POLYBROMINATHED DIPHENYL ETHERS (PBDEs) IN CONCEPCION BAY, CHILE AFTER THE 2010 TSUNAMI

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Introduction

Concepción Bay is a natural bay located on the coast of the Province of Concepción in the Bío Bío Region of central Chile. The environmental health of Concepción bay has a vital role in the sustainability of the socio-economic development of the neighbouring population in the region. The bay supports the adjacent coastal aquatic ecosystem, wild life and humans food chain. For instance, Concepción bay is used for several including maritime traffic, recreational activities (i.e., fishing and swimming), management areas for benthic resources, small economic entrepreneur (artisanal fisheries) and others. However, the Concepción Bay is surrounded by one of the most industrialized and urbanized areas of Chile[1,2]. The contribution of particulate organic matter (POM) in this bay is supported by its biological production, fluvial contributions, authorized sanitary discharges, shipyard, industrial wastewater and anthropogenic activity. Within the bay are many of the most important ports of the region and the country (Talcahuano, Lirquén and Tomé). Previous studies have reported high levels of Polycyclic Aromatic Hydrocarbons (PAHs) in sediments of the Concepción Bay[2]. However, information of others toxic chemicals in the Bay is scarce. In February 2010, the Concepción Bay was hit by an earthquake and tsunami event that might have "reset" the marine ecosystem of the Bay by changing the chemical composition of the sedimentary records and its geomorphology.

Flame retardants are brominated organic compounds (BFRs) that are produced and used widely to prevent the spread of fire. BFRs are estimated to represent 39% global market flame retardants from 2000, and its use in the electronics industry, in particular, accounted for 35-40% of flame retardant used[3]. Polybrominated diphenyl ethers (PBDEs) are one type of BFR commonly used for decades in plastics, foams, textiles and other materials. The use of PBDEs has increased in the last 20 years and, as a result, large amounts of these compounds have been released into the environment during its production and use. Commercial production of PBDEs began in the 1970s in Germany[4]. PBDEs are not manufactured in Chile, but Chile imported them as commercial mixtures and used them to various intermediate and finished products, such as appliances, furniture, car seats, and a variety of electrical and electronic components. The main commercial mixtures used worldwide are the penta-, octa- and deca-PBDE. PBDEs have high octanol-water partition coefficient (Kow) therefore they show highly lipophilic and hydrophobic property, they can be easily accumulated in the fatty tissue and can be passed through the food and trophic chain[5]. Due to their toxicity and persistence, the industrial production of some PBDEs is restricted under the Stockholm Convention[6]. The PBDE literature in the Chilean environment is very limited. In the past four years, only few studies has been conducted in Chile on emerging compounds such as PBDEs. For instance Montory et al.,[7] reported PBDE levels in wild chinook salmon (*Oncorhynchus tshawytscha*) in the Northern Patagonia and in farmed fish tissue (*Salmo Salar*) and recently, Baron et al.,[8,9] has reported levels of brominated flame retardants in central Chile.

The objective of this study is to contribute with new information of the environmental status of Concepción Bay by analyzing PBDEs in sediments and organisms from central Chile. This investigation is part of an ongoing project in central Chile aimed to study Persistent Organic Pollutants (POPs) and emerging compounds in sediments, water, organisms and air in order to know the chemical characterization of Concepción Bay after the 2010 Tsunami in central Chile.

Materials and methods

Study area

The Concepción Bay (36° 40'S, 73° 01'W), has a strong seasonality and high biological productivity of the water column due to wind driven upwelling[1]. The productivity of this system is supported by upwelling and intrusion of coastal waters with high nutrient content. The main activities that contribute to the load of organic and inorganic compounds in Concepción Bay are: Harbour activities (harbour cities of Talcahuano, Lirquén, Penco and Tomé), seasonal discharge of oil from oil processing industries, the activities of the industrial and artisanal fisheries, waste

water effluents and marine shipyards. The Andalién River flows into the southeast sector at the head of the bay contributing with untreated sewage from nearby towns and residual chemicals from agriculture and forestry in the Cordillera de la Costa[2].

Sampling of sediments and marine organisms

Surface sediment (15 g) were taken at three stations in the Concepción Bay (Talcahuano, Lirquén and Tumbes) (Figure 1) using Van Veen grab (0.3 m^2). Samples were transported to the laboratory in pre cleaned glass jars and then freeze dried at -50°C and 0.2 mbar for further chemical analysis.

Sediments and organism analysis

The species of organisms analyzed were taken in three locations in Concepción Bay (Tumbes, Talcahuano, and Lirquen) and correspond to primary consumers (including filtering): *Fisurella sp* (n= 4), *Chilensis Pyura* (n= 4), *Mytilus chilensis* (n= 6), *Venus antiqua* (n= 4), *Aulacomya atra* (n = 5). Results are expressed in pg/g or ng/g dry weight (d.w) in sediment and pg/g d.w lipid content. The lipid content of the species studied was ~ 5 %. The biotic material was spiked with ^{13}C extraction standards and extracted by sonication in DCM, triplicates were pooled and solvent was reduced under stream of nitrogen to a volume of approximately 10 mL. The reduced extract was split into 2 aliquots, 1/10 for PAHs analysis, 9/10 for POPs analysis. Clean-up of the POPs aliquot was performed on a modified silica column, 25 mm i.d. (3g silica+20g 44% H_2SO_4 silica+10g 22% H_2SO_4 silica+6g silica+10g Na_2SO_4), the column was prewashed with 80 mL *n*-hexane, sample was loaded and eluted with 150 mL *n*-hexane. The solvent was reduced in TurboVap II and transferred into a GC conical vial, recovery standards were added. Sediments were spiked with ^{13}C extraction standards and extracted using DCM in an automated Soxhlet extraction system (Büchi B-811). The extract was reduced under stream of nitrogen to about 10 mL and split into 2 aliquots, similar to biotic samples. The POPs aliquot was cleaned-up on a glass column filled with 1g $AgNO_3$ and 5 g 44% H_2SO_4 silica. Sample was loaded and eluted with 40 mL DCM:*n*-hexane mixture. The solvent was reduced in TurboVap II and transferred into a GC conical vial, recovery standards were added.

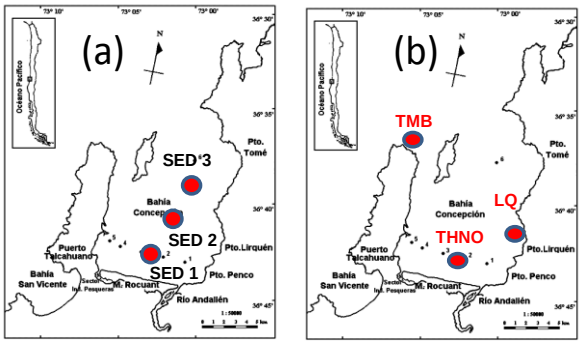

Figure 1. Sampling locations for (a) sediments at Talcahuano (n= 3) and (b) organisms at three stations in Concepción Bay, during May 2013. (Abbreviations for sediment stations: SED1= station 1 SED2= station 2, SED3= station 3; organisms: TMB= Tumbes, Talcahuano= THNO, and LQ= Lirquén)

Chemical analysis

Sediment and organisms samples were analyzed for 10 PBDE congeners (BDE-28, -47, -66, -99, -100, -85, -154, -153, -183, -209). The PBDE 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 x 0.10 m) (Restek, USA) coupled to an AutoSpec Premier MS (Waters, Micromass, UK). The mass spectrometer (MS) was operated in EI + mode in the resolution of> 10 000. For BDE-209, the resolution MS was set to > 5000. Injection was splitless 2 ul to 280 ° C, with He as carrier gas at 1 ml min^{-1}. GC temperature program was 80 °C (1 min hold), then 20° C min^{-1} to 250 °C, followed by 1.5 °C min^{-1} to 260 °C (2 min hold), and 25 °C min^{-1} at 320 °C (4.5 min hold)[10]. Results are expressed in ng g^{-1} dry weight (d.w)[10]. Chemical analyses were conducted at Masaryk University, Research Centre for Toxic Compounds in the Environment (RECETOX), Brno, Czech Republic.

Results and discussion

Concentrations of PBDEs in sediment and organisms

From the 10 PBDE congeners analyzed, generally congeners BDE-47, -99, -100 (low brominated congeners) and PBDE-209 (high brominated PBDE) were the four most frequently detected congeners in the samples analyzed (Table 1). Concentrations in sediments ΣPBDE-47, -99, -100 were low, showing a decreasing concentration from SED1 (90) to SED3 (20) (pg g^{-1} d.w). However, PBDE-209 showed significantly higher values ~20 ng g^{-1} d.w with a similar decreasing concentrations (ng/g d.w) pattern from SED1 (21) to SED3 (2) (Figure 2). These levels are similar to those

detected in marine sediments in Shanghai (China) (50 ng g^{-1} d.w) and North Sea (Belgium) (30 ng g^{-1} d.w). Nevertheless, these levels are low, when compared to an area "hot spot" (directly influenced by sources), as reported in the basin Sceldt in Belgium, with concentrations up to 1200 ng g^{-1} d.w (equivalent to 1 µg g^{-1} d.w)[11]. Moreover, it is interesting to compare our results with those reported by Baron et al.,[8] for sediments sampled in December 2009 (before the 2010 Tsunami) in Talcahuano, showing lower concentrations (factor of 10 times) of PBDE-209 (~2 ng g^{-1} d.w). These results might by influenced by two factors: First, we suggest that substantial input of contaminated material could have been associated with the 2010 Tsunami, including machinery, textiles, electronic equipment and other commercial products treated with PBDEs. It is also possible that the differences in sediment concentration reflect a change in the composition of the PBDE technical mixture in Chile. This is an area of further study.

Table 1. Concentrations of total PBDEs (ng g^{-1} d.w), expressed as ΣPBDE-47,-99, -100 and PBDE-209 in sediments of Concepción Bay during sampling in May 2013.

	This study		
Compounds (ng g^{-1} d.w)	SED 1	SED 2	SED 3
$\Sigma PBDE_{47, 99, 100}$	0.09	0.05	0.02
PBDE-209	21	5	2
	References*		
Compounds (ng g^{-1} d.w)	THNO		
$\Sigma PBDE_{47, 99, 100}$	0.26		
PBDE-209	1.72		

(*) Baron et al., 2013a[8], TMB= Tumbes, THNO= Talcahuano, LQ= Lirquen.

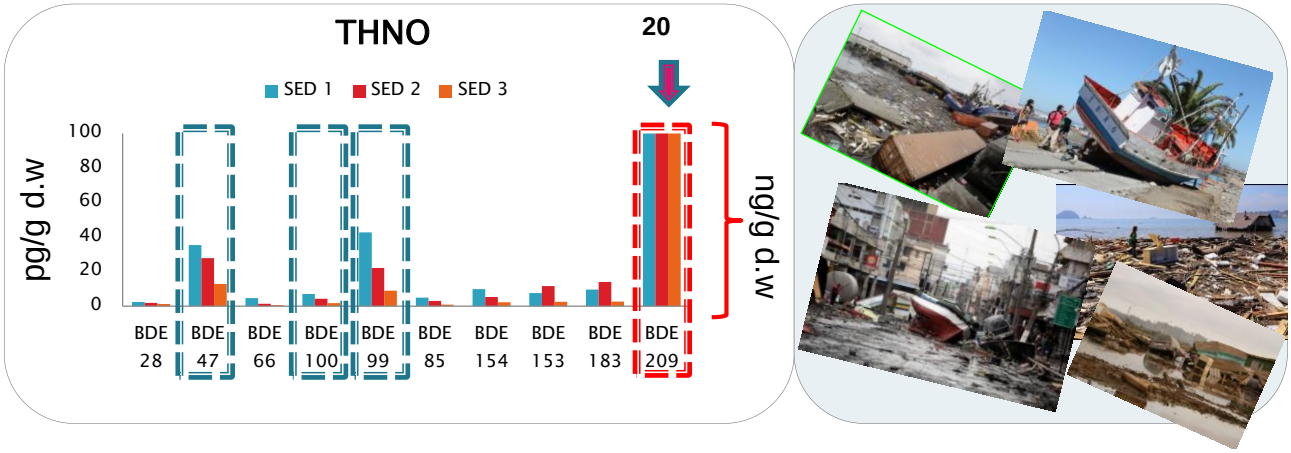

Figure 2. Shows (a) PBDEs concentrations (pg g^{-1} d.w) in sediment of Concepción Bay (Talcahuano station) and (b) pictures taken following the 2010 Tsunami in Central Chile (Source of Pictures: Diario el SUR).

In organisms (primary consumers), PBDEs concentrations were low, ΣPBDEs -47 , -99, -100, ~ 300 pg g^{-1} d.w and PBDE-209 in the range of 400 pg g^{-1} d.w (Table 2). Our results are lower than those detected by Baron et al.,[9], in organisms, in areas near Concepción Bay (Table 2). However, in organisms concentrations PBDE -47, -99, -100 (~ 400 pg g^{-1} d.w) were higher than those found in sediment (~ 40 pg g^{-1} d.w) (factor of 10 times higher). This difference is due to the fact that low brominated PBDE are more easily bio-accumulated in organisms and therefore their concentrations could be higher. Furthermore, it is important to consider that low brominated PBDEs are considered more dangerous because they bioaccumulate more efficiently.

PBDE congener patterns The PBDE family consists of 209 congeners. However, PBDE commercial mixtures used in industry are not only individual congeners, but rather are used as a mixture of congeners. Commercial mixtures of PBDEs most used in the past, are the penta-, octa- and deca- PBDE mixtures. The " penta- product " contains mainly 4-6 Br congeners and has been most widely investigated because of the abundance and rapid accumulation in biological samples from remote areas[12]. Similarly, commercial octa- is a mixture of homologs: hexa-, hepta-, octa-, nona- and deca brodiphenylethers. The commercial mixture of DecaBDE is also mixture of mainly nona and decaBDE.

From the results of this study, it seems that recent use and loading of PBDEs in the Concepción Bay area is dominated by decide. Further study is needed to determine if this shift in pattern is due primarily to change in use of PBDEs

associated with regulation of penta- and octa-mixtures, or if the 2010 Tsunami affected the loadings and distribution of PBDEs in the affected region.

Table 2. Concentrations of total PBDEs (pg g^{-1} d.w), expressed as ΣPBDE-47,-99,-100 and PBDE-209 in marine organisms collected from Concepción Bay during sampling in May 2013.

	$\Sigma PBDE_{47, 99, 100}$				PBDE-209			
Organisms	This study				This study			
Species	TMB	THNO	LQ	References*	TMB	THNO	LQ	References*
Fisurella sp			2	2			3	23
Mytilus Ch			5	n.a			3	n.a
Homalaspis plana			1	4			3	50
Venus antiqua		2		n.d		1		25
Aulacomya atra	4	12		n.a	3	14		n.a
Pyura chilensis	4			n.d	8			18

(*) Baron et al., 2013b[9], TMB= Tumbes, THNO= Talcahuano, LQ= Lirquen.

In this study PBDEs including BDE-47, -99, -100 and -209 were detected in all analyzed samples, sediments and organisms from Concepción Bay. Results showed that PBDEs in sediments (-47, -99, -100) were lower compared with PBDE-209 (showing 10 times higher concentrations). This results might be influenced by the intrusion of material from destroyed houses, cars, and electronics during 2010 Tsunami which has "reset" the coastal environment and also changing the chemical characterization of the marine sediments in the Bay. However, levels in organisms of ΣPBDE -47, -99, -100 and -209 did not exceed 1 ng g^{-1} d.w. This study is one of the few investigations in the country that contributes information on PBDE levels in Chile. Further research is still needed to identify PBDE commercial mixtures utilization in Chile and to know the current health status of Concepción Bay.

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