Legacy and emergent persistent organic pollutants (POPs) in NW Mediterranean deep-sea organisms

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Abstract

The levels and profiles of organochlorine (OC) contaminants, including polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethanes (DDTs), hexachlorocyclohexanes (HCHs) and penta- (PeCB) and hexachlorobenzene (HCB), as well as polybrominated diphenyl ethers (PBDEs) were determined in muscle samples of the deep-sea fish *Alepocephalus rostratus*, *Coelorinchus mediterraneus* and *Lepidion lepidion* and the red-shrimp *Aristeus antennatus* from the NW Mediterranean sea. Mean PCB and DDT levels ranged from the highest concentrations in the fish *A. rostratus* (Σ_7PCBs 6.93±0.71 ng/g w.w. and ΣDDTs 8.43±1.10 ng/g w.w.) to the lowest concentrations in the crustacean *A. antennatus* (Σ_7PCBs 1.17±0.24 ng/g w.w. and ΣDDTs 2.53±0.26 ng/g w.w.). The concentrations of ΣHCHs and HCB were more than one order of magnitude lower, ranging from 0.07-0.36 ng/g w.w. and 0.03-0.15 ng/g w.w., respectively, while PeCB was only detected in a few samples. PBDE levels were approximately ten times lower than PCB and DDT concentrations, ranging from 0.47 ± 0.20 ng/g w.w. in *A. antennatus* to 0.92 ± 0.13 ng/g w.w. in *A. rostratus*. The high-molecular-weight PCBs 153, 138 and 180 represented 69-79 % of Σ_7PCBs in fish and 60 % in the red shrimp. Moreover, in fish, the main DDT compound detected was the metabolite *p,p'*-DDE (70-80 % of ΣDDTs), indicative of old DDT residues. In contrast, o,*p'*-DDE was the main DDT metabolite (49 % of ΣDDTs) in shrimp, while the parent compound *p,p'*-DDT and its metabolite *p,p'*-DDE exhibited similar proportions of 16 % and 21 %, respectively. For PBDEs, the most abundant congeners were BDE 28, 47, 99, 100 and 154 in fish (>70 % Σ_{14}PBDEs), while BDE 153 and 209 were also important in *A. antennatus*, suggesting different uptake and/or biotransformation rates of PBDEs between fish and crustacea. In this sense, the ratios BDE99/100, BDE153/154, and BDE 47/99 were determined as proxies for BDE metabolization capacities and contrasted among species.

Keywords: persistent organic pollutants (POPs); organochlorine contaminants (OC); polybrominated diphenyl ether (PBDE); deep-sea; fish; crustacea; Mediterranean sea

1. Introduction

The deep-sea (> 200 m) has long been considered a pristine environment due to its remoteness from anthropogenic pollution sources. However, there has been growing concern over the impact of anthropogenic contaminants on deep-sea ecosystems (Ramirez-Llodra et al., 2011). In particular, several studies have shown that the deep-sea might act as a sink for highly persistent compounds that enter the marine environment (Kramer et al., 1984; Froescheis et al., 2000; Looser et al., 2000; Scheringer et al., 2004). In this context, persistent organic pollutants (POPs) are of particular concern due to their high hydrophobicity, toxicity and persistence (Scheringer et al., 2009). Because of their hydrophobic nature, POPs present in the aquatic systems have a high affinity to bind to suspended particles and previous findings have suggested a long-term vertical transport of organic contaminants from surface waters to the deep-sea floor (Dachs et al., 2002; Wania and Daly, 2002; Scheringer et al., 2004; Bouloubassi et al., 2006). Indeed, polychlorinated biphenyls (PCBs) and organochlorine (OC) contaminants, including dichlorodiphenyltrichloroethanes (DDTs) and hexachlorocyclohexanes (HCHs), have been found in deep-sea organisms all over the world (Berg et al., 1998; Looser et al., 2000; de Brito et al., 2002; Mormede and Davies, 2003; Ramu et al., 2006; Storelli et al., 2007; Unger et al., 2008; Takahashi et al., 2010; Webster et al., 2011).

Recent research efforts have confirmed that emerging contaminants such as polybrominated diphenyl ethers (PBDEs) are also subject to long-range transport being detected in aquatic organisms from remote areas, including deep-sea fish (Ramu et al., 2006; Covaci et al., 2008; Takahashi et al., 2010; Webster et al., 2011). PBDEs, which are structurally similar to PCBs, have been widely used as flame retardants in a wide array of products, including plastics, textiles and electronic devices. There are three technical mixtures of PBDEs, namely penta-, octa- and decaBDE, however, their production has been phased out under the Stockholm Convention due to their high toxicity and persistence. For instance, recent findings have shown that some PBDE congeners can result in neurotoxicity, reproductive and developmental effects and endocrine disruption, in particular, due to their structural similarity to the thyroid hormone thyroxine (Darnerud, 2003; Birnbaum and Staskal, 2004). In the European Union (EU), the use of the penta- and octa-formulations was banned in 2004, while the production of decaBDE was prohibited in 2008 (de Wit et al., 2010).

In comparison to OC contaminants such as PCBs, DDTs and HCHs, which started to be manufactured during the first half of the 20th century, PBDEs have been released into the environment since the 1970s. This 40 year time lag of emissions could explain why PBDEs levels have increased over the last decades while OC pollutant levels appear to have decreased (Gómez-Gutiérrez et al., 2007; Tanabe et al., 2008; Ross et al., 2009).

The northwestern Mediterranean Sea constitutes a highly industrialized area receiving multiple land-based sources of pollution through river inputs, waste water discharges and continental runoff, as well as atmospheric deposition. Recent studies have shown that the distribution of organic contaminants along the NW Mediterranean continental shelf and slope is closely linked to the dispersion dynamics of organic material and fine-grained particles (Salvadó et al., 2012a; Salvadó et al., 2012b). Moreover, in this region, the transfer of particle-bound contaminants to the deep-sea is further enhanced during episodic climatic events such as dense shelf water cascading (DSWC) (Salvadó et al., 2012c). During these events, which occur every 6-10 years in the NW Mediterranean, cold shelf water masses cascade down the continental slope transporting large amounts of sediment and organic matter to the deep-sea environment (Canals et al., 2006; Company et al., 2008). Hence, the impact of anthropogenic contaminants on deep-sea ecosystems might be relevant within the NW Mediterranean basin. This issue is particularly important considering the increasing interest in deep-sea fisheries due to depleted fish stocks of the world's oceans and the fact that the commercially exploited deep-sea shrimp species *Aristeus antennatus* represents one of the most valuable fishing resources within the region.

Despite of the relevance of pollutant concentrations in deep-sea organism for human and wildlife health, only a limited number of studies have thus far investigated the levels of POP contamination of the NW Mediterranean deep-sea fauna (Escartin and Porte, 1999; Porte et al., 2000; Solé et al., 2001; Borghi and Porte, 2002; Castro-Jiménez et al., 2012). However, none of these studies investigated the levels of emerging compounds such as PBDEs.

The present study aimed to investigate the bioaccumulation of OC and PBDE pollutants in deep-sea organisms from the NW Mediterranean (1) to determine baseline levels of both, legacy and emergent POPs in deep-sea biota; (2) to contrast POP levels among different deep-sea organisms; and (3) to investigate the influence of metabolic

capacities on the differences in POP distribution observed among species. To this end, we determined the levels of the ICES (International Council for Exploration of the Sea) 7 PCB congeners, DDT and its metabolites (DDTs), HCH isomers and penta- (PeCB) and hexachlorobenzene (HCB), as well as 14 BDE congeners in muscle tissue of different fish and a crustacean species from this region. The selected species represent the most abundant megafaunal species in the NW Mediterranean deep-sea and include three fish species belonging to different phylogenetic families, namely *Alepocephalus rostratus* (Alepocephalidae), *Coelorinchus mediterraneus* (Macrouridae) and *Lepidion lepidion* (Moridae), and the red-shrimp *Aristeus antennatus*, which is one of the most highly valuable fishery resources of the area.

2. Materials and Methods

2.1. Sample collection

Samples were collected within the area of the Blanes canyon (BC), NW Mediterranean sea (41◦15 N 2◦50 E) (Figure 1). The BC is one of the largest submarine canyons on the NW Mediterranean continental margin and its upper part is located approximately 4 km from the coastline. The hydrodynamic regime in the region is mainly characterized by the Northern Current, which follows the shape of the western Mediterranean continental slope, flowing in a southward direction. Furthermore, BC receives input of continental sediments via the Tordera River. Animals were caught during two cruises conducted in November 2008 and February 2009 onboard the R/V *Garcia del Cid*, using an OTMS otter trawl at depths ranging from 900-1500 m. Onboard, a portion of muscle tissue was dissected and frozen at -20 ºC until further treatment. Sample details are shown in Table 1(Polunin et al., 2001).

2.2. Sample extraction

Between 20 and 30 individual fish samples of each fish species and 3 pooled samples (5 individuals per pool) of the shrimp *A. antennatus* were analyzed. The extraction of organic pollutants was performed as described in (Koenig et al., 2012a) based on the protocol by Berdié and Grimalt (1998). Briefly, muscle tissue (2-4 g) was ground with anhydrous Na_2SO_4 and soxhlet-extracted with dichloromethane: hexane. Tetrabromobenzene (TBB) and PCB 200 were added as recovery standards. Extracts

were further purified with sulfuric acid. The cleaned extracts were concentrated by evaporation and redissolved in 100 µL of PCB 142 in isooctane as internal standard prior to the determination of organochlorine compound levels (*i.e.* CBs, HCHs, PCBs and DDTs). For PBDE analysis, samples were redissolved in 50 µL isooctane containing BDE 118 and [^{13}C]BDE 209 as internal standard. Lipid content was determined gravimetrically after drying an aliquot of the organic extracts to constant weight.

2.3. Instrumental analysis

To determine levels of PCBs (7 congeners: IUPAC # 18, 52, 101, 118, 138, 153, 180), DDTs (*o,p'*-DDT, *p,p'*-DDT, *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD), Pe-CB, HCB and HCH isomers (α-, β-, γ-, δ-HCH), samples were analyzed using a gas chromatograph (Model HP-6890) equipped with an electron-capture detector (µ-ECD). A 60 m x 0.25 mm I.D. DB-5 column (J&W Scientific, Folsom, CA, USA) coated with 5 % diphenylpolydimethylsiloxane (film thickness 0.25 µm) was used for separation. The oven temperature was programmed to increase from 90 °C (holding time 2 min) to 130 °C at a rate of 15 °C min^{-1} and finally to 290 °C at 4 °C min^{-1}, holding the final temperature for 20 min. The injector and detector temperatures were 280 °C and 320 °C, respectively. Injection was performed in splitless mode and helium was used as carrier gas (30.5 psi).

PBDE levels (14 congeners: BDE # 17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190, 209) were determined by gas chromatography coupled to negative ion chemical ionization mass spectrometry (GC-MS-NICI) as described in Vizcaino et al. (2009).

2.4. Quality assurance and control

To assess the possible inadvertent contamination of samples during analytical procedures, procedural blanks were performed for every set of six samples. Blanks were used to establish method detection (MDL) and quantification limits (MQL), which were defined as the mean of the blanks plus three times (MDL) or five times (MQL) the standard deviation. They were in the order of 0.03 and 0.05 ng g^{-1} w.w., respectively for organochlorine compounds. For PBDEs MDL and MDQ were in the order of 0.004 and 0.006 ng g^{-1} w.w., respectively, except for congeners 47, 99, 100, and 209 for which they were one order of magnitude higher, namely 0.04 and 0.06 ng/g w.w. respectively.

POPs levels were determined by internal standard method. Extraction and analytical performances were evaluated by surrogate standard recoveries, which ranged from 65 % to 90 %. Values reported in this study were corrected based on surrogate recoveries.

3. Results and discussion

3.1. OC levels

The concentrations of OC contaminants are presented in Table 2. Overall, PCB and DDT levels ranged from the highest concentrations in the fish *A. rostratus* (Σ_7PCBs 6.93±0.71 ng/g w.w. and ΣDDTs 8.43±1.10 ng/g w.w.) to the lowest concentrations in the crustacean *A. antennatus* (Σ_7PCBs 1.17±0.24 ng/g w.w. and ΣDDTs 2.53±0.26 ng/g w.w.). The concentrations of ΣHCHs and HCB were more than one order of magnitude lower, ranging from 0.07-0.36 ng/g w.w. and 0.03-0.15 ng/g w.w., respectively, while PeCB was only detected in a few samples above the detection limit. The OC relative abundance follows the sequence PCBs ≈ DDTs >> HCHs ≥ HCB and is generally in accordance with previous studies on deep-sea fish conducted in the Mediterranean (Porte et al., 2000; Storelli et al., 2009), the Atlantic (Berg et al., 1997; Mormede and Davies, 2003) and the Pacific Ocean (Ramu et al., 2006; Takahashi et al., 2010) and also with recent data on deep-sea sediments from the Gulf of Lions (NW Mediterranean) (Salvadó et al., 2012a). These results indicate that the bioaccumulation of HCHs and HCB in deep-sea biota is negligible compared to PCBs and DDTs, which is in agreement with the higher hydrophobicity and bioaccumulation potential of most PCBs and DDTs relative to HCHs and HCB. This effect, together with the enhanced vertical transport of these compounds due to their preferential association to suspended particulate matter (Dachs et al., 2002; Scheringer et al., 2009), would explain the dominance of PCBs and DDTs in deep sea species.

Differences in OC levels among species may result from various factors. One important factor is the age of the analyzed specimens, since POP levels have been shown to increase with increasing age in fish (Stow and Carpenter, 1994; Vives et al., 2004). No age determination was done in this study; however, for *A. rostratus* and *C. mediterraneus*, an average age of sampled individuals was estimated based on body length using previously published von Bertalanffy growth curves (Massutí et al., 1995;

Morales-Nin et al., 1996). *A. rostratus* is the most long-lived of the analyzed species, with a maximum age of > 20 years (Morales-Nin et al., 1996) and a mean estimated age of 10 years for specimens included in the present study. In contrast, *C. mediterraneus* can reach ages of the order of 10 years (Massutí et al., 1995) and the estimated age for the analyzed fish was 5 years. Although no growth parameters were available for *L. lepidion* and an average age for the studied specimens could not be calculated, preliminary age estimations have shown that specimens of sizes comparable to those in the present study generally do not exceed ages of 7 years (Morales-Nin, 1990). Similarly, no age could be estimated for the red-shrimp *A. antennatus*, however, this species is thought to live up to no more than 5 years (Company et al., 2008). Based on these estimations, *A. rostratus* would be the oldest organism and *A. antennatus* the youngest, while *C. mediterraneus* and *L. lepidion* exhibit similar and intermediate ages, which is consistent with the differential POP level distributions between species found in the present study.

Another important factor influencing the POP concentrations in biota is the lipid content. When expressing results on a lipid-weight basis, a different trend among species was observed, with highest values of OCs in *L. lepidion* (Σ_7PCBs 2125 ± 332 ng/g l.w. and ΣDDTs 1317 ± 239 ng/g l.w.) due to its low lipid content of muscle tissue (0.36 %, Table 1) and lower OC levels in *A. rostratus* (Σ_7PCBs 721.2 ± 72.8 ng/g l.w. and ΣDDTs 812 ± 102 ng/g l.w.), which also has the highest lipid content (1.3 %, Table 1). Moreover, *L. lepidion* also exhibits the highest nitrogen stable isotope ratio ($\delta^{15}N$) (Table 1), indicating that its higher trophic position could explain the higher lipid-normalized OC levels in this species. In general, organic contaminants are thought to bioaccumulate in relation to tissue lipid content (Hebert and Keenleyside, 1995; Randall et al., 1998), however, if such a relationship does not occur, the normalization of organic contaminant concentrations to lipid content may lead to erroneous conclusions (Hebert and Keenleyside, 1995). In the present study, only *A. rostratus* exhibited a lipid-dependent accumulation of OC compounds (PCB and DDT: Spearman rank $\rho = 0.7$, $p < .0001$). Hence, it is possible that the normalization to lipid-weight only reduced the relative POP levels for *A. rostratus* and thus resulted in a different profile among species as compared to POP concentrations on a wet-weight basis.

POP levels from the present study were compared with previously published results in deep sea organisms as concentrations per wet weight whenever possible or based on

lipid weight if applicable. The levels of OC contamination detected in the present study (Σ_7PCBs 1.17-6.93 ng/g w.w., ΣDDTs, 2.53-8.43 ng/g w.w.) are within the range of values previously measured in deep-sea fish from the same study area (i.e. NW Mediterranean) by Porte et al. (2000) (Σ_7PCBs 2.5-10.0 ng/g w.w.; ΣDDTs 1.9-10.2 ng/g w.w.) and Solé et al. (2001) (Σ_7PCBs 9.0-16.2 ng/g w.w.; ΣDDTs 7.4-12.6 ng/g w.w.). Although PCB and DDT contamination is thought to have decreased over the last decades, the present findings indicate that OC levels in NW Mediterranean deep-sea fish have remained relatively similar over the past decade. Based on lipid weight, concentrations of PCBs and ΣDDTs (Σ_7PCBs 145.2-2125 ng/g l.w.; ΣDDTs 321-1317 ng/g l.w.) in NW Mediterranean deep sea organisms appear to be higher than mean values reported in Atlantic deep-sea fish, where Σ_7PCBs ranged from 188 to 792 ng/g l.w. (Webster et al., 2009) and in various deep-sea fish species from the Pacific Ocean, such as the Sulu Sea (Σ_7PCBs 19-110 ng/g l.w.; ΣDDTs 69-270 ng/g l.w.) (Ramu et al., 2006) and off Tohoku, Japan (Σ_7PCBs 34-390 ng/g l.w.; ΣDDTs 36-220 ng/g l.w.) (Takahashi et al., 2010). However, an earlier study conducted in waters off Tohoku found similar OC levels to those described in this study (Σ_7PCBs n.d.-2200 ng/g l.w.; ΣDDTs 14-830 ng/g l.w.) (de Brito et al., 2002). In addition, due to the fact that some of the species analyzed by de Brito et al. (2002) and Takahashi et al. (2010) had high muscle lipid contents, up to 70 % and 25 %, respectively, the conversion of the reported OC concentrations to wet weight resulted in high PCB and DDT levels, reaching 80 ng/g w.w. and 30 ng/g w.w. (see de Brito et al., 2002), one order of magnitude higher than concentrations found in this study.

3.2. PBDE levels

The concentrations of PBDEs detected in the present study are shown in Table 3. They ranged from 0.47 ± 0.20 ng/g w.w. in *A. antennatus* to 0.92 ± 0.13 ng/g w.w. in *A. rostratus* and were approximately one order of magnitude lower than PCB and DDT concentrations, which is in agreement with former studies that simultaneously assessed OC and PBDE contamination in deep-sea fish from the Atlantic (Webster et al., 2009; Webster et al., 2011) and the Pacific Ocean (Ramu et al., 2006; Takahashi et al., 2010). Furthermore, this result is also consistent with sediment contamination data from the NW Mediterranean basin, where PCB and DDT contamination clearly exceeded PBDE levels (Salvadó et al., 2012a; Salvadó et al., 2012b). PCB and DDT levels are generally thought to have decreased in the environment due to the restrictions in their use and

production several decades ago, while environmental levels of PBDEs appear to have increased over the last decade due to their relatively recent emissions, even though PCBs and DDTs are still the most dominant contaminants in most marine organisms at present (Gómez-Gutiérrez et al., 2007; Tanabe et al., 2008; Ross et al., 2009).

To our knowledge, only one study has previously measured PBDEs in Mediterranean deep-sea fish (Covaci et al., 2008), however, reported levels were determined in fish liver and are thus not directly comparable to the results in muscle tissue presented in this study. In comparison to Mediterranean shallow-water species, similar PBDE levels have been detected in the European eel (*Anguilla anguilla*), with a range of Σ_{28}PBDEs 0.08–1.80 ng/g w.w. (including all 14 congeners analyzed in this work) (Labadie et al., 2010). Similarly, Corsolini et al. (2008) determined the sum of 19 PBDEs in swordfish (*Xiphias gladius*), and, although it is noteworthy that the more brominated BDEs (i.e. hepta- to decaBDE) were not included, reported values were similar to those found in this study, in the range of 0.04-1.91 ng/g w.w. Finally, significantly higher concentrations of PBDEs (Σ_{23}PBDEs 15.1 ng/g w.w.) have been observed in tuna (*Thunnus thynnus*) from Mediterranean sea (Borghesi et al., 2009).

Σ_{14}PBDE levels expressed on lipid weight basis varied between 61.9 ± 28.9 ng/g l.w. in *A. antennatus* and 188.8 ± 26.6 ng/g l.w. in *L. lepidion.* In comparison, Webster et al. (2009) reported slightly lower levels in deep-sea fish from North Atlantic Scottish waters, ranging from 11.7 to 50.5 ng/g l.w. for Σ_{17}PBDEs, which included all 14 congeners considered in our study except BDE 209. In contrast, the sums of 14 BDE congeners in Pacific deep-sea fish caught in the Sulu Sea (0.9-1.6 ng/g l.w.) (Ramu et al., 2006) and off Tohoku, Japan (1.3-8.5 ng/g l.w.) (Takahashi et al., 2010) were one to two orders of magnitude lower than our results. However, as mentioned earlier, some fish species included in the study by Takahashi et al. (2010) exhibited very high lipid contents in muscle tissue (1.2-25 %). Transforming reported values to wet weight concentrations results in levels in the range of 0.1-0.5 ng/g w.w., which are more similar to the present findings.

3.3. Compound distributions

Organochlorine compounds

PCB profiles in deep sea species were dominated by the high-molecular-weight (HMW) PCBs 153, 138 and 180, which represented 69-79 % of Σ_7PCBs in fish and 60 % in the red shrimp *A. antennatus* (Figure 2). While PCB 153 exhibited the highest abundance in fish, in the shrimp the most abundant congener was PCB 138. The differential PCB accumulation between the fish and the crustacean species has been described in a previous study and is likely related to differences in hepatic cytochrome P450-mediated metabolism of PCBs between fish and crustacea (Koenig et al., 2012b). Overall, the detected PCB profiles are in accordance with the general bioaccumulation patterns of PCBs in deep-sea fish reported in former studies (Porte et al., 2000; Solé et al., 2001; Mormede and Davies, 2003). The predominance of these compounds in biota can be explained by the higher bioaccumulative potential of the more hydrophobic higher chlorinated PCBs (i.e. hexa- to octachloro congeners) (McFarland and Clarke, 1989). In addition, as mentioned previously, highly chlorinated congeners have higher sediment affinities than low chlorinated compounds and are thus more prone to particle-bound transport from surface waters to the deep-sea (Dachs et al., 2002; Scheringer et al., 2004).

In fish, the main DDT compound detected was the metabolite *p,p'*-DDE, which comprised on average 70-80 % of ΣDDTs, while the parent compound *p,p'*-DDT contributed only 6-10 % to ΣDDTs (Figure 3). This result is a commonly observed distribution in marine organisms (Voorspoels et al., 2004), including deep-sea fish (Mormede and Davies, 2003; Takahashi et al., 2010) and is indicative of old DDT residues, which progressively degrade in aquatic environments into their even more persistent metabolites, primarily DDE (Wolfe et al., 1977). In shrimp however, o,*p'*-DDE was the main DDT metabolite and represented 49 % of ΣDDTs, while the parent compound *p,p'*-DDT and its metabolite *p,p'*-DDE exhibited similar proportions of 16 % and 21 %, respectively (Figure 3). Hence, the DDT/DDE ratio profile detected in shrimp would indicate a recent input of the parent compound *p,p'*-DDT within the study area, which is in contrast to the results observed in fish. Thus, it seems that, despite the wide use of the DDT/DDE ratio as a means to discriminate between recent and past use of DDT (Corsolini et al., 2008), these results indicate that it should be applied with caution as it can vary among different organisms.

The technical HCH mixtures, containing all four isomers with a α-HCH/γHCH ratio of 4-7, were gradually replaced by lindane, which is the only component exhibiting

significant insecticide activity and still being released, although to a limited extent, into the environment. Accordingly, the most abundant HCH isomer detected in the present study was γ-HCH (lindane), contributing approximately 50 % to ΣHCH in all species. Moreover, α-HCH/γ-HCH ratios ranged between 0.2 in *A. rostratus* and 1.0 in *L. lepidion*, showing a predominance of lindane over the technical mixture.

PBDE

In fish, the most important PBDE congeners detected were BDE 28, 47, 99 and 100, constituting from 68 % in *A. rostratus* to 89 % in *L. lepidion* of ΣPBDEs (Figure 4), similar to previous results observed in muscle tissue of deep-sea fish (Webster et al., 2009; Takahashi et al., 2010). These congeners are the main components in the commercial penta-BDE formulations (La Guardia et al., 2006). BDE 154 and 209 levels were also significant in all fish species. BDE 154 has been suggested to be a debromination product of BDE 183, the main congener in the technical octa-BDE mixtures (Stapleton et al., 2004; Roberts et al., 2011), while BDE 209 constitutes between 92 to 97 % of the total BDE content in the deca-BDE formulations (La Guardia et al., 2006). Therefore, PBDE composition observed in deep sea organisms are consistent with the composition of the technical mixtures used in Europe. This PBDE profile differs from that reported in deep-sea sediments from a nearby area (Gulf of Lions, NW Mediterranean) (Salvadó et al., 2012b), where BDE 209 was the predominant congener (78 %). These differences can be attributed to differences in bioavailability and biotransformation potential between compounds. BDE 209 is thought to have low bioavalability, in agreement with its high molecular size (Eljarrat et al., 2004), and it can be metabolized to less brominated congeners in some fish species (Kierkegaard et al., 1999; Stapleton et al., 2006), thus potentially explaining the relatively low proportion of BDE 209 found in the deep sea fish.

In contrast to fish, BDE 153 and 209 were the most abundant congeners in shrimp, although large variability was observed potentially because of the low sample sizes (n = 3 pools) (Figure 4). Previous studies have also observed high concentrations of BDE 209 (Ashizuka et al., 2008; van Leeuwen et al., 2009), as well as BDE 153 (Voorspoels et al., 2003) in shrimp, suggesting a higher uptake or lower biotransformation capacity of these congeners in crustacea.

Despite the correspondence between PBDE congeners found in deep sea organisms and main components in the technical mixtures, the relative abundance of these compounds differs from that found in the commercial formulations. These results can be explained by differences in metabolic transformation rates between congeners (Roberts et al., 2011). In this sense, BDE 99/100, 153/154 and 47/99 ratios have been used to assess differences in metabolic capacities as well as trophic position among various aquatic organisms (Voorspoels et al., 2003; Xiang et al., 2007; Dickhut et al., 2012). PBDE ratios determined in this study are summarized in Table 4. Usually, high BDE 99/100 ratios, similar to those found in the original commercial pentaBDE mixtures such as Bromkal 70 5-DE (approx. 5.3) or DE-71 (approx. 3.71), are found in sediments and lower organisms such as invertebrates, but decrease through the food chain due to higher biotransformation rate of BDE 99 in higher organisms (Christensen and Platz, 2001; Voorspoels et al., 2003; Xiang et al., 2007; Hu et al., 2010). This ratio varied between 0.99 to 1.91 in deep sea fish species (Table 4), indicating a significant degradation of BDE 99. The higher value found in shrimp (3.3) is in accordance with a number of studies reporting higher ratios in crustacea compared to fish (Voorspoels et al., 2003; Xiang et al., 2007; Hu et al., 2010). However, it should be noted that although *L. lepidion* has the highest trophic level (Table 1), it does not present the lowest BDE99/100 ratio, indicating that in the present study, the influence of metabolic capacities on this ratio may be more important than for instance the trophic position. The ratio between BDE 153 and BDE 154 has been similarly related to the metabolic capacities of different organisms (Xiang et al., 2007), with higher contributions of BDE 154 reflecting the higher biotransformation of more brominated congeners such as BDE 183 (Roberts et al., 2011). Values were <1 in fish, but shrimp exhibited a very high BDE153/154 ratio, pointing to a lower metabolic capacity of the crustacean in relation to fish, although it is noteworthy that this result is largely based on very high BDE 153 levels and a lack of BDE 154 in shrimp. However, a significant relationship between the ratios BDE99/100 and BDE153/154 in all three fish species ($\rho>0.4$, $p<0.05$) indicates the coherent covariation of these two parameters, reinforcing their use as proxies for the BDE metabolization abilities of different species. Furthermore, BDE 99/100 and BDE 153/154 ratios were highest in the shrimp, but also higher in *C. mediterraneus* compared to the two other fish species. These two species are infaunal feeders, closely associated to the sediment, while *A. rostratus* and *L. lepidion* feed on epibenthic and/or pelagic prey (see Table 1). Hence, it is possible that, in addition to differences in

metabolic capacities, these BDE congener ratios also reflect differences in feeding strategies among organisms.

BDE 47/99 ratios in deep sea fish varied between 1.17 and 1.36, with BDE 47 only representing 15-22 % of ΣPBDEs. This is in contrast to results found in liver of two Mediterranean deep-sea fish species, where BDE 47 contributed approximately 50 % to ΣPBDEs and BDE 99 was clearly depleted (Covaci et al., 2008). BDE 99 has been shown to be metabolized to BDE 47 in carp liver (Stapleton et al., 2004) and the congener ratio BDE 47/99 has been used to assess the level of metabolization of BDE 99 to BDE 47 (Wang et al., 2009). However, a different debromination pathway of BDE 99 has been detected in salmon and trout, suggesting significant differences in efficiency and metabolite formation of BDE 99 debromination among teleost species (Browne et al., 2009; Roberts et al., 2011) and the BDE 47/99 ratio does therefore not necessarily reflect the metabolization rate of BDE 99 in all species. In fact, the similar proportions of BDE 47 and 99 reported in the present study (Table 4) are consistent with BDE 47/99 ratios in the commercial penta-BDE mixtures, which primarily contain these two congeners at equal concentrations, suggesting a lack of debromination of BDE 99 to BDE 47. However, slightly lower BDE 47/99 ratios were observed in the shrimp (0.75) and *C. mediterraneus* (1.17), compared to the two other fish species (1.36), suggesting again the potential existence of different metabolic capacities and/or differences in BDE uptake related to feeding strategies between the two infaunal feeders and the more pelagic species.

These results indicate that metabolism plays an important role in the PBDE congener distributions in aquatic organisms, resulting in a selective accumulation of the lower brominated congeners. This is relevant to human as well as wildlife health, since lower brominated congeners have higher biomagnification potential and toxicological effects.

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Table

Table 1 Biological characteristics of deep-sea species. Values shown are mean ± standard error of mean

Species	**N**	**Length (mm)**	**Weight (g)**	**Lipid (%)**	**δ^{15}N (‰) [a]**	**Feeding strategies [b]**
Alepocephalus rostratus	30	311.2 ± 7.4	343.3 ± 28.3	1.32 ± 0.26	11.35-12.07	Non-migratory macroplankton (gelatinous)
Coelorinchus mediterraneus	25	73.4 ± 2.4*	27.8 ± 2.9	0.48 ± 0.07	12.40	Infauna
Lepidion lepidion	20	172.6 ± 6.9	37.9 ± 4.2	0.36 ± 0.04	11.27-13.42	Active predator supra- and epibenthic fauna
Aristeus antennatus	3 pools	40.4 ± 2.6	n.r.	0.79 ± 0.05	10.91-11.34	Infauna

[a] Polunin et al. (2001)
[b] Cartes et al. (2002)
* pre-anal length (PAL) recorded
n.r. not recorded

Table 2 Organochlorine levels in deep-sea fish and crustacean from NW Mediterranean. Values shown are mean concentrations (ng/g w.w.) ± standard error of mean (min.-max.).

	A. rostratus **(n = 30)**	***C. mediterraneus*** **(n = 25)**	***L. lepidion*** **(n = 20)**	***A. antennatus*** **(n = 3 pools)**
PeCB	0.02 ± 0.005 (n.d.-0.08)	0.01 ± 0.003 (n.d.-0.04)	n.d.	0.01 ± 0.003 (0.01-0.02)
HCB	0.15 ± 0.02 (n.d.-0.46)	0.05 ± 0.03 (n.d.-0.66)	0.05 ± 0.01 (n.d.-0.09)	0.03 ± 0.01 (0.01-0.04)
α-HCH	0.02 ± 0.01 (n.d.-0.11)	0.04 ± 0.01 (n.d.-0.15)	0.03 ± 0.01 (n.d.-0.09)	0.01 ± 0.01 (n.d.-0.03)
β-HCH	0.07 ± 0.02 (n.d.-0.51)	0.11 ± 0.04 (n.d.-0.68)	n.d.	0.03 ± 0.006 (0.02-0.04)
γ-HCH	0.17 ± 0.02 (n.d.-0.61)	0.019 ± 0.06 (n.d.-0.99)	0.03 ± 0.01 (n.d.-0.09)	0.03 ± 0.01 (n.d.-0.04)
δ-HCH	0.04 ± 0.02 (n.d.-0.51)	0.02 ± 0.01 (n.d.-0.14)	0.004 ± 0.004 (n.d.-0.08)	n.d.
ΣHCHs	**0.30 ± 0.05 (n.d.-1.2)**	**0.36 ± 0.10 (n.d.-1.80)**	**0.07 ± 0.02 (n.d.-0.20)**	**0.07 ± 0.03 (n.d.-0.10)**
ΣHCHs lw*	**49.8 ± 13.7 (n.d.-403.0)**	**130.9 ± 38.8 (n.d.-653.3)**	**20.2 ± 4.4 (n.d.-64.7)**	**8.5 ± 4.3 (n.d.-14.1)**
PCB 28	0.12 ± 0.02 (n.d.-0.35)	0.03 ± 0.01 (n.d.-0.19)	n.d.	0.06 ± 0.04 (0.02-0.13)
PCB 52	0.29 ± 0.05 (n.d.-1.04)	0.56± 0.12 (0.04-2.43)	0.65 ± 0.26 (0.03-4.68)	0.17 ± 0.02 (0.14-0.21)
PCB 101	0.59 ± 0.05 (0.18-1.23)	0.18 ± 0.02 (n.d.-0.35)	0.23 ± 0.04 (0.10-0.88)	0.09 ± 0.02 (0.06-0.12)
PCB 118	0.31 ± 0.05 (n.d.-0.85)	0.34 ± 0.10 (0.10-2.49)	0.37 ± 0.03 (0.18-0.68)	0.10 ± 0.04 (0.06--0.18)
PCB 153	2.36 ± 0.28 (0.42-5.69)	1.44 ± 0.31 (0.35-6.44)	2.53 ± 0.33 (0.83-5-65)	0.21 ± 0.04 (0.12-0.26)
PCB 138	1.83 ± 0.21 (0.35-4.34)	1.17 ± 0.25 (0.31-5.80)	1.41 ± 0.18 (0.52-3.56)	0.44 ± 0.13 (0.18-0.60)
PCB 180	1.44 ± 0.17 (0.26-3.35)	0.77 ± 0.16 (0.17-2.65)	1.03 ± 0.17 (0.12-3.21)	0.12 ± 0.04 (0.05-0.19)
ΣPCBs	**6.93 ± 0.71 (1.70-14.80)**	**4.48 ± 0.79 (1.20-18.10)**	**6.22 ± 0.64 (2.00-11.80)**	**1.17 ± 0.24 (0.70-1.50)**
ΣPCBs lw*	**721.2 ± 72.8 (190-1700)**	**1203 ± 219 (151-4320)**	**2125 ± 332 (463-5100)**	**145.2 ± 23.2 (99-1670)**
p,p'-DDT	1.83 ± 0.21 (0.35-4.34)	0.21 ± 0.03 (0.09-0.56)	0.18 ± 0.01 (0.10-0.31)	0.39 ± 0.24 (0.08-0.87)
p,p'-DDE	6.44 ± 0.91 (0.82.-16.52)	2.18 ± 0.45 (0.65-8.28)	3.38 ± 0.44 (0.37-6.87)	0.50 ± 0.24 (0.24-0.98)
p,p'-DDD	0.50 ± 0.07 (0.05.-1.48)	0.10 ± 0.01 (0.06-0.21)	0.08 ± 0.01 (n.d.-0.12)	n.d.
o,p'-DDT	0.32 ± 0.03 (0.06-0.70)	0.07 ± 0.01 (n.d.-0.15)	0.01 ± 0.01 (n.d.-0.07)	0.22 ± 0.06 (0.13-0.34)
o,p'-DDE	0.08 ± 0.01 (n.d.-0.34)	0.01 ± 0.003 (n.d.-0.05)	n.d.	1.33 ± 0.14 (1.06-1.47)
o,p'-DDD	0.94 ± 0.04	0.27 ± 0.01	0.23 ± 0.02	0.08 ± 0.01

	(n.d.-0.94)	(0.16-0.43)	(0.10-0.46)	(0.06-0.09)
ΣDDTs	**8.43 ± 1.10**	**2.83 ± 0.49**	**3.86 ± 0.47**	**2.53 ± 0.26**
	(1.30-21.20)	**(1.10-9.20)**	**(0.70-7.70)**	**(2.10-3.00)**
ΣDDTs lw*	**812 ± 102**	**761 ± 131**	**1317 ± 239**	**322 ± 32.3**
	(200-2635)	**(81.9-2197)**	**(287-4021)**	**(283-386)**

n.d.= not detected. * ng/lipid weight

Table 3 PBDE levels in deep-sea fish and crustacean from NW Mediterranean. Values shown are mean concentrations (ng/g w.w.) ± standard error of mean (min.-max.).

	A. rostratus **(n = 30)**	***C. mediterraneus*** **(n = 25)**	***L. lepidion*** **(n = 20)**	***A. antennatus*** **(n = 3 pools)**
BDE 17	0.06 ± 0.02 (n.d.-0.29)	0.05 ± 0.02 (n.d.-0.35)	0.001 ± 0.001 (n.d.-0.02)	0.003 ± 0.003 (n.d.-0.01)
BDE 28	0.10 ± 0.02 (n.d.-0.45)	0.12 ± 0.01 (0.03-0.23)	0.13 ± 0.01 (0.07-0.21)	0.06 ± 0.02 (0.03-0.08)
BDE 71	0.01 ± 0.003 (n.d.-0.05)	0.002 ± 0.001 (n.d.-0.01)	0.01 ± 0.005 (n.d.-0.09)	n.d.
BDE 47	0.15 ± 0.03 (n.d.-0.58)	0.14 ± 0.02 (n.d.-0.42)	0.15 ± 0.03 (n.d.-0.49)	0.06 ± 0.01 (0.04-0.08)
BDE 66	0.004 ± 0.004 (n.d.-0.11)	n.d.	n.d.	n.d.
BDE 100	0.14 ± 0.03 (0.03-0.77)	0.08 ± 0.01 (0.03-0.32)	0.10 ± 0.01 (0.03-0.23)	0.02 ± 0.003 (0.01-0.02)
BDE 99	0.16 ± 0.05 (n.d.-1.56)	0.13 ± 0.03 (0.05-0.67)	0.13 ± 0.04 (n.d.-0.66)	0.07 ± 0.03 (n.d.-0.11)
BDE 85	0.04 ± 0.01 (n.d.-0.17)	0.03 ± 0.01 (n.d.-0.15)	0.01 ± 0.002 (n.d.-0.04)	n.d.
BDE 154	0.11 ± 0.03 (0.02-0.79)	0.03 ± 0.01 (n.d.-0.17)	0.02 ± 0.004 (n.d.-0.08)	0.003 ± 0.003 (n.d.-0.01)
BDE 153	0.04 ± 0.01 (0.01-0.24)	0.01 ± 0.004 (n.d.-0.07)	0.001 ± 0.004 (n.d.-0.07)	0.09 ± 0.03 (0.03-0.14)
BDE 138	0.004 ± 0.001 (n.d.-0.03)	n.d.	n.d.	n.d.
BDE 183	0.008 ± 0.002 (n.d.-0.05)	0.002 ± 0.001 (n.d.-0.02)	n.d.	n.d.
BDE 190	0.01 ± 0.002 (n.d.-0.03)	n.d.	n.d.	n.d.
BDE 209	0.11 ± 0.05 (n.d.-1.66)	0.02 ± 0.01 (n.d.-0.09)	0.02 ± 0.01 (n.d.-0.22)	0.17 ± 0.17 (n.d. ± 0.52)
ΣBDEs	**0.92 ± 0.13 (0.29-3.02)**	**0.61 ± 0.07 (0.23-1.97)**	**0.58 ± 0.08 (0.20-1.63)**	**0.47 ± 0.20 (0.18-0.84)**
ΣBDEs lw*	**107.9 ± 15.8 (16.6-349)**	**172.1 ± 23.4 (14.5-501)**	**188.8 ± 26.6 (21.4-448)**	**61.9 ± 28.9 (23.1-1195)**

n.d.= not detected
*ng/lipid weight

Table 4 Mean PBDE ratios (min.-max.) in deep-sea fish and crustacean from NW Mediterranean.

Ratio	***A. rostratus*** **(n = 30)**	***C. mediterraneus*** **(n = 25)**	***L. lepidion*** **(n = 20)**	***A. antennatus*** **(n = 3 pools)**
BDE 99/100	0.99 (0.00-2.45)	1.91 (0.41-3.67)	1.32 (0.00-3.47)	3.33 (0.00-5.50)
BDE 153/154	0.37 (0.23-1.00)	0.63 (0.00-7.00)	0.28 (0.00-0.88)	14.0*
BDE 47/99	1.35 (0.00-3.73)	1.17 (0.00-1.57)	1.36 (0.00-2.14)	0.75 (0.73-0.78)

* BDE 154 only detected in one pooled sample

Fig.1 Map of study area within the NW Mediterranean. The map was created using the Ocean Data View (ODV) software package by Schlitzer, R., Ocean Data View, http://odv.awi.de, 2010.

Fig.2 Bioaccumulation profiles of ICES 7 PCB congeners in the three fish species, *Alepocephalus rostratus* (*Ar*), *Coelorinchus mediterraneus* (*Cm*), *Lepidion lepidion* (*Ll*) and the shrimp *Aristeus antennatus* (*Aa*). Values shown are mean proportions (PCB_x/Σ_7PCBs) ± standard error of mean.

Fig.3 Bioaccumulation profiles of DDT and its metabolites in the deep sea species studied.

Fig.4 Bioaccumulation profiles of 14 PBDE congeners in the three fish species, *Alepocephalus rostratus* (*Ar*), *Coelorinchus mediterraneus* (*Cm*), *Lepidion lepidion* (*Ll*) and the shrimp *Aristeus antennatus* (*Aa*). Values shown are mean ($PBDE_x/\Sigma_{14}PBDEs$) ± standard error of mean.

Figure 1

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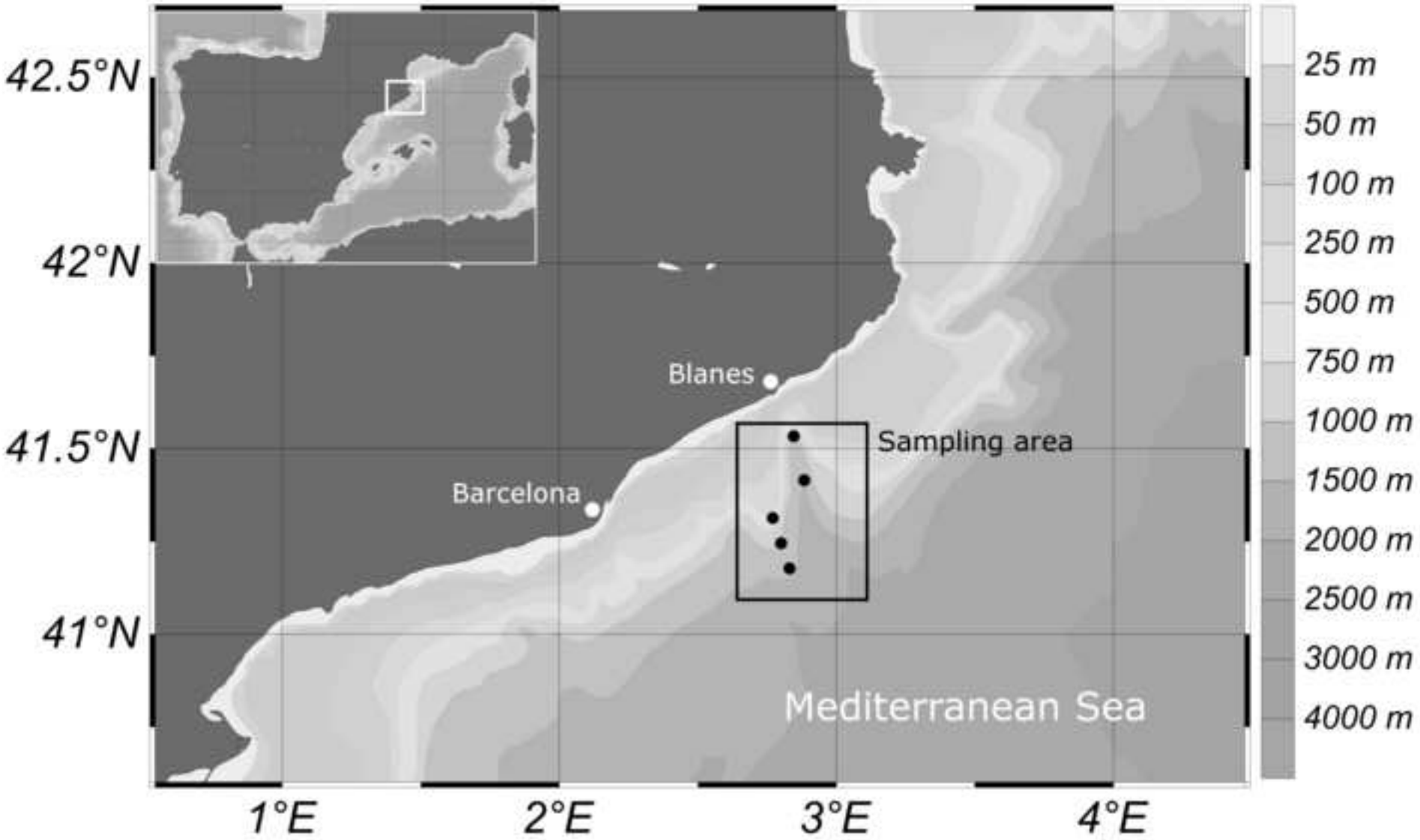

Figure2

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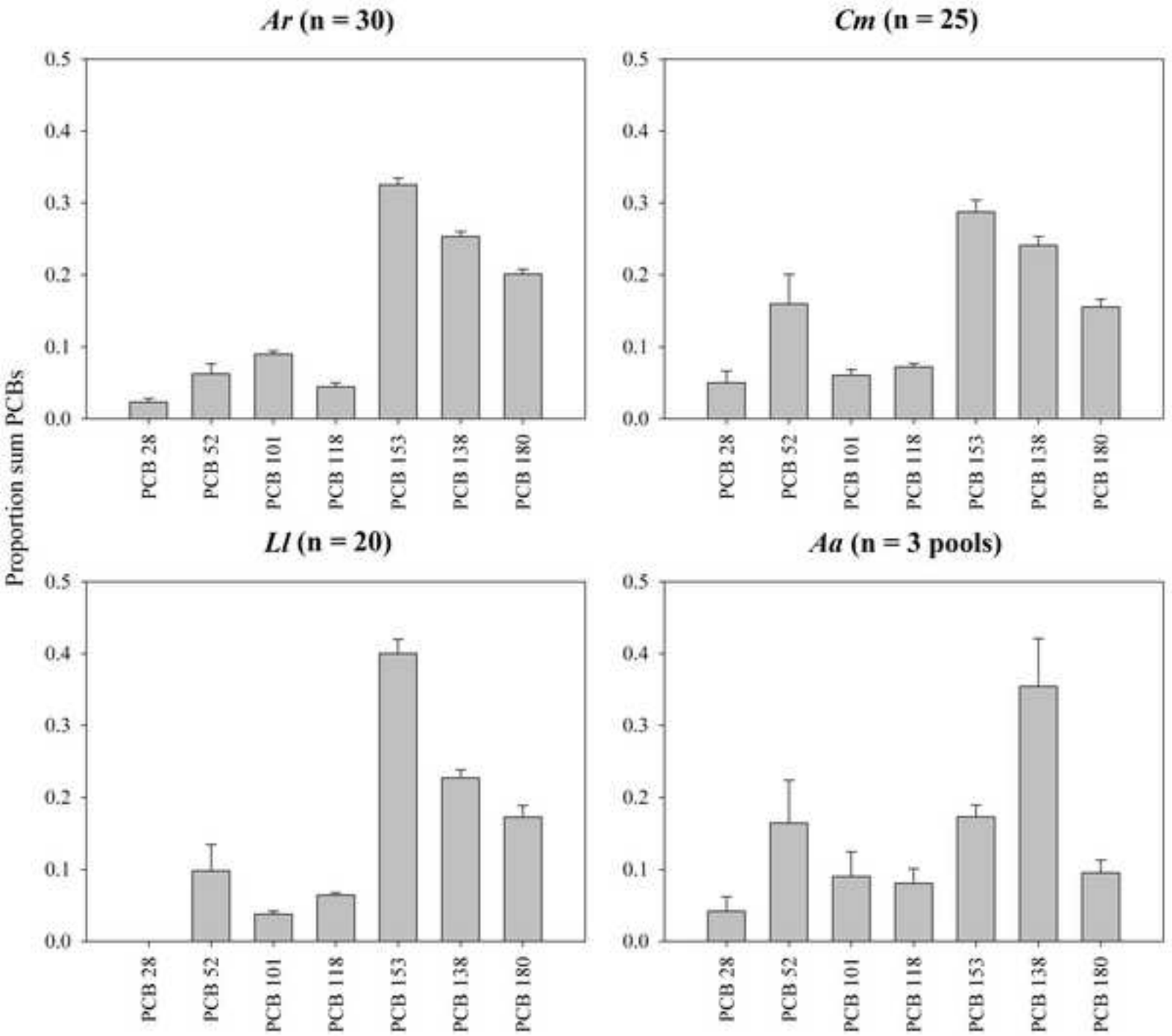

Figure 3

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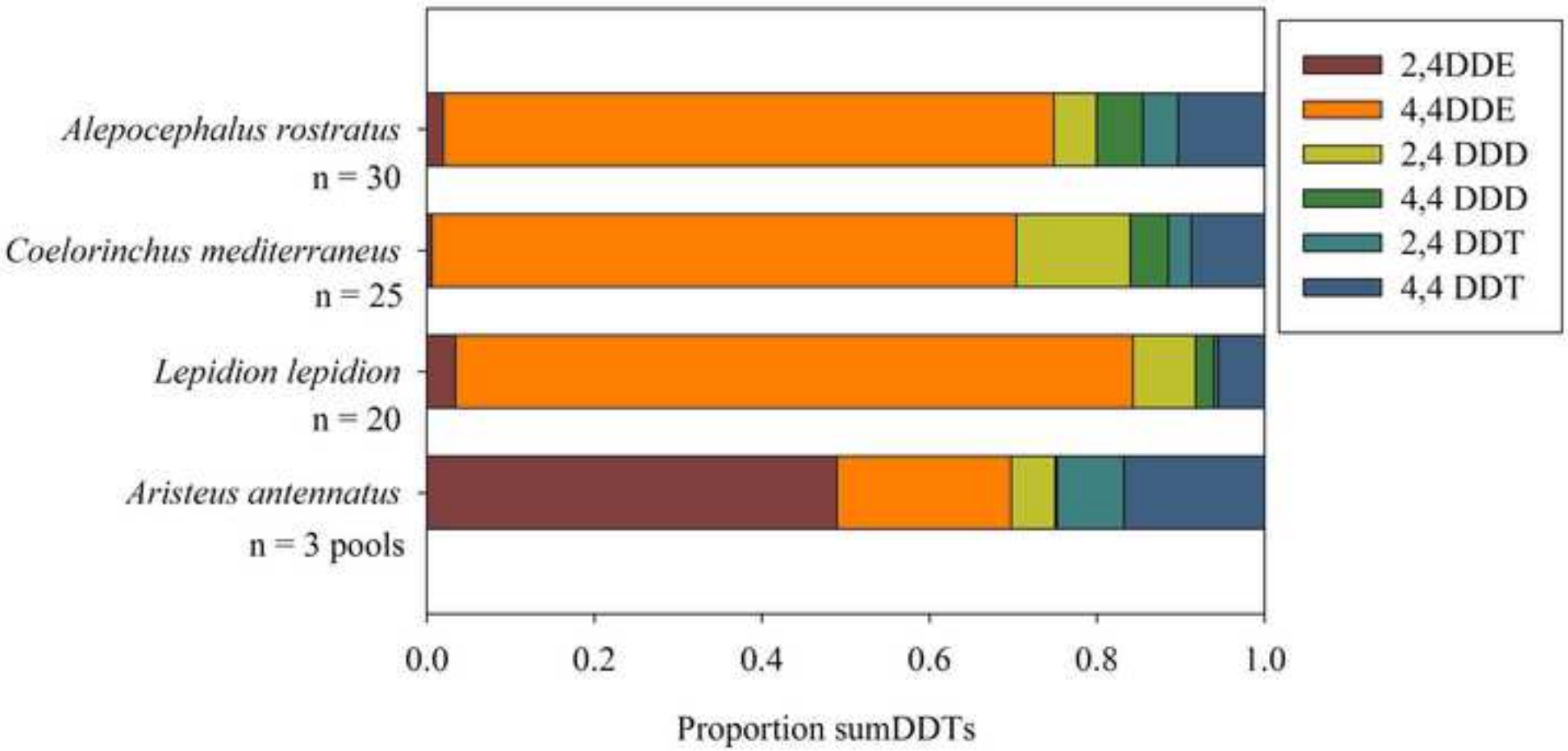

Figure4

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