Comparative occurrence and biomagnification of legacy persistent organic pollutants and alternative flame retardants in a macrotidal estuary: case study on the Gironde (SW France)

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Introduction

Flame retardants are substances used in plastics, textiles, electronic circuits and other materials to reduce their flammability. A number of these substances are chlorinated or brominated and are persistent in the environment, may bioaccumulate and have potential negative effects on human health and on the environment. In recent years, two groups of brominated flame retardants (BFRs), polybrominated biphenyls ethers (PBDEs) and hexabromocyclododecane (HBCD), have officially been listed in the Stockholm Convention and classified as persistent organic pollutants (POPs) and have been subjected to regulations and restrictions. This has paved the way for the use of alternative flame retardants which are increasingly being used, although they have similar properties to legacy POPs, including environmental persistence and potential for bioaccumulation[1]. However, the environmental fate of these FRs of emerging concern has little be documented so far, in particular in transitional waters such as estuaries. Thus, the aim of this work was to investigate the occurrence and to assess the biomagnification potential of selected legacy POPs and emerging FRs in the trophic web of a macrotidal estuary: the Gironde (SW France).

Materials and methods

Sampling, sample preparation and instrumental analysis

A total of 55 biota samples were collected between May and November 2012 in the mesohaline zone of the Gironde estuary, including fish (grey mullet, common seabass, common sole, anchovy, sprat, gobies) and invertebrates (copepods, crabs, white shrimps, brown shrimps, gammarids, ragworm, oysters, scrobicularidae and mysids). Samples were freeze-dried and finely ground prior to a further analysis. Target analytes included i) legacy POPs : PBDEs, HBCD and polychlorobiphenyles (PCBs), ii) brominated FRs such as DBE-DBCH, PBT, PBEB, TBP-DBPE, HBB, DBHCTD, EH-TBB, BTBPE, BEH-TEBP OBTMPI, DBDPE and iii) chlorinated FRs such as DDC-Ant, aCl10-DDC-CO, syn-DDC-CO, aCl11-DDC-CO, anti-DDC-CO[2].

Analytes were extracted using microwave-assisted extraction with dichloromethane; extracts were filtered, concentrated and aliquoted into two fractions. For the analysis of PCBs, PBDEs and HBCD isomers, the first aliquot was purified on H_2SO_4-impregnated silica gel (40% w/w), while the second aliquot was purified on activated alumina and H_2SO_4-impregnated silica gel (10% w/w) for the analysis of emerging FRs. Indicator PCBs (CB-28, -52, -101, -118, -153, -138 and -180) were analyzed by gas chromatography coupled to an electron capture detector and PBDEs (BDE-28, -47, -49+71, -99, -100, -153, -154, -183 and -209) by gas chromatography coupled with mass spectrometry in electron capture negative ionization mode (ECNI). HBCD isomers (α-, β- and γ-) were analyzed by ultra-performance liquid chromatography coupled with tandem mass spectrometry and emerging FRs by gas chromatography coupled to Time-of-Flight mass spectrometry operated in ECNI. $\delta^{15}N$ and $\delta^{13}C$ were determined using and Elemental Analyzer coupled with an Isotope Ratio Mass Spectrometer.

Calculation of trophic level (TL) and trophic magnification factors (TMF)

TL were calculated using the formula for two-source food webs[3,] where $\delta^{15}N_{base1}$ and $\delta^{15}N_{base2}$ are the mean $\delta^{15}N$ of the baseline organisms for the benthic and demersal food webs respectively, and α is a coefficient used to adjust the relative importance of each nitrogen food source for a given consumer: $TL = 2 + (\delta^{15}N_{predator} - (\alpha\ \delta^{15}N_{base1} + (1 - \alpha)\ \delta^{15}N_{base2})) / 3.4$.

TMF was determined by linear regression of log-transformed concentrations against TL. TMFs were calculated using three different models: linear regression, censored regression (cenken function, NADA package in R) which takes into account left-censored values and GLMM, implemented with the lmec function in R. The latter model considers both left-censored values and the heterogeneity in the number of individuals per taxon.

Results and discussion

Levels and contamination profiles

PCBs were the most detected compounds and their detection frequency ranged between 42–80 % for CB-52, -28 and -101 while other congeners were systematically detected. In fish and invertebrates, ∑PCBs were below the Maximum Allowable Level (125 ng.g^{-1} ww, Directive 1259/2011/CE). The highest levels of ∑PCBs in whole body (wb) were observed in common seabass (55 ± 29 ng.g^{-1} ww) and gobies (32 ± 6 ng.g^{-1} ww). The contamination profile was dominated by CB-153, CB-138 and CB-180, as classically observed in biota[4,5].

PBDEs were detected less often: the detection frequency of BDE-28, -153, -183 and -209 was in the range 5 – 22 % while that of the other congeners was higher (53 – 85 %). PBDE levels exceeded the EU Environmental Quality Standard (EQS_{biota}), set at 0.0085 pg.g^{-1} ww (Directive 2013/39/UE). The highest PBDE levels were observed in gobies (0.26 ± 0.05 ng.g^{-1} ww) and oysters (0.26 ± 0.10 ng.g^{-1} ww) while BDE-47 was the most abundant congener with a relative abundance of 43 ± 23 %.

HBCD was infrequently detected (5– 22 %) and ∑HBCD isomers was below the EQS_{biota} = 167 ng.g^{-1} ww (Directive 2013/39/UE). The highest levels were observed in copepods (36 ng.g^{-1} ww) and the contamination profile was dominated by α-HBCD and γ-HBCD with a relative abundance of 66 ± 45 % and 32 ± 42 %, respectively.

The levels of emerging FRs were much lower (median < 0.2 ng g^{-1}) and several compounds were not detected in biota. DBDPE, BTBPE BEH-TEBP, TBP-DBPE and aCl11-DDC-CO were detected in 15 – 42 % of samples. The syn- and anti- isomers of DDC-CO (Dechlorane Plus, DP), were detected in 100 and 96 % of biota samples, respectively. Another Dechlorane-related compound, DDC-Ant, exhibited a high detection frequency (75 %) and its levels were generally higher than those of DP (0.02 ± 0.05 vs 0.01 ± 0.01 ng.g^{-1} ww). The highest concentrations were observed in copepods for DDC-Ant (0.12 ± 0.18 ng.g^{-1} ww) and in sprat for DP (0.03 ± 0.02 ng.g^{-1} ww). The fractional abundance of DP isomers was calculated and f_{anti} exhibited large variations within and between species (fig. 1), in good agreement with the litterature[6].

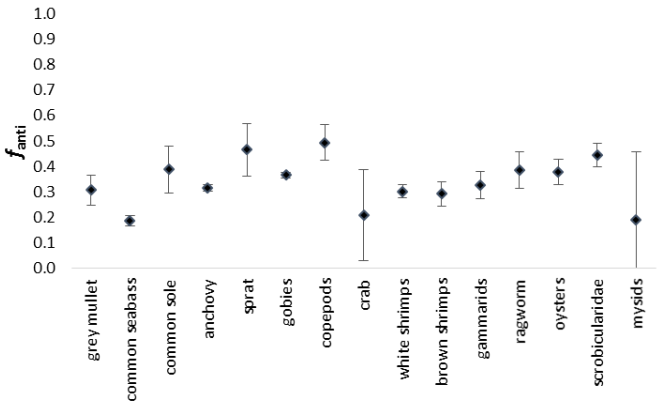

Fig. 1 Distribution of f_{anti} in aquatic biota

Trophic magnification factors

Oysters and scrobicularidae were selected as baseline organisms of the trophic web, based on both their known ecology and isotopic data (Fig. 2).

Since many left-censored values (<LOD) were observed, TMFs could only be calculated for PCBs, BDE-47, -49+71, -100, -154, and three compounds of the Dechlorane family: DDC-Ant, syn- and anti-DDC-CO (Fig. 3). TMF were expressed on both a lipid weight (lw) basis and a ww basis but more TMFs could be determined when concentrations were expressed on a ww basis. TMFs derived from the three statistical models were not significantly different but censored regression and linear regressions did not allow to calculate TMF for all the compounds listed above; thus, results obtained with the GLMM model (ww basis) were selected for further discussion. TMFs >1, indicative of biomagnification, were observed for all these compounds, except PCB-28 and -118. The highest TMF values were observed for PCB-52, PCB-101, BDE-154 and DDC-Ant.

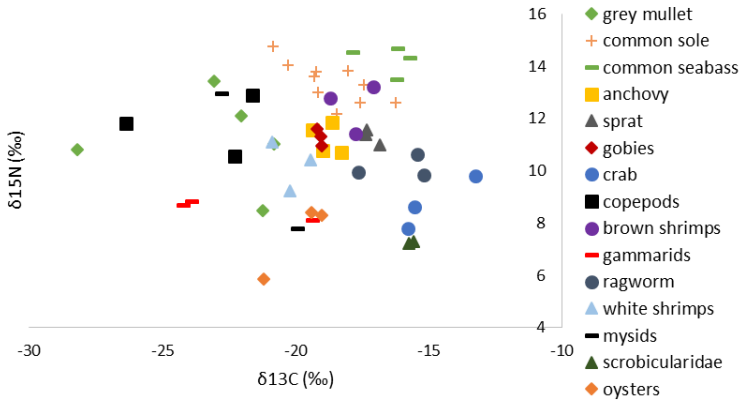

Fig. 2: Isotopic signature of fish and invertebrates

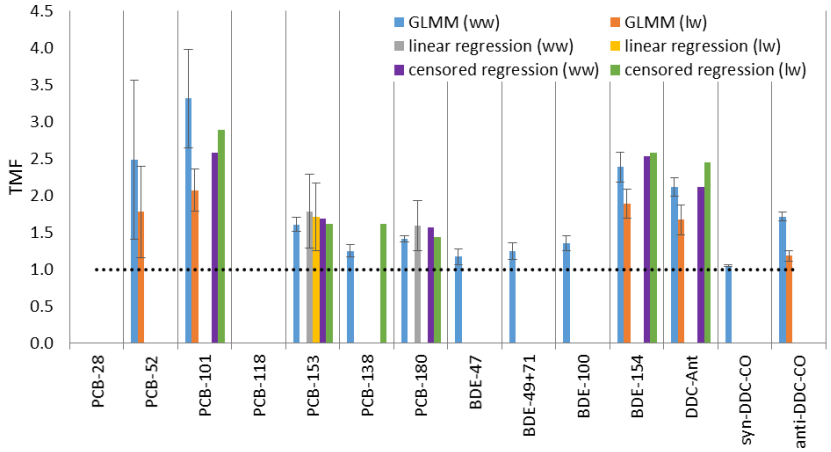

Fig. 3: TMF estimated on the basis of concentration adjusted to ww and lw with 3 models (error bars for the linear regression and GLMM models represent the 95 % confidence interval)

Acknowledgments

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