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High production volume chemicals in the most consumed seafood species in Tarragona area (Spain): Occurrence, exposure, and risk assessment

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ABSTRACT

Seafood consumption has become a potential exposure route towards high production volume chemicals (HPVs) due to the pathway of these compounds reaching the aquatic environment via industrial and domestic discharges. The present study focuses on the determination of phthalate esters (PAEs), organophosphate esters (OPEs), benzothiazoles (BTs), benzotriazoles (BTRs) and benzenesulfonamides (BSAs) in the ten most consumed fish species in Catalonia. A total of 120 commercially available seafood specimens were purchased throughout February 2019–February 2020 in three different stores (supermarket, local market, and local fishmonger) of the city of Tarragona, Spain, to cover the most typical places where seafood can be obtained. ΣOPEs, ΣBTs, ΣBSAs and ΣPAEs concentrations ranged between 5.99 and 139.45 ng g^{-1} w.w., 8.41–54.08 ng g^{-1} w.w., 8.38–304.47 ng g^{-1} w.w and 2.86–323.80 ng g^{-1} w.w., respectively. BTRs were not detected in any of the samples. PAEs and BSAs had similar contributions which combined represented nearly the 70% of detected compounds and sardine resulted as the species with the higher HPVs mean concentration. No considerable threat was posed due to the individual intake of these compounds via seafood consumption.

1. Introduction

The massive production of chemical compounds to cover the present day necessities has been the result of a rapid economic and industrial development of our society over the last century. Organisations such as the Organisation for Economic Co-operation and Development (OECD) (Organisation for economic co-operation and development, 2004) or the US Environmental Protection Agency (EPA) have listed the chemical compounds produced in more than 1000 or 500 tonnes per year, respectively, with the intention of generating useful data on these substances to provide screening information datasets (SIDS). The chemicals comprised in the list receive the name of High Production Volume chemicals (HPVs), and their prioritised study will be useful for the assessment of the exposure and risk towards both the environment and the population. HPVs constitute a diverse group of compound families including well-known compounds such as phthalate esters (PAEs), currently on the spotlight ones like organophosphate esters (OPEs) or even families yet to be further studied as benzothiazoles (BTs), benzotriazoles (BTRs) and benzenesulfonamides (BSAs). Most of these compounds are used in industrial as well as daily commodities, thus becoming generally present in our everyday life. Compounds such as OPEs or PAEs are used as plasticisers or flame retardants, mostly in food packaging, furniture, electronic devices, textiles and even toys (Maceira et al., 2020; Sakhi et al., 2014). On its part, BTs, BTRs and BSAs are usually found as corrosion inhibitors in antifreeze formulations or dishwasher detergents, as well as vulcanization accelerators in rubber, dye-synthesis precursors and even disinfectants (Herrero et al., 2014; Trabalón et al., 2017). Abrasion, dissolution and even volatilization are believed as the most common environment release mechanisms of OPEs and PAEs due to the lack of chemical bonding with the material (Wei et al., 2015). BTs, BTRs and BSAs fate mainly initiates with their release as domestic and industrial effluents with non-efficient removal at wastewater treatment plants (WWTP). All in all, HPVs release pathways coincide in their arrival to the aquatic environment, becoming a threat not only for the biodiversity and wildlife inhabiting, but also for the population ingesting seafood with possibly bioaccumulated HPVs. The fact that some of these compounds are believed to be mutagenic, carcinogenic, endocrine disruptors and even respiratory irritant and dermal sensitizers at high concentrations has led to the urge of screening and quantifying their presence in many environmental fates as well as commodities, including foodstuffs (Álvarez-Muñoz et al., 2015; Liao et al., 2018; Ye et al., 2014). In this case, seafood can be used for both

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elucidating the environmental status and potential threat that these compounds represent for the environment, while evaluating the exposure and risk for population associated to their consumption via dietary intake. Seafood includes all edible fish species from marine and freshwater environments as well as molluscs, crustaceans, and aquatic plants. Seafood consumption, as part of the Mediterranean diet, is relevant for the Spanish population. As an example, in 2021 the mean seafood consumption per capita was 22.72 kg, which represented a 13.12% of the average family budget destinated for food and beverages acquisition (Ministerio de Agricultura Pesca y Alimentación, 2022). It is therefore necessary to evaluate the possible bioaccumulation/biomagnification of HPVs in seafood to assess the risk of consumers.

In this study, samples of the ten most consumed seafood species of Tarragona, Spain, were purchased to determine nine organophosphate esters, six phthalate esters, five benzothiazoles, five benzenesulfonamides and four benzotriazoles. Based on the concentrations found in the samples, the study aims to calculate the exposure and risk for the population associated to the dietary intake of these HPVs via seafood consumption. To the best of our knowledge, this is the first monitorisation study including compounds of emerging concern such as benzothiazole and benzenesulfonamides. We believe the results obtained in the study may depict the contamination status of the seafood people is consuming along with an overview of the risk associated to different population subgroups, which may lead to future regulation of the use of some of these compounds.

2. Materials and methods

2.1. Standards and reagents

The present method compiles the determination of nine organophosphate esters (OPEs): triethyl phosphate (TEP), tributyl phosphate (TBP), tri-isobutyl phosphate (TiBP), tris (2- ethylhexyl) phosphate (TEHP), 2-ethylhexyl-diphenyl phosphate (EHDPP), triphenyl phosphate (TPP), tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCPP), tritolyl phosphate (TTP); five benzothiazoles (BTs): 1-H-benzothiazole (BTH), 2-chlorobenzothiazole (CIBT), 2-hydroxibenzothiazole (OHBT), 2-amino-1-H-benzothiazole (NH_2BT), 2-(methylthio)-benzothiazole (MeSBT); four benzotriazoles (BTRs): 1-H-benzotriazole (BTR), 4-methyl-1-H-benzotriazole (4TTR), 5-methyl-1-H-benzotriazole (5TTR), 5,6-dimethyl-1-H-benzotriazole (XTR); five benzenesulfonamides (BSAs): benzenesulfonamide (BSA), para-toluenesulfonamide (p-TSA), ortho-toluenesulfonamide (o-TSA), N-methyl-para-toluenesulfonamide (Me-p- TSA), N-ethyl-para-toluenesulfonamide (Et-p-TSA); and six phthalate esters (PAEs): diethylphthalate (DEP), dimethylphthalate (DMP), diethylhexyladipate (DEHA), di-iso-butylphthalate (DiBP), diethylhexylphthalate (DEHP), di-n-octylphthalate (DnOP). The previously listed standards were analytical grade with purity >98% and were purchased from Sigma Aldrich (St. Louis, USA). Five deuterated compounds acquired from LGC Standards (Teddington, UK) were used as internal standards: d_4-benzothiazole (d4-BT), d_4-benzotriazole (d_4-BTR), d_4-p-TSA (d_4-p-TSA), d_{27}-tributylphosphate (d_{27}-TBP) and d_4-diethylhexyl-phthalate (d_4-DEHP).

The acetonitrile and ethyl acetate used during the extraction procedure were GC grade with purity >99.9% from Scharlab (Barcelona, Spain), whereas ultrapure water was obtained from a Synergy water purification system from Millipore (Massachusetts, USA). Helium and nitrogen gas (>99.999% purity) were supplied by Carburos Metálicos (Tarragona, Spain). Salt packets of the original method to perform QuEChERS extraction, disposable syringes and PTFE filters were purchased from Scharlab. Lipifiltr push-trough cartridges were obtained from Carlo Erba (Barcelona, Spain).

2.2. Sample collection

Samples of 10 different seafood species were purchased in the supermarket, the local market and local fishmonger from Tarragona, Spain, to provide variability to cover the usual stores where local population acquire seafood. The samples were purchased every four months from February 2019 until February 2020. Seafood species included the ten most consumed seafood species from Catalonia, Spain based on the ENCAT 2003 survey (ENCAT, 2003) and included: codfish (*Gadus morhua*), shrimp (*Aristeus antennatus*), hake (*Merluccius merluccius*), sole (*Solea solea*), squid (*Loligo vulgaris*), mussel (*Mytilus galloprovincialis*), sardine (*Sardina pilchardus*), tuna (*Thunnus thynnus*), mackerel (*Scomber vincialis*) and salmon (*Salmo salar*). Lateral fillets of the fish samples were dissected and only the soft parts of the shrimp and mussel samples were kept. All samples were freeze-dried using a miVac Duo freeze-drying system from Genevac (Ipswich, UK) and then ground and homogenised. As the aim of the article was to cover the total dietary intake, samples of the different locations were mixed per species and sampling date, thus obtaining a total of 40 samples to analyse. Seafood species were also segregated upon their lipidic content. Thus, species were divided as low lipid content (cod, hake, shrimp, sole and squid) or high lipid content (sardine, tuna, mackerel, salmon, and mussel). The differentiation of lipid content was useful not only for the analysis of the samples, as the lipids may act as interferents during the extraction, but also to check the possible lipophilic character of some of the target HPVs. The moisture content was calculated as the difference between the weight prior and after lyophilisation. Once all the samples were lyophilised, composites of each of the species and each of the months were prepared (n = 40) and stored in the same conditions. All the samples were kept in glass containers and stored at −24 °C until their analysis.

2.3. Sample extraction

The samples were extracted using an adaptation of a previously described method for the determination of organophosphate esters from seafood samples (Castro et al., 2020). Briefly, 0.1g of the lyophilised sample was weighted in a 50 mL glass centrifuge tube with 10 mL of ultrapure water and 10 mL of acetonitrile. The mixture was vortex mixed for 1 min and subsequently, a QuEChERS extraction salt packet of the original method (1g of anhydrous sodium acetate + 4g of magnesium sulfate) was added to the tube and further mixed for 3 min. The tubes were later centrifugated at 4000 rpm for 5 min using a Hettich Universal 32R centrifugation system (Tuttlingen, Germany) and the acetonitrile layer (supernatant) was collected. The extract was further cleaned using a LipiFiltr push-through cartridge and evaporated to ~0.5 mL under a gentle nitrogen stream. Finally, the extracts were reconstituted with ethyl acetate to 2 mL after an internal standard spike of 50 μg L^{-1}. The extracts were then filtrated using a 0.22 μm PTFE syringe filter and analysed using GC-QqQ.

2.4. Instrumental analysis

An Agilent 8890 GC system coupled to an Agilent 7000D triple quadrupole mass spectrometer from Agilent Technologies (Palo Alto, CA, USA) was used for the analysis of the obtained extracts. The extracts were automatically injected by a PAL RSI 120 automatic injector from CTC Analytics (Zwingen, Switzerland). A total of 25 μL were injected in the system using an Agilent Mulit-Mode Inlet (MMI) in solvent vent mode. The initial temperature for the injector was 75 °C (held 0.37 min) and ramped to 325 °C (held for 5 min) at 600 °C/min. The optimised parameters for the solvent vent mode were as follows: vent flow of 120 mL/min and 5 psi for 0.37 min and purge to split vent at 60 mL/min at 2.87 min. The separation was performed using a ZB-50 capillary column (30 m × 25 mm i.d. and 0.25 μm film thickness) from Phenomenex with an oven temperature program starting at 75 °C (held for 2.87 min) and raising to 300 °C (held for 5 min) at 15 °C/min. The total run time of the analysis was of 22.87 min with a solvent delay of 6 min. Helium was used as carrier gas at a constant flow rate of 1.2 mL/min. The triple

quadrupole system operated in electron ionisation mode at 70 eV with ion source, quadrupole 1 and quadrupole 2 temperatures set at 230 °C, 150 °C and 150 °C, respectively. Agilent MassHunter Workstation (Quantitative and Qualitative Analysis) version 10.0 was used to perform the data analysis. Table S1 compiles the list of target compounds along with their retention times, quantitative and qualitative transitions, and collision energies.

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

Phthalates and organophosphates may be present in the ambient as well as in the material used for the extraction, especially if the material is made of plastic. Therefore, usage of plastic was avoided when possible and glass flacon tubes were used for the QuEChERS extraction. Even though minimizing the use of plastic, some of the compounds were still present in procedural blank extractions. Thus, two procedural blanks were included in every batch of analysed samples (10 samples per batch) to subtract the blank signal from the obtained sample signal. To ensure the quality of the determination, quality controls were included every 5 samples along with system blanks to check the suitability of the system and prevent carry-over. Concentrations in the samples were quantified depending on the lipidic content of the species using external calibration along with internal standard to correct injection variations and applying the convenient apparent recovery (low or high lipidic content). For low lipid content species, recoveries ranged between 72 and 92% for OPEs, 52–104% for PAEs, 50–105% for BTs, 70–102% for BTRs and 71–85% for BSAs, whereas the values for high lipid content species were 52–119% for OPEs, 62–132% for PAEs, 64–112% for BTs, 70–107% for BTRs and 67–84% for BSAs. Further quality parameters can be found in the supplementary material (Table S2).

2.6. Exposure and risk assessment

The presence of HPVs in seafood turns dietary intake into an alternate exposure route for these compounds to reach our organisms. Thus, exposure and risk assessment calculations are used as an effective tool to estimate the possibility of this compounds causing adverse health effects. Human exposure values (Et) were calculated using the mean wet weight concentrations found in the study along with the mean fish consumption (g day^{-1}) obtained from the ENCAT 2003 survey conducted in Catalonia, which data is segregated between fish species and gender/age (boys 10–19, girls 10–19, adult men 20–65, adult women 20–65, senior men >65, senior women >65) (Table S3). Equation (1) was used on this purpose, where E_t is the human exposure, C_f the mean consumption of the individual species *f* and $x_{t,f}$ the concentration of the individual compound *t*, for the species *f*. It was assumed that 100% of the HPVs present in the seafood were absorbed when ingested.

$$E_t = \sum_{f=1}^{p} C_f X_{t,f} \quad (1)$$

For the risk assessment, non-genotoxic and non-carcinogenic compounds were assessed using the NOAEL (*non-observed-adverse-effect-level*) approach, for which equation (2) is used. E_t, ADI_t and R_t are the dietary exposure, acceptable daily intake and risk factor for compound *t*, respectively. Acceptable daily intake values were the result of dividing the oral NOAEL values by an uncertainty factor of 100.

$$R_t = (E_t / ADI_t)*100 \quad (2)$$

As per carcinogenic compounds such as TBP and TCEP, the margin of exposure (MOEt) was calculated using equation (3), where MOEt is the margin of exposure for the compound *t*, E_t is the dietary exposure to compound *t* and BMD is the benchmark dose for which a measurable response of 5–10% range above the control is caused.

$$MOE_t = BMD_t / E_t \quad (3)$$

Calculations were performed for three different scenarios (EFSA, 2010; World Health Organization, 2011) assuming method limit of detection and quantification values for non-detected and below-LOQ compounds.

- Lower-bound scenario. Non-detected compounds concentrations are assumed as 0, while below-LOQ compounds are estimated as the LOD.
- Middle-bound scenario. Non-detected and below-LOQ compound are estimated as half the LOD and half the LOQ, respectively.
- Upper-bound scenario. Non-detected compounds are assumed as the LOD and below-LOQ compounds are estimated as the LOQ.

2.7. Statistical analysis

Principal components analysis (PCA) was used as multivariate statistical analysis to examine the possible patterns in HPVs associated to the lipidic content (low or high lipidic content). Data for the PCA construction was based in the individual concentrations of all the studied compounds for each of the analysed samples (n = 40). The statistical analyses were all performed using R (RStudio, 2022.02.3) with *FactoMineR* and *factoextra* packages.

3. Results and discussion

3.1. Occurrence of HPVs in commercial seafood

The target HPVs were divided in their respective families: OPEs, PAEs, BTs, BTRs and BSAs. One kind of each of the target HPVs (OPEs, PAEs, BTs and BSAs) was detected in all the analysed samples at the minimum, except for BTRs, which were not detected in any of the samples. Regarding the individual compounds' detection frequencies, these ranged between 8% for DEHP and 73% for BT. Among the analysed seafood species, the concentrations of ΣOPEs, ΣBTs, ΣBSAs and ΣPAEs ranged between 5.99 and 139.45 ng g^{-1} w.w. (GM: 31.99 ng g^{-1} w.w), 8.41–54.08 ng g^{-1} w.w (GM: 30.23 ng g^{-1} w.w), 8.38–304.47 ng g^{-1} w.w (GM: 56.75 ng g^{-1} w.w) and 2.86–323.80 ng g^{-1} w.w. (GM: 59.56 ng g^{-1} w.w), respectively. Thus, phthalate esters (PAEs) appeared as the group of compounds with the highest mean concentration as well as the group with the highest concentration of a single compound. Table 1 compiles the results obtained from each of the species, indicating the geometric mean, the minimum and maximum concentrations, and the detection frequency (DF%). Regarding the distribution of the detected compounds in the same group in terms of concentration, OPEs showed a trend of TTP < TiBP < TBP < EHDPP < TTP < TCPP < TCEP, with a difference of nearly an order of magnitude between the mean concentrations of TTP (1.74 ng g^{-1} w.w) and TCEP (18.04 ng g^{-1} w.w.). The presence of chlorinated organophosphate esters has been commonly reported in the literature by other authors, mainly by their lower degradation and higher persistence (Sundkvist et al., 2010). Studies on market basket total OPEs conducted in Australia for prawn, oyster and salmon (He et al., 2018) and the US for salmon, shrimp and lobster (Wang and Kannan, 2018) showed the presence of TCEP and TCPP at high detection frequencies and concentrations between 0.10 and 0.13, 0.40–1.39 ng g^{-1} w.w. and 0.06–2.16, 0.06–25.6 ng g^{-1} w.w., respectively. The same studies also reported the presence of other compounds such as TBP, TiBP, TPP and EHDPP at levels of low ng g^{-1} w.w. For BTs, the trend follows as MeSBT < NH_2BT < OHBT < BT, with the highest mean concentration being five times higher than the lowest one (3.37 ng g^{-1} w.w. for MeSBT and 15.40 ng g^{-1} w.w. for BT). Although their presence in the literature is scarce, some authors have documented the presence of benzothiazoles in seafood. Trabalón et al. (2017) reported concentrations between 6 and 82 ng g^{-1} d.w. of four benzotriazoles in seafood of common consumption (same as the present study), being BT the congener with the highest concentrations (up to 82 ng g^{-1} d.w. in squid), followed by NH_2BT, ClBT and MeSBT. Another study involving

Table 1
Mean concentrations, range and detection frequencies (%DF) of the determined HPVs in seafood (ng g^{-1} wet weight, w.w.) classified by species.

Species[a]		TBP	TiBP	TCPP	TCEP	EHDPP	TPP	TTP	BT	MeSBT	OHBT	NH_2BT	BSA	Et-p-TSA	DEP	DiBP	DEHA	DEHP	ΣOPEs	ΣBTs	ΣBSAs	ΣPAEs
Cod	mean	3.33	1.36	14.05	5.82	1.63	n.d.	8.09	34.1	n.d.	10.73	9.25	9.13	17.69	11.43	n.d.	1.22	n.d.	34.28	54.08	26.82	12.65
Gadus morhua	range	0.23 - 6.73	n.d. - 1.75	n.d. - 14.05	n.d. - 7.36	n.d. - 1.63	n.d.	n.d. - 9.55	n.d. - 72.08	n.d.	n.d. - 16.38	n.d. - 18.03	n.d. - 14.97	n.d. - 28.78	n.d. - 11.43	n.d.	n.d. - 1.22	n.d.				
	DF %	100	75	25	50	25	0	50	75	0	75	50	75	50	25	0	25	0				
Hake	mean	0.51	0.97	2.95	1.31	n.d.	n.d.	0.25	13.56	n.d.	3.52	2.3	4.77	3.61	9.03	1.31	n.d.	n.d.	5.99	19.38	8.38	10.34
Merluccius merluccius	range	n.d. - 0.89	n.d. - 0.97	n.d. - 2.95	n.d. - 1.51	n.d.	n.d.	n.d. - 0.25	n.d. - 35.90	n.d.	n.d. - 4.90	n.d. - 3.00	n.d. - 8.16	0.20 - 9.81	n.d. - 9.03	n.d. - 1.51	n.d.	n.d.				
	DF %	50	25	25	50	0	0	25	75	0	50	50	50	100	25	50	0	0				
Shrimp	mean	2.07	1.02	6.31	3.24	n.d.	0.6	3.4	27.91	n.d.	5	1.39	11.19	6.03	36.92	n.d.	1.52	10.92	16.64	34.3	17.22	49.36
Aristeus antennatus	range	n.d. - 3.33	n.d. - 1.02	n.d. - 9.61	n.d. - 4.69	n.d.	n.d. - 0.60	n.d. - 3.40	n.d. - 31.46	n.d.	n.d. - 12.01	n.d. - 1.39	n.d. - 11.19	n.d. - 11.34	n.d. - 36.92	n.d.	n.d. - 1.52	n.d. - 10.92				
	DF %	50	25	50	50	0	25	25	50	0	75	25	25	50	25	0	25	25				
Sole	mean	2.48	1.95	12.35	2.73	1.04	1.25	n.d.	1.64	1.02	38.18	2.38	19.21	6.98	15.03	0.95	3.26	8.26	21.8	43.22	26.19	27.5
Solea solea	range	n.d. - 4.29	n.d. - 3.64	n.d. - 16.41	n.d. - 4.46	n.d. - 1.04	n.d. - 1.76	n.d.	n.d. - 2.75	n.d. - 1.02	n.d. - 96.08	n.d. - 3.40	n.d. - 33.07	n.d. - 13.72	n.d. - 32.35	n.d. - 0.95	n.d. - 3.26	n.d. - 8.26				
	DF %	50	50	50	50	25	50	0	50	25	75	50	50	50	75	25	25	25				
Squid	mean	0.55	1.2	10.41	2.46	n.d.	n.d.	n.d.	30.41	6.8	3.14	5.21	4.82	7.05	n.d.	n.d.	1.03	13.75	14.62	45.56	11.87	14.78
Loligo vulgaris	range	n.d. - 1.18	n.d. - 1.53	n.d. - 18.99	n.d. - 4.71	n.d.	n.d.	n.d.	n.d. - 43.28	n.d. - 11.66	n.d. - 3.14	n.d. - 8.44	n.d. - 4.86	n.d. - 10.80	n.d.	n.d.	n.d. - 1.79	n.d. - 13.75				
	DF %	75	50	50	75	0	0	0	75	50	25	50	50	50	0	0	75	25				
Sardine	mean	1.31	4.37	10.2	n.d.	2.33	n.d.	9.46	4.9	0.87	5.17	4.15	11.57	7.58	102.07	n.d.	221.73	n.d.	27.67	15.09	19.15	323.8
Sardina pilchardus	range	n.d. - 2.4	n.d. - 4.37	n.d. - 10.2	n.d.	n.d. - 3.5	n.d.	n.d.- 9.46	1.10 - 7.00	n.d. - 1.37	n.d. - 5.17	n.d. - 4.15	n.d. - 11.57	n.d. - 7.58	n.d. - 117.5	n.d.	n.d. - 221.73	n.d.				
	DF %	50	25	25	0	50	0	25	100	50	25	25	25	25	75	0	25	0				
Tuna	mean	n.d.	1.84	n.d.	130.8	3.44	3.37	n.d.	2.65	1.74	4.86	6.88	47.85	74.33	19.43	n.d.	n.d.	n.d.	139.45	16.13	122.18	19.43
Thunnus thynnus	range	n.d.	n.d. - 3.6	n.d.	n.d. - 259.4	n.d. - 4.1	n.d. - 3.37	n.d.	n.d. - 5.1	n.d. - 1.74	n.d. - 5.3	n.d. - 7.9	n.d. - 86.2	n.d. - 148.20	n.d. - 19.50	n.d.	n.d.	n.d.				
	DF %	0	50	0	50	50	25	0	75	50	50	50	50	50	50	0	0	0				
Mackerel	mean	2.53	n.d.	2.73	5.59	2.37	n.d.	n.d.	31.59	4.62	3.74	5.82	165.71	138.76	2.86	n.d.	n.d.	n.d.	13.22	45.77	304.47	2.86
Scomber vincialis	range	n.d. - 3.4	n.d.	n.d. - 2.73	n.d.- 5.59	n.d. - 2.40	n.d.	n.d.	n.d. - 84.9	n.d. - 11.2	n.d. - 3.74	n.d. - 5.82	n.d. - 165.71	n.d. - 138.76	n.d. - 2.86	n.d.	n.d.	n.d.				
	DF %	50		25	25	50		0	75	75	25	25	25	25	25	0	0	0				
Salmon	mean	6.14	5.27	n.d.	7.59	7.94	n.d.	11.1	5.09	2.21	6.17	6.85	13.69	6.59	60.99	n.d.	n.d.	n.d.	38.04	20.32	20.28	60.99
Salmo salar	range	n.d. - 7.0	n.d. - 6.80	n.d.	n.d. - 11.20	n.d. - 11.3	n.d.	n.d. - 11.10	n.d. - 5.30	n.d. - 2.6	n.d. - 6.30	n.d. - 9.90	n.d. - 15.70	n.d. - 6.59	n.d. - 72.5	n.d.	n.d.	n.d.				
	DF %	50	50	0	50	75	0	25	75	50	50	75	75	25	75	0	0	0				

(*continued on next page*)

Table 1 (*continued*)

Species[a]		TBP	TiBP	TCPP	TCEP	EHDPP	TPP	TTP	BT	MeSBT	OHBT	NH_2BT	BSA	Et-p-TSA	DEP	DiBP	DEHA	DEHP	ΣOPEs	ΣBTs	ΣBSAs	ΣPAEs
Mussel *Mytilus galloprovincialis*	mean	1.03	1.62	n.d.	2.82	2.75	n.d.	n.d.	2.11	6.3	n.d.	n.d.	4.4	6.5	67.28	6.57	n.d.	n.d.	8.22	8.41	10.9	73.85
	range	n.d. - 1.5	n.d. - 2.5	n.d.	n.d. - 2.82	n.d. - 4.1	n.d.	n.d.	n.d. - 3.5	0.4–19.3	n.d.	n.d.	n.d. - 7.00	n.d. - 10.6	n.d. - 127.5	n.d. - 6.57	n.d.	n.d.				
	DF %	75	50	0	50	75	0	0	75	100	0	0	75	50	50	25	0	0				
All	mean	2.22	2.18	8.43	18.04	3.07	1.74	6.46	15.40	3.37	8.95	4.91	29.23	27.51	36.12	2.94	45.75	10.98	31.99	30.23	56.75	59.56
	range	n.d. - 7.0	n.d. - 6.80	n.d. - 18.99	n.d. - 259.4	n.d. - 11.3	n.d. - 3.37	n.d. - 11.10	n.d. - 84.90	n.d. - 19.3	n.d. - 96.08	n.d. - 9.90	n.d. - 165.71	n.d. - 148.20	n.d. - 117.5	n.d. - 6.57	n.d. - 221.73	n.d. - 13.75				
	DF %	55	44	25	45	35	11	15	73	40	45	40	50	48	43	10	18	8				

[a] Data shows the results of a composite mixture of each of the species containing the 4 monitoring campaigns (n = 4), while each of the monitoring campaigns contain specimens from 3 different acquisition channels (n = 3). Each of the analysis were performed in triplicate.

the determination of benzothiazoles and benzotriazoles in mollusc samples from the Bohai Sea also reported the presence of BT with a mean concentration of 595 ng g^{-1} d.w., OHBT with 20.1 ng g^{-1} d.w., MeSBT with 14.2 ng g^{-1} d.w. and NH_2BT with 0.165 ng g^{-1} d.w. (Jia et al., 2019). As it can be observed, the benzothiazoles determined in the present study are similar to the ones reported by other authors in terms of concentrations and detection frequency. Regarding the concentrations it can be observed that except for BT, which values are slightly higher, values for the other found congeners are similar. It should also be noted that the presented values are given in wet weight basis, which tends to be lower than the literature values given in dry weight. In the case of BSAs, only two compounds were detected, Et-p-TSA and BSA, with mean concentrations of 27.5 and 29.2 ng g^{-1} w.w. To date, there is no available data on the presence of these compounds in seafood species. However, literature on the presence of BSAs in water indicates the potential of waste-water treatment plants of causing bioconversion/biodegradation of sulfonamides of higher molecular weight into BSA and Et-p-TSA. Studies such as the ones carried out by Jover et al. (2009) and Herrero et al. (2013) found higher concentrations of these compounds in effluent waters when compared with the influent. This bioconversion and concentration enhancement could explain the apparition of these compounds in seafood species. Opposite to the presence of BSA and Et-p-TSA, high removal efficiency of p-TSA at WWTP explains the inexistence of this compound in the analysed samples (Richter et al., 2008). Lastly, PAEs followed a trend of DiBP < DEHP < DEP < DEHA, with DEHA mean concentration (45.8 ng g^{-1} w.w.) being 15 times higher than DiBP (2.94 ng g^{-1} w.w.). Even though literature depicts DEHP as the congener with the most detection frequency and with the highest concentrations (He et al., 2015; Hidalgo-Serrano et al., 2021; Hu et al., 2016), this fact disagrees with the PAEs distribution found in the present study. This could be directly linked to the apparition of an interference during the determination process disabling the determination of DEHP for high lipid content species. It should be noted that the punctual apparition of DEHA at high concentrations turns this compound as the one with the highest concentration, however, DEP appears as the phthalate ester with the highest detection frequency (43%). Concentration profiles for PAEs in fish are rather despair. Authors such as Gu et al. (Gu et al., 2014) reported total concentrations of Σ_5PAEs, in which DEHP was included, of 5–46.3 ng g^{-1} w.w. for fish, 3.3. – 219.3 ng g^{-1} w.w. for mollusc and 5.0–57.3 ng g^{-1} w.w. for shrimp. These values share similarities with the ones found in the present study in terms of concentrations. Table 2 compiles a summary of the concentrations of the HPV families reported in other studies. Distribution of the total HPVs concentrations in the analysed seafood samples is summarized in Fig. 1A.

In order to check possible correlations between the HPVs concentrations, a Pearson correlation test was performed. Fig. 1B shows the results of the correlations. As observed in the figure, most of the compounds show weak or non-significant correlation values. Positive correlations appear between TBP and TiBP, EHDPP and TTP, as well as between TiBP with EHDPP and TPP or TCEP with TPP. As observed, most of the compounds with positive correlation values belong to the same family. This correlation agrees with previous studies suggesting the diffusive spread of OPEs, which leads to similar profiles in different fates. A strong positive correlation is also found between BSA and Et-p-TSA, which may be explained due to a possible bioconversion of Et-p-TSA to BSA or a common higher molecular weight benzenesulfonamides to Et-p-TSA/BSA.

3.2. Comparison among seafood species

HPVs total concentrations and contributions were determined in the ten most consumed seafood species from Catalonia, Spain. The total contribution of the different compound families included in the target HPVs was evaluated among the ten seafood species. As observed in Fig. 2B, ΣPAEs and ΣBSAs represented the 65% of the total

Table 2
Comparison of HPVs concentrations reported by other studies.

Compounds	Country	Species	Detected congeners	Concentration (ng g^{-1} w.w.)	Ref.
PAEs					
	China	fish, mollusc, prawn	DMP, DEP, DBP, DEHP, DnOP	5–219.3	(Gu et al., 2014)
	China	mackerel, hairtail, bonito, catish, pomfret, gurnard, croaker, tuna, goby, herring, grey mullet,	DMP, DEP, DBP, DEHP, DnOP	2.32–1945	Hu et al. (2016)
	Italy	tuna	DEHP	9.3–13.9	Guerranti et al. (2016)
	Spain	cod, sole, mussel, squid, shrimp, hake, tuna, mackerel, sardine, salmon	DEP, DiBP, DEHP, DEHA	2.9–323.8	This study
OPEs					
	Belgium	salmon, cod, trout, plaice, sole, mackerel, tuna, herring, sardine, anchovy, halibut, monkfish eel, swordfish, perch, hake	TBP, TCEP, TCPP, TDCPP, TPP, EHDPP, TEHP	0.7–29.5	(Poma et al., 2018)
	Australia	salmon, oyster, prawn	TCEP, TCPP, TDCPP, TBP, TBOEP, TPP	0.9 - 3.5	He et al. (2018)
	US	salmon, shrimp, lobster	TMP, TEP, TPP, TBP, TiBP, TBOEP, TEHP, TCEP, TCPP, TDCPP, TPP, TMPP, EHDPP	1.5–105	Wang and Kannan (2018)
	Spain	sardine, anchovy, hake	TCEP, TPPO, TCPP, TDCPP, TPP, TBP, TBOEP, EHDPP, TEHP	1.39–73.4	Sala et al. (2022)
	Spain	cod, sole, mussel, squid, shrimp, hake, tuna, mackerel, sardine, salmon	TBP, TiBP, TCPP, TCEP, EHDPP, TPP, TTP	5.9–139.5	This study
BTs					
	Spain	cod, sole, mussel, squid, shrimp, hake, tuna, mackerel, sardine, salmon	BT, ClBT, MeSBT, NH2BT, OHBT	8–141	Trabalón et al. (2017)
	China	mollusc	BT, NH_2BT, OHBT, MeSBT, SCNMeSBT	229–13800	Jia et al. (2019)
	Taiwan	striped bass, tilapia, grouper, billfish	NH_2BT, OHBT	15.4–26.1	Chen et al. (2020)
	Spain	cod, sole, mussel, squid, shrimp, hake, tuna, mackerel, sardine, salmon	BT, ClBT, MeSBT, NH_2BT, OHBT	8.4–54.1	This study
BSAs					
	Spain	cod, sole, mussel, squid, shrimp, hake, tuna, mackerel, sardine, salmon	BSA, Et-p-TSA	8.9–304.5	This study

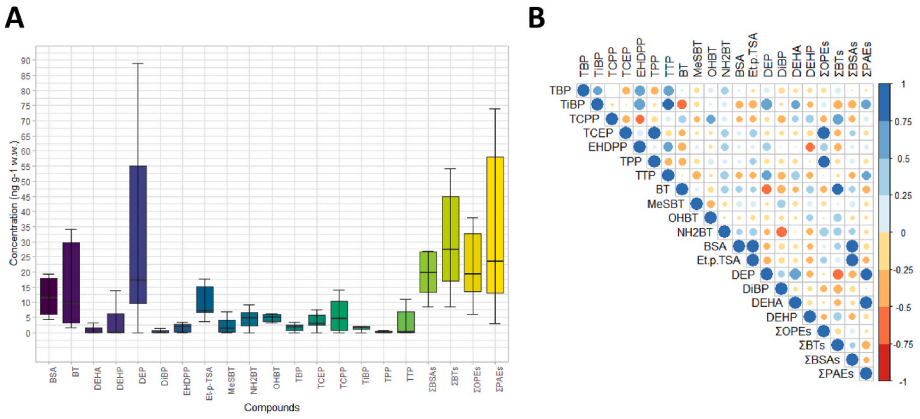

Fig. 1. A) Total concentrations of HPVs in the analysed samples. The box plot shows the 25th and 75th percentile concentrations (bottom and top edges of the box), the minimum and maximum concentrations (bottom and top whiskers) and the median concentration (line within the box). B) Pearson correlation among the concentrations of HPVs in seafood samples.

concentrations, with 34% and 31%, respectively. ΣBTs and ΣOPEs accounted the 19% and 16%. Regarding the levels of HPVs concentrations found in each of the species, the trend was hake < squid < mussel < shrimp < sole < cod < salmon < tuna < mackerel < sardine (Fig. 2C). Sardine presents the highest value with a total HPVs mean concentration of 386 ng g^{-1}, this value being nearly ten times higher than the species with the lowest concentration (hake, 44 ng g^{-1}). If compared between compound families, differences are found regarding the distribution of the HPVs among the studied species. Fig. 2A compiles the contributions of each of the HPVs families to the total concentrations of each of the species. It can be observed that species such as cod, hake, sole and squid have similar profiles, being benzenesulfonamides the group with the higher contribution, followed by OPEs/BTs with a similar contribution and finally PAEs. In contrast, for mussel, salmon, shrimp and sardine, phthalate esters represent from nearly a 50% of the contribution at the minimum (salmon and shrimp) to 70–80% (mussel and sardine). Most of these species are included in the higher lipid content subgroup except for shrimp. This trend could be explained by the known lipophilicity of phthalate esters, which would cause higher lipid content species such as sardine or salmon to bioaccumulate these compounds in greater

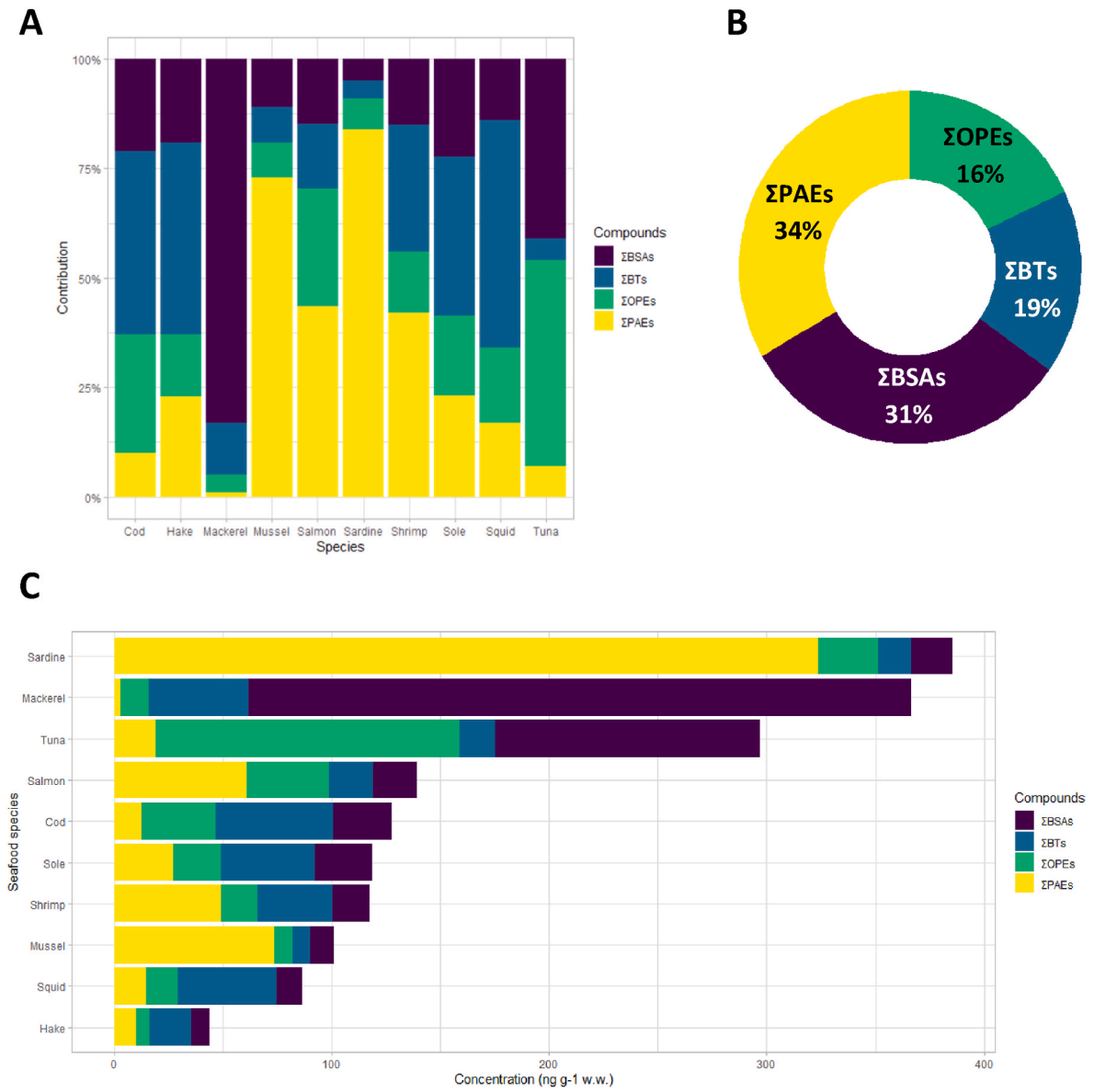

Fig. 2. A) Composition profiles of HPV families in the different seafood species. B) Total contribution (%) of the different HPV families to the total analysed samples. C) Total concentrations of HPVs in the analysed seafood species.

concentrations. Shrimp higher phthalate esters concentration levels could be possible explained by a contaminated source on its habitat or the presence of higher phthalate esters concentration in the waters were these were captured. Cross contamination coming from any of the manufacturing processes involved throughout the whole selling process should not be discarded, as these compounds can be found in packaging and other plastic made materials. Contrary to shrimp, tuna levels of PAEs are lower than expected for this high lipid content species. Despite most of the species having similar profiles, mackerel, as tuna and sardine, differs in its distribution. A larger percentage of BSAs, for both detected compounds BSA and Et-p-TSA is observed. As no data is found in the literature referred to the possible bioaccumulation or presence of these compounds in seafood or other aquatic organisms, no explanation can be given to this phenomenon. If focused on single HPVs family's contamination, hake appears as the species with the least concentration for OPEs (5.99 ng g^{-1} w.w) and BSAs (8.38 ng g^{-1} w.w.), whereas mussel and mackerel present the lowest concentrations of BTs (8.41 ng g^{-1} w.w.) and PAEs (2.86 ng g^{-1} w.w.), respectively. On the other hand, tuna, cod, mackerel, and sardine show the highest mean concentrations for OPEs (139.45 ng g^{-1} w.w.), BTs (54.08 ng g^{-1} w.w.), BSAs (304.47 ng g^{-1} w.w.) and PAEs (323.8 ng g^{-1} w.w.), respectively.

A principal component analysis was performed for all the analysed samples to check the possible correlation between the HPVs families' contributions and the species lipidic contents. Thus, samples were represented in biplots including PC1 (16.4%) vs PC2 (12.3%) and PC2 vs PC3 (10.7%) (Fig. 3A and B, respectively). Convex hulks for low lipid content species (yellow) and high lipid content species (blue) were mostly overlapped in both cases, thus indicating that no differentiation could be possibly made between low/high lipid content species when comparing their HPVs concentrations. All in all, the target HPVs comprised in the present study compile compounds with different characteristics, in which lipophilicity can be included. Compounds such as PAEs are highly fat dependant, whereas OPEs are believed to be non-lipophilic. As seen in Fig. 3C and D, contribution of PAEs to the PC1 and PC2 is minimal, except for DEP. Most of the compounds with the highest contributions are OPEs such as EHDPP and TiBP, which are believed to be non-lipophilic. Apart from OPEs, compounds such as MeSBT, BT, Et-p-TSA, NH_2BT or BSA have higher contributions than PAEs. To date,

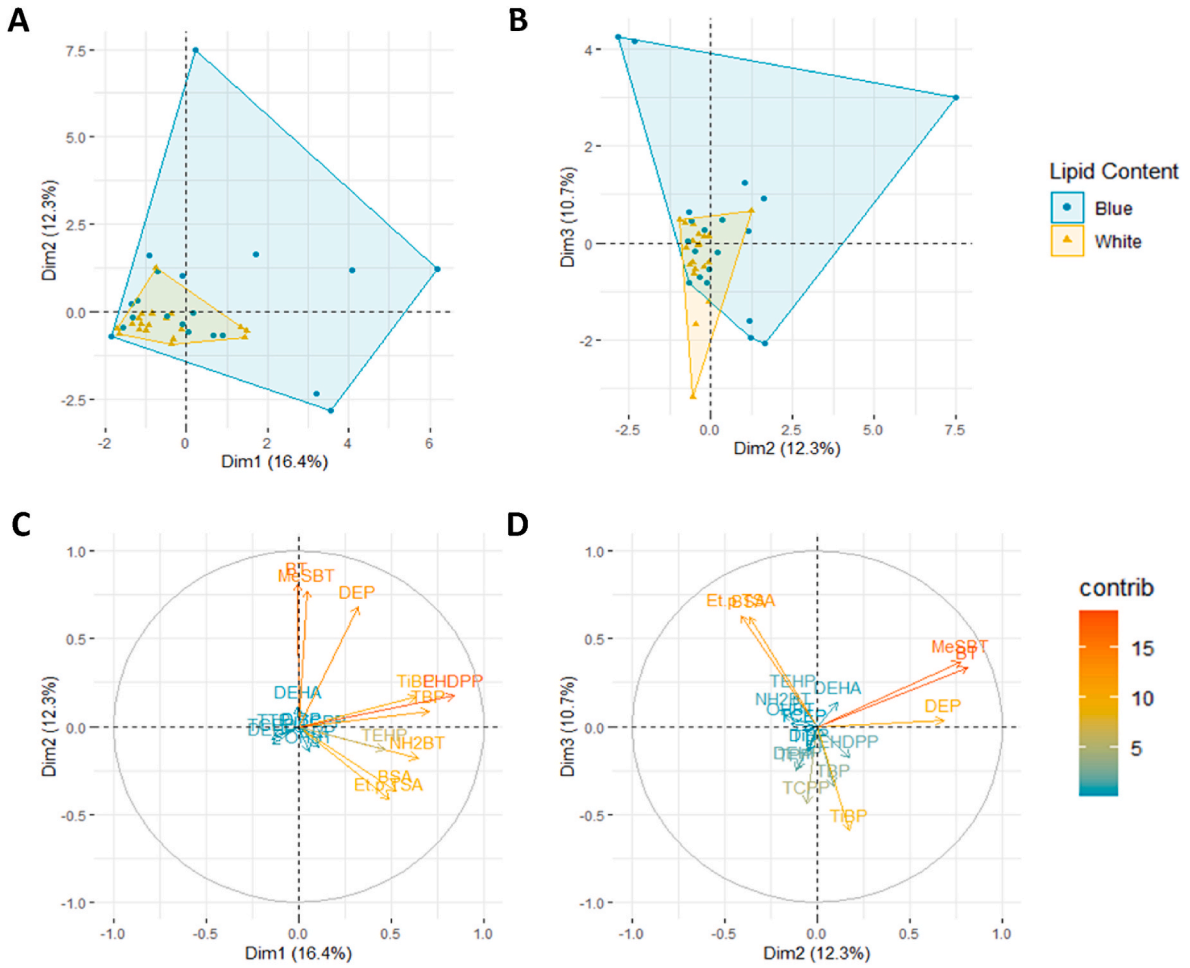

Fig. 3. Principal component analysis of HPVs in seafood. Convex hulls for low (white) and high (blue) lipidic content species delimited in different colours for PC1 vs PC2 (A) and PC2 vs PC3 (B). Subplots C and D show the congeners loadings and contributions for PC1 vs PC2 (C) and PC2 vs PC3 (D). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

there is not sufficient data regarding the lipophilicity of these compounds, however, given the obtained data, it seems that these may not be fat-dependant. Further experiments should be carried out in this topic to elucidate the relationship between BTs and BSAs and the lipid content.

3.3. Dietary intake of HPVs and risk characterization

The values regarding HPVs exposure via seafood consumption are gathered in Table 2. The table shows the results of the sum of the exposures of all the analysed species for each of the target HPV families. As no compounds were found below the method limit of quantification, the values for the lower-bound scenario correspond to the real exposure based on the concentrations determined in the present study. The exposure to the contaminants trends as follows: OPEs < BSAs < BTs < PAEs, which agree with the trend followed for the concentrations. Regarding the most affected groups, boys appear as the subgroup with the highest exposure values for 3 out of the 4 families, OPEs, BSAs and PAEs, with values of 32.8, 38.4 and 50.9 ng kg^{-1} bw day^{-1}, respectively. On the other hand, girls' subgroup tops on BTs exposure with 68.6 ng kg^{-1} bw day^{-1}. Compounds responsible of the higher contributions for each group were DEP (36.0 ng kg^{-1} bw day^{-1}), BT and OHBT (25.7 and 27.4 ng kg^{-1} bw day^{-1}), BSA (20.9 ng kg^{-1} bw day^{-1}) and TCEP (11.6 ng kg^{-1} bw day^{-1}). Sole appeared as the seafood species with the highest exposure contribution for BTs, BSAs and OPEs, whereas PAEs were more present in sardine. As seen in Table 3, values regarding the middle and higher-bound scenarios mainly differ in the incorporation of the BTRs exposure along with other non-detected compounds with no significant differences in the obtained values. In general, exposure was mostly linked to the consumption patterns of each of the subgroups, being their exposure greater when consuming species with a higher concentration of the compound. Extended data on single compounds exposure values for each of the species can be found in Table S2. Several studies have reported exposure values for some HPVs through seafood consumption. Trabalón et al. (2017) studies on the presence of benzothiazoles in seafood of common consumption reported values up to 48 ng kg^{-1} bw day^{-1} for Σ_5BTs, being MeSBT and BT the major contributors (22 and 11 ng kg^{-1} bw day^{-1}). Jia et al. (2019) exposure values for Σ_6BTs ranged between 76.1 and 121 ng kg^{-1} bw day^{-1}, with BT being responsible of approximately the 80% of the total exposure. OPEs exposure values from different seafood species from Nansha Islands (China), the western Mediterranean Sea (Spain) and the Great Lakes (Canada/USA) have been reported with values between 4.74 6.5 ng kg^{-1} bw day^{-1} (Σ_9OPEs) (Wang et al., 2022), 16.9 ng kg^{-1} bw day^{-1} (Σ_{13}OPEs) (Sala et al., 2022) and 2.56–31 ng kg^{-1} bw day^{-1} (Σ_{12}OPEs) (Choi et al., 2022), respectively. Regarding PAEs, most of the studies present in the literature focus on the exposure to DEHP, reporting values between 50 and 1390 ng kg^{-1} bw day^{-1}. As previously stated, no data on benzenesulfonamides is available to date. None of the obtained exposure values were higher than the acceptable daily intake (ADI), also known as reference dose (RfD), which ranged between $5.1x10^4 - 10^6$ ng kg^{-1} bw day^{-1} result of dividing the NOAEL values provided by the EPA by a safety factor of 100. Results

Table 3
Exposure values (ng kg^{-1} bw day^{-1}) of the different subgroups of population for three different scenarios.

		ΣOPEs	ΣBTs	ΣBSAs	ΣPAEs	ΣBTRs
BOYS	LB[a]	32.8	61.3	38.4	50.9	0.0
	MB[b]	33.0	61.4	42.3	51.2	7.9
	UB[c]	33.3	61.5	46.3	51.6	15.9
GIRLS	LB	19.1	68.6	24.1	48.4	0.0
	MB	19.4	68.8	27.7	48.8	7.3
	UB	19.6	68.9	31.4	49.2	14.6
ADULT MEN	LB	16.7	29.6	22.2	26.6	0.0
	MB	16.9	29.7	21.1	26.8	4.0
	UB	17.0	29.8	26.1	27.0	8.0
ADULT WOMEN	LB	17.5	31.6	23.4	28.9	0.0
	MB	17.7	31.7	25.5	29.1	4.3
	UB	17.8	31.8	27.6	29.3	8.5
SENIOR MEN	LB	17.2	37.4	21.2	28.0	0.0
	MB	17.4	37.5	23.7	28.3	5.0
	UB	17.6	37.6	26.2	28.5	10.0
SENIOR WOMEN	LB	14.5	34.8	28.0	33.2	0.0
	MB	14.6	34.8	30.0	33.4	4.2
	UB	14.8	34.9	32.1	33.6	8.3

[a] Lower-bound scenario.
[b] Middle-bound scenario.
[c] Upper-bound scenario.

gathered in Table 3 are several orders of magnitude lower than the ADIs, thus suggesting a low concern regarding the exposure to HPVs through seafood consumption.

The risk associated to the obtained exposure values was calculated for both non-carcinogenic and carcinogenic compounds using the equations previously described. Risk factors (Rt) values for the lower-bound scenario ranged between $1.38x10^{-5}$ – $1.12x10^{-3}$ for OPEs (TPP < TTP < TiBP < TCPP < EHDPP), $3.19x10^{-2}$ – $9.32x10^{-2}$ for BT, and $4.09x10^{-6}$ – $1.14x10^{-3}$ for PAEs (DEHP < DiBP < DEP < DEHA). As for TBP and TCEP, the margin of exposure values ranged between $4.12x10^{8}$ – $1.60x10^{9}$ and $2.33x10^{8}$ – $6.80x10^{8}$, respectively. As risk factor values are expressed as the percentage of the ADIs, the closer the obtained values are to 100, the higher is the risk. In this case, all the obtained values are found lower than 0.1%, thus posing a low risk of negative health effects related to the consumption of seafood. For TBP and TCEP, values of margin exposure are higher than the 10,000 limit set by the EFSA for genotoxic and carcinogenic compounds (Committee, 2012), thus meaning their presence in fish and their associated risk is of low concern. Fig. S4 compiles the risk factor values divided by compound families and scenarios.

4. Conclusions

The presence of several HPVs in the most consumed seafood species in Tarragona has been confirmed, being PAEs the group with the highest mean concentration followed by BSAs > BTs and > OPEs. Sardine appeared as the seafood species with the highest HPVs mean concentration, mainly due to a higher presence of PAEs, specially DEHA. To the best of our knowledge this is the first study focused on the monitoring of compounds such as BSAs and BTs. As observed in the results, their presence in seafood is higher than for compounds such as organophosphate esters, thus suggesting that their presence in aquatic environments could be even higher. No differentiation could be made between low and high lipid content species for their HPVs concentrations, thus indicating a potential lack of lipophilicity for most of the compounds. Exposure and risk related to the intake of HPVs through seafood consumption was assessed, concluding that the threat to population's health was of low concern. It must be noted that the obtained results were based on the diet of people from Tarragona consuming all the studied seafood species, which could differ from the average diet. We believe the present study enlightens the necessity of including novel or less studied HPVs families to the current field and hopefully helps to impulse new regulations on the use of some of these compounds in daily commodities.

CRediT authorship contribution statement

Óscar Castro: Conceptualization, Methodology, Validation, Investigation, Writing – original draft, Writing – review & editing. **Sílvia Borrull:** Methodology, Validation, Investigation. **Francesc Borrull:** Conceptualization, Methodology, Validation, Investigation, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Eva Pocurull:** Conceptualization, Methodology, Validation, Investigation, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Authors report financial support was provided by Spain Ministry of Science and Innovation.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fct.2023.113625.

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