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Persistent organic pollutants carried by synthetic polymers in the ocean environment

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Abstract

Thermoplastic resin pellets are melted and formed into an enormous number of inexpensive consumer goods, many of which are discarded after a relatively short period of use, dropped haphazardly onto watersheds and then make their way to the ocean where some get ingested by marine life. In 2003 and 2004 pre-production thermoplastic resin pellets and post-consumer plastic fragments were collected and analyzed for contamination for persistent organic pollutants (POPs). Samples were taken from the North Pacific Gyre, and selected sites in California, Hawaii, and from Guadalupe Island, Mexico. The total concentration of PCBs ranged from 27 to 980 ng/g; DDTs from 22 to 7100 ng/g and PAHs from 39 to 1200 ng/g, and aliphatic hydrocarbons from 1.1 to 8600 μg/g. Analytical methods were developed to extract, concentrate and identify POPs that may have accumulated on plastic fragments and plastic pellets. The results of this study confirm that plastic debris is a trap for POPs.

Keywords: Persistent organic pollutants; Plastic contaminants; PCBs in plastics; DDTs in plastics; PAHs in plastics; Plastic debris; Plastic pellets

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1. Introduction

Plastic materials comprise one of the most persistent macroscopic pollutants in oceanic waters and beaches in the world. There are many published reports about plastic debris found throughout the world's oceans (Colton et al., 1974; Shiber, 1979; Ryan, 1988; Shaw and Day, 1994; Golberg, 1995; Gregory, 1996; Guillet, 1997; Henderson, 2001; Ericksson and Burton, 2003; Otley and Ingham, 2003; McDermid and McMullen, 2004; Moore et al., 2001, 2002; Barnes, 2005).

The proliferation of plastic can be mainly attributed to inexpensive production costs and the light weight and varied properties of plastics. One pound of the most common pellets costs about $1US and contains approximately 25,000 pellets. Synthetic polymers are used to package almost everything in the consumer society. These favorable properties result in the production of high volumes of plastic goods, many classified as "throwaways" – single use products.

The physical characteristics of polyethylene- and polypropylene-based plastics show a high resistance to aging and minimal biological degradation. Marine litter is consistently between 60% and 80% plastic by mass (Derraik, 2002).

Plastics are primarily synthetic organic polymers derived from petroleum. When exposed to UV radiation in sunlight, these polymers break into smaller and smaller pieces, but they are still present as plastic, and they are not biodegradable in any practical human scale of time. This persistence of plastic leads to an increasing abundance in the ocean environment, which makes plastic debris more accessible to plankton and other marine life. Plastic debris and minute plastic particles, including pre-production plastic pellets, sometimes called nurdles or resin beads, are found floating in the ocean and stranded on beaches. Forty-four percent of all seabird species ingest floating plastic while feeding on or near the surface of the ocean,

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picking up anything that might resemble their natural food (Minchin, 1996; Auman et al., 1997; Blight and Burger, 1997; Bugoni et al., 2001; Cadée, 2002; Page et al., 2004).

Andrady (2000) found that degradation of plastic materials occurs slower in the ocean than on land, because cool ocean water inhibits the thermal loading that accelerates degradation on land. The length of time various plastic polymers persist in the ocean is not reliably known. Moore et al. (2001, 2002) found the mass of plastic material is 6 times that of plankton in the North Pacific Central Gyre and, 2.5 times that of plankton in California's southern coastal waters.

Most literature on plastic debris focuses on the classification and enumeration of the different kinds of plastic found on beaches and in seawater samples. Some papers report the measurement of PCBs and DDTs on plastic pellets made of polypropylene (PP) and polyethylene (PE) (Mato et al., 2001; Endo et al., 2005). We focus on these pollutants as well as other POPs to determine the amounts that are sorbed by various plastic samples.

The objective of this research is to analyze pre-production pellets, and post-consumer plastic fragments found in marine debris to quantify the concentration of pollutants including PCBs, PAHs, and organochlorine pesticides, such as DDTs, and aliphatic hydrocarbons. The existence and amount of many of these POPs in plastic marine debris has not been previously reported in the literature.

POPs are synthetic organic compounds which are widespread on land and in aquatic environments. They are considered among the most persistent anthropogenic organic compounds introduced into the environment. Some of these are highly toxic and have a wide range of chronic effects, including endocrine disruption, mutagenicity and carcinogenicity (Singh et al., 1998; Pauwels et al., 1999; Sultan et al., 2001; Tanabe, 2004). Furthermore, POPs are chemically stable, and therefore not easily degraded in the environment or in organisms. They are lipophilic and accumulate in the food chain.

Polychlorinated biphenyl's (PCB's) are mixtures of up to 209 individual chlorinated compounds (known as congeners), of which 113 are known to be present in the environment (Pascal et al., 2005; NWF, 1994). At least half of the PCBs produced are still in use, especially in older electrical equipment, or in storage. Thus, there remains a huge reservoir of PCBs with the potential to be released into the environment either through spills or leakage from transformers and other devices. Additionally, the migration of these chemicals from sediments that are known to contain high concentrations of PCBs to water provides an ongoing supply of the materials to the water phase (Brasher and Wolff, 2004; Barreira et al., 2005).

Organo-chlorine pesticides are synthetic compounds that are chemically stable and hydrophobic. They include DDT (dichloro-diphenyl-trichloroethane), a pesticide used in agriculture and as an insecticide. This pesticide was used in the late 1940s, greatly restricted in the 1970s and now banned for general use in the US and Canada. BHC (hexachlorocyclohexane), chlordane, and dieldrin, are other chlorinated pesticides used in agriculture.

Polycyclic aromatic hydrocarbons (PAHs) are a group of over 100 different chemicals that are formed during the incomplete burning of coal, oil, and gas, garbage, or other organic substances like tobacco or charbroiled meat. PAHs are usually found as a mixture containing two or more of these compounds. Soot contains PAHs. Some PAHs are manufactured. These pure PAHs usually exist as colorless, white, or pale yellow–green solids. PAHs are found also in coal tar, crude oil, creosote, and roofing tar. A few are used in medicines or to make dyes, plastics, and pesticides. These compounds are produced in many cases by anthropogenic activities. They can be separated into three non-exclusive categories based on their source: biogenic (PAHs formed by from natural processes like diagenesis), petrogenic (PAHs derived from petroleum), and pyrogenic (PAHs formed as a result of incomplete combustion of fuel) (Zeng and Vista, 1997). Many PAHs are toxic, and tend to bioaccumulate in aquatic organisms. There are 16 of these PAH compounds that are classified by the USEPA as priority pollutants based on their toxicity for humans (Bojes and Pope, 2007).

n-Alkanes, aliphatic hydrocarbons have not been found to affect the biota, however, they can help to differentiate between biogenic (marine or terrestrial) and petrogenic sources of organic matter. These compounds are microbially degraded relatively rapidly as compared to PAHs and organochlorine pesticides (Webster et al., 2003). However, biodegradation is more difficult in some *n*-alkanes, namely those in the C_{28}–C_{40} group (Brakstad and Bonaunet, 2006; Okoh, 2006)

2. Materials and methods

In 2003 and 2004, plastic samples were collected from the North Pacific Ocean, and from coastal sites in California, Hawaii and regurgitated stomach contents from a Laysan albatross colony on Guadalupe Island, Mexico (Fig. 1). Ocean samples were taken by the Oceanographic Research Vessel *Alguita*, and the others were taken using tweeze, scoops or taking directly into glass storage jars. In total, there were 26 sets of plastic samples. Some of the Industrial-site samples were taken from railyards where plastic pellets had been spilled while being offloaded to plastic processing facilities. The samples were stored at −20 °C until laboratory analysis.

The primary synthetic polymers in the sample of plastic fragments and pre-production pellets were identified by infrared spectroscopy, using a Shimadzu model 8300 Fourier Transform Infrared Spectrophotometer (FT-IR). Physical properties including buoyancy, color of flame, odor and melt characteristics were also recorded as supporting evidence.

The plastic samples were analyzed according to the method used by Partida-Gutiérrez et al. (2003) with the following modification; 1 or 2 g of dry plastic fragments

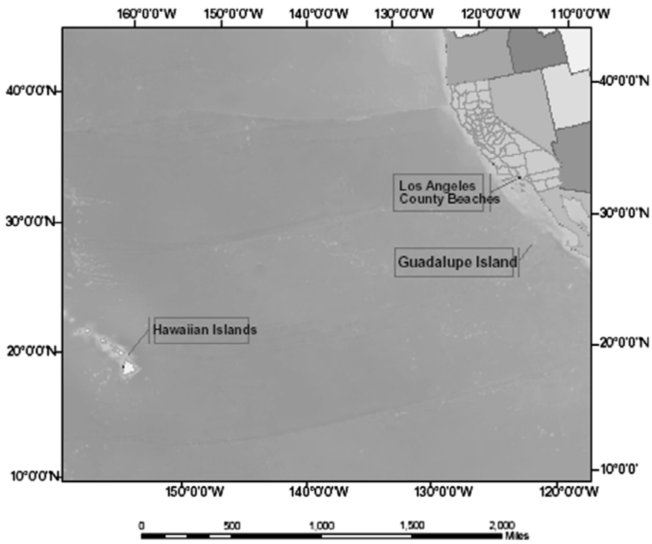

Fig. 1. Collection sites of plastic debris samples.

or/and pellets were placed in a glass extraction thimble, and a mixture of recovery standards was added. It is important to highlight that the samples were not sorted by size and shape. The sizes are listed in Table 1.

The plastic samples selected for examination for possible POP contaminants were Soxhlet extracted for 12 h (6 cycles/h) with 150 ml of dichloromethane. The aromatic and chlorinated hydrocarbon (PCBs, PAHs and Pesticides) fraction was analyzed by GC/MS using a JEOL GC/Mate II $^{\text{TM}}$ (double-focusing, reverse geometry mass spectrometer), with an Agilent 6890 gas chromatograph. The sample was injected in splitless mode (solvent delay: 1.5 min) into a BPX-5 column, 30 m × 0.25 mm i.d. × 0.5 μm thick film. The injector temperature was 270 °C and transfer line was 310 °C. The column temperature was programmed from 70 °C (1 min) to 300 °C (25 min), at a rate of 5 °C/min. The carrier gas was Helium (ultra high purity), programmed for a constant flow of 1.2 ml/min. The mass spectrometer was operated under selected ion monitoring mode (electron ionization, 70 eV, detector at 450 V), GC-interface 310 °C temperature and ion-chamber temperature 280 °C, resolving power 1000 with 10% valley. Quantification was done using the internal standard method, adding a known mixture of deuterated PAHs (1,4-dichlorobenzene-*d*4, naphthalene-*d*8, phenanthrene-*d*10, acenaphthene-*d*10, perylene-*d*12, chysene-*d*12), and a mixture of tetrachloro-*m*-xylene (TCMX) and PCB-209, and to aliphatic hydrocarbons the *n*-dodecane-*d*26 was added prior to extraction.

The identification and quantification of POPs was made by injection of mixtures of the following standards: PCB standard individuals, IUPAC numbers of congeners – 1, 11, 29, 47, 121, 136, 185, 194, 206, 5, 50, 104, 188, 87, 77, 154, 200, 208, 8,18, 28, 44, 52, 66, 101, 105, 118, 126, 128, 138, 153, 170, 180, 187, 195, 209; PAHs standard individuals – acenaphthene, acenaphthylene, antracene, Benzo(*a*)anthracene, benzo(*a*)pyrene, benzo(*b*+*k*) fluoranthene, benzo(*ghi*)perylene, benzo(*k*)fluoranthene, chysene, dibenz(*a*,*h*)anthracene, fluoranthene, fluorene, indeno(1,2,3,*c*,*d*)pyrene, naphthalene, phenanthrene, pyrene; DDT's and Pesticides standards-2,4′-DDD, 2,4′-DDE, 2,4′-DDT, aldrin, *a*-BHC, *b*-BHC, *d*-BHC, *d*-BHC, *g*-BHC, 4,4′-DDD, 4,4′-DDE, 4,4′-DDT, dieldrin, endosulfan I, endosulfan II, endosulfan sulfate, endrin, endrin aldehido, heptachlor, heptachlor epoxide-isomer B, methoxychlor; and aliphatic hydrocarbon standards-*n*-dodecane, *n*-tetradecane, *n*-hexadecane, *n*-octadecane, *n*-eicosane, *n*-docosane, *n*-tetracosane, *n*-hexacosane, *n*-octacosane, *n*-triacontane, *n*-dotriacontane, *n*-tetratriacontane, *n*-hexatriacontane.

The extraction recovery fraction was obtained using the standard DBOFB (4,4-dibromooctafluorobiphenyl) for PCBs and Pesticides, and *p*-terphenyl-*d*14 for PAHs prior to quantification. Procedural blanks were analyzed with each batch of samples (six samples per batch) and were taken through all phases of the analytical procedure. For every eight samples one duplicated sample was analyzed. The samples analyzed were found to fall in the range from 70% to 98% recovery. The detection limit of the organic compounds was calculated according to the methods proposed by Vial and Jardy (1999). The values ranged from 0.02 to 0.15 ng/g for PCBs, 0.05 to 0.8 ng/g for PAHs, 0.03 to 2.03 ng/g for pesticides and 0.02 to 6.18 μg/g for aliphatic hydrocarbons.

The quantification was based on the integrated peak area for the appropriate m/z value at the expected retention time with positive identification confirmed by the ion representing the base peak and the presence of two confirming ions. The retention time shift in the chromatogram was corrected using the internal standard and positive confirmation of the analyte within 0.2 min of expected retention time.

3. Results and discussion

The analyzed samples contained plastic fragments and pre-production pellets of different sizes and shapes (Table 1). The FT-IR analysis showed that the primary synthetic polymers in the samples were PP (polypropylene) and PE (polyethylene). The type of plastic fragments and pre-production pellets collected are shown in Fig. 2a, b and c. The main component in all plastic samples was PP (80–90%), and the remaining component was PE (Table 1). The authors recognize that the total surface area of the sample pieces was not uniform due to the nature of the debris material collected. The samples were taken from widely differing environments and it was not always possible to obtain samples of similar dimensions. In all cases, however, the samples analyzed were made up of multiples pieces and the process of averaging the measured pollutant per mass of sample provides a way to report the findings recognizing that the total surface are may vary with each sample. The extraction process is also an averaging process that pulls

Table 1
Description of plastic debris collected at each site

Sample ID (localization)	Color	Size (mm)	Type plastic
Tern Island I (*Hawaii Island*)	Red, orange, blue, white, blue–green, dark blue	27 × 13, 5 × 3, 16 × 4, 20 × 5, 15 × 5, 5 × 5, 20 × 18, 13 × 10, 13 × 5, 10 × 2, 20 × 8, 15 × 13	PP 90%; PE 10% (*Fragments*)
Tern Island II (*Hawaii Island*)	Black, green, blue, white, pink	16 × 9, 1 × 1, 8 × 6, 8 × 2, 3 × 4, 7 × 3	PP 90%; PE 10% (*fragments and pellets*)
Kamilo Beach (*Hawaii Island*)	White, clear, gray, black, pink	8 × 8, 5 × 3, 5 × 5, 5 × 8, 4 × 3	PE 85%; PP 15% (*pellets*)
Kualoa Park (*Hawaii Island*)	Blue, orange, black, pink, green, white	20 × 10, 7 × 5, 20 × 15, 10 × 8, 25 × 25, 70 × 1	PE 90%; PP 10% (*fragments and pellets*)
Guadalupe *Island*, *Mex.* (Albatross bolus)	Yellow, blue, green, light blue, white clear, orange	42 × 18, 32 × 15, 12 × 7, 20 × 10, 10 × 5, 5 × 3, 16 × 5, 9 × 4	PP 90%; PE 10% (*Fragments)*
Hermosa Beach (*L.A. USA*)	Purple, blue, white, green, pink	10 × 5, 32 × 4, 10 × 4, 14 × 8	PP 100% (*fragments*) PP 50%, PE 50% (*pellets*)
Golden Shore M.R. (*L.A. USA*)	White, clear, yellow, red, pink	4 × 2, 8 × 7, 10 × 7, 13 × 5, 20 × 10, 20 × 20,4 × 4	PP 50%, PE 50% (*fragments and pellets*)
Redondo Beach (*L.A. USA*)	Green, red, white, dark blue, clear	25 × 15, 10 × 5, 7 × 4, 20 × 15, 10 × 5,3 × 3, 20 × 9	PP 90%; PE 10% (*fragments and pellets*)
CCHW1 (a) (*L.A. USA – Industrial area)*	Red, blue(dark/light), white, purple, black, transparent, pink–green	6 × 5, 3 × 6, 5 × 5, 2 × 5, 2 × 4, 3 × 5, 3 × 8	PE 100% (*fragments*)
LB1311a (*L.A. USA – Industrial area*)	White, gray, green, red, purple, blue (light/dark), yellow, orange, transparent	40 × 4, 20 × 10, 10 × 6, 60 × 5, 30 × 15, 15 × 15, 24 × 7, 40 × 6, 10 × 9, 15 × 8	PE 20%, PP 80% (F*ragments*)
LB1312a (*L.A. USA – Industrial area*)	Transparent, yellow, black, white, gray, light green, red and white	3 × 4, 3 × 3, 4 × 5, 4 × 2	PE 10%, PP 90% (*pellets*)
SB1310 a (*L.A. USA – Industrial area)*	White, Clear, blue, yellow, light brown and gray	2 × 5, 4 × 6, 3 × 3	ABS 10%, PP 90% (*pellets*)
CCHW2 (a) (*L.A. USA – Industrial area*)	White, clear, light green–blue, light blue	2 × 5, 4 × 4	PE 10%, PP 90% (*pellets*)
LARHW2 (a) (*L.A. USA – Industria area*)	Green, light blue, dark blue, pink, orange, purple, black, clear, white, gray, neon green	23 × 15, 46 × 4, 21 × 7, 25 × 12, 15 × 15, 20 × 8, 23 × 17, 8 × 5	PE 20%, PP 80% (*fragments*)
LARHW1 (a) (*L.A. USA – Industrial area*)	White, transparent, blue (light), gray and black	2 × 5, 4 × 4, 4 × 3	PE 10%, PP 90% (*pellets*)
SB1309 a (*L.A. USA – Industrial area*)	Dark blue, light blue, green, pink, black, purple, white, transparent, light green, and yellow	13 × 9, 18 × 4, 8 × 4, 7 × 6, 11 × 10, 12 × 6, 14 × 5, 3 × 5, 22 × 4, 15 × 7	PE 50%, PP 50% (*fragments*)
San Gabriel River (1) (*L.A. USA*)	White, transparent, green, blue, black, yellowish, orange	5 × 3, 4 × 4, 3 × 3, 4 × 3	PE 80%, PP 10% (*pellets)*
San Gabriel River (2) (*L.A. USA*)	White, transparent, green, blue, black, yellowish, grey, red, pink	5 × 4, 6 × 4, 2 × 5, 7 × 5, 45 × 3, 15 × 7, 5 × 2, 7 × 5, 12 × 5, 12 × 1, 3 × 7	PE 20%, PP 10% (*fragments and pellets*)
TRM-1 (*L.A. USA – Industrial area*)	White, yellowish	5 × 3, 5 × 2, 4 × 3, 3 × 3	PE 100% (*pellets*)
TRM-2 (*L.A. USA – Industrial area*)	White, white dirty	5 × 3, 5 × 2, 4 × 3, 3 × 3	PE 100% (*pellets*)
TRM-3 (*L.A. USA – Industrial area*)	white	5 × 3, 5 × 2, 4 × 3, 3 × 3	PE 100% (*pellets*)
TRM-4 (*L.A. USA – Industrial area*)	White, yellowish, blue, white dirty	5 × 3, 5 × 2, 4 × 3, 3 × 3	PP 100% (*pellets*)
Site No. 6-1 (*L.A. USA – Industrial area*)	White, yellowish	5 × 3, 5 × 2, 4 × 3	PE 100% (*pellets*)
Site No. 6-2 (*L.A. USA – Industrial area*)	white	5 × 3, 5 × 2, 4 × 3, 3 × 3	PE 100% (*pellets and dust pellets*)
Site No. 6-3 (*L.A. USA – Industrial area*)	White, blue, grey, yellowish	5 × 3, 5 × 2, 4 × 3	PE 90% and PP 10% (*pellets*)
Surface seawater (*L.A. USA*)	Green, red, blue, white, transparent, orange	48 × 10, 150 × 5, 80 × 2, 35 × 8, 30 × 15, 5 × 4	PE 80% and PP 20% (*fragments*)

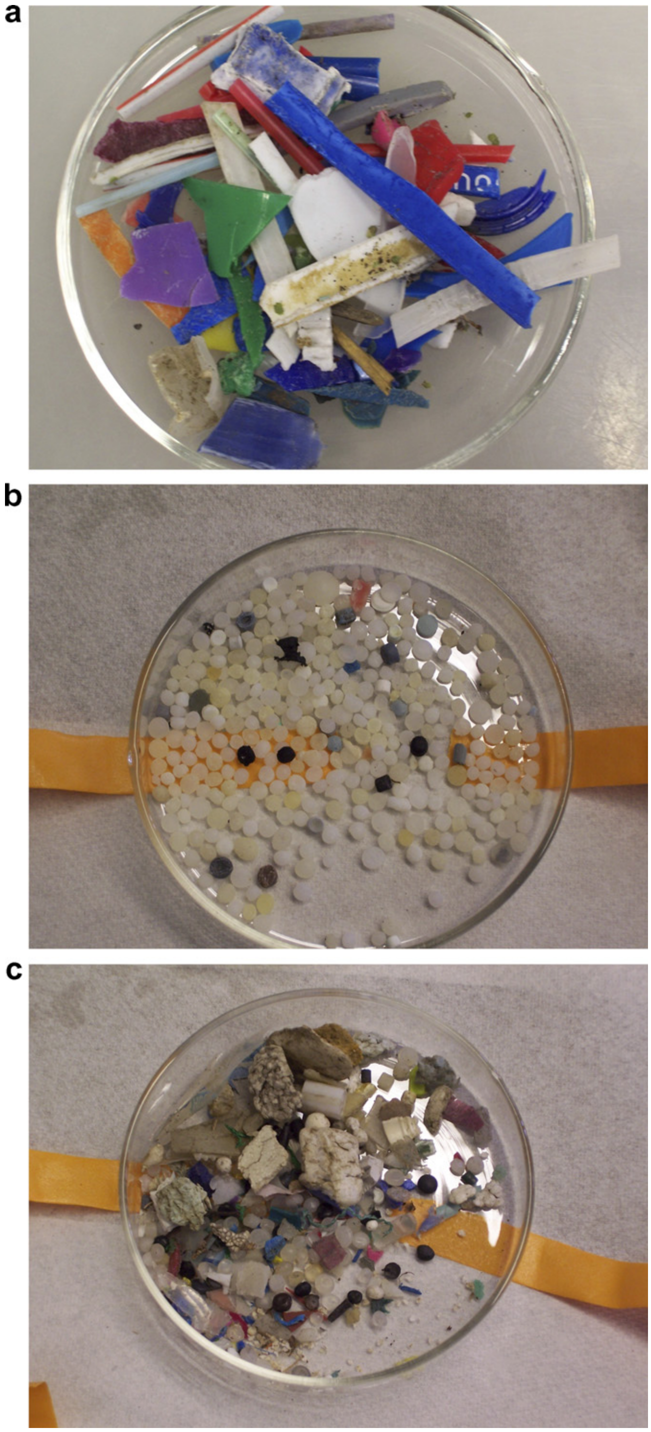

Fig. 2. Typical post-consumer plastic fragments and pre-production thermoplastic resin pellets from samples. (a) Plastic fragments, (b) plastic pellets, (c) mixed plastic (fragments and pellets).

Table 2
Persistent organic pollutants on samples from Beaches

Sample ID	∑PAH (ng/g)	∑PCBs (ng/g)	∑DDTs (ng/g)
Kamilo Beach (Hawaii)	nd	55	nd
Kualua Beach (Hawaii)	nd	nd	22
Tern Island (Hawaii)	500	70	nd
Tern Island II (Hawaii)	nd	980	nd
Albatross (Guadalupe Island, Mexico)	640	nd	nd
Hermosa Beach (California, USA)	nd	nd	140
Redondo Beach (California, USA)	1400	730	nd
Golden Shore Marine Reserve beach (California, USA)	1700	27	nd
San Gabriel River (1) (California, USA)	1200	nd	1100
San Gabriel River (2) (California, USA)	6200	nd	1000

nd, not detected at detection limit. Limit detection PCBs 0.02–0.15 ng/g, PAHs 0.05–0.8 ng/g and pesticides 0.03–2.03 ng/g.

Table 3
Persistent organic pollutants on samples from Industrial sites

Sample ID	∑PAH (ng/g)	∑PCBs (ng/g)	∑DDTs (ng/g)
CCHW1(a)	39	nd	nd
CCHW2 (a)	360	nd	nd
LB1311 (a)	150	nd	nd
LB1312 (a)	3900	nd	nd
LARHW1 (a)	1700	nd	nd
LARHW2 (a)	210	nd	nd
SB1309 a	1800	nd	nd
SB 1310 a	770	nd	170
Industry TRM-1	12,000	nd	1900
Industry TRM-2	88	nd	42
Industry TRM-3	74	nd	nd
Industry TRM-4	6100	nd	7100
Site No. 6-1	1800	nd	nd
Site No. 6-2	2600	nd	nd
Site No. 6-3	390	nd	nd
Surface sea water	9200	nd	nd

nd, not detected at detection limit. Limit detection PCBs 0.02–0.15 ng/g, PAHs 0.05–0.8 ng/g and pesticides 0.03–2.03 ng/g.

adsorbed materials off the surface exposed to the surrounding environmental conditions.

The quantities of persistent organic pollutants are presented in groupings of samples from beaches and samples from industrial sites as shown in Tables 2 and 3. All the samples contained detectable amounts of PAHs, except for four samples: Tern Island II, Kailua Beach, Kamilo Beach and Hermosa Beach. The PAH, pyrene, was detected in 65% of the samples. Fluoranthene was present in 62% of the samples. Naphthalene and phenanthrene were present in 54% of the samples. Acenaphthene was present in 42% of the samples. The remaining PAHs were present in smaller percentages.

The highest concentration of PAHs was found in the industrial-site samples. The sum of all observed PAHs (classified as priority pollutants by USEPA) was in the range of 39–1200 ng/g. The TRM-1, TRM-4 samples from a plastic pellet processor showed the highest concentration of total PAHs, with 6100 and 12,000 ng/g respectively. The pellets from TRM-1 and TRM-4 did not look new. In fact, many of these pellets were discolored (yellowed) and had cracks, characteristic of old pellets (Gregory, 1978; Endo et al., 2005). The fragment samples taken from the bank of the San Gabriel River, at the beach, and on the sea surface also presented high concentrations (6200–9200 ng/g).

The compositional patterns of PAHs may provide information about petrogenic sources. Oil seeps or petroleum spills are made up mostly of two- and three-ring PAHs. Pyrogenic PAHs from combustion, for example, vehicle exhaust, domestic heating with coal, and many industrial processes, produce mostly four- and five-ring PAHs. The ratio of the sum of the two- and three-ring PAHs to the sum of four- and five-ring is an indication of the source of the PAHs.

The presence of the EPA priority PAHs found in this study showed a dominance of four- and five-ring PAHs over the two- and three-ring PAHs. A decrease in this ratio indicates a shift from uncombusted to combusted organic matter as the dominant PAH source. The results of our study showed the ratio was 0.23, indicating that combusted fossil fuels were the principal source of PAHs.

There is another ratio that can aid source identification. This is the ratio of fluoranthene to pyrene. A fluoranthene/pyrene ratio of greater than 1 is considered to be a pyrolytic source. In our results, this ratio was of 1.53, providing additional evidence of combusted fuel as the source of the PAHs in our samples (Webster et al., 2003; Headley et al., 2002; Boonyatumanond et al., 2007).

The concentration of total PCBs detected (sum of all congeners detected) in plastic samples are summarized in Tables 2 and 3, ranging from 27 to 980 ng/g. These results are from the sampling sites at Tern Island I and II, Kamilo Beach, Redondo Beach, and Golden Shore Marine Reserve Beach. The highest concentration of total PCBs was found in Tern Island II and the lowest concentration of total PCBs was at Golden Shore Marine Reserve. The most abundant congeners were CB-52, 101, 118 and 170, where the highest concentration of PCB-101 was 200 ng/g. The second most abundant group of PCBs was congener CB-105, 138, and 153, showing a high concentration of PCB-138 (190 ng/g). Because there is no standard from previous studies with which to compare these results, we compared our results with data from sediments and found that the concentrations are very similar to the concentrations found in sediments from Baja California (Mexico) to California (USA) border zone, Salton Sea, and tidal marsh zones along coastal California, USA (Gutiérrez-Galindo et al., 1998; Partida-Gutiérrez et al., 2003; Sapozhnikova et al., 2004; Hwang et al., 2006).

The only pesticide detected in all the plastic samples was 4,4-DDT and its metabolites 4,4-DDE and 4,4-DDD. The measured sum of all DDT metabolites ranged from 22 to 7100 ng/g. All the samples contained 4,4-DDE, with the highest concentration (5600 ng/g) in the site called TRM-4, which is an industrial site. This result suggests that DDT may have been used as a pesticide in that area, probably in past decades when it was legal. Pellets analyzed from this site were weathered or discolored typical of old pellets. These results are presented in Tables 2 and 3 (sum of DDT and its metabolites). In Fig. 3, we observed that the samples with the highest concentration of total DDTs were samples TRM-1 and TRM-4, San Gabriel River 1 and San Gabriel River 2, in accordance with Endo et al. (2005). However, we were not able to detect PCBs on these pellets.

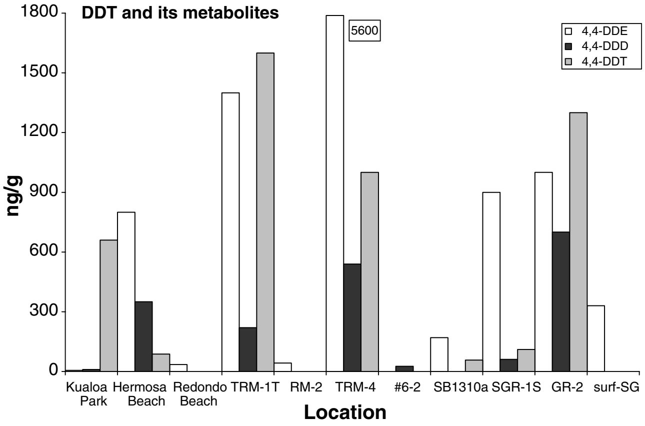

Fig. 3. Concentration of DDT and its metabolites, DDE and DDD in ng/g.

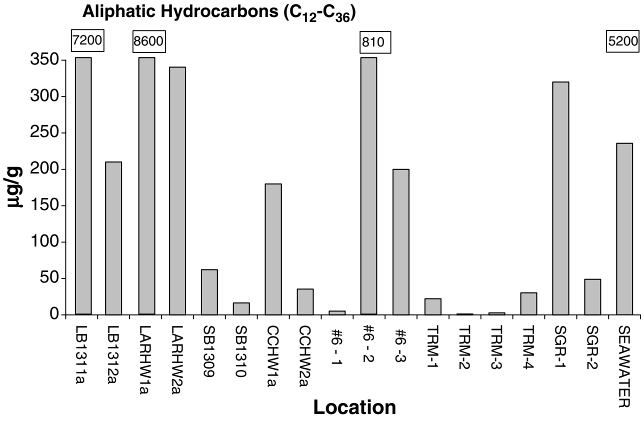

Fig. 4. Sum of total of aliphatic hydrocarbons (µg/g).

The concentration of total aliphatic hydrocarbons (sum of all normal alkanes present in the plastic samples, ranging in carbon chain length from C_{12} to C_{36} detected) is shown in Fig. 4. The samples in this graph are from the same sites listed in Table 1. The average total of *n*-alkanes relative to dry weight was 140 µg/g (17 samples), if we do not include the highest concentration samples (three samples) discussed below.

The three samples with the highest levels of *n*-alkanes were LB1311a with 7200 µg/g, LARHW1a, with 8600 µg/g, and the surface sea water sample, with 5200 µg/g. The first two are from industry sites and the third is from the ocean off the mouth of the San Gabriel River. We used dichloromethane to extract the samples to avoid potential problems using hexane. We believe that these observed *n*-alkanes hydrocarbons were adsorbed on the plastic's surface and were not extracted hydrocarbons from the synthetic polymers of the plastic samples.

4. Conclusions

The main plastic components of the samples of marine debris were polypropylene and polyethylene. Plastic debris was found to accumulate contaminants, perhaps because of its permeable lipophilic nature. We found PAHs in all the samples. The main source of these PAHs was pyrolytic, and the samples from California showed a strong influence from industrial and urban areas. The only pesticide that we found associated with the plastic debris was DDT and its metabolites DDD and DDE. PCBs were found only in the plastic debris collected on the beaches. The Tern Island site, while remote from civilization, was the site of a military base and is known to be contaminated with PCBs at a level requiring clean-up efforts (Miao et al., 2000). The plastic pieces taken from Laysan albatross regurgitated stomach contents on Guadalupe Island probably were originally foraged from an area north of the Island off the Pacific Coastal of the United States (Henry, unpublished data). There is a small military colony currently on the island, with some burning of fossil fuel for energy production.

The concentration ranges of the POPs are as follows: total PCBs 27–980 ng/g, total PAHs 39–1200 ng/g, DDTs 22–7100 ng/g, and aliphatic hydrocarbons 1.1–8600 μg/g.

The results of this study show that PCB-52, 101, 118, and 170 were the most common POPs detected, and fluoranthene was the most abundant PAH compound in plastic debris samples. Observations made during this study and by Mato et al. (2001), indicate the concentration of POPs in this plastic debris may be a function of the age of the plastic.

The work reported here is the first study showing the concentrations of persistent organic pollutants in post-consumer plastic debris samples. The increasing abundance of plastic debris allows marine organisms to mistake more plastic for their natural food and ingest more plastic as they feed. These plastics are important point sources carrying POPs. It is not only the initial organism that ingests the plastics that may be affected by the POPs, but also the organisms within its food web. Future studies should try to obtain fragments in the range of 1–5 mm in order to make possible comparison with the results reported by Mato and Endo.

It appears that the plastic debris fragments studied to adsorb, accumulate and transport persistent organic pollutants. Further study could be initiated to evaluate the possibility of the transfer of POPs between the plastic carrier particles and the tissues found in living organisms.

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