

Master Interuniversitario en
Oceanografía



FACULTAD
DE CIENCIAS
DEL MAR
UNIVERSIDAD DE LAS PALMAS
DE GRAN CANARIA

Persistent Organic Pollutants (POPs) in plastic pellets from Las Canteras Beach (Canary Islands)

Estela Lalueza Broto

**Máster Interuniversitario
de Oceanografía**

Curso 2016/2017

**Tutora: Alicia Herrera Ulibarri,
Departamento de Biología, ULPGC.**

**Cotutores: María Milagrosa Gómez
Cabrera, Departamento de Biología,
ULPGC y Andrés Cózar Cabañas,
Departamento de Biología, UCA.**

Abstract

Stranded pellets have been collected from Las Canteras beach, Gran Canaria, to analyze the corresponding UV filters (289.12 ng/g pellet), chlorpyrifos (4.72 ng/g pellet), OCPs (99.18 ng/g pellet), BDEs (0.89 ng/g pellet), OPFRs (27.09 ng/g pellet), PAHs (271.96 ng/g pellet) and PCBs (28.22 ng/g pellet) associated to these microplastics and try to determine their main sources. Of the total of 77 pollutants analyzed, only 52 compounds have appeared in the coastal zone. Most of the sources are of exogenous origin, adsorbed to the pellet during their residence on the sea surface, with the exception of UV filters, chlorpyrifos, PAHs and PCBs that are possibly related to tourism and the industrial activity of the zone.

Keywords: Microplastics, pellets, UV filters, Chlorpyrifos, OCP, BDE, OPFR, PAH, PCB.

Resumen

Se han recogido pellets en la arena de la playa de Las Canteras, Gran Canaria, para analizar los filtros UV (289.12 ng/g pellet), chlorpyrifos (4.72 ng/g pellet), OCPs (99.18 ng/g pellet), BDEs (0.89 ng/g pellet), OPFRs (27.09 ng/g pellet), PAHs (271.96 ng/g pellet) y PCBs (28.22 ng/g pellet) asociados a estos microplásticos y tratar de determinar sus principales fuentes. Del total de 77 contaminantes analizados han aparecido 52 compuestos en la zona costera. La mayoría de las fuentes son de procedencia exógena, adsorbidos a la superficie del pellet durante su estancia en la superficie del mar, a excepción de los filtros UV, chlorpyrifos, PAHs y PCBs que posiblemente estén relacionados con el turismo y la actividad industrial de la zona.

Palabras clave: Microplastics, pellets, filtros UV, Clorpirifos, OCP, BDE, OPFR, PAH, PCB.

INDEX

INTRODUCTION	5
1.1 Background.....	6
1.2 Stockholm Convention	8
1.3 Pollutants	9
UV Filters	9
Chlorpyrifos	10
Organochlorine Pesticides (OCPs).....	10
Polybrominated Diphenyl Ethers (PBDEs).....	13
Organophosphate Flame Retardants (OPFR)	13
Polycyclic Aromatic Hydrocarbons (PAH).....	14
Polychlorinated Biphenyles (PCBs).....	16
1.4 Objectives	16
2. MATERIAL AND METHODS	17
2.1 Study area	17
2.2 Field work	18
2.3 Laboratory work	18
GAS CROMATOGRAPHY	19
2.4 Data treatment.....	19
RESULTS.....	20
DISCUSION.....	24
CONCLUSIONS	1
Acronyms list.....	38
ANNEX I, Pollutants detailed information.....	39
ANNEX II, ANALITICAL PROTOCOL PROCEDURE.....	47
REFERENCES	48

LIST OF FIGURES

FIGURE 1. SUMMARY OF THE HISTORICAL STAGES OF PLASTIC WITH ASSOCIATED CONCERNS AND LEGISLATIVE MEASURES. PLASTIC PRODUCTION IN MILLIONS OF TONNES (MT) ARE SHOWN WITH SOLID RED LINE. BPA, BISPHENOL A; PVC, POLYVINYL CHLORIDE. FIGURE REPRODUCED FROM THOMPSON ET AL. (2009B).	5
FIGURE 2. COUNTRIES MAP WITH THE PARTIES COUNTRIES (GREEN) AND NON-PARTIES (GREY) IN THE STOCKHOLM CONVENTION. FROM WIKIPEDIA. NON PARTIES ARE ITALY, U.S.A., MALAYSIA, WESTERN SAHARA, SOUTH SUDAN, UZBEKISTAN, TURKMENISTAN AND PHILIPPINES.	8
FIGURE 3. LOCATION OF LAS CANTERAS BEACH, AT GRAN CANARIA ISLAND. SOLID YELLOW LINE INDICATES THE SAMPLING AREA (260M).	17
FIGURE 4. STRANDED PELLETS FROM LAS CANTERAS BEACH, DISPOSED IN STERILIZED PLASTIC BAGS. ...	18
FIGURE 5. UV FILTERS BAR CHART WITH MEAN VALUES OF EACH COMPOUND. MAXIMUM TO MINIMUM CONCENTRATION (NG/G PELLETT) FOR 2-ETHYLHEXYL P-METHOXYCINNAMATE (EHMC), HOMOSALATE AND 3-(4-METHYLBENZYLIDENE) CAMPHOR (4-MBC).	20
FIGURE 6. BOX DIAGRAM FOR UV FILTERS AND CHLORPYRIFOS. CONCENTRATIONS ARE SHOWN IN NG/G PELLETT.....	20
FIGURE 7. OCPS BAR CHART (LEFT) WITH MEAN VALUES OF EACH COMPOUND AND BOX DIAGRAM (RIGHT) FROM LAS CANTERAS BEACH. CONCENTRATIONS ARE SHOWN IN NG/G PELLETT.	21
FIGURE 8. BDES BAR CHART (LEFT) WITH MEAN VALUES OF EACH COMPOUND AND BOX DIAGRAM (RIGHT) FROM LAS CANTERAS BEACH. CONCENTRATIONS ARE SHOWN IN NG/G PELLETT.	21
FIGURE 9. BOX DIAGRAM FOR OPFRS. CONCENTRATIONS ARE SHOWN IN NG/G PELLETT.	22
FIGURE 10. OPFRS BAR CHART WITH MEAN VALUES OF EACH COMPOUND. CONCENTRATIONS ARE SHOWN IN NG/G PELLETT.	22
FIGURE 11. PAHS BAR CHART WITH MEAN VALUES OF EACH COMPOUND (NG/G PELLETT) FROM LAS CANTERAS BEACH.	22
FIGURE 12. BOX DIAGRAM FOR PAHS. CONCENTRATIONS ARE SHOWN IN NG/G PELLETT.....	23
FIGURE 13. PCBS BAR CHART WITH MEAN VALUES OF EACH COMPOUND. CONCENTRATIONS ARE SHOWN IN NG/G PELLETT.	23
FIGURE 14. BOX DIAGRAM FOR PCBS. CONCENTRATIONS ARE SHOWN IN NG/G PELLETT.	24

LIST OF TABLES

TABLE 1. MAIN CHARACTERISTICS OF LAS CANTERAS BEACH, ADAPTED FROM HERRERA ET AL. (2017).	17
TABLE 2. INFORMATION ABOUT THE SAMPLING DATE AND RELATED HIGH AND LOW TIDE HOURS.....	18
TABLE 3. UV FILTERS DATA COMPARISION OF THE PRESENT STUDY (NG/G PELLET) AND RODRIGUEZ ET AL. (2015) STUDY (NG/L).....	25

Del conocimiento viene la comprensión, y de la comprensión viene el cambio.

INTRODUCTION

Since Industrial Revolution, humankind has gradually polluted the environment, causing an excess of CO₂ in Earth's atmosphere (as well as the rising of seawater temperature, ocean acidification and ocean de-oxygenation), deforestation and pollution, being the chemical industry one of its main responsables. These have been the main environmental concerns until the last decade, when the scientific community noticed the excessive

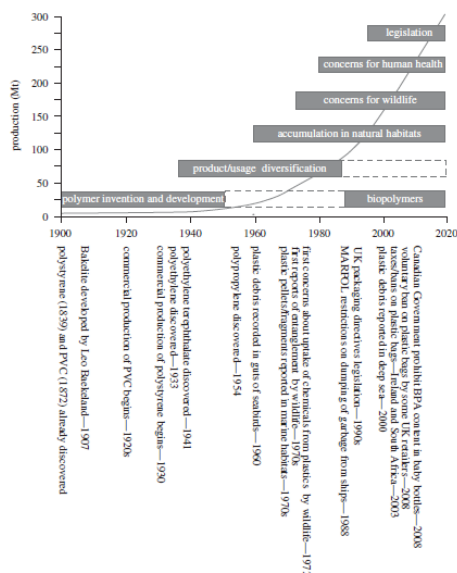


Figure 1. Summary of the historical stages of plastic with associated concerns and legislative measures. Plastic production in millions of tonnes (Mt) are shown with solid red line. BPA, bisphenol A; PVC, polyvinyl chloride. Figure reproduced from Thompson *et al.* (2009b).

plastic consumption carried out by humanity. Originally, this material was provisionally manufactured due to its difficult disintegration process. Nevertheless, plastic has been marketed since 1909 (bakelite, the first totally synthetic plastic, see Figure 1) and, nowadays, it can be found worldwide.

The amount of plastic consumed each year is hard to quantify, some authors estimate it is over 240 million tonnes each year (Browne *et al.*, 2011), even reaching 260 million tonnes (Thompson *et al.*, 2009), and discarded 'end-of-life' plastic accumulates, particularly in marine habitats (Browne *et al.*, 2011). Moreover, world population has increased by 250% in the last 50 years (Browne *et al.*, 2011). At the same time, research has also increased and, consequently, the awareness about the issue. Plastics made from any kind of material and with any sort of shapes and sizes have been studied, including clothing synthetic fibres or cleaning products. Clothing synthetic fibres have special

emphasis given their small size and their difficulty to be retained by treatment systems. Browne *et al.* (2011) demonstrated that a single garment is able to produce >1900 fibres per wash.

Mato *et al.* (2001) were the first to describe plastic resin pellets. They noticed that there are small granules (1-5 mm in diameter) that are widely distributed in the ocean all over the world because of their environmental persistence. Pellets are virgin plastic particles from which plastic products are made of. This primary material is carried into factories, where it is melted to be molded into a wide range of final products. Its environmental presence is generally unintended; in fact, it is due to losses during plastic manufacturing or transport (Carpenter *et al.*, 1972; Shiber, 1982).

Plastic particles are generally the most abundant type of debris encountered in the marine environment with estimates suggesting that plastics comprise between 60% and 80% of total marine debris (EPA, 2016). Currently, the potential danger observed are the persistent organic pollutants (POPs) associated to the pellets and fragments found, which have already entered the marine food webs and can cause fetal malformations, cancer, endocrine problems, infertility or even death. POPs can be adsorbed by plastics' surface during the manufacturing process (namely BDEs or Flame Retardants) or once they are in an aquatic environment as a consequence of their high hydrophobicity. The

concentration of POPs associated to plastic show great space variations, so they can reflect global pollution patterns (Teuten *et al.*, 2009). Previous studies related to this area of investigation are listed below.

1.1 Background

In March 1972, Carpenter and Smith published a study warning about the massive presence of plastic distributed along the Sargazo Sea's surface (290g per square kilometre) and the fact that this plastic could be a source of some of the polychlorinated biphenyls (PCBs) recently observed in marine organisms. Having observed the potential danger these plastics could entail, in September, Carpenter *et al.* (1972) detected PCBs in polystyrene pellets in a beach in the north-east of the USA with a concentration of five parts per million. Due to the fact that they could not provide evidence about the source of these PCBs (they suggested it was the adsorption from the surrounding seawater), their warning was ignored by the scientific community (Teuten *et al.*, 2009). They also found pellets in 8 out of the 14 fish species analysed. During the following 30 years several studies were published related to PCBs and other POPs found in the environment, organisms and food. However, until 2001 pellets were not studied, excluding the study carried out by Shiber (1982), in which pellets along Costa del Sol (13 beaches from Algeciras to Almeria, Spain) were collected, classified and quantified according to the kind of material.

Mato *et al.* (2001) analysed the content of PCBs, DDEs and nonylphenols (NP) in 4 Japanese beaches, finding these pollutants in all the samples but with different concentrations (adsorption coefficient of 10^5 - 10^6 from surrounding seawater). From this moment on, the number of studies about POPs in microplastics began to increase. Mato *et al.* (2001) suggested, based on the high accumulation potential, that plastic resin pellets serve as both a transport medium and a potential source of toxic chemicals in the marine environment. And in 2005, Endo *et al.* collected pellets from 47 Japanese beaches to verify if there was a regional variability of concentrations. They observed different concentration patterns in the research area and a great piece-to-piece variability, suggesting that discoloured pellets adsorb greater PCB concentrations (as a possible result of long water residence time).

Based on these findings, Takada (2006) suggested the International Pellet Watch (IPW), a global scale monitoring methodology where everyone can participate. This proposal consists in collecting stranded pellets and send them to Tokyo's laboratory (Tokyo University of Agriculture and Technology), where the headquarters are. That way, the global research related to pollutants associated to microplastics is enabled. It aims at quantifying and monitoring aquatic environment pollution in order to establish strategic plans to protect the environment worldwide. In 2009, studies based on data collected with the help of IPW began to be published, in which appeared more common responses among scientifics from all over the world: (a) type of plastic material (Mato *et al.*, 2002; Endo *et al.*, 2005; Ogata *et al.*, 2009; Teuten *et al.*, 2009; Hirai *et al.*, 2011), PE has higher affinity for hydrofobic compounds; (b) degree of weathering and colouring (Bakir *et al.*, 2012; Song *et al.*, 2017), discoloured pellets show greater PCB concentrations according to water residence time; (c) pollutants' transport and worldwide distribution via microplastics, reaching even the most remote and non-industrialized islands (Teuten *et al.*, 2009; Ogata *et al.*, 2009; Hirai *et al.*, 2011; Heskett *et al.*, 2012; Ryan *et al.*, 2012;

Batzan *et al.*, 2014; Herrera *et al.*, 2017). The study carried out by Ogata *et al.* (2009) is the one including the greater number of countries, showing bigger PCB concentrations in the west coast of the USA (San Francisco and Los Angeles), China (Hong Kong), Japan, Netherlands and India.

Regarding Canary Islands, Batzan *et al.* (2014) carried out a study concerning the abundance distribution and size of the marine debris in 125 beaches in Fuerteventura, Lanzarote y La Graciosa, observing a greater accumulation in north-oriented beaches. Subsequently, Herrera *et al.* (2017) have monitored and classified for one year marine debris abundance reaching Lanzarote, La Graciosa and Gran Canaria (a beach per island), observing different seasonal patterns at each location and suggesting it is mainly due to local-scale wind and wave conditions. Based on the type of debris found, the study confirmed that marine litter did not have local origin.

On the other hand, there are two studies about POPs in stranded pellets; (i) Heskett *et al.* (2012) analyzed PCBs, DDTs and HCH in 5 beaches all over the world, including North Pacific Gyre, Caribbean Sea, Indian Ocean and North (Fuerteventura) and South Atlantic Ocean, observing concentrations between 1-3 orders of magnitude smaller than those noticed in pellets from industrialized coastal shores and (ii) Sanz *et al.* (2017) examined OCPs, PCBs, PAHs and PBDEs in stranded pellets of beaches with SE orientation in Gran Canaria Island to raise awareness about priority pollutants adsorbed to these microplastic pellets.

The current worldwide plastic distribution is a fact, but this problem has not an easy solution due to its huge environmental impact. In the marine environment, hydrophobic compounds show a great affinity for plastics; marine debris is increasingly more abundant and keeps breaking up into smaller pieces without eventually decomposing. Numerous studies have demonstrated that these plastics have been ingested by many kind of marine species, incorporating to their tissues and, in most cases, causing death by suffocation (Tanaka *et al.*, 2013; Wright *et al.*, 2013; Rochman *et al.*, 2014; Watts *et al.*, 2014 and Bouwmeester *et al.*, 2015).

The analysis of these pollutants in seawater is extremely complicated due to their hydrophobic nature (they tend to “scape” from water). They mitigate their hydrophobicity adhering on plastics that are floating on the surface, causing an increasing adsorption of hydrophobic chemicals by plastics until equilibrium with the existing concentrations in marine environment is reached. Not every plastic reaches equilibrium with seawater, hence there is great concentration variability in the samples analysed so far. Stranded pellets from industrialized or urban areas show greater pollution due to their proximity to emission sources. However, studying non-industrialized beaches (or beaches with a minimum level of anthropogenic activities) which are far from the continent can reflect open ocean current state of pollution and, therefore, provide an approximate idea of the actual global pollution patterns. Increasing the amount of information about POPs will enable a better emission regulation and/or restriction, and consequently, a quicker and more effective substitution of these chemicals.

1.2 Stockholm Convention

Sponsored by the United Nations Environment Programme (UNEP), the convention is the result of a negotiation that has lasted for many years to get countries legally committed so they have the duty to urgently eliminate all POPs. The Stockholm Convention targets certain hazardous pesticides and industrial chemicals that can kill people, damage the nervous and immune systems, cause cancer and reproductive disorders and interfere with normal infant and child development. The negotiations for the convention ended up in May 2000 and it came into force in May 2004 with 152 Parties. At present, there are 181 countries that have ratified the convention (Figure 2).

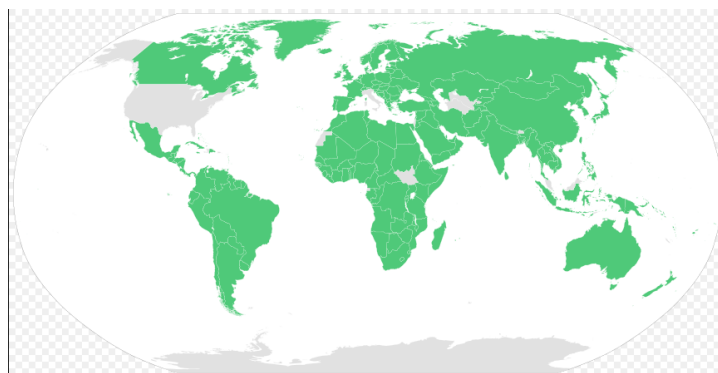


Figure 2. Countries map with the parties countries (Green) and non-parties (grey) in the Stockholm Convention. From Wikipedia. Non parties are Italy, U.S.A., Malaysia, Western Sahara, South Sudan, Uzbekistan, Turkmenistan and Philippines.

Based in Principle 15 of the Rio Declaration on Environment and Development, the objective of the Convention is to protect human health and the environment from persistent organic pollutants (Stockholm Convention on POPs, 2009).

The chemicals targeted by the Stockholm Convention are listed in the annexes of the convention text:

Annex A (Elimination)

Parties must take measures to eliminate the production and use of the chemicals listed under Annex A. Specific exemptions for use or production are listed in the Annex and apply only to Parties that register for them.

- **Pesticides:** Aldrin, Chlordane, Chlordane, Dieldrin, Endrin, Heptachlor, Alpha hexachlorocyclohexane, Beta hexachlorocyclohexane, Lindane, Mirex, Pentachlorophenol and its salts and esters, Technical endosulfan and its related isomers, Toxaphene.
- **Industrial Chemicals:** Hexabromodiphenyl ether and heptabromodiphenyl ether, Hexabromobiphenyl, Hexabromocyclododecane (HBCDD), Hexachlorobutadiene, Polychlorinated biphenyls (PCB), Polychlorinated naphthalenes, Short-chain chlorinated paraffins, Tetrabromodiphenyl ether and pentabromodiphenyl ether.
- **Industrial Chemical and Pesticides:** Hexachlorobenzene (HCB), Pentachlorobenzene.

Annex B (Restriction)

Parties must take measures to restrict the production and use of the chemicals listed under Annex B in light of any applicable acceptable purposes and/or specific exemptions listed in the Annex.

This POPs are DDT pesticide and the pesticide and industrial chemical Perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOS-F)

Annex C (Unintentional production)

Parties must take measures to reduce the unintentional releases of chemicals listed under Annex C with the goal of continuing minimization and, where feasible, ultimate elimination. To achieve this objective, reduction and elimination measures will be adopted, as well as the promotion of the use of substitute materials, products and processes, and the adoption of the best available techniques and environmental practices (Blount, 2002).

There are unintentional Products, mostly dioxins and furans: Hexachlorobenzene (HCB), Hexachlorobutadiene (HCBd), Pentachlorobenzene, PCBs, Polychlorinated dibenzo-*p*-dioxins (PCDD), Polychlorinated dibenzofurans (PCDF) and Polychlorinated naphthalenes.

1.3 Pollutants

UV Filters

UV filters are individual compounds or mixtures that block or absorb ultraviolet (UV) light, used in sunscreens, products for daily facial and body care or in photography (to reduce the level of ultraviolet light). UV filters can undergo transformation into less protective or more toxic products. These transformation products can have health and environmental effects. In fact, all substances described below are considered to be a priority for further work based on their potential for affecting endocrine systems (Killeen, 2008). However, these are permitted for use in sunscreens under the Cosmetic Products Safety Regulations 2008 and in Annex VII of the current EU Cosmetics Directive 76/768/EEC up to a specified maximum concentration (Annex II).

- **2-Ethylhexyl 4-(dimethylamino) benzoate (Padimate O).**
- **2-Ethylhexyl *p*-methoxycinnamate:** It is also used as a light stabiliser in plastics (Ashford, 1994) and one of the most tested and widely used UV filters.
- **3-(4-Methylbenzylidene) camphor (Enzacamene):** is listed on the ESIS database as an LPV chemical. This substance is not listed in Japan and is an unapproved new drug in the US.
- **3-Benzylidene camphor.**
- **Homosalate:** This substance is widely used in cosmetics.

Chlorpyrifos

Is an organothiophosphate cholinesterase inhibitor that is used as an insecticide and as an acaricide. Chlorpyrifos is a white crystal-like solid with a strong odor. It does not mix well with water, so it is usually mixed with oily liquids before it is applied to crops or animals or in a capsule form. They has been used as a pesticide since 1965 in both agricultural and non-agricultural areas (Kim *et al*, 2016):

In the home, it is used to control cockroaches, fleas, and termites and sometimes it is used in pet flea and tick collars. On the farm, it is used to control ticks on cattle and as a spray to control crop pests (such as corn, soybeans, fruit and nut trees or brussels sprouts).

Organochlorine Pesticides (OCPs)

Organochlorine pesticides are chlorinated hydrocarbons used extensively from the 1940s through the 1960s in agriculture and mosquito control. Most of them have been banned in North America and Europe, however these chemicals are still in use in Central America, India, China and countries in Africa (Chait, 2017). Organochlorines have extremely strong bonds between their chlorine and carbon components and are attracted to fats (high-fat dairy products, such as butter, high-fat cheeses, meat and fish).

The OCPs analyzed in the present study are detailed below, with supplementary information in Annex II:

- **Aldrin:** A pesticide applied to soils to kill termites, corn rootworm, and other insect pests. Humans are mostly exposed to aldrin through dairy products and animal meats (Stockholm Convention Clearing House Web Site, 2008).
- **Dieldrin:** Used principally to control termites and textile pests, but has also been used to control insect-borne diseases and insects living in agricultural soils. The pesticide aldrin rapidly converts to dieldrin, so concentrations of dieldrin in the environment are higher than dieldrin use alone would indicate. Dieldrin residues have been found in air, water, soil and animals, including humans. The primary source of exposure to the general population is through the food, e.g., dieldrin was the second most common pesticide detected in a US survey of pasteurized milk (Stockholm Convention Clearing House Web Site, 2008).
- **DDT** (dichlorodiphenyltrichloroethane) was widely used during World War II to protect soldiers and civilians from malaria, typhus, and other diseases spread by insects. Its insecticidal properties were discovered in 1939, being sprayed on a variety of agricultural crops, especially cotton. Nowadays, DDT continues to be applied against mosquitoes in several countries to control malaria. Its stability, its persistence (as much as 50% can remain in the soil 10-15 years after application), and its widespread use have meant that DDT residues can be found everywhere; residual DDT has even been detected in the Arctic. The short-term acute effects of DDT on humans are limited, but long-term exposures have been associated with chronic health effects (Stockholm Convention Clearing House Web Site, 2008). Typically, technical DDTs are composed of 77.1% p,p'-DDT, 14.9% o,p'-DDT, 4% p,p'-DDE, and 0.1% o,p'-DDE (WHO, 1979).

- **DDD** (dichlorodiphenyldichloroethane) and **DDE** (dichlorodiphenyldichloro-ethylene) are chemicals similar to DDT that contaminate commercial DDT preparations. DDT is degraded to DDD and DDE under aerobic and anaerobic condition, respectively, after their discharge to aquatic environments (Kale *et al.*, 1999; Chiu *et al.*, 2004; Ogata *et al.* 2009). DDE has no commercial use. DDD is also used to kill pests, but its use has also been banned. One form of DDD (o,p'-DDD or Mitotane, a synthetic derivative of DDT) has been used medically to treat adrenocortical tumors and causes CNS damage, but no bone marrow depression. It has limited clinical use (Kim *et al.*, 2016). The rest of ethane and ethylene metabolites (DDD-p,p' or Rhothane, DDE-o,p' and DDE-p,p') were used as pesticides.
- **Endosulfan** occurs as two isomers: alpha- and beta-endosulfan, biologically active. Endosulfan is a mixture of the two isomers along with small amounts of impurities. This insecticide has been used since the 1950s to control tsetse flies, crop pests and ectoparasites of cattle and as a wood preservative. “A total of between 18,000 and 20,000 tons of endosulfan are produced annually in Brazil, China, India, Israel and South Korea. The largest users of endosulfan (Argentina, Australia, Brazil, China, India, Mexico, Pakistan and the United States) use a total of about 15,000 tons of endosulfan annually. The use of endosulfan is banned or will be phased out in 60 countries that, together, account for 45 per cent of current global use. Endosulfan bioaccumulates and has the potential for long-range transport. It has been detected in air, sediments, water and in living organisms in remote areas, such as the Arctic, that are distant from areas of intensive use. Endosulfan is toxic to humans” (Stockholm Convention Clearing House Web Site, 2008).
 - **Alpha-endosulfan (Endosulfan I)** and **Beta-endosulfan (Endosulfan II)** are a polychlorinated compounds used for controlling a variety of insects. It is practically water-insoluble, but readily adheres to clay particles and persists in soil and water for several years (Kim *et al.*, 2016).
- **Endosulfan sulfate** is a sand-like powder which is not produced or used commercially. It occurs from the precursor endosulfan, which is used as pesticide. Can affect you when breathed in and may be absorbed through the skin (Kim *et al.*, 2016).
- **Endrin:** This insecticide is sprayed on the leaves of crops such as cotton and grains. It is also used to control rodents. Animals can metabolize endrin (it does not accumulate in their fatty tissue to the extent that structurally similar chemicals do), however, it has a long half-life, persisting in the soil for up to 12 years. In addition, endrin is highly toxic to fish (Stockholm Convention Clearing House Web Site, 2008).
- **Heptachlor** was used to kill soil insects, termites, and more widely to kill cotton insects, grasshoppers, other crop pests, and malaria-carrying mosquitoes. It is classified as a possible human carcinogen. Food is the major source of exposure for humans (Stockholm Convention Clearing House Web Site, 2008).

- **Hexachlorobenzene (HCB):** First introduced in 1945 to treat sedes because of its ability to kill fungi that affect food crops. “It is also a byproduct of the manufacture of certain industrial chemicals and exists as an impurity in several pesticide formulations. When people in eastern Turkey ate HCB-treated seed grain between 1954 and 1959, they developed a variety of symptoms, including photosensitive skin lesions, colic, and debilitation; several thousand developed a metabolic disorder called porphyria turcica, and 14% died” (Stockholm Convention Clearing House Web Site, 2008). HCB has been found in food of all types. A study of Spanish meat founded HCB in all samples (Herrera *et al.*, 1994).
- **Hexachlorocyclohexane (HCH)** is a synthetic chemical that exists in eight chemical forms called isomers. The different isomers are named according to the position of the hydrogen atoms in the structure of the chemical. Technical-grade HCH is a mixture of several isomers; it consists of approximately 60–70% α -HCH, 5–12% β -HCH, 10– 15% γ -HCH, 6–10% δ -HCH, and 3–4% ε -HCH (Dorsey, 2005).
 - **gamma-HCH (Lindane, γ -HCH):** This pesticide refers to products that contain >99% γ -HCH. The α -, β -, and δ -isomers, as well as technical-grade HCH are not synonymous with γ -HCH. Lindane has been used as a broad-spectrum insecticide for seed and soil treatment, tree and wood treatment and against ectoparasites in both veterinary and human applications. The production of lindane has decreased rapidly in the last few years (Stockholm Convention Clearing House Web Site, 2008).
 - **Alpha-HCH (α -HCH) and beta-HCH (β -HCH):** Although the intentional use of beta-HCH as an insecticide was phased out years ago, this chemical is still produced as unintentional by-product of lindane. Around 6-10 tons of the other isomers including alpha- and beta-HCH are created for each ton of lindane produced, so large stockpiles of alpha- and beta-HCH are therefore present in the environment. It is highly persistent in cold water regions and may bioaccumulate and biomagnify in biota and arctic food webs (Stockholm Convention Clearing House Web Site, 2008).
 - **delta-HCH (δ -HCH)** is used as an insecticide on fruit, vegetables, and forest crops and is also available as a prescription (lotion, cream, or shampoo) to treat head and body lice, and scabies (Kim *et al.*, 2016).
- **Methoxychlor** is a white crystalline solid which is often dissolved in a liquid carrier such as diesel oil, and it can easily penetrate the soil and contaminate groundwater and nearby streams. It is used as a pesticide. The primary hazard is the threat to the environment. The main route of exposure may occur during its manufacture or use as a pesticide (Kim *et al.*, 2016).
- **Mirex:** This insecticide is used mainly to combat fire ants, termites and as a fire retardant in plastics, rubber, and electrical goods. It has a half life up to 10 years, so it is considered to be one of the most stable and persistent pesticides (Stockholm Convention Clearing House Web Site, 2008).

Polybrominated Diphenyl Ethers (PBDEs)

PBDE are one of the five class of brominated flame retardants (BFRs) chemicals that exist as mixtures of distinct chemicals called congeners with unique molecular structures. “Them congeners may differ in the total number or position of bromine atoms attached to the ether molecule. Congeners with equal numbers of bromine atoms are known as homologs” (ATSDR, 2004; EPA, 2009). PBDEs do not chemically bind with the products to which they are added (furniture, electronics, etc.) so they easily release from these products and enter air and dust.

- c-triBDE's: **BDE 28**
- c-tetraBDE's: **BDE 47**
- c-pentaBDE's: **BDE 100, BDE 85, BDE 99**
- c-hexaBDE's: **BDE 153, BDE 154**
- c-heptaBDE's: **BDE 183**

Commercial mixture of octaBDE is highly persistent, has a high potential for bioaccumulation and food-web biomagnification, as well as for long-range transport. The only degradation pathway is through debromination (the replacement of bromine on the aromatic ring with hydrogen) and producing other bromodiphenyl ethers lower brominated and possibly more toxic. The Agency for Toxic Substances and Disease Registry (ATSDR, 2004) affirm that lower brominated tend to bioaccumulate more than higher brominated congeners and are more persistent in the environment. However, there are more tendency of higher brominated congeners to bind to sediment or soil particles (EPA, 2014).

Organophosphate Flame Retardants (OPFR)

With the phase out of some PBDEs, some OPFRs have been used as replacements. Flame retardants are chemicals that are added or applied to materials in order to slow or prevent the start/growth of fire. They have been used in many consumer and industrial products since the 1970s, to decrease the ability of materials to ignite (NIEHS, 2017). They are often added or applied to the following products.

- Furnishings (foam, upholstery, mattresses, carpets, curtains) and fabric blinds.
- Electronics and electrical devices (computers, laptops, phones, televisions) and household appliances, plus wires and cables.
- Building and construction materials, including electrical wires and cables, and insulation materials (polystyrene and polyurethane insulation foams).
- Transportation products and other parts of automobiles, airplanes, and trains.

Flame retardants can also enter the environment through burning or dismantling e-waste. During manufacturing, these chemicals can enter surrounding air, water and soil, travelling great distances on air and water currents. Levels of some retardants in the Arctic are extremely concerning. People are exposed primarily through diet and inhalation of off-gassing from products in the home and in cars, airplanes and workplaces. House dust is a significant source of exposure. Some of the potential health effects associated are endocrine and thyroid disruption, impacts to the immune system,

reproductive toxicity, cancer, neurologic function or adverse effects on fetal and child development (NIEHS, 2017). The studied flame retardants are the following:

- 2-Ethylhexyldiphenyl phosphate (EHDP)
- Tri (2-ethylhexyl) phosphate (TEHP)
- Tributyl phosphate (TBP)
- Triethyl phosphate (TEP)
- Triisobutyl phosphate (TiBP)
- Triphenyl phosphate (TPP or TPhP)
- Tris ((2-chloro-1-chloromethyl) ethyl) phosphate (TDCP)
- Tris (2-butoxyethyl) phosphate (TBEP)
- Tris (2-chloroethyl) phosphate (TCEP)
- Tris (2-chloroisopropyl) phosphate

Polycyclic Aromatic Hydrocarbons (PAH)

PAH are a large group of compounds, they consist of two or more fused aromatic rings made entirely from carbon and hydrogen. The physical and chemical properties of the individual PAH vary, but the semivolatile property of some PAH makes them highly mobile throughout the environment, deposition and re-volatilisation distributing them between air, soil and water bodies. A proportion of PAH is subject to long range atmospheric transport making them a transboundary environmental problem (European Communities, 2001). The PAHs analyzed in this study are explained below, which definitions appear in Kim *et al.* (2016):

- **Acenaphthalene:** Used in dye synthesis, insecticides, fungicides, and in the manufacture of plastics.
- **Acenaphthene:** Derived from coal tar and used to make dyes, pharmaceuticals, insecticides, fungicides, and plastics. The crystallizable acenaphthene fraction is obtained from the wash oil by redistillation.
- **Anthracene:** primarily used as an intermediate in the production of dyes, smoke screens, scintillation counter crystals, and in organic semiconductor research.
- **Benzo (a) anthracene:** primarily found in gasoline and diesel exhaust, tobacco and cigarette smoke, coal tar, coal combustion emissions, amino acids, fatty acids and carbohydrate pyrolysis products, wood and soot smoke. This substance is used only for research purposes.
- **Benzo (a) pyrene:** primarily found in gasoline and diesel exhaust, cigarette smoke, coal tar and coal tar pitch, charcoal-broiled foods and certain other foods, amino acids, fatty acids and carbohydrate pyrolysis products, soot smoke, creosote oil, petroleum asphalt and shale oils.
- **Benzo (b) fluoranthene:** primarily found in gasoline exhaust, tobacco and cigarette smoke, coal tar, soot, amino acids and fatty acid pyrolysis products.

- **Benzo (ghi) perylene** is present as a component of PAH content in the environment usually resulting from the incomplete combustion or pyrolysis of organic matters, especially fossil fuels and tobacco.
- **Benzo (k) fluoranthene:** is produced by the incomplete combustion of organic matter, primarily found in gasoline exhaust, cigarette smoke, coal tar, coal and oil combustion emissions, lubricating oils, used motor oils and crude oils. This substance is used only for research purposes.
- **Chrysene:** Is formed during distillation of coal, in very small amount during distillation or pyrolysis of many fats and oils. This substance does not usually occur as a pure substance but as a component of PAH mixtures. The substance decomposes on burning producing toxic fumes. Reacts violently with strong oxidants.
- **Dibenzo (a,h) anthracene** produced by the incomplete combustion of organic matter, primarily found in gasoline exhaust, tobacco smoke, coal tar, soot and certain food products, especially smoked and barbecued foods. This substance is used only for research purposes to induce tumorigenesis.
- **Fluoranthene** is usually resulting from the incomplete combustion or pyrolysis of organic matters, especially fossil fuels and tobacco. It is a constituent of coal tar and petroleum-derived asphalt.
- **Fluorene** is a combustible. It has a violet fluorescence, hence it's name. For commercial purposes it is obtained from coal tar. It is insoluble in water and soluble in many organic solvents.
- **Indeno (1,2,3-c,d) pyrene** is produced by the incomplete combustion of organic matter, primarily found in certain foods, gasoline and diesel exhaust, cigarette smoke, coal tar and coal tar pitch, soot and petroleum asphalt.
- **Naphthalene** is obtained from either coal tar or petroleum distillation and is primarily used to manufacture phthalic anhydride, but is also used in moth repellents, household fumigant, dispersants in synthetic and natural rubbers, in leather industries, agricultural formulations (dispersants for pesticides) and dyes.
- **Phenanthrene** is the second most abundant coal tar constituent next to naphthalene. Coal tar distillation concentrates phenanthrene in the anthracene oil fraction. Once anthracene residues have been crystallized and filtered off, phenanthrene is recovered from the filtrate.
- **Pyrene:** Pyrene forms during incomplete combustion of organic compounds. It is usually used for PAHs as mixtures, e.g., coal tar pitch volatiles. However, pyrene may be encountered as a laboratory chemical in its pure form. Health effects of exposure to the substance have not been investigated adequately.

Polychlorinated Biphenyles (PCBs)

PCBs are a group of man-made organic chemicals consisting of carbon, hydrogen and chlorine atoms. The number of chlorine atoms and their location in a PCB molecule determine many of its physical and chemical properties. Due to their non-flammability, chemical stability, high boiling point and electrical insulating properties, compounds are used in industry as heat exchange fluids, in electric transformers and capacitors, and as additives in paint, carbonless copy paper, and plastics. Of the 209 different types of PCBs, 13 exhibit a dioxin-like toxicity. Their persistence in the environment corresponds to the degree of chlorination, and half-lives can vary from 10 days to one-and-a-half years (Stockholm Convention Web Site, 2008). 17 congeners are analyzed in the current study:

- Mono-ortho-Substituted PCBs, Dioxin-Like: **PCB 105, PCB 114, PCB 118, PCB 123, PCB 156, PCB 157, PCB 167 and PCB 189.**
- Di-ortho PCBs, Non-Dioxin-Like: **PCB 28, PCB 52, PCB 101, PCB 138, PCB 153 and PCB 180.** There are the most abundant PCBs.
- Non-ortho PCBs, Dioxin-Like (Coplanar PCBs): **PCB 77, PCB 81 and PCB 126.**

The dioxin-like PCBs are regulated under Annex A and the non-dioxin-like under Annex C.

1.4 Objectives

- Identify and quantify the 77 compounds belonging to the 7 groups of POPs associated with microplastics that reach Las Canteras beach (Gran Canaria).
- To determine the possible sources.
- To compare results with other similar studies, if it's possible.

2. MATERIAL AND METHODS

2.1 Study area

The study was conducted from April to May 2017 in Las Canteras beach, the main urban beach of Gran Canaria island (Table 1). It's location to the north of the island (exposed to the predominant wind and swells N-NE) together with the amount of tourists it receives (3.735.417 tourists from January to October 2017, Tourism Board of Las Palmas de Gran Canaria) make this beach one of the most vulnerable to exposure of marine plastic debris. However, this beach is cleaned twice a day by the town council due to the large tourist influx.

This beach was selected due to Batzan *et al.* (2014) observed significantly higher microplastic pollution levels on beaches with northern exposure in Canary Islands East region, and the great abundance of ships that, eliminating fishing vessels, researchers and ferries, reaching the amount of 179 between the La Luz and Las Palmas Port from March 1 to June 1, 2017 (Port Authority of Las Palmas, 2017).



Figure 3. Location of Las Canteras Beach, at Gran Canaria Island. Solid yellow line indicates the sampling area (260m).

Table 1. Main characteristics of Las Canteras beach, adapted from Herrera *et al.* (2017).

	Las Canteras beach
Location	28° 7.854'N, 15° 26.775'W
Total longitude (m)	2049
Turistic pressure	High
Orientation	N
Exposure	Open to NW, partially protected to NE
Intertidal zone (m)	60
Sediment type	Fine sands
Median sediment size (mm)	0.125

2.2 Field work

Las Canteras beach shows a non-uniform distribution of plastic debris. The northern area has a semi-submerged natural rock barrier that partially protects the beach from plastic pollution. Nevertheless, La Cicer's area (sampling site) does not show any natural barrier, so a greater quantity of stranded plastics are observed. The samples were picked up along the high tide line within a range of 260m (Figure 3) and before the beach cleaning, usually at 7:00 a.m. (Table 2). As the density and distributions of the pellets on the beaches varied greatly among the sites, no strict criteria were set in terms of distance range where the pellets were collected (Endo *et al.*, 2005). Therefore, the first centimetres of sediment were picked up with a commercial fishing net (1mm mesh width) using latex gloves. The mesh was then introduced in the water to remove the sand and it was stored in a plastic container until arriving at the laboratory, where the samples were left to dry at room temperature keeping them away from solar light. Once dry and with the help of stainless steel tweezers, sorting took place, separating pellets (1-5mm) from remnants of vegetal debris, tar and other plastic fragments (maximum size about 10mm). Once separated, they were distributed in 1g samples (aprox. 50 pellets) and stored in sterile air-tight plastic bags. A total of 50g of pellets were collected. Pellet colour classification was not taken into account as it was not the aim of this work.

Table 2. Information about the sampling date and related high and low tide hours.

Date (yyyy/mm/dd)	Hour (h)	Max. Low Tide (hour, m)	Max. High Tide (hour, m)
2017/04/05	6:00-7:30 a.m.	2:48h, -0.62m	9:13h, 0.48m
2017/04/07	6:00-7:30 a.m.	5:03h, -0.77m	11:15h, 0.75m
2017/05/04	00:00-2:00 a.m.	2:28h, -0.56m	8:49h, 0.59m
2017/05/07	6:00-7:30 a.m.	5:19h, -0.77m	11:30h, 0.79m
2017/05/30	6:00-7:30 a.m.	10:43h, -0.78m	17:06h, 0.91m

2.3 Laboratory work



Figure 4. Stranded pellets from Las Canteras beach, disposed in sterilized plastic bags.

Samples analyses were carried out by Clinical and Analytical Toxicology Service (SERTOX) of the University of Las Palmas de Gran Canaria. Unfortunately, only 5g (250 pellets) were analysed due to the high analytical cost the 77 chemical pollutants represented. Anyway, previous studies state that a good representation of local individual concentrations is obtained with average values from 5 pellet pools (Endo *et al.*, 2005; Ogata *et al.*, 2009 and Heskett *et al.*, 2012). Analytical protocol, previously developed by María Camacho and her collaborators (e.g. Camacho *et al.*, 2013), took place in SERTOX's facilities. The analytical protocol consists of 4 days per sample as it is displayed in the Annex II.

GAS CROMATOGRAPHY

Samples of micro-plastic were weight (1 g approximately) in a glass tube. A liquid-solid extraction was used for the extraction of target analytes. CHX and AE were used to extract hydrophobic substances from the plastic matrixes. 5000 uL of CHX:AE (1:1) were added to each samples and ultrasonic extraction was applied. An orbital rotator was used during 24 hours to solvent soaking and promotes extraction. After each 24 hours, the 5000 µl were transferred to a test tube and another 5000 µl of the organic solvent mixture were added to the plastic sample, repeating this process during 72 hours. The fourth day the three extraction of each day were mixed. A part of it was evaporated and concentrated under a gentle stream of N₂ for prior analysis (See protocol, Annex II). The determination of chemical was performed using a gas chromatography separation with a triple quadrupole mass spectrometer (GC System 7890B and MSMS 7010 of Agilent Technologies, Palo Alto, CA, USA). Chromatographic separations were performed employing two 15-m capillary columns (Agilent J&WHP-5MS), which were connected in series using a Purged Ultimate Union (PUU, Agilent Technologies). The use of these two columns allowed the employment of the back-flushing technique (constant flow rates of 1.2 ml/min of helium (99.999%) for column 2, and 1.0 ml/min for column 1). The temperatures of the GC oven were programmed as follows: a) initial temperature: 60 °C for 1 min; b) ramp 1: 40 °C/ min to 170 °C; c) ramp 2: 10 °C/min to 310 °C; d) hold time: 3 min. Total run time was 20.75 min. Injector and transfer line were set at 280 °C. Standards and samples were injected (1 µl) in the splitless mode. Retention Time Locking (RTL) of the analytes with chlorpyrifos-methyl (Rt = 9.143 min) as the time reference was used. The QqQ mass spectrometer was operated under the previously described conditions (Henriquez-Hernandez *et al.*, 2016). Nitrogen (99.99%) was used as the collision gas. Collision gas flow was set at 1.5 ml/min.

The quantification was bases on peak area, using ten-point calibration curves. These calibration curves were constructed using a least-squares linear regression from the injection of standard solutions (1% olive oil), ranging from 0.03 to 20 ng/ml. The limits of quantification (LOQ) varied among compounds and ranged from 0.03 to 0.15 ng/ml (Henriquez-Hernandez *et al.*, 2016). The results of this study have been expressed in ng contaminant per gram (ng/g).

➤ Quality assurance and quality control

In each batch of samples, three controls were included for every 18 vials (6 samples): 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). The results were considered to be acceptable when the concentration of the analytes determined in the QC sample was 15% of the deviation of the theoretical value.

2.4 Data treatment

Data analysis and graphs were performed with Excel program of the Microsoft Office 2013 package. To estimate the representative concentrations of the five samples, the average (average function) was used due to its better correlation with the NOAA's Mussel Watch than the arithmetic or geometric average (Ogata *et al.*, 2009; Heskett *et al.*, 2012).

RESULTS

Concentrations of 52 out of the total 77 POPs analysed have been identified in all the 250 pellets. In general, POP concentrations show a great variability from one sample to another, as it can be seen below according to the medians, maximum and minimum values shown in the box diagrams.

Only three of the 5 UV Filters analyzed are present in the pellets, neither 2-Ethylhexyl 4-(dimethylamino) benzoate nor 3-benzylidenecamphor concentrations have been found. The addition of UV Filters' averages a total of 289.12 ng/g pellet (Figures 5 and 6). The most abundant are the ones allowed in concentrations of 10% by Regulation (EC) No 1223/2009 of the European Parliament and the Council of 30 November 2009 on cosmetic products (see Annex I), corresponding to Homosalate and 2-Ethylhexyl p-methoxycinnamate (EHMC). Concentrations of 4% are allowed for 4-MBC, which present the highest variability in the samples.

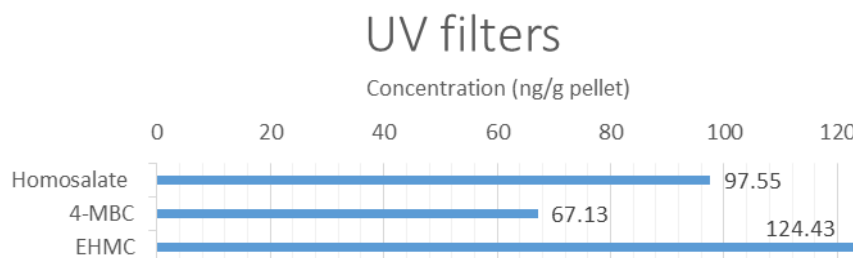
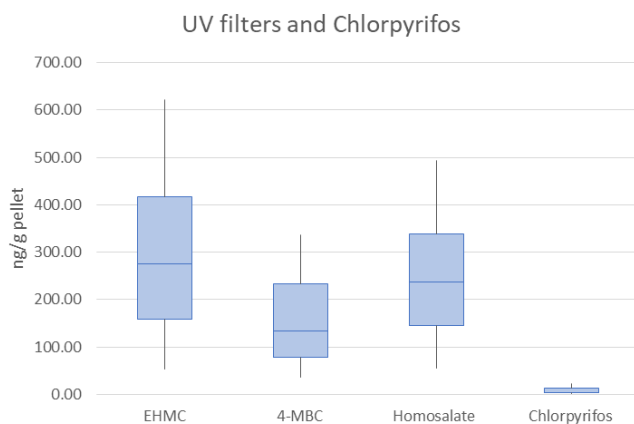


Figure 5. UV filters bar chart with mean values of each compound. Maximum to minimum concentration (ng/g pellet) for 2-Ethylhexyl p-methoxycinnamate (EHMC), Homosalate and 3-(4-Methylbenzylidene) camphor (4-MBC).



Chlorpyrifos (Figure 6) can be found in average concentrations of 4.72 ng/g pellet, being observed in every sample in spite of showing a great variability among them, having a minimum value of 1.28 ng/g pellet and a maximum value of 10.52 ng/g pellet. Its median value is 1.72 ng/g pellet.

Figure 6. Box diagram for UV filters and Chlorpyrifos. Concentrations are shown in ng/g pellet.

In the case of Organochlorine Pesticides (OCPs), 20 congeners were analysed, 11 of which were present in the pellets, showing a total value of 99.18 ng/g pellet. The OCPs that do not appear are methoxychlor, delta-HCH, beta-HCH, alfa-HCH, heptachlor, endosulfan sulfate, alfa-endosulfan, p,p'-DDT and p,p'-DDD. As reflected in Figure 7, p,p'-DDE, whose concentrations are much higher than than the rest of OCPs analysed

(77.26 ng/g pellet), is the most abundant and variable one. It present a value of 248.71 ng/g pellet in one sample, and the rest are values about 35 ng/g pellet.

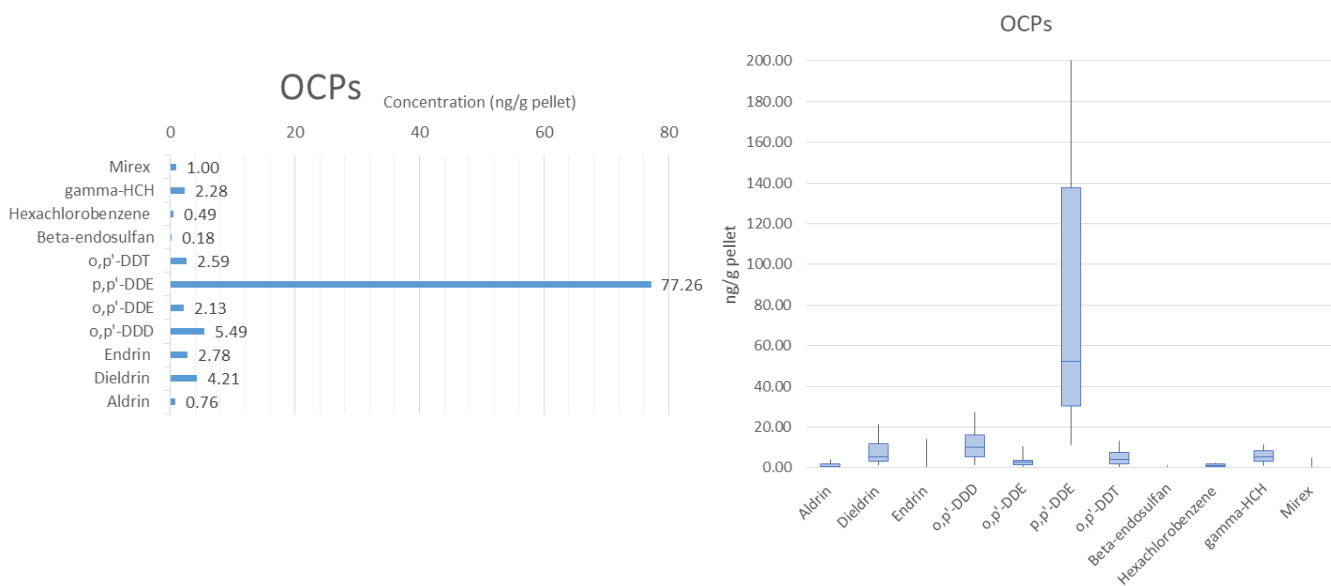


Figure 7. OCPs bar chart (left) with mean values of each compound and box diagram (right) from Las Canteras beach. Concentrations are shown in ng/g pellet.

Five out of the 8 Brominated Diphenyl Ethers (BDEs) studied have been appeared (Figure 8), with a total BDE concentration of 0.89 ng/g pellet, with maximum value of 0.84 ng/g pellet for BDE 47. BDE 85, BDE 154 and BDE 183 concentrations have not been found. BDE 47 (mean value 0.34 ng/g pellet) shows twice as concentration as the rest of the BDEs, being BDE 153 the less abundant one (0.03 ng/g pellet).

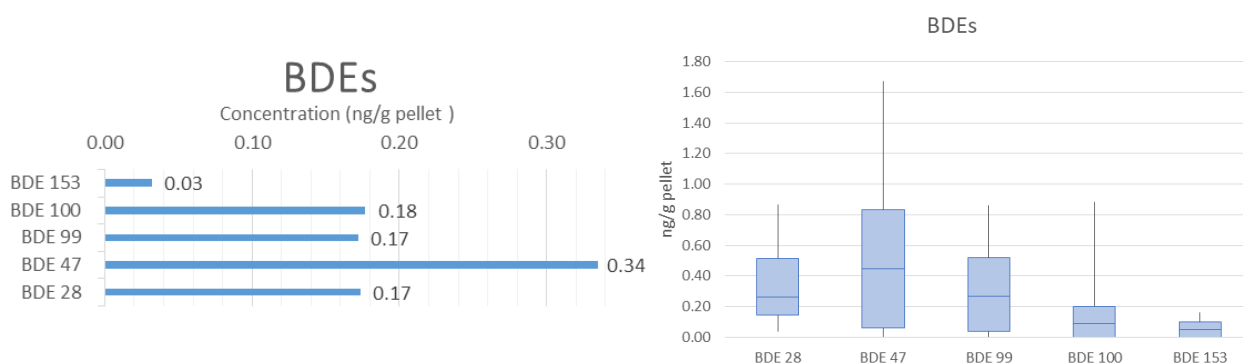


Figure 8. BDEs bar chart (left) with mean values of each compound and box diagram (right) from Las Canteras beach. Concentrations are shown in ng/g pellet.

The 10 Organophosphate Flame Retardants (OPFRs) examined did not show tris (2-butoxyethyl) phosphate or tri (2-ethylhexyl) phosphate concentrations. OPFRs shows less variability than others groups of POPs (Figure 9). The addition of the averages correspond to a 27.09 ng/g pellet value, being the most abundant one the tris (2-chloroisopropyl) phosphate (8.5 ng/g pellet), followed by triisobutyl phosphate (7.38 ng/g pellet) and 2-ethylhexyldiphenyl phosphate (5.88 ng/g pellet) (Figure 10). The minimum value found is 0.08 ng/g pellet in retardant Tris ((2-chloro-1-chloromethyl) ethyl) phosphate.

POPs in plastic pellets from Las Canteras Beach (Canary Islands)
Estela Lalueza Broto

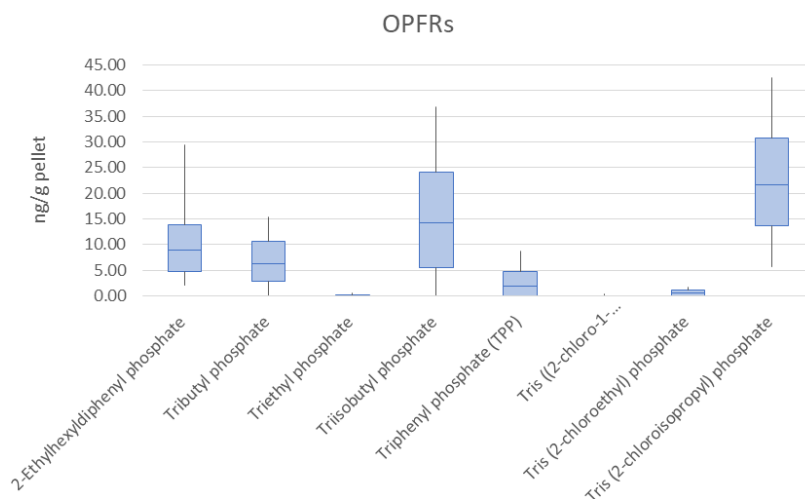


Figure 9. Box diagram for OPFRs. Concentrations are shown in ng/g pellet.

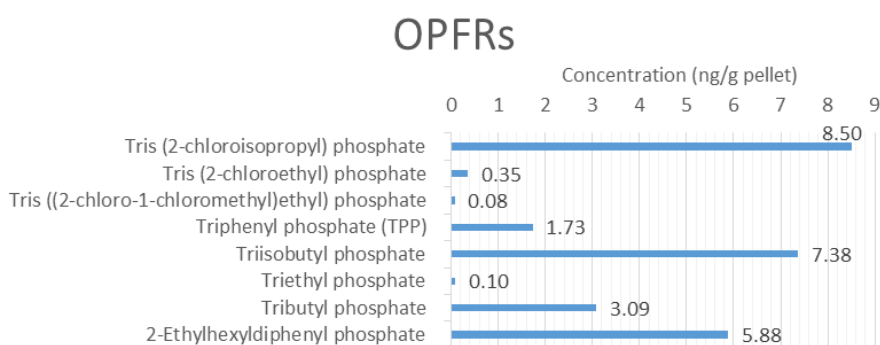


Figure 10. OPFRs bar chart with mean values of each compound. Concentrations are shown in ng/g pellet.

A total of 16 Polycyclic Aromatic Hydrocarbons (PAHs) were analysed, but fluoranthene, Benzo (b) fluoranthene and acenaphthene were not found in any sample. PAH total is 27.96 ng/g pellet and the case of naphthalene should be noted as it has concentrations of 144.21 ng/g pellet in all samples (Figure 11), with maximum and minimum of 663.97 and 10.83 ng/g pellet, respectively (290.56 ng/g pellet standard deviation) (Figure 12).

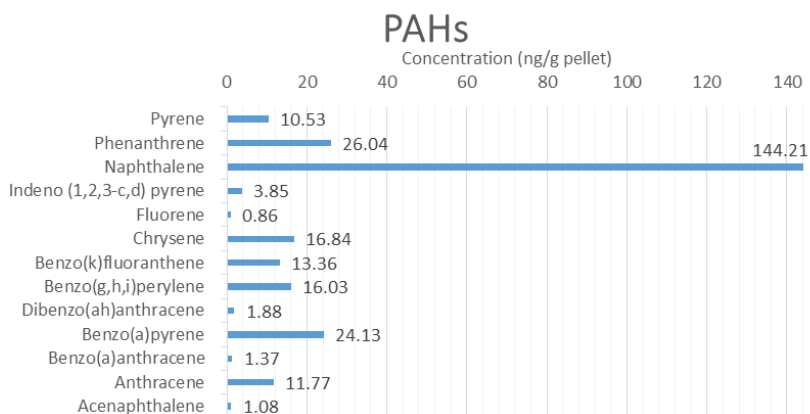


Figure 11. PAHs bar chart with mean values of each compound (ng/g pellet) from Las Canteras beach.

The compound less abundant is fluorene, with mean concentration of 0.86 ng/g pellet.

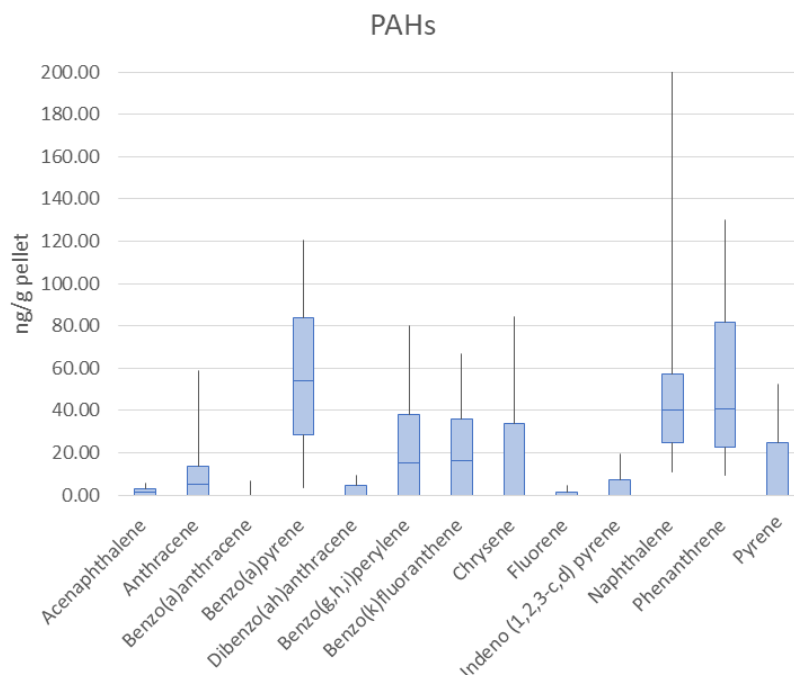


Figure 12. Box diagram for PAHs. Concentrations are shown in ng/g pellet.

Of the total 17 Polychlorinated Biphenyles (PCBs) analysed, the following congeners have not been found in any of the samples: PCB 81, PCB 28, PCB 157, PCB 126, PCB 118 and PCB 114. The total PCB content reaches a 28.22 ng/g pellet value. PCB 153 stands above the rest (12.09 ng/g pellet), followed by PCB 180 (9.60 ng/g pellet), as seen in Figure 13. PCB 101 and PCB 138 are found in concentrations of 2.64 and 2.14 ng/g pellet respectively, and the other PCBs' concentrations are lower than 1 ng/g pellet, having PCB 77 the minimum value (0.05 ng/g pellet). The higher standard deviation corresponds to the most abundants ones, PCB 153 and PCB 180 (Figure 14).

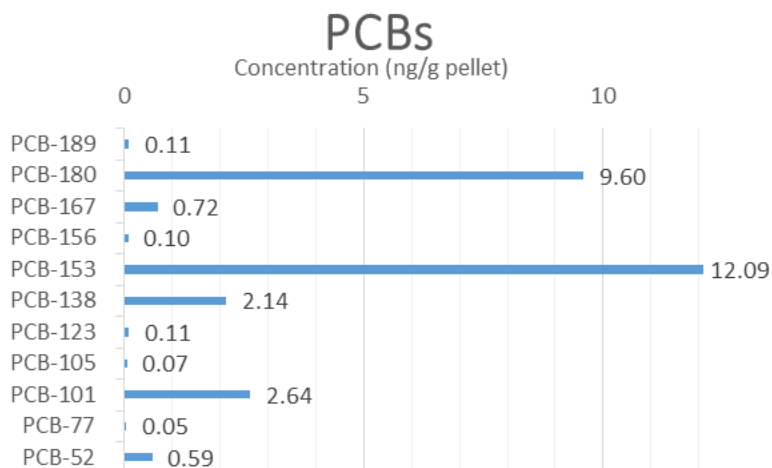


Figure 13. PCBs bar chart with mean values of each compound. Concentrations are shown in ng/g pellet.

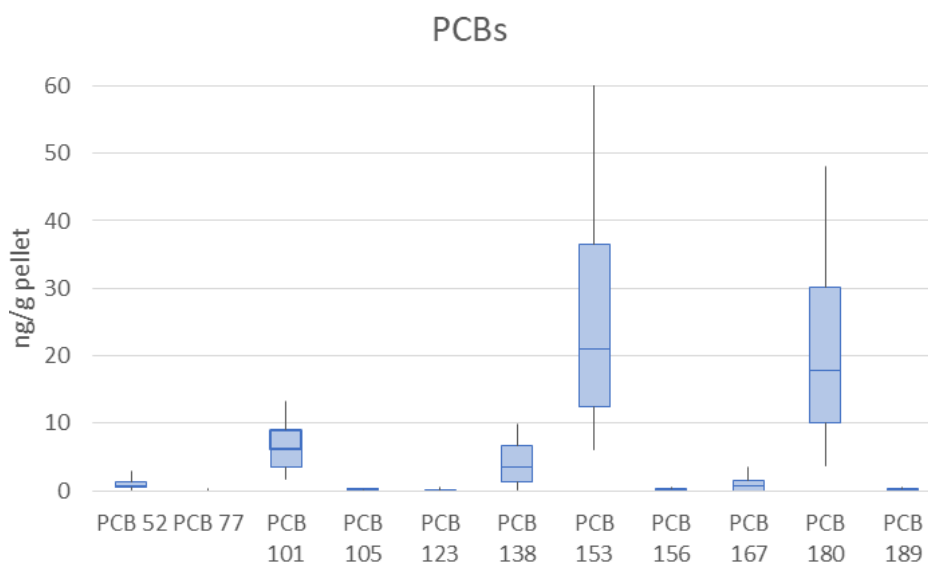


Figure 14. Box diagram for PCBs. Concentrations are shown in ng/g pellet.

DISCUSSION

Degree of weathering, type of material and colour have not been taken into account for the analysis of POP presence in stranded pellets, that is to say, pellets were randomly distributed in each 1g sample (50 pellets). The great variability of concentrations found among samples is similar to the variability shown in other studies, where pellets are classified by colour and/or material. For instance, Antunes *et al.* (2013) analysed them by color (white, aged, colored and black) and Endo *et al.* (2005) only analysed PE pellets. In both cases, the result was a great piece-to-piece variability between one and two magnitude orders, including the study by Heskett *et al.* (2012) carried out in 5 beaches located more than 100km away from the continent. The degree of weathering of every pellet could also influence pollutant concentration. Nevertheless, Endo *et al.* (2005) did not find any correlation between the degree of weathering and PCB concentration, concluding that the degree of weathering can affect PCB concentration in pellets either positively or negatively. On the contrary, the degree of discoloring seems to be similar; in the study carried out by Endo *et al.* (2005) discoloured pellets showed greater PCB concentrations than not discoloured ones, suggesting that the degree of discoloring could be related with pellet's water residence time, their slow sorption and the individual pathways of exposure to different concentrations of each pollutant. This sorption/desorption of hydrophobic organic compounds to pellets is controlled by diffusion into the polymer matrix, taking up to a year to reach equilibrium (Karapanagioti *et al.*, 2010; Heskett *et al.*, 2012). This idea has been well received by the scientific community and has been demonstrated in a large number of further studies (Ogata *et al.*, 2009; Hirai *et al.*, 2011; Heskett *et al.*, 2012, Antunes *et al.*, 2013). On the basis of the study carried out by Rochman *et al.* (2013) (12-month virgin pellet monitoring), Antunes *et al.* (2013) suggested that "lighter congeners of PAHs and PCBs with lower hydrophobicity reached adsorption equilibrium faster than the heavier ones, and moreover antagonistic/synergistic effects are known to occur and affect sorption capacities as shown by Bakir *et al.* (2012) for the PAH phenanthrene and DDT."

Previous studies of POPs in stranded pellets have shown a greater pollutant concentration in urban beaches than in rural ones, and similar concentration values between beaches which are far from the continent and open ocean (Endo *et al.*, 2005; Ogata *et al.*, 2009; Hirai *et al.*, 2011; Heskett *et al.*, 2012; Antunes *et al.*, 2013). These results are correlated with Mussel Watch and have been used as monitoring media of POPs since 1975 (Goldberg, 1975).

To our knowledge, this is the first study analysing UV filters in stranded pellets. Due to the large influx of tourists using sunscreens that Gran Canaria island receives, it is no surprise that these UV filters appear on the beaches. Comparing the values with a study using water samples carried out in 8 Gran Canaria's beaches (Rodriguez *et al.*, 2015), pellets show greater concentrations, between 1 and 2 magnitude orders higher (Table 3). The most abundant UV filters in that study (Rodriguez *et al.*, 2015) have not been analysed in this work, hence just the three UV filters appeared in the pellets have been compared. The addition of the UV filters found in water samples is higher in the south of the island, where beaches are semi-closed; the lowest values are from Las Canteras and Las Alcaravaneras. This value difference might be caused by UV filters' hydrophobicity, as they tend to adhere to solid particles, where greatest concentrations are found. Being a north-oriented open beach, Las Canteras could be receiving a greater quantity of pellets and fragments than southern semi-closed beaches (Batzan *et al.*, 2014) and, therefore, a greater UV filter concentration adsorbing to this plastic material. A further future review should be needed in order to see if there are significant differences of UV filter concentrations between water samples and pellet/plastic fragment samples among the different island's beaches.

Table 3. UV filters data comparison of the present study (ng/g pellet) and Rodriguez *et al.* (2015) study (ng/L).

	Present study (ng/g pellet)	Rodriguez <i>et al.</i>, 2015 (ng/L)
2-Ethylhexyl p-methoxycinnamate	124.4	7.9
Homosalate	97.6	13.3
3-(4-Methylbenzylidene) camphor	67.1	6.3

Chlorpyrifos have not been previously analysed in pellets or seawater samples. In a study regarding pesticide residues in bananas harvested in Canary Islands (Hernández-Borges *et al.*, 2009), 88% of the bananas analysed contained this pesticide as its use is permitted and limited to 3mg/kg (maximum residue limits for pesticides 2008) by the Spanish Ministry of Agriculture, Fishing and Food and the European Union. It can not be certainly concluded that chlorpyrifos found in the pellets (4.72 ng/g pellet) come from the island's agriculture or from Europe in general, being transported by the Canary Current adhered to pellets until they reach Las Canteras beach. It is evident that pellets show greater pesticide concentrations than the bananas studied by Hernández-Borges *et al.* (2009), the pesticide possibly arrives by sea run-off and accumulates in pellets due to its hydrophobicity. Consequently, this pesticide's concentrations in the environment might have been underestimated in the past, being necessary a new and more comprehensive review.

The studies concerning DDTs in pellets tend to show greater DDT concentrations than its degradation products, corresponding to recent entries of DDTs in the environment (Ogata

et al., 2009; Heskett *et al.*, 2012), excluding some non-urban beaches where DDEs do predominate compared to DDTs (Ogata *et al.*, 2009, Hirai *et al.*, 2011). However, nearly a 78% of DDTs found belong to p,p'-DDE and the bibliography suggests that the DDT spill is not recent, that is to say, the source of this pollutant does not come from Gran Canaria island. Pellets have been exposed to DDTs in the aquatic environment and transported to the beach by the Canary Current, reaching equilibrium with the pollutant before arriving at the beach. It is therefore probable that these pellets have remained for at least one year in the aquatic environment, long enough to reach that equilibrium (Karapangioti *et al.*, 2010). These values correspond to the ones obtained in the study conducted by Hirai *et al.*, (2011), in which DDE concentrations dominated Japanese beaches. This may be due to pellets being located on the ocean's surface, coming into contact with the atmosphere and resulting in an aerobic conversion from DDT to DDE, instead of DDD (Ogata *et al.*, 2009). Being a region located more than 100km away from the continent, concentrations should be similar to open ocean ones. Nevertheless, if we compare these values with the ones obtained by Ogata *et al.* (2009), it is observed that concentrations in Europe are much lower (e.g. 2ng/g pellet in Portugal and the UK) than the ones obtained in the present study (87.5 ng/g pellet), which are more similar to the concentrations found in cities such as San Francisco (96 ng/g pellet). Las Canteras would be on the fourth place in the ranking regarding greater DDT concentration in the global study carried out by Ogata *et al.* (2009), quite alarming data. Taking into account the prohibition of using DDTs as pesticides made in 1970 and the low values found in Europe, it would be surprising that they came exclusively from Europe. They may come from northern Africa, where DDT kept being used until 1995 due to a new malaria outbreak (Ryan *et al.*, 2012).

HCH values are similar to the ones found in India (Ogata *et al.*, 2009) and higher than the ones found in the USA, Asia and Europe. According to Ogata *et al.*, (2009) this is due to a lower hydrophobicity and a higher steam pression than the one shown by PCBs, so they do not tend to accumulate near their sources, evaporating and getting in the atmosphere (Mizukawa *et al.*, 2013). In this study, the only isomer appearing is gamma-HCH, the main component of lindane pesticide, so the concentrations found on Las Canteras beach may be associated to the use of this pesticide. The results from Ryan *et al.* (2012) show a generalized HCH concentration decrease in beaches in southern Africa in a monitoring carried out from 1984 to 2008, which refers to the effectivity of the pesticide prohibition made in the Stockholm Convention. These pesticides might have been intensively used in Gran Canaria island in the past, for tomato, advocado and banana production. However, remaining far from their sources and being higher than European and African ones, their presence could be explained by a greater residence time of the pellets in the aquatic environment than the ones found on European, Asian and African beaches, which show a greater HCH concentration.

Currently, PBDEs associated to plastics remain unstudied. The only publication in which they have been analysed was published by Hirai *et al.* (2011), although it focuses on the Pacific Ocean and a couple of Caribbean beaches (Costa Rica), so it is not really reliable to compare it to this study. A great BDE 183 abundance is shown in their results, particularly in the samples from Pacific Central Gyre, where it represents 60% of all the congeners analysed. BDE 183 significantly appears in Costa Rica as well, but BDE 147 is the most abundant, as in the present study. Nevertheless, BDE 183 does not appear in any of the samples analysed in Las Canteras. The most abundant BDEs are the less

brominated ones and, according to The Agency for Toxic Substances and Disease Registry (ATSDR, 2004), they have a greater tendency to bioaccumulate.

In the study conducted by Rochman *et al.* (2014) and focused on South Atlantic, the less brominated congeners predominated in 62% of the plastic samples collected from open ocean, as a probable result of environmental sorption during their water residence given that BDEs tend to be on the atmosphere. On the other hand, the remaining 38% of their samples was dominated by the more brominated congeners, which belong to the plastic ingredient added during its manufacturing. It seems that these BDEs come from an exogenous source and that they have been absorbed during pellets' residence on the oceanic surface.

At the moment, there is no available study about Organophosphate Flame Retardants (OPFR) in pellets or seawater samples. The addition of OPFRs contained in the pellets is 27.1ng/g pellet. More studies are necessary to understand the background levels of OPFR in the marine environment.

As the naphthalene represents 53% of the PAHs analysed, the main source may be petrogenic. Phenanthrene is the second largest component in naphthalene manufacturing and the second most abundant component in Las Canteras' pellets, representing the addition of both of them a total of 62.6% of PAHs. It is probable that these PAHs were adsorbed before reaching the beach given the amount of maritime traffic surrounding Canary Islands, which occasionally produces motor oil or petroleum spills. Even open sea ship cleanings have been seen, although they are forbidden. Companies such as Cepsa include several refineries in Spain. It has three, located in Huelva, Gibraltar and Tenerife, apart from transformation chemical plants in Cádiz and Huelva. Thus, apart from the possible adsorption of petrogenic products associated to Las Palmas' port, it has to be noticed the influence made by companies from Europe and by the maritime traffic between Europe and America, since during freight and/or tourist transport there might be fossil fuel losses. As it has been mentioned before, pellets reaching the island have possibly been at least one year floating on sea surface, so they may have been in contact with any fossil waste that is in open sea. Lima *et al.* (2005) classify PAH anthropogenic sources in two groups: petrogenic and pyrogenic, which can be distinguished by molecular profiles. We have not obtained enough data for distinguishing these ratios. However, Hirai *et al.* (2011) comment that components having lower molecular weight are petrogenic (e.g., naphthalene, phenanthrene and pyrene), while the ones having higher molecular weight are pyrogenic (e.g., benzo (a) anthracene). It is difficult to compare our results with available literature because in each study different congeners are measured. In spite of that, in order to make a comparison with each of the available studies, all the components that each author analysed have been combined. For example, Sanz *et al.* (2016) analysed 6 PAH from a beach located at the SW of Gran Canaria and the addition of the components reaches an average value of 28.25ng/g pellet, lower than the addition of the same components in the case of Las Canteras beach (57.37ng/g pellet). Fluoranthene does not appear in any of the two studies conducted in Gran Canaria island, whereas benzo (a) pyrene appears in Las Canteras beach in concentrations of 24.13ng/g pellet but does not appear at the SW part of the island. The difference might be caused by the greater amount of tourism in Las Canteras beach and, consequently, by the greater number of cigarette butts deposited on the sand. Hence, the source of benzo (a) pyrene could be the endogenous pollution caused by tourism. In the study regarding fragments conducted by Hirai *et al.* (2011) taking into account samples collected in the Atlantic

Ocean (Costa Rica), the addition of their PAH resulted in 77.7ng/g pellet, a lower quantity than the one observed in this study, 123.93 ng/g pellet. The difference might be related to the different level of industrialization existing in both regions or to the high level of maritime freight traffic which, as mentioned above, Gran Canaria island suffers from. Eventually, the study carried out by Antunes *et al.* (2013) analyses a total of 17 PAHs, two more than this study, without analyzing naphthalene. If the different components are not taken into account, the values obtained in this study are similar to the ones found in Portuguese beaches, which have rivers, ports and industrial activity. On the other hand, if naphthalene is not taken into account, the average addition remains at 127.75ng/g pellet, similar to the values obtained by Antunes *et al.* (2013) in white pellets (supposedly pellets that have recently been spilled in the environment) and generally, to some beaches where there are only river entries. In general, PAHs found in Las Canteras beach seem to be related to petrogenic sources, without being certain whether this pollution comes from the island or from open sea.

The markers of exposure (PCB 153, PCB 180, PCB 101 and PCB 138) are the most abundant PCBs in Las Canteras beach, as well as in the environment. These congeners also appear in the beach at the SW of Gran Canaria (Sanz *et al.*, 2016) in higher quantities. These PCBs are not as toxic as dioxin-like ones, but they have high and medium chlorine content (hexa-, hepta-, penta- and hexa-, respectively), so they tend to remain close to their emission sources, accumulating in the sediment (Meijer *et al.*, 2003; Mizukawa *et al.*, 2013). Over time, these PCBs can be resuspended and dissolve with water. If we compare these congeners with the ones studied by Mizukawa *et al.* (2013), it can be observed that the congeners from Las Canteras beach are more similar to Portuguese urban beaches (Porto and Lisboa) than to rural areas. However, concentrations are higher in these two Portuguese cities. According to the available bibliography, higher chlorine content biphenyls tend to appear in the most industrialized areas. They might come from legacy pollution trapped in the sediment, given the prohibition of 1970, while the less chlorinated biphenyls are more volatile and tend to be found in remote areas and the open ocean, mainly coming from atmospheric transport (Hirai *et al.*, 2011; Mizukawa *et al.*, 2013; Antunes *et al.*, 2013). In Las Canteras beach they have just appeared two low chlorine content biphenyls (PCB 52 and PCB 77), in concentrations lower than 0.6ng/g pellet. Thus, at least in this urban beach, PCB entries are mainly due to legacy pollution that might be reaching the beach through the ravine “La Ballena” that flows into the Cicer area in Las Canteras beach. These results match the ones given by Hirai *et al.* (2011), where middle chlorinate congeners (penta- and hexa-) are the ones which usually predominate in urban coasts. If we compare PCB concentrations to other studies, results are more similar to rural beaches than to urban ones (Antunes *et al.*, 2013; Mizukawa *et al.*, 2013). These values, at the same time, are closer to the ones from southern Asia, Australia and southern Africa, places where PCBs were not used during their economic growth in 1980s, and very similar to the ones found in Portugal by Ogata *et al.* (2009). It could seem good news given its lower concentrations. However, taking into account the island’s location, it is possible that most of these pellets are being transported to open ocean (Hirai *et al.*, 2011), possibly being introduced into marine food webs.

Due to the hydrophobicity of these contaminants, it has been proven they are found in higher concentrations in pellets than in other materials (water or food samples), making these pellets a great source of information of the actual amounts of POPs in the environment. It has to be taken into account the great potential danger of pellets to be ingested by marine fauna due to its high content of POPs.

CONCLUSIONS

- Las Canteras beach's plastic pellets come from exogenous sources. Any manufacturing companies of plastic containers are found in the Canary Islands. Therefore, stranded pellets in the sand come from accidental spills of cargo ships and during their residence on the sea surface, POPs have been adsorbing to the pellets, being the main pollutants sources from exogenous origin, with the exception of UV filters, chlorpyrifos, PAHs and PCBs that are possibly related to tourism and the industrial activity of this area.
- The study of POPs in the Canary Islands contributes greatly to the degree of knowledge of the current global situation due to its location, influenced by Europe and Africa.
- More studies of POPs in microplastics are needed to understand the actual situation of current pollution in the oceans, and it is advisable to classify microplastics by color and material in order to increase the degree of information they can provide.
- In future studies, it is advisable to use another type of container for the storage of samples (e.g. paper or aluminum), thus avoiding possible cross-contamination by plastics.

Acronyms list

4-MBC: 3-(4-Methylbenzylidene) camphor
AE: Ethyl acetate
ATSDR: Agency for Toxic Substances and Disease Registry
BDEs: Brominated Diphenyl Ethers
CC: Canary Current
CHX: Cyclohexane
CNS: Central Nervous System
DDD: dichlorodiphenyldichloroethane
DDE: dichlorodiphenyldichloro-ethylene
DDT: dichlorodiphenyltrichloroethane
EHDP: 2-Ethylhexyldiphenyl phosphate
EHMC: 2-Ethylhexyl p-methoxycinnamate
EPA: Environmental Protection Agency of U.S.
ESIS: European chemical Substances Information System
EU: European Union
GC: Gas chromatograph
HBC: Hexachlorobenzene
HBCDD: Hexabromocyclododecane
HCBD: Hexachlorobutadiene
HCH: Hexachlorocyclohexane
IPCS: International Programme on Chemical Safety
IPW: International Pellet Watch
LOQ: Limits of Quantification
LPV: Low Production Volume
NE: North East
NIEHS: National Institute of Environmental Health Sciences
NP: Nonyphenols
OCPs: Organochlorine Pesticides

OPFR: Organophosphate Flame Retardants
PAH: Polycyclic Aromatic Hydrocarbons
PBDEs: Polybrominated Diphenyl Ethers
PCBs: Polychlorinated Biphenyles
PCDD: Polychlorinated dibenzo-*p*-dioxins
PCDF: Polychlorinated dibenzofurans
PE: Polyethylene
PFOS: Perfluorooctane Sulfonic acid
PFOS-F: Perfluorooctane Sulfonyl Fluoride
POPs: Persistent Organic Pollutants
PP: Polypropylene
PUU: Purged Ultimate Union
QC: Quality Control
RTL: Retention Time Locking
SE: South East
SERTOX: Clinical and Analytical Toxicology Service
SPF: Sun Protection Factor
SW: South West
TBEP: Tris (2-butoxyethyl) phosphate
TBP: Tributyl phosphate
TCEP: Tris (2-chloroethyl) phosphate
TDCP: Tris ((2-chloro-1-chloromethyl) ethyl) phosphate
TEHP: Tri (2-ethylhexyl) phosphate
TEP: Triethyl phosphate
TiBP: Triisobutyl phosphate
TPP or TPhP: Triphenyl phosphate
UK: United Kingdom
UNEP: United Nations Environment Programme
USA: United States of America
UV: Ultraviolet

ANNEX I, Pollutants detailed information

This Annex shows all POPs analyzed in this study, with additional information of their corresponding CAS Number, chemical name (in the case of PBDEs and PCBs) and molecular formula. It also includes the POPs classification included in the Stockholm Convention and their hazard statements in accordance with the classification of the hazardous substance or mixture, in agreement with the corresponding Annex III, Codification of hazard statements, codification and use of precautionary statements and examples of precautionary pictograms of the United Nations Environment Program (2007). The hazard statements description is found at the end of the Annex.

Polibrominated Diphenyl Ethers (PBDEs)				
	Chemical Name	CAS N°	Stockholm Convention	Molecular Formula
BDE 153	2,2',4,4',5,5'-hexabromodiphenyl ether	68631-49-2	Listed under Annex A with a specific exemption for use as articles containing these chemicals for recycling in accordance with the provision in Part IV of Annex A (decision SC-4/14)	C ₁₂ H ₄ Br ₆ O
BDE 154	2,2',4,4',5,6'-hexabromodiphenyl ether	207122-15-4		C ₁₂ H ₄ Br ₆ O
BDE 183	2,2',3,4,4',5',6'-heptabromodiphenyl ether	207122-16-5		C ₁₂ H ₃ Br ₇ O
BDE 28	2,4,4'-tribromodiphenyl ether	41318-75-6	Not regulated by Stockholm Convention. GHS Hazard Statements: H362, H373, H400, H410	C ₁₂ H ₇ Br ₃ O
BDE 47	2,2',4,4'-tetrabromodiphenyl ether	5436-43-1	Listed under Annex A with a specific exemption for use as articles containing these chemicals for recycling in accordance with the provision in Part V of Annex A (decision SC-4/18)	C ₁₂ H ₆ Br ₄ O
BDE 100	2,2',4,4',6-pentabromodiphenyl ether	189084-64-8		C ₁₂ H ₅ Br ₅ O
BDE 85	2,2',3,4,4'-pentabromodiphenyl ether	182346-21-0		C ₁₂ H ₉ BrO
BDE 99	2,2',4,4',5-pentabromodiphenyl ether	60348-60-9		C ₁₂ H ₅ Br ₅ O

UV Filters and Chlorpyrifos				
	Maximum authorised concentration by Regulation (EC) No 1223/2009 of the European Parliament and of the Council of 30 November 2009 on cosmetic products	CAS N°	GHS Hazard Statements by Laboratory Chemical Safety Summary (LCSS)	Molecular Formula
2-Ethylhexyl 4-(dimethylamino) benzoate (Padimate O)	8%	21245-02-3	H315, H319, H335	C ₁₇ H ₂₇ O ₂
2-Ethylhexyl p-methoxycinnamate (EHMC)	10%	5466-77-3	H315, H319, H335	C ₁₈ H ₂₆ O ₃
3-(4-Methylbenzylidene) camphor (Enzacamene, 4-MBC)	4%	36861-47-9	<u>H361</u>	C ₁₈ H ₂₂ O
3-Benzylidene camphor Homosalate (HMS)	2%	15087-24-8	H361	C ₁₇ H ₂₀ O
Homosalate (HMS)	10%	118-56-9	H315, H319, H335, H413	C ₁₆ H ₂₂ O ₃
Chlorpyrifos (CPF)	Pesticide, oficial maximum residue limit: 3mg/kg	291-88-2	H301, H312, H319, H330, H400, H410	C ₉ H ₁₁ Cl ₁₃ NO ₃ PS

Organochlorine Pesticides (OCPs)				
	Stockholm Convention	CAS N°	GHS Hazard Statements by Laboratory Chemical Safety Summary (LCSS)	Molecular Formula
DDT-p,p' (Chlorophenothane)	Listed under Annex B with acceptable purpose for disease vector control	50-29-3	H301, H311, H351, H372, H400, H410	C ₁₄ H ₉ Cl ₅
DDT-o,p'		789-02-6	H301, H311, H330, H351, H372, H373, H400, H410	C ₁₄ H ₉ Cl ₅
DDD-o,p' (Mitotane)		53-19-0	H351	C ₁₄ H ₁₀ Cl ₄
DDD-p,p' (Rhothane, Dilene)		72-54-8	H301, H312, H351, H400, H410	C ₁₄ H ₁₀ Cl ₄
DDE-o,p'		3424-82-6	H302, H351, H400, H410	C ₁₄ H ₈ Cl ₄
DDE-p,p'		72-55-9	H302, H311, H315, H331, H332, H400, H410	C ₁₄ H ₈ Cl ₄
Endrin		Annex A	72-20-8	H300, H311, H400, H410
Aldrin	Annex A	309-00-2	H300, H301, H310, H311, H351, H372, H400, H410	C ₁₂ H ₈ Cl ₆
Dieldrin	Annex A	60-57-1	H300, H301, H310, H330, H351, H372, H400, H410	C ₁₂ H ₈ Cl ₆ O
Endosulfan alfa /I	Listed under Annex A with specific exemptions (decision SC-5/3)	959-98-8	H301, H302, H400, H410	C ₉ H ₆ Cl ₆ O ₃ S
Endosulfan beta /II		33213-65-9	H301, H302, H400, H410	C ₆ H ₆ Cl ₆ O ₃ S
Endosulfan sulfate	Not listed	1031-07-8	H300, H400, H410	C ₉ H ₆ Cl ₆ O ₄ S
Heptachlor	Annex A	76-44-8	H300, H310, H351, H373, H400, H410	C ₁₀ H ₅ Cl ₇
Hexachlorobenzene (HCB)	Listed under Annex A and Annex C	118-74-1	H350, H372, H400, H410	C ₆ Cl ₆

Gamma-hexachlorocyclohexane (γ-HCH; Lindane)	Listed under Annex A with a specific exemption for use as a human health pharmaceutical for control of head lice and scabies as second line treatment (decision SC-4/15)	58-89-9	H301, H311, H312, H330, H351, H400, H410	C ₆ H ₆ Cl ₆
Alfa-hexachlorocyclohexane (α-HCH)	Listed under Annex A (decision SC-4/10)	319-84-6	H301, H311, H312, H330, H351, H400, H410	C ₆ H ₆ Cl ₆
Beta-hexachlorocyclohexane (β-HCH)	Listed under Annex A (decision SC-4/11)	319-85-7	H301, H311, H312, H330, H351, H400, H410	C ₆ H ₆ Cl ₆
Delta-hexachlorocyclohexane (δ-HCH)	Not listed	319-86-8	H301, H311, H312, H330, H351, H400, H410	C ₆ H ₆ Cl ₆
Methoxychlor	Not listed	72-43-5	H303, H361, H371, H373, H400, H410	C ₁₆ H ₁₅ Cl ₃ O ₂
Mirex	Annex A	2385-85-5	H301, H302, H311, H312, H351, H361, H362, H400, H410	C ₁₀ Cl ₁₂

Organophosphate Flame Retardants (OPFRs)			
	CAS N°	GHS Hazard Statements by Laboratory Chemical Safety Summary (LCSS)	Molecular Formula
2-Ethylhexyldiphenyl phosphate (EHDP)	1241-94-7	H400, H410, H411	C ₂₀ H ₂₇ O ₄ P
Tri (2-ethylhexyl) phosphate	78-42-2	H315, H319, H335	C ₂₄ H ₅₁ O ₄ P
Tributylphosphate (TBP)	126-73-8	H302, H315, H351, H331, H401, H411	C ₁₂ H ₂₇ O ₄ P or (C ₄ H ₉) ₃ PO ₄
Triethylphosphate (TEP)	78-40-0	H302, H319, H336, H361, H371	C ₆ H ₁₅ O ₄ P or (C ₂ H ₅) ₃ PO ₄
Triisobutylphosphate (TiBP)	126-71-6	H315, H317, H319, H412	C ₁₂ H ₂₇ O ₄ P
Triphenylphosphate (TPP)	115-86-6	H400, H410, H411	(C ₆ H ₅) ₃ PO ₄ or C ₁₈ H ₁₅ O ₄ P
Tris ((2-chloro-1-chloromethyl)ethyl)phosphate (TDCP)	13674-87-8	H351, H411	C ₉ H ₁₅ Cl ₆ O ₄ P
Tris (2-butoxyethyl) phosphate (TBEP)	78-51-3	H302, H312, H315, H319, H332, H335	C ₁₈ H ₃₉ O ₇ P
Tris (2-chloroethyl) phosphate (TCEP)	115-96-8	H302, H320, H351, H360, H370, H373, H401, H411	C ₆ H ₁₂ Cl ₃ O ₄ P
Tris (2-chloroisopropyl) phosphate	13674-84-5	H302, H336, H361, H371, H373, H402, H412	C ₉ H ₁₈ Cl ₃ O ₄ P

PAHs (Polycyclic Aromatic Hydrocarbons)			
	CAS N°	GHS Hazard Statements by Laboratory Chemical Safety Summary (LCSS)	Molecular Formula
Acenaphthalene	208-96-8	H302, H310, H315, H319, H330, H335, H372, H373, H400, H410	C ₁₂ H ₈
Acenaphthahene	83-32-9	H319, H400, H410, H373	C ₁₂ H ₁₀
Anthracene	120-12-7	H304, H315, H317, H319, H350, H361, H412	C ₁₄ H ₁₀
Benzo (a) anthracene	56-55-3	H341, H351, H400, H410	C ₁₈ H ₁₂
Benzo (a) pyrene	50-32-8	H340, H350, H360, H373, H400, H410, H317	C ₂₀ H ₁₂
Benzo (b) fluoranthene	205-99-2	H350, H400, H410,	C ₂₀ H ₁₂
Benzo (g,h,i) perylene	191-24-2	H400, H410, H413	C ₂₂ H ₁₂
Benzo (k) fluoranthene	207-08-9	H350, H400, H410	C ₂₀ H ₁₂
Chrysene	218-01-9	H341, H350, H400, H410	C ₁₈ H ₁₂
Dibenzo (a,h) anthracene	53-70-3	H350, H400, H410	C ₂₂ H ₁₄
Fluoranthene	206-44-0	H351, H400, H410	C ₁₆ H ₁₀
Fluorene	86-73-7	H315, H319, H335, H400, H410	C ₁₃ H ₁₀
Indeno (1,2,3-c,d) pyrene	193-39-5	H351, H400, H410	C ₂₂ H ₁₂
Naphthalene	91-20-3	H228, H302, H351, H400, H410	C ₁₀ H ₈
Phenanthrene	85-01-8	H302, H317, H400, H410	C ₁₄ H ₁₀
Pyrene	129-00-0	H315, H319, H335, H400, H410	C ₁₆ H ₁₀

Polychlorinated Biphenyles (PCBs)				
Stockholm Convention: Listed under Annex A with specific exemptions and under Annex C	Chemical Name	CAS N°	GHS Hazard Statements by Laboratory Chemical Safety Summary (LCSS)	Molecular Formula
PCB-28	2,4,4'-trichlorobiphenyl	7012-37-5	H373, H400, H410	C ₁₂ H ₇ Cl ₃
PCB-52	2,2',5,5'-tetrachlorobiphenyl	35693-99-3	H373, H400, H410	C ₁₂ H ₆ Cl ₄
PCB-101	2,2',4,5,5'-pentachlorobiphenyl	37680-73-2	H373, H400, H410	C ₁₂ H ₅ Cl ₅
PCB-138	2,2',3,4,4',5'-hexachlorobiphenyl	35065-28-2	H373, H400, H410	C ₁₂ H ₄ Cl ₆
PCB-153	2,2',3,3',4,4'-hexachlorobiphenyl	11096-82-5	H373, H400, H410	C ₁₂ H ₄ Cl ₆
PCB-180	2,2',3,4,4',5,5'-heptachlorobiphenyl	35065-29-3	H373, H400, H410	C ₁₂ H ₃ Cl ₇
PCB-105	2,3,3',4,4'-pentachlorobiphenyl	32598-14-4	H302, H373, H400, H410	C ₁₂ H ₅ Cl ₅
PCB-114	2,3,4,4',5-pentachlorobiphenyl	74472-37-0	H373, H400, H410	C ₁₂ H ₅ Cl ₅
PCB-118	2,3',4,4',5-pentachlorobiphenyl	31508-00-6	H373, H400, H410	C ₁₂ H ₅ Cl ₅
PCB-123	2,3',4,4',5'-pentachlorobiphenyl	65510-44-3	H373, H400, H410	C ₁₂ H ₅ Cl ₅
PCB-126	3,3',4,4',5-pentachlorobiphenyl	57465-28-8	H373, H400, H410	C ₁₂ H ₅ Cl ₅
PCB-156	2,3,3',4,4',5-hexachlorobiphenyl	38380-08-4	H373, H400, H410	C ₁₂ H ₄ Cl ₆
PCB-157	2,3,3',4,4',5'-hexachlorobiphenyl	69782-90-7	H373, H400, H410	C ₁₂ H ₄ Cl ₆
PCB-167	2,3',4,4',5,5'-hexachlorobiphenyl	52663-72-6	H373, H400, H410	C ₁₂ H ₄ Cl ₆
PCB-189	2,3,3',4,4',5,5'-heptachlorobiphenyl	39635-31-9	H373, H400, H410	C ₁₂ H ₃ Cl ₇
PCB-77	3,3',4,4'-tetrachlorobiphenyl	32598-13-3	H373, H400, H410	C ₁₂ H ₆ Cl ₄
PCB-81	3,4,4',5-tetrachlorobiphenyl	70362-50-4	H373, H400, H410	C ₁₂ H ₆ Cl ₄

Description of the hazard statements based on the regulation (EC) No 1272/2008 of the European Parliament and of the council:

- H228** – Flammable solid.
- H300** – Fatal if swallowed.
- H301** – Toxic if swallowed.
- H302** – Harmful if swallowed.
- H304** – May be fatal if swallowed and enters airways.
- H310** – Fatal in contact with skin.
- H311** – Toxic in contact with skin.
- H312** – Harmful in contact with skin.
- H314** – Causes severe skin burns and eye damage.
- H315** – Causes skin irritation.
- H317** – May cause an allergic skin reaction.
- H318** – Causes serious eye damage.
- H319** – Causes serious eye irritation.
- H330** – Fatal if inhaled.
- H331** – Toxic if inhaled.
- H332** – Harmful if inhaled.
- H334** – May cause allergy or asthma symptoms or breathing difficulties if inhaled.
- H335** – May cause respiratory irritation.
- H336** – May cause drowsiness or dizziness.
- H340** – May cause genetic defects *exposure cause the hazard*.
- H341** – Suspected of causing genetic defects.
- H350** – May cause cancer.
- H351** – Suspected of causing cancer.
- H360** – May damage fertility or the unborn child.
- H361** – Suspected of damaging fertility or the unborn child.
- H362** – May cause harm to breast-fed children.
- H370** – Causes damage to organs.
- H371** – May cause damage to organs.
- H372** – Causes damage to organs through prolonged or repeated exposure *exposure cause the hazard*.
- H373** – May cause damage to organs through prolonged or repeated exposure *exposure cause the hazard*.
- H400** – Very toxic to aquatic life.
- H410** – Very toxic to aquatic life with long lasting effects.
- H411** – Toxic to aquatic life with long lasting effects.
- H412** – Harmful to aquatic life with long lasting effects.
- H413** – May cause long lasting harmful effects to aquatic life.

ANNEX II, ANALITICAL PROTOCOL PROCEDURE

First day

Weigh 1g of pellets in a glass tube. Balance (A&D brand), EK-i compact balance EK-610i (model).

Add 5000 μ L (5mL) of EA:CHX (Ethyl acetate:ciclohexane) (50:50) in each tube.

Magnetic vortex during 30s. Heidolph (brand), Reax top (model).

Sonicate 30 minutes. VWR (brand), Ultrasonic Cleaner (model).

Vortex 30s

Orbital shaker 24h

Second day

Introduce previous day samples for 30s in the vortex.

Transfer pipetting (1ml filter tips) the 5000 μ L to a 15ml falco.

Centrifugate each sample during 10min at 4200rpm. Eppendorf (brand), Centrifuge 5804R (model).

Filter the supernatant with 0.22 μ filters to a previously labelled test tube.

Cover the test tube and freeze it.

We use the pellets and repeat the same process:

Add 5000 μ L of EA:CHX (50:50)

Vortex 30s

Sonicate 30min

Vortex 30s

Orbital shaker 24h

Third day

Introduce samples from the orbital shaker in the vortex for 30s.

Transfer pipetting (1ml filter tips) the 5000 μ L to the 15ml falco.

Centrifugate each sample for 10min at 4200rpm.

Filter the supernatant with 0.22 μ filters to day 2 test tube.

Cover and freeze.

We use the pellets and repeat the same process:

Add 5000 μ L of EA:CHX (50:50)

Vortex 30s

Sonicate 30min

Vortex 30s

Orbital shaker 24h

Fourth day

Introduce samples from the orbital shaker in the vortex for 30s.

Transfer pipetting (1ml filter tips) the 5000 μ L to the 15ml falco.

Centrifugate each sample for 10min at 4200rpm.

Filter the supernatant with 0.22 μ filters to day 3 test tube.

Transfer to a 15mL Coper.

Evaporate under N₂ current until dryness (until 1.5mL remain) with a Sample concentrator. Techne (brand), Dri-block DB3 (model).

Resuspend in 100 μ L with CHX and transfer to GSMS chromatography vials.

REFERENCES

Agency for Toxic Substances and Disease Registry (ATSDR), 2004. Toxicological profile for Polybrominated Biphenyls.

URL: <https://www.atsdr.cdc.gov/toxprofiles/tp68.pdf>

Antunes, J. C., Frias, J. G. L., Micaelo, A. C., and Sobral, P., 2013. Resin pellets from beaches of the Portuguese coast and adsorbed persistent organic pollutants. *Estuarine, Coastal and Shelf Science*, 130: 62-69.

Ashford, R.D., 1994. *Ashford's dictionary of industrial chemicals*. London: Wavelength Publications. Date of consultation: 02/12/2017.

Bakir, A., Rowland, S. J., & Thompson, R. C., 2012. Competitive sorption of persistent organic pollutants onto microplastics in the marine environment. *Marine Pollution Bulletin*, 64 (12): 2782-2789.

Baztan, J., Carrasco, A., Chouinard, O., Cleaud, M., Gabaldon, J. E., Huck, T., and Vanderlinden, J. P., 2014. Protected areas in the Atlantic facing the hazards of microplastic pollution: first diagnosis of three islands in the Canary Current. *Marine pollution bulletin*, 80 (1): 302-311.

Blount, E. 2002. Informe sobre el Estado del Convenio de Estocolmo sobre los Contaminantes Orgánicos Persistentes. URL: <http://archivo-es.greenpeace.org/espana/Global/espana/report/other/informe-sobre-el-estado-del-co.pdf>

Bouwmeester, H., Hollman, P. C., & Peters, R. J., 2015. Potential health impact of environmentally released micro-and nanoplastics in the human food production chain: experiences from nanotoxicology. *Environmental science & technology*, 49 (15): 8932-8947.

Browne, M. A., Crump, P., Niven, S. J., Teuten, E., Tonkin, A., Galloway, T., & Thompson, R., 2011. Accumulation of microplastic on shorelines worldwide: sources and sinks. *Environmental science & technology*. 45 (21): 9175-9179.

Camacho, M., Luzardo, O. P., Boada, L. D., Jurado, L. F. L., Medina, M., Zumbado, M., & Orós, J., 2013. Potential adverse health effects of persistent organic pollutants on sea turtles: evidences from a cross-sectional study on Cape Verde loggerhead sea turtles. *Science of the total environment*, 458: 283-289.

Carpenter, E. J., Anderson, S. J., Harvey, G. R., Miklas, H. P., & Peck, B. B., 1972. Polystyrene spherules in coastal waters. *Science*, 178 (4062): 749-750.

Carpenter, E. J., & Smith, K. L., 1972. Plastics on the Sargasso Sea surface. *Science*, 175 (4027): 1240-1241.

Chait, J., 2017. What are Organochlorine Pesticides. *The balance Journal*. URL: <https://www.thebalance.com/what-are-organochlorine-pesticides-2538275>

Chiu, T.C., Yen, J.H., Liu, T.L., Wang, Y.S., 2004. Anaerobic degradation of the organochlorine pesticides DDT and heptachlor in river sediment of Taiwan. *Bull. Environ. Contam. Toxicol.* 72: 821–828.

Endo, S., Takizawa, R., Okuda, K., Takada, H., Chiba, K., Kanehiro, H., and Date, T., 2005. Concentration of polychlorinated biphenyls (PCBs) in beached resin pellets: variability among individual particles and regional differences. *Marine Pollution Bulletin*, 50 (10): 1103-1114.

European Communities, 2001. Ambient air pollution by Polycyclic Aromatic Hydrocarbons (PAH), position paper. ISBN 92-894-2057-X. URL: http://ec.europa.eu/environment/air/pdf/pp_pah.pdf

Goldberg, E.D., 1975. The mussel watch: a first step in global marine monitoring. *Marine Pollution Bulletin*. 6, 111.

Henriquez-Hernandez, L.A., Carreton, E., Camacho, M., Montoya-Alonso, J.A., Boada, L.D., Valeron, P.F., Cordon, Y.F., Almeida-Gonzalez, M., Zumbado, M., Luzardo, O.P., 2016. Influence of parasitism in dogs on their serum levels of persistent organochlorine compounds and polycyclic aromatic hydrocarbons. *Sci. Total Environ.* 562: 128–135

Hernández-Borges, J., Cabrera, J. C., Rodríguez-Delgado, M. Á., Hernández-Suárez, E. M., & Saúco, V. G., 2009. Analysis of pesticide residues in bananas harvested in the Canary Islands (Spain). *Food Chemistry*, 113 (1): 313-319.

Herrera, A., Ariño, A. A., Conchello, M. P., Lazaro, R., Bayarri, S., & Perez, C., 1994. Organochlorine pesticide residues in Spanish meat products and meat of different species. *Journal of food protection*, 57 (5): 441-444.

Herrera, A., Asensio, M., Martínez, I., Santana, A., Packard, T., and Gómez, M., 2017. Microplastic and tar pollution on three Canary Islands beaches: An annual study. *Marine Pollution Bulletin*.

Heskett, M., Takada, H., Yamashita, R., Yuyama, M., Ito, M., Geok, Y. B., and Powell, T., 2012. Measurement of persistent organic pollutants (POPs) in plastic resin pellets from remote islands: Toward establishment of background concentrations for International Pellet Watch. *Marine Pollution Bulletin*, 64 (2): 445-448.

Hirai, H., Takada, H., Ogata, Y., Yamashita, R., Mizukawa, K., Saha, M., and Zettler, E. R., 2011. Organic micropollutants in marine plastics debris from the open ocean and remote and urban beaches. *Marine Pollution Bulletin*, 62 (8): 1683-1692.

Kale, S.P., Murthy, N.B.K., Raghu, K., Sherkhane, P.D., Carvalho, F.P., 1999. Studies on degradation of C-14-DDT in the marine environment. *Chemosphere* 39: 959– 968.

Karapanagioti, H. K., Ogata, Y., & Takada, H., 2010. Eroded plastic pellets as monitoring tools for polycyclic aromatic hydrocarbons (PAH): laboratory and field studies. *Global Nest Journal*, 12 (3): 327-334.

Killeen, S., 2008. UV-Filters in Cosmetics—Prioritisation for Environmental Assessment. Environment Agency Handbook. URL: https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/291007/scho1008bpay-e-e.pdf

Kim, S., Thiessen, P.A., Bolton, E.E., Chen, J., Fu, G., Gindulyte, A., Han, L., He, J., He, S., Shoemaker, B.A., Wang, J., Yu, B., Zhang, J. and Bryant, S.H., 2016. PubChem Substance and Compound databases. *Nucleic Acids Res.* 2016 Jan 4; 44 (D1): D1202-13. URL: <https://pubchem.ncbi.nlm.nih.gov/>

Lima, A. L. C., Farrington, J. W., & Reddy, C. M., 2005. Combustion-derived polycyclic aromatic hydrocarbons in the environment—a review. *Environmental Forensics*, 6 (2): 109-131.

Mato, Y., Isobe, T., Takada, H., Kanehiro, H., Ohtake, C., and Kaminuma, T., 2001. Plastic resin pellets as a transport medium for toxic chemicals in the marine environment. *Environmental science & technology*, 35 (2): 318-324.

Meijer, S. N., Ockenden, W. A., Sweetman, A., Breivik, K., Grimalt, J. O., & Jones, K. C., 2003. Global distribution and budget of PCBs and HCB in background surface soils: implications for sources and environmental processes. *Environmental Science & Technology*, 37 (4): 667-672.

Mizukawa, K., Takada, H., Ito, M., Geok, Y. B., Hosoda, J., Yamashita, R., ... & Antunes, J. C., 2013. Monitoring of a wide range of organic micropollutants on the Portuguese coast using plastic resin pellets. *Marine pollution bulletin*, 70 (1): 296-302.

National Institute of Environmental Health Sciences (NIEHS), 2017. Flame Retardants. URL: https://www.niehs.nih.gov/health/topics/agents/flame_retardants/index.cfm
Update Date: 08/28/2017

Ogata, Y., Takada, H., Mizukawa, K., Hirai, H., Iwasa, S., Endo, S., and Murakami, M., 2009. International pellet watch: global monitoring of persistent organic pollutants (POPs) in coastal waters. 1. Initial phase data on PCBs, DDTs, and HCHs. *Marine pollution bulletin*, 58 (10): 1437-1446.

Port Authority of Las Palmas de Gran Canaria, 2017. Tráfico de buques, Histórico de Escalas 2017. Consulting date: 17/12/2017. URL: <http://www.palmasport.es/web/guest/historico-de-escalas>

Rochman, C. M., Hoh, E., Hentschel, B. T., & Kaye, S., 2013. Long-term field measurement of sorption of organic contaminants to five types of plastic pellets: implications for plastic marine debris. *Environmental Science & Technology*, 47 (3): 1646-1654.

Rochman, C. M., Lewison, R. L., Eriksen, M., Allen, H., Cook, A. M., & Teh, S. J., 2014. Polybrominated diphenyl ethers (PBDEs) in fish tissue may be an indicator of plastic contamination in marine habitats. *Science of the Total Environment*, 476: 622-633.

Rodríguez, A. S., Sanz, M. R., & Rodríguez, J. B., 2015. Occurrence of eight UV filters in beaches of Gran Canaria (Canary Islands). An approach to environmental risk assessment. *Chemosphere*, 131: 85-90.

Ryan, P. G., Bouwman, H., Moloney, C. L., Yuyama, M., & Takada, H., 2012. Long-term decreases in persistent organic pollutants in South African coastal waters detected from beached polyethylene pellets. *Marine pollution bulletin*, 64 (12): 2756-2760.

Sanz, M.R., Gabet, V.M., and Betancort, J., 2016. Priority pollutants in microplastics from beaches in Gran Canaria Island. DOI: 10.13140/RG.2.1.2584.7920.

Shiber, J. G., 1982. Plastic pellets on Spain's 'Costa del Sol' beaches. *Marine Pollution Bulletin*, 13 (12): 409-412.

Song, Y. K., Hong, S. H., Jang, M., Han, G. M., Jung, S. W., & Shim, W. J., 2017. Combined Effects of UV Exposure Duration and Mechanical Abrasion on Microplastic Fragmentation by Polymer Type. *Environmental Science & Technology*, 51 (8): 4368-4376.

Stockholm Convention Clearing House Web Site, 2008. All POPs listed in the Stockholm Convention. Consulting date: 05/12/2017 URL: <http://chm.pops.int/TheConvention/ThePOPs/AllPOPs/tabid/2509/Default.aspx>

Stockholm Convention on Persistent Organic Pollutants. Convention Text, as amended in 2009, 2009. United Nations Environment Programme, Geneva. URL: http://www.wipo.int/edocs/lexdocs/treaties/en/unep-pop/trt_unep_pop_2.pdf

Takada, H., 2006. Call for pellets! International Pellet Watch Global Monitoring of POPs using beached plastic resin pellets. *Marine Pollution Bulletin*, 52 (2006): 1547–1548.

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. *Marine pollution bulletin*, 69 (1): 219-222.

Teuten, E. L., Saquing, J. M., Knappe, D. R., Barlaz, M. A., Jonsson, S., Björn, A., and Ochi, D., 2009. Transport and release of chemicals from plastics to the environment and to wildlife. *Philosophical Transactions of the Royal Society of London B: Biological Sciences*, 364 (1526): 2027-2045.

Thompson, R.C., Swan, S.H., Moore, C.J., vom Saal, F.S., 2009b. Our plastic age. *Philosophical Transactions of the Royal Society B: Biological Sciences*. 364: 1973–1976.

Tourism Board of Las Palmas de Gran Canaria, 2017. Situación del sector turístico octubre 2017. Consulting Date: 07/12/2017. URL: http://www.grancanaria.com/turismo/fileadmin/PDF/informes/ICT_oct_17.pdf

United Nations Environment Programme, 2007. Annex III, Codification of hazard statements, codification and use of precautionary statements and examples of precautionary pictograms. URL:

http://www.unece.org/fileadmin/DAM/trans/danger/publi/ghs/ghs_rev02/English/07e_a_nnex3.pdf

U.S. Environmental Protection Agency (EPA), 2009. Polybrominated Diphenyl Ethers (PBDEs) Action Plan. URL: https://www.epa.gov/sites/production/files/2015-09/documents/pbdes_ap_2009_1230_final.pdf

U.S. Environmental Protection Agency (EPA), 2014. Technical Fact Sheet- Polybrominated Diphenyl Ethers (PBDEs) and Polybrominated Biphenyls (PBBs). URL: https://www.epa.gov/sites/production/files/2014-03/documents/ffrofactsheet_contaminant_perchlorate_january2014_final_0.pdf

Watts, A. J., Lewis, C., Goodhead, R. M., Beckett, S. J., Moger, J., Tyler, C. R., & Galloway, T. S., 2014. Uptake and retention of microplastics by the shore crab *Carcinus maenas*. *Environmental science & technology*, 48 (15): 8823-8830.

World Health Organization (WHO), 1979. DDT and its Derivatives, Environmental Health Criteria 9. International Programme on Chemical Safety. ISBN 92 4 154069 9. URL: <http://www.inchem.org/documents/ehc/ehc/ehc009.htm>

Wright, S. L., Thompson, R. C., & Galloway, T. S., 2013. The physical impacts of microplastics on marine organisms: a review. *Environmental Pollution*, 178: 483-492.

Descripción detallada de las actividades desarrolladas durante la realización del TFT:

El primer paso de todos fue ir a recoger los pellets a la playa de Las Canteras, siempre antes de que pasaran los de la limpieza a las 7 a.m., posteriormente se llevaban las muestras al laboratorio donde se dejaban secar y se separaban los pellets del resto del material recogido en la malla. Se ponían en bolsas de 1g y se llevaron a SERTOXX, situado en las instalaciones de la Facultad de Medicina de Las Palmas. Junto con el equipo de María Camacho se procedió al análisis de contaminantes, tardando 4 días para la extracción de los POPs. Por último, las muestras eran analizadas en el cromatógrafo de gases, obteniéndose el conjunto de datos con el que se redactó el TFM.

Formación recibida (cursos, programas informáticos, etc.):

Para la recogida de muestras fue necesaria una reunión con mi tutora, Alicia Herrera, la cual me explicó todo el procedimiento y en lo que consistía mi TFM. En la empresa SERTOXX aprendí el protocolo de análisis de contaminantes en microplásticos y tuve la oportunidad de practicar con ellos.

Nivel de integración e implicación dentro del departamento y relaciones con el personal:

Desde el primer día el trato en el departamento fue impecable, todos los compañeros me ayudaban día a día ante cualquier duda. Además, a parte del TFM también estuve colaborando en el análisis de microplásticos y fibras en el contenido estomacal de caballas, aprendiendo y realizando el procedimiento necesario para la visualización y recuento de los plásticos. Debido a que el análisis de los datos de mi TFM se realizaba en una empresa externa en la cual obtenía ya directamente los resultados, no tuve que ir al departamento una vez que los pellets eran separados y listos para transportarlos a SERTOXX.

Aspectos positivos y negativos más significativos relacionados con el desarrollo del TFT:

Los aspectos positivos son:

- Los conocimientos aprendidos para el análisis de contaminantes en microplásticos, así como la importancia y relevancia de los mismos. Son unas muestras muy fáciles de recoger, además de que limpias la playa, y obtienes unos datos muy valiosos y útiles con los que puedes relacionar la contaminación que realmente existe en el océano abierto, un tema muy poco estudiado a día de hoy.
- Al realizarse en inglés, hay muchas más oportunidades de poder presentar el TFM en simposios y congresos.

Estoy muy contenta con los resultados de mi TFM puesto que es el primer estudio desarrollado en la playa de Las Canteras, una playa que recibe miles de turistas al año y la cual es importante de cuidar y seguir manteniendo.

Todas las capacidades y competencias que he aprendido y desarrollado sobre los microplásticos, un tema que actualmente se encuentra en pleno auge dada la preocupación medioambiental que supone, tanto el plástico en sí como los POPs asociados.

Los aspectos negativos son:

- No haber podido realizar el estudio completo en todas las islas Canarias, o al menos 3 de ellas.
- Al no disponer de coche, no tuve la oportunidad de recoger pellets en más playas de la Isla y así poder comparar la distribución espacial de los mismos.
- Finalmente no se pudieron analizar los 50g de pellets debido al elevado coste que esto conllevaba.

Valoración personal del aprendizaje conseguido a lo largo del TFT.

Estoy muy contenta de haber aprendido tanto. Por un lado, cómo analizar los POPs en microplásticos y por otro, todo lo que he aprendido leyendo artículos de otras zonas y de contaminantes encontrados en la vida diaria, como alimentos, pinturas, muebles... No me imaginaba que los POPs se encontraran en tantas cantidades y distribuidos por absolutamente todo el planeta, ni los problemas que éstos suponen para la vida animal. Ahora me encuentro mucho más concienciada con el tema, el cual ya me gustaba antes de empezar el TFM, pero es que ahora parece que no puedo pensar en otra cosa en todo el día. Las cosas deben cambiar, no podemos seguir tan desinformados de la situación actual por la que estamos pasando y los innumerables problemas que los contaminantes están provocando en nuestra salud.