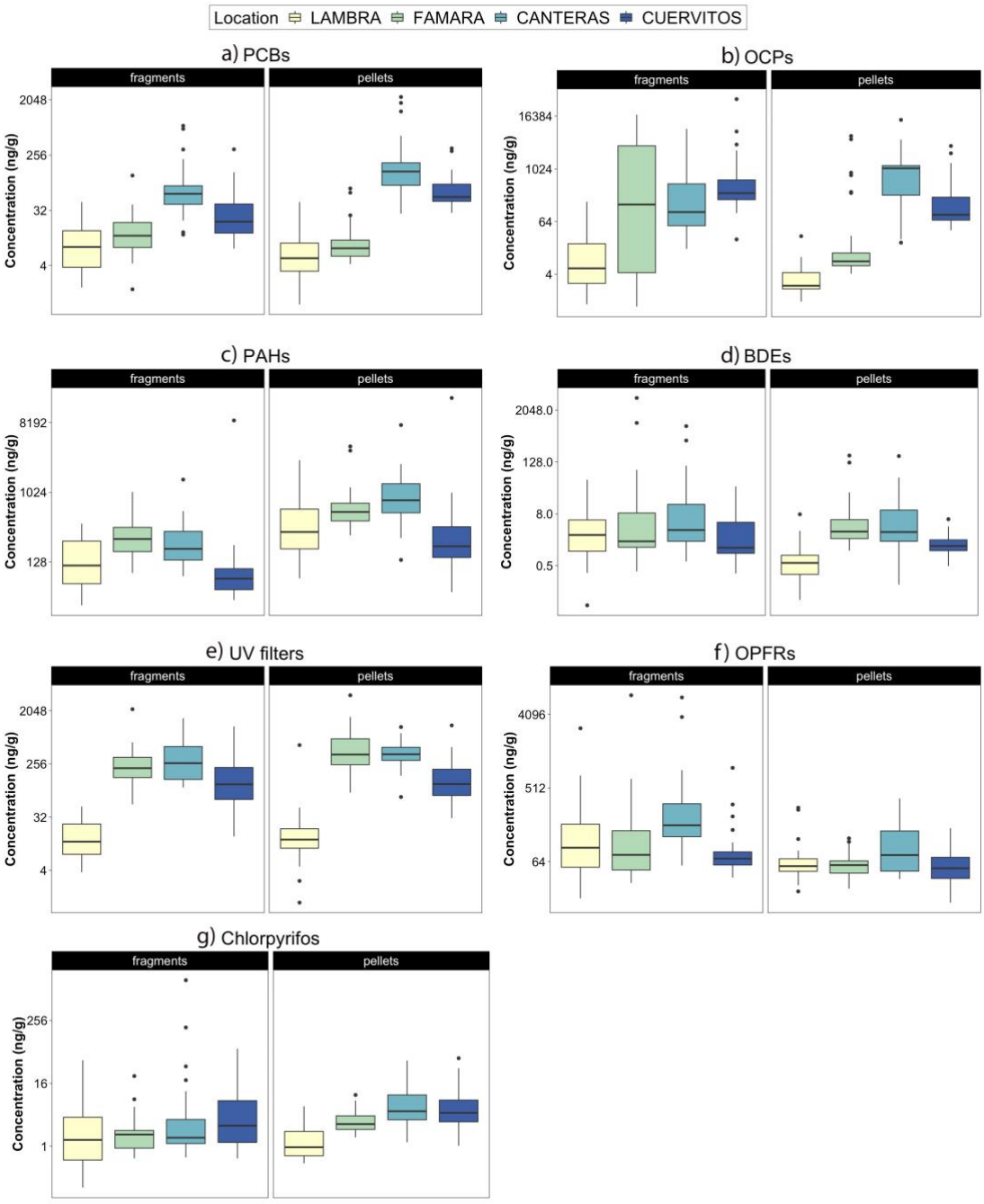
835 **Figure 1.** Map of the Canary Islands, indicating the location of the four beaches sampled.



836

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

838 (mesoplastic).



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840 **Figure 3.** Concentrations of the sum of chemical pollutants by chemical group in pre-production plastic pellets and in

841 plastic fragments (mesoplastic). **(a)** Polychlorinated biphenyls (PCBs). **(b)** Organochlorine pesticides

842 (OCPs). **(c)** Polycyclic aromatic hydrocarbons (PAHs). **(d)** Semi-persistent pollutants bromodiphenyl ethers

843 (BDEs). **(e)**Emerging pollutants used in UV-filters. **(f)** Organophosphate flame retardants (OPFRs). **(g)** Chlorpyrifos. Y

844 axis was $\log_2$ transformed in order to improve data visualization. The central thick line of each box designates the

845 median, the box height shows the interquartile range, the extreme lines shows the highest and lowest value excluding
846 outliers.
847
848