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Comparison of the presence of high production volume chemicals in farmed and wild fish highly consumed in catalonia and their risk assessment

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HIGHLIGHTS

- A wide range of concentrations of HPVCs was found in the fish species.
- No significant differences in HPVCs were found between wild and farmed fish.
- There is no risk associated with the intake of these contaminants.

GRAPHICAL ABSTRACT

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ABSTRACT

The decline in fish populations and the depletion of marine resources have sparked concerns about sustainable fish production, driving the innovation of new aquaculture methods. While some argue that wild fish are healthier than farmed fish due to less exposure to contaminants and pathogens, wild fish can accumulate contaminants from more contaminated water sources. The slower growth of wild fish and their longer exposure to the environment may contribute to higher pollutant levels in fish tissues. In this study, we focus on 25 contaminants considered as high production volume chemicals (HPVCs), such as organophosphate esters (OPEs), benzothiazoles (BTs), benzosulfonamides (BSAs) and phthalates (PAEs). The compounds were extracted from the edible part of the fish using the QuEChERS method and analysed by gas chromatography-tandem mass spectrometry.

A total of 74 samples were analysed from three of the most commonly consumed species in Catalonia, Spain (turbot, sea bass and sea bream). Two samples of each species were collected each month, one form farmed and one from wild origin. In general, the compounds were found in all the samples in a wide concentrations range, although no significant differences were observed between the mean concentration of wild and farmed samples. Although similar mean concentrations for the OPEs, BTs and BSAs were found between farmed and wild origin samples, PAEs were more frequently detected in farmed samples. Di-*n*-octyl phthalate and diethyl phthalate showed the highest concentrations in all fish samples, with values up to 19505 and 17605 ng g^{-1} (d.w.), in sea bass and sea bream, respectively. Di-(2-ethylexyl)-adipate proved to be the most relevant carcinogenic compound, with no associated health risk. Despite the detection of the studied HPVCs, no health risk was associated with the consumption of these three fish species.

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1. Introduction

Currently, chemical compounds are produced in large quantities to cover the needs of our developed society. The Organization for Economic Co-operation and Development (OECD) has compiled a list of chemicals that are produced at levels exceeding 1000 tonnes per year in at least one member country (OECD, 2004). They are well-known as high production volume chemicals (HPVCs) and comprise an extensive number of families such as phthalate esters (PAEs) and organophosphate esters (OPEs), as well as other families less studied such as benzothiazoles (BTs) and benzosulfonamides (BSAs), among others. Most of these compounds are present in our everyday life due to their use in industry and daily products. For instance, PAEs and OPEs are mainly used as plasticizers in toys, furniture and textiles (Castro et al., 2020; Sambolino et al., 2022) while BTs and BSAs are used as corrosion inhibitors in detergents or as vulcanization accelerators (Wang et al., 2016). After their industrial or domestic use, they are usually release to wastewater being non-efficiently removed in the water treatment plants. Consequently, they enter the aquatic system, posing a threat not only to fish but also to the population consuming this type of food. The fact that some of the listed HPVCs are considered endocrine disruptors, mutagenic and carcinogenic by long-term exposure, it has urged the need not only of knowing their presence in environmental matrices such as fish but also assess the potential human health risk due to the exposure to these compounds through diet (Castro et al., 2023a; Jia et al., 2019; Poma et al., 2018; Sala et al., 2022).

Although fish is an important source of nutrients for humans worldwide (FAO, 2020), the ever-increasing human population and thus increased demand on fish consumption have dramatically declined the wild fish stocks (Tomić et al., 2017). As a result, fish farming practices are increasing rapidly (Lundebye et al., 2017). Wild fish, which move freely in the sea and estuaries, are exposed to their environment for a longer time because they can be older, as they are not collected at a young age like in fish farms. (Henríquez-Hernández et al., 2017; Nácher-Mestre et al., 2010). In contrast, farmed fish are confined to a quality-controlled basin or cage (Zafeiraki et al., 2019). Consequently, wild fish may be more contaminated than farmed fish (Kalantzi et al., 2013; López-Mas et al., 2021; Simukoko et al., 2023). However, fish farms located along the coastline frequently replace pond water by fresh seawater, which could be contaminated with HPVCs (Mwakalapa et al., 2019). Thus, wild and farmed fish need to be analysed in order to know the presence of HPVCs.

Although PAEs and OPEs are widely studied in fish matrices, none of the studies focus on comparing wild and farmed fish samples. For example, Sambolino et al. (2022) reported a maximum concentration of 44 ng g^{-1} (w.w.) for di-(2-ethylhexyl)-phthalate (DEHP) and 10 ng g^{-1} (w.w.) for isobutyl phthalate (DiBP) in wild mackerel purchased from Tenerife, Spain. When Cheng et al. (2013) analysed fish from Hong Kong's market (with no information about the fish source), they found that the concentrations of PAEs ranged from 2 to 425 ng g^{-1} (w.w.), with DEHP having the highest concentration. OPEs have also been studied by several research groups (Castro et al., 2020; Liu et al., 2019; Pantelaki and Voutsa, 2020), reporting levels up to 2321 ng g^{-1} (w.w.) in fish samples from the Pearl River Delta, South China (Liu et al., 2019). The few studies on BTs and BSAs in wild fish correspond to previous research of the group. Trabalón et al. (2017) showed the presence of benzothiazole (BT) and 2-(methylthio) benzothiazole (MeSBT) in squid at levels up to 82 ng g^{-1} (d.w.).

Nevertheless, some studies have focused on comparing the concentrations of other families of contaminants in wild and farmed species. While concentrations of organohalogenated contaminants were comparable in wild and farmed cod and saithe, the same wild species showed 67% higher levels of perfluorooctane sulfonates than farmed ones (Bustnes et al., 2010). In contrast, farmed salmon showed higher concentrations of polybrominated diphenyl ethers than the wild one, probably due to its diet rich in fish oils and small pelagic species (Hites et al., 2004).

Because of the complexity of fish samples and the low levels at which HPVCs are present, reliable analytical methods are needed (Hassan and Farahani, 2011). Although few methods have been developed to determine the mentioned HPVC families in fish samples, most of them are based on the use of gas chromatography-mass spectrometry (Castro et al., 2020; Kalachova et al., 2013). Many techniques have been used for the extraction step, including solid-liquid extraction (SLE) (Qu et al., 2017), ultrasound assisted extraction (USAE) (Panio et al., 2020), pressurized liquid extraction (PLE) (Vallecillos et al., 2015) and Quick, Easy, Cheap, Effective, Rugged & Safe extraction method (QuEChERS) (Castro et al., 2020). However, a cleaning step after the extraction is mandatory due to the complexity of the matrix, being solid-phase extraction (SPE) the most common strategy (Petersen et al., 2011). In some studies solid-phase microextraction (SPME) (Panio et al., 2020) has been used for volatile HPVCs to avoid the presence of lipids and selectively extract the analytes. Currently, new commercially available LipiFiltr® cartridges from United Chemical Technologies (UTC) have provided an excellent level of cleanliness by removing most lipids, with good recoveries and easy handling thanks to their syringe inlet cartridge design (Castro et al., 2020).

All in all, there is a lack of information of the presence of HPVC in fish, mainly for BT and BSA families. And it is also of interest for both the scientific community and society, to know whether there is a human health risk by exposure to HPVCs through fish ingestion. Thus, in this study, three different species of wild-caught and farmed fish – sea bream (*Sparus aurata*), sea bass (*Dicentrarchus labrax*), and turbot (*Scophthalmus maximus*) collected from central market of the city of Tarragona – were analysed to compare the presence of twenty-five HPVCs from four families (PAEs, OPEs, BTs, BSAs) and to assess the human health risk. For the analyses, a previously developed method based on QuEChERS extraction followed by gas chromatography-tandem mass spectrometry was used (Castro et al., 2023b).

2. Materials and methods

2.1. Chemicals and reagents

The HPVCs selected were as follows: nine organophosphate esters (OPEs): triphenyl phosphate (TPP), triethyl phosphate (TEP), tris (2-ethylhexyl)-phosphate (TEHP), 2-ethylhexyl-diphenyl-phosphate (EHDPP), tri-iso-butyl phosphate (TiBP), tris (2-chloroethyl)-phosphate (TCEP), tributyl phosphate (TBP), tris (2-chloroisopropyl) phosphate (TCPP) and tritolyl phosphate (TTP); five benzothiazoles (BTs): benzothiazole (BT), 2-aminobenzothiazole (NH2BT), 2-(methylthio)-benzothiazole (MeSBT), 2-hydroxybenzothiazole (OHBT) and 5-chloro-1-benzothiazole (ClBT); five benzosulfonamides (BSAs): benzosulfonamide (BSA), *ortho*-toluenesulfonamide (*o*-TSA), N-methyl-*para*-toluenesulfonamide (Me-*p*-TSA), N-ethyl-*para*-toluenesulfonamide (Et-*p*-TSA) and *para*-toluenesulfonamide (*p*-TSA); six phthalate esters (PAEs): dimethyl phthalate (DMP), diethyl phthalate (DEP), isobutyl phthalate (DiBP), di-(2-ethylexyl)-adipate (DEHA), di-(2-ethylhexyl)-phthalate (DEHP) and di-*n*-octyl phthalate (DnOP). Deuterated tributyl phosphate (TBP-d27), deuterated benzothiazole (BT-d27), deuterated *ortho*-toluenesulfonamide (TSA-p-d4) and deuterated di-(2-ethylhexyl) phthalate (DEHP-d4) were used as internal standards for OPEs, BTs, BSAs and PAEs, respectively. All standards were purchased from Sigma Aldrich (St. Louis, USA).

Individual standard solutions at 100 mg L^{-1} and a working mixture solution at 1 mg L^{-1} were prepared in ethyl acetate and preserved at -5°C.

During the study, acetone, ethyl acetate and acetonitrile with a purity of > 99.9% from JT Baker (Deventer, The Netherlands) were used. Ultrapure water obtained from a Synergy purification system from Millipore (Massachusetts, USA) was also used. A QuEChERS extraction kit (Original Sachets) provided by Scharlab S.L (Barcelona, Spain) was

used for the extraction procedure. LipiFiltr® extraction filters were acquired from Carlo Erba (Barcelona, Spain). Helium gas with a purity of 99.999% was used for the gas chromatography system and nitrogen for the MS system, and were supplied by Carburos Metálicos (Barcelona, Spain).

2.2. Sampling and sample preparation

Samples of sea bream, sea bass and turbot (were purchased in the local market of the city of Tarragona (Spain) on a monthly basis over the course of one year, resulting in a total of seventy-four samples. We chose these species because they represent one of the most consumed fish for the population of Spain and they are easily found in the market from both sources, wild and farmed, during the sampling period. Each month, two specimens of each species were bought, one of wild origin, and the other from farm origin, both sourced from the same market stall.

Although fish shop staff could not always provide the information about the origin of the specimens, most of the wild ones came from the Mediterranean Sea while most of the farmed ones came from both the Mediterranean Sea (specially for sea bream and sea bass) and the Atlantic Ocean (specially for turbot). Prior to analysis, the individual weight, length and water content of the fish was measured, these data are given in Table S1. All three species are considered to be low in lipid content as they have less than 5 g of lipids per 100 g of fish. Turbot has a typical value of 3.6 g/100 g, sea bass 1.3 g/100 g and sea bream 1.0 g/100 g (Ministry of Agriculture Fisheries and Food, 2021).

The samples were dissected by separating all the lateral side and then frozen at −17°C. The frozen samples were then lyophilized using a miVac Duo system from Genevac (Ipswich, United Kingdom). The percentage of water loss was calculated by weighing the samples before and after they were lyophilized. Then, the samples were finely powdered and sieved through 500 μm sieve to achieve a small, uniformly homogenized particle size. The sample preparation method was carried out in the same way as in previous studies (Castro et al., 2020; Trabalón et al., 2015).

2.3. Sample extraction

The procedure employed for sample extraction of these compounds followed the method described by Castro et al. (2020). Briefly, 0.1 g of freeze-dried fish sample was introduced to a 50 mL centrifuge tube. Then, 10 mL of acetonitrile and 10 mL of ultrapure water were incorporated and vortexed for 1 min. QuEChERS salts (Original method) comprising 4 g of magnesium sulphate and 1 g of sodium chloride were then included and vortexed for 3 min. The tube was directly placed into the Hettich Universal 32R centrifuge (Tuttlingen, Germany) at 4000 rpm for 5 min. Using a pipette, the supernatant was removed and passed through to a syringe connected to a LipiFiltr® cartridge. The resulting extract was collected in a 20 mL vial and evaporated under a stream of nitrogen to approximately one drop. Then, 100 μL of 1 mg L^{-1} mixture solution of internal standards were introduced to provide a final concentration of 50 μg L^{-1}, and the content was transferred to a 2 mL flask. After transfer to the flask, it was filtered through a 0.22 μm PTFE filter (Sharlab) and the volume made up to 2 mL with ethyl acetate. In all steps, plastic materials were avoided as much as possible to prevent interferences mainly of phthalates.

2.4. Gas chromatography-mass spectrometry

The chromatographic method was based on a previous one by Castro et al. (2020). Analyses were carried out using an Agilent 7890A GC system, coupled with a triple quadrupole mass spectrometer (Agilent Technologies, Palo Alto, CA, USA). Chromatographic separation of the target compounds was achieved using a ZB-50 column (30 m × 0.25 mm i.d. x 0.25 μm film thickness) from Phenomenex (Torrance, CA, USA). The oven temperature gradient utilized was as follow: initially set at 75°C (then held for 2.87 min) and then ramped up to 300°C at 15 °C/min (held for 8 min). Helium was used as a carrier gas, maintained at a constant flow rate of 1.2 mL/min. The injection volume was 25 μL and an Agilent multimode input MMI (high volume injector) was employed in solvent ventilation mode, beginning at an initial temperature of 75°C (for 0.37 min) and then up to 325°C at 600 °C/min (for 5 min). Total analysis time was 25.87 min with a solvent delay of 3 min. Triple quadrupole mass spectrometer operated in electron ionization mode at 70 eV with an ionization source and quadrupoles 1 and 2 at temperature of 280°C, 150°C and 150°C, respectively.

Multiple reaction monitoring (MRM) mode was used for quantification using one quantifier transition (Q) and two qualifying transitions (q) for the confirmation of each compound. For confirmation purposes, retention time and the ratio between transitions were taken into account. The study employed the GC acquisition program Mass Hunter for software usage. The main MS/MS parameters are shown in Table S2.

2.5. Dietary exposure and risk characterization

The assessment of human dietary exposure (E_t) to chemical *t* involved a calculation that linked the consumption patterns of various fish species, as detailed in Table S3 (Spanish Government and Ministry of Agriculture, Fisheries and Food, 2021) with the concentrations of contaminants associated with each species. The exposure values were calculated using Equation (1):

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

where C_f represents the average fish consumption for each species f (g kg bw^{-1} day^{-1}), and $X_{t,f}$ represents the mean wet weight concentration of each contaminant for each species f (ng g^{-1}). The sum of these contributions from each species provides information on human exposure for each contaminant *t*. Two exposure scenarios – low (based on geometric mean) and high (95th percentile) – were simulated. The concentrations of non-detected or non-quantified compounds were considered as half the method detection limit or method quantification limit, respectively.

For risk assessment, the calculations suggested by the European Food Safety Authority (Committee, 2012) and the Environmental Protection Agency (EPA, 2022) were performed. For non-carcinogenic compounds, the non-observed-adverse-effect-level (NOAEL) approach was used to calculate the risk factor according to Equation (2):

$$R_t = \left(\frac{E_t}{ADI_t} \right) * 100 \quad (2)$$

where R_t is the risk factor, E_t is the dietary exposure of the chemical *t* (ng kg^{-1} bw day^{-1}) and ADI_t is the acceptable daily intake associated with chemical *t* (ng g^{-1} bw day^{-1}). Acceptable daily intake values were obtained by dividing the NOAEL of each compound by an uncertainty factor of 100. A value of R_t below 1 means that not risk is associated with the ingestion of the fish containing these contaminants at the concentrations found.

For carcinogenic compounds, risk was assessed using the margin of exposure according to Equation (3):

$$MOE_t = \frac{BMD_t}{E_t} \quad (3)$$

where, MOE_t is the margin of exposure of compound *t*, the benchmark dose (BMD_t) is the reference dose (estimated as the dose that elicits an average response in a 5–10% range above control) for compound *t* (ng g^{-1} bw day^{-1}), and E_t is the dietary exposure of compound *t* (ng g^{-1} bw day^{-1}). According to EFSA (Committee, 2012), MOE_t values higher than $1{\cdot}10^4$ are considered to be of low concern for carcinogenic effects.

Table 1
Range of concentrations (ng g^{-1} d.w.), detection frequencies (%DF) and the total average of the concentrations (ng g^{-1} d.w.) for each compound in wild and farmed turbot, sea bass and sea bream samples.

Compounds	Turbot						Sea bass						Sea bream					
	Farm			wild			Farm			wild			Farm			wild		
	range	%DF	average	range	%DF	average	range	%DF	average	range	%DF	average	range	%DF	average	range	%DF	average
Benzothiazole																		
BT	n.d-30	8	2.5	n.d-83	9	7.5	n.d-40	8	3.3	n.d-21	8	1.8	n.d-61	15	7.7	n.d-33	25	5.8
ClBT	n.d	0	n.d	n.d	0	n.d	n.d	0	n.d	n.d	0	n.d	n.d-8	15	0.7	n.d-1	17	0.1
MeSBT	n-*d*-14	42	3.7	n.d-9	45	3.1	n.d-11	33	2.6	n.d-11	25	2.1	n.d-9	46	1.7	n.d-12	50	2.7
OHBT	n.d-40	33	11.7	n.d-41	36	14.0	n.d-38	17	6.0	n.d-234	25	25.9	n.d-53	46	17.3	n.d-56	25	10.5
NH2BT	n.d-74	33	13.9	n.d-46	27	10.6	n.d-17	42	6.1	n.d-127	42	15.8	n.d-21	38	6.1	n.d-37	33	7.2
Total average	30.3			60.8			14.5			19.7			14.7			14.9		
Benzosulfonamide																		
BSA	n.d-77	50	8.0	n.d-80	27	8.5	n.d-13	42	1.9	n.d-286	42	25.4	n.d-310	54	40.3	n.d-144	25	13.7
o-TSA	n.d-8200	75	3440	n.d-8706	64	1718	n.d-3052	75	1007	n.d-1124	83	528	n.d-4048	92	931	n.d-5472	75	1145
Me-*p*-TSA	n.d-170	92	37.8	n.d-53	45	14.3	n.d-112	83	31.5	n.d-849	75	139	n.d-3140	54	268	n.d-154	67	45.7
p-TSA	n.d-111	58	27.5	n.d-138	55	21.8	n.d-87	42	17.2	n.d-471	58	71.1	n.d-876	62	107	n.d-535	58	84.3
Et-*p*-TSA	n.d-170	33	24.1	n.d-304	36	41.2	n.d-79	33	12.9	n.d-306	50	34.5	n.d-40	38	8.6	n.d-402	50	61.6
Total average	37.6			99.7			210			101			64.1			138		
Organophosphates esters																		
TEP	n.d-33	75	8.6	n.d-14	64	2.8	n.d-50	67	8.1	n.d-19	75	5.8	n.d-47	69	7.9	n.d-47	50	9.4
TBP	n.d-83	50	9.7	n.d-11	64	4.9	n.d-76	50	21.1	n.d-128	58	28.3	n.d-46	46	10.8	n.d-38	58	10.3
TiBP	n.d-9	25	1.4	n.d-21	27	3.2	n.d-10	25	1.7	n.d-17	42	4.4	n.d-40	31	5.0	n.d-22	42	3.8
TCPP	n.d-586	33	114	n.d-499	45	91.9	n.d-111	42	28.0	n.d-201	17	23.1	n.d-206	38	37.5	n.d-282	58	71.3
TCEP	n.d-7	8	0.6	n.d-21	18	2.4	n.d-1	8	0.1	n.d-3	25	0.6	n.d-15	23	1.3	n.d-224	50	21.1
TEHP	n.d-88	42	10.7	n.d-166	45	19.9	n.d-4	17	0.7	n.d-382	42	52.5	n.d-119	38	16.4	n.d-222	42	29.8
EHDPP	n.d-14	33	2.2	n.d-18	18	2.9	n.d-4	8	0.4	n.d-27	33	7.3	n.d-36	38	4.0	n.d-21	33	5.2
TPP	n.d-70	75	23.4	n.d-31	73	11.3	n.d-60	58	15.7	n.d-90	67	19.8	n.d-114	69	25.1	n.d-111	58	23.2
TTP	n.d-601	58	125	n.d-855	64	113	n.d-513	33	55.5	n.d-1344	58	218	n.d-812	54	147	n.d-964	50	100
Total average	28.6			26.9			19.9			27.2			17.8			38.5		
Phthalates																		
DMP	n.d-45	67	10.7	n.d-22	36	2.7	n.d-137	58	16.5	n.d-125	50	17.5	n.d-121	54	12.2	n.d-71	50	9.8
DEP	n.d-5410	75	1260	n.d-4724	73	742	n.d-19506	75	2477	n.d-2125	58	450	n.d-3049	62	736	n.d-3143	83	796
DiBP	nd.-8532	75	1554	n.d-5522	45	829	n.d-661	58	175	n.d-443	58	108	n.d-1112	46	231	n.d-984	58	209
DEHA	n.d-12220	92	3915	n.d-7932	64	1971	n.d-6576	75	2437	n.d-6431	75	2447	n.d-5375	62	1804	n.d-4314	75	1514
DEHP	n.d-13069	83	1631	n.d-2006	55	615	n.d-5765	50	601	n.d-7060	50	874	n.d-10283	62	1843	n.d-9802	67	1395
DnOP	n.d-16033	67	3121	n.d-7878	36	1174	n.d-8704	50	1129	n.d-2053	42	394	n.d-17606	31	1557	n.d-12775	50	2176
Total average	2127			1226			1927			1383			1991			1424		

n.d: not detected.

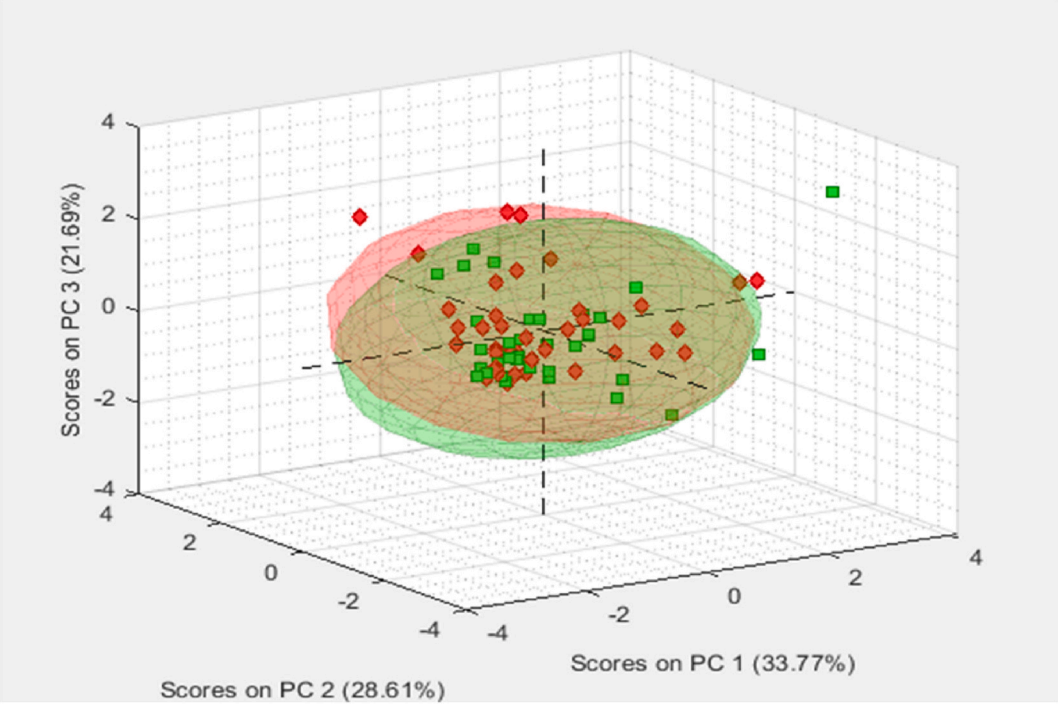

Fig. 1. Principal component analysis (PCA) of the concentrations of contaminants between the farmed fish and the wild fish.

3. Results and discussion

3.1. Validation of the analytical method

The analytical method was based on a previous method (Castro et al., 2020) and validated for the species analysed in this study by establishing the method linear range, the apparent recoveries (%R_{app}), the matrix effect, the method detection limits (MDLs), the method quantification limits (MQLs), the repeatability and the reproducibility. All parameters were calculated for each species by using a mixture of farmed and wild origin specimens.

As similar validation data was obtained for the three species, as example, data for turbot is shown in Table S4. All compounds showed good linearity ($R^2 > 0.999$) in the range of concentrations studied. Apparent recoveries, obtained by spiking (n = 5) at 1000 ng g^{-1} (d.w.) samples of each species, ranged from 24% to 87% for the turbot specie (the other species showed similar results). The R_{app} show somewhat low values but considering the complexity of the matrix and the large number of analytes that belong to different families, those values can be considered acceptable. It is also worth to remark that only 8 of 25 analytes had apparent recoveries below 40%. The matrix effect was calculated according to previous studies (Trabalón et al., 2015) and the extracts of the samples of each species were spiked (n = 3) after the extraction process at 1000 ng g^{-1} (d.w.) The matrix effect for all compounds and all three species was less than 21%, which indicates that it is negligible. Method detection limits (MDLs) were set as the concentration that gave a signal to background noise ratio of three and ranged from 0.1 to 13 ng g^{-1} (d.w.) for turbot. Method quantification limits (MQLs), set as the smallest concentration that can be quantified with the calibration line, ranged from 0.2 ng g^{-1} to 26 ng g^{-1} (d.w.) also for turbot. Repeatability and reproducibility, expressed as relative standard derivation (%RSD, n = 5, 1000 ng g^{-1} d.w.), were below 20% and 29%, respectively. As said, similar values were obtained for sea bream and sea bass.

3.2. Occurrence of HPVC in the wild and farmed species

A total of 74 samples of farmed fish (n = 39) and wild fish (n = 35) were analysed. Concentrations were initially calculated in dry weight (d.w.) although for the risk characterization they were converted into wet weight by applying the percentage of humidity content of each species (weights calculated before and after the lyophilization process for each sample).

Table 1 shows the average and range of concentrations, both expressed as dry weight, the detection frequencies (%DF) for each compound and each species and the total average for each compound family and specie. All the compounds determined were found to varying concentrations in the three fish species analysed.

As expected, phthalates presented the highest total average concentrations for all species independently of their origin. This is due to their widespread use in plastics and consumer products, their persistence in the environment, and their tendency to bioaccumulate in aquatic organisms, leading to higher concentrations in fish. However, farmed fish seems to have higher levels being its total average concentrations about 30% higher than those for wild fish. DEP and DnOP had the highest concentrations with values up to 19506 ng g^{-1} (d.w.) in farmed sea bass and 17606 ng g^{-1} (d.w.) in farmed sea bream, respectively. DEP, DEHA and DEHP had the highest frequencies of detection with respect the other compounds (up to 83, 92 and 83%, respectively). These results for phthalates are related to the high production of these compounds, with DEP being produced the most and having a maximum ubiquity of over 1000 tons of production per year (ECHA, 2022). The concentrations found in the present study were higher than those reported in the study by Valton et al. (2014), where phthalates were detected in wild common roach, captured in the Orge River (France), at 256 ng g^{-1} (d.w.) for DEP and 245 ng g^{-1} (d.w.) for DnOP.

OPEs were also present in most samples, with similar total average value for all species in both origins. The most frequently detected compounds were TEP and TPP (up to 75% in both cases, each in samples of farmed turbot). Also, TCPP and TTP were present at maximum concentrations of 586 ng g^{-1} (d.w.) in farmed turbot and 1344 ng g^{-1} (d.w.) in wild sea bass, respectively, which correspond to 140 and 423 ng g^{-1}

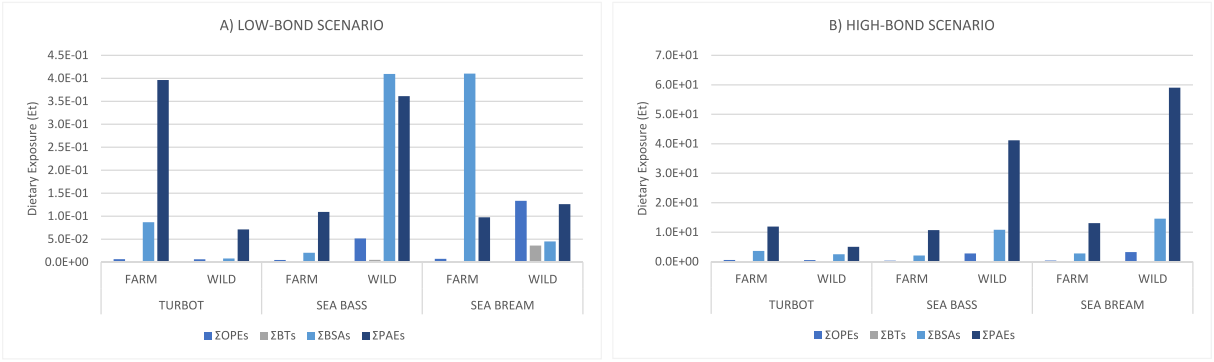

Fig. 2. Dietary exposure (ng kg^{-1} bw day^{-1}) of HPVCs for the general population of Tarragona in a) the low-bound scenario and b) the high-bound scenario.

in wet weight (w.w.), respectively. These results are similar to those found in perch species in the studies by Sundkvist et al. (2010) (770 and 180 ng g^{-1} (w.w.) for TPP and TCPP, respectively) and higher than those reported in mackerel species by Castro et al. (2020) (2.7 ng g^{-1} (w.w.) for TCPP). However, there are no studies that compare the same HPCVs from this study according to the capture origin.

BSAs and BTs were also found in most samples. Higher average concentrations of BSAs were found in wild turbot and sea bream, 99 and 138 ng g^{-1} (d.w.), respectively. However, sea bass showed higher average concentrations in farmed samples, with a value of 210 ng g^{-1} (d.w.). And for the BTs, the highest average concentrations compared to the other species, were found in wild and farmed turbot, with an average value of 60.8 and 30.3 ng g^{-1} (d.w.), respectively. For sea bass and sea bream, the average values of BT were very similar (14.5–19.7 ng g^{-1} d.w.). Much lower frequencies of detection were observed for BTs than phthalates and OPEs, especially in the case of ClBT, which was only found a few samples of sea bream. The concentrations of BTs were similar to those found by Trabalón et al. (2017); for example, the maximum for BT was 82 ng g^{-1} (d.w.) for a squid sample, which is very similar to the 83 ng g^{-1} (d.w.) found in wild turbot in the present study.

To observe the differences between farmed and wild samples, a principal component analysis (PCA) was done (Fig. 1) between farmed and wild species. With a total data variability of 84%, we can state that there is no clear distinction between farmed samples (red) and wild samples (green).

The high similarity between farmed and wild species may be due to the fact that they were all purchased from the local market to target the fish consumed and therefore the origin was not the same. It should be borne in mind that contamination levels may vary depending on geographical location and anthropogenic factors such as the use of chemicals in aquaculture, the feeding of fish (as contaminants may accumulate in their bodies) and the use of plastics, in the processing and/or handling of fish. From a consumption point of view, it is important to consider all these factors which may give more variability to the data but provide a more realistic human consumption study.

3.3. Dietary exposure and risk characterization

The results of dietary exposure associated with the consumption of turbot, sea bass and sea bream are shown in Fig. 2 (Fig. 2a and b show dietary exposure in the low bond (LB) and high bound (HB) scenarios, respectively). The two scenarios were calculated by separating the farmed and wild samples even through consumption could not be differentiated by origin.

In both scenarios, the highest dietary exposure corresponded to ΣPAEs followed by ΣBSAs, while the dietary exposures to ΣOPEs and ΣBTs were much lower due to the low concentrations found in the samples. According to the different origins, in the case of PAEs, as higher exposure values were found in samples of turbot from fish farm origin and in the sea bream and sea bass from wild origin. This, exposure to ΣPAEs ranged from $1.6{\cdot}10^{-1}$ to $8.8{\cdot}10^{-1}$ ng kg^{-1} bw day^{-1} for LB and from 9.1 to 83.6 ng kg^{-1} bw day^{-1} for HB. For OPEs, values were higher in wild samples of sea bream and sea bass, whereas turbot shows similar values between origins. Exposure to ΣOPEs ranged from $6.3{\cdot}10^{-3}$ to $5.1{\cdot}10^{-2}$ ng kg^{-1} bw day^{-1} for LB and from $6.3{\cdot}10^{-1}$ to 3.8 ng kg^{-1} bw day^{-1} for HB. In the case of BSAs, similar values were found in samples of turbot, while sea bream and sea bass show higher exposure values from wild origin. For ΣBSAs, exposure ranged from $2.7{\cdot}10^{-2}$ to $6.0{\cdot}10^{-1}$ ng kg^{-1} bw day^{-1} for LB and from 3.2 to 19.7 ng kg^{-1} bw day^{-1} for HB. And for BTs, higher values are found in samples of wild origin than those from farmed, in all three species. Exposure values for ΣBTs ranged from $9.9{\cdot}10^{-4}$ to $5.9{\cdot}10^{-3}$ ng kg^{-1} bw day^{-1} for LB and from $5.6{\cdot}10^{-2}$ to $4.6{\cdot}10^{-1}$ ng kg^{-1} bw day^{-1} for HB.

In the study by Castro et al. (2020), the highest dietary exposure values for ΣOPEs were obtained in fish samples of species different than the ones of the present study (1.2–1.9 ng kg^{-1} bw day^{-1} for LB and 2.5–4.7 ng kg^{-1} bw day^{-1} for HB). In another study (Gbadamosi et al., 2021), similar values were found for the dietary intake of various OPEs

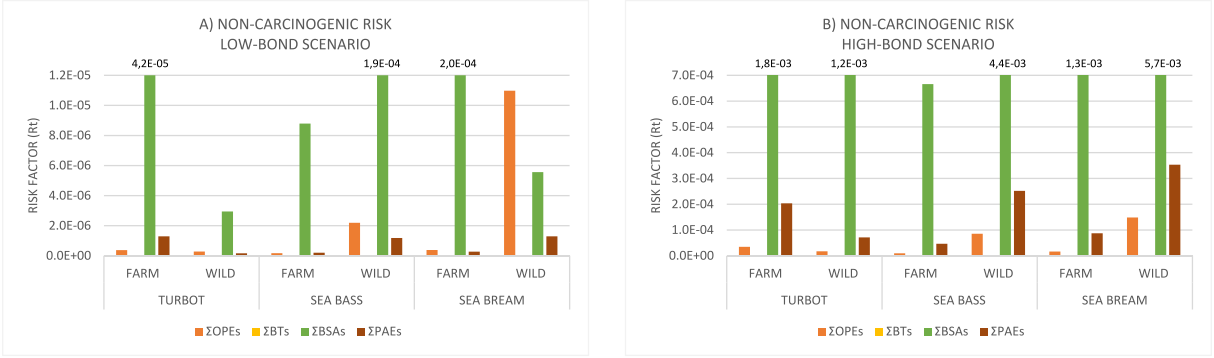

Fig. 3. Risk factor (R_t) of non-carcinogenic compounds associated with exposure to HPVCs for the Catalan population.

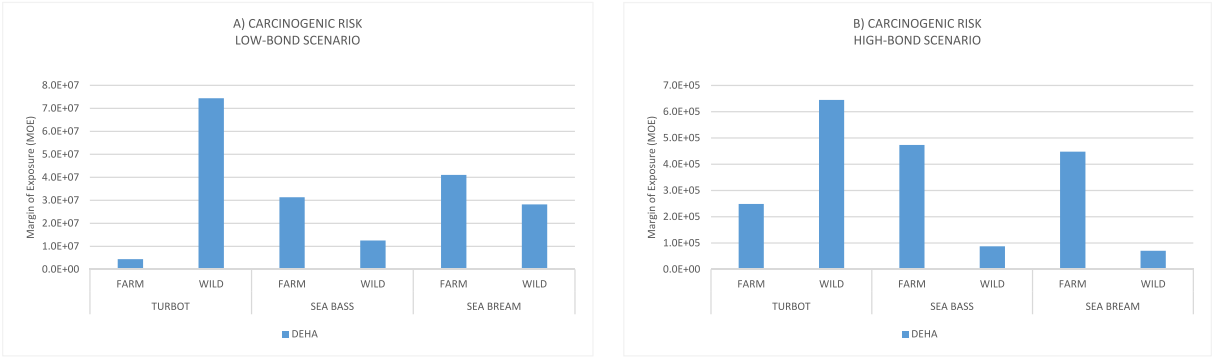

Fig. 4. Margin of exposure (MOE) of DEHA at low and high bound scenario.

(tris(2-chloroisopropyl)phosphate (TCIPP), triphenyl phosphate (TPHP), EHDPP, tris(2-butoxyethyl) phosphate (TBOEP), tris(1, 3-dichloro-2-propyl)phosphate (TDCIPP) and TCEP calculated by eel consumption with values between $3.4{\cdot}10^{-2}$ and $1.0{\cdot}10^{-1}$ ng kg^{-1} bw day^{-1}. In the same study, the results of the HB are also shown with values between of $8.4{\cdot}10^{-1}$ and 2.5 ng kg^{-1} bw day^{-1}.

The species with the highest dietary exposure index was sea bream mainly because it is the one that is most consumed by the Catalan population, followed next by sea bass and then by turbot. In both scenarios and all three species, ΣPAEs represent 57–82% of the total dietary exposure for all the samples analysed due to their high concentrations found, which suggests high exposure to these contaminants by consumption of the fish species mentioned. On the other hand, OPEs were present in all samples, through their concentrations were significantly lower than those of PAEs, representing on total average roughly 4% of the total dietary exposure. The percentage of their presence in the three fish species analysed was relatively low (ranging from 14% to 39%). BTs were not significantly present in any of the samples analysed, which suggests low exposure to this type of contaminants by consumption of any of the fish species under study.

To calculate the risk factor, we considered the carcinogenic and the non-carcinogenic compounds being TBP, TCEP, TEHP, DEHA and DEHP the only ones with carcinogenic characteristics.

For the non-carcinogenic compounds, the E_t for each contaminant and the ADI associated with the contaminant were used, as explained in section 2.5, equation (2). NOAEL values used to calculate ADI are collected in Table S5. Fig. 3 shows the risk factor values calculated that ranged from $6.6{\cdot}10^{-10}$ to $2.0{\cdot}10^{-4}$ ng kg^{-1} bw day^{-1} for LB and from $6.3{\cdot}10^{-18}$ to $5.7{\cdot}10^{-3}$ ng kg^{-1} bw day^{-1} for HB. Although the highest risk factor corresponds to wild sea bream in HB, no health risk is associated with the ingestion of the target species because in any case the risk factors are below 1(Committee, 2012). The total of the wild samples in the LB has an average risk of $1.8{\cdot}10^{-5}$ ng kg^{-1} bw day^{-1}, while the farmed samples have an average risk of $2.1{\cdot}10^{-5}$ ng kg^{-1} bw day^{-1}. In the HB a greater difference is observed, $1.0{\cdot}10^{-3}$ ng kg^{-1} bw day^{-1} for the wild samples and $3.5{\cdot}10^{-4}$ ng kg^{-1} bw day^{-1} for the farmed samples. In general, a higher risk factor is observed for samples of wild origin, especially in HB for sea bass and sea bream.

Similar results have been reported in other studies focused on similar HPVCs but different fish species, with values of $9.1{\cdot}10^{-5}$ to $1.5{\cdot}10^{-3}$ ng kg^{-1} bw day^{-1} for the risk factor for the same OPEs compounds (Castro et al., 2020). In the paper by Sala et al. (2022)' the risk factors were highest for TBOEP and tris(1,3-dichloro-2-propyl) phosphate (TDClPP), with values ranging from $7.3{\cdot}10^{-4}$ to $1.3{\cdot}10^{-3}$ ng kg^{-1} bw day^{-1} for LB and from $2.5{\cdot}10^{-4}$ to $7.2{\cdot}10^{-5}$ ng kg^{-1} bw day^{-1} for HB, respectively. These values were calculated by averaging the concentrations of three fish species (hake, anchovy, and sardine).

For carcinogenic compounds the margins of exposure were calculated from BMD_t and E_t defined in section 2.5 of equation (3). The results of the MOE values for all carcinogenic compounds ranged between $4.4{\cdot}10^{6}$ to $7.3{\cdot}10^{11}$ for LB and from $7.1{\cdot}10^{4}$ to $9.5{\cdot}10^{10}$ for HB. Generally, the highest values are found in species of wild origin, particularly in the sea bream species. The most relevant compound is DEHA, with a higher risk for all species. Therefore, the results (Fig. 4) were represented only for this contaminant since the others showed insignificant risk to the population. For LB scenario, the species with the highest risk was the farmed turbot with a value of $4.4{\cdot}10^{6}$, and the second was the wild sea bass with a value of $1.3{\cdot}10^{7}$. All other values were higher, thus further minimizing the risk. For HB scenario, the species with the highest risk was the wild sea bream with a value of $7.1{\cdot}10^{4}$, and the second was the wild sea bass with a value of $8.8{\cdot}10^{4}$. According to EFSA (EFSA, 2012b), these values indicate that risk associated to the intake of these contaminants via consumption of the three studied species is of low concern because they are above $1{\cdot}10^{4}$.

In the study by Castro et al. (2020) the carcinogenic risk values calculated for TCEP and TBP ranged from $4.7{\cdot}10^{7}$ to $11.0{\cdot}10^{7}$ ng kg^{-1} bw day^{-1} in fish species different from those in the present study but overall results were similar. In the present study, the risk values for TCEP and TBP ranged from $5.8{\cdot}10^{8}$ to $9.5{\cdot}10^{10}$. As these values are 5000 times higher than the threshold value of 10^{4} set by EFSA (Committee, 2012), the risk can be considered of low concern.

4. Conclusions

A wide range of concentrations of HPVCs was found in the three fish species analysed. No significant differences were observed between the mean concentrations of wild and farmed species for the contaminants OPEs, BTs and BSAs. However, a slight increase in the mean concentration was observed in the farmed samples compared to the wild samples for PAEs. DnOP and DEP showed the highest concentration levels in the sea bass and sea bream species (19505 and 17605 ng g^{-1} (d. w), respectively).

Dietary exposure assessment revealed higher values of all contaminants in wild samples of sea bream and sea bass. The high exposure of sea bream may be attributed to its status as one of the most consumed species by the Catalan population. The highest non-carcinogenic risk values were observed in species of wild origin, particularly in sea bream (83.6 ng kg^{-1} bw day^{-1} in HB scenario) and the highest carcinogenic risk values were observed for the DEHA that emerged as the most relevant compound, specifically in sea bream ($7.1{\cdot}10^{4}$ in HB scenario). However, the MOE values indicate that there is no carcinogenic risk associated with the intake of these contaminants through the consumption of the three analysed fish species.

CRediT authorship contribution statement

Sílvia Borrull: Writing – original draft, Validation, Resources, Investigation, Formal analysis. **Francesc Borrull:** Supervision, Funding acquisition. **Eva Pocurull:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Rosa Maria Marcé:** Writing – review

& editing, Supervision, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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.chemosphere.2024.143364.

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