



## Seafood consumption as a source of exposure to high production volume chemicals: A comparison between Catalonia and the Canary Islands

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### ABSTRACT

Seafood plays an important role in diet because of its health benefits. However, the fact that chemical compounds such as high production volume chemicals may be present in seafood means that its consumption can be a potential risk for population. To assess the occurrence of HPVs and estimate the exposure and risk associated with their consumption, specimens of the most consumed seafood species in Catalonia and the Canary Islands, Spain, were collected and analysed. Results showed higher levels of HPVs in samples from Catalonia and a prevalence of phthalate esters and benzenesulfonamides over the other target compounds in samples from both locations. Multivariate analysis showed spatial differences between the mean concentration profiles of HPVs for the samples from Catalonia and the Canary Islands. Exposures were higher for the samples from Catalonia, although the intake of HPVs via seafood was not of any real concern in either of the locations.

### 1. Introduction

The list of high production volume chemicals (HPVs) was compiled as a form of prioritizing chemicals and gathering information to produce screening information datasets (SIDS) about environmental, occupational and consumer exposure. Initially started by the OECD countries in the 1990s, the list included compounds with productions of over 1000 tonnes per year in the European Union (Organisation for economic co-operation and development, 2004). Families of compounds in the current list include many contaminants belonging to various compound groups such as legacy contaminants (e.g., some polycyclic aromatic hydrocarbons) and emerging contaminants (organophosphate flame retardants, synthetic phenolic antioxidants, benzotriazole ultraviolet stabilizers, etc.) (Castro et al., 2022b; Gimeno-Monforte et al., 2020). The present study focuses on the occurrence of four groups of HPVs: phthalate esters (PAEs), benzothiazoles (BTs), benzenesulfonamides (BSAs) and organophosphate esters (OPEs).

These families have a wide range of physicochemical properties so they are intended to be used in different applications. PAEs and some OPEs like tributyl phosphate (TBP) or triethyl phosphate (TEP) are used

as plasticizers to soften materials made of plastic, whereas other OPEs such as tris(2-chloroethyl) phosphate (TCEP) or triphenyl phosphate (TPP) are mainly used as an alternative to polybrominated diphenyl ethers (PBDEs) to prevent or delay fire ignition (Lee et al., 2019; Liu et al., 2022). These two groups are therefore found in such daily commodities as electronics, furniture, toys and even textiles (He et al., 2019; Net et al., 2015). On the other hand, benzothiazoles and benzenesulfonamides have been widely used as rubber vulcanization accelerators or anticorrosive agents in, respectively, antifreeze formulations, and disinfectants or fungicides (Herrero et al., 2014). As far as their toxicological properties are concerned, some of these compounds are endocrine disruptors (PAEs) (Ye et al., 2014), while others have been shown to be neurotoxic (OPEs) (Shi et al., 2018) and even carcinogenic (e.g. TBP, TCEP) (Greaves and Letcher, 2017). BTs have been linked with dermal sensitivity and respiratory irritation (Liao et al., 2018), whereas sulfonamide compounds such as p-TSA are considered moderately toxic (Herrero et al., 2014).

Because these compounds are not chemically bonded to materials, they can easily be released into the environment by abrasion, volatilization, and domestic/industrial discharges (Maceira et al., 2020). Their

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release into the environment has resulted in widespread occurrence in many environmental fates including air (Maceira et al., 2020; Naccarato et al., 2021), dust (Núñez et al., 2022), water (Díaz-Cruz et al., 2019; Mao et al., 2020; Peijnenburg and Struijs, 2006), biota (Barbieri et al., 2019; Castro-Jiménez and Ratola, 2020; Hidalgo-Serrano et al., 2021), and even biological samples (Li et al., 2017; Xu et al., 2019). Because effluents containing the remnants of these compounds that have not been removed by waste-water treatment plants (WWTP) (Herrero et al., 2014) enter water bodies and then reach the seas and oceans, they can be determined (Hidalgo-Serrano et al., 2019, 2022; Lian et al., 2021) and they become bioavailable to the inhabiting species (e.g. seafood). Several studies have reported the presence of HPVs in seafood samples around the world, especially PAEs and OPEs (Castro et al., 2022a). The extensive presence of these compounds in seafood samples along with the concern about how their negative health effects can impact the population has led to the need for further research. Studies that focus on determining HPVs in seafood samples mainly convey the need to provide tools to evaluate the exposure and risk associated to the dietary intake of HPVs via seafood.

The suspected toxicity of some of these compounds has prompted studies on dose-response relationships and the assessment of No-Observed-Adverse-Effect-Levels (NOAEL) values. These levels can then be used to evaluate the exposure and risk to the population. As part of risk analysis, exposure assessment is fundamental. The determination of HPVs in commercially available fish species and data concerning fish consumption enable the exposure via dietary intake of HPVs to be calculated. It is also necessary to point out that these assessment calculations take into consideration the amount of fish consumed as well as the concentrations of the compounds. Hence, different dietary patterns can lead to different exposures. Spanish gastronomy is rich and varied inside the country itself, which means that not all regions have a common diet and the seafood species consumed in each location depend on what is commercially available in that place. Being a Mediterranean coastal region, Catalonia usually offers local species from the Mediterranean Sea in its markets, and for non-local species mostly relies on imports. On the other hand, autochthonous seafood species are more widely consumed in the Canary Islands, an archipelago in the Atlantic Sea. Since HPV levels can vary according to fish species, diets with a prevalence of one species or another can lead to different exposures.

The present study aims to compare the concentrations of HPVs in the most consumed fish species from Catalonia and the Canary Islands. Once the HPVs have been determined, the exposure and risk associated with the dietary intake of these compounds will be calculated.

## 2. Materials and methods

### 2.1. Standards and reagents

Compounds from four different HPV families were included in the present study: organophosphate esters (OPEs), benzothiazoles (BTs), benzenesulfonamides (BSAs) and phthalate esters (PAEs). The organophosphate esters were tri-isobutyl phosphate (TiBP), tributyl phosphate (TBP), triethyl phosphate (TEP), 2-ethylhexyl-diphenyl phosphate (EHDPP), tris (2-ethylhexyl) phosphate (TEHP), tritoly phosphate (TTP), tris(2-chloroethyl) phosphate (TCEP), triphenyl phosphate (TPP), tris(2-chloroisopropyl) phosphate (TCPP); the benzothiazoles (BTs) were 2-amino-1-H-benzothiazole (NH<sub>2</sub>BT), 2-hydroxybenzothiazole (OHBT), 1-H-benzothiazole (BTH), 2-(methylthio)-benzothiazole (MeSBT), 2-chlorobenzothiazole (ClBT); the phthalate esters (PAEs) were dimethylphthalate (DMP), diethylhexylphthalate (DEHP), diethylphthalate (DEP), di-iso-butylphthalate (DiBP), diethylhexyladipate (DEHA) and di-n-octylphthalate (DnOP); the benzenesulfonamides (BSAs) were benzenesulfonamide (BSA), ortho-toluenesulfonamide (o-TSA), para-toluenesulfonamide (p-TSA), N-ethyl-para-toluenesulfonamide (Et-p-TSA) and N-methyl-para-toluenesulfonamide (Me-p-TSA). All the analytical standards were purchased from Sigma Aldrich (St.

Louis, USA) with a purity grade >98%. The deuterated compounds used as internal standards were acquired from LGC Standards (Teddington, UK): d<sub>4</sub>-benzothiazole (d<sub>4</sub>-BT), d<sub>27</sub>-tributylphosphate (d<sub>27</sub>-TBP), d<sub>4</sub>-diethylhexyl-phthalate (d<sub>4</sub>-DEHP) and d<sub>4</sub>-p-TSA (d<sub>4</sub>-p-TSA). Each of the internal standards was applied for the group of compounds of the same family as the deuterated compound.

Helium and nitrogen gas were supplied by Carbueros Metálicos (Tarragona, Spain) with >99.999% purity. The acetonitrile and ethyl acetate used for the extraction were GC grade from Scharlab (Barcelona, Spain) with a purity of >99.9% and the ultrapure water was obtained from a Millipore (Massachusetts, USA) Synergy water purification system. Original method salt packets for QuEChERS extraction and disposable PTFE 0.22 µm filters and syringes were purchased from Scharlab, while LipiFiltr push-through cartridges for the clean-up were purchased from Carlo Erba (Barcelona, Spain).

### 2.2. Sample collection and treatment

Samples of four different seafood species, mainly fish, were bought in two different locations. The samples of the most consumed species from Catalonia were bought in local markets from Tarragona, Spain and included: sole (*Solea solea*), cod (*Gadus morhua*), mackerel (*Scomber vinalialis*) and yellowfin tuna (*Thunnus thynnus*) specimens. The most consumed species from the Canary Islands – mackerel (*Scomber colias*), comber (*Serranus cabrilla*), common pandora (*Pagellus belloti*) and skipjack tuna (*Katsuwonus pelamis*) – were bought in local markets in Las Palmas de Gran Canaria (Canary Islands), Spain. Each of the species was bought in triplicate and subsequently mixed to create a composite sample. Once the samples had been purchased, lateral fillets were dissected and stored at –20 °C until lyophilization. Samples were then freeze-dried using a miVac Duo freeze-drying system from Genevac (Ipswich, UK). Once lyophilized, samples were ground and sifted through a 300 µm mesh to obtain a powder. The powders obtained for each of the species were kept in sealed glass containers until they were analysed.

### 2.3. QuEChERS extraction

Samples were extracted using a method developed previously. Briefly, 0.1 g of dry weight fish sample was weighed in a 50 mL glass centrifuge tube. Subsequently, 10 mL of ultrapure water and 10 mL of acetonitrile were added to the tube and the mixture was vortex mixed for 1 min. A packet of QuEChERS extraction salts containing 1 g of anhydrous sodium acetate and 4 g of magnesium sulfate was added to the tube and mixed for 3 min. The tubes were then centrifuged for 5 min at 4000 rpm using a Hettich Universal 32 R centrifuge (Tuttlingen, Germany). The upper layer (acetonitrile) was then collected and further cleaned using a LipiFiltr push-through cartridge. The extract was finally evaporated to circa 0.5 mL under a gentle nitrogen stream and reconstituted to 2 mL with ethyl acetate after incorporating the internal standard mixture at 50 µg L<sup>-1</sup>. The extracts obtained were filtered with a 0.22 µm PTFE syringe filter and kept at –20 °C until analysis with GC-QqQ.

### 2.4. Instrumental analysis

The extracts obtained from the QuEChERS extraction were analysed using an Agilent 8890 GC system coupled to an Agilent 7000D QqQ mass spectrometer from Agilent Technologies (Palo Alto, USA). The instrument included a PAL RSI 120 system from CTC Analytics (Zwingen, Switzerland) for the automatic injection of the extracts. A sample volume of 25 µL was injected into the Agilent Multi-Mode Inlet (MMI) using solvent vent mode. Solvent vent mode parameters were as follows: purge to split vent set at 60 mL/min at 2.87 min and vent flow of 120 mL/min and 5 psi for 0.37 min. The inlet ramped from 75 °C (held for 0.37 min) to 325 °C (held for 5 min) at 600 °C/min. The separation was achieved

using a ZB-50 capillary column (30 m × 25 mm i. d. And 0.25 µm film thickness) from Phenomenex with the following temperature program: initial temperature of 75 °C (held 2.87 min) raised to 300 °C (held 5 min) at 15 °C/min. The overall runtime was 22.87 min using a constant flow of 1.2 mL/min of helium as carrier gas. The mass spectrometry system operated in electron ionization mode (70 eV) at 230 °C, 150 °C and 150 °C for ion source, quadrupole 1 and quadrupole 2, respectively. Multiple reaction monitoring (MRM) mode was selected for the quantification using one quantifier transition (Q) and two qualifier transitions (q) for each of the target compounds. For qualitative and quantitative analysis, Agilent MassHunter Workstation was used in its 10.0 version.

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

The samples were quantified using internal standard calibration. Apparent recoveries were applied varying on the lipid content of the species, thus being low lipid content species: sole (*Solea solea*), cod (*Gadus morhua*), comber (*Serranus cabrilla*) and common pandora (*Pagellus belloti*), for which apparent recoveries ranged between 50 and 104% and high lipid content species: mackerel (*Scomber vinalis*), yellowfin tuna (*Thunnus thynnus*), mackerel (*Scomber colias*), and skipjack tuna (*Katsuwonus pelamis*) for which apparent recoveries ranged between 52 and 132%. Additional method quality parameters are found in Table S1. In terms of quality assurance, it should be noted that phthalate esters and some organophosphate esters may be present in plastic materials and the atmosphere, which could lead to background signals and, therefore, non-reliable determinations. To reduce this effect, plastic was avoided when possible and glass alternatives were used. Two procedural blank extractions were included in every batch of samples (10 samples per batch) to subtract the signal. Quality controls were also included in every 5 samples along with system blanks to check the system and prevent carry-over.

## 2.6. Exposure and risk assessment

Human exposure values (Et) were computed for three different scenarios. For the lower-bound scenario, compounds that were not detected or below the LOQ were estimated to be 0 and the LOD, respectively. The middle-bound scenario included half the LOD for compounds that were not detected and half the LOQ for compounds below the LOQ. Finally, the upper bound scenario was assessed with values of the LOD and the LOQ for compounds that were not detected and below the LOQ, respectively. The exposure values were calculated according to the following equation (Eq. 1):

$$E_t = \sum_{f=1}^p C_f X_{t,f} \quad \text{Eq.1}$$

where  $E_t$  was the human exposure ( $\text{ng kg}^{-1} \text{ b. w. day}^{-1}$ ),  $C_f$  the mean fish consumption of the individual fish species  $f$  and  $X_{t,f}$  the concentration found in the present study for the individual compounds  $t$  for the  $f$  species ( $\text{ng g}^{-1} \text{ w. w.}$ ). Data on fish consumption was obtained from the 2021 annual Spanish food consumption report conducted by the Spanish Ministry of Agriculture, Fisheries and Food (Ministerio de Agricultura Pesca y Alimentación, 2022). Consumption per capita of the most common fish species was segregated between the Catalonia population and the Canary Islands population. As no data is available specifically for the consumption of the autochthonous fish species from the Canary Islands, the consumption of comber, common pandora and skipjack tuna was assumed to be the same as other species with the same lipid content as the Catalan species. Hence, common pandora and comber were assumed to be the same as cod and sole, respectively, while skipjack tuna was assumed to be white tuna. Table 1 compiles the mean consumption values in  $\text{g day}^{-1}$  for the species selected.

All the calculations were performed assuming that ingested HPVs

**Table 1**

Consumption data ( $\text{g day}^{-1}$ ) of the selected fish species for each of the studied regions. Data extracted from the 2021 annual Spanish food consumption report (Ministerio de Agricultura Pesca y Alimentación, 2022).

Species	FOODX2 code	Location	
		Catalonia	Canary Islands
Sole ( <i>Solea solea</i> )	A02CB	0.63	0.78
Cod ( <i>Gadus morhua</i> )	A02BX	3.51	1.82
Mackerel ( <i>Scomber colias</i> )	A02DX	0.70	1.01
Tuna ( <i>Thunnus thynnus</i> )	A02DX	6.15	8.97

were 100% absorbed. The risk was assessed for the exposure values obtained in the three scenarios. For non-genotoxic and non-carcinogenic compounds, the NOAEL (*no-observed-adverse-effect-level*) approach was followed, for which the risk was calculated by dividing the dietary exposure (Et) previously obtained by the acceptable daily intake (ADi) multiplied by 100. At the same time, the acceptable daily intake was obtained by dividing the NOAEL value by an uncertainty factor of 100. For carcinogenic and genotoxic compounds such as TBP and TCEP, the benchmark dose (BMD) was used to calculate the margin of exposure (MOEt). In this case, the BMD that causes a response of 5–10% above the control was divided by the dietary exposure.

## 2.7. Statistical data analysis

PLS Toolbox 9.0 (Eigenvector Inc, Manson, WA, USA) for Matlab 2022a (Mathworks Inc, Natick, MA, USA) was used for data analysis. Principal component analysis (PCA) was used for exploratory data analysis. The different seafood species were classified using soft independent modelling of class analogies (SIMCA) and the  $k$ -nearest neighbors (knn) algorithm. Prior to calculating a model, data were autoscaled to take into account differences in the concentration scales of the compounds.

For the SIMCA model, the minimum number of PCs were selected that explained at least 95% of the variance for each class. In the SIMCA classification, samples were assigned to the class with the highest probability. In the knn classification,  $k$ , the number of nearest neighbors, was selected to be 1 because very few samples were available in each class. Sensitivity and specificity were the parameters used to assess the goodness of the classification (Ballabio et al., 2018).

## 3. Results and discussion

### 3.1. Occurrence of HPVs in samples from catalonia and the Canary Islands

OPEs, BSAs, PAEs and BTs were detected in all the samples from both locations. For Catalonia, BSAs were detected in 100% of the samples analysed followed by BTs (81%), OPEs (53%) and PAEs (44%). In the case of the Canary Islands, OPEs were detected in 66% of the samples closely followed by BSAs (63%), and then BTs (44%) and PAEs (31%). There are differences between the locations in terms of detection frequencies. While BSAs are frequently detected in both, OPEs are the most detected in the Canary Islands while the rate of BT detection in Catalonia is almost twice as much as it is in the Canary Islands. The frequency of PAE detection is the lowest in both locations, but slightly higher in the samples from Catalonia. Table 2 gathers the concentrations determined for each of the species of the two locations, Catalonia and the Canary Islands, their mean concentrations, range and detection frequency. In terms of concentrations, the samples from Catalonia showed the highest mean concentration for BSAs with  $94.2 \text{ ng g}^{-1} \text{ w. w.}$  (<MQL to  $166 \text{ ng g}^{-1} \text{ w. w.}$ ), then PAEs with  $83.6 \text{ ng g}^{-1} \text{ w. w.}$  (n.d. –  $290 \text{ ng g}^{-1} \text{ w. w.}$ ), OPEs with  $20.5 \text{ ng g}^{-1} \text{ w. w.}$  (n.d. –  $16.4 \text{ ng g}^{-1} \text{ w. w.}$ ) and finally BTs with  $15.4 \text{ ng g}^{-1} \text{ w. w.}$  (n.d. –  $24.3 \text{ ng g}^{-1} \text{ w. w.}$ ). For the Canary Islands samples, the highest mean concentration is also for BSAs with  $113 \text{ ng}$

**Table 2**  
Mean concentrations, range and detection frequencies (%DF) of the determined HPVs in seafood (ng g<sup>-1</sup> wet weight, w.w.) classified by species.

	Canary Islands								Catalonia							
	Common pandora	Mackerel	Skipjack tuna	Comber	TOTAL	Mean	Range	DF%	Sole	Cod	Mackerel	Yellowfin tuna	TOTAL	Mean	Range	DF%
<b><i>Benzothiazoles</i></b>																
BT	3.1	5.4	8.3	1.5	18.3	4.6	1.5–8.3	100	<MQL	24.3	4.5	1.4	30.3	10.1	<MQL - 24.3	100
OHBT	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0	6.8	1.6	3.7	4.4	16.5	4.1	1.6–6.8	100
NH2BT	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0	3.4	<MQL	5.8	2.9	12.1	4.0	<MQL - 5.8	100
MeSBT	2.2	0.5	n.d.	<MQL	2.7	1.4	n.d. - 2.2	75	1.0	n.d.	1.5	n.d.	2.6	1.3	n.d. - 1.5	50
ΣBTs	5.3	5.9	8.3	1.5	21.0	5.3	1.5–8.3	44	11.3	25.9	15.6	8.7	61.5	15.4	8.7–25.9	81
<b><i>Organophosphate esters</i></b>																
TBP	3.9	n.d.	2.1	4.6	10.6	3.5	n.d. - 4.6	75	4.3	6.7	3.4	n.d.	14.4	4.8	n.d. - 6.7	75
TiBP	0.8	n.d.	n.d.	1.7	2.5	1.2	n.d. - 1.7	50	3.6	1.7	n.d.	n.d.	5.3	2.7	n.d. - 3.6	50
TCPP	1.4	n.d.	n.d.	n.d.	1.4	1.4	n.d. - 1.4	25	16.4	14.0	2.7	n.d.	33.2	11.1	n.d. - 16.4	75
TCEP	2.2	2.3	2.1	0.4	6.9	1.7	0.4–2.3	100	1.0	7.4	n.d.	n.d.	8.36	4.18	n.d. - 7.4	50
TEHP	0.9	2.4	n.d.	<MQL	3.4	1.7	n.d. - 2.4	75	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0
EHDPP	3.1	0.3	n.d.	<MQL	3.4	1.7	n.d. - 3.1	75	1.0	1.6	2.4	4.1	9.2	2.3	1.0–4.1	100
TPP	n.d.	3.3	4.1	n.d.	7.4	3.7	n.d. - 4.1	50	1.8	n.d.	n.d.	3.4	5.1	2.6	n.d. - 3.4	50
TTP	1.4	n.d.	28.0	1.1	30.6	10.2	n.d. - 28.0	75	n.d.	6.6	n.d.	n.d.	6.6	6.6	n.d. - 6.6	25
ΣOPEs	13.6	8.3	36.2	7.9	66.0	16.5	7.9–36.2	66	28.1	38.0	8.5	7.5	82.2	20.5	7.5–38.0	53
<b><i>Benzenesulfonamides</i></b>																
BSA	242	<MQL	14	56.4	312	104	<MQL - 242	75	5.4	15.0	166	9.5	195	48.9	5.4–166	100
Et-p-TSA	n.d.	n.d.	140	<MQL	140	140	n.d. - 140	50	13.7	28.8	139	<MQL	181	60.4	<MQL - 139	100
ΣBSAs	242	n.d.	154	56.4	452	113	n.d. - 242	63	19.1	43.8	304	9.5	377	94.2	19.1–304	100
<b><i>Phthalate esters</i></b>																
DEP	n.d.	n.d.	184	n.d.	184	184	n.d. - 184	25	11.3	n.d.	n.d.	19.5	30.8	15.4	n.d. - 19.5	50
DiBP	122	20.9	1.8	n.d.	145	48.3	n.d. - 122	75	1.0	n.d.	n.d.	n.d.	1.0	1.0	n.d. - 1.0	25
DEHA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0	3.3	1.2	n.d.	n.d.	4.5	2.2	n.d. - 3.3	50
DEHP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0	8.3	n.d.	290	n.d.	298	149	n.d. - 290	50
ΣPAEs	122	20.9	185	n.d.	328	82.1	n.d. - 185	31	23.7	1.2	290	19.5	334	83.6	1.2–290	44

$\text{g}^{-1}$  w. w. (n.d. to  $242 \text{ ng g}^{-1}$  w. w.), then PAEs with  $82.1 \text{ ng g}^{-1}$  w. w. (n.d. –  $122 \text{ ng g}^{-1}$  w. w.), OPEs with  $16.5 \text{ ng g}^{-1}$  w. w. (n.d. –  $28.0 \text{ ng g}^{-1}$  w. w.) and finally BTs with  $5.3 \text{ ng g}^{-1}$  w. w. (n.d. –  $24.3 \text{ ng g}^{-1}$  w. w.). No significant differences were found in the concentrations of any of the target HPV families except for benzothiazoles, the levels of which in Catalonia ( $15.4 \text{ ng g}^{-1}$  w. w.) were significantly higher than in the Canary Islands ( $5.3 \text{ ng g}^{-1}$  w. w.) ( $p < 0.05$ ). Cod in Catalonia was the species with the highest mean concentration of OPEs and BTs ( $4.8$  and  $6.5 \text{ ng g}^{-1}$  w. w., respectively). As for BSAs and PAEs, mean concentrations were highest in mackerel from Catalonia ( $152$  and  $73 \text{ ng g}^{-1}$  w. w., respectively). The species with the highest mean concentrations of all the HPV families studied is from Catalonia. Nevertheless, skipjack tuna and common pandora, both from the Canary Islands, are the species with the second highest mean concentration for PAEs and BSAs, respectively.

Focusing on congeners, Fig. 1 displays the boxplot which shows that compounds such as  $\text{NH}_2\text{BT}$ , OHBT, DEHA and DEHP were only found in samples from Catalonia whereas TEHP was only found in the Canary Islands. Regarding the rest of the compounds, MeSBT, TPP, TTP, BSA, DiBP, Et-p-TSA and DEP were found at higher concentrations in the Canary Islands than in Catalonia, whereas BT, EHDPP, TBP, TCEP, TCPP and TiBP were higher in Catalonia. It can be observed that benzothiazoles are more frequently detected in the samples from Catalonia, thus being the cause of significant differences between the mean concentrations of BTs in the two locations.

The presence of these compounds in seafood samples has been reported by other authors. Studies such as the ones conducted by Poma et al. (2018) or Sala et al. (2022) reported the occurrence of the OPE congeners TBP, TCEP, TCPP, TEHP, EHDPP in samples of seafood from the Belgian market and different locations on the Mediterranean Sea, respectively. Both studies agree that aryl and chlorinated OPEs occur in most of the samples analysed at concentration levels between  $5.3$  –  $174$  and  $1.39$ – $73.4 \text{ ng g}^{-1}$  w. w., respectively. Phthalate esters occur in fish in a wide range of concentration levels. As they come from a variety of sources such as the aquatic environment, ingestion of microplastics and even migration from food packaging (Cheng et al., 2013; Sakhi et al., 2014), the concentrations reported for these compounds are generally different, with congeners such as DEHP and DBP usually being found (Hu et al., 2016). In the present study, phthalate esters were detected less frequently (31 and 44% in the Canary Islands and Catalonia, respectively), at concentrations between  $1.2$  and  $290 \text{ ng g}^{-1}$  w. w. DEHP is the compound with the highest concentration ( $290 \text{ ng g}^{-1}$  w. w. in Catalonia), but other compounds such as DiBP or DEP are also found at concentrations above  $100 \text{ ng g}^{-1}$  w. w. Benzothiazoles were not detected as frequently as they are in the literature. Trabalón et al. (2017) and Jia et al. (2019) reported the presence of BT, MeSBT,  $\text{NH}_2\text{BT}$  and OHBT among other congeners in fish samples from Tarragona and mollusk samples from the Bohai Sea in China, respectively. Concentration levels ranged from low  $\text{ng g}^{-1}$  ( $8$ – $88 \text{ ng g}^{-1}$  w. w.) in fish samples to up to  $13$ ,

$800 \text{ ng g}^{-1}$  w. w. in the most contaminated mollusk samples from China. In terms of the presence of BTs, the results of the present study agree with previously reported data, with levels in the low  $\text{ng g}^{-1}$  range, as expected. No data on the presence of BSAs in seafood has been reported to date. However, data on the presence of BSA and Et-p-TSA in WWTP influent and effluent waters suggest that these compounds are biomagnified by the procedures conducted at the plants (Herrero et al., 2014). Hence, these compounds are expected to be present in the aquatic environment and, therefore, in seafood. Their presence in samples from both locations suggests that these compounds are ubiquitous.

Multivariate statistical analysis was conducted using principal component analysis (PCA) to check for possible spatial-related patterns of HPVs in seafood species from both locations (Catalonia and the Canary Islands). The results of the PCA were displayed using PC1 (47.88%) vs. PC2 (39.38%) vs. PC3 (10.35%) scores. In this case, variables were reduced to the sum of the mean concentrations of each of the target HPV families ( $\Sigma\text{OPEs}$ ,  $\Sigma\text{BTs}$ ,  $\Sigma\text{PAEs}$  and  $\Sigma\text{BSAs}$ ). Fig. 2A shows the biplot (where the scores and the loadings of the PCA analysis are shown in the same plot) where a separation pattern can be observed for samples from Catalonia (Cat) and the Canary Islands (Can) along positive values of PC2 and PC3. For the sake of clarity, Figs. S2B and S2C (Supplementary Material) show the scores and loading plots to help the reader to better understand the position and the relationships of the scores and loadings in the 3D space. The relative position of the scores in Fig. 2 means that samples in Catalonia tend to higher concentrations of  $\Sigma\text{BTs}$  and  $\Sigma\text{OPEs}$

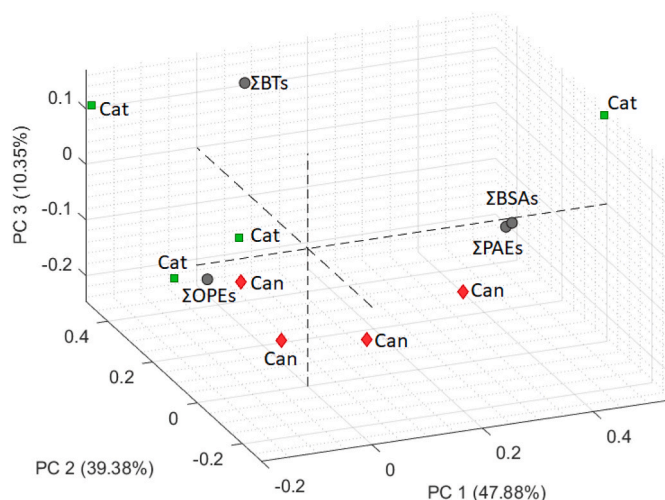


Fig. 2. Biplot showing the scores and loadings of the principal component analysis for the samples from Catalonia and the Canary Islands. Figures for scores (S2B) and loadings (S2C) can be found in the Supplementary Material (S2).

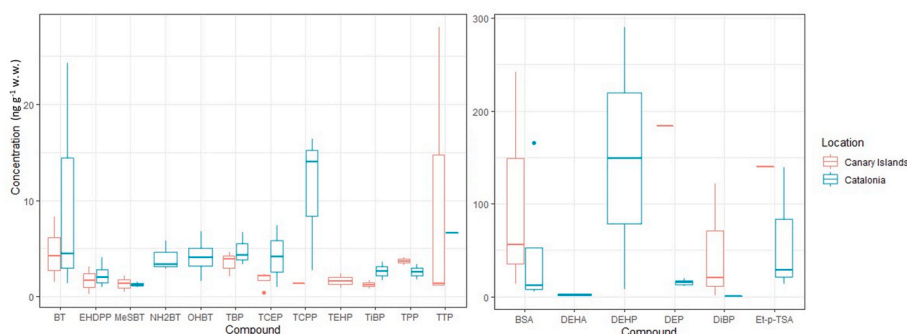


Fig. 1. Total concentrations of HPVs in the analysed samples for the Canary Islands (blue) and Catalonia (red) samples. The box plot shows the 25th and 75th percentile concentrations (bottom and top edges of the box), the maximum and minimum concentrations (bottom and top whiskers) and the median concentration (line within the box). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

and samples in the Canary Islands tend to higher concentrations of ΣPAEs and ΣBSAs, which can be seen along PC1. In this way, PC1 may discriminate HPV families that tend to give more concentration peaks (ΣPAEs and ΣBSAs) from HPV families with more homogeneous values (ΣBTs and ΣOPEs). Samples from the Canary Islands are less scattered than the samples from Catalonia, thus indicating that mean HPV concentrations are more similar in samples from the Canary Islands than in samples from Catalonia. This suggests that there may be spatial differences. These differences could also be linked to the fact that most of these species come from a common origin (the Atlantic Sea surrounding the Canary Islands), whereas the species usually consumed in Catalonia come from different origins. To check for this difference, two classification techniques (SIMCA and knn) were used to classify the samples from the two locations. Due to the small number of total samples (four samples for each class), only the results of classifying the samples used to make the models (training set) are presented. More samples need to be included in future studies for better validation with an external set of samples (test set) or internal validation using cross-validation. Considering these premises, all the specificities and sensitivities for the two classes (Catalonia and Canary Islands) were 1 for both SIMCA and knn, which indicates that the study of HPVs is a good option for differentiating between seafood samples from Catalonia and the Canary Islands.

### 3.2. Exposure and risk assessment

The seafood samples analysed in the present study are species that are commonly consumed by the population of both regions. Hence, data on the concentrations of HPVs found in the samples can be used to estimate the exposure and risk of people from both locations to HPVs in seafood via dietary intake. The calculations performed in the present study assume a 100% ingestion of the compounds present in the fish. Human exposure values (Et) for the families of compounds from the three scenarios studied are summarized in Table 3. If the upper-bound scenario values are compared, the biggest contributions from each of the families were made by TCPP (1.71 ng kg<sup>-1</sup> bw day<sup>-1</sup>) and TTP (0.82 ng kg<sup>-1</sup> bw day<sup>-1</sup>) for OPEs; BT (1.60 and 0.49 ng kg<sup>-1</sup> bw day<sup>-1</sup>) for BTs; BSA (10.02 and 8.31 ng kg<sup>-1</sup> bw day<sup>-1</sup>) for BSAs; and DEHP (15.28 ng kg<sup>-1</sup> bw day<sup>-1</sup>) and DEP (4.89 ng kg<sup>-1</sup> bw day<sup>-1</sup>) for PAEs. In Catalonia, cod was the species that made the biggest contribution of OPEs and BTs with values of 1.97 ng kg<sup>-1</sup> bw day<sup>-1</sup> and 1.38 ng kg<sup>-1</sup> bw day<sup>-1</sup>, respectively, whereas mackerel made the biggest contribution of BSAs and PAEs with values of 15.97 and 14.89 ng kg<sup>-1</sup> bw day<sup>-1</sup>, respectively. On the other hand, in the Canary Islands skipjack tuna made the biggest contributions of OPEs, PAEs and BTs (0.98, 4.94 and 0.24 ng kg<sup>-1</sup> bw day<sup>-1</sup>) and common pandora of BSAs (6.62 ng kg<sup>-1</sup> bw day<sup>-1</sup>). For both regions, BSAs represented the highest exposure levels (20.81 and 12.83 ng kg<sup>-1</sup> bw day<sup>-1</sup>), followed by PAEs (17.26 and 8.83 ng kg<sup>-1</sup> bw day<sup>-1</sup>), OPEs (4.33 and 1.82 ng kg<sup>-1</sup> bw day<sup>-1</sup>) and finally BTs (3.28 and 0.62 ng kg<sup>-1</sup> bw day<sup>-1</sup>). It must be noted that these

exposure values are the sum of the target compounds included in each of the families, so the number of congeners was different for each of the groups. All in all, exposure values for all the families of compounds are lower for the Canary Islands diet than the Catalonia diet, so people from Catalonia are more exposed to HPVs. However, none of the values obtained for either location were higher than the reference doses established by US EPA (USEPA, 2022) for compounds with values assigned. These values range from 600 to 100,000 ng kg<sup>-1</sup> bw day<sup>-1</sup> for OPEs (EHDPP and TEHP, respectively) and from 20,000 to 800,000 ng kg<sup>-1</sup> bw day<sup>-1</sup> for PAEs (DEHP and DEP, respectively). No reference doses are available for either benzothiazoles or benzenesulfonamides.

The risk factors for each of the compounds determined in the samples were calculated for the exposures in both regions. In Catalonia, the risk factors were between 3.59 × 10<sup>-7</sup>% (TEHP) and 2.26 × 10<sup>-4</sup>% (EHDPP) for OPEs; between 1.78 × 10<sup>-6</sup>% (DMP) and 1.18 × 10<sup>-4</sup>% (DnOP); 3.14 × 10<sup>-3</sup>% (BT) for BTs and between 1.24 × 10<sup>-6</sup>% (p-TSA) – 7.02 × 10<sup>-4</sup>% (o-TSA) for BSAs. For the Canary Islands, the values ranged between 5.31 × 10<sup>-7</sup>% (TEP) and 8.15 × 10<sup>-5</sup>% (TTP) for OPEs; between 5.31 × 10<sup>-8</sup>% (DEHP) – 2.18 × 10<sup>-4</sup>% (DiBP); 9.52 × 10<sup>-4</sup>% (BT) for BTs and between 6.43 × 10<sup>-7</sup>% (p-TSA) – 3.64 × 10<sup>-4</sup>% (o-TSA) for BSAs. Fig. 3 compiles the risk factors for each of the HPV families for both locations. It can be observed that Catalan overall risk is double that

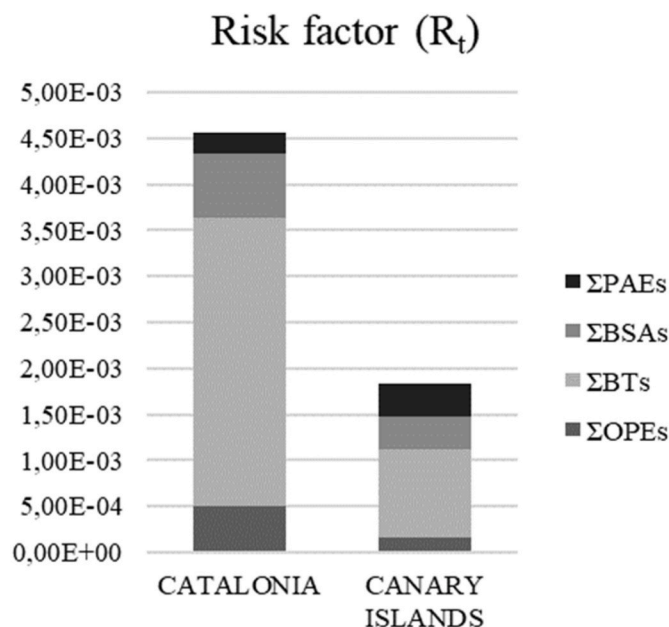


Fig. 3. Compiled risk factors for all the compounds with available risk values from both locations.

Table 3

Estimated exposure values (ng kg<sup>-1</sup> bw day<sup>-1</sup>) for Catalonia and Canary Island seafood species in three different scenarios: LB (lower-bound scenario), MB (middle-bound scenario) and UB (upper-bound scenario).

Region	Species	ΣOPEs			ΣBTs			ΣBSAs			ΣPAEs		
		LB	MB	UB	LB	MB	UB	LB	MB	UB	LB	MB	UB
Catalonia	Sole	1.44	1.45	1.46	0.60	0.61	0.64	0.98	1.16	1.34	1.22	1.23	1.24
	Cod	1.95	1.96	1.97	1.34	1.35	1.38	2.24	2.43	2.61	0.06	0.08	0.11
	Mackerel	0.43	0.45	0.47	0.80	0.81	0.81	15.60	15.78	15.97	14.85	14.87	14.89
	Yellowfin tuna	0.38	0.41	0.43	0.45	0.45	0.45	0.49	0.69	0.89	1.00	1.02	1.04
	TOTAL	4.21	4.27	4.33	3.18	3.22	3.28	19.31	20.06	20.81	17.12	17.19	17.27
Canary Islands	Common pandora	0.36	0.36	0.36	0.14	0.15	0.15	6.42	6.52	6.62	3.25	3.26	3.27
	Mackerel	0.22	0.23	0.24	0.16	0.16	0.17	0.00	0.10	0.21	0.55	0.56	0.57
	Skipjack tuna	0.96	0.97	0.98	0.22	0.23	0.24	4.08	4.18	4.27	4.92	4.93	4.94
	Comber	0.22	0.22	0.23	0.04	0.05	0.06	1.50	1.60	1.70	0.02	0.02	0.04
	TOTAL	1.76	1.78	1.81	0.56	0.59	0.62	12.01	12.40	12.80	8.74	8.78	8.83

of the Canary Islands. As risk factors are expressed as a percentage of the acceptable daily intake, values close to 100% are believed to be of extreme concern for the health of a population, whereas as the percentage decreases, so does the risk. As the values found in the present study are several orders of magnitude below 100%, the concern about the risk caused by consuming these compounds via seafood is low. For the carcinogenic compounds with an available BMDL value, TCEP and TBP, the estimated values of the margin of exposure (MOE) were  $1.08 \times 10^7$  and  $1.57 \times 10^7$  for Catalonia and  $2.83 \times 10^7$  and  $3.77 \times 10^7$  for the Canary Islands, respectively. These values are two orders of magnitude above the value set by EFSA for which MOE values equal to or higher than 10,000 are considered of little concern from a public health point of view (Committee, 2012). Therefore, there is little risk associated with the intake of TBP and TCEP via seafood from both locations.

All in all, no risk is associated with the intake of either non-carcinogenic or carcinogenic compounds via seafood from any of the studied diets.

#### 4. Conclusions

The presence of several HPV chemicals has been successfully proved in seafood samples from both Catalonia and the Canary Islands. Benzenesulfonamides were the group of compounds with the highest detection frequency (100%) and mean concentration in both locations ( $113 \text{ ng g}^{-1} \text{ w. w.}$  for the Canary Islands and  $94.2 \text{ ng g}^{-1} \text{ w. w.}$  for Catalonia), whereas PAEs, even though the detection frequency was low, were found to be the HPV family with the second highest mean concentration ( $82.1$  and  $83.6 \text{ ng g}^{-1} \text{ w. w.}$ , respectively). Samples from both Catalonia and the Canary Islands showed HPV profiles with the highest contributions from BSAs and PAEs, and the lowest from BTs and OPEs. Species from Catalonia (cod and mackerel) had the highest total concentrations of all the families studied. Significant differences between the individual mean concentrations of the target families in the two locations were found only for BTs, for which concentrations were higher in Catalonia than in the Canary Islands. Using multivariate analysis and classification techniques, samples from the two locations were successfully differentiated on the basis of their HPV concentration profiles. In terms of exposure and risk, none of the samples from Catalonia or the Canary Islands posed a high level of concern for the intake of HPVs via seafood.

#### CRedit authorship contribution statement

**Óscar Castro:** Conceptualization, Methodology, Validation, Investigation, Formal analysis, Writing – original draft, Writing – review & editing. **Silvia Borrull:** Methodology, Validation, Investigation. **Jordi Riú:** Methodology, Validation, Investigation, Formal analysis, Writing – original draft, Writing – review & editing. **Sandra Gimeno-Monforte:** Methodology, Resources, Writing – review & editing. **Sarah Montesdeoca-Esponda:** Methodology, Resources, Writing – review & editing. **Zoraida Sosa-Ferrera:** Methodology, Resources, Writing – review & editing. **Jose Juan Santana-Rodríguez:** Methodology, Resources, Writing – review & editing. **Eva Pocurull:** Conceptualization, Methodology, Validation, Investigation, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Francesc Borrull:** 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.2023.113729>.

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