Novel Flame Retardants in Marine Debris of Coastal Areas in Central Chile

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1 Introduction

Plastics are multipurpose and have replaced almost any material, they are cheap, light and have high resistance, that is why their production has increased successively over last years, with a world production of 367 Mt in 2020[1]. Plastics can serve as an important source of pollutants which are primarily used as plastic additives. Flame retardants (FRs) are compounds applied to consumer products and materials to slow down or to hinder their combustion[2], being useful to improve the life cycle of products[3]. Particularly, brominated flame retardants (BFRs) are synthetic compounds which are added to enhance the safety of a variety of commercial, consumer and industrial products to inhibit the propagation of fire, such as furniture, electrical and electronic equipment (EEE), plastics, toys, textiles, and clothing[4]. During the last few years BFRs have been progressively regulated (elimination of its production and use) by the Stockholm Convention and implemented by the European Commission[5]. These regulations have prompted the manufacture of replacement products, such as novel flame retardants (nFRs) (also known as "alternative," "emerging," "new," "current-use")[6]. There are about 75 nFRs that have been manufactured, for which their production volume, high distribution in the environment, bioaccumulation, and toxic potential position them as priority contaminants[7]. Regarding plastic pollution, 9 million tons of plastic per year are dumped and enter marine estuaries, coasts, or hydrological basins through different sources[8], which are estimated to reach the sea. The non-regulation and the non-cleaning of beaches generate a great disorder and contamination, which later results in an extensive mass of floating garbage due to the Humboldt current in most of the coasts of the north, center and south of our country[9]. Recently, in Chile only few studies have reported toxic substances in marine debris[10,11,12], between those chemicals, flame retardants (PBDEs) and perfluoroalkyl compounds (PFASs) were reported in a coastal area in Central of Chile. The aims of this study were: to evaluate the levels of nFRs (PBBZ, BTBPE, HBB, PBEB, pTBX, PBT, alphaTBCO, alphaTBECH, betaTBECH, HCDBCO, DPTE, BATE, AntiDP, SynDP, T23BPIC, TBCT, betaTBCO, DBDPE and gama+deltaTBECH) in marine plastic litter (MPL) from coastal areas of central Chile. This investigation contributes with new and valuable information on chemical composition of MPL and to reduce its impacts on the marine ecosystem.

2 Material and Methods

Marine litter was collected at six beaches in November 2017: Dichato (D), Coliumo (C) (located in the Coliumo Bay, in the northern part of Concepcion Bay), Negra (N), El Morro (M), Bellavista (B) and Desembocadura BioBío (DB) (located at the northern part of the mouth of the Bíobío River) (Fig. 1). Further details for the sampling protocol were presented elsewhere by Gómez et al.[11].

Chemical analysis was done using ultrasonic extraction to analyze samples (UAE, Banderlin Sonorex) three times (3 × 15 min) with 10 mL hexane. After the extraction, the sample volume was reduced under a gentle stream of nitrogen at ambient temperature. Sample cleanup, compounds instrumental and quality assurance/control (QA/QC) details were reported elsewhere by Corsolini et al.[13]. The recoveries of ^{13}C-labeled compounds were within an acceptable range according to EPA method 1614 (25–150%).

The limits of quantification (LOQs) were set as the mean value of target compounds detected in procedural blanks plus ten times of standard deviations. For the undetectable compounds in blanks, the LOQs were set as a signal to noise ratio of 10. The LOQs ranged from 0.1-222 pg g^{-1} for nFRs. Three solvent blanks were used to evaluate contamination from the laboratory procedures. The concentrations of average and SD of the detected FRs with MLOQ are summarized in Table 1.

3 Results

From all nineteen nFRs analyzed only nine (50%) were routinely detected (Table 1). Chemicals showed the following decreasing pattern: BTBPE > AntiDP > HBB > SynDP > PBBZ > PBT > alphaTBCO > a-TBECH > b-TBECH.

The 1, 2-bis (2,4, 6-tribromophenoxy) ethane (BTBPE) was the most abundant compound with levels ranging from 600 to 424 000 pg g^{-1} (70 815 ± 173 024) (Figure1; Table 1) and was detected at Bellavista. AntiDP, ranged from 20 to 20 000 pg g^{-1} (4 260 ± 8 581); and SynDP ranged from 100 to 5 000 pg g^{-1} (1 019 ± 1 987).

The hexabromobiphenyl (HBB) ranged from 2 600 to 14 000 pg g^{-1} (7 328 ±3 722) with the highest concentration found in Coliumo (Fig. 1). Levels of PBBZ ranged from 300 to 1 000 pg g^{-1} (583 ± 311) (with the highest concentrations in Bellavista) and PBT levels were 170 to 850 pg g^{-1} (431 ± 229) (Fig. 1; Table 1). For α-1,2,5,6-Tetrabromocyclooctane (alphaTBCO), level was 624 pg g^{-1} (104 ± 255) and the highest concentration was found in Morro. In this study, Tetrabromoethylcyclohexane (alpha and betaTBECH) levels were also detected. AlphaTBECH (160 to 240 pg g^{-1} (160 ± 84) showed the highest concentration registered in Dichato; and for betaTBECH (110 to 200 pg g^{-1} (123 ± 69)) the highest concentration was in Bellavista (Figure 1; Table 1).

Table 1: Concentrations of nFRs (pg g^{-1}) measured in marine plastic litter samples from six beaches of Central Chile.

Compound	BTBPE	antiDP	HBB	synDP	PBBZ	PBT	alphaTBECH	betaTBECH
Dichato	<LOQ	26	6320	108	428	325	239	165
DB	<LOQ	985	2630	306	304	169	160	124
Coliumo	<LOQ	251	13700	113	903	850	<LOQ	<LOQ
Negra	618	232	7120	147	535	453	175	134
El Morro	<LOQ	234	5450	371	303	431	166	112
Bellavista	424000	19600	8750	5070	1030	358	218	206
Average	70815	4260	7328	1019	584	431	160	124
SD	173025	8581	3722	1987	311	229	84	69

LOQ: for BTBPE<69.2 - <222, for alphaTBECH is <0.22 and for betaTBECH is <0.16. Abbreviations: SD: standard deviation, BTBPE: 1, 2-bis (2,4,6-tribromophenoxy) ethane, DechloranePlus(anti- and syn-), HBB: Hexabromobiphenyl, PBBZ: pentabromobenzene, PBT: polybutylene terephthalate, Tetrabromoethylcyclohexane (alpha and betaTBECH).

4 Discussion

It is difficult to identify sources of chemicals associated to MPL. Previously, the characterization of plastic polymers was reported in Gomez et al.[11]. The analyzed coastal areas showed the prevalence of plastics such PP, PVC, in the spring of 2017. Such information could provide insights about additives found in plastics (or in this case to MPL). For example, it has been reported that PVC can contain chlorine like chlorinated paraffins or bromine, which can act by removing the radicals H+ and OH- in the gaseous phase of the flame. Among the flame retardants for PVC, antimony trioxide[15] is the best known for its high cost/benefit ratio and its effectiveness in putting out fire without altering dielectric properties of the finished product. In addition, the use of alpha and betaTBECH has also been detected in PVC electrical cable coating, other used nFRs are TBPH, TBC and T23BPIC[16].

5 Conclusions

Levels of nFR in MPL in the literature are poorly reported, which hinders the comparison of results in other coastal areas of the world. In this study BTBPE and other nFRs were particularly high at Bellavista site (beach location) which highlights the importance to improve the management of solid waste like MPL along the coastal tidal zones because of the likely exposure to people during the summer months. Further research is still ongoing in order to evaluate MPL impact in the coastal ecosystem.

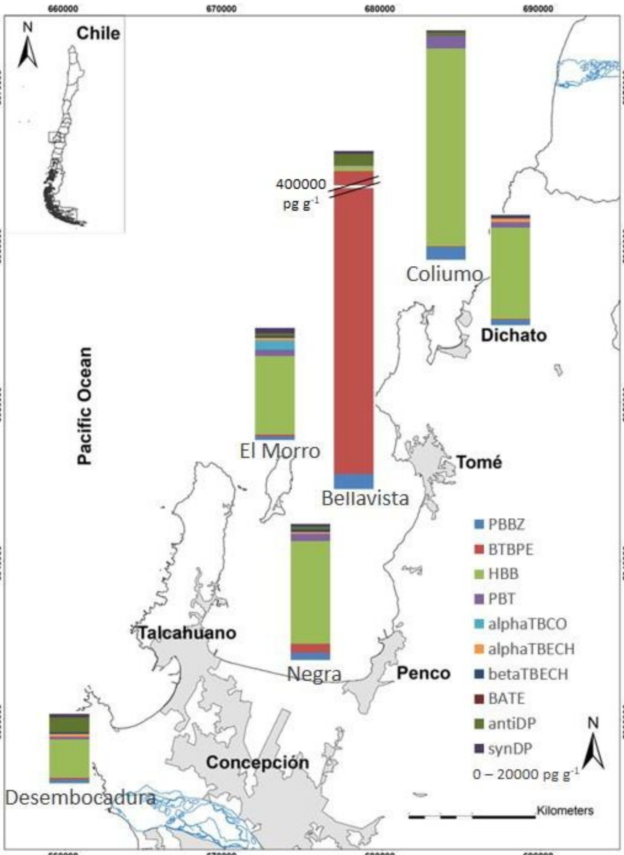

Figure 1: Sample sites and concentration of BTBPE, AntiDP, HBB, SynDP, PBBZ, PBT, alphaTBCO, alphaTBECH, betaTBECH and BATE (pg g^{-1}) in macroplastic samples from coastal areas, central Chile.

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7 References
1. PlasticEurope. 2021. Plastics - The Facts 2021: An analysis of European plastics production, demand and waste data.
2. de Wit, C.A. 2002. An overview of brominated flame retardants in the environment. Chemosphere 46, 583–624
3. Hahladakis, J.N., Velis, C.A., Weber, R., Iacovidou, E., Purnell, P. 2018. An overview of chemical additives presents in plastics: migration, release, fate and environmental impact during their use, disposal and recycling. J. Hazard. Mater., 344, pp. 179-199.
4. Li, X., Ren, Q., You, X. 2019. Material flow analysis of discarded refrigerators from households in urban and rural areas of China. Resour. Conserv. Recycl. 149: 577–585
5. EU Regulation. 2017. Commission Regulation (EU) 2017/227. Annex XVII to Regulation (EC) No 1907/2006 of the European Parliament and of the Council concerning the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) as regards bis(pentabromophenyl)ether.
6. SC-POPs, 2017. Stockholm convention. Texts and Annexes Revised in 2017, available at: http://chm.pops.int/
7. McGrath, T. J., Ball, A. S., Clarke, B. O. 2017a. Critical review of soil contamination by polybrominated diphenyl ethers (PBDEs) and novel brominated flame retardants (NBFRs); concentrations, sources and congener profiles. Environ. Pollut. 230, 741-757.
8. Jambeck, J.R., Geyer, R., Wilcox, C., Siegler, TR., Perryman, M., Andrady, A., Narayan, R., Law, K.L. 2015. Plastic waste inputs from land into the ocean. Science, 347(6223), 768–771.
9. SINIA-MMA. 2021. Informa del Estado del Medio Ambiente/Capítulo6/Océanos (https://sinia.mma.gob.cl/wp-content/uploads/2021/04/6-oceanos.pdf)
10. Pozo, K., Urbina, W., Gómez, V., Torres, M., Nuñez, D., Přibylová, P. (2020). Persistent Organic Pollutants Sorbed in Plastic Resin Pellet - "Nurdles" from Coastal Areas of Central Chile. Mar. Pollut. Bull. 151, 110786.

11. Gomez, V., Pozo, K., Nunez, D., Pribylova, P., Audy, O., Baini, M., Fossi, M.C., Klanova, J. 2020. Marine plastic debris in central Chile: characterization and abundance of macroplastics and burden of persistent organic pollutants (POPs). Mar. Pollut. Bull. 152.
12. Gómez, V., Torres, M., Karásková, P., Přibylová, P., Klánová, J., Pozo, K. 2021. Occurrence of Perfluoroalkyl Substances (PFASs) in marine Plastic Litter From Coastal Areas of Central Chile. Mar. Pollut. Bull. 172, 112818–112826.
13. Corsolini, S., Metzdorff, A., Baroni, D., Roscales, J.L., Jimenez, B., Cerro-Galvez, E., Dachs, J., Galban-Malagon, C., Audy, O., Kohoutek, J., Pribylova, P., Poblete-Morales, M., Avendano-Herrera, R., Bergami, E., Pozo, K. 2021. Legacy and novel flame retardants from indoor dust in Antarctic: Sources and human exposure. Environ. Res. 196
14. Chen, S. J., Ma, Y. J., Wang, J., Chen, D., Luo, X. J., Mai, B. X. 2009. Brominated flame retardants in children's toys: concentration, composition, and children's exposure and risk assessment. J. Environ. Sci. Technol. 43(11), 4200-4206.
15. van der Schyff, V., du Preez, M., Blom, K., Kwet Yive, N, S., Klánová, J., Přibylová, P., Audy, O., Martiník, J, Bouwman, H. 2021. Chlorinated and brominated persistent compounds in hard coral, soft coral, and parrotfish from remote Mascarene islands. Chemosphere, 267, 129316.
14. Czégény, Z., Jakab, E., Blazsó, M., Bhaskar, T., Sakata, Y. 2012. Thermal decomposition of polymer mixtures of PVC, PET and ABS containing brominated flame retardant: Formation of chlorinated and brominated organic compounds., J. Anal. Appl. Pyrolysis. 96, 69-77.
15. Wellington Reporter. 2011. New brominated flame retardant. Tris(2,3-dibromopropyl)isocyanurate. Product updates from Wellington Laboratories. December 2, 2011.