UNIVERSITÀ DI SIENA 1240

Dipartimento di Scienze fisiche, della Terra e dell'ambiente

Dottorato in Scienze e tecnologie ambientali, geologiche e polari

33° Ciclo

Coordinatore: Prof. Simone Bastianoni

Characterization and abundance of macroplastics and microplastics in biotic and abiotic matrices in Concepción Bay, Chile

Settore scientifico disciplinare: *CHIM/12*

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Seriale Certificato: 782418713957579617698452943345655248 02
Valido dal 28/12/2020 al 28/12/2023
ArubaPEC S.p.A. NG CA 3

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Anno accademico di conseguimento del titolo di Dottore di ricerca

2020/21

Università degli Studi di Siena

Dottorato in Scienze e tecnologie ambientali, geologiche e polari
33° Ciclo

Data dell'esame finale

11 gennaio 2021

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Abstract

In the last decade, increasing concern has been raised to protect the marine environment from plastic pollution. Plastic has the potential to break down into microscope and nanoscope particles (secondary microplastics). Among them, microplastics (MPs) (also known as emergent pollutants=EC) are fragments of grain size lower than 5 mm.

The characteristics of plastics such as colour, heat resistance, etc., change thanks to the adhesion of chemical substances, called additives. In some cases, the additive ingredients constitute up to 50% of the proportion of the plastic product. Phthalate esters, bisphenol A (BPA), brominated flame retardants (BFRs) are among many other plastic additives known as toxic compounds to organisms when released to the environment. Also, because of their properties, plastics sorbed a complex mixture of chemical contaminants present in the surrounding environment.

It is estimated that of the total annual plastic consumption in Chile, only 8.5% is recycled. However, this includes both post-industrial waste and household solid waste. If only the recycling of household plastic waste is measured, the recycling percentage is only 1.4% of the total plastic consumed each year in Chile.

This study evaluated the state of contamination by plastics (micro and macroplastics) on the coasts of the province of Concepción, Chile, specifically in Coliumo Bay, Concepción Bay and on the adjacent beach at the mouth of the Biobío River. The main results of this study were to conduct the first information of POPs sorbed in macroplastics collected on beaches of coastal areas in Chile and characterization and abundance of microplastics collected in the sand and fish.

Identification/characterization of polymer types in plastics was done using Fourier-transform infrared (FT-IR) spectroscopy and an optical microscope with an integrated camera. This is essential because it allows an assumption on the source of the plastic pollutants and governs its origin from the break down of macro, larger or extra-large plastic components or nearby recreational and industrial activities. In the coast of central Chile, fragment and fibres account for 100% of the collected MP particles, indicating the presence of secondary MPs in Concepcion Bay and the most frequent plastics identified were polystyrene foam beads (46% in sand) and Polyethylene (PE) (75% in fish). Black fragments were the most abundant microplastics both in the biotic and abiotic samples of Concepción Bay. The abundance of microplastics in the sand was 0.035 ± 0.04 items/g and 1 item/individual in fish (*Trachurus murphyi* (Chilean jack mackerel) and *Merluccius gayi* (Hake)). Regarding macroplastics, the average abundance was 2 items/m^2 less than in other studies. The highest abundance of macroplastic types were the fragments and the most frequent plastics identified were polypropylene (PP) (38%), mostly white. Also, to determine the chemical load, such as persistent organic pollutants (POPs) found in plastic waste, they were analysed using ultrasonic extraction and gas chromatography–mass spectrometry (GC-MS) for POPs determination. Screened compounds were PBDEs (n = 10), PCBs (n = 7), and OCPs (n = 13). High concentrations of PBDEs were found ranging from 2.1 to 1300 ng/g in the spring of 2017 and 392 to 3177 ng/g in the summer of 2018. Σ_7PCBs ranged from 0.9 to 93 ng/g during the spring of 2017 and 0.3 to 4.5 ng/g for the summer of 2018. The concentrations of OCPs (DDX and HCHs) were low and were only detected in the summer of 2018.

The plastics found in this study are commonly used in commercial, fishing, and household activities. These findings reinforce the need to improve effective sustainable management actions of solid waste treatment and disposal in the Coastal cities of Chile, also taking into account the chemical burden associated with plastic waste.

ACKNOWLEDGMENT

This research was supported by FONDECYT grant No.1161673 (PI: Ph.D. Karla Pozo) and the RECETOX Research Infrastructure (LM2015051 and CZ.02.1.01/0.0/0.0/16_013/0001761) at Masaryk University.

I thank CIPA (Centro de Investigación Polímeros Avanzados) (CONICYT Regional, GORE BIO BIO, R17A10003), and Ph.D. Dariela Nuñez.

I thank CMA (Centro de microscopia avanzada) Universidad de Concepción in Chile and Joanna Tereszczuk for teaching me the basics of using FT-IR microscope.

I thank INFOP (Instituto de Fomento Pesquero) for the fish samples.

I thank Universidad Católica de la Santísima Concepción, Facultad de Ciencias and Universidad San Sebastian, Facultad de Ingeniería y Tecnología of Chile.

I thank the logistic support of Mariett Torres, Williams Urbina and Luciano Vera.

I would like to thank my mentor, Ph.D. Karla Pozo for her expert advice and encouragement throughout my research project and study and for allowing me to work with her.

I also would like to thank my Supervisor Prof. Maria Cristina Fossi for accepting to be my tutor and for giving me the opportunity to work with her. I also thank the support of Ph.D. Matteo Baini.

Finally, I would like to give special thanks to my husband, my family, and friends for their encouragement during the study.

List of Abbreviation

ABS	Acrylonitrile butadiene styrene
ASIPLA	According to the Chilean plastic industry
ATSDR	Agency for toxic substances and disease registry
BCN	Biblioteca del Congreso Nacional de Chile
BFRs	Brominated flame retardants
BPA	Bisphenol A
CEG	Criteria Expert Group
CCI	Clean-coast index
CIPA	Centro de Investigación Polímeros Avanzados
CMA	Centro de Microscopía Avanzada
CONA	Comité oceanográfico nacional - Chile
DCM	Dichloromethane
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
DDX	Sumatoria DDTs, DDEs, and DDDs
deca-BDE	Decabromodiphenyl ether
EBFRIP	The European Brominated Flame Retardant Panel
EFSA	European Food Safety Authority
US EPA	United States Environmental Protection Agency
EPS	Expanded polystyrene foams
EU	European Union
FT-IR	Fourier-transform infrared
G7	Group of Seven
GC-MS	Gas chromatograph-mass spectrometry
HBCD	Hexabromocyclododecane
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexane
IARC	The Agency for Research on Cancer
IDL	Instrumental detection limits
IFCS	Intergovernmental Forum on Chemical Safety
IFOP	Institute of Fisheries Promotion
INC	Intergovernmental negotiating committee
INE	Instituto Nacional de Estadísticas
IPCS	International Program on Chemical Safety
IPW	International Pellet Watch
LOQ	Limits of quantification
MP	Microplastics
MSFD	Marine Strategy Framework Directive
OCPs	Organochlorine pesticides
octa-BDE	Octabromodiphenyl ethers
PAEs	phthalic acid esters
PAHs	Polycyclic aromatic hydrocarbons
PBBs	Polybrominated biphenyls

PBDEs	Polybrominated diphenyl ethers
PCBs	Polychlorinated biphenyls
PD	Plastic debris
PE	Polyethylene
PES	Polyester
PET	Polyethylene terephthalate
penta-BDE	Pentabromodiphenyl ethers
PFASs	Perfluoroalkylated substances
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonate
POPs	Persistent organic pollutants
POPRC	Persistent Organic Pollutants Review Committee
PP	Polypropylene
PS	Polystyrene
PVA	Poly(vinyl alcohol)
PVC	Polyvinyl chloride
rpm	Revolution per minute
SC	Stockholm Convention
SPLACH	Scientific Alliance of Plastic Pollution of Chile
SUBPESCA	Subsecretaría de Pesca y Acuicultura
TBBPA	Tetrabromobisphenol A
TDPA™	Totally Degradable Plastic Additive
UNEP	The United Nations Environment Programme
XPS	Extruded polystyrene foams

Table of Contents

List of Figures

List of tables

Chapter 1. Introduction

1.1 Microplastics

1.1.1 What are microplastics?

Plastics are synthetic organic polymers, which are derived from the polymerisation of monomers extracted from oil or gas (Derraik, 2002; Ríos et al., 2007; Thompson et al., 2009; Cole et al., 2011). These attributes have led to the extensive use of plastics in near inexhaustible applications (Andrady, 2011) ranging from applications for domestic, industrial, and medicinal use, to a series of attributes such as lightweight, durable, inert and corrosion-resistant plastics (PlasticsEurope, 2010). Since mass production began in the 1940s, the amount of plastic being manufactured has rapidly increased, with 230 million tonnes of plastic being produced globally in 2009 (PlasticsEurope, 2010), accounting for 8% of the global oil production (Thompson et al., 2009, Cole et al., 2011).

Whilst the societal benefits of plastic are far-reaching (Andrady and Neal, 2009), this valuable commodity has been the subject of increasing environmental concern (Cole et al., 2011). Primarily, the durability of plastic that makes it such an attractive material to use also makes it highly resistant to degradation, thus disposing of plastic waste is problematic (Barnes et al., 2009; Sivan, 2011). For the massive increase of single-use plastics (e.g. plastic tableware), the proportion of plastic contributing to municipal waste constitutes 10% of waste generated worldwide (World Bank, 2012). While some plastic waste is recycled, most of it ends up in a landfill where it may take centuries for this material to breakdown and decompose (Barnes et al., 2009; Moore, 2008).

Although macroplastic debris has been the focus of environmental concern for some time, it is only since the turn of the century that tiny plastic fragments, fibres, and granules, collectively known as ‘‘microplastics’’ have been considered as a pollutant on their own (Ryan et al., 2009; Thompson et al., 2004). Andrady (2011) has suggested adding the term ‘‘mesoplastics’’ to the scientific nomenclature, to differentiate between small plastics visible to the human eye, and those only discernible with the use of a microscope.

Therefore, in this study sizes of ≤0.5-5.0 mm are considered as microplastics and sizes 5.01-25 mm as mesoplastics (Fossi et al., 2017), the larger plastics are called macroplastics.

1.1.2 Primary microplastics

Plastics that are manufactured to be of a microscopic size are defined as primary microplastics. These plastics are typically used in facial-cleansers, cosmetic microbeads used in cosmetics and personal care products, industrial scrubbers used for abrasive blast cleaning, microfibres used in textiles, and virgin resin pellets used in plastic manufacturing processes. Under the broader size definitions of microplastic, virgin plastic production pellets (typically 2–5 mm in diameter).

Microplastic ‘‘scrubbers’’, used in exfoliating hand cleansers and facial scrubs, have replaced traditionally used natural ingredients, including ground almonds, oatmeal, and pumice (Derraik, 2002; Fendall and Sewell, 2009). Since the patenting of microplastic scrubbers within cosmetics in the 1980s, the use of exfoliating cleansers containing plastics has risen dramatically (Fendall and Sewell, 2009; Zitko and Hanlon, 1991). Typically marketed as ‘‘micro-beads’’ or ‘‘micro-exfoliators’’, these plastics can vary in shape, size and composition depending upon the product (Fendall and Sewell, 2009).

Primary microplastics have also been produced for use in air blasting technology (Derraik, 2002; Gregory, 1996). This process involves blasting acrylic, melamine or polyester microplastic scrubbers at machinery, engines and boat hulls to remove rust and paint (Browne et al., 2007; Derraik, 2002; Gregory, 1996). As these scrubbers are used repeatedly until they diminish in size and their cutting power is lost, they will often become contaminated with heavy metals (e.g. Cadmium, Chromium, Lead) (Derraik, 2002; Gregory, 1996).

1.1.3 Secondary microplastics

Secondary microplastics describe tiny plastic fragments derived from the breakdown of larger plastic debris, on both land and sea (Ryan et al., 2009; Thompson et al., 2004; Cole et al., 2011). Over time, the culmination of physical, biological and chemical processes can reduce the structural integrity of plastic debris, resulting in fragmentation (Browne et al., 2007).

Exposure to sunlight for long periods can result in the photodegradation of plastics; ultraviolet (UV) radiation in sunlight causes oxidation of the polymer matrix, leading to bond cleavage (Andrady, 2011; Barnes et al., 2009; Browne et al., 2007; Moore, 2008; Ríos et al., 2007). In the marine environment, photo-oxidation may be minimal due to the cold and haline conditions. However, plastic debris on beaches has high oxygen availability and direct exposure to sunlight, the wind will degrade rapidly, eventually turning brittle, forming cracks and ‘‘yellowing’’ (Andrady, 2011; Barnes et al., 2009; Moore, 2008; Cole et al., 2011). With a loss of structural integrity, these plastics are increasingly susceptible to fragmentation resulting from abrasion, wave-action, and turbulence (Barnes et al., 2009; Browne et al., 2007). This process is ongoing, with fragments becoming smaller over time until they become microplastic in size (Fendall and Sewell, 2009; Ríos et al., 2007; Ryan et al., 2009). It is considered that microplastics might further degrade to be nanoplastic in size.

The development of biodegradable plastics is often seen as a viable replacement for traditional plastics. However, they can also be a source of microplastics (Thompson et al., 2004). Biodegradable plastics are typically composites of synthetic polymers and starch, vegetable oils or specialist chemicals (e.g. TDPA™) designed to accelerate degradation times (Derraik, 2002; O’Brine and Thompson, 2010; Ryan et al., 2009; Thompson et al., 2004) that, if disposed of appropriately, will decompose in industrial composting plants under hot, humid and well-aerated conditions (Moore, 2008; Thompson, 2006). However, this decomposition is only partial: whilst the starch components of the bio-plastic will decompose, an abundance of synthetic polymers will be left behind (Andrady, 2011; Roy et al., 2011; Thompson et al., 2004). In the relatively cold marine environment, in the absence of terrestrial microbes, decomposition times of even the degradable components of bioplastics will be prolonged, increasing the probability of the plastic being fouled and subsequently reducing UV permeation on which the degradation process relies (Andrady, 2011; Moore, 2008; O'Brine and Thompson, 2010). Once decomposition does finally occur, microplastics will be released into the marine environment (Roy et al., 2011).

1.2 Impact of Marine Plastic Garbage

1.2.1 Impact of marine microplastics

The presence of small plastic fragments in the open ocean was first highlighted in the 1970s (Carpenter and Smith, 1972), and a renewed scientific interest in microplastics over the past decade has shown that these contaminants have become widespread and located within the marine environment, with the potential to cause damage to biota (Rand et al, 2010; Sutherland et al., 2010). Due to its small size, microplastics are considered bioavailable for organisms throughout the food chain. Their composition and the relatively large surface area make them prone to absorb pollutants, such as organic pollutants transmitted by water and the leaching of plastics that release compounds that are considered toxic. Therefore, the ingestion of microplastics can thus involve the introduction of toxins to the base of the food chain, acquiring potential for bioaccumulation (Teuten et al., 2009).

The estimated global load of plastic on the ocean surface is in the order of tens of thousands of tons (Cózar et al., 2014), a far lower level than expected; these data were later confirmed by an assessment of plastic pollution in the world's oceans (Eriksen et al., 2014).

A range of marine taxa, including birds, sea turtles, and marine mammals, are known to be affected by entanglement and ingestion, with consequences including impaired movement, decreased feeding ability, reduced reproductive output, lacerations, ulcerations, and death (Laist, 1997; Derraik, 2002; Moore, 2008; Gregory, 2009). Because of their small size, microplastics have the potential to be ingested by a wide range of marine organisms. Laboratory studies have shown that invertebrates: crustaceans, barnacles, polychaete worms, mussels, and amphipods will ingest microplastic fragments (Thompson et al., 2004; Browne et al., 2008; Graham &Thompson, 2009; Lusher et al., 2013).

The proportion of microplastics has about the same size interval as that of zooplankton (Cózar et al., 2014; Collignon et al., 2014; Fossi et al., 2016). Zooplanktivorous predators, such as the mesopelagic fish are prone to ingest this type of substance. Microplastic could have both physical and chemical effects (impacts) on the organisms that ingest them. If ingested, microplastics may pass through the gut or may be retained in the digestive tract (Browne et al., 2008). Fibres may knot or clump and could be hazardous if they block feeding appendages or hinder the passage of food. Hoss and Settle (1990) suggested that if plastic particles were accumulating in high numbers in the intestines of smaller animals, they may have a similar impact to larger items of debris and clog digestive systems (Derraik, 2002; Gregory, 2009; Ryan et al., 2009). The accumulation of debris in the digestive tract may also cause a false sense of satiation leading to decreased food consumption (Ryan, 1987; Lusher et al., 2013). There is also concern that, if ingested, small items of plastic debris might facilitate the transport of chemical contaminants to organisms such as persistent organic pollutants (POPs).

Ingestion of microplastics by individual organisms at lower trophic levels could also have consequences for organisms at high trophic levels if any contaminants that are transferred have the potential for biomagnification (Teuten et al., 2009). Despite these concerns, there have been few studies specifically examining the occurrence of microplastic in natural populations. The available data is Davison and Asch (2011) who found mesopelagic fish to have ingested plastic fibres, filaments, and films (mean length 2.2 mm). A recent study on plastic ingestion by catfish from estuarine waters in Western South Atlantic found out that all ontogenetic phases of the three species of catfish ingested plastic (Possatto et al., 2011). However, few studies have formally identified the material found using Fourier Transform Infrared Spectroscopy (FT-IR). This is considered essential to confirm the identity of pieces <1 mm.

Possible impacts on nearshore environments from small plastic debris (Carson et al., 2011), whether pre-production pellets or fragments of larger items include ingestion by a variety of organisms (Graham and Thompson, 2009; Laist, 1997), sediment contamination from leached plasticizers (Oehlmann et al., 2009) or the adsorption of persistent organic pollutants (Mato et al., 2001; Ríos et al., 2007).

Marine plastic debris, particularly microplastics with their large surface-to-volume ratio, are susceptible to contamination by many contaminants dissolved in water, including metals (Betts, 2008; Ashton et al, 2010), endocrine disrupters (Ng and Obbard, 2006) and persistent organic pollutants (POPs) (Ríos et al., 2007; Cole et al., 2011).

1.2.2 Impact of macroplastics on marine organisms

The entanglement is one of the main problems of the macroplastics in the marine organisms in conjunction with the ingestion. A study realized by Kühn et al. (2015) details the harmful impacts on the interaction between marine plastic debris and wildlife. In this study, the increase in the number of species known to have been affected by the entanglement or ingestion of plastic waste was determined. The affected species have doubled since 1997, from 267 to 557 species among all wildlife groups. For sea turtles, the number of affected species increased from 86% to 100%, for marine mammals from 43% to 66%, and seabirds from 44% to 50%.

Some animals can intentionally ingest plastic waste, and this depends on a wide range of factors. These can vary between different groups of animals (Shaw et al., 1994; Laist, 1997).

Some of these factors are the foraging strategies, for example, the omnivorous diving seabirds (Provencher et al., 2010) are more pelagic than seabirds with specialized diets (Ryan 1987) and surface capture (KK). Marine turtles often ingest plastic bags as they may mistake them for jellyfish, a common component of their diet (Carr 1987; Lutz 1990; Mrosovsky et al., 2009; Tourinho et al., 2010; Townsend 2011; Campani et al., 2013; Schuyler et al., 2014). This can be deduced for the rest of the species (big fish, whales, etc).

Another factor that is often considered to influence the consumption of litter is the colour since specific colours can attract predators when they resemble the colour of its prey. In seabirds, this has been suggested as they naturally feed mainly on light brown crustaceans so mostly darker plastic granules have been found suggesting that they were mistaken for food (Day et al., 1985).

The ingestion of macroplastics can lead to direct death since the gastrointestinal tract is completely blocked or severely damaged. The ingested plastic can lead to rapid death. Even small pieces can cause a blockage. Several studies have described the deleterious effects of garbage in the sea on different organisms. For example, cases of mortality among Magellanic penguins, Brandao et al. (2011), in seabirds, Pettit et al. (1981) and Colabuono et al. (2009), and cases of mortality among marine turtles, Mrosovsky et al. (2009) and Tourinho et al. (2010). But, direct lethal result from ingestion probably does not occur with a relevant frequency at the population level (Kühn et al., 2015).

Apart from being a potential danger to organisms, the floating anthropogenic litter provides a habitat for a diverse community of marine organisms (Kiessling et al., 2015). A total of 387 taxa, including pro- and eukaryotic microorganisms, seaweeds and invertebrates have been found rafting on floating litter in all major oceanic regions. Among the invertebrates, species of bryozoans, crustaceans, molluscs and cnidarians are most frequently reported as rafters on marine litter. Micro-organisms are also ubiquitous on marine litter although the composition of the microbial community seems to depend on specific substratum characteristics such as the polymer type of floating plastic items. Sessile suspension feeders are particularly well-adapted to the limited autochthonous food resources on artificial floating substrata and an extended planktonic larval development seems to facilitate colonization of floating litter at sea. Properties of floating litter, such as size and surface rugosity, are crucial for colonization by marine organisms and the subsequent succession of the rafting community. The rafters themselves affect substratum characteristics such as floating stability, buoyancy, and degradation. Under the influence of currents and winds, marine litter can transport associated organisms over extensive distances. Because of the great persistence (especially of plastics) and the vast quantities of litter in the world's oceans, rafting dispersal has become more prevalent in the marine environment, potentially facilitating the spread of invasive species.

1.3 Persistent Organic Pollutants (POPs) in Microplastics

The marine plastic remains are associated with a large number of chemicals including chemicals added or produced during manufacturing and those present in the marine environment that accumulate onto the debris from surrounding seawater (Rochman, 2015). Plastic debris acts as a vector for organic contaminants because of their hydrophobic nature (Mato et al., 2001; Karapanagioti and Klontza, 2008) (Figure 1. 1). Plastic pellets are used as passive samplers and a low-cost monitoring medium to assess organic contaminants in the marine environment (Ogata et al., 2009; Teuten et al., 2009; Heskett, et al., 2012; Ríos Mendoza et al., 2017).

Recent investigations have demonstrated the ingestion of microplastics in various marine organisms with different feeding strategies particularly in those species which cannot discriminate the food source (Browne et al., 2008; Andrady, 2011). Besides, it has been demonstrated that marine microplastics (polyvinyl chloride, polyethylene, polypropylene, polystyrene) contain a wide range of organic contaminants including polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), petroleum hydrocarbons, organochlorine pesticides (DDTs, HCHs), polybrominated diphenyl ethers (PBDEs), alkylphenols and bisphenol A (BPA), at concentrations from sub ng/g to µg/g (Mato et al., 2000; Ríos et al., 2007; Teuten et al., 2009). The physicochemical properties of microplastics, such as size, shape, density, colour and chemical composition, greatly affect their transport in the environment and their bioavailability (i.e., toxicological effects) on marine organisms.

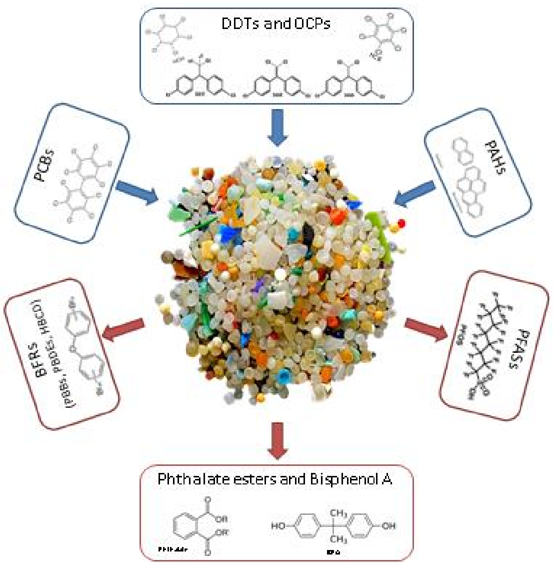

Figure 1. 1. Contamination of persistent organic pollutants in microplastics.

1.3.1 POPs plastic additives

To be able to change characteristics of the final products (Teuten et al., 2009; Ríos Mendoza et al., 2017) such as colour, resistance to heat and aging, flexibility and performance, plastic additives are used as organic composite (Ríos Mendoza et al., 2017). In some cases, the additive ingredients constitute up to 50% of the proportion of the plastic product (Bauer and

Herrmann, 1997; Rochman, 2015; Ríos Mendoza et al., 2017). Phthalate esters, bisphenol A (BPA), brominated flame retardants (BFRs) are among many other plastic additives known as toxic compounds to organisms when released into the environment. Fragments of postconsumer plastic may have more additives than plastic pellets since they are added during moulding (Teuten et al., 2009; Ríos Mendoza et al., 2017).

As mentioned earlier, the phthalate esters or phthalic acid esters (PAEs) have been widely used in plastic manufacturing since the 1930s to act as an additive, which gives flexibility to vinyl resins. As phthalate esters are not bound with covalent chemical bonds, they can migrate to the surface and be lost by a variety of physical processes, and therefore their input into the environment is due to the slow release from plastic material (Staples, 2003; Ríos Mendoza et al., 2017). In scientific studies at the global level, it has been demonstrated that they are one of the persistent organic pollutants (POPs) most frequently detected in the environment (Daiem and Berge, 2012; Gao and Wen, 2016; Ríos Mendoza et al., 2017). Several phthalates are "plausibly" endocrine disruptors (Waring and Harris, 2011). The long-term health effects of exposure to endocrine disruptors, such as phthalates, are unclear (Waring and Harris, 2011).

Also, the perfluoroalkylated substances (PFASs), which include perfluorooctane sulfonate (PFOSs) and perfluorooctanoic acid (PFOA), because of their characteristics including high thermal, chemical and biological inertness and that are generally hydrophobic but also lipophobic (EFSA, 2008) have been extensively used in polymer production, metal plating, electronic semiconductors, aqueous firefighting foams, impregnating agents, paper, cookware, textiles and carpet coatings, ski waxes, stain repellents, surface coatings, insecticides and cleaners (Kelly et al., 2009; Alder and van der Voet, 2015; Ríos Mendoza et al., 2017). These compounds can cause various health problems, are carcinogenic and can damage the thyroid and the reproductive system.

Bisphenol A, BPA, [2,2(4,40-hydroxyphenyl)propane] is a candidate to join the list of POPs of the Stockholm Convention. It is used as an intermediate in the production of polymeric materials, primarily epoxy resins and polycarbonate plastic, and is also used as a raw material for other products such as flame retardants (Staples, 2003; Ríos Mendoza et al., 2017) and the manufacture of tetrabromobisphenol A (TBBPA) (EU, 2003, Ríos Mendoza et al., 2017). Its introduction into the environment includes releases during handling, unloading, heating, as well as accidental spills or other releases (Staples, 2003; Ríos Mendoza et al., 2017). Bisphenol A is an endocrine disruptor. It is capable of causing imbalances in the hormonal system at very low concentrations with possible repercussions on health (Rochester, 2013).

Phthalate esters (PAEs), one type of common industrial compound, have been widely used in various applications including textiles, medical devices, electronics, plastics, and personal care items (Horn et al., 2004). Because of the potential cytotoxicity and estrogenic effects (Mankidy et al., 2013), PAEs have been considered to be endocrine disruptor chemicals and toxic environmental priority pollutants. During the manufacturing, application and disposal processes, PAEs could be released into the environment and they have been detected frequently in sediments, surface water, estuarine and marine waters (Li et al., 2016; Turner and Rawling; 2000; Zeng et al., 2008). Due to the high octanol-water partition coefficients, strong sorption of PAEs by soil and sediment organic matters, biochar, and other carbonaceous sorbents have been reported (Gao et al., 2013; Ghaffar et al., 2015; Jin et al., 2015; Liu et al., 2019).

Some substances, such as BFRs, are mixed into these polymers to reduce the flammability of the petroleum-based combustible materials. Those additives include polybrominated biphenyls (PBBs), PBDEs, hexabromocyclododecanes (HBCDs) that are not chemically bound to the plastic and may leach into the environment (de Wit, 2002; Covaci et al., 2011; Ríos Mendoza et al., 2017) and TBBPA that are chemically bonded to the plastics (Alaee et al., 2003).

Polybrominated Biphenyls were introduced as flame retardants in the early 1970s and were incorporated into acrylonitrile butadiene styrene (ABS) plastics (IPCS, 1994). PBBs are almost insoluble in water and enter into the aquatic environment through industrial waste discharge as well as from leaching of polluted soils. The effects of PBBs were found to be essentially the same as those seen for PCBs (de Wit, 2002).

Polybrominated Diphenyl Ethers (PBDEs) are one of the most widely used and studied BFRs and have been extensively used as three formulations: deca-BDE (98% decabromodiphenyl ether), octa-BDE (mix of hexa-, hepta-, and octabromodiphenyl ethers) and penta-BDE (penta- and tetrabromodiphenyl ethers) (la Guardia et al., 2006; Lee and Kim, 2015). PBDEs are added to a variety of products, such as plastics, textiles, and furniture foam, due to their flame-retardant capacity (Rahman et al., 2001). These chemicals are slowly and continuously released into the environment through several different pathways (Chen and Hale, 2010; Hale et al., 2003; Ríos Mendoza et al., 2017). The Agency for Research on Cancer (IARC) has classified PBDEs as a Group 3 carcinogen (not classifiable as to its carcinogenicity to humans) (ATSDR, 2017)

Hexabromocyclododecanes (HBCDs or HBCDDs) are used in expanded (EPS) and extruded (XPS) polystyrene foams, which are used as insulation in buildings, roads to prevent frost-heaving, as packing material for food, laboratory chemicals, and electronic appliances (de Wit et al., 2010; Wünsch, 2000; Ríos Mendoza et al., 2017). Low water-soluble-HBCD input in the environment can occur due to emissions during production, by leaching from consumer products, or by disposal into the environment (Rani et al., 2014; Ríos Mendoza et al., 2017). It is very toxic to aquatic organisms. Although there is a great lack of information on the toxicity of HBCD in humans, vulnerable groups could be at risk, particularly to the observed neuroendocrine and developmental toxicity of HBCD (SC, 2018a).

1.3.2 POPs sorbed to microplastics

Because of their physical and chemical properties, plastics accumulate a complex mixture of chemical contaminants present in the surrounding seawater (Mato et al. 2001; Teuten et al., 2007, 2009; Frias et al., 2010; Holmes et al., 2012; Engler, 2012; Rochman et al., 2013; Rochman, 2015), adding to the cocktail of chemicals already present from manufacturing. As a result of widespread global contamination of chemical contaminants (Ogata et al., 2009) and plastic debris (Thompson et al., 2004; Barnes et al., 2009; Browne et al., 2011), marine plastic debris is recovered globally with measurable amounts of POPs (e.g. polychlorinated biphenyls (PCBs), PAHs and OCPs) and other persistent bioaccumulative and toxic substances (Rochman, 2015).

The incorporation of chemicals in microplastic debris is related to their sorption path onto the resin surface or into the polymer phase itself (Rice and Gold, 1984; Ahn et al., 2005). The variability in sorption among polymers should be considered (Karapanagioti and Klontza, 2008; Teuten et al., 2007). For example, PE has a higher affinity for PCBs (Endo et al., 2005; Rochman et al., 2013) and phenanthrene (Karapanagioti and Klontza, 2008) than PP. Hydrophobic contaminants are present in the environment as complex mixtures and their sorption onto plastics can occur simultaneously or differentially affecting their transport and desorption (Rochman, 2015; Bakir et al., 2012; Ríos Mendoza et al., 2017).

It is difficult to fully understand the impact on the environment caused by the sorbed contaminants on microplastics (Hammer et al., 2012). As an example, the transfer of sorbed contaminants from ingested plastic to marine organisms, reported by several authors (e.g., Rochman et al. (2014), Ryan et al. (1988), Tanaka et al. (2015)) is dependent on the organism, the nature of the chemical substance involved, the size of the plastic particle and the surrounding physical and chemical environment (Teuten et al., 2009; Bakir et al., 2014a; Bakir et al., 2014b; Ríos Mendoza et al., 2017).

Polychlorinated Biphenyls (PCBs) are synthetic organic compounds obtained from the chlorination of biphenyls. Theoretically, there are up to 209 congeners that can be generated; 113 are known to be present in the environment (Pascal et al., 2005). The low chemical and biological degradation rates of PCBs (Jones and Voogt, 1999) lead to their substantial use in electrical equipment and flame retardants (Shulz et al., 1989; Ríos Mendoza et al., 2017).

PCBs in microplastic debris have been reported in different places (Figure 1. 2) even in remote islands, as reported in Refs. (Heskett et al., 2012; Hirai et al., 2011). Even though their production and use are forbidden in many countries, several tonnes are estimated to be in use or present in old, abandoned equipment, mainly related to shut down power plants (Ríos et al., 2007; Almeida et al., 2007) which can leak and release PCBs into the environment. Recently, a volunteer-based global monitoring program (International Pellet Watch, IPW) has been designed to monitor the pollution status of the oceans for persistent organic pollutants (POPs) such as PCBs and organochlorine pesticides in resin pellets (plastic raw material) from the surrounding seawater and beaches. The results show the presence of PCBs (0.01 - 2746 ng/g) (Figure 1. 2), OCPs (0.02 - 1061 ng/g) and HAPs (<0.03 - 17 ug/g) in plastics pellets found on beaches worldwide. Generally, high concentrations were found in the northern hemisphere where there is greater anthropogenic and industrial activity.

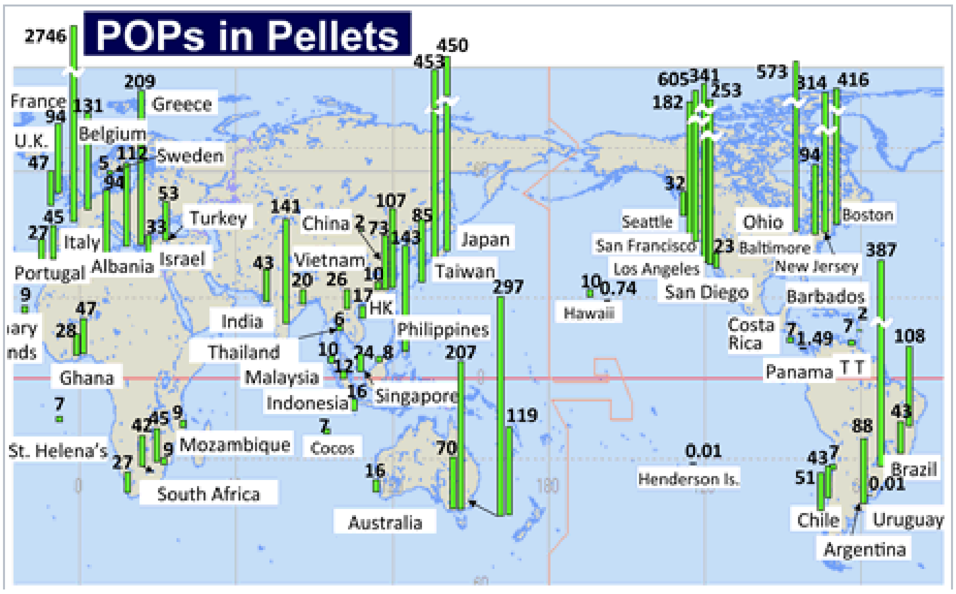

Figure 1. 2. PCB concentration in beached plastic resin pellets (ng/g), source: IPW, http://www.pelletwatch.org.

Sources of Polycyclic Aromatic Hydrocarbons (PAHs) are normally classified into three groups, biogenic, pyrolytic, and petrogenic. Biogenic PAHs are attributed to the biosynthesis of hydrocarbons by marine or terrigenous organisms or early diagenetic transformation of nonhydrocarbon natural products to hydrocarbons (UNEP, 1992; Ríos Mendoza et al., 2017). Pyrolytic sources include the incomplete combustion of organic matter such as fossil fuel combustion, waste incineration, and asphalt production. Petrogenic sources are usually associated with inputs of crude oil or its derivatives (Law and Biscaya, 1994; Ríos Mendoza et al., 2017). The data published in the IWP page reveal that the concentrations of PAHs (<0.03-17 ug/g) were higher in the United Kingdom (Forth Estuary), besides these concentrations represent a high capacity of adsorption of PAHs in comparison with the other pollutants.

Organochlorine Pesticides (OCPs) are synthetic compounds that are hydrophobic and chemically stable. Because of their properties such as persistence, biomagnification and long-range transport, their use and production are forbidden in many countries (Jones and Voogt, 1999; Ríos Mendoza et al., 2017).

Among OCPs, dichlorodiphenyltrichloroethane (DDT) is the one largely used in agriculture and against vectors and pests that cause tropical diseases, such as Malaria and Leishmaniasis (D´Amato et al., 2002; Ríos Mendoza et al., 2017) in many countries such as South Africa (Ryan et al., 2012), China (Zhang et al., 2015), and Brazil (Rochman et al., 2014). Concentrations of DDT in microplastic also depend on their proximity to the sources (Ríos Mendoza et al., 2017). Have been found high concentrations of DDT (7100 ng/g) in plastic pellets near an industrial area in Los Angeles (The United States) and the extensive use of this compound when it was still legal.

The use of technical Hexachlorocyclohexane (HCH) (insecticide) was the most extensive during the 1970s and early 1980s followed by a rapid decrease as a result of restrictions and prohibitions in many countries (Li, 1999). HCH can be found in microplastic, but usually in low concentrations, which reflect the less retention of HCH due to relatively lower hydrophobicity and higher vapour pressure in comparison to PCBs (Ogata et al., 2009). The concentrations of HCH found in several countries during the initial phase of the International Pellet Watch programme ranged from 0.14 to 37.1 ng/g, which demonstrated that these compounds were used at that time in some countries, such as Mozambique (Ogata et al., 2009). Hexachlorobenzene (HCB) is an organochloride with the molecular formula C_6Cl_6. It is a fungicide formerly used as a seed treatment, especially on wheat to control the fungal disease bunt (Mackay et al., 1992; Pozo et al., 2014). HCB may be released into the environment as a product of incomplete waste combustion in incinerators and as a by-product of industrial processes (Tanabe et al., 1997; Lohse, 1988; Pozo et al, 2014). In plastic pellets collected on the southeastern coast of Brazil, Taniguchi et al. (2016) reported concentrations from 1.8 to 55.8 ng/g for HCB.

1.4 Stockholm Convention on Persistent Organic Pollutants (POPs)

The Stockholm Convention on Persistent Organic Pollutants was adopted on 22 May 2001 and entered into force on 17 May 2004.

Being aware that persistent organic pollutants (POPs) pose major and increasing threats to human health and the environment, in May 1995 the Governing Council of UNEP requested in its decision 18/32 an international assessment process to be undertaken of an initial list of 12 POPs and that the Intergovernmental Forum on Chemical Safety (IFCS) develop recommendations on international action for consideration by UNEP Governing Council and World Health Assembly no later than 1997 (UNEP, 2020a).

In June 1996, IFCS concluded that available information was sufficient to demonstrate that international action, including a global legally binding instrument, was required to minimize the risks from the 12 POPs through measures to reduce and/or eliminate their emissions or discharges.

In February 1997, the UNEP Governing Council in its decision 19/13C invited UNEP to prepare for and convene an intergovernmental negotiating committee (INC), with a mandate to prepare an international legally binding instrument for implementing international action, initially beginning with the 12 POPs and requested that the INC establish an expert group to develop criteria and a procedure for identifying additional POPs as candidates for future international action.

The first meeting of the INC to develop an internationally legally binding instrument for implementing international action on POPs was held in June 1998 in Montreal, Canada, at which the Criteria Expert Group (CEG) requested above was established. Subsequent meetings of the INC were held in Nairobi, Kenya, in January 1999, in Geneva, Switzerland, in September 1999, in Bonn, Germany, in March 2000, and Johannesburg, South Africa, in December 2000, where the negotiations were successfully completed.

The CEG completed its mandate in two meetings: the first in Bangkok, Thailand, in October 1998 and the second, in Vienna, Austria, in June 1999.

The Convention was adopted and opened for signature at a Conference of Plenipotentiaries held from 22 to 23 May 2001 in Stockholm, Sweden.

The Conference of the Plenipotentiaries also adopted several resolutions that were included in the appendix to the Final Act, such as on interim arrangements, on the Secretariat (e.g. inviting UNEP to convene further sessions of the INC during the interim period), and on liability and redress. On this latter issue, a workshop on liability and redress was held on 19-21 September 2002 in Vienna, Austria.

The Convention entered into force on 17 May 2004, ninety days after submission of the fiftieth instrument of ratification, acceptance, approval, or accession in respect of the Convention (SC, 2018b).

The seventh meeting of the Persistent Organic Pollutants Review Committee (POPRC-7) took place from 10–14 October 2011 in Geneva, considered three proposals for listing in Annexes A, B and/or C of the Convention: chlorinated naphthalenes, hexachlorobutadiene and pentachlorophenol, its salts and esters (Table 1.1). The proposal is the first stage of the POPRC's work in assessing a substance and requires the POPRC to assess whether the proposed chemical satisfies the criteria in Annex D of the Convention. The criteria for forwarding a proposed chemical to the risk profile preparation stage are persistence, bioaccumulation, the potential for long-range environmental transport and adverse effects.

POPRC-8 proposed hexabromocyclododecane for listing in Annex A ().

Table **1. 1**), with specific exemptions for production and use in expanded polystyrene and extruded polystyrene in buildings. This proposal was agreed upon at the sixth Conference of Parties on 28 April-10 May 2013 (UN, 2001; SC, 2018c).

POPRC-9 proposed di-, tri-, tetra-, penta-, hexa-, hepta- and octa-chlorinated napthalenes, and hexachlorobutadiene for listing in Annexes A and C. It also set up further work on pentachlorophenol, its salts and esters, and decabromodiphenyl ether, perfluorooctanesulfonic acid, its salts and perfluorooctane sulfonyl chloride (SC, 2018d).

POPRC-15 proposed PFHxS for listing in Annex A without specific exemptions (UNEP, 2020b).

Table 1. 1. All POPs listed in the Stockholm Convention.

Compounds	Class	Classification under the Stockholm Convention
Aldrin	Pesticide	Annex A (Elimination)
Chlordane	Pesticide	Annex A (Elimination)
Chlordecone	Pesticide	Annex A (Elimination)
Dieldrin	Pesticide	Annex A (Elimination)

Endrin	Pesticide	Annex A (Elimination)
Heptachlor	Pesticide	Annex A (Elimination)
Hexachlorobenzene (HCB)	Pesticide/Industrial chemical	Annex A (Elimination)
Alpha-hexachlorocyclohexane	Pesticide	Annex A (Elimination)
Beta-hexachlorocyclohexane	Pesticide	Annex A (Elimination)
Lindane	Pesticide	Annex A (Elimination)
Mirex	Pesticide	Annex A (Elimination)
Pentachlorobenzene	Pesticide/Industrial chemical	Annex A (Elimination)
Pentachlorophenol and its salts and esters	Pesticide	Annex A (Elimination)
Technical endosulfan and its related isomers	Pesticide	Annex A (Elimination)
Toxaphene	Pesticide	Annex A (Elimination)
DDT	Pesticide	Annex B (Restriction)
Decabromodiphenyl ether	Industrial chemical	Annex A (Elimination)
Hexabromobiphenyl	Industrial chemical	Annex A (Elimination)
Hexabromocyclododecane (HBCDD)	Industrial chemical	Annex A (Elimination)
Hexabromodiphenyl ether and heptabromodiphenyl ether	Industrial chemical	Annex A (Elimination)
Polychlorinated naphthalenes	Industrial chemical	Annex A (Elimination)
Short-chain chlorinated paraffins (SCCPs)	Industrial chemical	Annex A (Elimination)
Tetrabromodiphenyl ether and pentabromodiphenyl ether	Industrial chemical	Annex A (Elimination)
Perfluorooctane sulfonic acid, its salts, and perfluorooctane sulfonyl fluoride	Pesticide/Industrial chemical	Annex B (Restriction)
Hexachlorobenzene (HCB	Unintentional production	Annex C (Unintentional production)
Hexachlorobutadiene (HCBD)	Unintentional production	Annex C (Unintentional production)
Pentachlorobenzene	Unintentional production	Annex C (Unintentional production)
Polychlorinatedbiphenyls (PCB)	Unintentional production	Annex C (Unintentional production)
Polychlorinated dibenzo-p-dioxins (PCDD)	Unintentional production	Annex C (Unintentional production)
Polychlorinated dibenzofurans (PCDF)	Unintentional production	Annex C (Unintentional production)
Polychlorinated naphthalenes	Unintentional production	Annex C (Unintentional production)

1.5 International and National Microplastic Regulations

In light of the growing concern about the negative impacts of plastics pollution in the environment and potential human exposure risk, governments are increasingly acting to address this problem at the local, national, and international levels (Xanthos and Walker, 2017). Globally, several international governance bodies have spoken out regarding the need to tackle marine plastic pollution. For example, the United Nations (UN) Environment Assembly has enacted resolutions in which all UN member states committed to addressing global plastic pollution, including several marine plastic debris and microplastics resolutions (Carlini and Kleine, 2018; Niaounakis, 2017; UNEP, 2016). Similarly, the Group of Seven (G7) Summit acknowledged in 2015 that marine pollution is a global challenge affecting marine and coastal ecosystems and human health and ultimately passed an Ocean Plastics Charter in 2018 that committed to taking specific actions to reduce plastics in the marine environment (Niaounakis, 2017; G7, 2018). And, the G20 agreed to an Action Plan on Marine Litter in 2017 (G7, 2017).

A variety of legislative instruments have been developed to control, reduce and manage the use of plastics in everyday life to minimize adverse effects. Existing legislation largely covers levies, bans, and voluntary efforts through "reduction and reuse campaigns" (Lam et al., 2018).

The countries have primarily focused their efforts on regulating single-use plastics, mainly with plastic bags and straws. However, it is still necessary to move forward so that the laws extend their reach to other PUSU products that are equally polluting and harmful to the environment including cutlery, dishes, glasses, plates, plastic cups, etc.

Measures to reduce the impacts of microplastics have begun to be taken in different parts of the world, industry and government , especially micro-beads, in the marine environment, for example, in Australia, the United Kingdom, and the United States (NSW EPA, 2016). The presence of microbeads in cosmetic products has prompted the enactment of legislation to reduce the production and consumption of plastic materials, thus reducing adverse impacts on the environment and potential human health risks.

Recently, the federal government of the United States brought in the Microbead-Free Water Act 2015, which aims to ban the manufacture and sale of microbeads in cosmetic products since July 2018. The Canadian Parliament passed a law to ban the manufacture of microbeads in June 2017. The Australian Microplastics Working Group was established to search for voluntary industry agreements for the elimination of microspheres in personal care, cosmetics, and cleaning products (NSW EPA 2016, Lam et al., 2018).

The European Union (EU) approved a Directive to regulate certain single-use plastic products (De Vido, 2020), which aims to prevent and reduce its impact on the environment, particularly in the aquatic environment, and on human health, as well how to promote the transition to a circular economy with business models, innovative and sustainable products and materials, contributing to the efficient operation of the internal market.

The European proposal establishes the obligation of the Member States to adopt measures such as reduction of consumption (25%) of food containers with or without lids, glasses, and post-consumer waste from tobacco filters that contain plastics. And marking restrictions for cotton buds, cutlery (forks, knives, spoons, chopsticks), plates, straws, drink stirrers, sticks for holding and attaching balloons, oxo-degradable plastic products, food and beverage containers made of expanded polystyrene, and fishing equipment containing plastics.

On the other hand, in Chile, from August 2018, the law regulating the use of plastic bags has been enacted. This law is an important step in reducing plastic pollution since it prohibits the delivery of plastic shopping bags.

The next step is to move forward with the implementation of the Extended Producer Responsibility Law (*Programa legislativo*, 2020) that encourages the recycling of plastic packaging.

Other countries in the region have also decided to legislate to reduce plastic pollution. Antigua and Barbuda was the first country in the Americas to ban plastic bags in 2016. Following Colombia, the ban on plastic bags has been in force since 2016. In the country, 30 × 30 cm bags are prohibited and a tax is charged for those who want to buy plastic bags in stores and supermarkets to protect the environment. Similarly, Puerto Rico began to prohibit the use of plastic bags to transport purchased items. The measure does not apply to prepared food sales premises or airport duty-free zones. Another country that has decided to take measures is Mexico, which from 2021 will begin to govern the law that prohibits the use of non-biodegradable plastic bags, within the framework of the Solid Waste Law. In May 2019, Peru approved the regulation of law 30884, which regulates single-use plastics and other disposable containers. In July 2019, Panama will prohibit the use of single-use plastic bags for the transport of products and merchandise. Belize and Bahamas have strategies in place to reduce plastic use and are promoting conservation strategies for the Caribbean Sea which is the 2nd most polluted with plastics. Meanwhile, Ecuador is transforming the remote Galapagos Islands into a plastic-free archipelago by banning the use and sale of plastic products such as straws, bags, and bottles.

1.6 Microplastics in Chile

Chile is a maritime country since it has a coast that stretches for more than 4,000 km (from 18° S to 56° S). Therefore, plastic pollution is a real threat, potentially damaging marine and coastal ecosystems, food security, and public health.

For this reason, the network of the Scientific Alliance of Plastic Pollution of Chile (SPLACH) has recently been created, which unites Chilean scientists working in plastic pollution, whose objective is to promote collaborative research focused on this environmental stressor. This network has been created to encourage research on plastics, filling some of the important knowledge gaps to inform society and decision-makers.

The first investigations on marine plastic waste were carried out in the southern zone of Chile when surveying sightings of plastic waste from the fishing industry, which strongly impacted this region (Hinojosa and Thiel, 2009; Bravo et al., 2009) (Table 1. 2). Subsequently, studies in Chile focused on determining marine litter on beaches throughout the country focused on citizen science (Bravo et al., 2009; Hidalgo-Ruz and Thiel, 2013; Hidalgo-Ruz et al., 2018).

Subsequent studies focused on the intake of microplastics by marine organisms ranging from sea lions, fish, spider crabs to krill (Bravo Rebolledo, 2014; Andrade and Ovando, 2017; Ory et al., 2017, 2018; Perez-Venegas et al., 2017, 2020; Pozo et al., 2019).

Plastic pollution has also been studied in remote Chilean oceanic islands (Easter Island and Juan Fernández), which receive large volumes of marine litter from the Chilean mainland and the fishing industry (Barnes et al., 2018; Luna-Jorquera et al., 2019).

In the case of Chile, the contamination by plastics is not higher than in other countries where the impact is greater. However, plastic pollution is far worse than expected (Urbina et al., 2020).

Table 1. 2. Scientific Articles in Chile related to microplastics

Scientific Articles in Chile Related to Microplastics	Author
Floating marine debris in fjords, gulfs and channels of southern Chile	Hinojosa & Thiel., 2009
Anthropogenic debris on beaches in the SE Pacific Chile: results from a national survey supported by volunteers	Bravo et al., 2009
Accumulation of microplastic on Shorelines Worldwide: Sources and Sinks	Browne et al., 2011
Microplastics in the Marine environment: A review of the methods used for identification and quantification	Hidalgo-Ruz et al., 2012
Distribution and abundance of small plastic debris on beaches in the SE Pacific (Chile): A study supported by a citizen science project	Hidalgo-Ruz & Thiel, 2013
Plastic pollution in the South Pacific subtropical gyre	Eriksenn et al., 2013
Plastic pollution in the World's oceans: More than 5 Trillion Plastic pieces weighing over 250,000 tonnes afloat at sea	Eriksenn et al., 2014
The Potential for young citizen scientist projects: a case study of Chilean Schoolchildren collecting data on marine litter	Eastman et al., 2014.
Los desechos marinos y el lobo fino antártico: ingesta y enmallamiento	Bravo Rebolledo, 2014
First Record of microplastics in stomach content of the southern King crab Lithodes santolla, Nassau bay, Cape Horn, Chile	Andrade & Ovando, 2017
Amberstripe scad Decapterus muroadsi (Carangidae) fish ingest blue microplastics resembling their copepod prey along the coast of Rapa Nui (Easter Island) in the South Pacific subtropical gyre	Ory et al., 2017
Polyethylene microbeads induce transcriptional responses with tissue-dependent patterns in the mussel Mytilus galloprovincialis	Détrée & Gallardo, 2017
Coastal debris survey in a Remote Island of the Chilean Northern Patagonia	Perez-Venegas, 2017
Who cares about dirty beaches? Evaluating environmental awareness and action on coastal litter in Chile	Kiessling et al., 2017
Is the feeding type related with the content of microplastics in intertidal fish gut?	Mizraji et al. 2017
Spatio-temporal variation of anthropogenic marine debris on Chilean beaches	Hidalgo-Ruz et al., 2018

First detection of plastic microfibres in a wild population of South American fur seals (Arctocephalus australis) in the Chilean Northern Patagonia	Perez-Venegas, 2018
Impacts of marine plastic pollution from continental coasts to subtropical gyres—fish, seabirds, and other vertebrates in the SE Pacific	Thiel et al. 2018
Low prevalence of microplastic contamination in planktivorous fish species from the southeast Pacific Ocean	Ory et al., 2018
Marine plastics threaten giant Atlantic Marine Protected Areas.	Barnes et al., 2018
Marine Protected Areas invaded by floating anthropogenic litter: An example from the South Pacific.	Luna-Jorquera et al., 2019
Marine debris occurrence along Las Salinas beach, Viña Del Mar (Chile): Magnitudes, impacts and management	Rangel-Buitrago et al. 2019
Presence and characterization of microplastics in fish of commercial importance from the Bío-Bío region in central Chile	Pozo et al., 2019
Persistent organic pollutants sorbed in plastic resin pellet—“Nurdles” from coastal areas of Central Chile	Pozo et al., 2020
Marine plastic debris in Central Chile: Characterization and abundance of macroplastics and burden of persistent organic pollutants (POPs)	Gómez et al., 2020
Monitoring the occurrence of microplastic ingestion in Otariids along the Peruvian and Chilean coasts	Perez-Venegas et al., 2020
A country's response to tackling plastic pollution in aquatic ecosystems: The Chilean way	Urbina et al., 2020

1.7 Study Area

1.7.1 Central zone of Chile

The Central zone of Chile (Figure 1. 3) (CROFO, 2013) is one of the five natural regions in which the Chilean economic development agency, Corfo, divided Chile in 1950. Its limits are the Aconcagua River on the north and the Biobío River on the south. It limits to the north with the Norte Chico, to the east with Argentina and to the south with the Southern Zone of Chile. It includes the Valparaíso Region (including the Juan Fernández Islands), the Metropolitan Region, O'Higgins, Maule, and the Bío-Bío regions.

Historically, it has been the main area of the country and the one with the greatest number of inhabitants (it gathers near 79% of the total population of the country). In addition, it concentrates the highest percentage of the country's economic productivity, due to its favourable Mediterranean and continental climate in the interior.

In a strict sense, it is not a valley, but a narrow plain with smaller valleys flanked on the east by the Andes mountain range and on the west by the Coast. The three main cities in the country are located in this area: Gran Santiago, Gran Valparaíso, and Gran Concepción. Other important cities are Quillota, Los Andes, San Antonio, Melipilla, Rancagua, Talca, Curicó, Chillán, and Los Ángeles. Santiago and Valparaíso are the most politically important cities in the area and the country. The Executive and Judicial powers are in Santiago, and the Legislative power is in Valparaíso.

Figure 1. 3. Map of Chile

1.7.1.1 Economic characteristics

Its economy is composed of the extraction of natural resources, through mining, forestry, agriculture, fishing, and port activity (BCN, 2017).

Mining: Copper is mainly one of the minerals that can be found in this area, El Teniente site, located in the O'Higgins Region, was already known during the colony, but its exploitation was not significant until the beginning of the 20th century. Next to it, in the Metropolitan Region, there is a minor site known as La Disputada.

Coal is another mineral extracted from this area, with the most well-known sites located in Lota and Lebu.

Forestry: it is composed mainly of the pine trees processed in pulp mills located in the city of Constitución (Maule Region).

Agriculture: Its main crops correspond to cereals such as wheat, corn, and legumes; fruit trees, especially the production of apples, table grapes, pears, almonds, plums, and peaches, and vegetables such as lettuce, cucumbers, pumpkins, tomatoes, etc. In the central regions located to the south, agriculture produces rice, wheat, legumes and potatoes, as well as beets and raps. The fruit sector is favored by soil conditions and climate. It is important to emphasize that the vineyards are an important resource of the area and the production of wine is one of the most important at a domestic level. The following valleys stand out: Casablanca Valley, San Antonio Valley/Leyda Valley, Maipo Valley, Cachapoal Valley, Colchagua Valley, and Curicó Valley/Lontué Valley.

Fishing: The main products extracted from the sea are the horse mackerel, albacore, anchovy, sardine, cod, cockfish, conger, hake, croaker, silverside, sole, Chilean abalone, black mussel, Magellan mussel, small razor clam, sea squirt, hedgehog, crab, shrimp, lobster, and giant acorn barnacle.

Port activity: in the Central zone of Chile, there are the three most important ports in the country, from north to south: Valparaíso, San Antonio, and Talcahuano/San Vicente. Of these, Valparaíso and San Antonio (Valparaíso Region) are the most important at the domestic level since they have greater cargo transfer and greater proximity to the capital city. Valparaiso stands out as it is the only port having an important passenger terminal. There are also smaller ports such as Quintero, Penco/Lirquén, and Coronel.

Plastic industry: In Chile, the plastic industry started in the 1930s and it was mainly focused on the use of Bakelite. After the 1950s, melamine was incorporated for producing panels and covers. According to the Chilean plastic industry (ASIPLA), in 2016 Chile exported ~70,700 tonnes of raw materials (resins) and ~76,300 tonnes of manufactured products mainly to other South American neighbours. The same year, however, Chile imported ~736,631 and ~304,533 tonnes of resins and manufactures products, respectively, mainly from the USA (29%), Brazil (15%), and China (12%) (ASIPLA 2016).

The open economic policy and the lack of regulations on plastic waste led Chile to become the number one country in plastic waste generation in South America, with an annual average of 456 kg per capita, above Brazil (383 kg), Uruguay (376 kg), Panama (343 kg) and Argentina (341 kg) (UNEP, 2018).

1.7.2 Central coastal zone of Chile

Chile is located on the western slope of South America and for its boundary to the west with the Pacific Ocean, it has one of the most extensive coasts in the world, with approximately 4,200 km in a straight line and more than 80 thousand km considering the outline of all the islands, channels and fjords located in the southern part of the country. This relationship with the sea allows having one of the richest and most productive marine ecosystems and the earth (SUBPESCA, 2015).

This is how on the coasts you can find several currents or masses of water that move in several directions and that travel in parallel with the ocean. The most known and important is the so-called Humboldt Current or Humboldt Current System, which also adds the West

Wind Drift or Antarctic Circumpolar Current. As for the Humboldt Current, this is an ocean current that flows along the western coasts of Chile and Peru.

The Humboldt Current is a surface current generated by the Pacific Ocean pressure system and the strong winds from the West. This current constitutes a northern extension of subantarctic waters of low salinity, low temperature, and high content of oxygen. Also, throughout its four thousand kilometres of extension, it is divided into a coastal branch and an oceanic branch, which reach an approximate depth of 300 and 400 meters respectively. For this reason, the Humboldt Current System is often referred to (Figure 1. 4).

Figure 1. 4. Marine currents in the Southeast Pacific, source: redrawn from CPPS 2000b, https://www.slideserve.com/moral/humboldt-current-system

One of the main characteristics of the Humboldt Current is with its effects it creates one of the most productive marine areas of the Pacific Ocean. This is mainly due to the presence of areas of upwelling or outcrops of water that are produced by the action of the wind, which displaces large amounts of surface water, creating a space that is filled by the ascent of deeper waters. These waters are cold and very rich in nutrients, with basic components for the maintenance of life, and come from the decomposition of the organisms of the sea and/or the waste that arrives at it. When reaching the surface, these waters rich in nutrients, together with the action of solar energy, facilitate the proliferation of microscopic algae that form the phytoplankton, which serves as food for small fish. And so begins a food chain that continues in the zooplankton, the fish, and the large inhabitants of the sea (SUBPECA, 2015).

A large quantity of fishery resources is generated, which transforms this current into one of the richest areas in fish species, and at the same time, it makes industrial fishing a very important sector for the economy of Chile and Peru. From the above, it should be noted that Chile has a wide variety of plant and animal species. According to the Fisheries Statistical Yearbook of 2014 of the National Fisheries and Aquaculture Service (SUBPECA, 2015), there is a total of 161 species in exploitation and cultivation: 14 algae, 87 fish, 34 molluscs, 23 crustaceans, two echinoderms, and one tunicate. The coast is highly impacted by human activities such as urban settlements, industrial development, fishing, aquaculture, and tourist activities (SUBPESCA, 2015).

The central coast of Chile (33°-37° 30 'S) has a general orientation NW-SO. A characteristic feature is the existence of extensive erosion terraces, true plains of probable marine origin. Its successive steps can rise up to more than 400 m above sea level and extend more than 30 km inland, as a result of a long evolution that probably began in the Miocene, on a coastal edge affected by upheaval tectonics. The novel fact is the occurrence of long beaches and extensive fields of dunes. These segments of sand accumulation are directly linked to the abundant alluvial load, mainly sediments of volcanic origin carried to the ocean by large rivers, coming from the Andes mountain range and characterized by a Hydrographic regime of Mediterranean type. The mouths of these rivers, affected by the flow of the tide, correspond to estuaries. The advanced segment of the coast that forms the Arauco Peninsula (37º 30 'S) matches with a block of tertiary-age marine sedimentary rocks, carved into living cliffs by the sea. The continental shelf widens to the south and shows submarine canyons, such as the one in San Antonio (33º 35 'S) (CONA, 2010).

As stated in part 1.7.1.1, in the central coastal area of Chile, there are the three most important ports in the country, from north to south: Valparaíso, San Antonio, and Talcahuano/San Vicente. Of these, Valparaíso and San Antonio (Valparaíso Region) are the most important at the national level since they have greater cargo transfer and are closer to the capital city. Valparaiso stands out as it is the only port to have an important passenger terminal. There are also smaller ports such as Quintero, Penco/Lirquén, and Coronel.

In the central zone of the country, the fishing ports of San Antonio, Tomé, Talcahuano, San Vicente, Coronel and Lota are key to the national fishery. There, the horse mackerel is increasingly destined to be frozen and preserved, although an important fraction goes to the production of fishmeal and fish oil. Also, this zone has one of the main fisheries for common hake (SUBPESCA, 2012).

1.7.3 Demography of the province of Concepción

The Bío-Bío Region (VIII Region) is located at the southern limit of the central zone, specifically between 36°00 'and 38°30' south latitude. It limits to the north with the Maule Region, to the south with the Araucanía Region, to the west with the Pacific Ocean and to the east with the Argentine Republic. It has an area of 37,068.70 km^2, representing 4.9% of the national territory. This region presents traditional longitudinal relief units. According to the National Statistics Institute, INE, the projected population in 2016 will reach 2,127,902 inhabitants and a density of 57.4 inhabitants per square kilometer (INE, 2016).

Regarding the climatic conditions, this zone is defined as a transition between a warm temperate Mediterranean climate and a temperate humid or rainy climate. These conditions allow the development of very particular vegetation which is different from other regions. The hydrographic network of the region is organized through two large pits, Itata and Bío-Bío (INE, 2016)

The Bío-Bío region is one of the most important regions in the country. After Santiago, Concepción-Talcahuano conurbation is the second urban conglomerate in the country, surpassing even Valparaíso-Viña del Mar. Also, the region is one of the main concentrators of important economic activities. This region hosts activities as diverse as the steel industry (Huachipato), traditional agriculture, pulp industry, forestry, electricity generation, fishing industry, etc. (INE, 2016).

The industrial sector contributes almost a third of the regional gross domestic product and employs more than sixty thousand people. The production of steel, which contributes 100% of Chilean steel, stands out. The chemical industry is represented by the petroleum refinery and the petrochemical industries of the city of Concepción, which produce ethylene and derivatives. The paper industry also develops a great activity for the foreign market. In Talcahuano, there are fishing processing industries, a sector in which the region ranks second in the country, immediately after Tarapacá. There are about fifteen fish meal plants, seven canneries, seventeen frozen product plants, and shipyards (Aedo and Larraín Ruiz-Tagle, 2004).

The rivers in this region are characterized by having a rain and snow regime with two full periods in the year, one in the summer and another in the winter. The two most important rivers that flow through the region are Itata and Bíobío.

The Itata River is born in the external part of the Andes Mountain Range by the confluence of the Cholguán and Itatita rivers, draining in a North-West direction, crossing the Intermediate Depression. Some of the main tributaries that it receives in its route are the Diguillín, Larqui, and Ñuble rivers. Its hydrographic basin is 11,200 km^2, after traveling 230 km it flows into the Pacific Ocean with a flow of 140 m^3/sec (DGA, 2004).

The Biobío River, one of the most important rivers in the country, is born in the Gualletué and Icalma lakes. Along its route, it is collecting a series of tributaries, where the Vergara and Laja rivers stand out. Its hydrographic basin is of 24,000 km^2. In its lower course, it carries a flow that fluctuates between 700 and 1,000 m^3/sec, being advantaged in its flow only by the Baker River. It presents two maximum flows in the year, being the highest in the winter and a minimum between January and April (DGA, 2004).

At a national level, the Biobío basin represents an important centre of economic development. The most dynamic productive sectors are linked to the forestry sector, the agricultural sector (located mainly in the provinces of Ñuble and Bío-Bío), the industrial sector (represented mainly by the metallurgical, chemical, oil refining, textile, pulp industries, among others) and the hydroelectric sector that constitutes the main source of electrical power supply nationwide.

The Biobío River rises on the eastern bank of the Gualletué Lake in the Andes Mountain Range, and its upper course develops in an intermontane valley of glacial origin, generating numerous meanders, through a steppe landscape in which low bushes abound (Colbún, 2018). It crosses the central plain and then empties its waters in San Pedro, in the northern sector of the Arauco Gulf, in the outskirts of Concepción. It has a distance of 380 km., ranking second in Chile due to its length, after the Loa River (DGA, 2004).

The Bío-Bío region is composed of the provinces of Arauco, Bío-Bío, Concepción, and Ñuble. Its main urban centre is the Gran Concepción. The province of Concepción is the one that houses the majority of the regional population, as well as all the communes that make up the Gran Concepción.

The province of Concepción is one of the most important industrial poles of the country, highlighting the fishing industry, forestry, steel, and manufacturing, besides being the distribution centre of services in the region where it is located.

According to the Chilean census of 2012, its population is 967,757 inhabitants. It has an area of 3,439 km² and its capital is the city of Concepción. Its main districts are Concepción, Talcahuano, Hualpén, San Pedro de la Paz, Chiguayante, and Tomé (INE, 2016).

1.7.4 Industrial history of the province of Concepción

The province of Concepción and the commune of Talcahuano, due to its geographical location, natural conditions and proximity to energy supply centres such as the coal mines of Lota and Coronel, had from 1950 an important industrial, fishing, military and port growth, which generated an accelerated urban growth. The coexistence of active urban and industrial areas in the rugged territory, with abundant bodies of water and with an extension of only 142.8 km^2, have made the city especially sensitive to the degradation of its natural resources and those affected by its environment. This situation led to a crisis in recent decades, giving rise to a municipal strategy started in 1993 and which is the subject of this Case Study. This situation was aggravated by the chronic shortage of resources of the City Council, and the lack of infrastructure and control mechanisms for environmental control (Aedo and Larraín Ruiz-Tagle, 2004).

The pollution caused by the different anthropic activities, exceeded the natural capacity of the community, altering and greatly affecting its natural resources (bays of Concepción and San Vicente, Canal El Morro, air and soil of the community), thus deteriorating the quality of life of its inhabitants (health and material possessions). Pollution, along with urban disorder, including its coastal area, created a potential for critical risk in economic development. An example of this was the massive clam death in 1986 and the fire of San Vicente in 1993, with the loss of 80 million dollars and a life. According to the City Council, what was at stake was "*... both the destruction of natural resources and the rejection by the domestic and international market of products manufactured in the area since they were considered to be contaminated, as well as the general image of the Community.*" This was decisive in motivating the design of a plan that was committed to all the actors involved, including the generators of problems, the recipients of the problems, and those responsible for solving them (Valenzuela, 2003).

The City Council, as the administrative body of the Commune against this serious environmental deterioration, which affected the quality of life of its inhabitants, the economic development and the sustainability as a commune, assumes at the beginning of the 90s, the firm intention of solving this serious problem by designing and developing plans, projects and programs to reverse this deterioration. This is how the City Council, in coordination with other public, private, and community organizations, expressed their greatest commitment and concern to reduce pollution, especially water resources, and territorially ordered the city to make different activities compatible and make them sustainable over time (Valenzuela, 2003). This is how today Concepción Bay is less environmentally impacted.

1.7.5 Environmental impact in the province of Concepción

The fishing sector is the main responsible for the pollution that affects the bay formed by Talcahuano, Concepción, Penco, and Tomé, where the biggest problem is the waste deposit (Liquid Industrial Waste) by the fishmeal industry (Valenzuela, 2003).

In the last 20 years, the distribution area and concentration of organic matter have increased in the superficial sediments of Concepción Bay. Heavy metals (cadmium, zinc, chromium) are deposited in bivalve molluscs and fish; and some of the exported fishery products have been rejected abroad due to their high content of these metals. In addition, on the coasts of the area, sulfuric acid, detergents, lanolin, phosphates, sodium hydroxide, pesticides, herbicides, and chemical process residues from the wood and cellulose industries can be found.

Industrial waste from the fishing and forest industry is also discharged into fluvial systems, affecting wide sections of the Bío-Bío and Itata rivers and their tributaries. There is also no sewage treatment system, which contributes to aggravate this problem. The Andalién and Bío-Bío rivers in the sectors of Negrete and Nacimiento, and Laja, San Rosendo, Hualqui, Chiguayante, Concepción, San Pedro and Talcahuano have the highest levels of organic and faecal contamination from industrial discharges from pulp production, paper, sugar, tannery, and refinery.

Chapter 2. Thesis objectives

2.1 General Objectives:

This thesis will aim to characterize marine plastic debris and microplastics in Concepción Bay during different seasons. To assess the occurrence of them in organisms (gastrointestinal content of fish species) and sand, and its relevance for a route of transport of pollutants in the marine environment of central Chile.

2.2 Specific Objectives:

2.2.1. Conduct sampling of sand and fish from Concepción Bay, Coliumo Bay and Biobío River, the sampling will take place during the winter, spring and summer periods.

2.2.2. Evaluate the presence of microplastic in the gastrointestinal content of fish species of Concepción Bay.

2.2.3. Characterize the marine plastic debris and microplastics found in the different matrices of Concepción Bay through the Fourier Transform Infrared Spectroscopy (FT-IR).

2.2.4 Quantify the persistent organic pollutant (PBDEs, PCBs and OCPs) load in environmental samples of plastic debris taken from the sand of the beaches of Concepción Bay.

Chapter 3. Materials and Methods

3.1 Study area

Concepción Bay is a Chilean natural bay, with a shallow and semi-enclosed area of 190 km^2 located 36°40 "S; 73°02 "W (Figure 3. 1), the coast of the Province of Concepción of the Bío-Bío Region and is bounded by Quiriquina Island, located to the north (Ahumada and Chuecas, 1979) and the communes of Talcahuano, Penco, Lirquén, and Tomé.

Six beaches were selected along the coastline of the province of Concepción (Gómez et al., 2020). Negra Beach (N) in Penco, near the mouth of the Andalien River, which is a river that passes through part of the city of Concepción, and the communes of Penco and Talcahuano, ending at Concepción Bay. It has a length of 130 km, born of the junction of the Poñén Creek, which comes from the north watershed line and, Curapalihue, coming from the south. This basin is part of the Bío-Bío Region. It has innumerable turns into the coastal range, the last one of which is an arc open to the south that borders the city of Concepción, where in the full alluvial plain usually divides into two or more tributaries before emptying in a great widening of the south coast of Concepción Bay.

El Morro Beach (M), located 500 meters from the Main Square of Tomé, has an extension of 500 meters of white sand. It is suitable for swimming and leisure activities. Bellavista Beach (B) located on the coastline, entering the city of Tomé, has an extension of 900 meters of grey and fine sand. It is very suitable for swimming and leisure activities. Given the ease of access and movement, it is very crowded in the summer.

The *desembocadura* beach (DB) (river mouth) beach is near the mouth of the Biobío River which is a river that crosses part of the southern zone of Chile and is one of the main rivers of the country, as much by its geographical characteristics as by its economic and historical importance. It is the second-longest river in Chile, with a length of 380 km. It is born in the Galletué Lake and Icalma Lake, located in the northeastern end of the Araucanía Region in the Andes, near the international border with Argentina. From there, it crosses much of the southern part of the Central Valley, passing through the provinces of Bío-Bío and Concepción, in the Bío-Bío Region. Finally, it ends in the city of Concepción. The River carries the inputs for the industrial and urban activity of the Biobío Basin.

Samples of the beaches of Dichato and Coliumo were also taken. The first is the main beach of a coastal town called Dichato (D), located in the municipality of Tomé in the Bío-Bío Region, Chile. The town is located 37 kilometers north of the city of Concepción. It is a very closed bay, with calm but very cold waters, suitable for water sports, very popular in the summer. The main source of income for the inhabitants of Dichato is fishing. It deals with activities of artisanal capture of fish and shellfish that are commercialized locally. Marine concessions have also been delivered, called "management areas", where molluscs are grown. Since the 1980s, tourism has become important, through recreational services, typical food restaurants and accommodation in small hotels, residential areas, and private cabins. Coliumo (C) is an artisan fishermen's cove located 10 km from Tomé, and 39 km from Concepción. It has about 931 inhabitants. Coliumo is well-known for its location as one end of the bay, with calm and cold waters, suitable for artisanal fishing and the cultivation and extraction of shellfish.

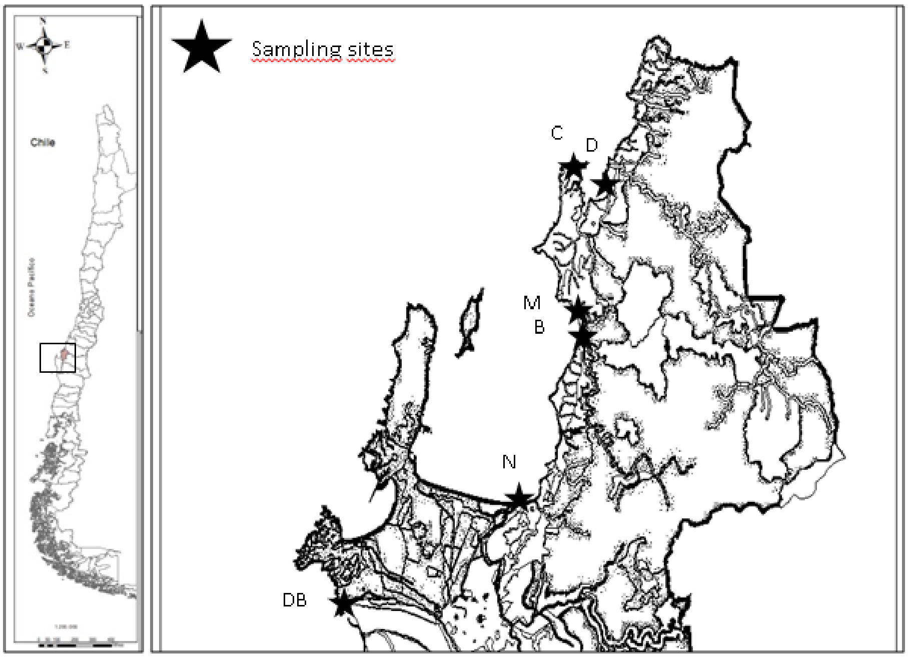

Figure 3. 1. Study area. (D = Dichato Beach; C = Coliumo Beach; M = El Morro Beach; B = Bellavista Beach; N = Negra Beach; DB = Desembocadura Biobío River Beach).

3.2 Sampling

All samples sand were collected between 2016 and 2018 during the four seasons of the year: summer, autumn, winter, and spring in Concepción Bay (Figure 3. 1; Table 3. 1).

The samples were taken in different areas of the coastal edge of Concepción Bay (Andalién River, Negra Beach, Penco (N), El Morro Beach (M), Bellavista Beach (B)), that could contribute to the discharge of microplastics and Coliumo bay (Coliumo beach (C) and Dichato beach (D)). Also, the area of the Biobío River (Desembocadura beach (DB) was added. This is the main effluent of the region and one of the largest rivers in the country.

Fish samples (hake and sardine) were provided by the Institute of Fisheries Promotion IFOP of the Bío-Bío Region. For the 2017 period, 10 fish (Hake, n = 5 and Jack mackerel, n=5) were provided to analyse the gastrointestinal content.

Table 3. 1. Summary of microplastics and macroplastics sampling campaigns in the different environmental matrices.

Matrices	Site	Sampling periods 2016 Winter	2016 Spring	2016 Summer	2017 Autumn	2017 Winter	2017 Spring	2018 Summer	2018 Winter
Sand	Negra Beach, Penco (N)	x	x	x	x	x	x *		x *
	El Morro Beach, Tomé (M)	x	x	x	x	x	x *	x *	
	Bellavista Beach, Tomé (B)	x	x	x	x	x	x *	x *	x *
	Coliumo beach (C)	x	x	x	x	x	x *	x *	x *
	Dichato beach (D)	x	x	x	x	x	x *	x *	x *
	Desembocadura beach, Biobío River (DB)						*	x *	x *
Biota (Fish)	Concepción Bay					x		x	

X = microplastic; * = macroplastic.

3.2.1 Microplastic in sand

For microplastic sand sampling to collect from the top 2 cm, they will be collected in 250 g of sand in glass bottles privily washed, calcined and rinsed with acetone. Subsequently, 25 g of sand are weighed into a beaker and 200 ml of saline solution (NaCl 36%) are added to it for flotation (Besley et al., 2017). After that, it is given an ultrasonic bath for 15 minutes and it is left to rest for 20 more minutes to later filter the supernatant using Pasteur pipettes and vacuum filtration equipment with GF/F 47 mm filters (previously calcined at 450ºC).

3.2.2 Microplastics in organisms

Samples of pelagic fish were collected in Concepción Bay using a traditional fixed trap provided by the Institute of Fisheries Promotion IFOP of the Bío-Bío Region. We worked with the gastrointestinal content of fish (*Trachurus murphyi* (Jack mackerel, n=5), *Merluccius gayi* (Hake, n=5). The selected species have great economic importance for Chile since they represent one of the main resources of the fishing sector in the country (> 80% human consumption) (SUBPESCA, 2019), where the Bío-Bío region is in first place in economic and social importance (36%) (Pozo et al., 2019). Fish were frozen within 2 h of capture and subsequently thawed out at room temperature before the examination. For each fish, basic measurements were recorded including length, from mouth to central point of caudal fin (mm), body weight (g) and girth, and the maximum distance between dorsal and ventral sides (mm). The stomach content was removed by dissection from each fish, from the top of the oesophagus and cut away at the vent (Pozo et al., 2019). To minimize the risk of contamination, fish were opened with a scalpel and digestive tracts were immediately placed in plastic zip-lock bags and stored for up to 3 hours before transferring to clean Petri dishes for inspection with a dissecting microscope (Browne et al., 2008; Lusher et al., 2013).

Subsequently, the stomach contents of the individuals were digested with 200mL of KOH 15%, it was vigorously shaken for 5 to 10 minutes using a baguette, then they were stored in a place without light for 24 hours. After 24 hours, 100mL of 15% KOH solution was added, stirring with a loaf. Then it is left to rest for 2 hours and is shaken again with a loaf for 5 minutes to finally leave the samples again in a place without light for 72 hours, shaking from time to time.

Once the digestion is finished, the organic matter of each sample is filtered, for which pasteur pipettes and a vacuum filtration equipment with GF / F 47mm filters (previously calcined at 450ºC) are used. Using metal tweezers, the filters are stored in glass Petri dishes (60x15mm).

3.2.3 Macroplastic in sand

Plastic debris (PD) or macroplastics were collected from the beach of coastal areas around Concepción Bay during November 2017, March 2018 and July and August 2018. For the collection of samples, 3 transects (every 5 meters approximately) were taken, perpendicular to the coast. The transects were sampled from the highest site of the beaches (base of dunes or the start of a road) (quadrant 1) to the low tide line (quadrant 3). Each transect had 3 quadrants of 3 × 3 m (Figure 3. 2), delimited by ropes and sticks, following the proposal of Bravo et al. (2009) and Hidalgo-Ruz et al. (2018). The sand of each quadrant was sieved in situ through a metal sieve screen (1 mm) and collected in aluminium foil envelopes (Taniguchi et al., 2016), contact with plastic materials was avoided. The samples were finally kept at 20 °C until their analysis.

The PD found were measured for their diameters and then sorted by colour, shape, and size (MSFD, 2013, Baini et al., 2018).

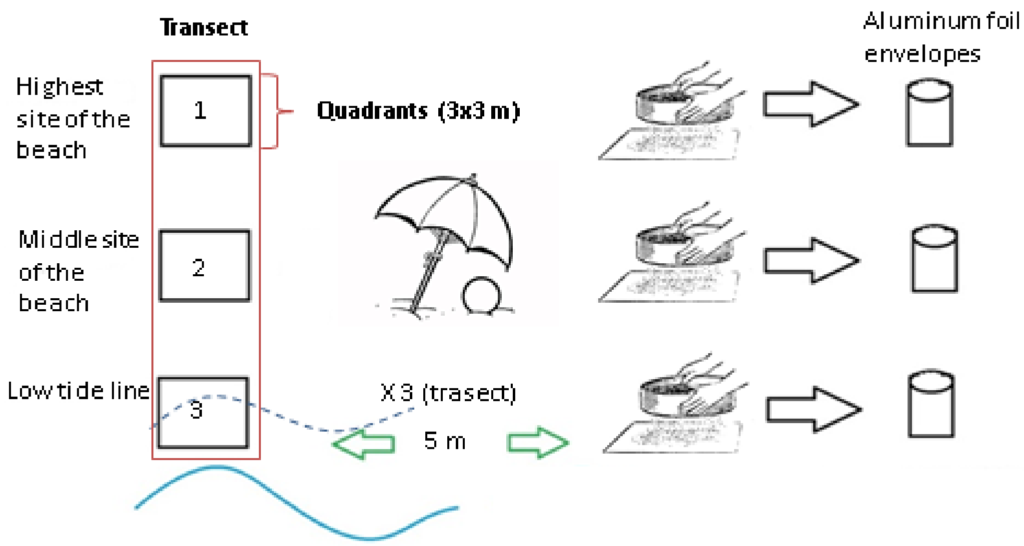

Figure 3. 2. Sampling design (black stars=show sampling sites=highest site of the beach; 2=middle site of the beach; 3=low tide line).

3.3 Physical analysis

After the samples were collected, the samples were taken to the laboratory for analysis and filtering, where the resulting filters were analysed under the optical microscope with an integrated Leica DM 750 camera (Universidad Católica de la Santísima Concepción) and an optical microscope (Faculty of Engineering and Technology, Universidad San Sebastían). The particles were photographed and digitized. Subsequently, the particles showing microplastic characteristics were counted and measured in length.

3.4 Chemical Analysis

3.4.1 Determination of polymers

The particles showing microplastic characteristics were analyzed using a Fourier-transform infrared (FT-IR) spectroscopy (FT-IR Microscope Spotlight 400 & Spectrum Frontier, Perkin Elmer, CMA, Universidad de Concepción, Chile) (FT-IR Spectrum Two, Perkin Elmer, CIPA, Universidad del Bío-Bío, Chile) (Figure 3. 3) to obtain the spectrum of the pre-identified particles. The obtained spectra were compared with a database of reference standard compounds to identify the polymers present in the particles. For macroplastic polymer analysis to carry out in the Agilent Cary 630 FTIR spectrometer (Dipartimento di Scienze Fisiche, della Terra e dell'Ambiente, Università degli Studi di Siena).

Figure 3. 3. FT-IT analysis equipment used in this thesis.

3.4.2 Determination of POPs

In order to quantify the concentrations of PBDEs, PCBs and OCPs in macroplastics, the samples taken at different beaches of Concepción Bay (Chile) and Biobío River, at two different periods (November 2017 and March 2018). The samples were separated into two groups, the first group corresponds to macroplastic samples collected in 5 beaches of the Concepción Bay and a beach at the mouth of the Biobío River (November 2017). The second group corresponds to samples of macoplastics collected in 4 beaches of Concepción Bay and a beach at the mouth of the Biobío River (March 2018). Both were frozen in liquid nitrogen and crushed in homogenization equipment of cryogenic samples (Retsch MM301) (Kühn et al., 2018) and were taken for analysis in duplicate, with their respective Blank.

Samples were weighed about 1 g for analysis. The samples were extracted by an ultrasonic bath with 15 ml of hexane for 15 min (3 times). The samples were reduced to 5 ml, 3 ml of concentrated sulfuric acid was added and they were heated at 45 ° C for 15 min. When the organic and inorganic phases were not well defined, they were centrifuged at 15,000 rpm x 10 min. The organic phase was separated from the inorganic phase with a Pasteur pipette and washed with hexane. All samples were concentrated under gentle nitrogen to 1 ml.

The clean-up of the samples was carried out in columns of acid silica gel and sodium sulfate, eluting with 6 ml DCM (Figure 3. 4) and 40 ml of DCM/hexane 1: 1. After the clean-up, the samples were concentrated under gentle nitrogen at 35° C up to a volume of 100 µl, 50 µl of nonane and hexane were added and then concentrated to 50 µl (Gómez et al., 2020, Appendix 1).

Figure 3. 4. Clean-up in acid columns.

3.4.2.1 Chemical analysis and Target compounds

PCBs and OCPs (DDT and derivatives) were identified on an Agilent 7890A gas chromatograph-mass spectrometry (GC-MS) equipped with a Rxi 5Sil MS capillary column (30 m x 0.25 mm x 0.10 µm) (Restek, USA) coupled to Agilent 7000B QQQ mass spectrometer. Samples were screened for (target/qualified ion) five isomers of hexachlorocyclohexane (α-, β-, γ-, δ-, ε-HCHs) (purchased from Ultra Scientific, North Kingstown, RI, USA), six isomers of DDT and its derivatives (o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD, o,p'-DDT and p,p'-DDT) (purchased from Ultra Scientific, North Kingstown, RI, USA) and seven PCB indicator PCB congeners (PCB28, 52, 101, 118, 138, 153, and 180) (purchased from Supelco NC, USA). 10 congeners of PBDEs were screened (BDE28, 47, 66, 85, 99, 100, 153, 154, 183, and 209) (purchased from Wellington, ON, Canada). Their analyses were performed by gas chromatography-mass spectrometry (GC-MS) on a 7890A GC instrument (Agilent, USA) equipped with an Rtx-1614 column (15 m × 0.25 mm × x 0.10 µm) (Restek, USA) coupled to an AutoSpec Premier MS (Waters, Micromass, UK). The high-resolution mass spectrometer (HRMS) was operated in EI + mode in the resolution of >10 000.

3.4.2.2 Quality control and quality assurance (QA/QC)

PCBs were quantified with 8 point calibration with concentrations from 1 ng/ml to 4000 ng/ml. Linearity was maintained in the whole range. Calibration standards for PCBs were provided from LGC Standards. PCB121 was used as an internal (syringe) standard, PCB30 and PCB185 as extraction standards. Instrumental detection limits (IDL) and limits of quantification (LOQ) were calculated from the lowest calibration point as an amount producing a signal to noise 3 (LOD) and 10 (LOQ). All PBDE standards were obtained from Wellington. POP concentrations in the samples were recovery-corrected using surrogate compounds (i.e., PCBs (30 and 185), and 13C12-labeled PBDEs spiked before analysis (100 µl). Procedural blanks (n=14) were also assessed.

3.5 Statistical-based Method for the Evaluation of the Abundance of Plastic Debris in the Central Coast of Chile

Statistical one-way ANOVA tests were performed to compare the abundance of plastic debris on beaches between quadrants and identify differences for the abundance of plastic debris between the spring of 2017 and the summer of 2018.

The dataset was processed using one-way ANOVA, with Tukey tests to make multiple comparisons. The Statistix 10 software performed the analyses. The results were considered statistically significant at $p < 0.05$.

Chapter 4. Results and Discussion

4.1 Abundance

4.1.1 Microplastics Abundance

The results of the abundance of microplastics in Concepción Bay in sand and fish taken in the campaigns of the period between 2016 and 2018.

4.1.1.1 Abundance of microplastics in sand

In 2016, (winter and spring) and 2017 (summer and autumn) 20 sand samples were collected. 35 particles were found in the filters of these sand samples, in which 43% of the total particles were analyzed in FT-IR and only 27% of the particles were identified as microplastics. In 2018, (summer) 6 samples were collected, of which 10 particles were found and 90% of them were identified as microplastics (Figure 4. 3).
The abundance of microplastics in the sand was 0.035 ± 0.04 items/g, the highest abundance of microplastics in sand samples was in the summer of 2018 in coliumo beach(0.12 items/g). The concentration of microplastics on the beaches of Concepción Bay was lower than that reported in the beach sand of Bohai Sea, China, which ranged from 0.1 to 0.2 items/g (Yu et al., 2016) and a similar concentration than that reported in the beach sand of India, which ranged from 0.045 to 0.22 items/g (Tiwari et al., 2019). The sampling protocols in these studies were similar to those carried out in this thesis. However, efforts have been recently made to standardize sampling and sample processing methodologies (Besley et al., 2017) to make reliable comparisons in the future.

4.1.1.2 Abundance of microplastics in fish

In this study, 5 samples were taken from each species, (Trachurus murphyi (Chilean jack mackerel) and Merluccius gayi (Hake), in which the stomach content was analyzed. They were analyzed under an optical microscope and FT-IR on the filters corresponding to two Hake and one Jack mackerel.

Of the total number of particles found, 63% was analysed, of which 80% was microplastics. A previous study of microplastics in fish of Concepción Bay (Pozo et al., 2019, Appendix 1) showed a low abundance of microplastics (30% in Sardines, 10% in Chilean jack mackerel and 10% in Hake), while Pejerrey—the fish species obtained from the mouth of the Biobío River—presented the highest detection frequency of microplastics (70%), followed by Robalo (30%) and Jerguilla (20%). The results showed that the highest abundance of microplastics was found in the hake samples (60%) in comparison with Chilean jack mackerel (20%) (Table 4. 1), with an average abundance of 1 item/individual. Huang et al. (2020) reported a higher MP presence from the fish in China, totalling 30 species out of the 32 under study, with an average abundance of 2.83 items/individual.

Table 4. 1. Fish species (number and sizes examined) and frequency of debris occurrence for Microplastics analysis in Oceanic and Coastal fish species from central Chile.

Species (common name)	Number of individuals	Number of stomachs with microplastics
Trachurus murphyi (Chilean jack mackerel)	5	1
Merluccius gayi (Hake)	5	3

4.1.2 Macroplastics Abundance

The results showed a large amount of plastic debris on the beaches sampled in spring (November 2017), summer (March 2018) and winter (July – August 2018), along the coast of the province of Concepción (Figure 4. 1).

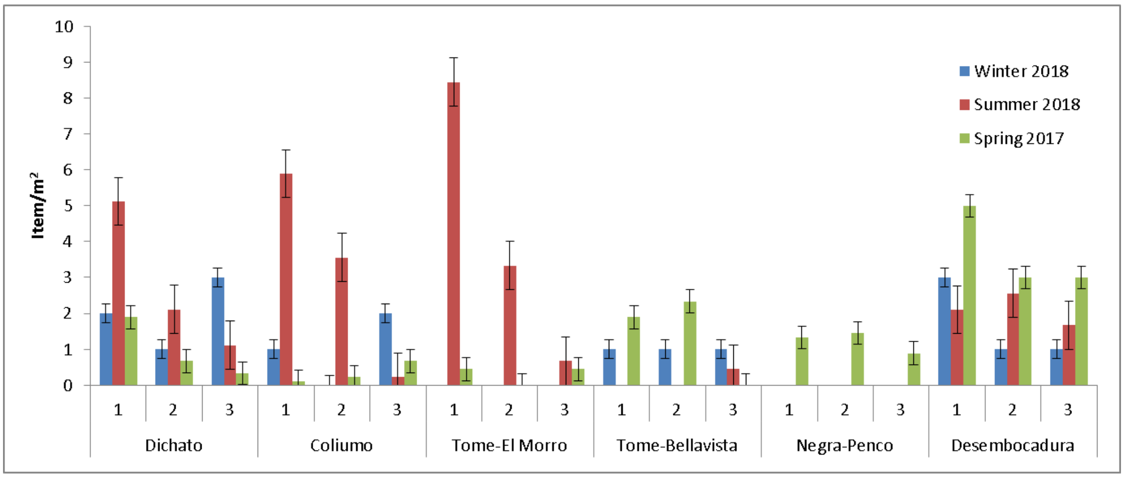

Figure 4. 1. Macroplastic abundance (ítem/m^2) found in beaches located in central Chile for quadrant (1=highest site of the beach; 2=middle site of the beach; 3=low tide line).

The results showed a significant difference for the macroplastic abundance between spring 2017, summer 2018 and winter 2018 periods ($p < 0.05$, $p = 0.004$) (Table 4. 2). In summer, a higher abundance of macroplastics was detected with average values of 2.9 ± 3.1 items/m^2, ranging from 1.1 items/m^2 on Bellavista Beach (B) to 4 items/m^2 in El Morro Beach (M). In winter, an average of 1.2 ± 1.2 items/m^2 was found, ranging from 1.0 items/m^2 on Bellavista Beach (B) to 2 items/m^2 in Dichato Beach (D). According to the clean-coast index (CCI) (Alkalay et al., 2007), these beaches are filthy (fragments>1 item/m^2). A recent study conducted along the Chilean Coast determined an average abundance of 2.15 items per m^2 for the year 2016 (Hidalgo-Ruz et al., 2018). Studies in other areas worldwide have reported densities accounting for 1 item/m^2 range on beach sectors (Galgani et al., 2015). Furthermore, in studies conducted on the beaches in South Korea, the highest macroplastic abundance with 2.7 items/m^2 was recorded in Dukpo Beach (Lee et al., 2013), with 10 items/m^2 in Po-Hang (Lee et al., 2015). Ivar do Sul et al. (2009) reported a high abundance of macroplastics on the beaches of Fernando de Noronha Island in Brazil (29 items/m^2).

Table 4. 2. One-Way A0V statistical analysis for abundance of PD by season. Statistix 10 software (p <0.05).

Source	DF	SS	MS	F	P
Season	2	39.405	19.7026	6.98	0.0041
Error	24	67.707	2.8211		
Total	26	107.112			

DF =Degrees of freedom; SS = sum-of-squares; MS = Mean squares; F ratio = F; P values = P.

Table 4. 3. One-Way A0V statistical analysis for plastic on the beach by Quadrant in winter 2018, summer 2018 and spring 2017. Statistix 10 software (p <0.05).

Period	Source	DF	SS	MS	F	P
Spring 2017	Quadrant	2	0.5013	0.25063	0.43	0.6647
	Error	10	5.8895	0.58895		
	Total	12	6.39077			
Summer 2018	Quadrant	2	39.7717	19.8850	7.84	0.0107
	Error	9	22.8150	2.5350		
	Total	11	62.5867			
Winter 2018	Quadrant	2	2.7450	1.37250	1.92	0.2023
	Error	9	6.4375	0.71520		
	Total	11	9.1825			

DF =Degrees of freedom; SS = sum-of-squares; MS = Mean squares; F ratio = F; P values = P.

The results show significant differences between quadrants (1, 2 and 3) during summer 2018 (p <0.05, p = 0.0107) (Table 4. 3), in relation to the distribution of PD along the beach (the highest site of the beaches (quadrant 1) and the low tide (quadrant 3)). The highest abundances of PD were found in the upper areas of the beaches (quadrant 1). These results are comparable with those reported in Chile by Hidalgo-Ruz et al., 2018. However, in the periods of spring 2017 and winter 2018 there is not a significant difference (p >0.05, p = 0.6647, p >0.05, p = 0.2023, respectively).

4.2 Morphology of microplastics and macroplastics

4.2.1 Microplastics

All collected MP (analysed in FT-IR) were sorted according to size (<0.5 mm, 0.5-1 mm, 1-2.5 mm and 2.5-5 mm), shape (fibre, fragment and pellet), and colour categories.

4.2.1.1 Morphology of microplastics in sand

The results indicated that the sizes of collected microplastics in the sand were in a range of 2.5-5 mm, with around 57% of total MPs, the most abundant MP shape was pellet/ball (50%). The colour with the highest frequency of detection was white (50%) (Table 4. 4). Previous studies showing that fibre is the most abundant type of microplastics in the environment (Lots et al., 2017; Piñon-Colin et al., 2018; Horn et al., 2019; Chen and Chen, 2020). Even so, some studies found fragments as the major type of microplastics in sand beaches (Bancin et al., 2019; Bayo et al., 2019; Piperagkas et al., 2019). High concentrations of pellets have been reported on other beaches near Concepción Bay (Pozo et al., 2020). The variation may result from a different source of microplastics or dissimilar methodologies used. With respect to colour, a diverse range of colours of microplastics in the marine environment has been reported, and the most common colours were white or related (Hidalgo-Ruz et al., 2012). However, it has been reported that the most abundant colours of microplastics found in the beach sand from the Baja California Peninsula, Mexico, were black (Piñon-Colin et al., 2018), like this thesis. Some previous studies suggested that the varied colours indicate diverse origins of microplastics in the environment (Stolte et al., 2015; Bimali Koongolla et al., 2018).

4.2.1.2 Morphology of microplastics in fish

The physical analysis showed that microplastic size ranged between <0.5 and 6 mm. Comparing our results with other studies, the ingestion of microplastics by different groups of fish has commonly been characterized ranging from 0.8 to 5 mm (Browne et al., 2008; Boerger et al., 2010; Foekema et al., 2013). Foekema et al. (2013) reported in North Sea fish a low number of microplastics of small dimensions. The authors suggested that microplastics would not cause physical damage to the carriers in terms of the blockage of their gastrointestinal tract, a false sensation of satiety, or injuries in the digestive tract due to sharp particles. However, the microfibre dimensions reported by Foekema et al. (2013) were larger (>) 0.5 mm (2.5 to 5 mm) and were detected in coastal fish species. This result deserves attention because bigger size particles may affect the ingestion rate in fish species and consequently, in the long term, have health impacts in the population dynamics of fisheries' stocks. The fragment is the most frequent shape (100%) and red and black are the predominant colours (100%) (Table 4. 4; Figure 4. 4). Fibre and fragment are the most commonly detected shapes of microplastics in fish, which is consistent with their predominance in global waters (Boerger et al., 2010; Lusher et al., 2016; Alomar and Deudero, 2017; Wang et al., 2017). A study of microplastics in fish from the North Pacific Central Gyre reported greater fragment abundance (97%) (Boerger et al., 2010), as in Tokyo Bay, Japan (86%) (Tanaka and Takada, 2016). Regarding the predominance of red and black colours, previous studies are consistent since red microplastics have been found in species of fish larvae, who had preferences for the ingestion of red fibres (Steer et al., 2017). Also, Mizraji et al. (2017) found that red microplastics predominated among coastal fish, whereas in North Atlantic species of mesopelagic (Lusher et al., 2016) and species in Musa Estuary and Persian Gulf (Abbasi et al., 2018) ingestion of black microplastics was found.

Table 4. 4. Table of physical characterization of microplastics in different matrices of Concepcion bay during 2016 and summer 2018.

		Sand	Fish
Size	<0.5 mm	0%	50%
	0.5-1 mm	14%	50%
	1-2.5 mm	21%	0%
	2.5-5 mm	57%	0%
Colour	White	50%	0%
	Black	43%	50%
	Red	7%	50%
	Blue	0%	0%
	Transparent	7%	0%
	Other colours	7%	0%
Shape	Fibre	0%	0%
	Pellet/beads	50%	0%
	Fragment	21%	100%

4.2.2 Macroplastics

Several types of macroplastics were present on beaches of Concepción Bay. Among the macroplastics (> 2.5 cm), a large number of remaining plastics found were plastic bottles, fishing nets, cables, foam fragments, bags, and pieces of other synthetic materials, and bits and fragments of plastic foam (**Table 4. 5**). Therefore, the plastic pollution sources on the screened beaches are from sea and land sources. The fragments of plastics found come mainly from construction, tourism, and recreational activities performed on the coasts, as well as fishing, as on many other marine beaches reported elsewhere (UNEP, 2016).

Table 4. 5. Composition of macroplastics (~0.5- >25 cm) collected from >9 m-transects at 6 central Chile sandy beaches in the austral spring of 2017, summer of 2018, and winter 2018 (3 total transect, with 3 quadrants of 3x3m).

Type of plastic items	N° items	%
Ropes/fibre	19	9
Industrial pellet	2	1
Plastic/rigid pieces	54	25
Piece of bag/film	4	2
Fishing gears	18	8.5
Foamed plastics	64	30
Flexibles packing	15	7
Other plastics	36	17
Total	212	100

The physical characterization showed that the size of macroplastics ranged between 0.5 to 600 cm, and the most usual size was between <2.5 (45%), these are the called mesoplastics. The most frequent shape were fragments (30%). Also, the predominant macroplastic colour found was white (35%), followed by purple and orange (other) (14%) (Figure 4. 1). In other parts of the world, a greater abundance of white microplastics has been reported (Maharana et al., 2020). Regarding the size in general, a higher concentration of mesoplastics was found (Figure 10), with particles ranging between 5 mm to 2.5 cm. The DB site had the highest mesoplastic concentration values in the summer and winter of 2018. Lee et al. (2017) reported an average concentration of 13.2 items/m^2 for meso-sized plastic marine debris on 20 beaches in Korea and on the Southeast coast of India. Mesoplastics of the type of fibre, fragments and film are also reported (Jeyasanta et al., 2020). Globally, the proximity to anthropogenic input sites has been found to be a determinant key of mesoplastic concentration in numerous locations (Lozoya et al., 2016). Mesoplastics are formed by the decomposition of larger plastics through mechanical forces, by photolysis, thermooxidation, and thermodegradation and possibly by biodegradation processes (Zhao et al., 2016), which is why the most abundant forms are the fragments of bigger and harder plastics.

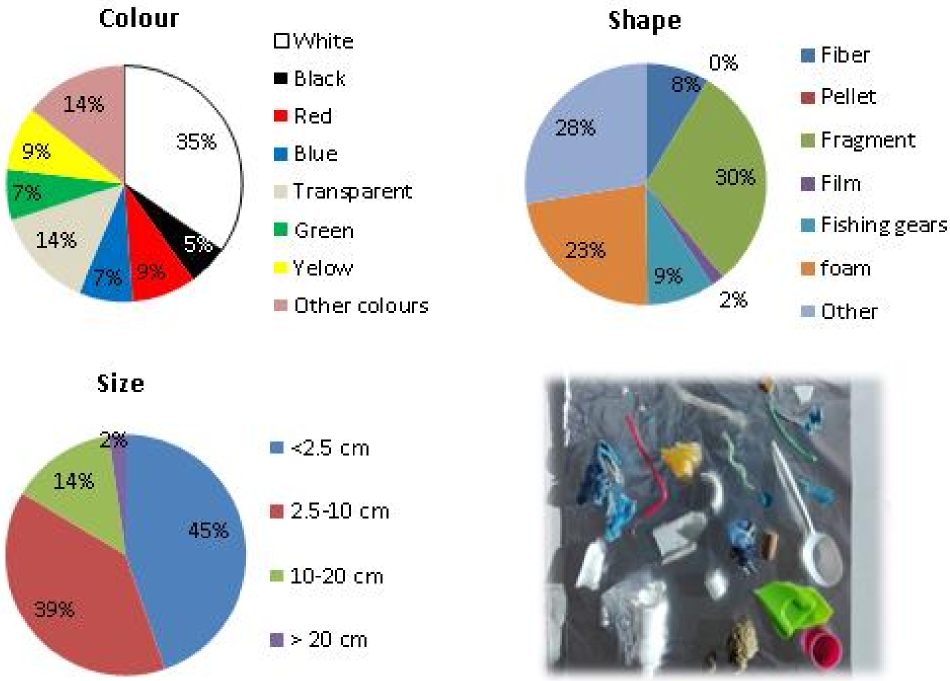

Figure 4. 2. Proportions of the physical characterization (colour, shape, and size) of macroplastics found on beaches of Concepción Bay.

4.3 Polymer analysis of microplastics and macroplastics

4.3.1 Microplastics

Different instruments were used depending on the size of the particles, the smallest particles were analyzed with the Spotlight 400 Microscope and Perkin Elmer Spectrum Frontier, the medium ones with the Perkin Elmer FT-IR Spectrum Two, and the largest ones (microplastics > 1 mm and macroplastics) with the Agilent Cary 630 FTIR spectrometer.

4.2.1.1 Polymer analysis of microplastics in sand

The polymer analysis showed that the microplastics in the sand of beaches in Concepcion bay were composed mainly of polystyrene foam beads (46%) and polypropylene and polyethylene fragments (31%). Also, other polymers such as polytetrafluoroethylene, neoprene and rubber were identified (Figure 4. 3). Consequently, microplastic sources are the deterioration of large plastics. PS, PP, and PE are the most abundant polymers found in many other coastal marine studies (Claessens et al., 2011; Wessel et al., 2016; Karthik et al., 2018; Sagawa et al., 2018; Simon-Sánchez et al., 2019). Anjos et al. (2020) and Delvalle de Borrero et al. (2020) have also observed these same polymer types as the main microplastic pollutants found in the Latin American countries (Mazariegos-Ortíz et al., 2020). PS was previously reported to cause toxicity in zebrafish (Jin et al., 2018), being transferred from Mytilus edulis and Carcinus maenas via the trophic chain (Farrell and Nelson, 2013).

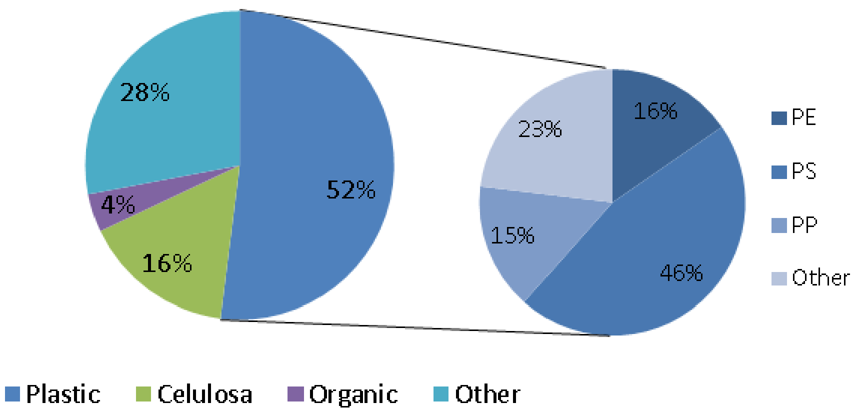

Figure 4. 3. Proportions of the composition of the particles and proportions of the polymer of microplastics found in the sand of Concepción Bay.

4.2.1.2 Polymer analysis of microplastics in fish

The chemical characterization of microplastics showed only two types of polymers (Figure 4. 4, Figure 4. 5). Polyethylene (PE) was the most abundant with 75% and poly(vinyl alcohol) (PVA) (25%). A previous study reported PE concentrations in fish in this study area (Pozo et al., 2019). PE is the most common plastic; its primary use is in packaging (plastic bags, plastic films, geomembranes, containers including bottles, etc.). PVA is a thermoplastic used in the production of different types of paper (e.g. coated, release, inkjet). Thanks to their hydroxyl groups (-OH), which establish hydrogen bonds with similar groups present in the fibres.

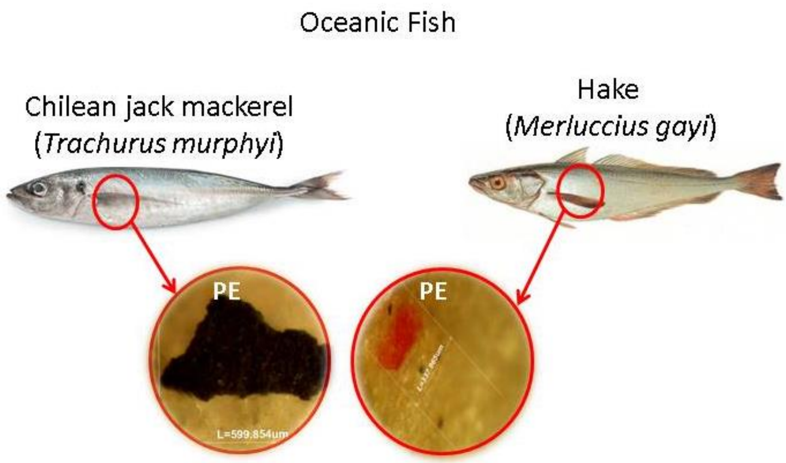

Figure 4. 4. Microplastics found in two species of fish of Concepión Bay.

Studies revealed that pelagic fish (i.e., Chilean horse mackerel) are more likely to encounter low-density polymers (e.g., polypropylene and polyethylene), while demersal species (i.e., Hake) may be more susceptible to high-density microplastics. (e.g., polyvinyl chloride and polyethylene terephthalate) (Lusher et al., 2013), that is why polymers like PVA were found in the hake samples.

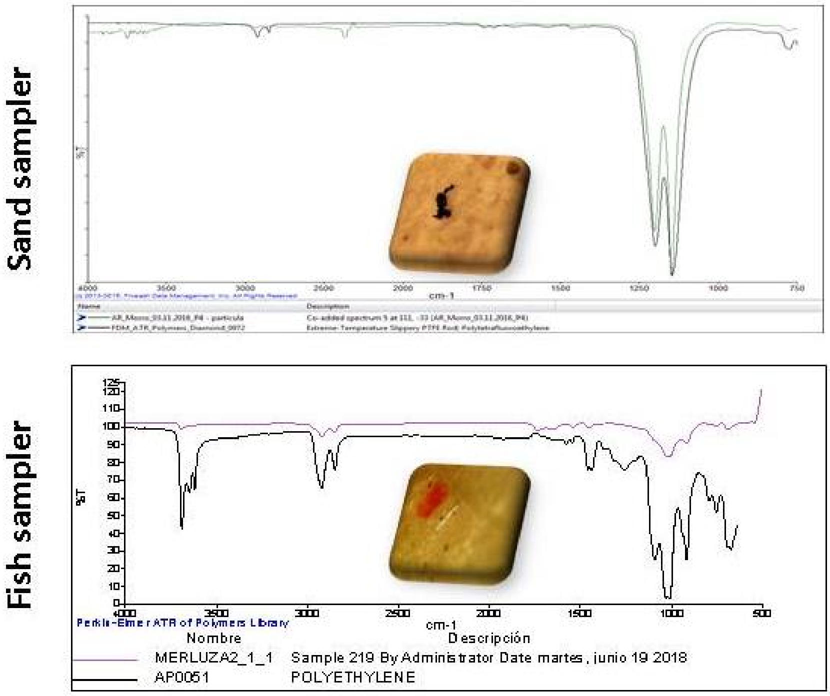

Figure 4. 5. Infrared spectra from the MP observed in the sand (Spotlight 400 Microscope and Perkin Elmer Spectrum Frontier) and fish (Perkin Elmer Spectrum Two FT-IR) of Concepcion Bay.

4.3.2 Macroplastics

The macroplastic samples (100%) collected on the different beaches in the three sampling periods were analyzed on the Agilent Cary 630 FT-IR spectrometer (Figure 4. 6). The chemical analysis of PD showed that the most frequent plastics identified were polypropylene (PP) (38%), and Polystyrene (27%) (Figure 4. 7). These findings are consistent with other studies reported on the Baltic beaches of the Kaliningrad region, Russian beaches, where the prevalent fragments found were polypropylene, foamed polystyrene, foamed polyurethane, and PVC (Esiukova, 2017). On the beaches in Kuching, Sarawak, and Malaysia, polypropylene and polyethylene were the dominant plastic polymers detected (Noik and Tuah, 2015).

PP IR spectra produced distinctive peaks with wavelengths ranging from 2950 to 2720 cm^{-1}. In this spectrum (Figure 15), three groups of bands are clearly observed corresponding to tension movements of the C-H links to 2900 cm^{-1} and C-C tension movements at 1350 - 1450 cm^{-1} and at flexion movements of $–CH_3$ between 1200-1000 cm^{-1} (Velandia Cabra, 2017). PP is typically used in packaging applications (bags, bottles, beverage container caps, and drinking straws), fishing-related applications (nets, rope, and tape), making toys and home appliances (Maharana et al., 2020).

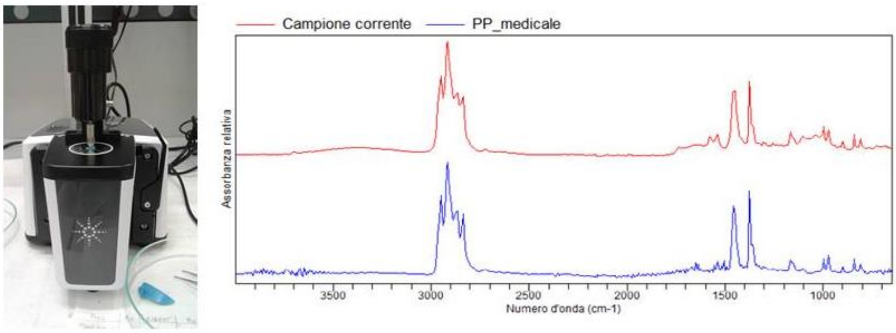

Figure 4. 6. Polypropylene infrared spectra using Agilent Cary 630 FT-IR spectrometer from a macroplastic on Dichato Beach.

Figure 4. 7 shows that in rural beaches (located near a small town) (Dichato (D) and Coliumo (C)), PP was more abundant in all periods except in winter for Dichato, where PS was more abundant. In addition, a greater abundance of PET was observed in spring for Coliumo. On the urban beaches (Bellavista (B), El Morro (M) and Negra (N)), PCV and Nylon were the predominant polymers in spring in Bellavista and El Morro beaches, respectively. In summer, PET and PS polymers prevailed in Bellavista, but in winter there was a homogeneous abundance of macroplastics. At the Desembocadura of the Biobío River (DB), there was an abundance of PS in winter.

Some beaches like Coliumo presented> 30% unspecific polymers. Among them was the Polyurethane Foam, used as buoys by fishermen.

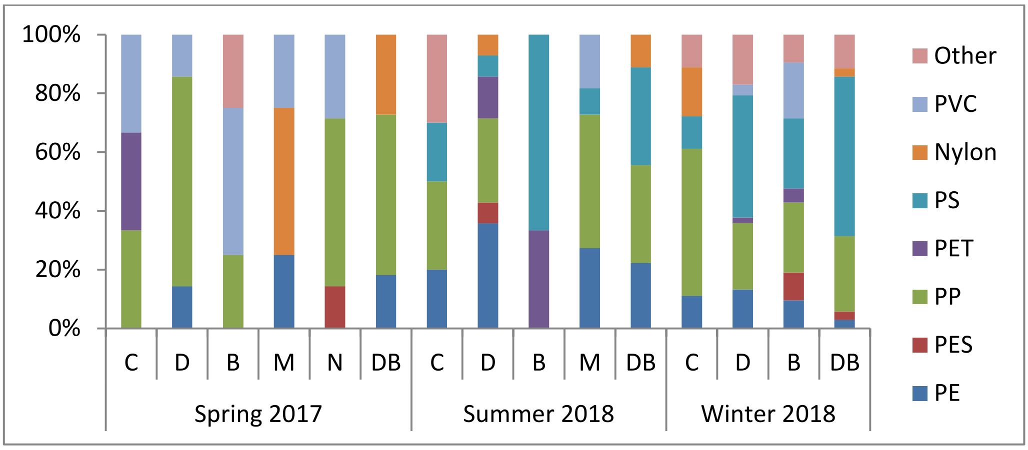

Figure 4. 7. Abundance (%) of polymer types (PE = polyethylene; PES = polyester; PP = polypropylene; PET = polyethylene terephthalate; PS = polystyrene; Nylon; PVC = polyvinyl chloride; others = unspecific polymers) of plastics collected from different beaches of Concepción Bay identified by FT-IR spectroscopy.

4.4 Analysis of POPs in Macroplastics

Persistent organic pollutants (POPs) were analyzed for 42 different chemical compounds, finding 29 of them (70%) in >60% of the samples (macroplastic taken in the spring 2017 and summer 2018 campaigns) (Table 4. 6).

Table 4. 6. Concentration of POPs for PBDEs, PCBs and OCPs (ng/g) in macroplastic in Concepción Bay (D = Dichato Beach; C = Coliumo Beach; M = El Morro Beach; B = Bellavista Beach; N = Negra Beach; DB= Desembocadura of Biobío River Beach).

		2017						2018				
POPs	LOQ	D	C	M	B	N	DB	D	C	M	B	DB
BDE28	0.01-0.09	<0.01	<0.01	0.02	0.07	0.10	<0.01	<0.03	<0.05	<0.04	<0.09	<0.05
BDE47	0.04-0.25	<0.08	0.09	<0.064	1.57	1.29	0.73	0.58	0.98	0.22	<0.04	0.83
BDE66	0.07-0.43	<0.14	<0.14	<0.11	<0.14	<0.07	<0.12	<0.07	<0.43	<0.07	<0.04	<0.13
BDE85	0.04-2.20	<0.06	<0.06	<0.04	<0.06	<0.06	<0.04	<0.18	<2.20	<0.36	<0.62	<0.19
BDE99	0.03-1.42	<0.04	0.10	1.43	1.90	0.91	0.78	0.30	1.47	0.18	<0.40	2.26
BDE100	0.02-0.33	<0.03	0.02	0.33	0.43	0.19	0.16	0.08	1.12	<0.16	<0.31	0.51
BDE153	0.25-1.83	<0.32	<0.33	0.25	20.48	<0.33	<0.26	<0.49	4.73	<1.05	<1.39	<0.99
BDE154	0.12-1.03	<0.15	<0.16	0.14	2.37	<0.16	<0.13	0.31	9.00	<0.36	<1.03	<0.43
BDE183	0.13-1.87	<0.17	<0.18	<0.13	126.19	<0.18	<0.14	0.95	<1.87	<0.40	6.16	1.17
BDE209	0.47-6.17	2.11	9.63	30.20	1147	2.55	79	513	3160	559	1460	387
$\sum_{10}$PBDE		2.11	9.84	32.13	1300	5.05	81	515	3177	559	1466	392
PCB 118	0.01-0.02	0.09	0.07	1.08	5.07	8.11	0.96	0.32	0.56	<0.01	<0.02	<0.01
PCB 28	0.005-0.01	0.17	0.06	0.26	0.38	0.73	0.49	0.11	0.32	<0.01	<0.01	<0.01

PCB 52	0.01-0.02	0.25	0.11	0.73	2.61	6.34	0.74	0.24	0.87	0.30	<0.02	0.24
PCB 101	0.01-0.03	0.30	0.13	1.92	6.17	26.37	2.08	0.81	0.86	0.47	<0.02	<0.01
PCB 138	0.02-0.04	0.15	0.12	1.51	6.61	17.55	2.10	0.89	0.45	0.34	<0.04	0.31
PCB 153	0.01-0.03	0.33	0.28	3.13	8.73	30.69	3.69	1.69	0.96	0.59	0.34	0.73
PCB 180	0.01-0.03	<0.02	0.08	0.32	3.86	3.00	1.03	0.51	<0.02	<0.2	<0.03	0.53
$\sum_7$PCB		1.30	0.85	8.95	33.41	92.75	11.08	2.16	1.63	1.70	0.34	1.28
OP_DDT	0.01-0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	2.13	16.00	2.49	<0.02	<0.01
PP_DDD	0.01-0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	1.72	10.80	2.51	<0.02	0.48
OP_DDE	0.01-0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.18	1.44	0.38	<0.02	<0.01
PP_DDE	0.01-0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	1.20	32.15	1.60	0.55	0.93
OP_DDD	0.01-0.03	<0.02	<0.01	<0.02	<0.01	<0.02	<0.02	0.32	2.67	0.51	<0.03	0.21
PP_DDT	0.01-0.03	<0.02	<0.01	<0.02	<0.02	<0.02	<0.02	8.07	48.05	6.41	<0.03	0.84
∑DDTs								13.6	111	13.9	0.55	2.45
A_HCH	0.01-0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.02	<0.01	<0.02	<0.01
B_HCH	0.01-0.03	<0.02	<0.01	<0.02	<0.01	<0.02	<0.02	<0.02	<0.02	<0.02	<0.03	<0.01
G_HCH	0.01-0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	22.60	0.79	<0.02	<0.01
D_HCH	0.02-0.04	<0.03	<0.02	<0.03	<0.02	<0.03	<0.03	<0.03	<0.04	<0.04	<0.04	<0.02
∑HCH									22.6	0.80		

LOQ for PBDE = calculated by TargetLynx for S/N (peak-to-peak) equal to 9, based on the individual standard response in the sample, LOQ for PCB and OCPs = were calculated from the lowest calibration point (S/N 9).

Σ_{10}PBDEs showed values of 2.1 ng/g to 1 300 ng/g (238 ± 521 ng/g) during the spring of 2017 and 392 to 3 177 ng/g (1 222 ± 1 174 ng/g) during the summer of 2018 (Table 4. 7). From Σ_{10}PBDE congeners analyzed, BDE209 accounted for 99% of the total PBDE composition (Table 4. 6 and Table 4. 7). The highest concentrations were detected on Coliumo Beach in the samples of the summer of 2018 (Figure 4. 8). These findings are similar to other investigations reported in other areas of the world. For instance, the values reported in the literature range between 0.1 and 3 924 ng/g on beaches in the Canary Islands (Camacho et al., 2019), and from 0.02 and 412 ng/g on urban beaches in Costa Rica, Vietnam, USA, and Japan (Hirai et al., 2011).

Figure 17 shows that in the Bellavista beach, both in spring and summer, the concentrations were high as well as on the beach of the Desembocadura of the Biobío River, this can be because the sources are punctual and are not affected by the seasons of the year. On the other hand, on the beaches of Dichato, Coliumo and El Morro, the beaches located north of the bay in the vicinity of the mouth of the Itata River show a difference between both periods, this can be due to the discharge of the river since the discharges in the coastal system have a series of physical, biological, chemical and geological implications (Saldías, 2011) or the increase in plastic pollution in the summer period.

At Coliumo beach, the most substantial proportion of macroplastics was identified as PP and others (polymer mix). In the spring 2017 campaign, the highest concentrations were detected in Bellavista beach, with a predominant composition of BDE209 (88%) and BDE183 (10%) (Table 4. 6). This pattern may be influenced by the different types of polymers found at Bellavista, which were mainly PVC. It is known that PVC is used to cover cables, which are also protected with PBDEs (Wang et al., 2012). The use of penta- and deca-bromodiphenyl ethers in PVC has also been described elsewhere (EBFRIP, 1990; Rahman et al., 2001). The unexpected detection of BDE183 (only at Bellavista Beach) can be ascribed to aerobatic debromination of BDE209, as previously reported (Shi et al., 2013). The high PBDE levels detected on this site are influenced by four main factors. First, PP has been reported to contain PBDEs, as an additive, in particular, deca-bromodiphenyl ethers (EBFRIP, 1990; Rahman et al., 2001). This is also consistent with the dominance of PBDE209 in this study (which is approximately 90% composition in such PBDE mixture). Second, previous studies have determined the relationship between polymer types and the physicochemical properties of pollutants. For example, PP has a high partitioning affinity to PBDEs due to its high log KPP-W (> 5) (Schenker et al., 2005). Third, the increase in tourist activity (90% increase) in the Bay of Coliumo during the summer season. Fourth, there is a convergence of the oceanic currents (the superficial currents (S-NW) and a deep current (NNE)) in the lower corner of the bay, facilitating the accumulation of macroplastics on the beach, where the sampling was conducted (SUBPESCA, 2018).

Table 4. 7. Concentrations (Median ± DS) of total PBDEs, PCBs, and OCPs (DDTs, HCHs) measured in plastic debris from six beach sites of Concepción Bay.

Period	Location	Compound [concentrations in ng/g]			
		Σ_{10}PBDEs	Σ_7PCBs	DDTs	HCHs
Spring 2017	Dichato (D)	2.1 ± 0..0	1.3 ± 0.1	<LOQ	<LOQ
	Coliumo (C)	9.8 ± 4.8	0.9 ± 0.1	<LOQ	<LOQ
	El Morro (M)	32.1 ± 12.2	9.0 ± 1.0	<LOQ	<LOQ
	Bellavista (B)	1300 ± 400	33.4 ± 2.8	<LOQ	<LOQ
	Penco, Negra beach (N)	5.0 ± 1.0	92.7 ± 11.8	<LOQ	<LOQ
	Desembocadura (DB)	80.9 ± 39.3	11.1 ± 1.1	<LOQ	<LOQ
Summer 2018	Dichato (D)	515 ± 229	4.6 ± 0.5	13.6 ± 2.9	<LOQ
	Coliumo (C)	3177 ± 1289	4.0 ± 0.3	111.2 ± 18.3	22.6 ± 0.0
	El Morro (M)	559 ± 323	1.6 ± 0.1	13.9 ± 2.2	0.8 ± 0.0
	Bellavista (B)	1466 ± 729	0.3 ± 0.0	0.6 ± 0.0	<LOQ
	Desembocadura (DB)	392 ± 173	1.8 ± 0.2	2.5 ± 0.3	<LOQ

<LOQ = Below LOQ

Regarding the group of PCBs, in this study, Σ_7PCBs were low, ranging from 1 to 93 ng/g (25 ± 36 ng/g) for samples taken during the spring of 2017 and 0.3 to 5 ng/g (2 ± 2 ng/g) for samples obtained in the summer of 2018. The highest concentrations were detected at Negra Beach (Spring 2017), located in Penco City (Table 4. 7; Figure 4. 8). These results are lower than those reported in San Diego, California, beaches (USA) (3 and 47 ng/g) (Van et al., 2012), in beaches of Canary Islands (1 and 772 ng/g) (Camacho et al., 2019) and between 1 and 436 ng/g in urban beaches (Costa Rica, Vietnam, USA, and Japan) (Hirai et al., 2011).

PCB153 (12%), a high molecular weight PCB, was the most predominant congener, followed by PCB101 (10%) and PCB138 (10%). The dominance of high molecular weight PCBs could be affected by the high industrial activity in the city of Penco during the 20th century. Penco was one of the most important industrial centres in southern Chile, hosting the National Factory of Flat Glasses located in Lirquén, the National Factory of Dinnerware, the South

American Phosphate Company, the coal mines of Lirquén and Cerro Verde, the Port of Lirquén, among other activities of secondary economic importance (Figueroa, 2012).

Figure 4. 8 shows that on the beaches of El Morro, Bellavista, and the Desembocadura of the Biobío River, the concentrations were higher in spring compared to summer, increasing up to 100 times its value. On the other hand, the beaches of Dichato and Coliumo show an increase in the concentration of PCBs in the summer period.

Regarding the group of chlorinated pesticides, OCPs, concentrations were only detected in the samples taken in the summer of 2018. Levels of DDTs ranged from 1 to 111 ng/g (28 ± 47 ng/g). The highest concentrations were detected at Coliumo Beach in the summer of 2018 (Table 4. 6 and Table 4. 7). The pp'-DDT was the most predominant isomer (> 50%) and pp'-DDE was 26%. The DDT/(DDE+DDD) ratio>1 suggested a fresh application of DDT (Li et al., 2006). These findings are likely the result of two sources: i) the use of an old stock of DDT or ii) the use of other pesticide mixtures, for example, the use of Dicofol, which contains DDT impurities (Eng et al., 2016), in agricultural activities in the surrounding area of the Coliumo Bay.

These results are similar to values detected in urban beaches (Costa Rica, Vietnam, USA, and Japan) (0.6 to 138 ng/g) (Hirai et al., 2011), lower than the Canary Island beaches (0.4 to 3 776 ng/g) (Camacho et al., 2019) and higher than San Diego, California, beaches (USA) (1.5 to 75 ng/g) (Van et al., 2012).

HCHs (α- and γ-) in macroplastics ranged from 1 to 23 ng/g (5 ± 10 ng/g) (Table 4. 6 and Table 4. 7). However, HCHs levels in PD have not been previously reported.

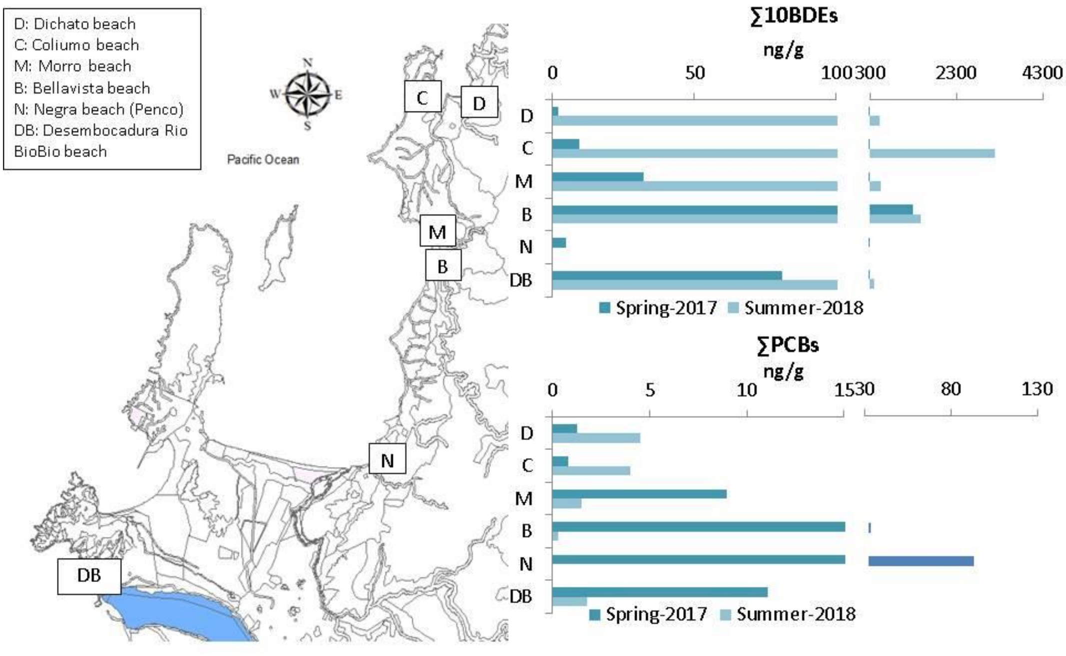

Figure 4. 8. Concentrations (ng/g) of $\sum_{10}$PBDES and $\sum_{7}$PCBs in macroplastics on beaches of Concepción Bay (D = Dichato Beach; C = Coliumo Beach; M = El Morro Beach; B = Bellavista Beach; N = Negra Beach; DB= Desembocadura of Biobío River Beach).

Chapter 5. Conclusion

1) This study developed an evaluation of the state of contamination by plastics (micro, meso and macroplastics) on the coasts of the province of Concepción, particularly in the coast of Central Chile in Coliumo and Concepción Bay and on the adjacent beach at the mouth of the Biobío River in abiotic and biotic matrices.
2) The abundance of plastic debris (meso and macroplastics) and microplastics detected in this study was lower compared to other studies around the globe. We suggest that the size of the surrounding cities and consequently the high population density have an important influence which is measured with the amount of waste. However, we investigated the factor that could affect the amount of marine debris in the study beaches and we found out that these beaches are regularly cleaned by companies managed by the Municipality (through the Department of Ornament and Environment) corresponding to each commune (even so the regularity of cleaning is low and is carried out superficially).
3) Based on our obtained results, fragment and fibers account for 100% of the collected MP particles in abiotic and biotic matrices, indicating the presence of secondary MPs derived from larger plastics.
4) Black fragments and polymers of polypropylene (PP), polyethylene (PE) and polystyrene (PS) were the most abundant MPs in both the biotic and abiotic samples from Concepción Bay. The identification and characterization of polymer types in plastics are essential because it allows an assumption on the sources of the plastic. These findings are consistent with the high abundance of plastics in the industrial market i.e., polypropylene, polyethylene and polystyrene are the most commonly used in industrial, commercial, fishing, and household activities. These types of plastics represent 39% of the European demand for plastics (Plastic Europe, 2010). In addition, the black fragments are used in low-density PP bags, these are widely used in small businesses, neighbourhood stores and popular fairs in Chile, PE bags are also widely used for garbage and PS in styrofoam containers. Black plastics are also used in agriculture as pipes or containers for plants and also in the industry. We suggest that the polymers found probably from the same garbage that people leave on the beaches. In the case of microplastics, the samples taken from the sand in this study can even be reaching the sea where the fishing zones (~40 nautical miles) is located and influence the organisms (fish).
5) In the same way, the macroplastics and mesoplastics found in the sand of the beaches of the province of Concepción were the PP, mainly fragments and white colour. These plastics came from larger plastics, they were the remains of bottles, toys, styrofoam containers and fishing gear, where it is estimated that more than 80% of the waste washed up on the beaches comes from the waste of the same users of beaches.
6) Different measures around the world have been implemented to reduce the impact of plastics on the environment. An example of them are the regulations mentioned in chapter 1.5 of this thesis, in addition to some environmental management measures, one example is the case of Spain that have developed daily cleaning strategies in high season (summer) in the morning and afternoon, for emptying bins,

manual sand sweeping, selective collection, mechanical screening of the sand on the beach and the cleaning and irrigation services with water of the paved areas, thus making sure to keep the beaches clean and free of plastic contamination. They have also implemented boats that are responsible for cleaning floating debris on the surface of seawater. The device has two vessels that operate every day. Also, users can find out about beach conditions through digital platforms (web sites and AP mobile). These strategies serve as an example for countries such as Chile, which despite scarce municipal resources can encourage daily cleaning, the use of garbage cans on the beaches, manual sweeping and selective collection and boats that are responsible for cleaning floating waste in seawater and in the future the use of mechanical screening of beach sand and thus reduce microplastics in the sand, it is also important to encourage the reduction of the consumption of plastics in general and raise awareness in the population.

7) Furthermore, these findings reinforce the need to improve effective sustainable management actions of solid waste treatment and disposal in the coastal cities of Chile. An example of this is Italy, where citizens grow up in a public system where more than 47% of waste is collected selectively and the education sector and local initiatives join awareness campaigns on recycling. The most recycled and reused plastic are bottles (PET) and, on the other hand, mixed plastic that is recycled for construction, as an insulating material, for false ceilings and walls, or on asphalt; and in steel mills instead of carbon, and thanks to water vapour it reduces CO_2 emissions. Since 2019 the Italian Government approved the “End of Waste” decree where some materials, such as plastics and diapers are no longer considered garbage, but reusable raw material. However, Chile is advancing in policies related to plastic waste and we hope that in a near future it will be possible to take concrete measures to reduce this debris on the coastal area. On the other hand, although there are companies and associations of recyclers in Chile and the society is increasingly aware of the problem of plastics, it is necessary to improve the communication between the government and society to identify a sustainable mechanism to handle the garbage at a small scale (small towns, artisanal fishery populations, low-income areas) in the local and national perspective.
8) In the case of biotic samples of fish of commercial importance, more research is needed to establish the risk of human exposure to this species and the potential impact of microplastics on Chilean fishing activities. Although microplastics were found in digestive tracts, they are not consumed by humans but by other species. It is also necessary to do more studies in species such as bivalves where the consumption of these organisms can directly affect humans. It is also important to mention that the microplastics analysis is also needed in seawater in industrial fishing areas since fishery inputs can play an important role in the marine ecosystem since they act as sources of MPs that contribute to the direct ingestion of MPs.
9) Regarding the chemical loading on the macroplastics, this study is the first information of POPs sorbed in macroplastics collected on beaches of the province of Concepción in Chile. In this study, high concentrations of flame retardants (PBDEs) and PCBs were found. This information is very important as it provides new information on solid waste management and shows the need to determine the chemical load. The future of plastics is still unknown but could represent a potential

exposure for wildlife and for humans, especially, on tourist beaches that are highly crowded during the summer season. Nevertheless, further research is still needed to elucidate proper environmental strategies to reduce the impact of plastic on the environment.

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APPENDIX 1. Scientific Articles

Marine Pollution Bulletin 152 (2020) 110881

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Baseline

Marine plastic debris in Central Chile: Characterization and abundance of macroplastics and burden of persistent organic pollutants (POPs)

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Abstract

In this study, we characterized plastic debris (PD) found on beaches from Concepción Bay in central Chile during spring 2017 and summer 2018. The identification of polymers was carried out using FT-IR. Persistent organic pollutants (POPs) were extracted with hexane using ultrasonic bath and further quantified through GC-MS. The highest abundance of PD was obtained during the summer (4.1 ± 3.7 items/m^2), with the most common size range between 2.5 - 10 cm (42%) and the most frequent shape were fragments (44%). FT-IR analysis showed that polypropylene was the most recurrent plastic polymer found. The $\sum_{10}$PBDEs ranged from 2.1 to 1300 ng/g in spring 2017 and 392 to 3177 ng/g in summer 2018. $\sum_{7}$PCBs ranged from 0.9 to 93 ng/g during the spring 2017 and 0.3 to 4.5 ng/g for summer 2018. This study is the first with information on POPs occurrence in the plastic debris of central Chile.

Key words: Plastic debris, POPs, beach, macroplastics, Central Chile

During the 20th century, the development of the plastics industry played an essential role in the improvement of the quality of life. However, nowadays, the unsustainable disposal of these residues is a relevant environmental problem (Llorca et al., 2014). The packaging sector is the primary user of plastic materials, where Polypropylene (PP) is the more common type of plastic, representing around 19% of the total demand (Plastics Europe, 2017). As a consequence of their heavy usage and resistance to degradation, large areas of the oceans contain plastic debris (NOAA, 2019). Macroplastics are generally defined by having a size >25mm (Romeo et al., 2015). However, despite their larger size, it has been reported that they are regularly ingested and retained by various marine species, including seabirds, fish, and cetaceans (Derraik, 2002; Teuten et al., 2007; Fossi et al., 2017).

Plastic fragments on the beaches are derived either (1) from inland sources being transported to coasts by water streams, wind, drainage systems, or human activity, or (2) directly from the oceans where low density floating varieties accumulate and are transported across great distances (Frias et al., 2010). Plastic debris (PD) acts as a vector of organic pollutants because of their hydrophobic nature (Mato et al., 2001; Karapanagioti and Klontza, 2008). Among the many types of contaminants, the most commonly found are polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), nonylphenol (NP), polycyclic aromatic hydrocarbons (PAHs), and polybrominated diphenyl ethers (PBDEs). This latter is a plastic additive that changes some characteristics of final products (Teuten et al., 2009) such as color, resistance to heat and aging, flexibility, and performance. In some cases, the additive ingredients constitute up to 50% of the proportion of the plastic product (Bauer and Herrmann, 1997; Rochman, 2015).

Recent studies have been devoted to characterizing the anthropogenic marine debris (AMD) along the Chilean Coast, revealing that the most abundant AMD are plastics and cigarette butts coming from local sources increasing over time (Hidalgo-Ruz and Thiel, 2013 and 2018). However, there is still a lack of information regarding PD spatial distribution, loading of chemicals, and their sources.

The objectives of this study were first to physically and chemically characterize the macroplastics collected from tourist beaches of Central Chile and second, to determine and quantify the persistent organic pollutants (POPs) present in these PDs. POPs have been restricted under the Stockholm Convention (SC) (UNEP, 2015), which Chile signed in May 2001 and ratified in 2005. The results obtained herein will contribute new information to motivate the development of national strategies aiming to reduce the impact of PD in the marine ecosystem.

Six beaches were selected along the coastline of the province of Concepción (Fig. 1). A description of each sampling site is presented in textS1 (Supporting material).

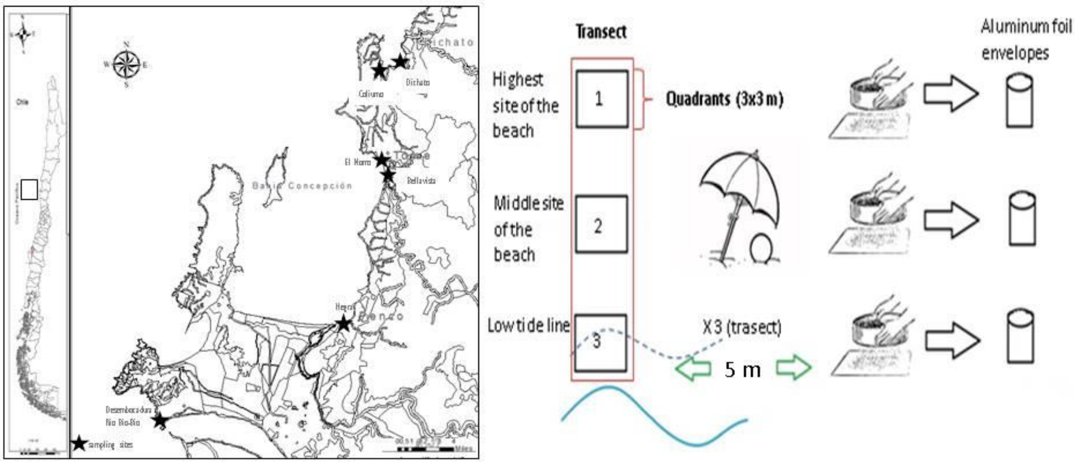

Fig. 1. Locations of beach surveys a) location and b) sampling design (black stars=show sampling sites= highest site of the beach; 2= middle site of the beach; 3= low tide line)).(Van et al., 2012,; Hidalgo-Ruz et al., 2018).

PD was collected, at each beach, in November 2017 and March 2018 (Table S1) at the following locations: in Dichato (D), Coliumo (C), El Morro (M), Bellavista (B), Negra, (N) and Desembocadura (DB). For the collection of samples,three transects (approximately every 5 meters) were taken perpendicular to the coast. Transects were sampled from the highest site of the beaches (base of dunes or start of a road) (quadrant 1) to the low tide line (quadrant 3). Each transect had 3 quadrants of 3 × 3 m (Fig. 1), delimited by ropes and sticks, following the proposal of Hidalgo-Ruz et al., 2018. The sand of each quadrant was sieved in situ through a sieve metal screen (1 mm) and collected in aluminum foil enveloppes (Taniguchi et al., 2016); skin contact with plastic materials was avoided. The samples were finally kept at 4°C until their analysis.

The PDs found were measured for physical properties such as color, shape, and size (MSFD, 2013) using a caliper (model Festa 150/0.02mm) and stainless steel metal ruler (12 inches (300 mm)) and chemically analyzed (polymer type and chemical burden of POPs).

The identification of polymers was carried out with Agilent Cary 630 Fourier transformed infra-red spectrometer (FT-IR) (Fossi et al., 2017).

The determination of the chemicals in the PD samples was carried out through chemical extraction; determination and quantification of the chemicals were conducted using gas chromatography-mass spectrometry (GC-MS). First, 1 g of the sample was frozen in liquid nitrogen and crushed using homogenization equipment for cryogenic samples (Retsch, MM301) (Kühn et al., 2018). POPs were extracted using hexane and an ultrasonic bath for 15 minutes and concentrated under a gentle nitrogen atmosphere up to 1 ml. Silica gel and sodium sulfate columns were used to clean-up the samples, eluting with DCM/hexane 1:1. After clean-up, the samples were concentrated up to a volume of 100 µl under a gentle nitrogen stream at 35° C, then 50 µl of nonane and hexane were added, and further concentrated up to 50 µl. This final extract was used to quantify PCBs (7 congeners: 28, 52, 101, 118, 138,153 and 180), OCPs (13 compounds) including DDT isomers (o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD, o,p'-DDT and p,p'-DDT), HCHs isomers (α-HCH, β-HCH, γ-HCH, δ-HCH, ε-HCH), PECB and HCB, PBDEs (10 congeners: BDE28, 47, 66, 85, 99, 100, 153, 154, 183, 209). PCBs and OCPs were analyzed on an Agilent 6890 gas chromatograph-mass spectrometry (GC-MS) equipped with a 30 m by 0.25 mm i.d, DB-5 (5% diphenyl dimethyl polysiloxane) capillary column with a film thickness of 0.25 mm. For PBDEs, a gas chromatography-mass spectrometry (GC-MS) on a 7890A GC instrument (Agilent, USA) equipped with an RTX-1614 column (15 m × 0.25 mm x 0.10 m) (Restek, USA) was chosen to perform the analysis, coupled to an AutoSpec Premier MS (Waters, Micromass, UK). The mass spectrometer (MS) was operated in EI + mode in the resolution of > 10 000.

PCBs were quantified with 8 point calibration with concentrations from 1 ng/ml to 4000 ng/ml, linearity was maintained in the whole range. Calibration standards for PCBs were provided from LGC Standards. PCB121 was used as an internal (syringe), standard PCB30, and PCB185 as extraction standards. Instrumental detection limits (IDL) and limits of quantification (LOQ) were calculated from the lowest calibration point as an amount producing a signal to noise 3 (LOD) and 10 (LOQ). All PBDE standards were obtained from Wellington. POPs concentrations in the samples were recovery-corrected using surrogate compounds (i.e., PCB (30 and 185), and 13C12-labeled PBDE spiked before analysis (100 µl). Procedural blanks (n=14) were also assessed.

The dataset was processed using ANOVA one way, withTukey tests to make multiple comparisons. The Statistix 10 software performed the analyses. The results were considered statistically significant at $p < 0.05$.

Results showed a large amount of plastic debris on the beaches sampled in both seasons, spring (November 2017) and summer (March 2018), along the coast of the province of Concepción.

Several types of PD were present on remote rural beaches (located near a small town) (D and C). Among the macroplastics (> 25 cm), a large number of remaining plastics found were: plastic bottles, fishing nets, cables, fragments of pens, bags, and pieces of other synthetic materials, and bits and fragments of foam plastic (Table S2). Therefore, the plastic pollution sources on the screened beaches are fromsea and land sources. The fragments of plastics found come mainly from construction, tourism, and recreational activities performed on the coasts, as well as fishing, as on many other marine beaches reported elsewhere (UNEP, 2016).

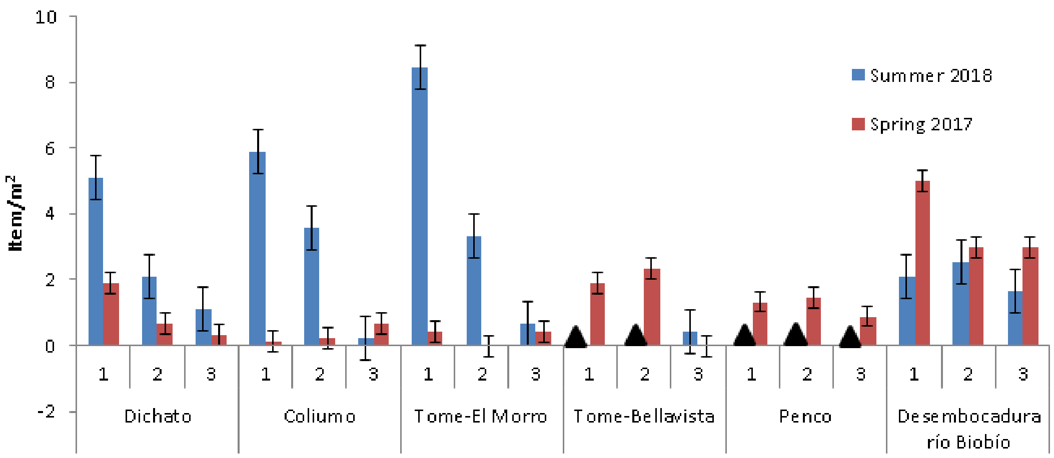

Fig. 2. Macroplastic abundance (ítem/m2) found in beaches located in central Chile for quadrant (1= highest site of the beach; 2= middle site of the beach; 3= low tide line; ▲ *= no sample available for municipality cleaning operation).*

The results showed a significant difference for the PD abundance between the spring 2017 and summer 2018 periods ($p <0.05$, $p = 0.007$) (Table S3). In summer, a higher abundance of PD was detected with average values of 2.9 ± 1.0 items/m^2, ranging from 1.1 items/m^2 on the beach (B) to 4 items/m^2 in (M). In spring, an average of 1.0 ± 0.5 items/m^2 was found, ranging from 0.3 items/m^2 (site M) to 1.4 items/m^2 in (B) (Fig. 2). According to the clean-coast index (CCI) (Alkalay et al., 2006), these beaches are extremely dirty (fragments>1 plastic parts/m^2). A recent study conducted along the Chilean Coast determined an average abundance of 2.15 items per m^2 for the year 2016 (Hidalgo-Ruz et al., 2018). Studies in other areas worldwide x have reported densities accounting for 1 item/m^2 range on beach sectors (Galgani et al., 2015). Furthermore, in studies conducted on the beaches in South Korea, there were recorded the highest PD abundance with 2.7 items/m^2 in Dukpo Beach, (Lee et al., 2013), with 10 items/m^2 in Po-Hang (Lee et al., 2015); and Ivar do Sul et al. (2009) reported a high abundance of PD on the beaches of Fernando de Noronha Island in Brazil (29 items/m^2).

The results show significant differences between quadrants (1, 2 and 3) during summer 2018 ($p < 0.05$, p=0.0107) (Table S4), in relation to the distribution of PD along the beach (the highest site of the beaches (quadrant 1) and the low tide (quadrant 3). The highest abundances of PD were found in the upper areas of the beaches (quadrant 1). These results are comparable with those reported in Chile by Hidalgo-Ruz et al., 2018.

The physical characterization showed that the size of macroplastics ranged between 0.3 and 100 cm, and the most usual size was between 2.5 and 10 cm (42%). The most frequent shape was in the form of fragments (44%). Also, the predominant PD color found was white (22%), followed by purple and orange (26%). The chemical analysis of PD showed that the most frequent plastics identified were mostlypolypropylene (PP) (38%), polyethylene (PE) (10%), PVC (10%), PS (9%), Nylon (8%), polyester (4%), and PET (2%) (Fig. 3). These findings are comparable with other studies reported from the Baltic beaches of the Kaliningrad region, Russia from, where the prevalent fragments found were polypropylene, polyethylene, foamed polyethylene, foamed polystyrene, foamed polyurethane, and PVC (Esiukova, 2017). On the beaches in Kuching, Sarawak, and Malaysia, polypropylene, and polyethylene were the dominant plastic polymers detected (Noik and Tuah, 2015).

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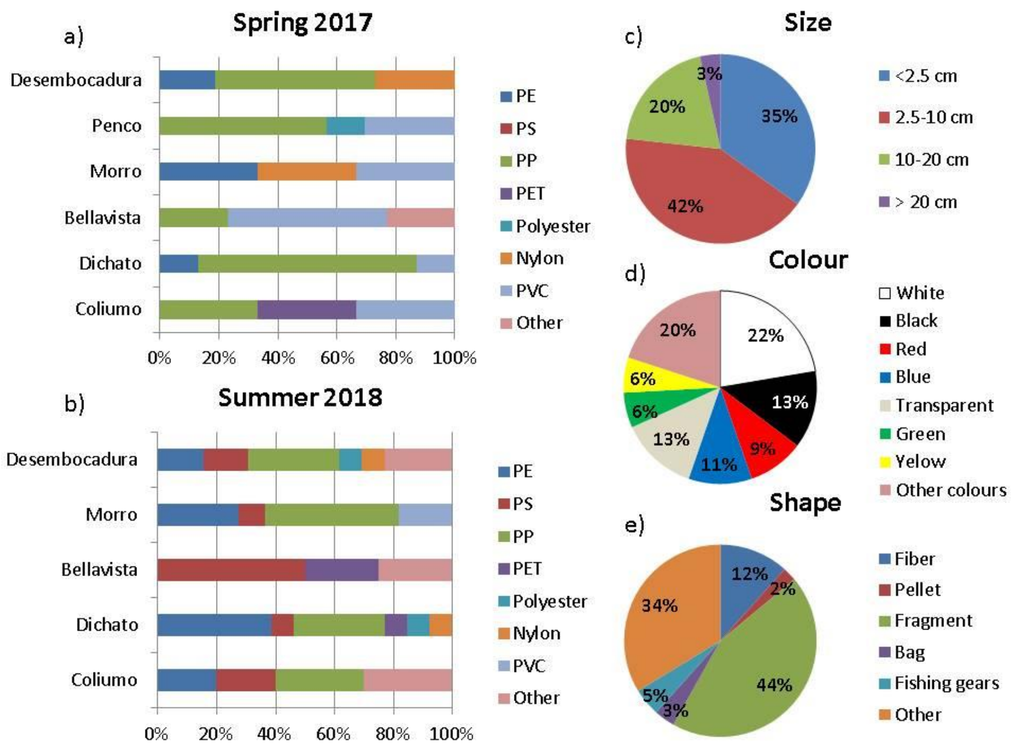

Fig. 3. Proportion of macroplastic (% of number of items per m^2) of each polymer groups detected at beaches of Central Chile a) in spring 2017; b) in summer 2018; c) Physical characterization of macroplastic size; d) color; and e) shape.

POPs were analyzed for 42 different chemical compounds, and we found 29 of them (70%) in>60% of the samples. The burdens of chemicals in PD were mainly characterized by flame retardants such as PBDEs (Table 1). Σ_{10}PBDEs showed values of 2.1 ng/g to 1 300 ng/g (238 ± 521 ng/g) during the spring of 2017 and 392 to 3 177 ng/g (1 222 ± 1 174 ng/g) during the summer of 2018 (Table S5). From Σ_{10}PBDE congeners analyzed, BDE209 accounted for 99% of the total PBDE composition (Fig. 4; Tables 1 and S1). The highest concentrations were detected on Coliumo Beach in the summer 2018 samples (Fig. 4). These findings are similar to other investigations reported in other areas of the world. For instance, the values reported in the literature range between 0.1 and 3 924 ng/g on Canary Islands beaches, and from 0.02 and 412 ng/g on urban beaches in Costa Rica, Vietnam, USA, and Japan (Hirai et al., 2011).

At Coliumo beach, the most substantial proportion of the PD was identified as PP and others (polymer mix). In the spring 2017 campaign, the highest concentrations were detected in Bellavista beach, with a predominant composition of BDE209 (88%) and BDE183 (10%) (Fig. 4). This pattern may be influenced due to the different types of polymers found at Bellavista, that was mainly PVC. It has is known that PVC is used to cover cables which are also protected with PBDEs (Wang et al., 2012). The use of penta- and deca-bromodiphenyl ethers in PVC has also been described elsewhere (EBFRIP, 1990; Rahman et al., 2001). The unexpected detection of BDE183 (only at Bellavista beach) can be ascribed to aerobatic debromination of BDE209, as previously reported (Shi et al., 2013). The high PBDE levels detected at this site are influenced by four main factors; first, PP has been reported to contain PBDEs, as an additive, in particular, deca-bromodiphenyl ethers (EBFRIP, 1990; Rahman et al., 2001). This is also consistent with the dominance of PBDE209 in this study (which is approx. 90% composition in such PBDE mixture); second, previous studies have determined the relationship between polymer types and pollutants physicochemical properties. For instance, PP has a high partitioning affinity to PBDEs due to its high log KPP-W (> 5) (Schenker et al., 2005) (Table S6); third, the increase in tourism activity (90% increase) in the Bay of Coliumo during summer season; and fourth, there is a convergence of the oceanic currents (the superficial currents (S-NW) and deep one (NNE)) in the lower corner of the bay facilitating the accumulation of macroplastics on the beach, where the sampling was conducted (SUBPESCA, 2018).

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Regarding the group of PCBs, in this study Σ7PCBs were low, ranging from 1 to 93 ng/g (25 ± 36 ng/g) for samples taken during spring 2017 and 0.3 to 5 ng/g (2 ± 2 ng/g) for samples obtained in summer 2018. The highest concentrations were detected at Negra Beach (Spring 2017) located in Penco City (Table 1; Fig. 4). These results are lower than those reported in San Diego, California beaches (USA) (3 and 47 ng/g) (Van et al., 2012), in beaches of Canary Islands (1 and 772 ng/g) (Camacho et al., 2019) and between 1 and 436 ng/g on urban beaches (Costa Rica, Vietnam, USA, and Japan) (Hirai et al., 2011).

The PCB153 (12%), a high molecular weight PCB, was the most predominant congener, followed PCB101 (10%), PCB138 (10%). The dominance of high molecular weight PCBs could be affected due to the high industrial activity at Penco city during the 20th century. Penco was one of the most important industrial centers in southern Chile hosting the National Factory of Flat Glasses located in Lirquén, the National Factory of Loza, the South American Phosphate Company, the coal mines of Lirquén and Cerro Verde, the Port of Lirquén, among other activities of secondary economic importance (Figueroa, 2012). The main plastic polymer detected was polypropylene (PP).

Regarding the group of chlorinated pesticides, OCPs, concentrations were only detected in the samples taken in the summer of 2018. Levels of DDTs ranged from 1 to 111 ng/g (28 ± 47 ng/g). The highest concentrations were detected at Coliumo Beach in summer 2018 (Fig. 4; Table 1). The p,p'-DDT was the most predominant isomer (>50%) and pp´-DDE was 26%. The DDT/(DDE+DDD) ratio >1 suggested a fresh application of DDT (Li et a., 2006). The DDT/(DDE+DDD) ratio >1 suggested a fresh application of DDT (Li et a., 2006). These findings are likely the result of two sources: i) the use of old stock of DDT or ii) the utilization of other pesticides mixtures for example Dicofol which contains DDT impurities (Eng et al., 2016), use in agricultural activities in the surrounding area of Coliumo bay (See text S1).

Table 1. Concentrations (Median ± DS) of total PBDEs, PCBs, and OCPs (DDTs, HCHs) measured in plastic debris from six beach sites of the Concepción Bay.

Period	Location	Compound [concentrations in ng/g]			
		ΣPBDEs	ΣPCBs	ΣDDTs	ΣHCHs
Spring 2017	Dichato (D)	2.1 ± 0..0	1.3 ± 0.1	<LOQ	<LOQ
	Coliumo (C)	9.8 ± 4.8	0.9 ± 0.1	<LOQ	<LOQ
	Morro (M)	32.1 ± 12.2	9.0 ± 1.0	<LOQ	<LOQ
	Bellavista (B)	1300 ± 400	33.4 ± 2.8	<LOQ	<LOQ
	Penco, Negra beach (N)	5.0 ± 1.0	92.7 ± 11.8	<LOQ	<LOQ
	Desembocadura (DB)	80.9 ± 39.3	11.1 ± 1.1	<LOQ	<LOQ
Summer 2018	Dichato (D)	515 ± 229	4.6 ± 0.5	13.6 ± 2.9	<LOQ
	Coliumo (C)	3177 ± 1289	4.0 ± 0.3	111.2 ± 18.3	22.6 ± 0.0
	Morro (M)	559 ± 323	1.6 ± 0.1	13.9 ± 2.2	0.8 ± 0.0
	Bellavista (B)	1466 ± 729	0.3 ± 0.0	0.6 ± 0.0	<LOQ
	Desembocadura (DB)	392 ± 173	1.8 ± 0.2	2.5 ± 0.3	<LOQ

<LOQ = Below LOQ

This results are similar to values detected in urban beaches (Costa Rica, Vietnam, USA, and Japan) (0.6 to 138 ng/g) (Hirari et al., 2011), lower than Canary Islands beaches (0.4 to 3776 ng/g) (Camacho et al., 2019) and higher than San Diego, California beaches (USA) (1.5 to 75 ng/g) (Van et al., 2012).

HCHs (α- and γ-) in macroplastics ranged from 1 to 23 ng/g (5 ± 10 ng/g). However, HCHs levels in PD has not been previously reported.

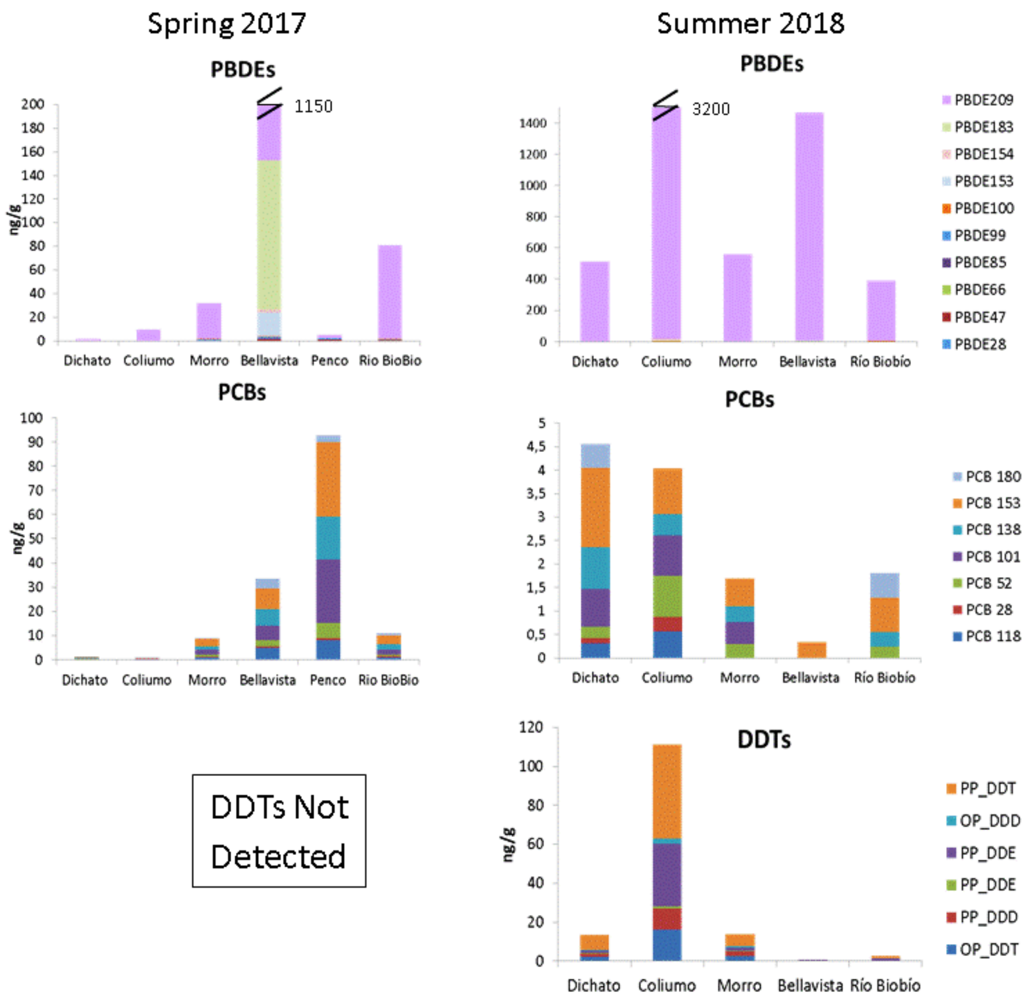

Fig. 4. POPs concentration in the PD collected on the beaches of the Concepción bay in the periods of spring 2017 and summer 2018.

The present study provides new information on plastic debris pollution from six touristic beaches, along the coast of Biobío region, in central Chile. In general, PD distribution was high at the top quadrant compared to the bottom area. We observed the difference between seasons, showing a higher abundance of PD during the summer on touristic beaches. The physical characterization showed high numbers of PD in the size of 2.5 to 10 cm, followed by<2.5 cm (mesoplastic), with a prevalence of white color fragments. Polypropylene and polyethylene were the most abundant polymers. Of all POPs analyzed, BDE209 showed the highest prevalence of PBDEs, followed by>PCBs (PCB153)>DDT (pp'-DDE). These findings are similar to the results obtained from other beaches in the world (Table S7). Nevertheless, further research is still needed to correlate the relationship between the type of polymers and POPs.

Furthermore, this information could contribute to future national trategies of plastic pollution and the identification of potential sources to reduce the impact of plastic debris in the marine environment.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

The authors thank FONDECYT grant n°1161673 (PI: Karla Pozo) and the logistic support of Williams Urbina and Mariett Torres. Thank you to CIPA (Centro de Investigación Polímeros Avanzados) (CONICYT Regional, GORE BIO BIO, R17A10003), and CMA (Centro de microscopia avanzada) Universidad de Concepción in Chile. This research was supported by the RECETOX Research Infrastructure (LM2015051 and CZ.02.1.01/0.0/0.0/16_013/0001761) at Masaryk University.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2019.110881.

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Marine Pollution Bulletin 151 (2020) 110786

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Persistent organic pollutants sorbed in plastic resin pellet — "Nurdles" from coastal areas of Central Chile

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Abstract

Plastic resin pellets were collected from coastal areas (n = 7) of central Chile. Pellets were analyzed usingFourier-transform infrared spectroscopy for polymer identification and gas chromatography–mass spectrometryfor Persistent Organic Pollutants (POPs) determination. Screened compounds were PBDEs (n = 10), PCBs(n = 7), and OCPs (n = 13). Pellets were only found at Lenga Beach (San Vicente Bay), which is likely influencedby the presence of industrial activities in the surrounding coastal area. The diameter of the pellets was 4.0 ± 0.6 cm (n = 370), the color varied from white (32%) to yellowing (68%), and the most prevalent polymer identified was high-density polyethylene (99%). POPs concentrations (ng/g-pellet) ranged from 10 to 133 for Σ_{10}PBDEs, from 3 to 60 for Σ_7PCBs and between 0.1 and 7 for DDTs. Levels of POPs are consistent with other investigations around the world and highlight the sorbtion capacity of plastics resin pellets, and consequently transport of POPs into coastal environments.

Key words: Microplastics, Pellets, POPs, San Vicente Bay

1. Introduction

Plastic pollution has been a major concern worldwide. Two main scenarios have been globally described, the macro scenario characterized by the presence of macroplastics with dimensions >25 mm (Romeo et al., 2015) and the micro scenario characterized by the presence of microplastics with dimension<5 mm (Derraik, 2002). Macroplastic pollution has been well described due to the damage it has produced in the aquatic environment, causing the death of the marine fauna and the pollution of the environment (Kühn et al., 2015). Microplastic pollution is characterized by the small dimensions of the fragments. The primary sources of microplastics are identified as i) derived from hand and facial cleansers, cosmetic preparations, air blast cleaning media, microfibers coming from urban liquid waste (domiciliary waste and from plastic processing plants) and ii) secondary sources coming from unintentional plastic resin pellets spills and the fragmentation of macroplastic as a result of its photodegradation and abrasion due to wave action (Gouin et al., 2011).

Plastic resin pellets, commonly referred to as nurdles, are a type of marine debris originated from plastic particles used to manufacture large scale plastic products (i.e., industrial feedstock of plastic products) and can be spilled into the environment during production, packaging, and transportation. Typically, such pellets are in the shape of a cylinder or disk with diameters of<5 mm. They are generally constituted of polyethylene (PE), polypropylene (PP), polyvinylidene fluoride (PVDF), polyoxymethylene (POM) and polycarbonate. Because their melting temperature range up to 352 °F (177.8 °C), plastic pellets are used for their resistance to corrosion, their wide range of chemicals, creep, impact and flame resistance. Nurdles can be released to the environment as a loss of industrial process production or as a result of spills during terrestrial and marine transport (Ryan et al., 2018). Due to their characteristic buoyancy and lightness, polyethylene (PE) and polypropylene (PP) pellets can play a role as vectors of chemicals, which are transported by surface runoff, streams, rivers and eventually end up in the ocean (Yeo et al., 2015). In addition, because of their chemical nature, plastic resins sorb and concentrate pollutants (Mato et al., 2001; Wardrop et al., 2016), in particular hydrophobic chemical products, including polycyclic aromatic hydrocarbons (PAH) and Persistent Organic Pollutants (POPs) such as polychlorinated biphenyls (PCB), polybrominated diethyl ethers (PBDEs), and other organic chemicals (Koelmans, 2015).

POPs are substances of international concern because they are resistant to environmental degradation through chemical, biological, and photolytic processes. Due to their persistence, POPs bioaccumulate with potential adverse impacts on human health and the environment. For these reasons, the Stockholm Convention (SC) on POPs, which is a global treaty, has a pursuit to protect human health and the environment (UNEP, 2014). From 152 signatory countries, Chile has ratified the SC in 2005.

Despite of the last decade, questions about their role as vectors enhancing the bioaccumulation of POPs in aquatic environments are still pending (Gouin et al., 2011; Teuten et al., 2007, 2009; Hammer et al., 2012; Browne et al., 2013; Rochman, 2015; Lusher, 2015). In nature, complex mixtures of toxicants are present and can be transferred by ad- and absorption on microplastics, causing synergic interactions between them to enhance toxicity in the organism (Jung et al., 2018). For instance, PBDEs are assimilated in the amphipod Allorchestes compressa by microplastic ingestion (Chua et al., 2014); the algae Tetraselmis chuii growth was affected when exposed to microplastics plus pharmaceuticals (Prata et al., 2018) and finally, Pomatoschistus microps's activity of isocitrate dehydrogenase was decreased by combined exposure to pyrene and polyethylene microbeads (Oliveira et al., 2013).

The coastal areas of central Chile are characterized by the presence of a high number of different industrial activities (Ahumada and Vargas, 2005; Parra and Faranda, 1993; Gonzalez et al., 1999; Pozo et al., 2012 and Pozo et al., 2014). Three main embayments are located in this part of the country: Concepción, Coronel and San Vicente bay. These three embayments are highly influenced by industrial activities such as harbor, artisanal fishing, and tourism, which have considerably contributed to the deposition of chemicals and loads of others solid wastes in this coastal ecosystem (Ahumada and Vargas, 2005; Parra and Faranda, 1993; Gonzalez et al., 1999; Pozo et al., 2012 and 2014). Since these coastal areas, in particular, the beach sites, are also commonly used for touristic purposes during the summer period, the potential risk of human exposure to those chemicals should be taken into account. Evidence of plastic resin pellets associated with POPs adsorption have been reported under the pellet watch network (Takada, 2013), reporting levels of PCBs in the range of 5 to 605 ng/g-pellet (Ogata et al., 2009); however, since then, no information has been available for POP levels in other coastal areas of central Chile with microplastics as sorbent materials. Gouin et al. (2011), has evaluated the physicochemical capacities of accumulation of persistent bioaccumulative toxic substances (PBT) in microplastics, revealing its role as a vector of chemicals. Therefore, the aim of this study was to determine and characterize (physically and chemically) plastic resin pellets found in coastal areas of central Chile and their chemical burden, in particular POPs, such as PCBs, PBDEs and organochlorine pesticides (OCPs: DDTs, HCHs, HCB, PeCB). This investigation will provide new information for spatial distribution and likely a time trend for previously measured POPs.

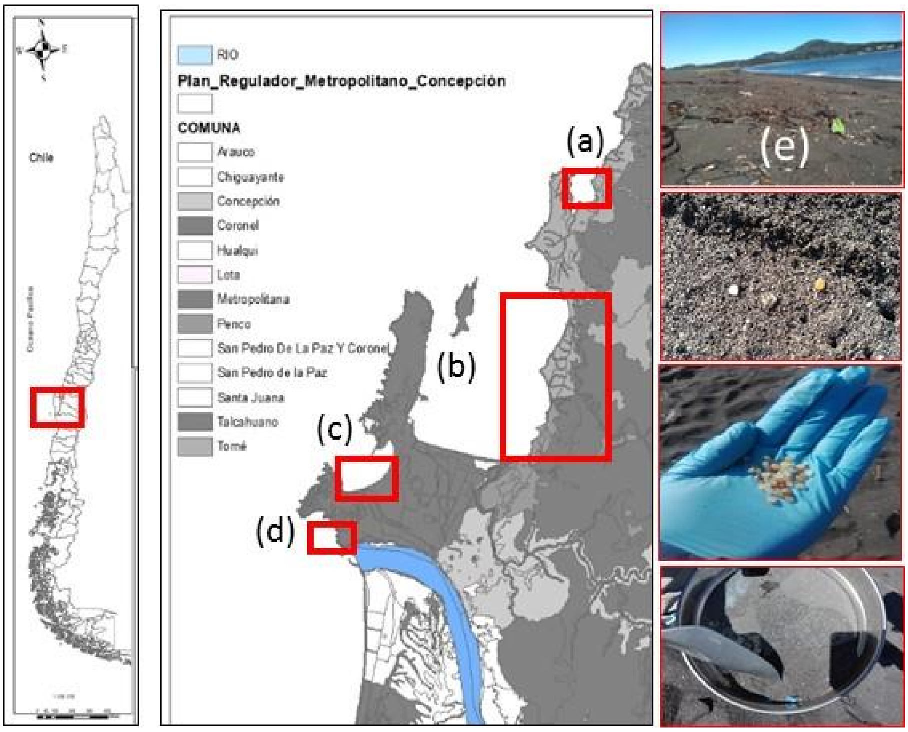

Figure 1. Location of the sampling site a) Coliumo Bay (Coliumo and Dichato site), b) Concepción Bay (Penco, Tomé), c) San Vicente Bay (Lenga beach) and Hualpén Peninsula, d) Desembocadura Beach close to the mouth of Biobío River, and e) Pictures of sampling campaign, including plastic pellets found.

2. Material and Methods

Plastic resin pellets (> 1 g for each site) were sampled in the central coast of Chile at Coliumo Bay (36° 31.77'S, 72° 57.37'W) (Coliumo and Dichato), Concepción Bay (36°32'2.44"S, 72°56'46.86"W) (Penco, Bellavista and El Morro beach), San Vicente Bay (36°43'14.99"S, 73°7'14.99"W) (Lenga Beach) and Peninsula de Hualpén (36° 41'22"S, 73° 06' 09"W) (Desembocadura beach) (Table SM1), during winter 2018 (July 20 and August 20, 2018). Pellet samples were only found at Lenga Beach (Fig. 1). At each site, samples were collected from the low tide line and the upper line of the beach (Fig. 1b). Firstly, pellets were physically analyzed by the determination of i) diameter, ii) thickness and iii) color (white or yellowing pellets; the latter were correlated to aged pellets). Secondly, the samples were chemically characterized through the analysis of i) polymer identification using µFTIR analysis and ii) sorbed POPs using GC-MS. Pellets were sampled along 7 sampling sites at

Lenga Beach; however, as the abundance of pellets were very low at some locations, they were grouped into three final groups (Site 1: obtained from the area close to the pipeline, site 2: obtained from the central part of the beach and closed to artisanal fishing, and site 3: site close to artisanal fishing and close to the pipeline (Table SM1).

2.1. Polymer identification

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR FT-IR) (Jung et al., 2018) (Spectrum Two, Perkin Elmer) was performed using a resolution of 4 cm^{-1} and measuring in the range of 400–4000 cm^{-1}. The obtained spectra were compared with an in-house polymer spectra library for polymer identification. Physical analysis of pellets was carried out by caliper (model festa 150/0.02 mm), the pellets separated by color by the naked eye, between white (new) and yellowing (aged) pellets for each site (Ogata et al., 2009), weighing about 1 g.

2.2. Chemical analysis

The samples were subjected to solvent extraction using 15 ml of hexane in ultrasonic bath during 15 min (3 times). After extraction, samples were reduced to 5 ml, 3 ml of concentrated sulfuric acid was added and they were heated at 45 °C for 15 min to eliminate interferences for chlorinated and brominated compounds analysis. Samples were then centrifuged at 15000 rpm × 10 min. The organic phase was separated from the inorganic with a Pasteur pipette and washed with hexane. All samples were concentrated under a gentle nitrogen flow to 1 ml. The clean-up of the samples was carried out in columns of acid silica gel and sodium sulfate, eluting with 6 ml of dicloromethane (DCM) and 40 ml of DCM/hexane 1:1. After the clean-up, the samples were concentrated under a gentle nitrogen flow at 35 °C up to a volume of 100 µl, then 50 µl of nonane and hexane were added and then concentrated to 50 µl.

2.3. Chemical analysis and target compounds

PCBs and OCPs (DDTs, HCHs, HCB, PeCB) were identified on an Agilent 7890A gas chromatograph–mass spectrometry (GC–MS) equipped with a Rxi 5Sil MS capillary column (60 m × 0.25 mm × 0.10 µm) (Restek, USA) coupled to Agilent 7000B QQQ mass spectrometer. Samples were screened for (target/qualified ion): five isomers of hexachlorocyclohexane (α-, β-, γ-, δ-, ε-HCHs) (purchased from Ultra Scientific, North Kingstown, RI, USA), six isomers of DDT (o,p′-DDE, p,p′-DDE, o,p′-DDD, p,p′-DDD, o,p′-DDT and p,p′-DDT) (purchased from Ultra Scientific, North Kingstown, RI, USA) and seven PCB indicators (PCB28, 52, 101, 118, 138, 153, and 180) (purchased from Supelco NC, USA). 10 congeners of PBDEs were screened (PBDE28, 47, 66, 85, 99, 100, 153, 154, 183 and 209) (purchased from Wellington, ON, Canada). Their analyses were performed by gas chromatography - mass spectrometry (GC–MS) on a 7890A GC instrument (Agilent, USA) equipped with a Rtx-1614 column (15 m × 0.25 mm × 0.10 µm) (Restek, USA) coupled to an AutoSpec Premier MS (Waters, Micromass, UK). The high resolution mass spectrometer (HRMS) were operated in EI + mode in the resolution of>10,000.

2.4. Quality control and quality assurance (QA/QC)

PCBs were quantified with a calibration of eight points with concentrations from 1 ng/ml to 4000 ng/ml, linearity was maintained in the whole range. Calibration standards for PCBs were from LGC. PCB30 and PCB185 are recovery extraction standards (from Absolute Standards). Recoveries for PCB30 were in the range 69 to 74% and for PCB185 were 87 to 98%. 13C12-labeled PBDEs (28, 66, 85, 100, 153, 154, 183, 209) spiked before analysis (100 µl and concentration or amount of Standards) with recoveries fluctuating between 70 and 95%.

Instrumental limits of detection and limits of quantification were calculated from the lowest calibration point as an amount producing signal to noise 3 (LOD) and 10 (LOQ). Procedural blanks (n = 14) were also assessed and showed low percentage of targeted chemicals with 1.2% for PCBs, 10% for DDTs, 1.5% for HCB, 2% for PeCB, and PBDEs were below detection limit (Table SM2).

3. Results and Discussion

Results show the occurrence of POPs in plastic resin pellets obtained from San Vicente Bay in Central Chile (Table 1). From all the studied areas (n = 7 beaches), pellets were only found at Lenga Beach in San Vicente bay.

The physical and chemical characterization of the pellets showed an average size diameter of 4.0 ± 0.6 mm and color abundance of white (32%) (W) and yellowing (68%) (Y) pellet. Yellowing occurs as the results of oxidation of phenolic antioxidation agents to byproducts with quinoidal structures that cause yellow color (Ogata et al., 2009). Hence, yellowing pellets are influenced by the weathering effect like water floating, sunlight, and sand exposition for longer period of time which enhance the chance to sorb chemicals.

The identification of plastic polymer was carried out using ATR FTIR technique. Results showed high-density polyethylene as the most abundant polymer type (99%) except for a single pellet detected at site 1 (high intertidal), which corresponds to a dark gray pellet identified as isostactic polypropylene (Fig. 2a, b). Previous studies have reported similar abundance of polymers in pellets i.e., polypropylene, polyethylene, polystyrene (Mato et al., 2001). The prevalence of pellets at Lenga Beach and polymer type could be associated with the industrial activity characterized by the production of thermoplastic resins in the surrounding coastal area. Indeed, the regional report released by the Communal regulatory Plan of Hualpén, Biobío region, shows that there are approximately 20 industries in the area, and among them, a few plastic/resin pellet producers. Also, Lenga beach is located in the vicinity of the San Vicente Harbor (approximately 5 km) which could contribute with the unknown spill of nurdles (PRCH, 2018).

Table 1. Concentration of POPs for ∑10PBDEs, ∑7PCBs and OCPs (ng/g-pellet) in plastics pellets in Lenga Beach of San Vicente Bay, Central Chile.

	Site 1 (W)	Site 1 (Y)	Site 2 (W)	Site 2 (Y)	Site 3 (W)	Site 3 (Y)
Σ10PBDEs	137	14	1.55	0.43	0.10	0.05
Σ7PCBs	9.64	6.29	58.4	30.0	12.20	3.17
ΣDDTs	0.18	0.54	0.78	2.75	0.96	7.40
PECB	0.43	0.38	3.11	0.85	0.39	0.11
HCB	2.85	2.80	3.60	4.37	1.80	0.63

Abbreviations for pellet color: W=white, Y=Yellowing color.

POP levels sorbed on plastic pellets showed the highest concentrations for brominated compounds i.e., PBDEs with a range of 10 to 133,000 pg/g-pellet (133 ng/g-pellet) followed by PCBs<10 ng/gpellet, DDTs<7 ng/g-pellet, HCB<4 ng/g-pellet, and PeCB<3 ng/gpellet. HCHs were not detected in any pellet analyzed (Fig. 3). To analyze the prevalence of chemicals detected, the physico-chemical properties for PE-octanol-water partitioning of each compound are presented in Table SM3 in the supporting material.

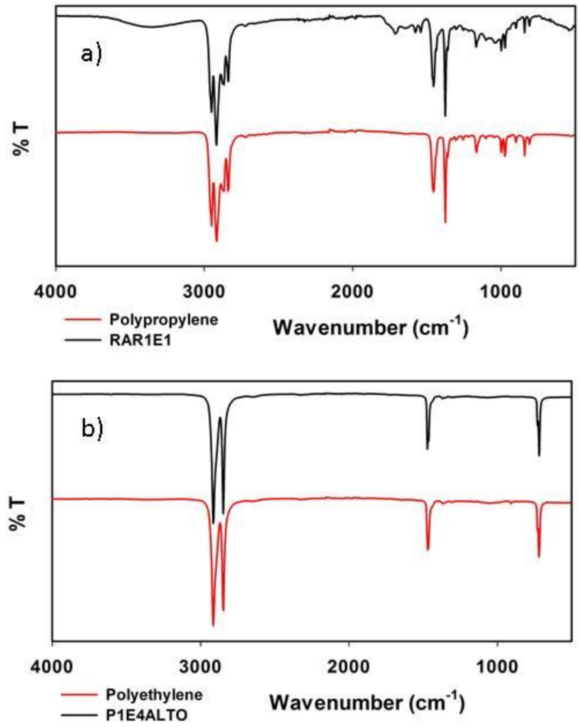

Figure 2. Spectra using FT-IR a) Shows the profile of reference standard of polypropylene (red color) and sample (black color) and b) the figure depicts the comparison of the signal emitted by yellowing pellet (black color) (station 4).

Polybrominated diphenyl ethers are organobromine compounds used in a wide array of products such as flame retardant, building materials, electronics, furnishings, motor vehicles, airplanes, plastics, polyurethane foams, and textiles (UNEP, 2009a). In this study, the spatial distribution and fingerprints were different for each chemical group studied. PBDE levels showed a clear decreasing pattern from site 1 which is located beside a gas pipeline, with values of 10 pg/g-pellet to 133,000 pg/g-pellet (133 ng/g-pellet found at site 3) (Fig. 3). From Σ10PBDEs congeners analyzed, BDE209 accounted for 50 to 98% of the total PBDEs composition (Fig. 2), except site 3 (white pellet samples = 47% BDE47). It has been reported that BDE47 has a greater log $K_{PE\text{-}W}$ than the BDE209 (O'Connor et al., 2016). These results were lower than those detected in other selected studies. For instance at the Pellet watch network PBDEs ranged from 14 to 21 ng/g-pellet (sum of 46 BDE congeners) at several locations, and also lower than those reported in western European countries (0.69–13 ng/g-pellet), in the USA (17–39 ng/g-pellet), and in African countries (< 3.9 ng/g-pellet) including Kenya, Mozambique, South Africa (Pellet watch program website). Similar PBDE concentrations have been reported in other regions such as, Brazil (< 0.26 to 5.56 ng/g-pellet) (Taniguchi et al., 2016, BDE209 was not analyzed), Canary Islands beaches (0.0 to 180 ng/g-pellet) (Camacho et al., 2019) and in the Pacific Ocean (0.3 to 129 ng/g-pellet) (Hirai et al., 2011). The deca-BDE or BDE209 is added to plastic products in high concentrations (µg/g) (Hirai et al., 2011), so we could indicate that this type of pellet absorbs the PBDEs from the environment by its eluded log k_{OW} (> 6), since supposedly they are virgin polymers manufactured in the vicinity of the study site.

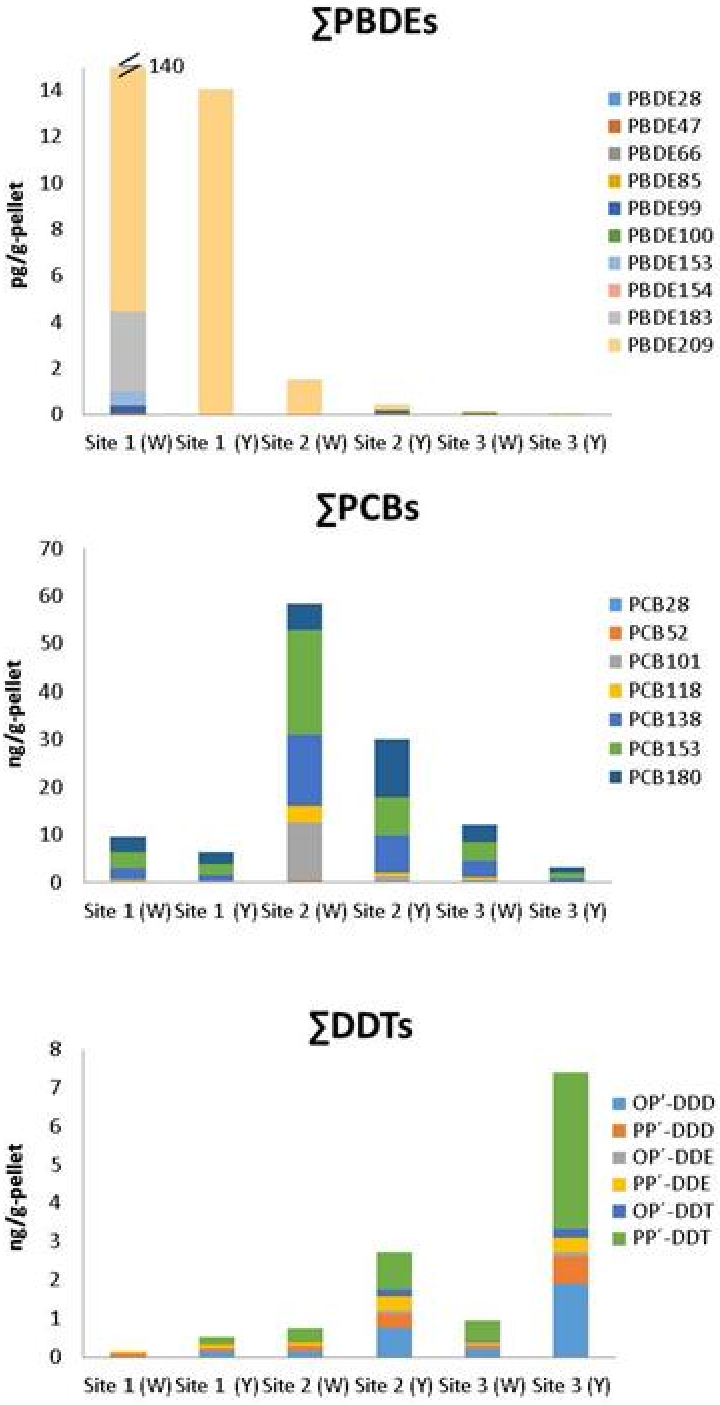

Figure 3. POP concentrations (ng/g-pellet) for PBDEs, PCBs, DDTs in Lenga Beach at San Vicente Bay, Central Chile (W= white and Y= yellowish pellet type).

Polychlorinated biphenyls are organic chlorine compounds with the formula C12H10–xClx. PCBs were once widely deployed as dielectric and coolant fluids in electrical apparatus, carbonless copy paper, in heating transfer fluids and also in open applications (e.g. cables, sealants, and paintings) (Weber et al., 2018). Chile, as a signatory country of the Stockholm Convention, has implemented inventories of PCBs (CONAMA, 2008). In this study, PCB levels were low ranging from 3 to 60 ng/g-pellet. The highest concentrations were detected at site 2, in the middle of the Lenga Beach area (Fig. 3). These concentrations are comparable with pellet samples found in Portugal beaches, 0.01 to 68 ng/g-pellet (Frias et al., 2010; Mizukawa et al., 2013), South African coasts (1 to 23 ng/g-pellet) (Ryan et al., 2012), with the remote islands of the Pacific, Atlantic, Indian Ocean and Caribbean Sea (0.1 to 9.9 ng/g-pellet) (Heskett et al., 2012) and the coasts of Vietnam (4 to 24 ng/g-pellet) (Le et al., 2016). Yet, lower than those reported by Antunes et al. (2013) in Portugal beaches (2 to 223 ng/g), than the coasts of Greece (0.001 to 70 ng/g-pellet) (Karapanagioti et al., 2011), than those found in the Japanese coasts with 4 to 117 ng/g-pellet (Mato et al., 2001) and 28 to 2300 ng/g-pellet (Endo et al., 2005). Previous studies have reported that PCBs tend to remain in pellets because of their high log K_{PEW} (> 5) and to be highly chlorinated (Endo et al., 2013); PCB180 ($logK_{PE\text{-}W}$ = 7.53; Perron et al., 2009; O'Connor et al., 2016) has the highest $K_{PE\text{-}W}$ of all the PCBs analyzed in this study. This is consistent with the PCBs abundance found in pellet at Lenga beach showing a prevalence of High Molecular Weigh (HMW) PCBs (PCB180 (30-40%), PCB153 (25-30%) and PCB138 (20-30%)) of the total PCBs.

Organochlorine pesticides have been widely used in Chile since the 1950s (SAG, 1980). Dichlorodiphenyltrichloroethane, commonly known as DDT, is a colorless, tasteless, and almost odorless crystalline chemical compound, an organochlorine, originally developed as an insecticide, and ultimately becoming infamous for its environmental impacts. In Chile, DDTs has been banned since 1984 by SAG (SAG, 1980). In this study, levels of DDTs ranged from 0.1 to 7.4 ng/g-pellet. These levels are similar to DDTs values found in remote islands of the Pacific, Atlantic, Indian and Caribbean Seas ranging between 0.8 and 4.1 ng/g-pellet (Heskett et al., 2012). Nevertheless, DDTs showed lower concentrations than those detected in the Portuguese coast (0.32 to 41 ng/g-pellet) (Antunes et al., 2013; Frias et al., 2010; Mizukawa et al., 2013), in Greece (0.2–25 ng/g-pellet) (Karapanagioti et al., 2011) (by a factor of 3 times lower), than those DDTs reported in South African coasts (a factor of 10 times lower with 50–73 ng/g-pellet) (Ryan et al., 2012), and lower than those found in the coasts of Vietnam (7.8–357 ng/g-pellet) (by a factor of ~50 times) (Le et al., 2016).

From the six isomers analyzed, pp'-DDT was the predominant isomer detected (70%), followed by pp'-DDE (20%) and pp'-DDD (20%). This finding could suggest that the pellets were exposed to fresh DDT, as in its technical formulation. In a previous study, a similar fresh DDT signature was determined in the air (4 to 30 pg/m3) from the urban areas of the Concepción city (Pozo et al., 2017). However, DDT composition was different for site 1W (white pellet) with pp'-DDE and pp'-DDT accounting for 12 and 18%, respectively and 30% for pp'-DDD than the one detected in site 1Y (yellowing pellet) with pp'-DDE 16%, pp'-DDT accounting for ~34% and pp'-DDD with 14%. DDT is basically degraded by two reactions: (i) dehydrohalogenation reaction, enzymatic conversion of DDT to DDE (1,1-dichloro-2,2-bis (p-chlorophenyl) ethylene), and (ii) reductive dechlorination of DDT to DDD (1,1-dichloro-2,2-bis (p-chlorophenyl) ethane) which is a reaction of substitution of a chlorine atom with one of hydrogen (Lin and Chang, 2007; Sudharshan et al., 2012). In both cases, the degradation products are also very persistent and have chemical, physical, and toxicological properties similar to the original product and last up to 50% in the soil for a period of 10 to 15 years after application (Morrison et al., 2000). Therefore, although white pellets are considered to be newer than yellowing pellets, the predominance of the degradation products of DDT could be stronger related to the location where the pellets were sampled, since these white pellets were sampled in the furthest site from the estuary (Figure SM1).

Hexachlorobenzene (HCB) is an organochloride with the molecular formula C_6Cl_6. It is an industrial product which can also be found in technical formulations of pesticides, formerly used as a seed treatment, especially on wheat to control the bunt fungal disease (Matanguihan et al., 2011). It can be released into the atmosphere from chlorine pesticide breakdown, chlorine solvent incineration and incomplete combustion of waste, biomass, coal, and fuel (Bailey, 2001; Guida et al., 2018). HCB has not been imported, manufactured, or marketed in Chile; its environmental levels are presumably derived from industrial activities (Pozo et al., 2014). HCB in pellet samples were low and ranged from 0.6 to 4 ng/g-pellet. Records of HCB in coastal areas of Chile have been reported in the Biobío region at of Lenga estuary in sediments (1–870 ng/g-pellet) (Pozo et al., 2014) and in Los Lagos region in Valdivia in seabird eggs (102–236 ng/g-pellet) (Cifuentes et al., 2003).

Pentachlorobenzene is a chemical compound with the molecular formula C6HCl5 that is a chlorinated aromatic hydrocarbon. PeCB was used in PCB products, in dyestuff carriers, as a fungicide, flame retardant and asa chemical intermediate e.g. previously for the production of quintozene. PeCB is also produced unintentionally during combustion, thermal, and industrial processes. It also presents itself as an impurity in products such as solvents or pesticides (UNEP, 2009b). PeCB was listed as a POPs on the Stockholm Convention in the last decade. PeCB in pellet samples ranged from 0.1 to 3 ng/g-pellet (Table 1). In Chile, no PeCB data has been previously reported in the scientific literature.

Hexaclorociclohexanes (HCHs) with the molecular formula C6H6Cl6. The most extensive use of technical HCH (organochlorine insecticide) was during the 1970s and early 1980s followed by a rapid decrease as a result of restrictions and prohibitions in many countries (Li et al., 2000). In this study, HCHs were not detected. These findings may be related first to the effective prohibition of HCHs in the country. HCHs technical mixture was banned in 1984 (SAG, 1980) and in particular, Lindane has been prohibited for sanitary purposes by the Chilean Ministry of Health (MINSAL, 2009; Pozo et al., 2017). Since γ-HCH is the main component (with 90%) of Lindane, its presence in the environment could have decreased in the last years. Second to HCHs physicochemical properties. γ-HCH have a polyethylene (PE)-water partition coefficient low (log KPE-W < 3) which enhance its solubility in water (Hale et al., 2010; O'Connor et al., 2016), therefore, the concentrations of this chemical would depend on the type of polymer found in the environment. In this study, PE would not be an efficient trap of HCHs. Nevertheless, in other areas of the world the scientific literature report HCHs levels in Greek coasts (0.01–1.5 ng/g-pellet) (Karapanagioti et al., 2011), in South African coasts (1–107 ng/g-pellet) (Ryan et al., 2012), in remote Pacific, Atlantic, Indian and Caribbean Islands (0.6–19.3 ng/g-pellet) (Heskett et al., 2012), on the coasts of Portugal (0.088–1.2 ng/g-pellet) and off the coasts of Vietnam (0.01–0.82 ng/g-pellet) (Le et al., 2016).

The pellet weathering effect was also analyzed through the elaboration of fig. S1 which shows POP concentration patterns in white and yellowing pellets. For PBDEs and PCBs, higher levels were detected in white (new pellets) than in the yellowing (aged) pellets. These results are different than those reported by Ogata et al., 2009 where high levels of PCBs were detected in yellowing pellets than in white ones. These differences are likely attributed to sampling sites areas (with low or high levels of chemicals). This is the case of PCBs at Lenga beach which shows higher levels, by a factor of five times higher (with exception one outlier for PBDEs), than other chemicals analyzed.

Interestingly, DDT concentrations and isomers distribution behave differently showing higher levels at yellowing (aged pellet) than white (new). These results may suggest past use of DDTs due to longer exposure time of pellets in the environment. In this regard the ratio of parent DDT to its metabolite, DDE, was used to estimate the recent input of technical DDT.

The ratio obtained at Lenga Beach was DDT/DDE>1 and may be an indication of the presence of DDT in the last 5 years (Li et al., 2009).

4. Conclusions

Plastic resin pellets (nurdles) were only found at Lenga Beach located in San Vicente Bay of Central Chile. The prevalent polymer plastic-type detected was high-density polyethylene, which showed a selective capacity to trap chemicals depending on their physicochemical properties ($K_{ow} > 5$). From all POPs analysis ΣPCBs showed the highest concentrations, followed by PBDEs (with exception of one outlier value at Site 1), with BDE209 as the main congener, and finally by organochlorine pesticides.

These findings are consistent with other investigations around the world and highlight the capacity of microplastics, plastic resin pellets, to trap and consequently transport POPs into coastal environments. Interestingly, pellet color showed differences for PBDEs and PCBs than DDTs showing evidence of weathering and source influence.

The fate of pellets is still unknown, but could represent a potential exposure for wildlife and for humans, in particular, on touristic beaches that are highly crowded during the summer season. Nevertheless, further research is still needed to elucidate proper environmental strategies to reduce their impact in the environment.

Authors contribution

Karla Pozo: Coordinator of the Project and sampling design. Analysis of data and discussion. Revision of entire manuscript.

Williams Urbina: Sampling at the study area, Analysis of pellets using FT-IR, and organization of data.

Victoria Gómez: Analysis of data and comparison, with other studies and discussion of results, analysis of physic-chemicals data and correlations between pellet type and chemicals.

Mariett Torres: Elaboration of analytical protocols, and material for sampling campaigns during the entire period of the projects. Elaboration of Maps using GIS tool.

Dariela Nuñez: Co-investigator of the research Project, contribution under the analysis of FT-IR at CIPA, discussion of results.

Petra Příbylová: Coordination of lab work and discussion of results for chemicals.

Ondřej Audy: Coordination of lab work and discussion of results for chemicals.

Bradley Clarke: Interpretation of data and discussion of results. Revision of entire manuscript.

Andres Arias: Interpretation of data and discussion of results.

Norma Tombesi: Interpretation of data and discussion of results.

Yago Guida: Interpretation of data and discussion of results. Analysis of physic-chemicals data and correlations between pellet type and chemicals.

Jana Klánová: Part of research project, supervision of laboratory data and discussion of results.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors thank Fondecyt grant no 1161673 (PI: Karla Pozo) and CIPA, CONICYT Regional, GORE BIO BIO, R17A10003, in Chile. This research was supported by the RECETOX Research Infrastructure (LM2015051 and CZ.02.1.01/0.0/0.0/16_013/0001761).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2019.110786.

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Marine Pollution Bulletin 140 (2019) 315–319

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Baseline

Presence and characterization of microplastics in fish of commercial importance from the Biobío region in central Chile

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Abstract

In this study we have identified and characterized microplastic particles (MPs) found in six fish species of commercial importance in central Chile. The fish species belong to different trophic levels and were obtained from the oceanic and coastal habitats. To analyze MPs, the fish gastrointestinal content was extracted, analysed and characterized using a microscopy equipped with Fourier-transform infrared spectroscopy (FT-IR). The MPs found in fish samples were mainly constituted by red microfibers (70–100%) with sizes ranging between 176 and 2842 µm. Polyester, polyethylene (PE) and polyethylene terephthalate (PET) were identified as the prevalent polymers detected. The coastal species showed the presence of microfibers with a higher size and abundance (71%) compared to oceanic species (29%), suggesting there is a greater exposure risk. These findings are consistent with results found in other investigations worldwide. However, further research is still needed to accurately establish the potential exposure risk for the public consuming these fish and the impact of MPs in the Chilean fishery activities.

Keywords: Microplastics, Microfibers, FTIR, Fish species, Biobío region, Chile.

In the last decade, a large amount of plastic waste has been accumulating in the world's oceans (Jambeck et al., 2015). The plastic waste found in the sea is subjected to mechanical forces and solar radiation, triggering a slow fragmentation process that produces fragments smaller than 5 mm, called microplastics (Arthur et al., 2009). This form of contamination would represent a threat to marine ecosystems, since these plastic particles would be mixed with the food sources of marine organisms and could be accidentally or deliberately ingested when they are mistaken for food (Bergmann et al., 2015). Although microplastic pollution research has increased in recent years, the evidence of the effects of plastic particle intake by marine biota is still scarce (Galloway, 2015; Koelmans, 2015). Recent investigations have estimated that plastic intake would cause physical and chemical injuries, with negative consequences for survival and reproductive performance organisms (Rochman, 2015; Von Moos et al., 2012; GESAMP, 2015; Wardrop et al., 2016). In addition, the ingestion of microplastics can lead to potentially fatal injuries, such as blockages in the entire digestive system or abrasions by sharp objects (Wright et al., 2013). Plastics could be eliminated along with feces or they could be retained during an important part of fish life (Boerger et al., 2010), causing a bioaccumulation and subsequent biomagnification (Perez-Venegas et al., 2018). In addition, other phenomenon such as translocation of the intestine to the circulatory system, have been described in an invertebrate manipulation experiment carried out by Browne et al. (2008), in which the authors demonstrated a trophic transfer that occurs between mussels and crabs because small microplastic particles (5 µm) can be translocated from the gut to the circulatory system in mussels. Thus, microplastic could potentially enter the food chain in natural environments (Farrell and Nelson, 2013).

Plastics are resistant to degradation and will persist in the environment for centuries being transported far from its original source (Lohmann, 2017). In Chile, plastic contamination has been investigated along the Northern and Southern coast (Hidalgo-Ruz and Thiel, 2013; Perez-Venegas et al., 2017). Recently, Perez-Venegas et al. (2018) has reported the prevalence of microfibers, as microplastics, in the wild population of South American fur seals (Arctocephalus australis), in Northern Chile; Gómez et al. (2015); Baeza et al. (2016); Vera et al. (2017) have characterized the type of microplastics (Polyethylene terephthalate = PET and Polyester) found in sand and water samples from Concepción Bay while Acuña-Ruz et al. (2017, 2018) has applied remote sensing methodology to estimate the marine trash found on the coast of Chiloe Island. Nevertheless, there is a lack of information regarding microplastics identification and characterization and no information is available about their abundance in organisms, accumulation patterns or sources in Chile. Andrade and Ovando (2017) reported the presence of microplastics in the stomach contents of the king crab (Lithodes santolla) in Cape Horn, Chile (the occurrence in their stomachs was 27%). Ory et al. (2018) has analyzed the gut contents of planktivorous fish (seven species), captured along the coast of the southeast Pacific, that were examined for microplastic contamination. In addition, Mizraji et al. (2017) compared the content of microplastics among intertidal fish with a different feeding type; results showed that omnivorous fish presented a higher amount of microplastic fibers than herbivores and carnivores. Only a small fraction of all studied fish (2.1%; 6 individuals) contained MPs in their gastrointestinal content.

Chile is among the ten most important fishing countries in the world, with its fisheries being a relevant economic source, corresponding to the 4% of the Country's GDP (Gross Domestic Product). The fishing and aquaculture sectors are one of the pillars of the Chilean economy, with a total production of 3.6 million tons and total exports of 4337 million dollars of fish and fishery products in 2012 (FAO, 2014). In particular, the Biobío region is the most important fishing region in the country (36%), being also among the main regions dedicated to algae, rainbow trout and mollusc aquaculture (Subpesca, 2018). However, despite the relevance of this economic sector in Chile no scientific data is available about the incidence of microplastics in marine products.

In this context, the objective of this study was to assess the presence of microplastics in the gastrointestinal content of fish with commercial importance obtained from the oceanic habitat (benthic environment) and the coastal habitat from the mouth of the Biobío River in central Chile. In addition, the phenomenon of bioaccumulation in fish species of different trophic levels is preliminary explored in this study.

Fish species analyzed from the ocean habitat were: *Trachurus murphyi* (TM) (common name Chilean jack mackerel; n=10), a carnivorous specie representing a high trophic level, *Strangomera bentincki* (SB), (common name Sardine; n=10), a planctivora specie representing a low trophic level, with coastal and oceanic life habits, and *Merluccius gayi* (MG) (common name Hake; n=10). Samples were provided in October 2016 by the Instituto de Investigación Pesquera (Research Institute for Fishery=INPESCA) located in the city of Talcahuano, in the Biobío region.

The species analyzed from the coastal habitat were: *Eleginops maclovinus* (EM) (common names Patagonian blenny and Robalo, in Spanish; n=10), a carnivorous specie representing a high trophic level (HTL) and *Aplodactylus punctatus* (AP) (Jerguilla, n=10), one herbivorous specie representing a low trophic level (LTL). These samples were captured in November of 2016 by artisanal fishing, in areas surrounding the mouth of the Biobío River. In addition, *Basilichthys australis* (BA) (common name Pejerrey, in Spanish; n=10), a detritivore specie that inhabits in the mouth of the Biobío River, was also analyzed.

The gastrointestinal content of each fish sample was extracted and freeze-dried. Samples of 0.1 g were taken to be subjected to digestion of the organic matter in glass tubes. To facilitate the identification of plastic material in the stomach content, digestion of the organic matter was carried out by adapting the enzymatic digestion protocol developed by Lindeque and Gary (2003). This procedure consisted of using 250 μg mL^{-1} of Proteinase-K per 0.1 g of dry gastrointestinal content. Then, 7.5 ml of homogenization solution (buffer 400mM Tris-HCl buffer, 60mM EDTA, 105mM NaCl, 1% SDS) was added to the glass bottles with the gastrointestinal content; the bottles were subsequently mixed using a vortex every 10 min and incubated at 50 °C for 20 min. Then, 250 μgmL−1 Proteinase-K was added to the samples and incubated at 60 °C for 3 h, and were subsequently mixed using a vortex every 15 min. After the digestion of the organic matter, the stomach content was filtered using Whatman glass microfiber filters (47mm in diameter and 0.7 μm pore) with the help of a vacuum pump to retain the non-organic material in the filter. The filters were kept frozen in individual Petri dishes for further analysis. During the analysis, all the laboratory surfaces were cleaned with acetone to ensure quality control and quality assurance (QA/QC). The utensils used were calcined at 500 °C for 4 h in a Thermolyne 600 furnace. In addition, “blanks” were prepared using sodium sulfate, filtered and observed with an optical microscope (Foekema et al., 2013). The identification of microplastics particles were carried out with a high-resolution optical microscope having an integrated camera model Leica DM 750. The particles were photographed and digitized. Subsequently, the particles showing microplastic characteristics were counted and measured in length. Filters of each species were analyzed using a Fourier-transform infrared (FTIR) microscope (FT-IR Microscope Spotlight 400 & Spectrum Frontier, Perkin Elmer) to obtain the spectrum of the pre-identified particles. The obtained spectra were compared with a database of reference standard compounds to identify the polymers present in the particles. To allow the analysis of the results we have organized the discussion section in: i) polymer types present in the samples (number, shape, size and colour) (Norén, 2007; MSFD, 2013) and chemical analysis (FT-IR microscope detection), ii) type of habitat, and iii) trophic level.

Results showed the presence of low number microfibers (total of n=20; 100%) (Fig. 1a, d and Table 1). Microfibers are also a type of microplastic, which include small fibers that may enter the water environment from clothing made of synthetic materials, like polyester, polyethylene or nylon (Steer et al., 2017). These results are consistent with those obtained in a study analyzing three important commercial fish species: the sea bass (Dicentrarchus labrax), the common twobanded seabream (Diplodus vulgaris) and the European flounder (Platichthys flesus) from the Mondego estuary (Portugal), showing a total of 96% fibers detected (microfiber) and polyester as the main polymer (Bessa et al., 2018). Lusher et al. (2013) also reported ingestion of microplastics in ten species of fish, from the English Channel, pelagic species (n=5) and demersal species (n=5) with 68% of abundance for fibers (microfiber), studies conducted on the coast of central Chile by Mizraji et al. (2017) showed that fibers represent the most abundant form in fish and omnivores have a greater amount of microplastic type than those recorded in herbivores and carnivores. The ingestion of microplastics varies in species with different food sources, such as omnivores. Ory et al. (2018) has also found that 80% of the Decapterus muroadsi fish from Easter Island had ingested mainly blue polyethylene fibers which are similar in colour and size to the blue copepod consumed by Decapterus muroadsi.

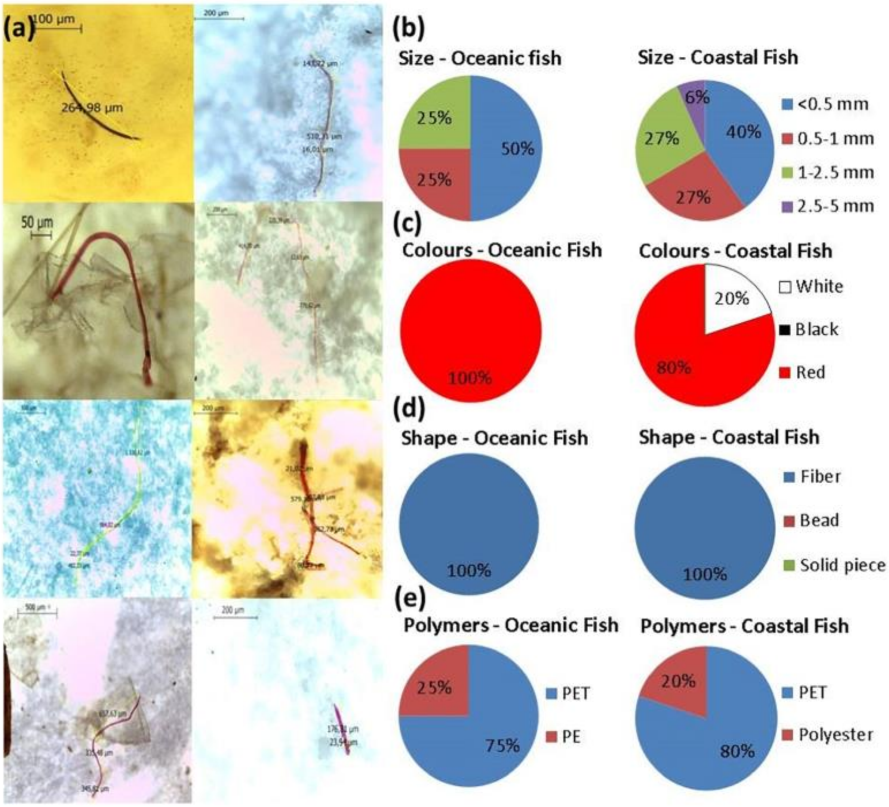

Fig. 1. Characterization of microplastic particles (MPs) in oceanic and costal fish. (a) MPs predominantly constituted to microfibers found in the filters of the stomach contents - Images captured under the optical microscope. Physical and chemical characteristic of microfibers: (b) size, (c) colour, (d) shape and (e) polymer type in oceanic and coastal fish species.

The physical analysis showed that microfiber size ranged between 0.1 and 2.8mm (Fig. 1b). From these particles, the most abundant microfibers were smaller than 0.5mm (< 0.5 mm). In oceanic fish ~50% of microfibers were<0.5 mm, while in coastal species only 40% (Fig. 1b). Comparing our results with other studies, the ingestion of microplastics by different groups of fish have commonly been characterized ranging from 0.8 to 5mm (Browne et al., 2008; Boerger et al., 2010; Foekema et al., 2013). Foekema et al. (2013) reported in North Sea fish a low number of microplastics of small dimensions. The authors suggested that microplastics would not cause physical damage to the carrier in terms of blockage of their gastrointestinal tract, false sensation of satiety or injuries in the digestive tract due to sharp particles, however; the microfibers dimensions reported by Foekema et al. were larger (>) 0.5mm (2.5 to 5 mm) and were detected in coastal fish species. This result deserves attention because particles of a bigger size may affect ingestion rate in fish species and consequently, in the long term, have health effects in the population dynamics of fisheries' stocks.

In addition, Browne et al. (2008) indicated that the accumulation risk in tissues of organisms increases as plastics are fragmented into smaller particles.

In this study, red and white microfibers were detected in the sampled fish; showing 100% of red microfibers in oceanic fish species while in coastal species we observed red (80%) and white (20%) microfibers (Fig. 1c). These results are similar to those recently reported by Steer et al. (2017), who described species of fish larvae with preferences for ingestion of red over black fibers. This is consistent with Mizraji et al. (2017) where red fibers were predominant among coastal fish. The chemical characterization of microfibers showed only two types of polymers. Polyethylene terephthalate (PET) was the most abundant with 75% in oceanic fish and 80% coastal fish (Fig. 1e). Nevertheless, Polyethylene (PE), the second polymer, accounted for 25% of detection (Fig. 1e), being only detected in oceanic fish. PE is the most common plastic, its primary use is in packaging (plastic bags, plastic films, geomembranes, containers including bottles, etc.). Polyester presents an abundance of 20% only in fish from the coastal area (Fig. 1e). Polyester is a popular material for commercial marine utensils and instruments, including fishing nets (Steer et al., 2017), and PET is a material widely used in fibers for clothing, as well as in containers for liquids and foods (Naji et al., 2017).

Our results showed a different microfiber distribution patterns between ocean and coastal habitats. In oceanic fish, a lower microfiber content was found than in coastal fish. The contained microfibers: SB (Sardines), which showed a low abundance of microfibers (30%), while TM (Chilean jack mackerel) was even lower (10%) like MG (Hake) (10%). In coastal species, microfibers were found in all the samples analyzed. Interestingly, BA (Pejerrey), the fish species obtained from the mouth of the Biobío River, presented the highest detection frequency of microplastics (70%); followed by EM (Patagonian blenny=Robalo) (30%) and AP (Jerguilla) (20%) (Fig. 2a, b). These results suggest that marine species living in the coastal area would have a greater chance of being exposed to microplastics (microfibers), enhancing MPs ingestion due to their vicinity to anthropogenic activities.

Table 1. Fish species (number and sizes examined) and frequency of debris occurrence for Microplastics analysis in Oceanic and Coastal fish species from Central Chile.

Species (common name)	Number of individuals	Average fish length ±SD (cm)	Number of stomachs with debris
Trachurus murphyi (Chilean jack mackerel)	10	45.9 ± 4.63	1
Strangomera bentincki (Sardine)	10	13.1 ± 0.61	3
Merluccius gayi (Hake)	10	61.9 ± 19.7	1
Eleginops maclovinus (Patagonian blenny)	10	34.7 ± 3.30	3
Aplodactylus punctatus (Jerguilla)	10	37.7 ± 2.71	2
Basilichthys australis (Pejerrey)	10	24.8 ± 1.08	10
Total	60	36.4 ± 16.9	20

Similar results have also been reported in previous investigations (Browne et al., 2008; Boerger et al., 2010; Foekema et al., 2013; Choy and Drazen, 2013). One plausible explanation is related to the impact of riverine inputs from the Biobío River, considering that rivers are the main emitters of plastic waste to the oceans (Jambeck et al., 2015). Particularly, the Biobío River would be an important source of MPs, due to its proximity to urban centers and high degree of anthropic activities.

This river receives the urban wastewater and the water discharge from different types of industries (Parra et al., 2009; Pozo et al., 2012). Studies have shown that wastewater from urban areas contains microplastics (Habib et al., 1996); and they have reported that an important source of MPs appears to be through sewage contaminated by fibers from washing clothes, mainly polyester fibers (Browne et al., 2008).

In order to preliminary assess the transfer of microplastics between trophic levels, the selected fish species were analyzed considering their position in the trophic food chain. Results showed that BA (Pejerrey) (LTL) had 70% detection frequency of microfibers compared with EM (Patagonian blenny=Robalo) (HTL) with 30% of microfibers, whereas in TM (Chilean jack mackerel) with 10% of microfibers (Table 1). Previous studies suggested that the residence time of the microplastic in the organism would be rather brief and these materials would be discarded together with the feces (Possatto et al., 2011; Foekema et al., 2013). Nevertheless, in this study we considered that the transfer of MPs through the marine trophic web was not possible to be properly evaluated due to two factors: i) the low number of samples analyzed, and ii) the low abundance of microfibers detected. From another point of view, these results could have a positive interpretation, because they would suggest a low abundance of MPs in the gastrointestinal content of fish species of high trophic levels in central Chile, but higher than those reported in the southeast Pacific Ocean

(Ory et al., 2018). However, further research is still needed to evaluate the transfer of microplastics in the marine environment, particularly, in fish species of commercial importance.

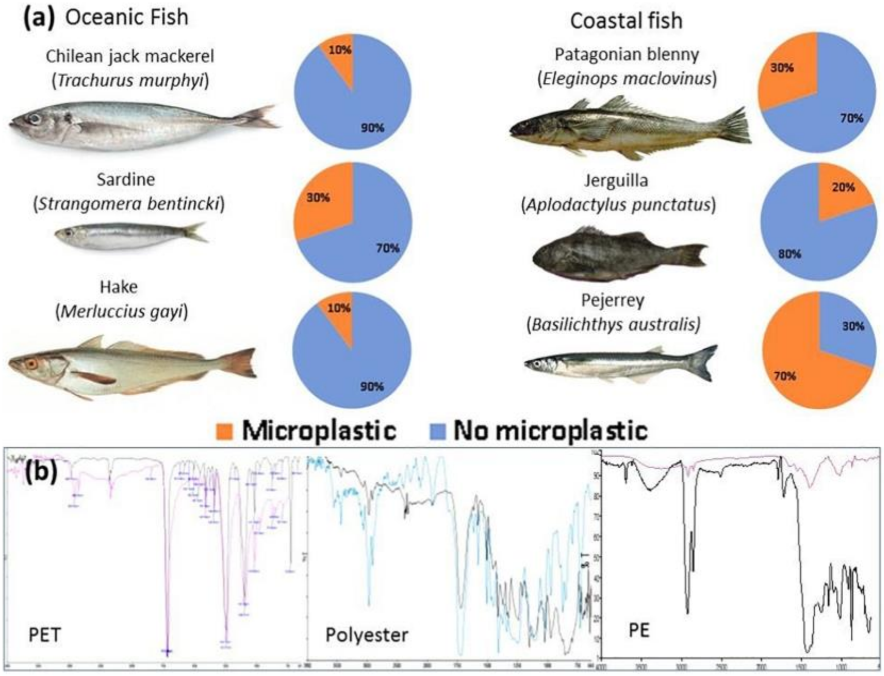

Fig. 2. (a) Frequency of microfibers in the six fish species, (b) Spectrum of FT-IR analyses of the polymers found in the stomach content of coastal and oceanic fish.

In conclusion, we can state that microplastics were detected, in the form of microfibers, in the gastrointestinal content of fish species from central Chile. The chemical characterization showed polyethylene terephthalate (PET), polyethylene (PE) and polyester as the main polymers identified in this study. Fish species (LTL) from the coastal sites (mouth of the Biobío River) showed the highest numbers and sizes of microfibers, overtaking organisms (HTL) from oceanic habitat. Riverine inputs may play an important role in the coastal ecosystem since they act as sources of MPs contributing to the direct ingestion of MPs. The results of this study suggest the consumption of these type of microfibers is primarily related to the habitats of the fishes and it is linked with the food they eat rather than their trophic level position. However, since the trophic transfer of microplastics was not possible to be evaluated in this study, further research is needed to establish the risk for human exposure from commercially important fish species and the potential impact of microplastics in the Chilean fishery activities.

Acknowledgements

The authors thank FONDECYT grant n°1161673 (PI: Karla Pozo) and CIPA, CONICYT Regional, GORE BIO BIO, R17A10003, in Chile. This research was supported by the RECETOX Research Infrastructure (LM2015051 and CZ.02.1.01/0.0/0.0/16_013/0001761). The authors also thank Prof. Anny Rudolph and Prof. Antonio Brante for supervision of undergraduate students.

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APPENDIX 2. Poster

Marine debris in Central Chile: Characterization of macroplastics in Concepción Bay

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Introduction: Plastic debris can be transported over long distances from the sites of origin and accumulates via ocean currents in oceanic gyres. Recent studies have been devoted to characterize the Marine Debris (MD) along the Chilean coast, where it has been shown that the most abundant AMD are plastics and cigarette butts which can be attributed to local sources with increase over time. In this study we have physical and chemical characterized plastic debris (PD) and determine Persistent Organic Compounds (POPs) levels from five touristic beaches in central Chile during two different periods (spring 2017 and summer 2018).

Concepción Bay (Figure 1) has a vital role in the sustainability of the socio-economic development and health of the neighboring population in the region.

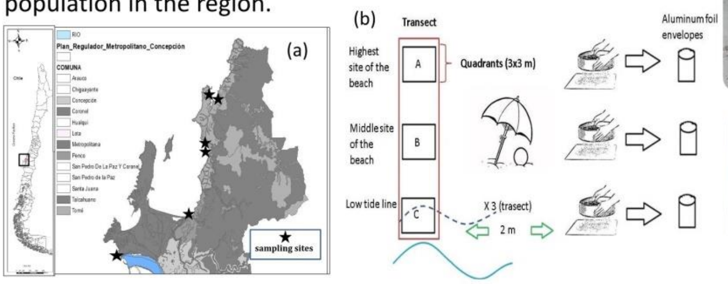

Figure 1. (a) Location and sampling sites; (b) Schematic overview of beach sampling design.

Materials and methods

Sample collection: The sampling was carried out using three transects and three quadrants (3x3 m) for each beach (Figure 1. (b)).

Chemical analysis: The polymer analysis was carried out with FT-IR. The POPs analysis was carried out with an extraction by ultrasound and detection by GC-MS.

Statistical Analysis: The plastics data set was processed using a ANOVA one way, a Turkey test to make multiple comparisons. The analyses are performed with the Statistix 10 software.

Results and discussion

The physical characterization showed the most frequent size was PD between 2,5-10 cm (42%), with the most frequent shape for plastic pieces (50%) and the predominant PD colour found was white (22%) (Figure 2 (a), (b) and (c)). The results showed significant difference between the spring 2017 and summer 2018 periods ($p < 0.05$) (Figure 2 (d)), with the highest abundance of PD detected during the summer (4.1 ± 3.7 items/m^2). According to clean-coast index (CCI)[1] these beaches are extremely dirty, more than 1 item/m^2. A recent study conducted throughout Chile determined an average abundance of 2.15 items per m^2 for the year 2016[2]. This results are comparable with other studies in Russian beaches[3] and Malaysians Beaches[4]

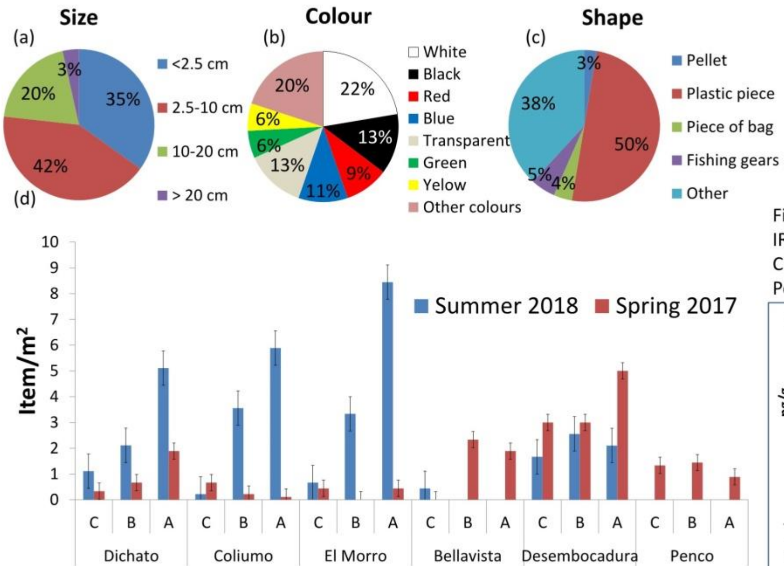

Figure 2. Physical characterization: (a) macroplastic size; (b) color; (c) shape, and (d) abundance on touristic beaches of Central Chile, during spring 2017 and summer 2018.

Conclusions: These data are the first information of POPs in Plastic debris in touristic beaches of the Concepción bay and are also comparable with other studies reported in the scientific literature. The concentrations of PCBs were lower and reported in other studies. However, the concentration of PBDEs were higher than other areas of the world.

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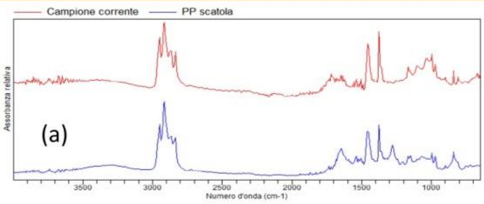
Acknowledgment: This research was funded by FONDECYT project (No. 1130329, K. Pozo) and supported by the RECETOX Research Infrastructure (LM2015051 and CZ.02.1.01/0.0/0.0/16_013/0001761). Thanks to the PhD Program in Environmental, Geological and Polar Sciences and Technologies of the Department of Environmental Sciences, University of Siena.



The chemical analysis of PD showed that the most frequent plastics polymer was Polypropylene (Figure 3a and b). POPs levels are shown in Figure 4.

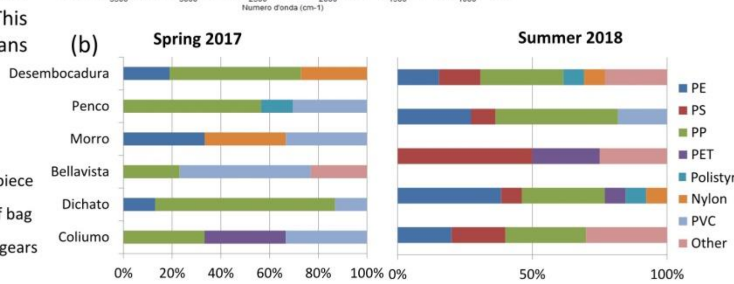
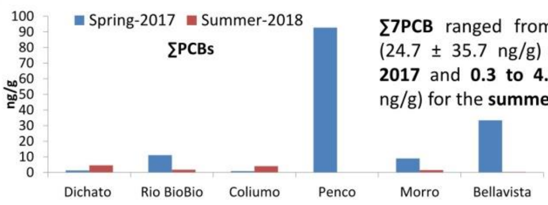
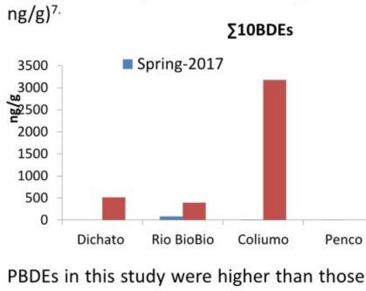


Figure 3. Polymers characterization (n=89 samples analysed) of macroplastics, (a) FT-IR spectrum and (b) Polymers composition,, found in touristic beaches of Central Chile, during spring 2017 and summer 2018. (PE= Polyethylene, PS= Polystyrene, PP= Polypropylene, PET= Polyethylene terephthalate, PVC= Polyvinyl chloride)



∑7PCB ranged from **0.9 to 93 ng/g** (24.7 ± 35.7 ng/g) during the **spring 2017** and **0.3 to 4.5 ng/g** (2.4 ± 1.8 ng/g) for the **summer 2018** samples.

This PCB levels are lower than those reported in San Diego, California (USA) (2.5 to 47 ng/g)[5], in Canary Islands beaches (1 to 772 ng/g)[6] and in urban beaches (1 to 436 ng/g)[7].



∑10BDEs levels showed values of **2.1 ng/g to 1300 ng/g** (238 ± 521 ng/g) for the **spring 2017** and **392 to 3177 ng/g** (1222 ± 1174 ng/g) for the **summer 2018** samples.

PBDEs in this study were higher than those reported in urban beaches (0.02 and 412 ng/g)[7] and similar to those reported in Canary Islands beaches (0.1 and 3924 ng/g)[6].

Figure 4. POP levels in Macroplastics sampled in touristic beaches of Central Chile.

Characterization of microplastics along the coast of Concepción bay, Central Chile

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INTRODUCTION

In recent years, there has been increasing concern about "microplastic particles" (MP) (plastic fragments smaller than 5 mm) in the environment. Due to their small size, MP are considered bioavailable for organisms throughout the food chain and for humans. In Chile, recent studies have detected microplastic in abiotic matrices along the Chilean coast. In this study we assess the occurrence of MP in sand samples from Concepcion Bay which is a coastal ecosystem with a vital role in the economic sustainability of the Biobío region of central Chile. The bay holds several beaches, along the coast, used for recreational activities by the population during the summer period. In this study we have physically and chemically characterized MP, in sand samples, of the beaches of Concepción bay, in central Chile, during two years in different seasons in order to preliminary assess population exposure to MP.

MATERIALS AND METHODS

Sand samples (250 g) were collected in four location of Concepción bay at six beaches: i) at Dichato, ii) in Coliumo, iii) in Tome town (at Bellavista, El Morro, and Estación beach) and iv) in Penco, during four seasons (September 2015 (winter) - March 2018 (Summer)) (Figure 1). Samples were taken in glass bottles and analyzed using a saline solution (NaCl 1.2 kg/L)[1,2] and filtered using a filtration system under vacuum, with glassfiber filters (Whatman GFF)[1]. Then, the samples were analyzed physically (for size, colour and shape) using optical microscope with an integrated camera, Leica DM 750 and chemically screened under a Spotlight 400 FT-IR microscope and Spectrum Frontier, Perkin Elmer (Figure 2).

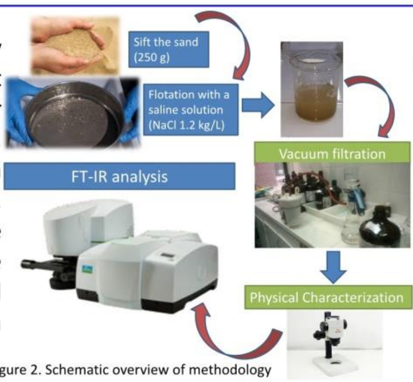


Figure 2. Schematic overview of methodology

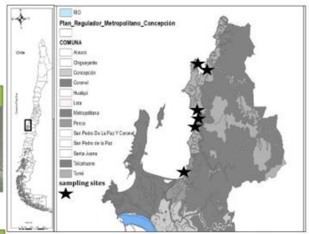
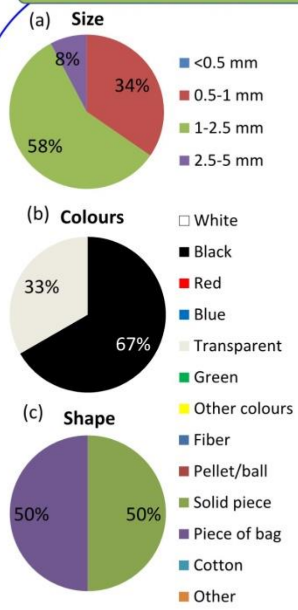


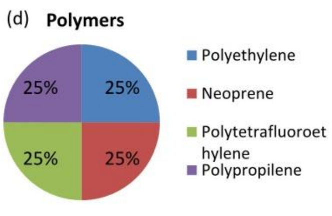
Figure 1. Concepción Bay location and sampling sites.

RESULTS AND DISCUSSION

The preliminary results of MP in sand samples showed, in general, an average abundance of 0.07 ± 0.04 MP items/g, showing greater abundance in summer season.

A total of 46% of the particles was analyzed in the FT-IR, where **25% of the particles were MPs**. The MPs physical characterization showed the predominance size was 1-2.5 mm; the shape was 50% solid pieces and 50% pieces of bag; the colour with the highest frequency of detection was black colour (67%), and transparent colour (33%). The **polymer analysis** showed mainly the abundance of **polyethylene (25%),** followed by **Neoprene (25%), Polytetrafluoroethylene (PTFE) (25%) and Polypropylene 25%**.





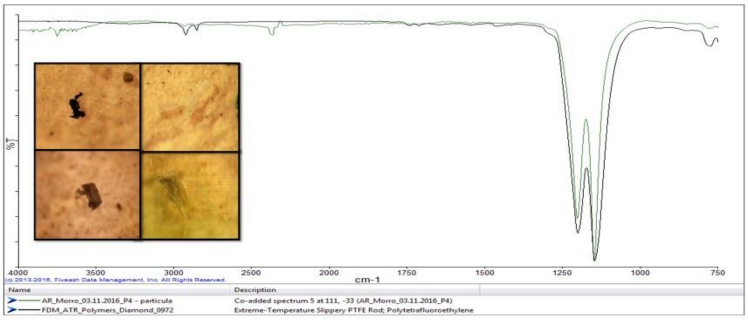


Figure 3. Physical characterization (a) size; (b) color; (c) shape; (d) polymers.

These results are consistent with other studies conducted in China, where the most abundant polymer was Polyethylene[3] and the presence of non-plastic particles like cellulose[3,4]. A large amount of polyethylene (49%) and polypropylene (38%) particles are also found on the beaches of South Korea[5]. The polymers type found on the sand samples from the beaches of the Concepción Bay are mainly used in a wide variety of applications including packaging, containers, pipes, electrical insulation, coating and kitchen utensils.

CONCLUSION

These data are the first information of MP in Concepción Bay and are consistent with other studies in the scientific literature. The areas with the greatest presence of MPs were, El Morro beach, in Tome small town, and at Dichato, both located on the north-east coast of the Concepción Bay, both with a strong touristic activity in the summer period. Further studies are required to evaluate the environmental hazards of microplastics, especially as they may “act as vector of contaminants” into the coastal areas.

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Acknowledgment: This research was funded by FONDECYT project (No. 1130329, K. Pozo) and supported by the RECETOX Research Infrastructure (LM2015051 and CZ.02.1.01/0.0/0.0/16_013/0001761). Thanks to the PhD Program in Environmental, Geological and Polar Sciences and Technologies of the Department of Environmental Sciences ,University of Siena.

DioXin 2018
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Persistent Organic Pollutants (POPs) in the marine food web from Central Chile

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Introduction

Many studies have estimated human exposure to toxic chemicals have concluded over 90% of the intake is from contaminated food[1]. Persistent Organic Pollutants (POPs) are ubiquitous in the environment and they are a global international concern[2]. They have been identified as harmful substances due to their toxicity, persistence and bioaccumulation in humans and wildlife. Limited data is available concerning the levels of POPs in seafood from Chile. In particular, organic chemicals (PCBs, PBDEs, chlorinated pesticides (OCPs))[3,4] have been measured in farmed fish products from Southern Chile. Concepción Bay is a costal embayment located in the Biobío Region of central Chile.

Figure 1. Concepción Bay location.

Concepción Bay (Figure 1) has a vital role in the sustainability of the socio-economic development and health of the neighboring population in the region. The bay supports the adjacent coastal aquatic ecosystem, wild life and human food chain. **The objective of this study was to determine POPs in a variety of marine organisms, primary, secondary and tertian consumers from Central Chile.**

Materials and methods

In this study, we have analyzed marine organisms (from different trophic levels) (Figure 2).

Tertiary consumers: *Trachurus picturatus murphyi* (n = 8), *Brama australis* (n = 4), *Merluccius gayi gayi* (n = 4).

Secondary consumers: *Alpheopsis chilensis*.

Primary consumers: *Pyura chilensis*, *Venus antiqua*, *Fissurella nigra*, *Choromytilus chorus*, *Aulacomya atra* and *Tegula atra*.

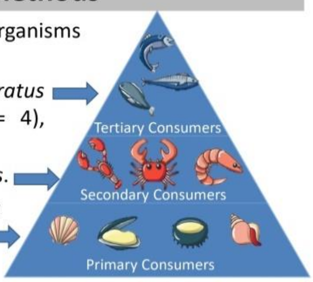

Figure 2. Marin food Chain

Chemical analysis: Samples were homogenized with anhydrous sodium sulphate, then spiked with 13C extraction standards and extracted using DCM in an automated Soxhlet extraction system (Büchi B-811). Fractionation was achieved on a silica gel column; a sulphuric acid modified silica gel column was used for PCB/OCP samples. For PFC prior to extraction all samples were spiked with labelled standards (M8PFOA, M8PFOS). All samples were extracted with 5 mM ammonium acetate in methanol using a B–811 automated extraction unit (Büchi, Switzerland).

Organism samples were analyzed for DDTs, 9 PCB congeners, 10 PBDE congeners, and PFCs. The PBDE analyses were performed by gas chromatography– mass spectrometry (GC–MS) on a 7890A GC instrument (Agilent, USA)[5]. PFCs were measured using high performance liquid chromatography (UHPLC) with an Agilent 1290 (Agilent Technologies, Palo, Alto, California, USA[6].

Results and discussion

DDTs: Levels of DDTs (total 6 isomers) (ng/g dry weight (dw) ranged from not detected (nd) to 2(mean ± SD= 0.8 ± 1.4) in primary, from 0.1 – 0.9 (0.5 ± 0.6) for secondary consumers however, in the tertiary consumers ranged from 0.1 – 15 (2 ± 4) (Figure 3). These results are comparable with other remote areas of the world where DDT levels were low[7].

Polychlorinathed biphenyls (PCBs): The results obtained in this study showed low concentrations of ∑7PCBs (ng/g d.w) in organisms and ranged from nd to 22 (5.5 ± 9.4) in primary, from 0.04 – 0.7 (0.4 ± 0.5) for secondary consumers and from 0.04 to 15 (2 ± 4) for tertiary consumers (Figure 3). In general, these results were below to the limits established by the European Union for mollusk and fish (0.075 mg/Kg, UE No. 704/2015).

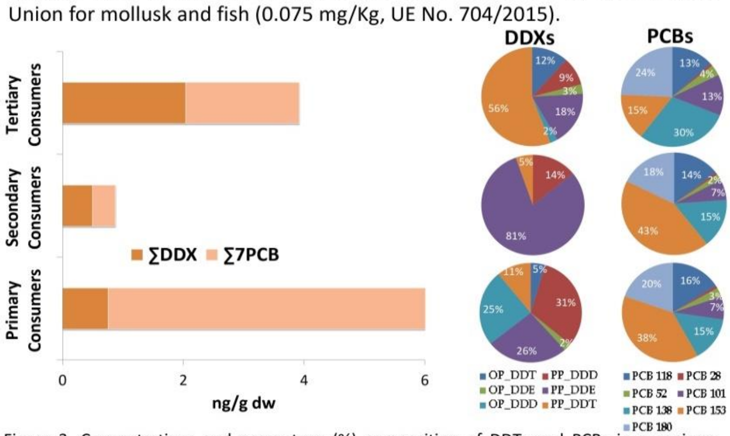

Figure 3. Concentrations and percentage (%) composition of DDTs and PCBs in organisms (primary, secondary and tertiary consumers) from central Chile.

Polybrominated diphenyl ethers (PBDEs): The results obtained in this study showed concentrations of ∑10PBDEs (pg/g d.w) in organisms ranged from 44 to 493 (189 ± 267) in primary, from 5 – 74 (40 ± 49) for secondary consumers and from not detected (nd) to 4559 652 ± 1235) to tertiary consumers (Figure 4). These values are similar than those reported fro PBDEs previously in the Concepcion bay (Pozo et al., 2015).

PFC: The results obtained in this study showed low concentrations of PFOA and PFOS (pg/g d.w) in organisms and ranged from nd to 346 (55 ± 157) and nd – 3810 (714 ± 1518) respectively in primary consumers, for secondary consumers nd – 198 (198 ± 0) and 25 – 78 (52 ± 38) respectively, and for tertiary consumers nd – 646 (190 ± 313) and 39 – 18500 (4274 ± 7404) respectively (Figure 4). These results obtained can be compared with results obtained from the Mediterranean Sea[8,9].

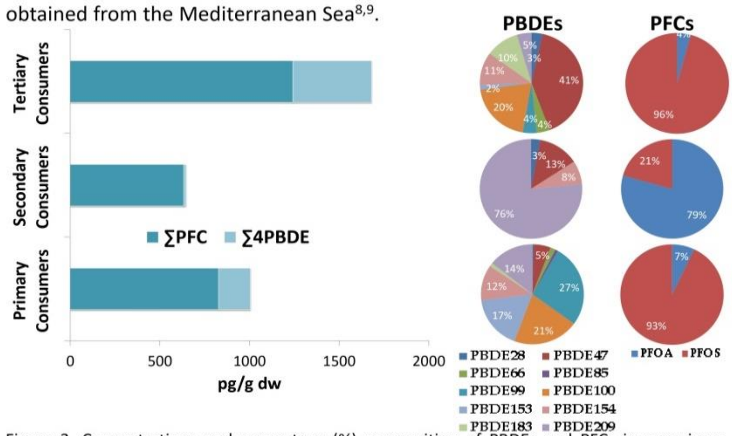

Figure 3. Concentrations and percentage (%) composition of PBDEs and PFCs in organisms (primary, secondary and tertiary consumers) from central Chile.

Conclusion

PBDEs showed the highest levels detected (pg/g dw) in this study. The predominant congeners were PBDE47, 99 and 209; followed by the PFCs (PFOA and PFOS). The organisms of higher trophic level were those that presented the highest concentrations of these pollutants. PCBs concentrations were higher than DDX, the predominate congeners were for PCB28, 138 and 180. These pollutants were more abundant in the organisms of low trophic level. This is the first report in which the POPs concentration and emerging pollutants are estimated in organisms of different trophic levels in the coastal zone of central Chile.

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Acknowledgements

This research was funded by FONDECYT project (No. 1130329, K. Pozo) and supported by the RECETOX Research Infrastructure (LM2015051 and CZ.02.1.01/0.0/0.0/16_013/0001761). Thanks to the PhD Program in Environmental, Geological and Polar Sciences and Technologies of the Department of Environmental Sciences of the University of Siena.