Potential transfer of organic pollutants from littoral plastics debris to the marine environment[☆]

Víctor M. León [a, *], Inés García [a], Emilia González [a], Raquel Samper [a], Verónica Fernández-González [b], Soledad Muniategui-Lorenzo [b]

[a] *Instituto Español de Oceanografía, Centro Oceanográfico de Murcia, Apdo. 22, C/ Varadero 1, 30740 San Pedro del Pinatar, Murcia, Spain*
[b] *Grupo de Química Analítica Aplicada, Instituto Universitario de Medio Ambiente (IUMA), Centro de Investigaciones Científicas Avanzadas (CICA), Departamento de Química Analítica, Facultade de Ciencias, Universidade da Coruña, Campus A Coruña, E-15071, A Coruña, Spain*

ABSTRACT

Plastic polymers act as passive samplers in air system and concentrate hydrophobic organic contaminants by sorption or specific interactions, which can be transported to other systems such as the marine environment. In this study plastic debris was sampled in the surrounding area of a Mediterranean lagoon in order to determine the concentration of persistent and emerging organic contaminants. More specifically, desorption of 91 regulated and emerging organic contaminants (polycyclic aromatic hydrocarbons, polychlorinated biphenyls, organochlorinated pesticides, current-use pesticides, personal care products, other pesticides and plastic additives) was characterized for the first 24 h from different polymers to seawater and the remaining content of these contaminants was also extracted by ultrasonic extraction with methanol. All samples were analyzed by Stir Bar Sorptive Extraction coupled to GC/MS. A significant fraction of sorbed contaminants in polymers was desorbed in the first 24 h, particularly for triazines and organophosphorus pesticides due to their lower hydrophobicity than other considered analytes. The remaining contaminants contained in plastics can be also transferred to seawater, sediments or biota. Considering 24 h desorbed fraction plus the remaining methanol extracted fraction, the highest transfer levels corresponded to personal care products, plastic additives, current-use pesticides and PAHs. This is the first study to show the relevance of the transport of organic contaminants on plastic debris from littoral areas to the marine environment.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

The presence and impact of plastic and microplastics in the marine environment is not a new phenomenon, but in recent years it has received particular attention from the social and scientific communities (Andrady, 2011; Cózar et al., 2015). The presence of plastics in the environment is a consequence of their worldwide use in the majority of human activities (domestic, industry, agriculture, fisheries, etc.) a large proportion of which is as single-use applications that are neither recovered nor recycled. Consequently plastics and plastic debris can reach the marine environment through direct discharges and be transported from continental areas (air, rivers, etc.). Land-based sources, including beach litter, contribute about 80% of plastic debris (Andrady, 2011). Microplastics are also found in the marine environment due to their direct introduction through runoff, including those used in consumer products, and to the weathering breakdown of larger plastic debris (Andrady, 2011). The most commonly used plastics are polyethylene (PE), polypropylene (PP) and polyethylene terephthalate (PET) and are therefore also those most frequently found in the marine environment (Iñiguez et al., 2017).

Plastic debris causes physical problems in marine fauna, which can confuse it with food (Thomson et al., 2004; Andrady, 2011). Many different organisms ingest plastics and microplastics, including bivalves (Ward and Shumway, 2004), crustaceans (Murray and Cowie, 2011), fish (Boerger et al., 2010; Bellas et al., 2016), marine mammals (Denuncio et al., 2011) and seabirds (Avery-Gomm et al., 2012). The chemical toxicity of microplastics has been also demonstrated on sea urchin (Martínez-Gómez et al., 2017).

Plastics also act as passive samplers in continental areas, accumulating hydrophobic organic contaminants (HOCs) which are present in the surrounding environmental compartments (air, water, soil, etc.). Plastic debris may also transport persistent organic pollutants sorbed to these materials to new locations and transfer their chemical components to the surrounding environment (Mato et al., 2001; Teuten et al., 2009; Andrady, 2011; Engler, 2012). However, the low density of some plastics favours their transport not only through water courses but also, and probably more relevantly, by wind transport due to the concentration of human activities in coastal areas. The high accumulation potential suggested that plastic resin pellets serve as both a transport medium and a potential source of toxic chemicals in the marine environment (Mato et al., 2001). The sorption of HOCs to marine plastics may affect the food-web bioaccumulation and bioavailability of HOCs. Several studies have modelled the effect of plastics on the transfer of HOCs to marine organisms (Teuten et al., 2007; Bakir et al., 2016; Paul-Pont et al., 2016; Koelmans et al., 2013, 2014, 2016). The combined intake from food and water was the main route of exposure to DDT, phenanthrene and bis-2-ethylhexyl phthalate, with negligible input from microparticles of polyvinyl chloride (PVC) and PE (Bakir et al., 2016). In this sense polystyrene (PS) microbeads play a minor role in transferring fluoranthene to mussels in comparison with waterborne and foodborne exposures, but direct toxic effects of this plastic were also observed (Paul-Pont et al., 2016). On the other hand positive correlations were found between ingested plastic particles and the concentrations of polychlorinated biphenyls (PCBs) or polybrominated diphenyl ethers in birds (Ryan et al., 1988; Tanaka et al., 2013). However, the ingestion of microplastic by lugworm and cod was expected to result in a marginal contribution to NP and BPA exposure (Koelmans et al., 2014). In this sense a recent critical review suggested that the effects of ingestion of microplastics on bioaccumulation most probably are limited for most marine habitats (Koelmans et al., 2013). Therefore it could be hard to confirm these effects by field data, but it does not imply that plastics do not have deleterious effects on marine life (Koelmans et al., 2016). Further studies are thus required because plastic can accumulate HOCs from air or aquatic environments (Mato et al., 2002) and subsequently transport and transfer them to other compartments. The accumulation of every contaminant depends on the ratio of surface area to volume, the sorption capacity of each material, weathering, the exposure period and its concentration in the surrounding matrix (Endo et al., 2005). In fact, HOCs have a higher affinity for polyethylene than PP (Mato et al., 2002; Karapanagioti and Klontza, 2008), whilst PE, PP and PVC have a greater affinity for these compounds than for natural sediments tested by Teuten et al. (2007). Weathered PE and PP showed higher partition ratios for phenanthrene than unweathered polymers (Karapanagioti and Klontza, 2008). The hydrophobic surfaces of pellets accumulate other compounds in beached plastic pellets, such as DDT and its metabolites, polycyclic aromatic hydrocarbons (PAHs), etc. (Teuten et al., 2009; Frias et al., 2010; Hirai et al., 2011; Van et al., 2012; Zhang et al., 2015). In the majority of studies persistent organic contaminants and PAHs were considered but many more substances can also be sorbed. Moreover, plastics and microplastics can also transfer monomers, base polymers and chemical additives (PBDEs, bisphenol-A, nonylphenol, etc.) contained in the different materials (Teuten et al., 2009). In fact, two recent non-targeted screening analyses looking at the chemicals associated with plastic debris detected a total of 231—251 organic compounds on plastics, including hydrocarbons, UV-stabilizers, anti-oxidants, plasticizers, flame retardants, lubricants, intermediates and compounds for dyes and inks (Gauquie et al., 2015; Rani et al., 2015).

However, to the best of the authors' knowledge no previous information is available regarding the transfer of HOCs from littoral/continental plastics to coastal areas. Furthermore, the majority of previous studies have mainly focused on the sorption of PAHs, organochlorinated contaminants or plastic additives desorption in seawater (Mato et al., 2001; Teuten et al., 2009), and recently on the sorption of carbamazepine, 4-methylbenzylidene camphor, triclosan and 17α-ethinyl estradiol to PE (Wu et al., 2016), but no data are available in relation to contaminants of emerging concern such as current-use pesticides (CUPs) and other personal care products (PCPs). In this study the occurrence of plastics is characterized in several areas from the perimeter of a Mediterranean coastal lagoon and the transfer of 91 HOCs (PAHs, PCBs, OCPs, CUPs, PCPs, other pesticides and plastic additives) from different polymers (materials, weathering and origin) to seawater is estimated by stir bar sorptive extraction (SBSE) coupled to thermodesorption unit and GC/MS (Moreno-González et al., 2013). More specifically, the desorption of these pollutants from littoral plastics and microplastics to seawater was characterized for the first 24 h and the remaining organic contaminants content in these materials was also determined by MeOH ultrasonic extraction, as an indicator of the maximum desorbable amount over time and their potential transfer from plastics to the marine environment (seawater, sediments or biota).

2. Materials and methods

2.1. Materials

Seawater used for the preparation of seawater standards and seawater transfer experiments was obtained 10 miles from the coast and filtered (0.22 μm). The commercial polydimethylsiloxane stir bars employed (Gerstel, Mulheim a/d Ruhr, Germany) were 20 mm × 0.5 mm. A 15 position magnetic stirrer (Gerstel, Mulheim a/d Ruhr, Germany) was used to stir samples at 750 rpm.

OPPs were purchased from Ultra Scientific (Rhode Island, USA). Standards containing organochlorinated pesticides, PCBs, PAHs, triazines and individual standards of the remaining analytes were purchased from Dr. Ehrenstorfer GmH (Augsburg, Germany). The complete list of analyzed substances is shown in Table S1 (Supplementary Material section). Atrazine-D5, deuterated PAH mix, triclosan-D10 and chlorpyrifos-D10 were obtained from Dr. Ehrenstorfer (Augsburg, Germany).

2.2. Study area and sampling campaign

The Mar Menor is a Mediterranean coastal lagoon located in southeast Spain. This lagoon is subject to heavy seasonal tourist activity and urban development and is surrounded by Campo de Cartagena, an intensive agricultural area where the use of plastic has greatly increased in recent decades. All these activities are relevant sources of plastic debris in littoral areas.

Plastic and microplastics were sampled in Spring 2015 from 5 coastal areas adjacent to the Mar Menor lagoon (P1—P5, Fig. 1) exposed to a variety of predominantly anthropogenic activities (tourist, agricultural, urban, etc.). Plastic debris were randomly sampled by hand at five coastal areas (P1—P5) in order to obtain a sufficient mass of plastic (0.2—2.0 g) for the analysis of regulated and emerging organic contaminants, being mainly macroplastics. These macroplastic samples corresponded to continental debris transported by air from surrounding areas or deposited directly by tourists in the littoral. Attending to the environmental conditions of the study area and the characteristics of these samples we can consider that they were not previously immersed in seawater and accumulated environmental contaminants mainly from air. Consequently they can be used to simulate the desorption and

Fig. 1. Location of sampling areas in the Mar Menor lagoon.

transfer of contaminants from littoral areas to marine ecosystem. All samples were kept refrigerated in amber glass bottles, previously cleaned with MeOH and bidistilled water, until their arrival at the laboratory, where they were frozen until analysis.

2.3. Plastic debris characterization

The different plastic polymers, formats and uses were characterized and classified. Some samples were selected for analysis of the organic contaminant content in each sampling area (5—8% of total samples per area) in order to get information about the most common polymers found in each area. Samples were identified by the polymer abbreviation (PE, PP, PA for polyamide, etc) and the number of sample in each sampling area. In some cases, when the material nature of a sample was not visually recognized (too small piece or not clear origin/use), a small fraction was characterized by attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FT-IR) in a Spectrum 400 FT-IR/FT-NIR Spectrometer and a horizontal ATR PIKE Miracle with a Perkin Elmer diamond/ZnSe crystal plate. Individual particles were placed on the ATR crystal and FTIR absorption spectra were recorded as an average of 50 scans in the mid-infrared range 4000-650 cm^{-1}. The polymer type was identified based on the absorption frequencies for specific chemical bond types present in relevant polymer samples. Spectrum software was used to analyse recorded IR spectra and the material was identified by a spectrum search in commercial and customized polymer libraries. These libraries contained spectra of all common polymers, natural and weathered materials with different uses, colours, etc.

2.4. Desorption experiment in seawater

The transfer of semivolatile organic pollutants from littoral plastics to seawater was determined using stir bar sorptive extraction technique (SBSE), simulating their first immersion in the sea. More specifically, 0.2—2 g of each plastic polymer was deployed

in a stainless steel cage (0.6 mm mesh size) immersed in 100 mL of seawater (100 mL amber Erlenmeyer) for 24 h at room temperature (22-24 °C) and stirred with a 20 mm*0.5 mm coated-polydimethylsiloxane stir bar at 700 rpm (Fig. 1S). Every sample corresponded to a single piece but in some cases it was fragmented to insert it in the desorption cage. The concentration of 91 organic pollutants, including pesticides, PAHs, PCBs, personal care products (PCPs) and some plastic additives was determined by SBSE followed by gas chromatography with mass spectrometry (Agilent Technologies 6890N GC and 5975B inert XL MSD) (SBSE/GC/MS). The analytical method was based on that proposed by Moreno-González et al. (2013) but excluding the sodium chloride addition to simulate desorption to seawater. External calibration standards (10—200 ng/L) were used applying the same analytical procedure using seawater spiked with the mix-standard stock (50—500 µg L^{-1}). Blanks (seawater with and without the stainless steel cage) were also analyzed applying the same procedure as for the rest of samples. Limits of quantification of the applied procedure for each considered analyte are shown in Table S1, together with their log Kow.

2.5. Methanol extractable amount in plastics

The remaining amount of organic pollutants in plastic used for desorption experiments in seawater were extracted using ultrasonication with methanol. Mato et al. (2001) used hexane for Soxhlet extraction of PP, showing that MeOH was adequate for DDE and PCBs extraction for this polymer but it was also available to extract a fraction of plastic additives such as NP from PP resin pellet. The main goal of this study is to determine sorbed analytes, not present in plastic formula, and consequently the fraction of plastic additives was not considered in the methanol extracted fraction. In our study methanol (100%) was the organic solvent selected because it provoked fewer visible alterations to plastic surfaces and a more efficient extraction than other water soluble solvents (acetone, MeOH/H$_2$O mix) in a previous test. Three successive ultrasonic extractions were applied with 5—15 mL of MeOH for 15 min in a glass centrifuge tube completely covering the plastic with the solvent under similar conditions to those of a previously validated sediment-extraction procedure (Moreno-González and León, 2017). All the extracts were combined and concentrated until a final volume of 5 mL using a rotary evaporator. 2 mL of the obtained extract were then diluted in 100 mL of seawater in a 100 mL amber Erlenmeyer flask (Fig. 1S) spiked with internal standards and analyzed by SBSE/GC/MS (Moreno-González et al., 2013) using specific standards prepared in the same way as the samples. Desorbed concentrations to seawater and total concentration on plastics were expressed to plastic dry weight. Plastic-free blanks were also analyzed applying the same procedure as for the rest of samples.

3. Results and discussion

3.1. Abundance/density/distribution of plastics in littoral areas

Sampled plastics and microplastics (>0.1 cm) from each area were classified according to their polymer composition, size, use, colour, etc. The number of items of plastic debris randomly sampled for organic contaminant analysis varied between 81 (P1) and 202 (P3) (Table 1) and the surface area varied between 4.2 and 290.5 cm^2. The plastics found were mainly used for food and cosmetic packaging (tourist pressure) with some contribution from other activities such as fishing, agriculture, etc. The polymer composition was visually identified and confirmed using infrared spectroscopy in some samples, but not for all cases (29—54% were

Table 1
Proportion of different polymer numbers (polyethylene, PE; polypropylene, PP; polyvinyl chloride, PVC; polystyrene, PS; polyamide, PA; polyurethane, PUR; other polymers and non-analyzed/identified samples, N.A.) found in the sampling areas (%) and total number of items of plastic debris sampled (n).

Sampling point	PE (%)	PP (%)	PVC (%)	PS (%)	PA (%)	PUR (%)	Others (%)	N.A. (%)	n
P1	36.0	8.1	1.5	6.6	7.3	5.2	5.8	29.5	197
P2	37.0	12.4	1.2	6.2	2.5	5.0	2.5	32.2	81
P3	26.2	4.5	2.0	6.9	3.5	1.0	9.4	46.5	202
P4	18.9	3.7	3.1	8.5	6.7	3.0	3.7	52.4	164
P5	12.4	8.3	3.1	4.1	3.1	2.1	12.4	54.5	97

not identified nor analyzed). Concretely ATR-FT-IR was only used for the identification of polymers in samples selected for contaminant analysis when it was necessary (43 samples). Attending to the identified materials, the most common polymer was PE at the 5 sampling points, representing between 30 and 60% of identified plastic debris, a figure in accordance with the production of this polymer, which represented 45% of global plastics production in 2007 (Brien, 2007). The PE group includes different plastic formats (HPDE, LPDE, PET, etc.) used for many and diverse applications (domestic, agricultural, food preservation, etc.), although its primary use is in packaging (plastic bags, plastic films and containers including bottles, etc.). In fact this polymer is the most commonly used for packaging (many different plastic formats and applications), which is the largest sector for the plastics industry, representing 39.6% of the total European plastics demand in 2013 (PlasticsEurope, 2015). The use of plastics in European agriculture is also continuously increasing in certain agricultural applications, such as covering greenhouses, tunnels and mulching, essentially in Italy, Spain and France (Scarascia-Mugnozza et al., 2011). In this sense PE is the most commonly used raw material for these applications (Scarascia-Mugnozza et al., 2011).

The next most abundant polymers were PP (8–20%) and PS (10–18%), mainly used for food packaging. PVC, PA and polyurethane (PUR) were also found in all areas. Materials were both recent and aged (visual determination), the majority corresponding to a medium-high state of degradation, probably the consequence of an environmental exposure period lasting from several months to years. The proportion of polymers found in the Mar Menor surrounding area is similar to those found in other coastal areas. Polyethylene vinyl acetate, low-density PE and PS were the three major plastic types found in all the sites from the Bohai Sea, a large semi-enclosed inner sea located in the northeast of China (Yu et al., 2016). Most of the plastic pellets sampled along the coast of Goa (India) were made of PE and PP (Veerasingam et al., 2016), whilst in Mediterranean surface waters PE was also the predominant polymer form with an overall frequency of 52%, followed by PP (16%), polyamides (PA) (4.7%) PVC (2.6%), PS (2.8%) and polyvinyl alcohol (1.2%) (Suaria et al., 2016).

3.2. Desorption of organic pollutants from plastics to seawater

47 items of plastic debris from among the different materials and sites were selected for organic contaminant analysis, analyzing between 5 and 8.5% of total samples obtained per sampling area. PAHs, CUPs, PCPs and plastic additives were desorbed from plastic polymers to seawater in the first 24 h (Tables 2 and 3). 63 of 91 pollutants analyzed were found in one or more of the desorbed fractions. The highest number of substances detected per plastic debris was 29, found in PP and PVC samples from areas P2 and P4, respectively. The mean number of substances found per sample varied from 6.2 at P5 to 23.3 at P2. P5 is the sampling area sited at longer distance of main pollutant sources, however, P2 is subjected to many human activities because it is close to important urban and touristic nuclei (Los Narejos), agricultural plots and Murcia-San

Javier Airport. Extraction replicates (n = 2–3) of some plastic samples (PE plastic bags and other PE samples in P1 and P3, respectively) were performed showing similar results for the majority of analytes (SD was lower than 30% for contaminants found at concentrations higher than the limit of quantification), indicating the reproducibility of the desorption and extraction procedures (Figs. 2 and 3).

Plastic additives (mainly tributyl acetylcitrate and tris-(2-chloropropyl)phosphate) and PCPs were the major contaminants released to seawater from plastic debris in all studied areas, the highest mean contribution per area being 492 ng/g and 444 ng/g respectively (P2) (Table 2). Plastic additive desorption was present in 85.1% of samples, being particularly high from PS and PA (Table 3). In four samples the concentration of plastic additives (tributyl-2-acetyl citrate and tris-2-chloropropyl)phosphate) was significantly higher than calibration standards and the obtained concentrations were therefore replaced by 1000 ng/g (maximum concentration in the linear range) to avoid any overestimation in the results for these compounds.

The most commonly desorbed contaminants from plastic debris, apart from the plastic additives, were OPPs (85.1% of total samples), PAHs (83.0%), triazines (74.5%), PCPs (68.1%), other pesticides (53.2%), OCPs (46.3%) and PCBs (4.3%). Those data showed the influence of agricultural, touristic and urban activities on the presence of pollutants in the sorption surfaces, as it was also evidenced in air in the same area (Carratalá et al., 2017). The highest mean desorbed concentrations per study area (Table 2) were found for PAHs (5.6 ng/g) in P3, and for OCPs (11.3 ng/g), triazines (10.9 ng/g), OPPs (17.9 ng/g), PCPs (116 ng/g) and other pesticides (9.1 ng/g) at P2. The plastic samples from the P2 area also showed the highest concentrations for the majority of contaminant groups, probably due to the intensive tourist pressure at this beach (Los Narejos) and the proximity of other relevant sources (agricultural plots, San Javier-Murcia airport, etc.). These results confirm that many HOCs present in air (Carratalá et al., 2017), fresh water, soil, etc., can be accumulated in plastics and transferred to marine seawater once they reach the marine environment.

Turning now to specific contaminants, the most prevalent were chlorpyrifos-methyl and terbuthylazine (70.2% of total samples), chlorpyrifos (68.1%), phenanthrene (63.8%), musk-ketone (51.1%), tributhylphosphate and fluorene (42.6%), and acenaphthylene and benzophenone (40.4%) (Figs. 4 and 5; Tables 2S and 3S). Chlorpyrifos and terbuthylazine were also the most ubiquitous CUPs in the Mar Menor lagoon seawater (Moreno-González et al., 2013). Chlorpyrifos was the most widely used insecticide in the Murcia Region in 2006 and terbuthylazine is a commonly-used herbicide in lemon tree crops, one of the most relevant in Campo de Cartagena, and uncultivated areas (Sanz-Navarro, 2008). These semi-volatile pesticides and others (i.e.: chlorpyrifos-methyl, pendimethalin, propyzamide,…) were also found in air around Mar Menor lagoon using passive samplers (Carratalá et al., 2017). Depending on the properties of the compounds and polymers, the proportion of contaminant desorbed and the desorption kinetic varied significantly, as was also found in previous studies (Endo et al., 2013).

Table 2
Mean and maximum concentrations per plastic mass unit (ng/g plastic) of the different contaminant groups desorbed from plastic to seawater over 24 h and subsequently extracted with MeOH for each sampling area. The desorbed proportion expressed as a percentage is also included.

	Sampling area	Desorption in seawater (24 h) (ng/g plastic)			MeOH extraction (ng/g plastic)			N total	Desorption[b] (%)	
		Mean	S.D.	Maximum	Mean	S.D.	Maximum		Mean	Maximum
PAHs	P1	0.31	0.44	1.50	30.65	39.05	138.30	11	1.5	4.7
	P2	24.90	19.99	67.20	30.93	38.52	114.80	7	51.9	70.6
	P3	5.21	8.65	27.40	75.05	142.69	496.60	11	14.1	65.2
	P4	1.39	3.19	9.20	38.41	27.77	80.10	8	2.2	14.8
	P5	n.d.	–	n.d.	6.73	10.02	28.20	7	0.4	1.1
OCPs	P1	3.88	8.33	23.80	0.97	1.64	5.30	11	62.9	100.0
	P2	29.11	66.40	179.20	n.d.	–	n.d.	7	–	–
	P3	2.17	3.61	11.20	2.38	3.17	8.40	11	35.2	100.0
	P4	0.59	1.18	3.20	3.88	10.80	30.60	8	–[a]	–
	P5	0.06	0.13	0.30	0.63	1.28	3.40	7	–[a]	–
PCBs	P1	n.d.	–	n.d.	5.16	17.13	56.80	11	–	–
	P2	0.14	0.38	1.00	n.d.	–	n.d.	7	–	–
	P3	0.03	0.09	0.30	31.94	53.64	140.30	11	–	–
	P4	n.d.	–	n.d.	0.04	0.11	0.30	8	–	–
	P5	n.d.	–	n.d.	n.d.	–	n.d.	7	–	–
Triazines	P1	2.04	2.54	7.80	18.15	40.43	138.40	11	41.4	100.0
	P2	15.54	15.59	39.70	6.44	11.92	32.00	7	70.7	100.0
	P3	3.73	7.54	25.80	8.82	12.57	42.80	11	41.1	94.8
	P4	2.09	4.41	12.70	9.60	11.97	36.90	8	16.1	51.7
	P5	0.78	0.52	1.20	9.70	8.76	20.30	7	27.5	78.2
OPPs	P1	1.42	1.55	4.80	4.04	6.74	20.70	11	63.4	100.0
	P2	46.76	57.35	168.80	0.16	0.42	1.10	7	99.4	100.0
	P3	8.53	9.76	31.00	40.35	106.41	359.40	11	55.8	100.0
	P4	7.50	18.82	54.00	5.99	10.58	31.00	8	38.7	100.0
	P5	0.12	0.13	0.30	32.37	49.30	104.60	7	25.1	100.0
Other Pesticides	P1	0.80	1.95	6.50	145.82	476.77	1583.30	11	23.9	63.1
	P2	5.49	12.77	34.30	n.d.	–	n.d.	7	100.0	100.0
	P3	5.69	6.14	19.20	5.34	8.99	25.50	11	57.7	100.0
	P4	6.30	15.00	42.90	61.65	138.50	401.20	8	28.1	100.0
	P5	0.28	0.26	0.50	1.90	2.15	6.40	7	26.3	100.0
PCPs	P1	45.91	151.87	503.80	401.95	646.89	2205.90	11	6.6	70.6
	P2	444.40	542.35	1589.00	672.99	676.02	1886.30	7	48.1	80.1
	P3	59.25	107.80	330.80	159.59	227.96	655.70	11	27.5	99.5
	P4	95.40	160.58	474.60	449.39	335.02	1060.70	8	12.9	58.8
	P5	0.10	0.17	0.40	57.84	117.32	321.60	7	20.6	60.7
Plastic additives	P1	156.78	218.95	661.10				11		
	P2	492.64	308.14	1056.50				7		
	P3	228.40	466.12	1552.70				11		
	P4	126.81	146.45	459.50				8		
	P5	56.12	78.13	172.30				7		
NP	P1	0.05	0.15	0.50				11		
	P2	n.d.	–	n.d.				7		
	P3	0.01	0.03	0.10				11		
	P4	n.d.	–	n.d.				8		
	P5	n.d.	–	n.d.				7		

[a] OCPs were not found simultaneously with both extraction procedures in every sample.
[b] Desorption percentage was calculated as mean of all desorption rates.

Thus, the log $K_{PE/SW}$ (partition coefficient between PE and seawater) ranged from 4.44 (phenanthrene) to 7.61 (benzo(ghi) perylene) (Endo et al., 2013). These coefficients varied between 4 and 6.69 and 5.39 and 7.15 in the case of log $K_{PP/SW}$ (partition coefficient between PP and seawater) and log $K_{PS/SW}$ (partition coefficient between polystyrene and seawater), respectively. Weathering has also been shown to have a significant effect on sorption and desorption kinetics and the capacity of plastic to sorb chemicals (Jahnke et al., 2017).

Considering all samples, the highest mean desorption fraction was found for the less hydrophobic compounds (log Kow <5, Table 1S) such as OPPs (55.5%), followed by triazines (32%) and other pesticides (31%) (Fig. 6A). The most hydrophobic contaminants (log Kow >5, Table 1S) (PCBs, OCPs and PAHs) showed the lowest desorption rates from plastic materials (e.g. 12.4% for PAHs), particularly for PCBs (Table 2, Fig. 6A), according to the results of a recent study (Lee et al., 2018). The desorption of organic contaminants decreased with their hydrophobicity as it is shown in Fig. 6 for the different contaminant groups (A) and the individual contaminants (B) considered in this study. The correlation between desorption and hydrophobicity (log Kow) of the different groups of contaminants (Fig. 6A) was low due probably to the heterogeneity of the pollutants and samples considered (origin, exposition period, ageing, etc.). Regarding the different polymers tested, desorption of triazines and OPPs was higher from PA and rubber than from other polymers (Table 3). This desorption was also close to total content for OCPs, other pesticides and PCPs from rubber, although care must be taken when considering this result because it corresponds to a single sample.

In order to compare the distribution profiles of different groups of contaminants factorial analysis was applied considering all data available for 24 h desorption. First factor analysis depended on contaminants related to urban, touristic and agriculture sources (PAHs, PCPs, plastic additives, triazines and OPPs). The highest

Table 3

Mean and maximum concentrations per plastic mass unit (ng/g plastic) of the different contaminant groups desorbed from plastic to seawater over 24 h and subsequently extracted with MeOH for each polymer type. The desorbed proportion expressed as a percentage is also included.

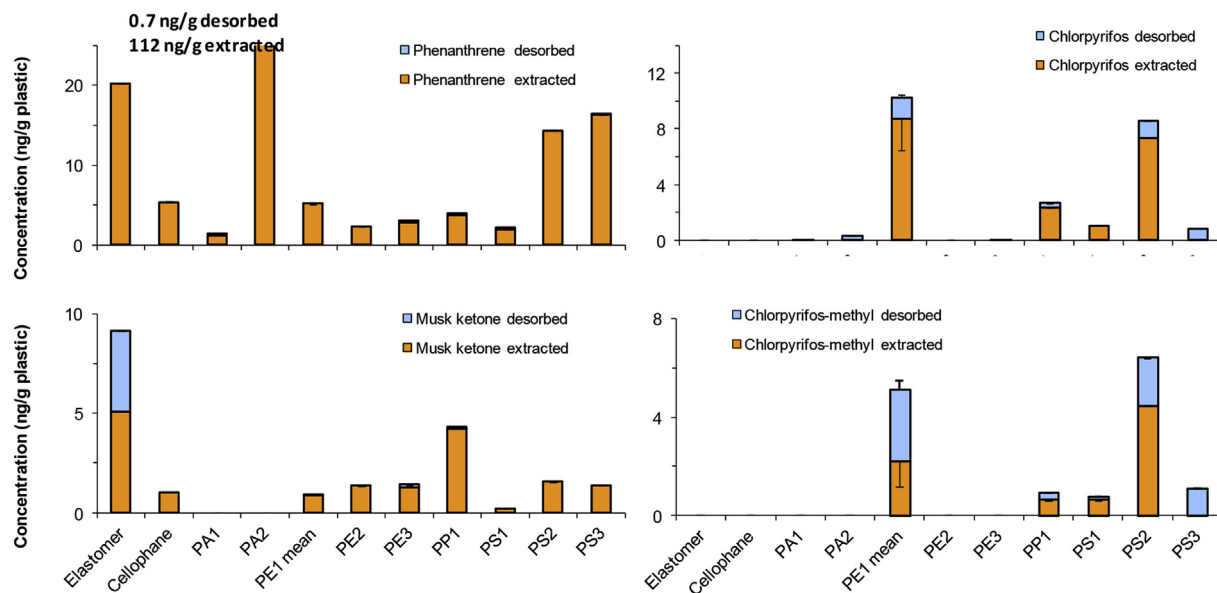|	Polymer	Desorption in seawater (24 h) (ng/g plastic)			MeOH extraction (ng/g plastic)			N total	Desorption (%)
		Mean	S.D.	Maximum	Mean	S.D.	Maximum		
PAHs	PE	4.26	9.02	26.90	26.09	26.46	79.80	13	7.9
	PP	3.73	6.81	20.50	51.58	147.66	496.60	11	18.8
	PS	11.58	27.25	67.20	55.65	36.13	114.80	6	8.0
	PVC	4.40	5.09	9.20	16.78	24.66	53.20	4	11.2
	PA	7.32	11.53	27.40	42.80	48.51	138.30	6	17.5
	PUR	0.20		0.20	54.15	36.70	80.10	2	0.3
	R	20.10		20.10	15.80		15.80	1	55.9
	E	1.50		1.50	45.20		45.20	1	3.2
OCPs	PE	0.37	0.83	2.60	4.04	8.53	30.60	13	–
	PP	21.49	59.25	179.20	0.57	1.07	3.30	11	–
	PS	1.95	3.84	9.70	0.63	1.00	2.20	6	42.7
	PVC	0.80	1.60	3.20	0.25	0.50	1.00	4	–
	PA	4.15	6.86	17.10	n.d.		n.d.	6	–
	PUR	n.d.		n.d.	1.70	2.40	3.40	2	–
	R	13.20		13.20	n.d.		n.d.	1	100.0
	E	23.80		23.80	5.30		5.30	1	81.7
PCBs	PE	n.d.		n.d.	26.27	50.76	140.30	13	
	PP	0.11	0.33	1.00	n.d.		n.d.	11	
	PS	n.d.		n.d.	1.68	4.12	10.10	6	
	PVC	n.d.		n.d.	n.d.		n.d.	4	
	PA	0.05	0.12	0.30	9.47	23.19	56.80	6	
	PUR	n.d.		n.d.	n.d.		n.d.	2	
	R	n.d.		n.d.	n.d.		n.d.	1	
	E	n.d.		n.d.	n.d.		n.d.	1	
Triazines	PE	2.30	3.33	10.50	4.72	5.58	15.70	13	30.8
	PP	4.52	11.45	35.00	8.05	7.85	20.30	11	24.0
	PS	7.52	15.79	39.70	47.50	45.72	138.40	6	14.5
	PVC	3.30	6.27	12.70	3.23	6.05	12.30	4	21.5
	PA	6.77	9.68	25.80	2.33	2.44	6.40	6	65.7
	PUR	0.40	0.56	0.80	9.40	0.28	9.60	2	7.8
	R	12.40		12.40	n.d.		n.d.	1	100.0
	E	7.80		7.80	5.80		5.80	1	57.1
OPPs	PE	21.54	46.06	168.80	8.26	12.85	31.00	13	61.3
	PP	3.79	5.09	15.20	22.40	40.67	104.60	11	52.1
	PS	7.32	14.53	36.90	62.67	145.44	359.40	6	48.5
	PVC	16.15	25.72	54.00	0.18	0.29	0.60	4	25.3
	PA	4.55	5.81	15.60	0.22	0.53	1.30	6	92.1
	PUR	0.05	0.07	0.10	5.15	6.43	9.70	2	1.2
	R	25.70		25.70	1.10		1.10	1	95.8
	E	n.d.		n.d.	20.70		20.70	1	0.0
Other	PE	2.96	5.60	19.20	5.18	8.36	25.50	13	37.8
	PP	1.69	3.47	10.40	1.15	1.91	6.40	11	38.4
Pest.	PS	0.55	1.21	3.00	8.58	17.38	43.80	6	0.1
	PVC	10.83	21.38	42.90	0.90	1.05	2.00	4	1.3
	PA	2.92	4.20	9.30	271.13	643.05	1583.30	6	48.3
	PUR	n.d.		n.d.	201.65	282.21	401.20	2	0.0
	R	34.30		34.30	n.d.		n.d.	1	100.0
	E	6.50		6.50	4.00		4.00	1	62.1
PCPs	PE	45.71	129.75	484.90	280.98	265.50	824.00	13	6.4
	PP	93.06	188.02	562.60	67.97	75.18	181.80	11	41.5
	PS	266.48	648.35	1589.90	501.50	458.05	1087.50	6	12.2
	PVC	168.55	224.65	474.60	558.83	898.16	1886.30	4	4.0
	PA	100.02	123.49	330.80	647.23	810.74	2205.90	6	23.0
	PUR	58.60		58.60	539.05	737.72	1060.70	2	5.2
	R	118.30		118.30	72.00		72.00	1	62.1
	E	503.80		503.80	209.50		209.50	1	70.6
Plastic Addit.	PE	136.04	224.04	627.40				13	
	PP	139.83	133.42	371.80				11	
	PS	274.13	408.56	1056.50				6	
	PVC	170.38	242.55	514.80				4	
	PA	368.32	597.94	1552.70				6	
	PUR	459.50		459.50				2	
	R	160.80		160.80				1	
	E	661.10		661.10				1	

Fig. 2. Concentration per plastic mass unit (ng/g plastic) of the different contaminant groups desorbed from plastic to seawater over 24 h and subsequently extracted with MeOH for each sample analyzed from the sampling area P1. Standard deviations for the desorbed (upper bar) and extracted (lower bar) fractions of the replicates of the sample PE1 (n = 3) are also shown in the graph.

significant correlations were found between PAHs and PCPs (0.864 p < 0.01) showing their similar distribution in Mar Menor littoral related mainly to urban and touristic activities. However, OCPs and other pesticides were included in factor 2 and 3 respectively showing inputs associated to other sources.

In the case of individual contaminants (Figs. 4 and 5; Tables 2S and 3S), the highest concentrations found in seawater corresponded to plastic additives, showing contributions higher than 1000 ng/g for tributyl acetyl citrate and tris-2-chloropropylphosphate due to fact that they can be desorbed from plastic components. In fact release rates may be higher for aged plastics (Koelmans et al., 2013; Rochman et al., 2013). The second most relevant group was PCPs, which showed the highest desorption for ethylhexyl salicylate (816.0 ng/g), galaxolide (479.4 ng/g), benzophenone (334.1 ng/g), tonalide (96.9 ng/g) and triclosan (37.6 ng/g). The high concentrations of these contaminants in plastics are directly related with the high levels of tourist activity around this lagoon. Ethylhexyl salicylate, polycyclic musks and benzophenone are used for cosmetics such as sun creams, while triclosan is commonly used as an antibacterial and anti-fungal agent in consumer products. In the case of current-use pesticides the highest desorption (Table 2S) was found for chlorpyrifos-methyl (44.9 ng/g plastic), boscalid (31.5 ng/g) and pendimethalin (8.4 ng/g) from PVC samples (sampling station P4); and for diazinon (154.6 ng/g), prometon (29.7 ng/g), terbutryn (27.5 ng/g), ametryn (23.0 ng/g), propyzamide (18.3 ng/g), chlorpyrifos (12.4 ng/g), terbuthylazine (12.3 ng/g) and benalaxyl (8.4 ng/g) from different polymers and sites. The agricultural application of pesticides in the surrounding area favours the presence and accumulation of insecticides, herbicides, etc. on plastic debris, particularly in those also used in agriculture. The presence of pesticides and PAHs in this area was also confirmed in particulate and dissolved fractions from air samples using polyurethane as a passive sampler, with chlorpyrifos and chlorpyrifos-methyl being the most commonly detected compounds in 2010 (Carratalá et al., 2017). On the other hand, the majority of PAHs were not transferred to seawater in 24 h, as shown for phenanthrene in Fig. 4.

Previous studies have shown an increase of the sorption capacity for PAHs, HCHs and PCBs in the order PP, PE to PS (Lee et al., 2014), while the partition coefficients of phenanthrene were in the order PE > PP > PVC (Teuten et al., 2007). Many of these studies, however, focused on the sorption capacity of samples and not on the reversibility of this process. The desorption rate can be crucial for estimating the potential transfer of contaminants from plastic to each marine compartment. By polymer, the maximum desorbed concentrations were found for triazines, OPPs and PAHs from polystyrene (PS), for OCPs and PCBs from PE and for PCPs from other polymers (Table 3). PS is commonly used for packaging and agricultural applications (e.g. seed trays) and consequently the exposure of this polymer to current-use pesticides can be particularly high in crop-growing areas. Although sorption and desorption capacity depends on the contaminant group and polymer properties, in the case of environmental polymers prior exposure to pollutant sources (distance, physicochemical and meteorological conditions, etc.) can also be a relevant factor.

These results confirm that a significant fraction of sorbed contaminants on littoral plastics, particularly for those less strongly sorbed, is released into seawater only 24 h after their input in the marine environment. The most hydrophobic compounds (PAHs, PCBs and OCPs) showed lower desorption rates, and consequently they can be transported sorbed on plastics to the marine environment. Thus, longer desorption periods could permit the transfer of a higher fraction of contaminants to seawater. In fact, a longer period is required for the complete desorption of highly hydrophobic contaminants (log Kow>5) from plastic polymers, as has been observed for phenanthrene (5 days required) and DDT (15 days) from PVC and PE (Bakir et al., 2014). In other studies after 3 months of PCBs desorption from PE pellets, the smallest congener (CB 8) was almost entirely desorbed, whereas major fractions of highly chlorinated congeners remained in the pellets (Endo et al., 2013). Consequently the input of plastics can have an impact not only as a result of their presence in the sea but also of the significant input of contaminants desorbed from these materials.
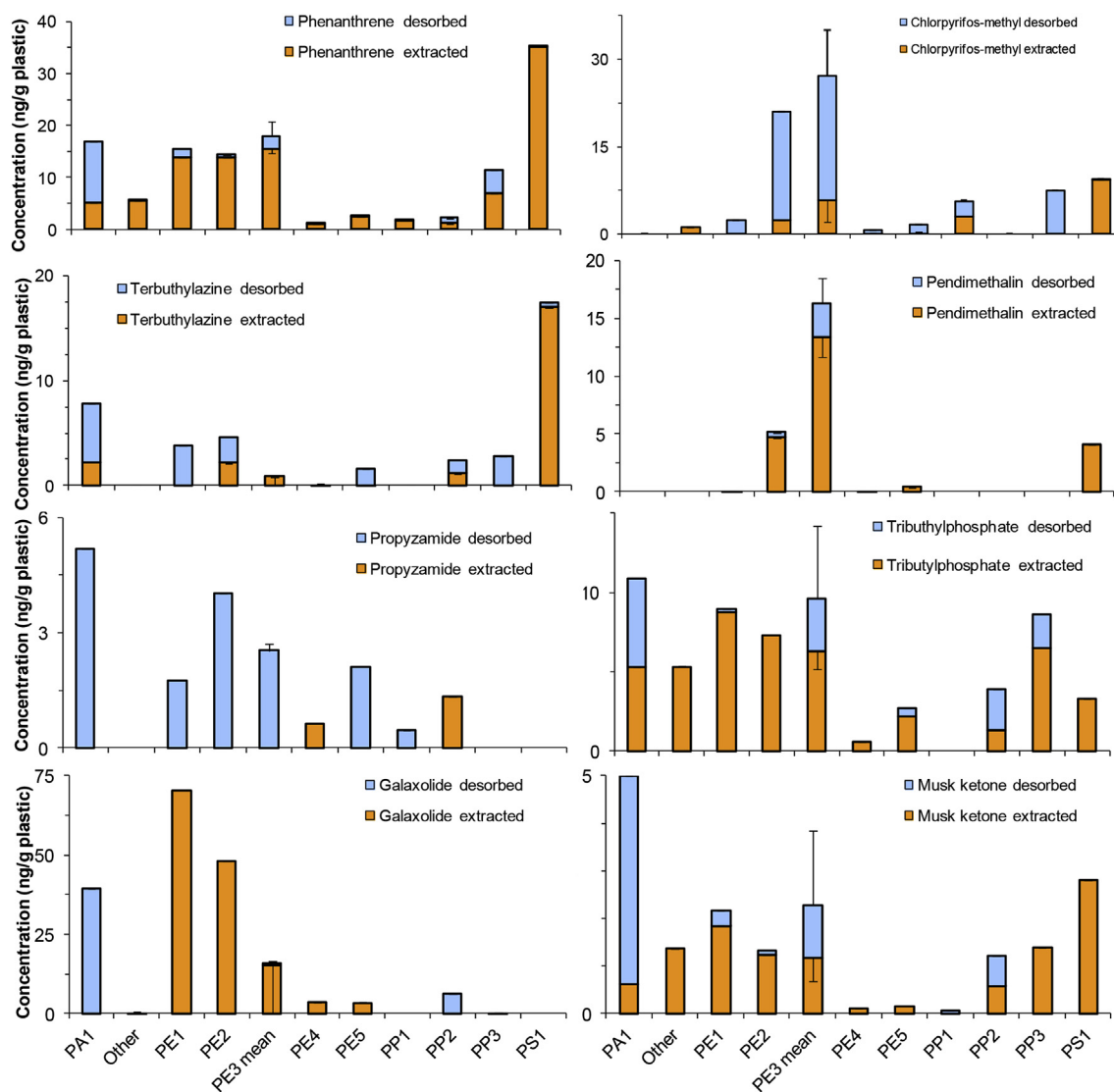
Fig. 3. Concentrations per plastic mass unit (ng/g plastic) of the different contaminant groups desorbed from plastic to seawater over 24 h and subsequently extracted with MeOH for each sample analyzed from the sampling area P3. Standard deviations for the desorbed (upper bar) and extracted (lower bar) fractions of the replicates of the sample PE3 are also shown in the graph.

3.3. Potential transport of organic pollutants in plastics

After first 24 h desorption from plastics to seawater, the remaining organic contaminants present in plastics were extracted with methanol. MeOH extraction favoured the desorption of plastic additives, including those ones included as polymer constituents, which were found in 95.8% of samples. Consequently this fraction was not considered in this study because it should be higher than desorption in seawater and it could be not environmentally relevant.

66 of 91 pollutants analyzed were found in one or more of the extracted samples. The maximum number of substances detected per plastic sample was 35, this being in PE samples from sampling area P3, whilst the minimum number of contaminants detected was 7 (P5). The mean number of substances found per sample varied from 14.0 to 24.7 for areas P5 and P3, respectively, which were higher than those found for the desorbed fraction.

The most commonly detected contaminants in the extracted fraction were PAHs (present in 97.9% of total samples), PCPs (93.8%), triazines (77.1%), OPPs (62.5%), other pesticides (60.4%), OCPs and

PCBs (39.6%). However, in the desorbed fraction OPPs were the most prevalent group, probably due to the weaker sorption of these substances to plastic debris. In the case of specific contaminants, the most prevalent ones in the extracts were phenanthrene (95.8% of samples), fluorene (89.6%), tributhylphosphate (87.5%), musk-ketone, fluoranthene and naphthalene (83.3%) and pyrene and tonalide (81.3%) (Tables 2S and 3S). Thus, PAHs were the most commonly found contaminants in the extracts, rather than pesticides, which were the prevalent ones in the 24 h desorbed fraction.

The highest concentration of PAHs was found in plastics from P3 (Table 2), probably due to the proximity of this point to several roads, including a motorway. The maximum concentrations of PAHs and PCBs were lower than those found in plastic pellets from other areas (Zhang et al., 2015), although PAHs concentrations were of the same magnitude as those in other studies (Frias et al., 2010; Van et al., 2012). The highest concentration of PAHs was found in a PP sample (496.6 ng g^{-1}, Table 3) and in the majority of cases the most abundant proportion corresponded to phenanthrene, as was also observed in air samples from this area (Carratalá et al., 2017), except in one sample from P3, in which acenaphthylene was found
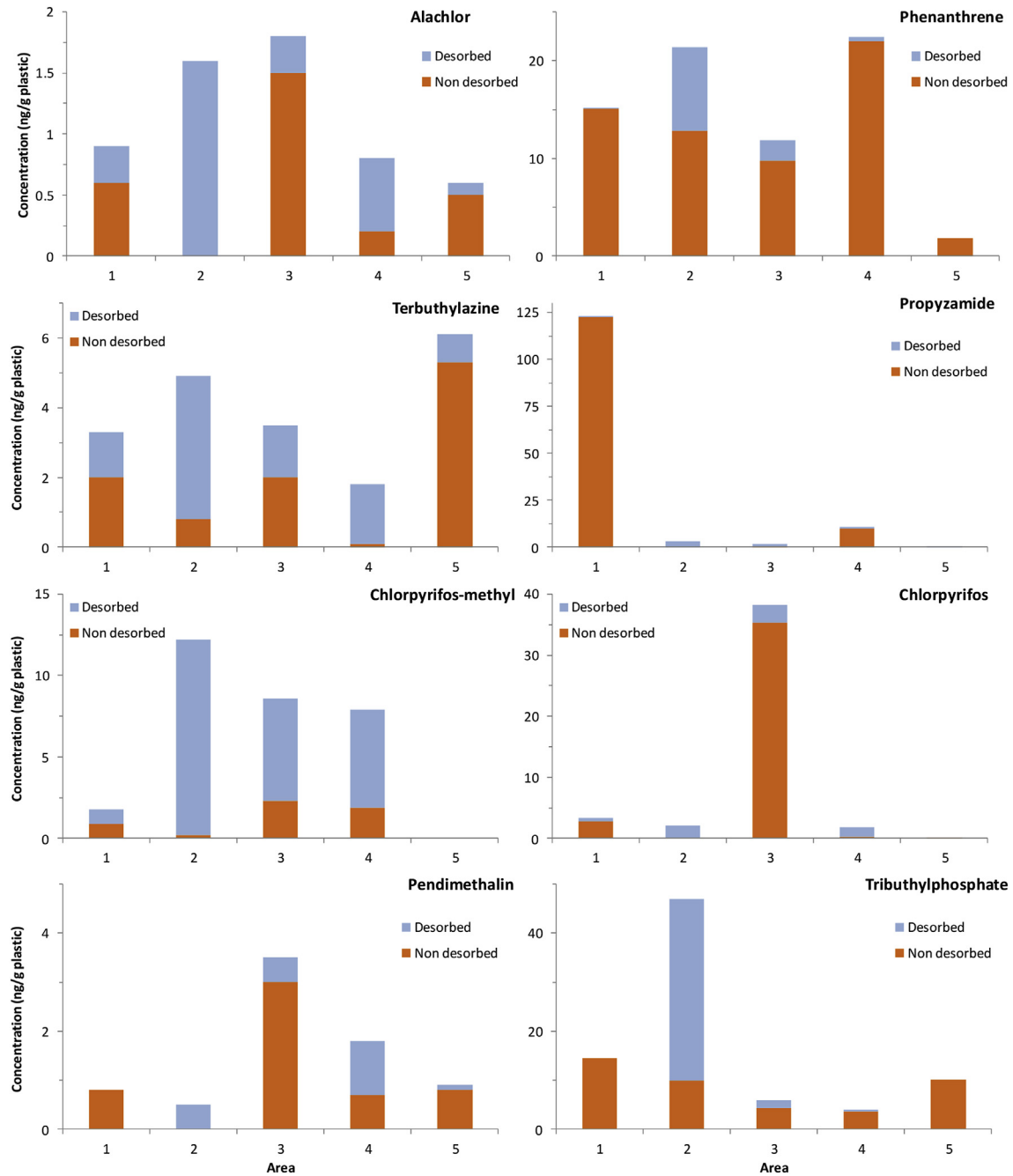
Fig. 4. Concentrations per plastic mass unit (ng/g plastic) of the most relevant OCPs, PAHs and pesticides desorbed from plastic to seawater over 24 h and subsequently extracted with MeOH for each sampling area (P1 to P5).

at 361 ng g^{-1}. However, in Portuguese beaches the most abundant PAH was pyrene (Frias et al., 2010). In another study, total PAHs concentrations in microplastics deployed for one year in San Diego Bay were higher in PE than PP (Rochman et al., 2013). In our study there is no information about the exposure period for every plastic sampled, and therefore no direct comparison between the sorption capacities of the different polymers can be derived from our study. However, the results obtained offer a real view of the potential transport of pollutants present in plastic debris from littoral areas and the readily desorbed fraction in seawater.

The most hydrophobic contaminants considered in this study, PCBs, were only found in the extracted samples. The highest concentration of PCBs was found at sampling point P3, particularly in a PE sample (Tables 2 and 3). p,p'-DDT and p,p'-DDE were found in some plastic samples at similar concentrations as in Portuguese beaches (<0.1–4.05 ng/g, Frias et al., 2010), but at lower concentrations than in Chinese beaches (1.15–126.95 ng/g, Zhang et al., 2015).

Although a significant proportion of OPPs, triazines, other pesticides and PCPs was desorbed during the first 24 h, high concentrations were still present in the extracts obtained from specific samples (Tables 2 and 3). In fact, higher concentrations of CUPs were found in the plastic extracts than in the desorbed fraction, as in the case of propyzamide, boscalid and chlorpyrifos (1583, 395 and 350 ng g^{-1} plastic, respectively; Table 2S). Similarly the highest concentrations of PCPs were also found in the methanolic extracts
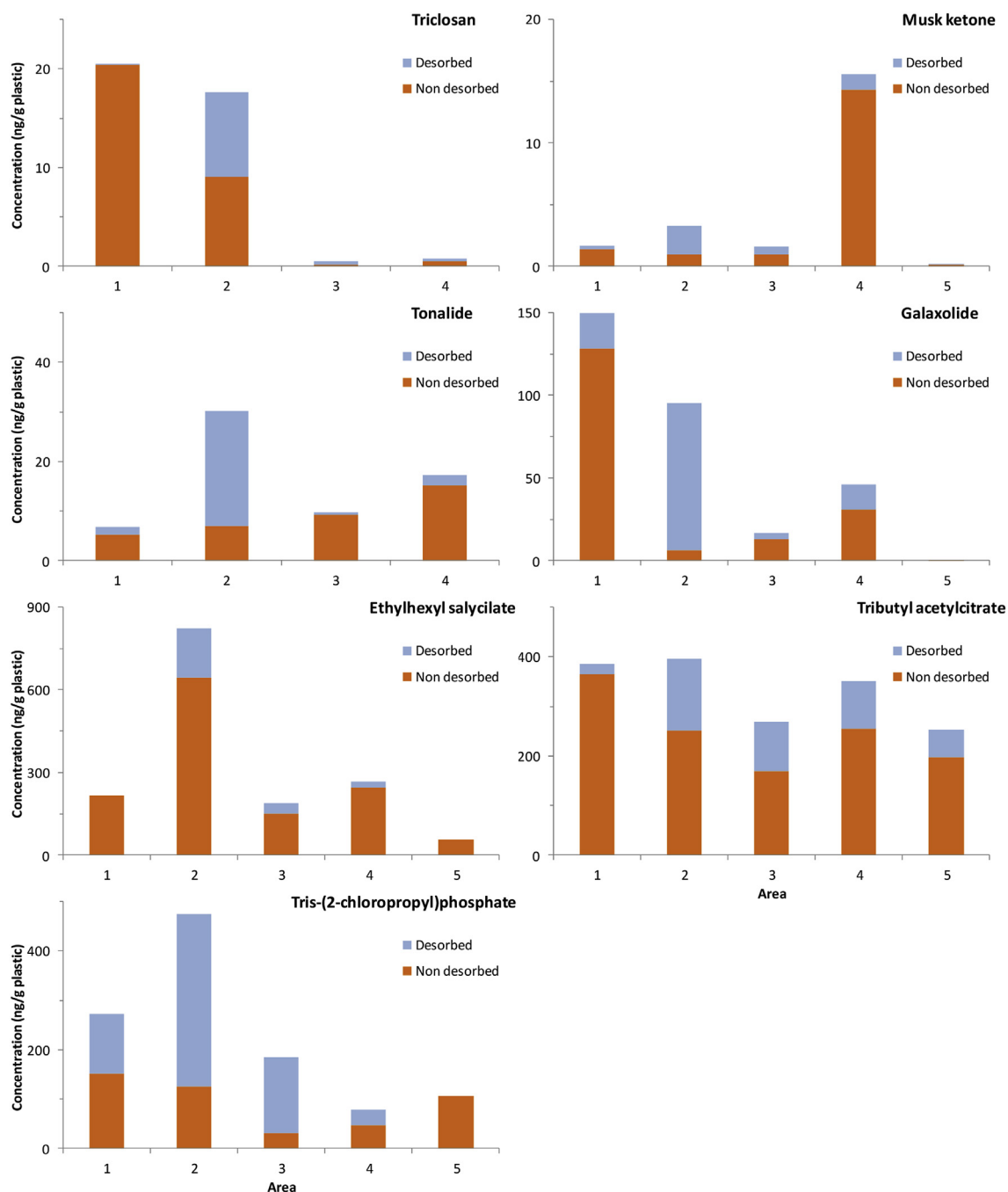
Fig. 5. Concentrations per plastic mass unit (ng/g plastic) of the most relevant PCPs and plastic additives desorbed from plastic to seawater over 24 h and subsequently extracted with MeOH for each sampling area (P1 to P5). Data not included corresponded to areas where this compound was not detected (n.d.) in any sample from this sampling point.

for galaxolide, benzophenone, triclosan, musk ketone and tonalide (1583, 588, 159, 110 and 109 ng g^{-1} plastic, respectively; Table 3S). The lowest concentrations and smallest number of contaminants were found in plastics sampled from the littoral area located at greater distances from the main pollution sources (P5).

In order to compare distribution profiles of different groups of contaminants factorial analysis was also applied considering all data available for MeOH extraction. First factor analysis depended on PCPs and other pesticides, which showed significant correlation (0.636 p < 0.01). However, OCPs and other pesticides were included in factor 2 and 3 respectively showing inputs associated to other sources.

Organic contaminants, not desorbed in the first 24 h, represent the fraction of these compounds which can be potentially transfered to organisms (i.e.: ingestion), sediments (deposition, flocculation, etc.) or seawater (desorption). In all probability part of the contaminant content could be desorbed from plastic with longer exposure periods in seawater, while the rest can be transferred to sediments or biota. The persistence and effects of these contaminants will depend on the physicochemical and environmental conditions and their specific properties. This study has shown the significance of both transfer pathways (fast desorption and total content) for the majority of considered contaminants in a coastal area.
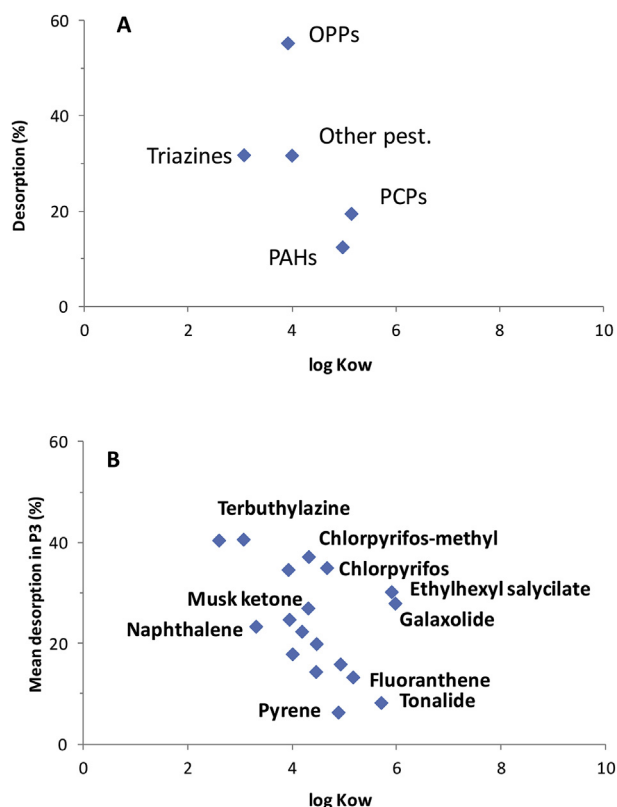
Fig. 6. Relationship between mean desorption (%) of different group of contaminants from plastics of all areas and their mean hydrophobicity expressed as mean log Kow (A), and between mean desorption from P3 samples and the hydrophobicity of individual contaminants (log Kow).

3.4. Environmental implications

The worldwide use of plastic materials, in many cases for a single use, combined with negligence on the part of their users, favour their presence in the continental environment and their transport over long distances (i.e.: aerial and river transport), particularly for smaller fragments, due to their low density. The input of organic contaminants from continental to coastal areas has frequently been shown to be the result of their sorption to particulate materials, but this transport can also be particularly relevant when associated to plastic debris. This study has shown that plastic debris of different origins and polymers accumulates the prevalent HOCs of the surrounding area (e.g. PAHs, pesticides and PCPs in the case of the Mar Menor lagoon). Items of plastic debris can thus be considered a means of transport of many persistent and emerging contaminants from polluted areas to other systems, including the marine environment. A significant contribution of organic contaminants from plastics has also been observed after only a few hours following the immersion in seawater. In fact, 1—2 mg of PCPs or CUPs and 0.5 mg of PAHs can be transported by 1 kg of plastic, together with the important contribution associated to the desorption of plastic additives and components. Previous studies have focused on the sorption of contaminants once plastics reach the marine environment, but this is the first study that shows the input of organic contaminants in the marine environment through different kinds of littoral plastic debris and the relevance of this process. Obviously the relative relevance of each contaminant group will differ from one area to another depending on the prevalent anthropogenic activities, but the role of plastics as a contamination vector from continental areas to the sea has been confirmed in this study through the simulation of the desorption of organic contaminants from real plastic debris. The transport of sorbed contaminants also takes place in other particulate materials (soil, vegetable debris, etc.), being probably more relevant due to their greater masses in the environment, but the low density of plastics can favour their aerial or watercourse transport over longer distances. Once items of plastic debris reach the sea part of the sorbed contaminants are transferred to seawater, and simultaneously additional contaminants present in the marine environment can be sorbed to their surface from the surrounding environment and transferred to biota or sediments. Consequently, given the huge amounts of these materials that continuously reach the marine environment this transport should be considered to be environmentally relevant. Additional effort is therefore required in plastic waste management so as to minimize the impact of plastic debris reaching the marine environment (adverse physical effects, plastic components and the desorption of other contaminants), particularly as a result of tourist activities (beach picnics, pleasure boats, etc.), agricultural uses and everyday life in coastal urban nuclei.

4. Conclusions

Plastics act as passive samplers in the environment, accumulating HOCs which are partially transferred to the marine system once they enter the seawater column. More than 60 contaminants were found in some plastic samples (PAHs, OPPs, PCPs, triazines, other pesticides, PCBs and plastic additives), the highest contribution corresponding to the leaching of plastic additives. A significant proportion of those contaminants can be desorbed from plastics to seawater in the first 24 h (average rate 20—55%), particularly in the case of less hydrophobic compounds (OPPs, triazines and PCPs). The most commonly detected contaminants (>70% of total samples) in the 24 h desorbed fraction were OPPs, PAHs, and triazines. However, in the fraction retained by plastic the predominant contaminants were PAHs, PCPs and triazines. A slower desorption rate was observed for the more HOCs (PAHs, OCPs and PCBs; log Kow >5), which can be transported over longer distances sorbed on plastic materials. In this study a significant contribution of organic contaminants from plastics to the marine environment has also been confirmed. The maximum concentrations in the studied area show that 1.8 mg of PCPs, 0.4 mg of OPPs, 0.1 mg of triazines, 1.7 mg of other pesticides and 0.5 mg of PAHs can be transported per kilogram of plastic, in addition to the significant contribution associated to the desorption of plastic additives and components.

The input of plastics from inland areas to coastal seawater is relevant not because of the impact of the plastics themselves, but also because of the organic contaminants which are sorbed on them. Additional efforts should therefore be made to reduce these inputs by improving the recovery and recycling of plastic materials after use.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2018.01.114.

References

Andrady, A.L., 2011. Microplastics in the marine environment. Mar. Pollut. Bull. 62, 1596—1605.

Avery-Gomm, S., O'Hara, P.D., Kleine, L., Bowes, V., Wilson, L.K., Barry, K.L., 2012. Northern fulmars as biological monitors of trends of plastic pollution in the eastern North Pacific. Mar. Pollut. Bull. 64, 1776—1781.

Bakir, A., Rowland, S.J., Thomson, R.C., 2014. Transport of persistent organic pollutants by microplastics in estuarine conditions. Estuar. Coast. Shelf Sci. 140, 14—21.

Bakir, A., O'Connor, I.A., Rowland, S.J., Hendriks, A.J., Thomson, R.C., 2016. Relative importance of microplastics as a pathway for the transfer of hydrophobic organic chemicals to marine life. Environ. Pollut. 219, 56—65.

Bellas, J., Martínez-Armental, J., Martínez-Cámara, A., Besada, V., Martínez-Gómez, C., 2016. Ingestion of microplastics by demersal fish from the Spanish Atlantic and Mediterranean coasts. Mar. Pollut. Bull. 109, 55—60.

Boerger, C.M., Lattin, G.L., Moore, S.L., Moore, C.J., 2010. Plastic ingestion bhy planktivorous fishes in the north Pacific Central Gyre. Mar. Pollut. Bull. 60, 2275—2278.

Brien, S., 2007. Presentation at the world vinyl forum 2007. Sept 2007. Retrieved from. http://vinyl-institute.com/Publication/WorldVinylForumIII/VinylIndustryUpdate.aspx.

Carratalá, A., Moreno-González, R., León, V.M., 2017. Occurrence and seasonal distribution of polycyclic aromatic hydrocarbons and legacy and current-use pesticides in air from a Mediterranean coastal lagoon (Mar Menor, SE Spain). Chemosphere 167, 382—395.

Cózar, A., Sanz-Martín, M., Martí, E., González-Gordillo, J.I., Úbeda, B., Gálvez, J.A., Irigoien, X., Duarte, C.M., 2015. Plastic accumulation in the Mediterranean sea. PLoS One 10 (4), e0121762. https://doi.org/10.1371/journal.pone.0121762.

Denuncio, P., Bastida, R., Dassis, M., Giardino, G., Gerpe, M., Rodríguez, D., 2011. Plastic ingestion in franciscana dolphins, Pontoporia blainvillei (Gervais and d'Orbigny, 1844), from Argentina. Mar. Pollut. Bull. 62, 1836—1841.

Endo, S., Takizawa, R., Okuda, K., Takada, H., Chiba, K., Kanehiro, H., Ogi, H., Yamashita, R., Date, H., 2005. Concentration of polychlorinated biphenyls (PCBs) in beached resin pellets: variability amon individual particles and regional differences. Mar. Pollut. Bull. 50, 1103—1114.

Endo, S., Yuyama, M., Takada, H., 2013. Desorption kinetic of hydrophobic organic contaminants from marine plastic pellets. Mar. Pollut. Bull. 74, 125—131.

Engler, R.E., 2012. The complex interaction between marine debris and toxic chemicals in the ocean. Environ. Sci. Technol. 46, 12302—12315.

Frias, J.P.G.L., Sobral, P., Ferreira, A.M., 2010. Organic pollutants in microplastics from two beaches of the Portuguese coast. Mar. Pollut. Bull. 60, 1988—1992.

Gauquie, J., Devriese, L., Robbens, J., De Witte, B., 2015. A qualitative screening and quantitative measurement of organic contaminants on different types of marine plastic debris. Chemosphere 138, 348—356.

Hirai, H., Takada, H., Ogata, Y., Yamashita, R., Mizukawa, K., Saha, M., Kwan, C., Moore, C., Gray, H., Laursen, D., Zettler, E.R., Farrington, J.W., Reddy, C.M., Peacock, E.E., Ward, M.W., 2011. Organic micropollutants in marine plastics debris from the open ocean and remote and urban beaches. Mar. Pollut. Bull. 62, 1683—1692.

Iñiguez, M.E., Conesa, J.A., Fullana, A., 2017. Pollutant content in marine debris and characterization by thermal decomposition. Mar. Pollut. Bull. 117, 359—365.

Jahnke, A., Arp, H.P.H., Escher, B.I., Gewert, B., Gorokhova, E., Kühnel, D., Ogonowski, M., Potthoff, A., Rummel, C., Schimitt-Jansen, M., Toorman, E., MacLeod, M., 2017. Reducing unertainty and confronting ignorance about the possible impacts of weathering plastic in the marine environment. Environ. Sci. Technol. Lett. 4, 85—90.

Karapanagoioti, H.K., Klontza, I., 2008. Testing phenanthrene distribution properties of virgin plastic pellets and plastic eroded pellets found on Lesvos Island beaches (Greece). Mar. Environ. Res. 65, 283—290.

Koelmans, A.A., Besseling, E., Wegner, A., Foekema, E.M., 2013. Plastic as a Carrier of POPs to aquatic organisms. A model analysis. Environ. Sci. Technol. 47, 7812—7820.

Koelmans, A.A., Besseling, E., Foekema, E.M., 2014. Leaching of plastic additives to marine organisms. Environ. Poll 187, 49—54.

Koelmans, A.A., Bakir, A., Burton, G.A., Janssen, C.R., 2016. Microplastic as a vector for chemicals in the aquatic environment: critical review and model-supported reinterpretation of empirical studies. Environ. Sci. Technol. 50, 3315—3326.

Lee, H., Shim, W.J., Kwon, J.H., 2014. Sorption capacity of plastic debris for hydrophobic organic chemicals. Sci. Total Environ. 470—471, 1545—1552.

Lee, H., Byun, D.E., Kim, J.M., Kwon, J.H., 2018. Desorption modeling of hydrophobic organic chemicals from plastic sheets using experimentally determined diffusion coefficients in plastics. Mar. Pollut. Bull. 126, 312—317.

Martínez-Gómez, C., León, V.M., Calles, S., Gomáriz-Olcina, M., Vethaak, A.D., 2017. The adverse effects of virgin microplastics on the fertilization and larval development of sea urchins. Mar. Environ. Res. 130, 69—76.

Mato, Y., Tomohiko, I., Takada, H., Kanehiro, H., Ohtake, C., Kaminuma, T., 2001. Plastic resin pellets as a transport medium for toxic chemicals in the marine environment. Environ. Sci. Technol. 35, 318—324.

Mato, Y., Takada, H., Zakaria, M.P., Kuriyama, Y., Kanehiro, H., 2002. Toxic chemicals contained in plastic resin pellets in the marine environment —spatial difference in pollutant concentrations and effects of resin type. Kankyo Kagakukaishi 15, 415—423.

Moreno-González, R., Campillo, J.A., León, V.M., 2013. Influence of an intensive agricultural drainage basin on seasonal distribution of organic pollutants in seawater from a Mediterranean coastal lagoon (Mar Menor, SE Spain). Mar. Pollut. Bull. 77, 400—411.

Moreno-González, R., León, V.M., 2017. Presence and distribution of current-use pesticides in surface marine sediments from a Mediterranean coastal lagoon (SE Spain). Environ. Sci. .Pollut. Res. (en prensa). https://doi.org/10.1007/s11356-017-8456-0.

Murray, F., Cowie, P.R., 2011. Plastic contamination in the decapod crustacean Nephrops norvegicus (Linnaeus, 1758). Mar. Pollut. Bull. 99, 178—185.

PlasticsEurope, 2015. Plastics — The Facts 2014/2015. An Analysis of European Plastics Production, Demand and Waste Data. www.plasticseurope.org.

Paul-Pont, I., Lacroix, C., González-Fernández, C., Hegaret, H., Lambert, C., Le Goïc, N., Frère, L., Cassone, A.L., Sussarellu, R., Fabioux, C., Guyomarch, J., Albentosa, M., Huvet, A., Soudant, P., 2016. Exposure of marine mussels Mytilus spp. To polystyrene microplastics: toxicity and influence on fluoranthene bioaccumulation. Environ. Pollut. 216, 724—737.

Rani, M., Shim, W.J., Han, G.M., Jang, M., Al-Odaini, N.A., Song, Y.K., Hong, S.H., 2015. Qualitative analysis of additives in plastic marine debris and its new products. Arch. Environ. Contam. Toxicol. 69, 352—366.

Rochman, C.M., Hoh, E., Hentschel, B.T., Kaye, S., 2013. Long-term fiel measurement of sorption of organic contaminants to five types of plastic pellets: implications for plastic marine debris. Environ. Sci. Technol. 47, 1646—1654.

Ryan, P.G., Connell, A.D., Gardner, B.D., 1988. Plastic ingestion and PCBs in seabirds: Is there a relationship? Mar. Pollut. Bull. 19, 174—176.

Sanz-Navarro, J., 2008. Utilización de plaguicidas en las asociaciones de tratamientos integrados en agricultura de la Región de Murcia. Consejería de Sanidad Región de Murcia, Dirección General de Salud Pública, Servicio de Sanidad Ambiental de Murcia, ISBN 978-84-96994-14-0.

Scarascia-Mugnozza, G., Sica, C., Russo, G., 2011. Plastic materials in European agriculture: actual use and perspectives. J. Ag. Eng. Riv. di Ing. Agr. 3, 15—28.

Suaria, G., Avio, C.G., Mineo, A., Lattin, G.L., Magaldi, M.G., Belmonte, G., Moore, C.J., Regoli, F., Aliani, S., 2016. The Mediterranean Plastic Soup: synthetic polymers in Mediterranean surface waters. Nat. Sci. Rep. 6 https://doi.org/10.1038/srep37551.

Tanaka, K., Takada, H., Yamashita, R., Mizukawa, K., Fukuwaka, M.A., Watanuki, Y., 2013. Accumulation of plastic-derived chemicals in tissues of seabirds ingesting marine plastics. Mar. Pollut. Bull. 69, 219—222.

Teuten, E.L., Rowland, S.J., Galloway, T.S., Thomson, R.C., 2007. Potential for plastics to transport hydrophobic contaminants. Environ. Sci. Tech. 41, 7759—7764.

Teuten, E.L., Saquing, J.M., et al., 2009. Transport and release of chemicals from plastics to the environment and to wildlife. Phil. Trans. R. Soc. B 364, 2027—2045.

Thomson, R.C., Olsen, Y., Mitchell, R.P., Davis, A., Rowland, S.J., John, A.W., McGonigle, D., Russell, A.E., 2004. Lost at sea: where is all the plastic. Science 304, 838.

Van, A., Rochman, C.M., Flores, E.M., Hill, K.L., Vargas, E., Vargas, S.A., hoh, E., 2012. Persistent organic pollutants in plastic marine debris found in beaches in San Diego, California. Chemosphere 86, 258—263.

Veerasingam, S., Saha, M., Suneel, V., Vethamony, P., Rodrigues, A.C., Bhattacharyya, S., Naik, B.G., 2016. Characteristics, seasonal distribution and surface degradation features of microplastic pellets along the Goa coast, India. Chemosphere 159, 496—505.

Ward, E.J., Shumway, S.E., 2004. Separating the grain from the chaff: particle selection in suspension- and deposit-feeding bivalves. J. Exp. Mar. Biol. Ecol. 300, 83—130.

Wu, C., Zhang, K., Huang, X., Liu, J., 2016. Sorption of pharmaceuticals and personal care products to polyethylene debris. Environ. Sci. Pollut. Res. 23, 8819—8826.

Yu, X., Peng, J., Wang, J., Wang, K., Bao, S., 2016. Occurrence of microplastics in the beach sand of the Chinese inner sea: the Bohai Sea. Environ. Pollut. 214, 722—730.

Zhang, W., Ma, X., Zhang, Z., Wang, Y., Wang, J., Wang, J., Ma, D., 2015. Persistent organic pollutants carried on plastic resin pellets from two beaches in China. Mar. Pollut. Bull. 99, 28—34.