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Occurrence and behavior of natural and anthropogenic (emerging and historical) halogenated compounds in marine biota from the Coast of Concepcion (Chile)

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HIGHLIGHTS

- Anthropogenic and natural halogenated compounds were detected in Chilean biota from different trophic levels.
- Concentration levels of classical FRs (PBDEs) were higher than those of emerging FRs.
- PBDEs and MeO-PBDEs showed biomagnification capacity (BMF>1), whereas halogenated norbornenes presented BMF<1.
- Biomagnification capacity of naturally occurring MeO-PBDEs was higher than that of PBDEs.

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ABSTRACT

Fifty-five biota samples from the Coast of Concepcion (Chile) were analyzed for PBDEs, emerging brominated FRs, halogenated norbornenes and naturally-occurring MeO-PBDEs. PBDEs, MeO-PBDEs and halogenated norbornenes were detected at concentration levels ranging from 11 to 170, nd to 118 and nd to 5.8 ng/g lw, respectively. However, emerging brominated FRs such as decabromodiphenylethane (DBDPE), hexabromobenzene (HBB) and pentabromoethylbenzene (PBEB) were not detected in any sample.

Bioaccumulation and bioconcentration processes were evaluated for the different families of compounds. Biomagnification factors (BMFs) were calculated, and some PBDE congeners (BDE-28, BDE-183 and BDE-209) as well as MeO-PBDEs presented BMF > 1, being values of the naturally occurring MeO-PBDEs higher than those obtained for PBDEs. As regards halogenated norbornenes, BMF < 1 were found.

1. Introduction

Flame retardants (FRs) are a group of compounds added or applied to a material to increase the fire resistance of that product. The most widely used families of compounds for this purpose are the halogenated flame retardants (HFRs). Among them, polybrominated diphenyl ethers (PBDEs) have been used for many years and in great amounts, and exist in 3 main commercial mixtures: Penta-BDE, Octa-BDE and Deca-BDE. They have been found in environmental matrices, such as sediments (Hale et al., 2006), air (Harner et al., 2006) or sludge (Guerra et al., 2010), and also in biological matrices such as fish (Christensen et al., 2002), bird eggs (Guerra et al., 2012) or breast milk (Lacorte and Ikonomou, 2009). Different toxicological properties of PBDEs have been reported: effects on the thyroid hormone homeostasis (Freitas et al., 2011), interaction with the estrogenic receptor (Montaño et al., 2012) or the fact that they can act as endocrine disruptors (Simon et al., 2010). As a result, Penta-BDE and Octa-BDE mixtures are currently listed and consequently banned due to the Stockholm Convention (Renner, 2004). The use of Deca-BDE mixture in the EU was also banned in 2008 (Justice, 2008) and it has been said that its production in the USA will stop by the end of 2013 (Covaci et al., 2011).

Due to these restrictions, different compounds have been proposed as an alternative to PBDEs, including emerging chemicals such as decabromodiphenylethane (DBDPE), hexabromobenzene (HBB) and pentabromoethylbenzene (PBEB). Moreover, halogenated norbornenes were first used as substitutes for Mirex when it was banned as FR in 1976 and now dechlorane plus (DP) has been proposed by the UE as

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an alternative to Deca-BDE. Although they have been used for many years, they were not found in the environment until 2006 (Hoh et al., 2006). Since then, different studies have reported levels of these contaminants in sediment (Shen et al., 2011b; Sverko et al., 2008), air (Venier and Hites, 2008) or sludge (De la Torre et al., 2010), and also in biological matrices such as fish (Shen et al., 2011a), eggs (Guerra et al., 2011) or human serum (Zheng et al., 2010). These levels are still lower than other classical FRs such as PBDEs. However, they will probably increase due to the recent restrictions over PBDEs.

On the other hand, more than 4000 naturally-produced halogenated molecules have been found in the marine environment, such as methoxylated PBDEs (MeO-PBDEs). Their main sources seem to be blue mussels, sponges and red algaes (Malmvärn et al., 2005), and they have been measured at high concentrations in marine animals, especially in top predators such as dolphins (Alonso et al., 2012) or killer whales (Nomiyama et al., 2011a). Besides, some studies show that they may have similar toxic properties to PBDEs (Wiseman et al., 2011).

The aim of this study was to evaluate the concentration levels of "classical" and emerging HFRs, as well as naturally occurring brominated compounds, in an aquatic food web from an area in the South Central Chilean coast. Moreover, the results will be of interest in order to study the bioaccumulation and bioconcentration processes of emerging FRs. To the best of our knowledge, this is the first study which reports levels of HFRs in an industrial area from Chile. In addition, there is a lack of studies about MeO-PBDEs and halogenated norbornenes in the Southern hemisphere.

2. Materials and methods

2.1. Study area and sample collection

The samples analyzed were collected during February of 2010 in the frame of the BROMACUA project. In a previous sampling campaign, sediments from 4 different areas were sampled in order to evaluate the area with the highest contamination levels of FRs (Barón et al., 2013). Thus, in the sampling campaign during the earlier 2010 the Lenga estuary was chosen to carry out the study in biota samples (Fig. 1). However, it was not possible to collect all the biota samples in this place so samples were collected in the nearby area called Chome and Perone. This area has a high industrial charge, being part of a large petrochemical complex. In fact, an industrial growth of 2.1% was estimated between November of 2010 and November of 2011 (INE, 2011). In recent years this area has suffered heavy environmental damages: a fuel spill of 350 m^3 in 2007 and an earthquake with its epicenter at 150 km of the estuary in 2010.

A total of 55 biota samples, divided into 3 different trophic levels (primary, secondary and tertiary consumers), were collected. This division was made based in the alimentation source of the species. Species listed as primary consumers were 5 different species of filtering (they get their nutrients by directly filtrating water): giant barnacle (*Austromegabalanus pstittacus*, MP), keyhole limpet (*Fisurella* sp., FS), sea squirt (*Pyura chilensis*, PC), clam (*Venus antiqua*, VA) and razor shell clam (*Tagelus dombeii*, NV). The species listed as secondary consumers were 2 crustaceans, crab (*Homalaspis plana*, HP) and crab with Spanish common name "panchote" (*Taliepus dentatus*, TD), and 2 fish, peruvian morwong (*Cheilodactylus variegatus*, CV) and damselfish (*Chromis crusma*, CA). These 4 species are herbivorous or they eat small organisms. Finally, tertiary consumers were the two available predators: sandperches (*Pinguipes chilensis*, PR) and Chilean abalone (*Concholepas concholepas*, CC). In Supporting information 1 the number of samples collected for each species as well as the number of individuals used for each pool sample is listed.

2.2. Standards and reagents

The standard mixture of PBDEs (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209), the standard mixture of MeO-PBDEs (5-MeO-BDE-47, 6-MeO-BDE-47, 4′-MeO-BDE-49, 2′-MeO-BDE-68, 5′-MeO-BDE-99, 5′-MeO-BDE-100, 4′-MeO-BDe-101 and 4′-MeO-BDE-103), PBEB, HBB, DBDPE, BDE-181 and ^{13}C-BDE-209, used as internal standards, and *syn*- and *anti*-isomers of DP were purchased from Wellington Laboratories Inc. (Guelph, ON, Canada). Dec 602 (95%), Dec 603 (98%) and Dec 604 (98%) were purchased from Toronto Research Chemical Inc. (Toronto, ON, Canada). Mirex (98%) and ^{13}C-*syn*-DP (98%), used as internal standard, were obtained from Cambridge Isotope Laboratories Inc. (Andover, MA).

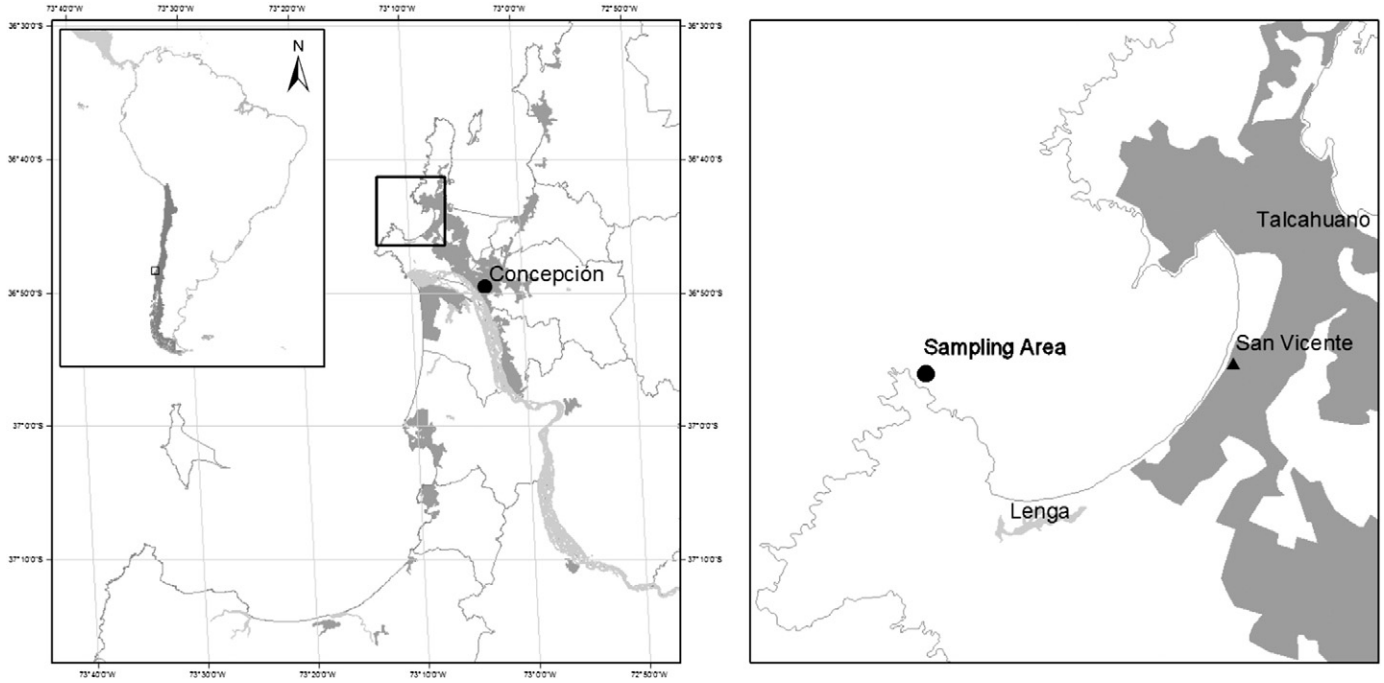

Fig. 1. Map of Chilean coast showing the study area for biota collection.