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

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Introduction

Seafood is one of the major sources of protein for people in the world and is an important part of the human diet. Many studies that have estimated human exposure to toxic chemicals have concluded that over 90% of the intake is from contaminated food[1,2,3,4,5]. Persistent Organic Pollutants (POPs) are ubiquitous in the environment and they are a global international concern[6]. They have been identified as harmful substances due to their toxicity, persistence and bioaccumulation in humans and wildlife. The Stockholm convention is a global treaty aimed to protect human health and the environment from POPs. Limited data is available concerning the levels of POPs in seafood from Chile. In particular organic chemicals (PCBs, PBDEs, chlorinated pesticides (OCPs))[7,8] have been measured in farmed fish products from Southern Chile. Concepción Bay is a costal embayment located in the Biobío Region of central Chile. The environmental state of Concepción Bay 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). The species of organisms (n=8 for each specie) analyzed correspond to primary consumers (including filtering): *Pyura chilensis*, *Venus antiqua*, *Fissurella nigra*, *Choromytilus chorus*, *Aulacomya atra* and *Tegula atra*. Secondary consumers: *Alpheopsis chilensis*. Tertiary consumers: *Trachurus picturatus murphyi* (n = 8), *Brama australis* (n = 4), *Merluccius gayi gayi* (n = 4). Before extraction, organism samples were spiked with 13C extraction standards and extracted in an ultrasonic bath for 15 minutes with 50 mL of DCM, three times. Final solvent extracts (150 mL) were pooled and the solvent was reduced under stream of nitrogen to a volume of 10 mL. The reduced organism extract was split into 2 aliquots, and 9/10 for OCPs, PCBs, PBDE analysis. Clean-up of the PBDE, PCBs and OCPs aliquot was performed on a modified silica column, 25 mm i. d. (3 g silica + 20 g 44% H2SO4 silica + 10 g 22% H2SO4 silica + 6 g silica + 10 g Na2SO4), the column was prewashed with 80 mL n-hexane, and the sample was loaded and then eluted with 150 mL n-hexane. The solvent was reduced in TurboVap II and transferred into a GC conical vial, recovery standards were added. The total lipid content of the species studied was determined by weight difference and accounted for ~5 (±2) %. 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). The filtrate was concentrated to 0.5 mL under a gentle stream of

nitrogen and diluted with 0.5 mL 5mM ammonium acetate in water. Extracts were centrifuged (1800 G, 10 min) and 100 µL transferred to LC minivials for analysis (Labicom, Czech Republic).
Organism samples were analyzed for OCPs (DDTs, HCHs, PECB, HCB), 9 PCB congeners (PCB - 118, -28, -52, -101, -138, -153, -180, -9, -11), 10 PBDE congeners (BDE-28, -47, -66, -99, -100, -85, -154, -153, -183, -209), and PFC. 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 x 0.25 mm x 0.10 m) (Restek, USA) coupled to an AutoSpec Premier MS (Waters, Micromass, UK)[9,10]. PFCs were measured using high performance liquid chromatography (UHPLC) with an Agilent 1290 (Agilent Technologies, Palo, Alto, California, USA) connected to a QTRAP 5500 mass spectrometer (AB Sciex, Foster City, California, USA). Details for chemical analysis were reported elsewhere[11].

Results and discussion

DDT

Total DDT concentrations (sum of p,p'-DDT, o,p-DDT, p,p'-DDE, o,p-DDE, p,p'-DDD and o,p-DDD) (Table 1), (ng/g dry weight (dw)) for primary consumers were low, with range of nd – 4.1 ng/g dw (with a mean ± SD= 0.8 ± 1.4), for secondary consumers, 0.9 – 0.1 ng/g dw (0.5 ± 0.6), however, in the tertiary consumers 0.1 – 15 ng/g dw (2 ± 4) reach higher values than primary and secondary consumers (Figure 1). These differences might be associated with the differences in the accumulation patterns in the trophic food chain. DDT have high octanol–water partition coefficient (Kow)[12], therefore they show highly lipophilic and hydrophobic properties that they can be easily accumulated in the fatty tissue and can be passed through the food and trophic chain[10,12]. These results are comparable with other remote areas of the world where low levels of DDT have been detected in primary consumers 0.2 - 2.3 ng/g (0.9 ± 1.0)[13] 1.9 – 50 ng/g[14], for secondary consumers (Shrimp) higher values have been found in Mexico and El Salvador (>4.0 ng/g)[15,16], for tertiary, these results, are comparable to reported concentrations in fish from China (0.5 – 6.4 ng/g)[17].

Polybrominated diphenyl ethers (PBDEs)

Total ∑10PBDEs (sum of BDE-28, -47, -66, -85, -99, -100, -153, BDE-154, -183 and -209) (Table 1) concentrations ranged widely in primary consumers, from 44 to 493 pg/g dw (189 ± 267) (with exception of *Pyura Chilensis* = 1633 pg/g dw of ∑10PBDEs). For secondary consumers the total levels of PBDEs were lower with a range of 5 – 74 pg/g dw (40 ± 49) and for tertiary consumers the total levels of PBDEs were higher than the primary and secondary consumers, the range was nd - 4559 pg/g dw (652 ± 1235) (Figure 1). High levels of PBDE-209 (41%) were recorded in all species, this finding is quite interesting, as BDE-209 is often assumed not to be bioavailable[18,19] because of its high molecular weight, however the occurrence of BDE-209 in our samples further confirms its occurrence in the environment[19]. These results are comparable to the concentrations found in China, with PBDE (64 to 2300 pg/g) for shellfish samples and (6.3–199 pg/g) for fish[19,20,21]. In addition, these values are similar to those reported previously in the Concepcion bay (ΣPBDE-47, -99, -100 and PBDE-209) by Pozo et al., 2015[10], but lower than those reported by Baron et al., 2013[22].

Polychlorinated Biphenyls (PCBs)

∑7PCBs (PCB-118, -28, -52, -101, -138, -153, -180) in primary consumers ranged from not detected (nd) to 22 ng/g dw (5.5 ± 9.4) with the highest concentrations found in *Tegula atra*. For secondary consumers the total levels of PCBs were low with a range of 0.04 – 0.7 ng/g dw (0.4 ± 0.5) and for tertiary consumers the total levels of PCBs ranges between 0.04 to 15 ng/g dw (2 ± 4) (Figure 1). These concentrations are comparable with the results obtained in Norwegian organisms (mussel, clam and lobster) and in central and southern Italy (∑7PCBs= 6, 1 and 0.2 ng/g, respectively)[23], and with studies carried out in Spain on fish muscles (*P. blennoides*) (1.0 ± 0.2 ng/g[24]). In general these results were below the limits established by the European Union for mollusk and fish (0.075 mg/Kg, UE No. 704/2015)[26].

Perfluoroalkyl Contaminants (PFC)

PFBS, PFHxS and PFDS were detected at high concentrations in primary consumers (>2000 pg/g dw), while PFBA, PFPA and PFHxA were detected in high concentrations in secondary consumers (>500 pg/g dw) and for tertiary consumers higher concentrations of PFPA, PFOS and EtFOSE (>1500 pg/g dw) were detected. In general, the lowest concentrations detected were for PFNS, PFDA, MeFOSA, EtFOSA and FOSA. Mean values for PFOA was 55 ± 157 pg/g dw and for PFOS was 714 ± 1518 pg/g dw in primary consumers while for secondary consumers values were 198 ± 0.0 pg/g dw for PFOA and 52 ± 38 pg/g dw for PFOS (Figure 1). These results are lower than those data obtained in Italy[23] and Spain[24] (PFOA range: nd – 16000 pg/g dw and PFOS range: 148 – 3000 pg/g dw). For tertiary consumers the average concentration was 190 ± 66 pg/g dw for PFOA and 4274 ± 7402 pg/g dw for PFOS. These results obtained can be compared with results obtained from pelagic and benthic Mediterranean fish[27,28].

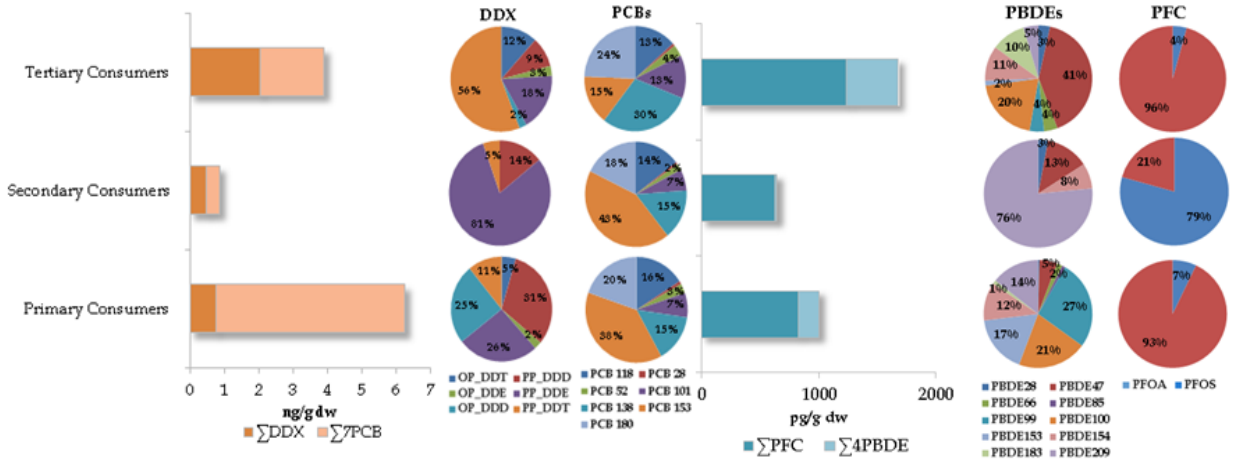

Figure 1. Concentrations and percentage (%) composition of DDTs, PCBs, PBDEs and PFCs in organisms (primary, secondary and tertiary consumers) from central Chile.

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