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Persistent Organic Pollutants Burden, Trophic Magnification and Risk in a Pelagic Food Web from Coastal NW Mediterranean Sea

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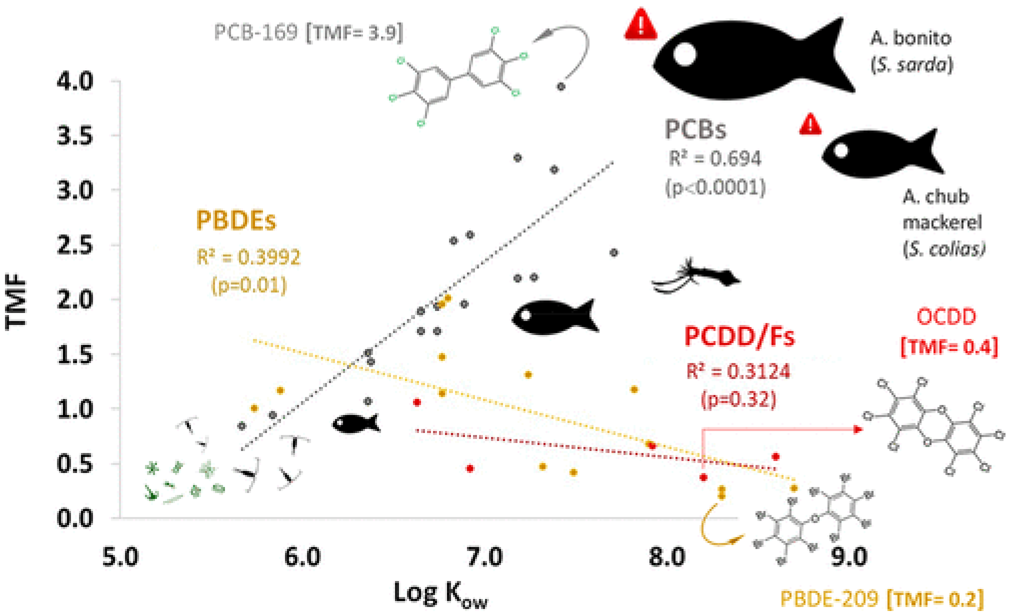
Abstract :

The storage capacity, trophic magnification and risk of sixty-two POPs have been evaluated in a well-characterized pelagic food web (including phytoplankton, zooplankton, six fish, and two cephalopods species) from an impacted area in NW Mediterranean Sea. Our results show the high capacity of the planktonic compartment for the storage of polybrominated diphenyl ethers (PBDEs) and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), consistent with their estimated low trophic magnification factors (TMF) of 0.2–2.0 (PBDEs) and of 0.3–1.1 (PCDD/Fs). ∑PBDEs dominated in the zooplankton size-class 200–1000 µm (~330 ng g–1 lw, median), whereas ∑PCDD/Fs accumulated preferentially in phytoplankton size-class 0.7–200 µm (875 pg g–1 lw, median). In contrast, polychlorinated biphenyls (PCBs) were preferentially bioaccumulated in the higher trophic levels (six fish species and two cephalopods) with TMFs = 0.8–3.9, reaching median concentrations of 4270 and 3140 ng g–1 lw (∑PCBs) in Atlantic bonito (Sarda sarda) and chub mackerel (Scomber colias), respectively. For these edible species, the estimated weekly intakes of dioxin-like POPs for humans based on national consumption standards overpassed the EU tolerable weekly intake. Moreover, the concentrations of nondioxin-like PCBs in S. sarda were above the EU maximum levels in foodstuffs, pointing to a risk. No risk evidence was found due to consumption of all other edible species studied, neither for PBDEs. The integrated burden of POPs in the food web reached ~18 µg g–1 lw, representing a dynamic stock of toxic organic chemicals in the study area. We show that the characterized food web could be a useful and comprehensive "bioindicator" of the chemical pollution status of the study area, opening new perspectives for the monitoring of toxic chemicals in Mediterranean coastal waters.

Graphical abstract



Keywords : environmental exposure, bioaccumulation, flame retardants, dioxins, PCBs, fish, cephalopods, plankton

1. Introduction

The chemical contamination of the marine environment is a global and transversal issue with important ecological and socio-economic implications, yet not well quantified nor efficiently managed.[1,2] Populations living in coastal areas, as well as marine organisms, are exposed to multiple sources of chemical contamination, particularly in semi-enclosed environments such as the Mediterranean Sea. The Mediterranean is a sensitive environment with the particularity of being a hotspot of both marine biodiversity (up to 18% of the world's marine diversity) and chemical contamination (e.g. organic and inorganic contaminants, plastic debris). [3-5] Among the contaminants impacting this marine environment, persistent organic pollutants (POPs) and related chemicals are well documented in non-biotic compartments[6-10] and different marine organisms.[5,8,11-17] POPs are organic contaminants of major concern due to their high toxicity, long-range transport and bioaccumulation potential, and their high resistance to degradation.[18] Even if these toxic chemicals have been banned by international regulations, such as the Stockholm Convention on POPs (SC), their ubiquity in the marine environment many years after their release may still pose potential risks.

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) are widespread POPs with different environmental sources. While PCDD/Fs can occur as unintentional by-products in a number of industrial processes and domestic heating[19,20], PCBs are legacy industrial chemicals used in many applications (e.g. lubricants, transformers, oil additives). [21] Major primary sources for these two families of legacy POPs are considered under control in most parts of the world today.[22] However, ongoing primary releases from diffuse sources such as open fires and uncontrolled waste incineration, urban/industrial centres, as well as secondary sources such as net re-emissions from environmental reservoirs are still possible. [21,22] PBDEs were mostly used (and are still in some regions) as flame retardants[23] and, in contrast to PCDD/Fs and PCBs, have been only recently restricted at global scale by the SC.[24] These chemicals constitute complex mixtures in the environment to which marine organisms and humans are exposed. Their accurate determination in the biotic compartment represents a very important first step to apprehend potential risks. However, despite the fact that POPs are often measured in organisms from different trophic levels (TLs), these organisms do not always belong to the same food web, making it difficult to properly investigate their trophic magnification, subsequent impacts and more generally the environmental status of marine waters, as requested by the European Marine Strategy Framework Directive. [25]

Here, we report results for PCDD/Fs, PCBs, and PBDEs in 26 biotic samples consisting of phyto- and zooplankton, six fish species and two cephalopods, all belonging to the same trophic web from an impacted coastal area, the Bay of Marseille, in the NW Mediterranean Sea. The overall aims of this work were: (1) to characterize a pelagic food web representative of the coastal NW Mediterranean, including species consumed by humans, which could help the monitoring and assessment of chemical pollution in the area; (2) to determine the burden and storage capacity of a cocktail of 62 toxic organic chemicals in the selected food web; (3) to assess their potential trophic magnification, exposure to humans and risks *via* consumption of fishery products.

2. Materials and Methods

2.1. Study area

Samples were collected in the Bay of Marseille in the south of France (NW Mediterranean Sea) (Figure S1). This bay is highly impacted by multiple contamination sources, such as the Marseille sewage treatment plant, with its outlet (WWTP Cortiou) located around 10 km south-east of the sampling site,[26] and the port, industry, agriculture and tourism, in particular. The Bay of Marseille is naturally influenced by high solar radiation,[27] intrusions of the Northern Current on the shelf, [28] and occasionally by intrusions of the Rhone river plume and the coastal Huveaune River, giving rise to episodic high inputs of particle and dissolved organic matter. [29-31] Inputs of a wide diversity of POP families and related organic contaminants of emerging concern have been reported in the area coming from the Rhone River, [32-36] the Marseille WWTP at Cortiou and the Huveaunne, [35,37-39] and the atmosphere. [10] Marine organisms and pelagic food webs in the Bay of Marseille are certainly exposed to those contaminants (Figure S1).

2.2. *Sampling*

Phyto- and zooplankton samples were collected at the SOLEMIO station (43.24°N; 5.29°E, Figure S1) on 15th March 2017 on board the RV ANTEDON II. Phytoplankton and suspended particulate matter (mostly microphytoplankton and detritus particles) were obtained by filtering ~60 L of surface water collected with an inner lining Teflon GoFLo 12 L bottle through ten pre-combusted 47mm glass fiber filters (GFFs, 0.7 µm) and treated as one sample. Zooplankton was vertically sampled, from 0 to 50 m depth, using a zooplankton net of 150 µm mesh, and then sequentially separated by using stainless steel sieves. Due to the limited amount of sampled material, the various fractions were pooled together into two overall size classes ('Z1': 200-1000 µm, and 'Z2': >2000 µm) for POPs analyses. However, all zooplankton size-classes were considered for the food web structure determination (Figure S2). Their groups and species as well as biochemical composition are detailed elsewhere.[40] Teleosts and cephalopods were sampled by professional fishers in the Bay of Marseille near SOLEMIO and specimens were acquired in the Marseille fish market on the same day. Sampled species were: (1) the planktivorous fish bogue (*Boops boops*, Linnaeus, 1758); (2) the mesopredators *Trachurus trachurus* (Linnaeus, 1758), *Trachurus mediterraneus* (Steindachner, 1868), *Scomber colias*

(Gmelin, 1789), the European hake (*Merluccius merluccius*, Linnaeus, 1758), and the cephalopod squid *Illex coindetii* (Vérany, 1839), *Todarodes sagittatus* (Lamarck, 1798), and (3) the top predator Atlantic bonito (*Sarda sarda*, Bloch, 1793). All these fish and cephalopods are commonly caught by local fisheries and consumed in the region. Three individuals of different size were considered by species, except for the cephalopod *T. sagittatus* for which only one specimen was available. In the laboratory, the fresh organisms were cleaned, measured and weighed (Table S1). Plankton analyses were made on the entire individuals, while dorsal muscle was sampled for teleosts and mantle for squid. Dissection was done on a clean glass table strictly avoiding contact with plastics or any other material which could be a source of organic matter. All the samples were then frozen at -20°C, freeze-dried and ground into a homogenized fine powder prior to analyses (see text S1 for details). We acknowledge that the overall contaminant transfer in the food web will be dictated by the consumption of the entire prey individuals in the ecosystem. However, the choice of the sampling in this study concerned only the muscle for cephalopods and fishes as generally represents the major contaminant exposure route for humans, therefore enabling a risk assessment (section 3.5). Further analyses in higher lipid-rich organs such as the liver and gonads may reveal a higher total POP burden and a potentially higher biomagnification.

2.3. Stable isotope and biochemical analyses

Three replicates were performed on phytoplankton and zooplankton size classes, while the three individuals of teleosts and cephalopods were considered as replicates for $\delta^{13}C$, $\delta^{15}N$, %C, %N, and total lipid analyses. Stable isotope measurements were performed with a continuous-flow isotope-ratio mass spectrometer coupled to an elemental analyzer in LIENSs Laboratory, La Rochelle University (France). Details for total lipid determinations are presented in Text S1. For fish samples, $\delta^{13}C$ values were corrected for the effects of lipids when the C/N >3.5.[41] TLs were estimated using the zooplankton 200-300 µm size class (composed mostly of small herbivorous copepods) as 'baseline' with trophic position defined as 2.[40,42] A classical enrichment factor of 3.4‰ between prey and predator was applied except for the top predator *S. sarda* for which a value of 2.4‰ was used [43] (See Text S1 for all details).

2.4. POPs analysis

All samples were freeze-dried and zooplankton and fish samples homogenized by using a ball mill mounting stainless steel cells. The corresponding amounts of sample (0.14-0.25 g dw, Table S1) were spiked with ^{13}C-labeled standards of PCDD/Fs, PCBs, and PBDEs prior to Soxhlet extraction (24h) with a n-hexane: DCM (9:1) mixture. Extracts were rota-evaporated and cleaned-up using the automated sample preparation system DEXTech+.[14] The six indicator PCBs ($_{ID}$PCBs), the eight mono-*ortho* dioxin-like PCBs ($_{DL}$PCBs) and PBDEs (27 congeners) were collected in a first fraction, while the seventeen 2,3,7,8-substituted PCDD/Fs along with the four non-*ortho* $_{DL}$PCBs were obtained in a second fraction, summing up a total of 62 POPs. Final extracts were rota-evaporated to ~ 1 mL, transferred to vials, and dried under a gentle nitrogen steam. Fractions were reconstituted in a few microliters of the respective PCDD/F, PCB, and PBDE ^{13}C-labeled injection standards prior to instrumental analysis. Quantification was carried out by isotopic dilution according to 1613 US EPA method [44] on a gas chromatograph (Trace GC ultra, Thermo Fisher Scientific) coupled to a high-resolution mass spectrometer (DFS, Thermo Fisher Scientific). Details can be found in Text S1.

2.5. Quality assurance / quality control (QA/QC)

Field blanks for phytoplankton samples (n=2), consisting of baked GFFs, which were placed in the freeze-dryer and then processed with the samples, were performed. Analytical laboratory blanks (n=6) accounting for all the sample processing steps were also performed. After sampling, GFFs were wrapped in aluminium foil again and stored in the dark at -20°C. Laboratory blank levels were generally low for the three POP classes compared to their concentrations in the samples, averaging from not detected (n.d.) to 25 pg (PCBs), from n.d. to 0.13 pg (PCDD/Fs), and from n.d. to 7 pg (PBDEs) depending on the congener and sample (Table S3). Laboratory blanks showed lower or similar levels to field blanks, so no contamination occurred during sampling, storage and analysis. Results were blank-corrected by subtracting the average field and laboratory blanks values for phytoplankton and the rest of samples, respectively. Chromatographic peaks were only considered when the ratio between the two monitored ions was within ±15% of the theoretical value, and the signal-to-noise (S/N) ratio>3 (limit of detection, LOD). Limits of quantification (LOQs) corresponded to S/N≥10. Calibration curves were daily checked. Median LODs (n=26) ranged from 0.2 to 2.3 pg (PCBs), from 0.1 to 0.8 pg (PCDD/Fs) and from 0.3 to 14.0 pg (PBDEs) depending on the compound and sample (Table S4). Median method recoveries varied from 60 to 111 % (PCBs), from 79 to 102 % (PCDD/Fs) and from 61 to 102 % (PBDEs) (Table S5). Results were corrected by recoveries.

2.6. Data analysis

Non-parametric tests (Kruskal−Wallis and Wilcoxon rank-sum) were used in order to investigate significant differences among pollutant levels. The effect of multiple comparisons was considered by applying the false discovery rate method. Non-detected values were imputed to the LOD/2 to run these tests (Text S2 and Table S6). The software employed was STATA/SE 16.1. However, the concentration sums presented in sections

3.3.1 and 3.3.2 consider only the detected values, and the concentrations expressed as World Health Organization-toxic equivalents (WHO_{05}-TEQ) presented in section 3.5 for $_{DL}$POPs are reported as upper bound values (i.e. the n.d. values were substituted by the corresponding LODs before the blank correction) to facilitate their comparison with available threshold values. The sample BB-1 was excluded from the data set for PBDEs due to suspected specific contamination. Trophic magnification factors (TMFs) for individual POPs were calculated using the slope (*m*) of the linear regression between the log_{10} of the lipid-normalized contaminant concentration in the food web organisms and their corresponding TLs (calculated as indicated above) [45, 46] (section 3.4.). For PBDEs and PCDD/Fs, which exhibited more n.d. values, only congeners with >30% detection frequency and detected in at least 7 different species and plankton size-classes were considered for the TMF calculation. In order to derive the estimated weekly intake (EWI) of $_{DL}$POPs and ∑PBDEs (section 3.5.), the weekly consumption data for France for demersal (*M. merluccius)* and pelagic (rest of species) fish and cephalopod (222, 132 and 9.2 g/week, respectively)[47] were multiplied by the WHO_{05}-TEQ (PCDD/Fs + $_{DL}$PCBs) and the ∑PBDEs (only detected values) concentration, respectively, measured in the corresponding species and divided by 70 Kg (average human bodyweight, bw), as previously described. [15] Risk quotients (R), were calculated as the concentration in the sample and its corresponding EWI, to threshold values, legally binding or not, derived by international authorities to protect humans consuming fishery products and aquatic ecosystems (R>1 indicating risk).

3. Results and discussion

3.1. Food web characterization

The stable isotope ratios of the species and size classes analysed in the Bay of Marseille pelagic food web are presented in Figure S2A and Table S7. Both $\delta^{13}C$ and $\delta^{15}N$ are significantly different between species and/or size classes (Kruskal-Wallis, $p < 0.0001$). Zooplankton > 2000 µm mainly constituted of gelatinous organisms had the lowest stable isotope ratios related to their filter feeding regime based on small pico (0.2-2 µm) and nano (2-20 µm) phytoplankton. These small size classes of phytoplankton are supposed to be the main source of the zooplankton food web in the North-Western Mediterranean area [48] but they could not be sampled for this study in sufficient quantities for POPs analyses. Particles issued from the Cortiou WWTP with low stable isotope ratios are also susceptible to be consumed by the different zooplankton size classes and decrease their stable isotope ratios during particulate rain or hydrodynamic conditions. [26,42] Micro-phytoplankton size class may represent the prey of many planktivorous fish such as *B. boops,* and all the juveniles of the studied fishes and squid. Herbivorous zooplankton 200-300 µm had also low stable isotope value and were considered as baseline for the estimation of the TL of the other consumer groups. The $\delta^{15}N$ ratios increased between low TL groups (phyto- and zooplankton) and high TL groups (fish and squid, TL > 3) consistent with their TL position (Figure S2B/Table S7). Predators such as the fish *S. sarda* and squid *T. sagittatus* showed the highest stables isotope ratios related to their high TL (5.3 and respectively 4.2).

3.2. Distribution of POPs and storage capacity in the food web

Overall, PCBs exhibited a high detection frequency (DF) of 73-100% for most congeners (Figure S3), and dominated total POP concentrations from zooplankton to top predators, accounting for 69% to around 100% of the ∑POPs (Figure 1A). PBDEs showed a generally lower DF with most congeners in the range 0-60%, although a certain number of congeners such as BDEs-28, -47, -49, -71, -99, -100 and -154 were highly detected (DF= 84-100%). PBDEs dominated only in phytoplankton, reaching 64% of total POPs concentrations, while accounting for 0.3 – 31% of the total contaminant stock in the rest of the samples. PCDD/Fs levels were below LODs in many cases and DF was mostly in the range 0-40% and only 2,3,7,8-TCDF (88 %) and 1,2,3,4,6,7,8-HpCDD (96%) were highly present. The contribution of PCDD/Fs to the total POPs burden in the studied food web was minor, representing < 0.5% of the total POPs. These contaminants accumulated preferentially in the lowest trophic levels (LTL) like PBDEs (Figure 1B). LTL, considered as the planktonic compartment (i.e. phytoplankton 0.7-200 µm, zooplankton 200-1000 µm and zooplankton > 2000 µm), seemed to play a predominant role driving the food web burden and storage capacity of ∑PBDEs and ∑PCDD/Fs exhibiting 12-fold and 5-fold higher median concentration than in higher trophic levels (HTL), respectively (Figure 1C). This trend was followed by individual PBDEs and PCDD/Fs too (Figure S4-S5) showing similar or significantly higher ($p<0.01$-0.04, Kruskal-Wallis) median concentrations in LTL. In contrast, the ∑PCBs burden in the food web may be dominated mostly by HTL showing a significantly 9-fold higher median concentration ($p=0.02$, Kruskal-Wallis) than the LTL (Figure 1B). Individual PCB congeners generally followed the same trend except for CBs-28 and -52, which exhibited similar or significantly higher median concentrations ($p=0.03$, Kruskal-Wallis) in LTL as PBDEs and PCDD/Fs (Figure S6). In other words, the lipid-normalized cumulative concentrations of PBDEs and PCDD/Fs in the phytoplankton and the two zooplankton size classes were similar or significantly higher than the cumulative concentrations of the 21 fish and 2 cephalopod individuals studied, pointing to the high capacity of the planktonic compartment for the accumulation and storage of these two POPs families. In contrast, fishes and cephalopods represent efficient biotic storage compartments for PCBs.

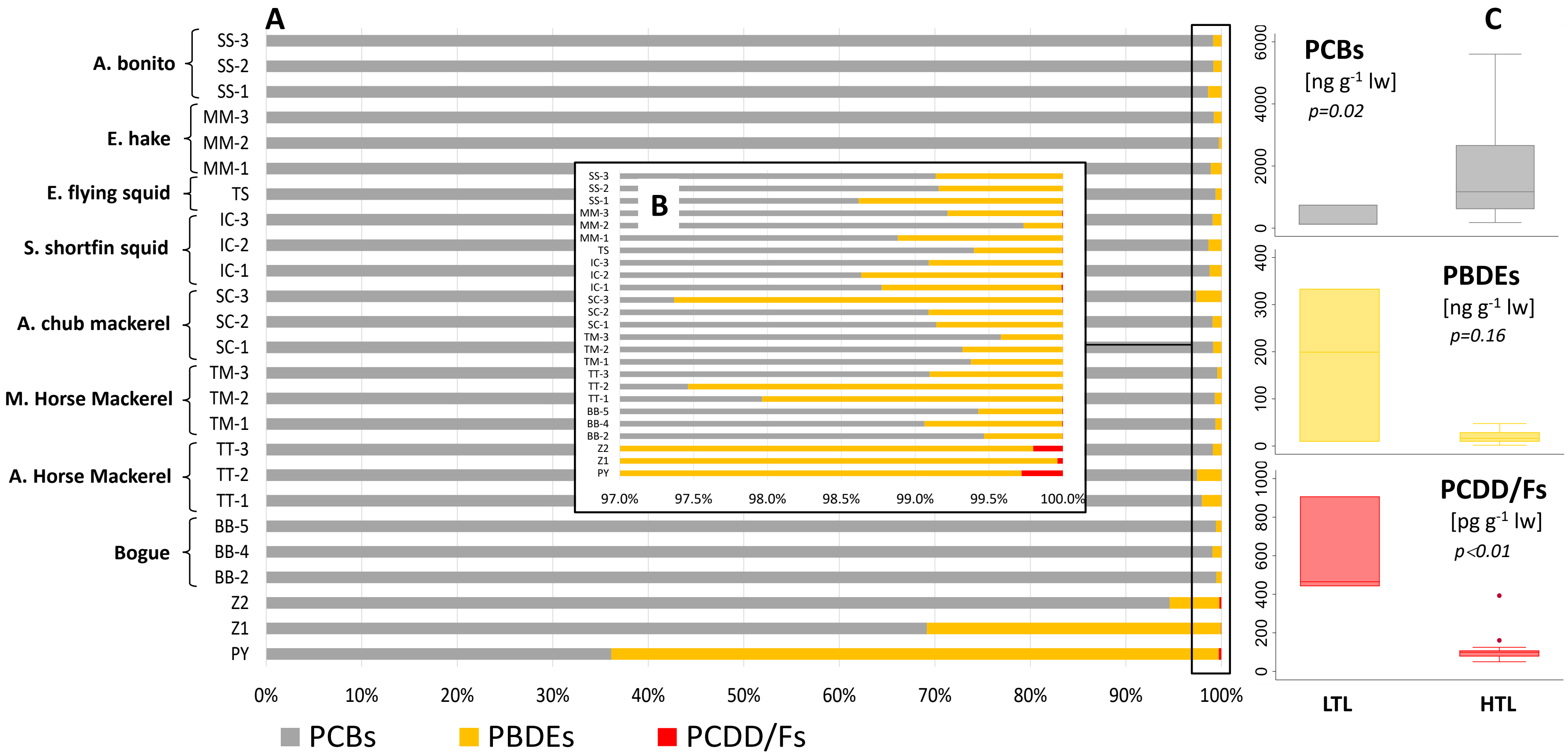


Figure 1. POPs relative burden in the food web (A) with a zoom showing the higher % of PCDD/Fs found in the planktonic compartment (B), and box plots (C) of the lipid normalized total concentrations of ∑PCBs, ∑PBDEs (ng g^{-1} lw) and ∑PCDD/Fs (pg g^{-1} lw) in the lowest trophic levels (LTL) considered as the planktonic compartment for the purpose of this comparison (i.e. *PY=phytoplankton 0.7-200 µm, Z1=zooplankton 200-1000 µm and Z2=zooplankton > 2000* µm, n=3) and the higher trophic levels (HTL) considered as the other organisms from the food web (fishes and cephalopods, n=22) Kruskal-Wallis test p-value. *BB=B. boops; TT=T. trachurus; TM=T. mediterraneus; SC=S. colias; IC=I. coindetii; TS=T. sagittatus; MM=M. merluccius; SS=S. sarda*.

3.3. Environmental concentrations and patterns

3.3.1. Overall concentrations

$\sum_{18}$PCB concentrations varied from 3.3 to 496 ng g^{-1} dw (from 113 to ~5600 ng g^{-1} lipid weight - lw) in the different individuals from the studied food web. The total PCB load was dominated by $\sum_{ID}$PCBs, accounting for 83-92% of $\sum_{18}$PCBs with concentrations ranging from 3.0 to 454 ng g^{-1} dw (~100 to 5130 ng g^{-1} lw). $\sum_{DL}$PCBs represented only between 8 and 17% of the total PCBs with levels between 0.3 and 42 ng g^{-1} dw (13 to 470 ng g^{-1} lw). $\sum_{26}$PBDE concentrations varied from 0.08 to 25 ng g^{-1} dw (1.0 to 333 ng g^{-1} lw) whereas three orders of magnitude lower $\sum_{17}$PCDD/F concentrations were measured, ranging from 0.3 to 110 pg g^{-1} d.w (3.4 to 875 pg g^{-1} lw). Results for individual PCBs, PBDEs and PCDD/Fs in each sample are presented in Tables S8-10. In addition, in order to facilitate data comparability, POPs concentrations are also expressed on a wet weight (ww) basis (Table S11).

3.3.2. Levels and patterns in the different organisms

Although concentrations of a number of POPs, mostly PCBs and PBDEs, were found significantly different among the different TLs in a first data analysis ($p<0.01–0.04$, Kruskal-Wallis) (Table S6), when comparing by pairs of TLs (Wilcoxon rank-sum test) and correcting by the effect of multiple comparisons (section 2.6, Text S2), these differences were not statistically significant. These analyses are certainly hampered by the limited amount of data. However, some trends are worth discussing. Although some bioaccumulation was observed in the 200-1000 µm zooplankton for the sum of PCBs, the species exhibiting the highest median $\sum_{18}$PCB concentration was the Atlantic bonito (*S. sarda*) (4270 ng g^{-1} lw), presenting the highest position in the food web (i.e TL=5.3), followed by the Atlantic chub mackerel (*S. colias*) (3140 ng g^{-1} lw). The European flying squid (*T. sagittatus*) and the Mediterranean horse mackerel (*T. mediterraneus*) were also among the highest concentrations with 2670 ng g^{-1} lw (only one sample) and 2280 ng g^{-1} lw (Table 1). Similar trends were found for individual PCBs, except for CB-28 and -52 which accumulated preferentially in the planktonic compartments with no clear trends in the other TLs (Figure S7). A consistent PCB pattern was observed in the whole food web, with PCB-153 as the most abundant congener in all TLs (27-42% of the median $\sum_{18}$PCBs), except for the TL 1 (phytoplankton) where PCB-101 and -52 were more abundant. The predominance of PCBs-101 and -52 has been reported in the dissolved water phase in other NW Mediterranean coastal areas.[49] Likely their preferential bioconcentration at the very first TLs could explain this differential pattern found in phytoplankton. PCB-118 was the most abundant $_{DL}$PCBs contributing ~53 – 74% of the median $\sum_{DL}$PCBs (Figure S8).

Table 1. Median concentrations (only detected values) of indicator, dioxin-like, and total PCBs ($\sum_{ID}$PCBs, $\sum_{DL}$PCBs, $\sum_{18}$PCBs, respectively), total PBDEs ($\sum_{26}$PBDEs) and total PCDD/Fs ($\sum_{17}$PCDD/Fs) in the different plankton size-classes, fish and cephalopods species of the food web under study. Values are expressed in dry, wet and lipid weights (dw, ww, lw, respectively). Concentrations are in ng g^{-1} except for PCDD/Fs (pg g^{-1}).

Median concentrations*	$\sum_{ID}$PCB [ng g^{-1}]			$\sum_{DL}$PCB [ng g^{-1}]			$\sum_{18}$PCB [ng g^{-1}]			$\sum_{26}$PBDEs [ng g^{-1}]			$\sum_{17}$PCDD/Fs [pg g^{-1}]		
Foodweb Species	*dw*	*ww*	*lw*	*dw*	*ww*	*lw*	*dw*	*ww*	*lw*	*dw*	*ww*	*lw*	*dw*	*ww*	*lw*
Phytoplankton (0.7-200 µm)	12.5	2.5	99.2	1.7	0.3	13.8	14.2	2.8	113.0	25.0	5.0	199.0	109.9	22.0	874.6
Zooplankton (200-1000 µm)	39.3	7.9	653.0	5.7	1.1	95.4	45.1	9.0	748.3	20.1	4.0	333.3	23.7	4.7	393.4
Zooplankton (>2000 µm)	3.0	0.6	112.7	0.3	0.1	12.9	3.3	0.7	125.6	0.2	0.04	6.9	7.0	1.4	265.9
Boops boops	38.4	9.2	629.4	6.2	1.5	102.2	44.7	10.7	732.3	0.5	0.1	5.3	2.1	0.5	28.8
Trachurus trachurus	55.7	11.1	858.5	5.6	1.1	79.2	61.3	12.3	937.6	1.0	0.2	19.5	0.7	0.1	9.2
Trachurus mediterraneus	180.2	36.0	2023.4	18.9	3.8	256.0	200.3	40.1	2279.4	0.8	0.2	15.6	0.9	0.2	16.2
Scomber colias	203.0	58.9	2734.2	19.1	5.5	286.4	222.1	64.4	3140.8	1.9	0.6	28.7	2.6	0.8	38.8
Merluccius merluccius	36.8	8.8	538.1	3.9	0.9	45.9	41.1	9.9	584.0	0.3	0.08	4.8	1.6	0.4	23.8
Illex coindetii	69.3	16.6	1229.4	8.1	2.0	155.5	77.5	18.6	1384.9	0.8	0.2	14.9	6.2	1.5	152.2
Todarodes sagittatus	181.8	43.6	2355.8	24.4	5.9	316.3	206.2	49.5	2672.1	1.2	0.3	16.1	6.5	1.6	84.5
Sarda sarda	444.0	106.5	3903.9	41.6	10.0	367.5	485.7	116.6	4271.4	4.2	1.0	37.1	3.9	0.9	43.3

*only one sample was available for phytoplankton, the two zooplankton size clasess and the cephalopod *Todarodes sagittatus*

Median $\sum_{26}$PBDE concentrations clearly dominated in the 200-1000 µm zooplankton (~330 ng g^{-1} lw) and phytoplankton (199 ng g^{-1} lw), whereas $\sum_{17}$PCDD/Fs accumulated preferentially in phytoplankton (875 pg g^{-1} lw) followed by 200-1000 µm zooplankton (~390 pg g^{-1} lw). The ∑PBDE predominance in zoo- and phytoplankton was driven by the higher contribution of BDE-209 (70-75% of the detected ∑PBDEs). The high $\sum_{17}$PCDD/F levels found in the LTL were driven by the higher abundance of octachlorodibenzo-p-dioxin (OCDD) accounting for the 64-80% of the detected ∑PCDD/Fs (Figure S9). Indeed, the predominant of OCDD/Fs in zooplankton has been reported in other marine food webs.[50] Both BDE-209 and OCDD are highly hydrophobic POPs with log octanol-water partition coefficients (log K_{ow}) of 8.7 and 8.2, respectively, indicating high partition potential on hydrophobic components such as lipids or organic carbon-rich particles. The combination of the following factors may explain this observation: The 200-1000 µm plankton size classes in the study area, mostly composed of copepods, have been reported to have a high concentration of protein and lipid.[40] Moreover, the composition of smallest size class (0.7–200 µm) is dominated by microphytoplankton and detritus (mostly from the Marseille WWTP effluents and Rhone inputs), and small copepod stages[26,40,42], proving active surfaces for the accumulation of highly hydrophobic contaminants. A previous study showed important atmospheric inputs of particle-bound PBDEs (~550 ng m^{-2} y^{-1}) and PCDD/Fs (~15 ng m^{-2} y^{-1}) in the area, also with a clear predominance of BDE-209 and OCDD in the atmospheric particle patterns.[10] This atmospheric loading may constitute a relatively constant and direct source of these congeners to surface waters, facilitating their way to the LTL of the food web.

Regarding HTLs, *S. sarda* and *S. colias* presented the highest ∑PBDE median concentrations of 37 and 29 ng g^{-1} lw, respectively, followed by *T. trachurus*, *T. sagittatus* and, *T. mediterraneus* exhibiting median concentrations in the range 16-20 ng g^{-1} lw

(Table 1). Although individual PBDEs generally followed this trend too (Figure S10), some differences were found in the PBDE patterns. In the group of species showing higher ∑PBDE median concentrations (i.e. *S. sarda*, *S. colias*, *T. trachurus*, *T. mediterraneus*, and *T. sagittatus*), the PBDE pattern was characterized mostly by the predominance of BDE-47 and -100 (32-46% and 13-31% of the detected ∑PBDEs, respectively) and a lower contribution of PBDE-209 (4-16% of the detected ∑PBDEs) (Figure S11A). The predominance of these congeners, particularly BDE-47, has been reported for other marine organisms.[14,17,51] Furthermore, the patterns in *M. merluccius* and *I. coindetii*, two out of the three species showing the lowest median values, showed a more even relative distribution of BDE-47 and BDE-209, accounting for the 24-32 and 32-39% of the detected ∑PBDEs, respectively (Figure S11B). These are piscivorous and invertivorous species feeding mainly on pelagic species. Interestingly, the pattern found in *B. boops* showed a similar BDE-209 contribution as *M. merluccius* and *I. coindetii* but lower relative contribution of BDE-47 and higher % of BDE-99, resembling instead that of phytoplankton and 200-1000 µm zooplankton (Figure S11B,C). The fact that *B. boops* is essentially zooplanktivorous[40] could partially explain this pattern. The 200-1000 µm zooplankton have been reported as the zooplankton class-size with the highest energy content in the study area, making it preferable prey for zooplanktivorous fish such as the bogue. [40] However, a differential metabolic capacity of *B. boops* could also contribute to the observed pattern. Species-specific differences in metabolic rates of PBDE in fish has been already reported.[52] A higher median BDE-99/BDE-100 ratio (reported as an indicator of fish capacity to metabolize PBDEs)[49, 53] for *B. boops* (0.9) was observed in comparison to the combined ratio for *M. merluccius* and *I. coindetii* (0.2), suggesting a less efficient capacity of *B. boops* to metabolize PBDEs. For comparison, the ∑PBDE concentrations in HTL organisms in this study (0.02-1.0 ng g^{-1}ww, Table S11B) were similar or slightly lower to those reported in fish from other Mediterranean locations. Values ranging from 0.07 to 3.4 ng g^{-1}ww were measured in wild fish from the Adriatic, Ionian and Tyrrhenian Seas (E Mediterranean)[17] and average concentrations ranging from ~1.0 to 3.9 ng g^{-1} ww were reported for fish and seafood collected in Valencian markets (Spain, NW Mediterranean)[54]. The fact that the authors of these studies reported the upper bound concentrations and that other fish species were also studied could explain an important part of the concentration variability.

Regarding HTL, ∑PCDD/Fs accumulated preferentially in the cephalopods exhibiting median concentrations of 152 and 84 pg g^{-1} lw in the Southern shortfin squid (*I. coindetii*) and European flying squid (*T. sagittatus*), respectively. The pattern in these organisms was characterized by a predominance of OCDD (around 50% of the detected ∑PCDD/Fs) and was quite similar to that of the planktonic compartment (Figure S12A). Individual congeners followed the same concentrations trend, except for 2,3,7,8-TDCF which also accumulated in *S. colias, B. boop, S. sarda and T. trachurus* (Figures S13), as reflected too in their respective patters (Figure S12B) with this congener accounting from ~60 to 76% (median) of the detected ∑PCDD/Fs. *M. merluccius* and *T. mediterraneus* showed a comparable contribution of 1,2,3,4,6,7,8-HpCDD, 2,3,7,8-TDCF, and OCDFs representing 30-40% of the detected ∑PCDD/Fs depending on the congener and species (Figure S12C).

3.4.Trophic magnification

TMFs were calculated for the eighteen PCBs, fourteen PBDEs and five PCDD/Fs (Figure S14, Table S12). The majority of POPs (60%) with calculated TMFs bioamplified

(TMF>1), 32% biodiluted (TMF<1) and the remining 8% exhibited no apparent tendency (TMF~1)[45] (Figure 2A).

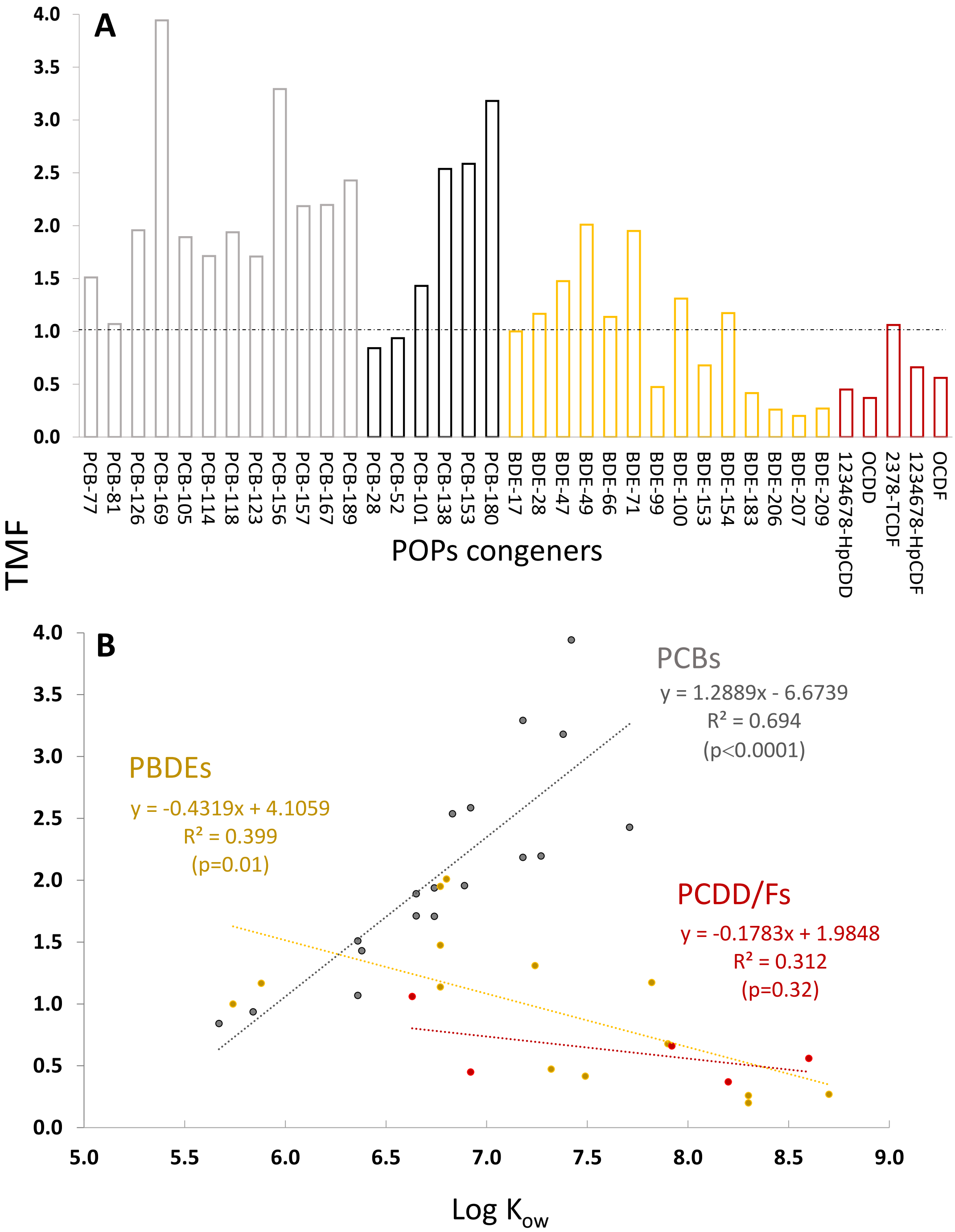


Figure 2. Trophic magnification factors (TMFs) for individual PCBs, PBDEs and PCDD/Fs (A) and their relationship with the POPs' log K_{ow} (B) for the NW Mediterranean Sea food web. Only congeners with DF > 30% and covering at least seven different species and plankton size-classes were considered. The horizontal dotted line indicates TMF=1. Light and dark grey, yellow and red indicates $_{DL}$PCBs, $_{ID}$PCBs, PBDEs and PCDD/Fs, respectively. The standard errors and confidence intervals of the slopes used to derive the TMFs can be consulted in Table S12.

PCBs showed the highest biomagnification potential (>80% congeners with TMF>1) with TMFs ranging from 1.4 (PCB-101) to 3.9 (PCB-169). Our results indicate that even if PCB-153, one of the most studied PCBs in aquatic organisms, exhibited a lipid-normalized concentration of 4-5 orders of magnitude higher than PCB-169 and PCB-126 (Table S8), its estimated trophic magnification potential (TMF_{CB-153} = 2.6) is around 35% weaker than that for PCB-169 and only 24% higher than that of PCB-126 (TMF=1.9). PCBs-126 and -169 are indeed the most toxic $_{DL}$PCBs (toxic equivalent factor, TEFs=0.1 and 0.03, respectively).[55] This may have implications for the appropriate environmental exposure assessment to the most toxic PCBs in the study area, which may be overlooked by only studying the most abundant PCBs, which is often the case, and warrants further research. Only PCB-28 (TMF=0.8) and -52 (TMF=0.9) did not biomagnify, consistent with their higher abundance in the food web LTL (section 3.3.2). A significant positive correlation (R^2=0.69, $p<0.0001$) was found between the TMF_{PCBs} and the log K_{ow} (Figure 2B) confirming the general higher trophic magnification for the more hydrophobic PCBs in this Mediterranean food web, as previously reported for other aquatic ecosystems[46]. This biomagnification potential is consistent too with the higher PCB concentrations generally found in the Atlantic bonito (Tables 1, S7 and Figure S7).

In contrast to PCBs, only 50% of PBDE congeners biomagnified, exhibiting generally lower TMFs ranging from 1.1 (BDE-66) to 2.0 (BDE-49). The other congeners showed a trophic dilution in the food web with TMFs varying from 0.2-0.7 (Figure 2A, Table S12). A negative significant correlation (R^2=0.40, $p=0.01$) was found for TMF_{PBDEs} and the log K_{ow} indicating a lack of biomagnification of the heaviest PBDEs like BDE-206, 207 and 209 among others (Figure 2B), consistent with their higher predominance in the planktonic compartment. It is worth mentioning that no or little trophic magnification

(0.5< TMF< 1.5) was found for most of the PBDEs considered in the European Quality Standard for PBDEs (i.e. BDE-28, -47, -99, -100, -153, -154) in fishes (EQS_{biota})[56]. Moreover, a generic biomagnification factor (BMF) of 5 is used to cover the biomagnification of those PBDEs from lower TLs to fish species of higher TLs [57], which is much higher than our filed-derived TMFs. PCDD/Fs showed TMFs ranging from 0.4 to 1.1 indicating mostly trophic dilution, with a non-significant negative correlation (R^2=0.31, p=0.32) between $TMF_{PCDD/Fs}$ and log K_{ow}. This lack of significant correlation with log K_{ow} has also been reported in other aquatic food webs. [58] Similarly to PBDEs, a BMF=10 is considered for PCDD/Fs and $_{DL}$-PCBs to account for their biomagnification in aquatic food webs [59], which is much higher than the TMFs measured in this study. These facts raise the importance of using site and food web specific biomagnification values in order to perform a more reliable site-specific risk assessment instead of applying generic default values.

Overall, our results indicate that the POPs biomagnification in the studied food web is strongly congener and species dependent. The fact that POPs congeners with similar K_{ow} showed distinct bioaccumulation patterns, particularly the more hydrophobic PCBs, PBDEs and PCD/Fs indicated that lipophilicity was not the only factor explaining their trophic magnification. This differential behaviour has also been reported in other aquatic food webs.[58] Indeed, the interplay of the specific contaminant bioavailability and metabolic transformation may have driven their final biomagnification. The observed trophic dilution of higher hydrophobic PBDEs in wild fish could be mostly attributed to the metabolic debromination of HMW PBDEs as previously reported. [52] However, the biodilution of higher hydrophobic PCDD/Fs, exhibiting negligible metabolization rates in most cases, may be better explained by a reduced membrane permeability due to their larger molecular size compared to the lower chlorinated congeners. [50]

Field-derived TMFs for the studied POPs in marine food webs are scarce in the literature for comparison. In addition, TMFs in marine systems have been reported to be highly variable and a number of factors such as type, structure and length of the food web and the site study specificities and season of the year, may have an important influence on the final TMF value [60,61]. Therefore, the comparability of TMFs must be carefully interpreted. TMFs of 1.3 and 1.2 were reported for PCB-153 and BDE-47, respectively, in a study conducted in the Gulf of Lion during the period 2004-2006 and in a shorter foodweb[60]. These values are slightly lower than those calculated for the same contaminants in this study ($TMF_{PCB-153}$ = 2.6 and TMF_{BDE-47} = 1.5). The fact that we studied a longest food web, including a higher top predator (Atlantic bonito), could explain our higher values. TMFs within the same range were reported for a pelagic food web in the western Scheldt estuary (Netherlands)[62] for BDE-28, -47, and -100. This work highlighted too the trophic dilution of BDE-209 with a very similar TMF of 0.2. However, they found BDE-99 biomagnifying (TMF=2.4) in their studied food web, while a TMF=0.5 was found for the same congener in our study. The reported predominance of BDE-99 in the western Scheldt Estuary organisms [62] , likely linked to historical local sources, could explain this difference, since this congener was not predominant in our food web. TMFs for PCBs and PBDEs within the same range were reported for a pelagic food web in coastal Atlantic Ocean[63]. However, our TMFs for these two families of POPs were generally lower than the average (± standard deviation) TMFs reported for a global compilation also including fresh water ecosystems, which ranged from 1.7 ± 1.1 to 8.1 ± 6.9 for PCBs and from 0.3 ± 0.3 to 3.2 ± 1.9 for PBDEs [61], although a large variability was reported too (Figure S15).

To the best of our knowledge, we report here the first field-derived TMFs for PCDD/Fs in a Mediterranean food web, which are very similar to those reported in other aquatic ecosystems[61] (Figure S15).

3.5. Toxicity potential and risk assessment

3.5.1. $_{DL}$POPs

Concentrations expressed as upper bound WHO$_{05}$-TEQ were derived for $_{DL}$PCBs and the 2,3,7,8-PCDD/Fs in the food web organisms using the latest available TEFs[55] in order to study their toxicity potential against humans. Concentrations ranged 0.008 - 5.2 and 0.2 – 0.8 WHO$_{05}$ TEQ pg g^{-1} ww for Σ_{DL}PCBs and Σ_{17}PCDD/Fs, respectively, resulting in TEQ$_{Total}$ (Σ_{29}dioxin-like POPs) of 0.2-5.7 pg g^{-1} ww (Figure 3A, Table S13).

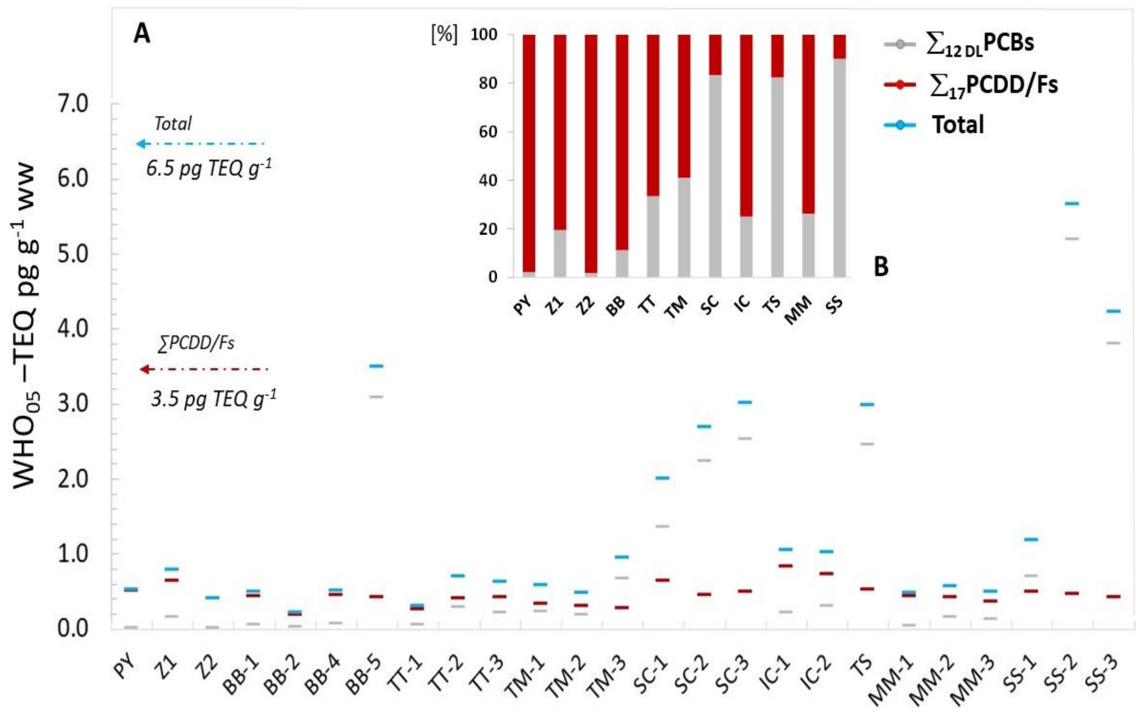


Figure 3. Calculated WHO$_{05}$-TEQ (pg g^{-1} ww) in all samples from the pelagic food web in coastal NW Mediterranean Sea (A) and median relative contribution (%) of Σ_{12DL}PCBs (grey) and Σ_{17}PCDD/Fs (red) to the total WHO$_{05}$-TEQ (PCBs+PCDD/Fs) in blue (B), except for PY, Z1, Z2 and TS, which are single values. The horizontal dotted lines show the EU concentration thresholds in sea foodstuffs and wild fish (see text for details). *PY=phytoplankton 0.7-200 µm; Z1=zooplankton 200-1000 µm; Z2=zooplankton > 2000 BB=B. boops; TT=T. trachurus; TM=T. mediterraneus; SC=S. colias; IC=I. coindetii; TS=T. sagittatus; MM=M. merluccius; SS=S. sarda*.

The species *S. sarda*, *T. sagittatus* and *S. colias* exhibited the highest median TEQ_{Total} values of 4.2, 3.0, and 2.7 pg g^{-1} ww, respectively (Table S13). These TEQs were driven by the predominant contribution of $_{DL}$PCBs (82-90%) in those species (Figure 3B). Median TEQ_{Total} values in the remaining trophic levels varied from 0.4 to 1.1 pg g^{-1} ww. PCDD/Fs exhibited a generally higher contribution (53-98%) on these species, except for some isolated samples such as BB-5 and TM-3, which show a higher concentration of PCB-126, increasing the relative contribution of $\sum_{DL}$PCBs TEQ on those samples. The $\sum_{DL}$PCB TEQ concentrations measured in the studied food web were within the range or higher than those reported for other fish species in the Mediterranean. For example, levels of 0.4-1.2 (*Sardina pilchardus*), 0.08-0.4 (*Engraulis encrasicolus*) and 0.07-0.27 (*B. boops*) pg TEQ g^{-1} ww have been recently reported.[14] Our concentrations in fish samples, excluding those of the top predator Atlantic bonito, ranged from 0.02 to 3.1 pg TEQ g^{-1} ww for $\sum_{DL}$PCBs, with values varying from 0.05 to 3.1 pg TEQ g^{-1} ww for *B. boops*. Our $\sum_{DL}$PCB TEQ values were also higher than those reported for chub mackerel (*Scomber japonicas*) (0.002 -0.008 pg TEQ g^{-1} ww) and horse mackerel *(T. trachurus)* (0.004 – 0.016 pg^{-1} ww) caught in the Adriatic Sea.[64] For comparison, our $\sum_{DL}$PCB levels in *T. trachurus* varied from 0.05 to 0.3 pg TEQ g^{-1} ww (Table S13). A recent study measured dioxin-like POPs in Mediterranean bluefin tuna (*Thunnus thynnus*), reporting 0.7 and 1.9 pg TEQ g^{-1} ww for $\sum_{DL}$PCBs and $\sum$PCDD/Fs, respectively.[65] Our results in the Atlantic bonito ranged from 0.7 to 5.2 and from 0.4 – 0.5 pg TEQ g^{-1} ww for $\sum_{DL}$PCBs and $\sum$PCDD/Fs, respectively. However, the concentrations reported for the bluefin tuna were lower bound values (non-detected values were considered as zero). These comparisons are only indicative due to the associated variability related to the different species considered, sampling year and season and the quantification strategies adopted in each specific study.

At European level, two pieces of legislation, Commission Regulation 1259/2011[66] and Directive 2013/39/EU[56], set a maximum level for $_{DL}$POPs in seafood and marine organisms aiming at protecting human health *via* consumption of fishery products (but also aquatic top predators from secondary poisoning for the EQS_{biota}). The same threshold level of 6.5 pg TEQ g^{-1} ww for the $\sum_{17}$PCDD/Fs + $\sum_{12DL}$PCBs in fish muscle and fishery products, and wild fish (EQS_{Biota}) has been established. In addition, regulation 1259/2011 also set a threshold value of 3.5 pg TEQ g^{-1} ww for $\sum_{17}$PCDD/Fs only. The concentrations measured in the various species considered did not exceed any of these thresholds, although certain *S. sarda* and *S. colias* individuals (i.e. SS-2-3 and SC-3) approached the 6.5 pg TEQ g^{-1} ww threshold for total $_{DL}$POPs (Figure 3A) with risk quotients (R) between 0.5 and 0.9 (Table S14). The $_{DL}$POPs EWIs considering fish and cephalopod consumption data in French population (section 2.6) were calculated for each sample and varied from 0.1 to 11 pg TEQ Kg^{-1} bw $week^{-1}$. All individuals of *S. colias* and *S. sarda* exceeded the tolerable weekly intake (TWI) of 2 pg TEQ Kg^{-1} bw $week^{-1}$ set by the European Food Safety Authority[67] with R values ranging from 1.1-5.3 and 1.9-2.8 for *S. sarda* and *S. colias*, respectively (Table S14). The major contributors to the EWI and subsequent risk for humans associated with the consumption of *S. colias* and *S. sarda* were $_{DL}$PCBs, particularly PCB-126.

Moreover, Regulation 1259/2011 sets a maximum level of 75 ng g^{-1} ww for the sum of the six non-dioxin-like PCBs in seafood, also referred as $_{ID}$PCBs in this work. The $\sum_{ID}$PCBs concentrations in the studied food web were for most samples below that threshold (Table S11), varying from 0.6 to 59 ng g^{-1} ww. However, some *S. colias* individuals again approached the threshold (R=0.8 for SC-1-2) and two out three samples of the top predator *S. sarda* (i.e. SS-2-3) exceeded it with concentrations between 106-109 ng g^{-1} ww (R=1.4, Table S14) pointing to a risk for humans to non-dioxin-like PCBs due to consumption of this last species. It has been reported that non-dioxin-like PCBs, which are weak aryl hydrocarbon receptor agonists, can modulate the overall toxic potency of 2,3,7,8-TCDD and related compounds[55] and therefore their co-occurrence cannot exclude cumulative effects including synergic harmful effects.

3.5.2. PBDEs

Regarding PBDEs, the EQS_{Biota} of 0.0085 ng g^{-1} ww (as $\sum_6$PBDEs including BDE-28,-47,-99,-100,-153,-154) based on human toxicity[56] was used for a first risk evaluation. This threshold value was exceeded in every single individual in all TLs (Table S14), indicating a risk for humans consuming the edible species, again pointing to *S. sarda* (R=54-97) and *S. colias* (R=15-65) as the most ‘risky' fish. However, some authors argue that the existing EQS_{Biota} for PBDEs is extremely low leading to environmental concentrations exceeding the threshold value in most study cases.[51,68] For OSPAR, there are still questions on the reliability and appropriateness of some of the thresholds set as EQS_{biota}, based on human protection, to support environmental assessment. This issue has recently resulted in the proposal to adopt the Canadian Federal Environmental Quality Guidelines (FEQGs) based only on wildlife protection.[69] Comparing our concentrations with the proposed FEQGs, which have been set for a number of individual PBDE congeners (i.e BDE-28, 47, 99, 100, 153, 154, 183 and 209), there is no indication of apparent risk for wildlife species (Table S15). However, it should be noted that the FEQGs are derived for whole organisms, and PBDE were measured in muscle in this study. The $\sum$PBDEs EWI in France ranged from 0.02 to 1.9 ng Kg^{-1} bw $week^{-1}$, the highest value corresponding to *S. sarda*, followed by *S. colias* (0.7-1.2 ng Kg^{-1} bw $week^{-1}$). For comparison, an average estimated intake of 0.14 ng Kg^{-1} bw d^{-1} *via* fish and seafood consumption for adults has been reported for Valencia (Spain) in the NW Mediterranean

Sea[54], corresponding well with our higher end estimate (0.17 ng Kg^{-1} bw d^{-1}). There is no TWI for ∑PBDE to the best of our knowledge, but the US Agency for Toxic Substances and Disease Registry and the US Environmental Protection Agency have established acute/sub-chronic Minimal Risk Levels[70] and chronic oral reference doses[71], respectively, for some of the most abundant PBDE congeners (i.e BDE-47, BDE-99, BDE-153, BDE-209). These health standards ranged from 3 to 7000 ng Kg^{-1} bw d^{-1} depending on the congener, showing that there is no risk associated with these congeners for humans consuming the studied Mediterranean fishery products.

Our study demonstrates that the edible species Atlantic bonito (*S. sarda*) and Atlantic chub mackerel (*S. colias)* bioaccumulated the highest concentrations of POPs which may pose a risk for humans consuming these species caught in the Gulf of Lion (NW Mediterranean Sea) mostly due to $_{DL}$POPs exposure. The cephalopods southern shortfin squid (*I. coindetti*) and European flying squid *(T. sagittatus*) showed a high potential for the accumulation of PCDD/Fs, however no indications of risk can be observed according to our evaluation. An in-depth review of available thresholds for PBDEs concentration in biota and the determination of tolerable daily intakes for more congeners are urgently needed to provide a more comprehensive risk assessment. We consider the calculated EWI as a lower-end estimate of their total exposure, since their intake through other food items is not accounted for and external exposure routes were not takein into consideration for in this evaluation. For example, the reported median outdoor inhalation intake in the study area for $_{DL}$POPs (0.028 pg TEQ Kg^{-1} bw $week^{-1}$) and ∑PBDEs (0.015 ng Kg^{-1} bw $week^{-1}$)[10] could range up between 0.4 - 1.3% and 0.8-2.1 % their respective total intakes. These results warrant further research on the overall intake rates of the three POP families by humans and their cumulative risks in this impacted region of NW Mediterranean Sea.

Our results would be highly valuable to set up-to-date and comparable concentration thresholds in biota considering trophic level normalization as recommended by EU guidance on the implementation of EQS_{biota} [72] and OSPAR.[73] Besides, the characterized food web, as a whole, may be a useful and site-specific comprehensive ‘bioindicator’ of the chemical pollution status, representing a dynamic stock of toxic organic chemicals in the study area. A lower-end estimation of its integrated POPs burden in the study season, calculated considering the sum of the median concentrations in all TLs, reached ~ 18 µg g^{-1} lw. This value could be considered a benchmark for further studies using the same food web, opening new perspectives for the monitoring of toxic chemicals in Mediterranean coastal waters. Future studies should investigate the effect of seasonality on the food web storage capacity and resulting integrated POPs burden, including a larger number of samples and considering whole organisms as well as fillet. A better characterization of POP accumulation processes in the planktonic compartment is needed, in view of its high storage capacity for some of these toxic chemicals and the potential implications for their biogeochemical cycling in marine environments, even if the collection of enough material for the size-class specific analysis is particularly challenging.

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Supporting information available

Additional data and details on the sampling and analytical procedures, QA/QC, concentration of individual congeners, TMFs, risk ratios among others are available free of charge via the Internet at http://pubs.acs.org/

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