PERSISTENT ORGANIC POLLUTANTS SORBED IN PLASTIC RESIN PELLET FROM COASTAL AREAS OF CENTRAL CHILE

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Introduction

In the last decade increasing concern has been raised by the Plastic pollution worldwide. Two main scenarios characterize this type of global issue, first the macro scenario, macroplastics of dimensions >25mm[1] and microplastic particles- (particles or fragments of dimension <5mm[2]. The macroplastics pollution has been well identified mainly because the observable damage produced by big pieces of plastics detected in the marine fauna and that have caused death or pollution in the aquatic environment[3]. While for microplastic, the small dimension of MP is a key factor to identify this issue. The primary sources of microplastics are identified as i) as derived from hand and facial cleansers, cosmetic preparations, air blast cleaning media, microfibers coming from urban liquid waste (Houses waste and from plastic processing plants) and ii) secondary sources (unintentional spills of plastic resin pellets, other sources like derived from fragmentation of macro-plastic as a result of photodegradation and abrasion due to wave action)[4].

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., are 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 <5 mm. Due to their buoyancy and lightness characteristics, polyethylene (PE) and polypropylene (PP) pellets can play a role as vector and facilitate the transport by surface runoff, streams, rivers and eventually end up in the ocean [5]. In the other hand, because of their chemical nature, plastic resins sorb and concentrate pollutants [6-7], in particular hydrophobic chemical products, such as Persistent Organic Pollutants (POPs) including polybrominated diphenyl ethers (PBDEs)[8]. POPs are substances of international concern because they persistence, and potential of bioaccumulation process[9]. The coastal areas of central Chile are characterized by heavy industrial activities[10-11]. The aims of this study were to determine and characterize (physically and chemically) plastic resin pellets and their chemical burden in particular POPs for PBDEs in coastal areas of Central Chile. This investigation will provide new information for spatial distribution and likely a time trend for previously measured POPs.

Material and Methods

Plastic resin pellets were sampled in the central coast of Chile at Desembocadura Beach, Lenga Beach and Concepción Bay (Penco, Tome, Coliumo e Dichato). Pellet samples (>1 g for each site), were only recovered at Lenga beach, located in San Vicente Bay (36°45′S, 73°10′W), in the Peninsula of Hualpén in Central Chile (Figure 1). At each site samples were collected from the low tide line and from the upper line on the beach (Figure 1). Firstly, pellets were physically analyzed by the determination of: i) diameter, ii) thickness and iii) color (white/ yellowed; the latter were correlated to aged pellets). Secondly, the samples were chemically characterized through the analysis of i) sorbed POPs and ii) plastic composition.

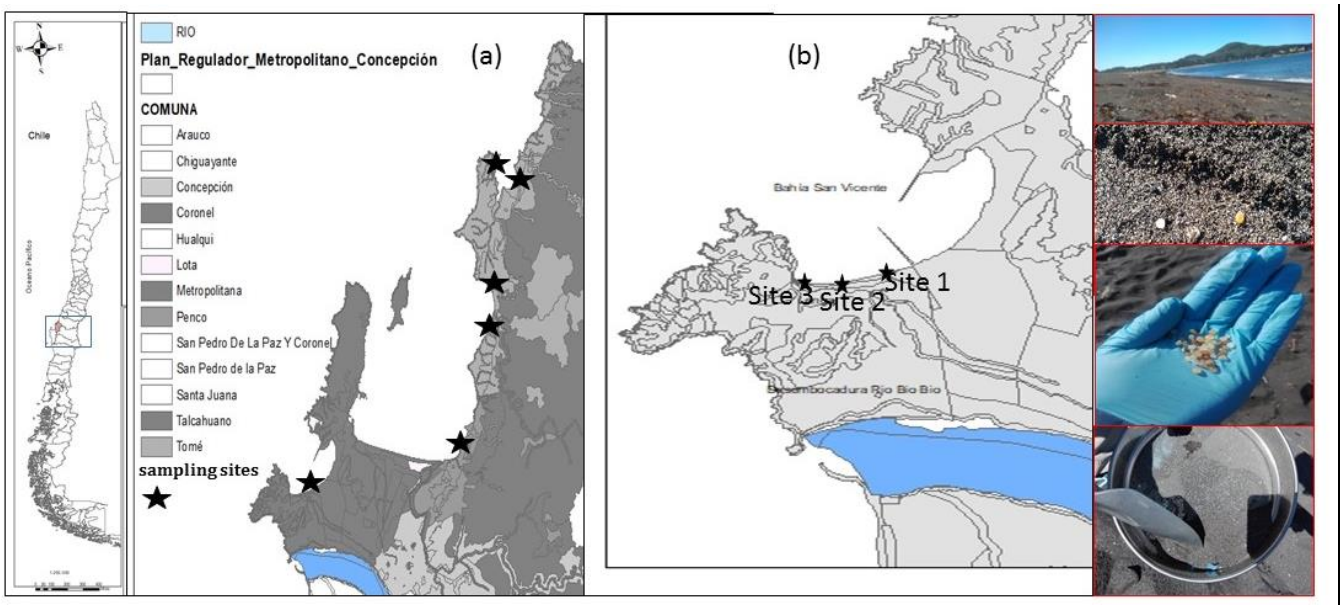

Figure 1. Location of sampling site (a) in Lenga beach (red dotted line along the coast) at San Vicente Bay (b) in central Chile. ((c) Pictures of sampling campaign and plastic pellets).

Chemical analysis.
The samples (1 g) were extracted by ultrasonic bath with 15 ml of hexane during 15 minutes (3 times). After extraction, samples were reduced to 5 ml and 3 ml of concentrated sulfuric acid was added and they were heated at 45°C for 15 min to eliminate interferences for chlorinated compounds analysis. Samples were then centrifuged at 15000 rpm x 10 min. The organic phase was separated from the inorganic with a Pasteur pipette and washed with hexane. All samples were nitrogen blow-down 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 dichloromethane (DCM) and 40 ml of DCM/hexane 1:1. After clean-up, the samples were concentrated at 35°C up to a volume of 100 µl and were added 50 µl of nonane and hexane and then re-concentrated to 50 µl.

Target compounds
10 PBDE congeners were screened (BDE28, 47, 66, 85, 99, 100, 153, 154, 183 and 209) (purchased from Wellington Laboratories (Ontario, Canada). The analysis was 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 x 0.10 m) (Restek, USA) coupled to an AutoSpec Premier MS (Waters, Micromass, UK). The mass spectrometer (MS) were operated in EI + mode in the resolution of > 10 000.

Pellet analysis
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.

Quality Control and Quality assurance (QA/QC)
Instrumental limits of detection (LOD) and limits of quantification (LOQ) were calculated from lowest calibration point as an amount producing signal to noise 3 (LOD) and 10 (LOQ). Recoveries for PCB121 and PCB30 were in the range 69 to 74%. All PBDE standards were from Wellington Laboratory. POPs concentrations in the samples were recovery-corrected using recoveries of surrogates (i.e., deuterated ^{13}CPBDEs, spiked before analysis (100 µl and concentration or amount of Standards). Recoveries of ^{13}CPBDEs were 75±5%. Procedural blanks (n=14) were also assessed and no record of targeted compounds were detected.

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=6 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 3.9 ± 0.7 mm and color abundance of white (32%) and yellowed (68%). The identification of plastic polymer was carried out using FT-IR technique. Results showed high-density polyethylene as the most abundant polymer type (99%) with exception of only one pellet detected at site 1 (high intertidal), which corresponds to dark gray pellet identify as isotactic polypropylene. The prevalence of pellets only at Lenga beach and type of polymers could be associated

to the production of thermoplastic resins in the surrounding coastal area influenced by industrial activity. Indeed, the regional report released by the Communal regulatory Plan (PRCH, Spanish initials)[12] of Hualpén shows that there are approximately 20 industries, and among them, a few plastic/resin pellets producers. In addition, Lenga beach is also located in the vicinity of the San Vicente Harbour (approximately 5 Km) which could contribute with unknown spill of nurdles. These findings are similar to those reported in previous work where several POPs were assessed in polymers such as polyvinylchloride (PVC), polyethylene (PE), polystyrene (PS) and polyoxymethylene (POM)[8].

Polybrominated diphenyl ethers (PBDEs) which are organobromine compounds are used in a wide array of products as flame retardant including building materials, electronics, furnishings, motor vehicles, airplanes, plastics, polyurethane foams, and textiles[13]. In this study, PBDEs levels range from 10 to 133 000 pg/g-pellet (133 ng/g-pellet) and showed a clear decreasing pattern from site 1 (located beside a gas pipeline) 133 000 pg/g-pellet (133 ng/g-pellet) to site 3 with 10 pg/g-pellet. PBDE209 was prevalent and accounted for 50 to 98% of the total PBDEs composition (Figure 2). With exception of site 1. These results were higher than those reported in Brazilian beach pellets with a range of <0.26 to 5.56 ng/g-pellet[14], PBDEs in pellets from remote and urban beaches in the Pacific Ocean 0.3 to 129 ng/g-pellet[15] and Canary Islands beaches (0.05 – 180 ng/g-pellet)[16].

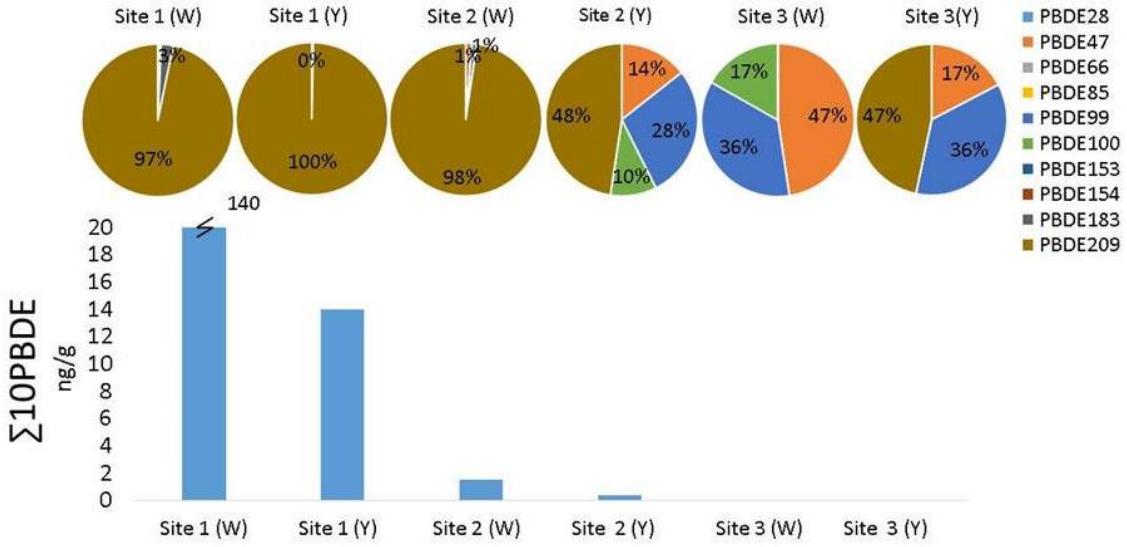

Figure 2. POPs concentration (ng/g-pellet) for ΣPBDEs Lenga Beach at San Vicente Bay, Central Chile.

Conclusions

From all sampling sites pellets were only found at Lenga Beach located in San Vicente Bay of Central Chile. The prevalent polymer plastic type was high-density polyethylene. PBDEs showed the high levels compare with other studies, with PBDE209 as the main component of plastics pellets. These findings are consistent with other investigations around the world and highlight the capacity of plastics resin pellets to trap and consequently transport POPs into coastal environments. The fate of pellets is still unknown, however, could represent a potential human exposure, in particular, at touristic beaches highly crowded during summer seasons. Nevertheless, further research is still need to elucidate proper environmental strategies to reduce their impact to the population and wild life.

Acknowledgements

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