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Levels, patterns and risk assessment of PCDD/Fs and dl-PCBs through dietary exposure in the Valencian Region (Spain)

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A R T I C L E I N F O

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A B S T R A C T

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and dioxin like polychlorinated biphenyls (dl-PCBs) levels were measured in representative vegetable oils and animal origin foodstuffs collected in a Total Diet Study carried out in the Valencian Region (Spain). A total amount of 3,300 food samples were collected and grouped into 5 main food groups: vegetable oils, meat and meat products, eggs, milk and dairy products and fish and sea products. The samples were analysed using gas chromatography coupled to high-resolution mass spectrometry (GC-HRMS). The food group which presented the highest concentration in wet weight (ww) for the sum of PCDD/Fs and dl-PCBs was fish and sea products (0.5 pg TEQ g^{-1} ww), whereas meat and meat products (0.6 pg TEQ g^{-1} lipid) showed the highest levels expressed in lipid terms. Occurrence data of PCDD/F and dl-PCBs were combined with consumption data to estimate the dietary exposure of adults (>15 years) and children (6–15 years). Finally, the estimated weekly intake (EWI) was calculated using a deterministic approach and considering the food consumption of the population, with fish and sea products being the main food group contributor. Likewise, considering the worst-case scenario (Upper Bound, UB), average EWI were 1.8 and 3.4 pg TEQ kg^{-1} body weight (bw) $week^{-1}$ for adults and children, respectively. For children, the average EWI was almost twice above the tolerable weekly intake (TWI) of 2 pg TEQ kg^{-1} bw $week^{-1}$ set by EFSA in 2018. In terms of risk characterisation, the overall obtained results showed that 19 % of adults and 43 % of children may exceed the TWI when using UB.

1. Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), commonly known as dioxins, and polychlorinated biphenyls (PCBs) are harmful organic compounds, part of the so-called “dirty-dozen” and listed in the Stockholm Convention as persistent organic pollutants (POPs) for reduction or elimination (UNEP, 2009). PCDD/Fs are unintentionally by-products produced during waste combustion and incineration process, particularly when process implicates organic and inorganic chlorinated chemicals. PCBs have been employed in commercial products in the past as a dielectrics isolating fluids in capacitors and transformers, heat exchangers fluids, plasticizers and printing inks due to their exceptional properties (Grešner et al., 2021; Shen et al., 2017).

An amount of 75 PCDDs and 135 PCDFs constituted the total congeners of dioxins compounds but 17 congeners with chlorine substitution in the 2, 3, 7 and 8 positions coated special importance by their toxicity for human health, being 2378-TCDD identified as the most toxic congener. Likewise, 209 PCBs compounds are distinguished but only 12 are named dioxin-like PCBs (dl-PCBs) due to their similar structurally and toxicological properties to PCDD/Fs. Toxicological effects include dermal toxicity, damage to the immune system and adverse effects on reproduction, development, endocrine and neurologic functions (EFSA Panel on Contaminants in the Food Chain (CONTAM) et al., 2018;

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Ssebugere et al., 2019). International Agency for Research on Cancer (IARC) also classified 2378-TCDD, 23478 PCDF and dl-PCBs as carcinogenic to humans (IARC, 2012; IARC, 2016).

PCDD/Fs and dl-PCBs are persistent in the environment since they can be transported over long distances in different pathways like air, sediment, soil, water and plants (Canlı et al., 2022; Güzel et al., 2022). Due to their lipophilicity, low water solubility and poor degradation, they can bioaccumulate in animal fat tissues thereby being present in the food chain (Güzel et al., 2020). As a consequence, ingestion is the main route of PCDD/Fs and dl-PCBs for humans, due to the fact that more than 90 % of total exposure occurs from food, mainly by animal origin such as eggs, dairy products, meat, and fish (Kanan and Samara, 2018; Shen et al., 2017). In order to protect public health, a tolerable intake level of 14 pg TEQ kg^{-1} bw per week was set in the early 2000s (TWI_{2001}), but after a reassessment of the toxicity of these compounds, the updated value was set by EFSA in 2018 (TWI_{2018}) at 2 pg TEQ kg^{-1} bw per week, seven times lower than the previously considered value (EFSA et al., 2018).

Gas chromatography coupled to high resolution mass spectrometry (GC-HRMS) is a confirmatory method that is considered the gold standard for the analysis of these compounds analysis due to its high sensitivity and selectivity when a substantial number of analytes are analysed simultaneously. Hence, determination with GC-HRMS offers unambiguous identification and quantification of PCDD/Fs and dl-PCBs present in a sample. This technique enable to obtain the congener profiles, and also allows to know which of those are the most abundant in each food group (EFSA et al., 2018; Reiner, 2016). In contrast, DR CALUX® (Chemical-Activated Luciferase gene expression) bioassay is a screening fast and inexpensive validated method for the determination of PCDD/Fs and dl-PCBs in a large number of samples but it does not quantify specific congeners and has no ability to discriminate between all compounds with AhR affinity. Thus, the results obtained employing this bioassay method could be overstated or underestimated on Upper Bound (UB) and Lower Bound (LB) scenarios, respectively (Quijano et al., 2018).

Previously, PCDD/Fs and dl-PCBs dietary intake exposure and risk assessment have been assessed in the Valencian Region (Spain) by Quijano et al., 2018 using DR CALUX® bioassay to determine the levels of these compounds.

The present work assesses the PCDD/Fs and dl-PCBs dietary exposure and risk assessment in a population living in the Valencia Region of Spain by GC-HRMS. The main objectives of this study are i) to determine by GC-HRMS the concentrations of PCDD/Fs and dl-PCBs in the food groups with the highest fat content, as these food items are the major contributors to the human dietary exposure to these contaminants., ii)To achieve more precise and accurate results using GC-HRMS which allows to obtain congener profiles enriching the results previously obtained by DR CALUX® in this region., iii) to assess temporal trends, iv) to improve the risk assessment from dietary exposure through more exhaustive results and taking into account the updated guideline values proposed by EFSA.

2. Materials and methods

2.1. Food sampling

The dietary study was distributed in 33 food items grouped into the five mainly fatty consumed food groups in the assessed Region, which were the following: milk and dairy products (22 %), meat and meat products (12 %), fish and sea products (4 %), vegetable oils (2 %) and eggs (2 %) (Fullana et al., 2010).

In order to include seasonal foods, four sampling periods were defined: January-March, April-June, July-September and October-December. Thus, 100 samples were collected for each food item to reduce the variability, obtaining a total amount of 3300 samples. Likewise, in order to reduce the number of analyses, composite samples were formed from 10 samples of each food item (collected in the same seasonal period), being 330 the total number of composite samples analysed, 10 for each of the 33 food items included in this work (see Table SD-1).

2.2. Consumption data

The consumption data used to estimate PCDD/Fs + dl-PCBs intake were obtained from a dietary study conducted and validated by the Valencian Public Health Directorate. The food consumption survey was carried out in three different seasons which were June-July 2010, September-November 2010 and November-February 2010/2011. The survey included the consumption data of: a) 195 young people (6–15 years of age, 43.5 kg body weight average) and b) 1281 adults (16–95 years of age, 71.2 kg body weight average). Therefore, a total of 1476 subjects from the Valencian Region were interviewed face-to-face to collect the details about the variety and amount of food and beverages consumed in the previous 24 h as well as body weight information.

Data on food consumption for the two populations selected are shown in Table SD-2.

2.3. Sample preparation and analysis

Mass-labelled $^{13}C_{12}$-PCDD/F and $^{13}C_{12}$-dl-PCB working solutions as well as the commercial calibration standards and solvents used were previously described by Hernández et al., (2020). For the clean-up, three columns of CLDS-ABN-STD (silica), CLDA-BAS-011 (alumina), and CLDC-CCE-034 (carbon) were used and supplied by Fluid Management System (Watertown, Massachusetts, USA). On the other hand, sodium sulfate anhydrous was purchased from VWR (Radnor, Pennsylvania, USA) and diatomaceous Earth was supplied from PanReac AppliChem (Barcelona, Spain).

Food samples were prepared according to the sample treatment already described by our research group (Hernández et al., 2020, López et al., 2021). Briefly, volumes of 20 μL and 50 μL of the 1613EPA-LCS and WP-LCS working solutions (surrogate solutions) were added to the food samples. Depending on the units in which the results were expected to be expressed, the surrogates were added: a) before the extraction step for food samples, expressed as pg g^{-1} wet weight (ww) or b) after extraction step for food samples, expressed as pg g^{-1} lipid weight (lw). In the first case, after 30 min of interaction, the extraction was performed using a pressurised liquid extraction system (PLE) with 66 mL stainless steel cells (ASE 350, Dionex, Sunnyvale, CA, USA). Then, a clean-up was carried out on a multi-column system (Power-Prep^{TM}, Fluid Management Systems, USA).

GC-HRMS system was also previously described by López et al., 2021. Briefly, the mass resolution was set at approximately 10,000 R using a TG-Dioxin capillary column (60 m × 0.25 mm × 0.25 μm) and coupled to a DFS High Resolution Mass Spectrometer (Thermo Scientific, Bremen, Germany).

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

The present work has been carried out under ISO/IEC/EN 17025 quality assurance system. Furthermore, this study followed the quality assurance requirements in Commission Regulation 2017/644 concerning sampling and analysis for the monitoring of PCDD/Fs levels, dioxin-like PCBs, and non-dioxin-like PCBs (European Commission, 2017). Moreover, a procedural reagent blank was employed every 8 batches in order to assess and correct any contamination from laboratory background, where the sum of PCDD/Fs and dl-PCBs in pg TEQ/g had to be lower than 1/5 of the established maximum content (always taking as a reference the most restrictive value) and the content of each individual congener was lower than the calculated LOQ. A sample blank spiked to 1/5 of the established maximum content was introduced every 6 batches.

Spiked samples as internal quality control and certified reference material (CARP-2, Wellington Laboratories, Canada) were also analysed twice a year and the results obtained were satisfactory in all analysis. Spiked samples recovery was accepted when the total TEQ recoveries were between 80 and 120 %. Likewise, surrogate recoveries were only accepted if they were between 60 and 120 % or if being lower or higher, their contribution did not exceed the 10 % of the total PCDD/Fs + dl-PCBs in TEQ terms.

2.5. Exposure and risk assessment

PCDD/Fs and dl-PCBs exposure for adults and children has been estimated using the deterministic method for chronic exposure. The estimated weekly intake (EWI) was assessed as follows combining information on food consumption for each individual (in g/week) and PCDD/Fs and dl-PCBs levels (in pg g^{-1}).

$EWI = C{\cdot}A$ (1)where EWI is exposure weekly intake expressed as pg TEQ kg^{-1} bw $week^{-1}$, C is a matrix of dimension 1476 × 33 containing information on the food consumption (g $week^{-1}$) for each individual (per kg bw) and A is a matrix of dimension 33x10 containing the PCDD/Fs and dl-PCBs levels in the 10 samples of each of the analysed foods that were consumed (pg TEQ g^{-1}). Finally, the PCDD/Fs and dl-PCBs exposure for each individual was summarised by considering the average exposure in the 10 analysed samples. Thus, the effect of cooking or processing was not taken into account for the calculation of the PCDD/Fs and dl-PCBs levels in the different food groups assessed.

Likewise, the risk characterization of PCDD/Fs and dl-PCBs was evaluated taking into account the tolerable weekly intake (TWI) proposed by the Scientific Committee on Food (SCF) in 2001 as 14 pg TEQ_{1998} kg^{-1} bw $week^{-1}$ (TWI_{2001}) (SCF, 2001) and the updated value suggested by European Food Safety Authority (EFSA) in 2018 as 2 pg TEQ_{2005} kg^{-1} bw $week^{-1}$ (TWI_{2018}) (EFSA et al., 2018).

3. Results and discussion

3.1. PCDD/F and dl-PCB levels by congeners

Table 1 and Table SD-3 describe the median, range and frequency of detection (FD) of the PCDD/F and dl-PCB individual congeners for the different assessed food groups. PCDD/Fs and dl-PCB levels in foodstuffs are shown both on a lipid and on ww sample basis depending on the study group concerned. Thus, results are expressed according to the EU 2017/644 Regulation in Table 1. PCDD/Fs and dl-PCBs levels in eggs, meat and meat products, milk and dairy products and vegetable oils are expressed in pg g^{-1} lipid. Otherwise, fish and sea products are only presented in pg g^{-1} ww. Furthermore, several food groups (eggs, meat and meat products, milk and dairy products) were also expressed in pg g^{-1} ww in order to compare with previous studies, as shown in Table SD-3.

Overall, obtained concentrations for PCDD and PCDFs by congeners, expressed as lipid terms, ranged from 0.001 pg g^{-1} lipid (234678-HxCDF, 1234789-HpCDF, OCDF, 2378-TCDD) to 318.6 (OCDD) pg g^{-1} lipid. Regarding to ww terms, the obtained results ranged from $5.8{\cdot}10^{-6}$ pg g^{-1} ww (2378-TCDD) to 28.5 pg g^{-1} ww (OCDD). Median values for the highest detected congener (OCDD) ranged from 0.2 (Milk and dairy products) to 1.1 (Meat and meat products), expressed in lipid terms. Otherwise, obtained OCDD median in pg g^{-1} ww oscillated from 0.04 (Milk and dairy products) to 0.2 (Meat and meat products). The congeners with the highest FD for PCDD/Fs in the assessed samples (n = 330) were OCDD, 12378-PCDF and 1234678-HpCDD with FD of 69 %, 58 % and 57 %, respectively. These congeners were also the most predominants in a similar previous study assessed in the same region (Marin et al., 2011). On the other hand, all HxCDF congeners and the majority of PCDD showed FD below than 30 %.

Additionally, although OCDD was highly detected and concentrated in all food groups, in fish and sea products the most detected congener was 2378-TCDF and the most concentrated were 23478-PeCDF and 2378-TCDF.

For dl-PCBs, PCB-118 was the congener with the highest FD, being the only one detected in all the assessed samples. Furthermore, PCB-156 and PCB-167 were detected in more than 90 % of them. Overall, concerning the levels of dl-PCBs, ranged from 0.007 pg g^{-1} lipid in milk and dairy products to 1547.2 pg g^{-1} lipid in meat and meat products in all food groups. In ww terms, dl-PCBs levels ranged from $2.3{\cdot}10^{-6}$ to 5347.7 pg g^{-1} ww both in fish and sea products.

Likewise, the highest concentrations of PCB-118 were found in the different assessed food groups, with median values ranging from 7.9 (vegetable oils) to 152.7 pg g^{-1} lipid (eggs). Otherwise, median of PCB-118 in pg g^{-1} ww ranged from 3.9 (milk and dairy products) to 177.7 (fish and sea products).

Comparing with other studies, the obtained results are similar to those presented by Barone et al. (2019) in meat samples in Italy, where OCDD and HpCDD were also the most detected PCDDs congeners. However, dl-PCBs profiles are different, being the PCB-189 the most abundant in Barone et al. (2019) whereas PCB-118 was the most predominant in the present study. Likewise, the detected profiles in Catalonia (Spain) in 2008 (EDT Catalonia, 2008) were very similar to this research, showing the highest concentration for OCDD in meat and meat products and the highest levels for OCDD and 2378-TCDF in fish and sea products.

3.2. Profiles for PCDD/F and dl-PCB

The profile for each congener and food group was calculated considering the toxicity of each compound and the UB scenario. The obtained profiles for total pg-TEQ_{2005} g^{-1} lipid levels and pg-TEQ_{2005} g^{-1} ww in all analysed samples are depicted in Fig. 1. In all cases, 12378-PeCDD presented the highest contribution to the total ∑PCDD/Fs and PCB-126 was the most contributed congener to ∑dl-PCBs levels, probably since these two congeners have the highest toxic equivalency factor (TEF). The showed profiles were comparable to those obtained by Marin et al., 2011 in the same assessed region.

3.3. Total TEQ in food groups

Table 2 shows the levels associated to the presence of ∑PCDD/Fs, ∑dl-PCBs and ∑PCDD/Fs + dl-PCBs both in pg-TEQ g^{-1} lipid and in pg-TEQ g^{-1} ww in each food group, based on UB approach. Concentrations for PCDD/Fs ranged from 0.003 to 4.5 pg-TEQ_{2005} g^{-1} lipid, levels for dl-PCBs ranged from 0.002 to 2.4 pg-TEQ g^{-1} lipid and concentrations of the sum of PCDD/Fs + dl-PCBs oscillated from 0.005 to 6.8 pg-TEQ g^{-1} lipid. Likewise, in ww terms, ∑PCDD/Fs, ∑dl-PCBs and ∑PCDD/Fs + dl-PCBs concentrations ranged from $3.1{\cdot}10^{-5}$ to 1.6 pg-TEQ g^{-1} ww, from $2.7{\cdot}10^{-6}$ to 4.8 pg-TEQ g^{-1} ww and from $6.8{\cdot}10^{-5}$ to 4.9 pg-TEQ g^{-1} ww, respectively.

Regarding the obtained concentrations in each food group, meat and meat products and eggs presented the highest median concentration in pg-TEQ g^{-1} lipid of ∑PCDD/Fs, whereas the values for vegetable oils presented the minimum median observed for ∑dl-PCBs. The highest concentration for ∑dl-PCBs corresponded to milk and dairy products. In pg-TEQ_{2005} g^{-1} ww terms, the highest concentrations were associated to fish and sea products with a large difference with the other groups in ∑dl-PCBs and ∑PCDD/Fs + dl-PCBs. For ∑PCDD/Fs levels, the highest concentrations were found in meat and meat products.

Overall, the estimated levels for all assessed groups in this study are significantly lower than the limits set by Regulation 2023/915 setting maximum levels in foodstuffs.

Moreover, the obtained concentrations in fish products were five times lower than the levels obtained by Marin et al. (2011) in the same assessed region and two times lower than the concentrations detected in Catalonia in 2008 (EDT Catalonia, 2008). Furthermore, the levels detected were significantly lower than the PCDD/Fs and dl-PCBs levels

Table 1
PCDD/Fs and dl-PCBs concentrations in the different studied foods.

Congeners	Meat and meat products (N = 120)[a]			Milk and dairy products (N = 60)[a]			Vegetable oils (N = 20)[a]			Eggs (N = 10)[a]			Fish and sea products (N = 120)[b]			Overall FD[c]
	FD[c]	Median	min–max	FD[c]	Median	min–max	FD[c]	Median	min–max	FD[c]	Median	min–max	FD[c]	Median	min–max	
PCDD/Fs																
2378-TCDF	35	0.1	0.005–0.8	22	0.03	0.006–0.2	55	0.04	0.02–0.1	100	0.2	0.1–0.2	71	0.1	0.002–0.8	49
12378-PeCDF	58	0.2	0.008–1.4	65	0.1	0.005–0.6	45	0.09	0.1–0.1	100	0.2	0.2–0.2	55	0.05	0.008–0.3	59
23478-PeCDF	27	0.2	0.005–8.6	33	0.1	0.002–0.3	10	0.07	0.04–0.1	30	0.1	0.1–0.1	42	0.1	0.007–0.4	33
123478-HxCDF	25	0.2	0.006–3.3	23	0.1	0.004–0.2	10	0.07	0.03–0.1	10	0.1	0.1	16	0.03	0.004–0.2	20
123678-HxCDF	14	0.5	0.005 – 4.0	20	0.1	0.01–0.2	0	–	–	10	0.1	0.1	20	0.02	0.005–0.2	16
234678-HxCDF	19	0.3	0.01–4.3	28	0.1	0.001–0.1	0	–	–	0	–	–	15	0.02	0.006–0.1	18
123789-HxCDF	14	0.2	0.02–1.3	8	0.02	0.006–0.05	15	0.03	0.03–0.1	0	–	–	54	0.04	0.01–0.2	27
1234678-HpCDF	49	0.1	0.006–7.0	37	0.1	0.003–0.5	10	0.12	0.1–0.2	10	0.1	0.1	28	0.02	0.003–0.2	36
1234789-HpCDF	12	0.2	0.007–0.7	10	0.02	0.001–0.2	25	0.04	0.01–0.1	0	–	–	18	0.01	0.002–0.2	14
OCDF	33	0.3	0.009–3.6	17	0.1	0.001–1.0	20	0.10	0.03–0.6	0	–	–	33	0.04	0.008–0.4	27
2378-TCDD	13	0.03	0.002–0.2	13	0.001	0.001–0.05	10	0.02	0.02–0.02	0	–	–	22	0.02	0.005–0.06	16
12378-PeCDD	9	0.2	0.04–1.1	10	0.1	0.004–0.1	5	0.02	0.02	0	–	–	19	0.04	0.004–0.2	13
123478-HxCDD	12	0.1	0.005–0.7	17	0.05	0.005–0.2	10	0.05	0.02–0.1	0	–	–	12	0.02	0.006–0.1	12
123678-HxCDD	23	0.3	0.01–1.6	25	0.1	0.007–0.2	10	0.06	0.02–0.1	0	–	–	24	0.02	0.004–0.1	22
123789-HxCDD	20	0.1	0.02–1.1	23	0.1	0.003 – 0.2	5	0.1	0.1	0	–	–	16	0.02	0.005–0.2	18
1234678-HpCDD	62	0.3	0.008–10.6	53	0.3	0.005–1.0	70	0.09	0.1–0.3	80	0.2	0.2–0.3	50	0.03	0.01–0.3	57
OCDD	80	1.1	0.02–318.6	70	0.2	0.01–4.7	90	0.3	0.1–1.1	100	1.0	0.4–1.4	52	0.08	0.005–1.1	69
PCBs non-ortho																
PCB-77	93	2.2	0.2–30.3	87	0.5	0.05–17.0	85	0.9	0.3–1.2	100	9.1	7.4–11.0	97	3.3	$2.3\cdot10^{-6}$ – 93.3	77
PCB-81	67	0.5	0.03–14.2	42	0.2	0.007–11.7	55	0.2	0.2–0.3	100	1.1	0.9–1.4	84	1.4	0.03–21.4	69
PCB-126	41	0.9	0.05–21.7	47	1.4	0.02–2.5	15	0.1	0.1–0.2	70	0.7	0.4–0.9	91	2.6	0.05–37.1	60
PCB-169	42	0.4	0.04–5.6	27	0.6	0.3 – 1.0	10	0.2	0.1–0.2	30	1.0	1.0–1.1	86	1.0	0.05–25.1	53
PCBs mono-ortho																
PCB-105	98	17.5	1.4–374.8	100	31.2	0.3–74.7	100	3.0	1.9–6.6	100	55.3	30.4–65.4	100	53.9	0.8–1354.4	99
PCB-114	66	1.9	0.1–53.1	60	2.3	0.02–7.1	55	0.3	0.1–0.4	50	3.5	3.0–3.7	86	5.7	0.07–75.5	71
PCB-118	100	75.1	4.3–1547.2	100	97.9	1.1–263.9	100	7.9	4.3–17.9	100	152.7	76.7–178.6	100	177.7	2.4–5347.7	100
PCB-123	82	3.1	0.3–174.5	88	4.0	0.1–17.9	85	1.0	0.5–1.6	100	12.5	8.3–13.6	98	37.8	0.5–722.7	90
PCB-156	99	17.4	1.0–107.4	100	13.2	0.04 – 30.0	95	1.0	0.7–3.7	100	28.1	13.8–40.8	100	34.7	0.2–1247.1	99
PCB-157	89	3.5	0.2–28.3	58	3.2	0.02–6.6	50	0.3	0.1 – 1.0	100	3.6	1.9–4.4	94	12.4	0.06–359.1	83
PCB-167	95	5.6	0.2–78.6	85	7.4	0.03–18.2	85	0.9	0.5–2.1	100	16.3	7.5–25.2	99	32.4	0.2–1056.4	94
PCB-189	84	2.4	0.2–14.2	58	2.3	0.01–6.5	15	3.2	1.6–12.1	100	5.84	2.2–10.3	87	6.9	0.7–257.7	77

[a] ($pg\cdot g^{-1}$ lipid).
[b] ($pg\cdot g^{-1}$ ww).
[c] FD (Percentage samples > LOD).

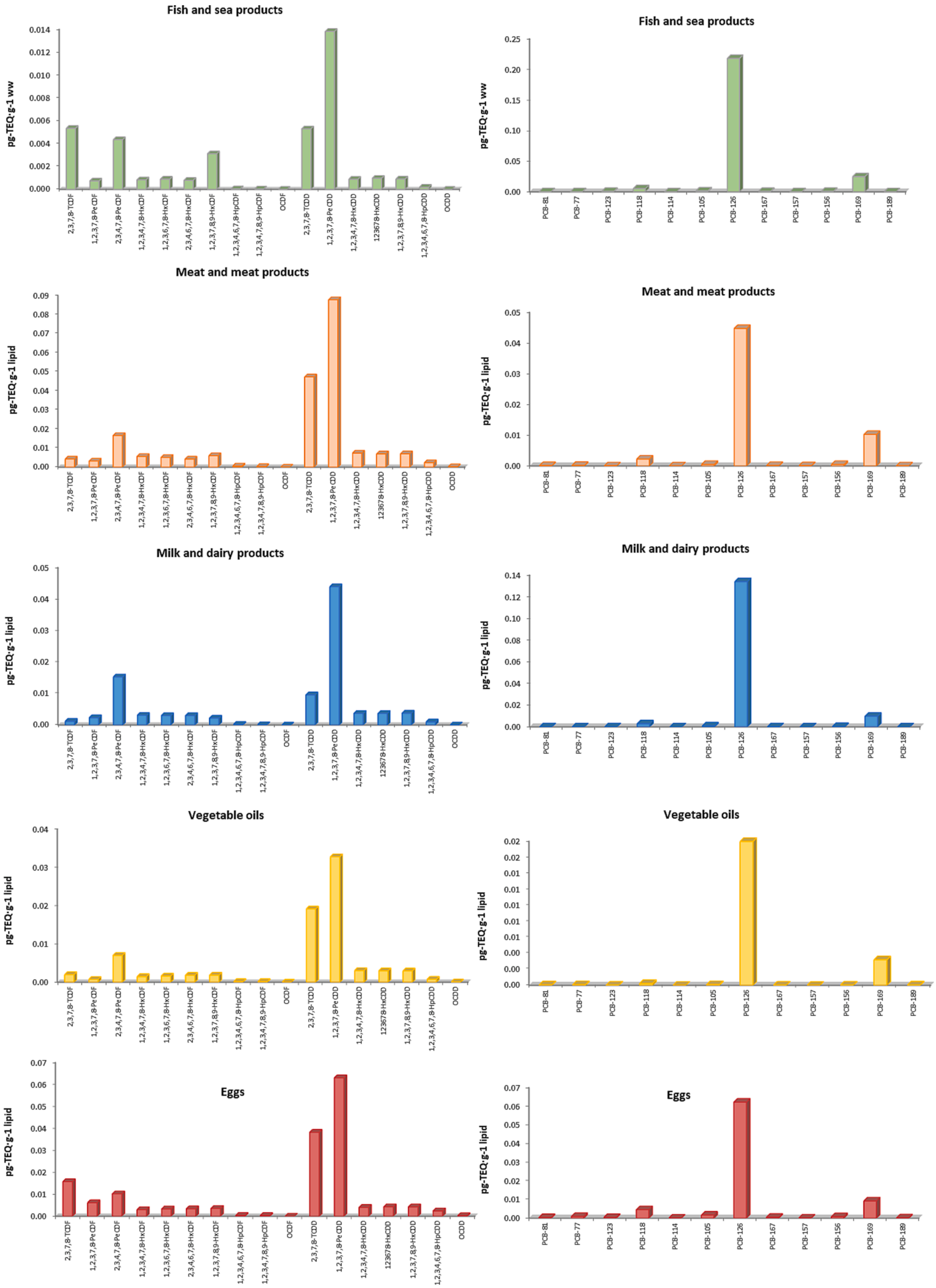

Fig. 1. Profiles of total pg-TEQ$_{2005}$ g^{-1} lipid (eggs, milk and dairy products, vegetable oils, meat and meat products) and pg-TEQ$_{2005}$ g^{-1} ww (fish and sea products) levels for each congener in all food groups.

Table 2
PCDD/Fs, dl-PCBs and PCDD/Fs + dl-PCBs concentrations (pg-TEQ_{2005} g^{-1}) corresponding to food groups (UB).

	∑PCDD/Fs			∑dl-PCBs			∑PCDD/Fs + dl-PCBs		
	Median	AM[a]	min - max	Median	AM[a]	min - max	Median	AM[a]	min - max
Concentrations expressed on fat basis									
Meat and meat products	0.2	0.4	0.008–4.5	0.06	0.1	0.004–2.4	0.3	0.6	0.02–6.8
Milk and dairy products	0.1	0.2	0.003–1.0	0.2	0.1	0.002–0.5	0.3	0.3	0.005–1.2
Vegetable oils	0.1	0.1	0.06–0.4	0.02	0.02	0.01–0.03	0.1	0.1	0.08–0.4
Eggs	0.2	0.2	0.09–0.2	0.1	0.1	0.06–0.1	0.2	0.3	0.2–0.3
Concentrations expressed on wet weight									
Fish and sea products	0.04	0.1	0.009–0.4	0.3	0.4	0.003–4.8	0.3	0.5	0.02–4.9
Meat and meat products	0.04	0.1	$2.7 \cdot 10^{-4} - 1.6$	0.01	0.02	0.001–0.08	0.05	0.1	0.004–1.6
Milk and dairy products	0.01	0.1	$3.1 \cdot 10^{-5} - 0.2$	0.006	0.05	$2.7 \cdot 10^{-6} - 0.2$	0.02	0.1	$6.8 \cdot 10^{-5} - 0.4$
Eggs	0.02	0.02	0.008–0.02	0.008	0.008	0.005–0.01	0.02	0.02	0.02–0.03

[a] *Arithmetic Mean.*

found in the European Survey carried out by EFSA in 2012. On the other hand, PCDD/Fs and dl-PCBs levels obtained in this study were two times above than the levels detected in Chinese markets (Sun et al., 2021).

Meat and meat products PCDD/Fs and dl-PCBs concentrations were 40 % lower than levels showed by Marin et al. (2011) in the same assessed region, four times lower than the obtained levels in the survey of dietary exposure for PCDD/Fs and dl-PCBs carried out by EFSA in 2012 around Europe, and two times lower than concentrations reported by Sun et al. (2021) in China. Additionally, levels in this study were five times higher than the study of dietary exposure carried out in Catalonia in 2008.

Looking at the study by Xu and Cai (2015), in the sum of PCDD/Fs and dl-PCBs, similar levels were found for fish and vegetable oils but the mean values for meat are higher than in this work. However, the biggest differences are found for eggs and dairy products, with concentrations 10 and 3 times higher than in this study, respectively.

Sirot et al. (2012) showed results for fish and eggs very similar to this study. For meat, however, the value was almost 3 times smaller than this work. In addition, a different pattern regarding to fish was found in the article published by Stadion et al. (2022) with concentrations twice higher as in this study.

It should be noted that when comparing the results described by Quijano et al. (2018) using the CALUX bioassay and this study through GC-HRMS system for the same analysed samples, the obtained levels are 2 or 3 times lower for fish and sea products, milk and dairy products and eggs using the latter technique. Therefore, this general decrease of the concentrations in the studied matrices could be due to the over-estimation of the CALUX analytical method.

3.4. Estimate of dietary exposure to PCDD/Fs and dl-PCBs

The estimated weekly intake (EWI) among adults and young people in the LB and UB scenarios are presented in Table 3. Using the worst-case scenario (UB), average EWI of ∑PCDD/Fs + dl-PCBs was 1.8 pg TEQ kg^{-1} bw $week^{-1}$ and 3.4 pg TEQ kg^{-1} bw $week^{-1}$ for adults and children, respectively.

Table 3
Estimation of the PCDD/Fs + dl-PCBs dietary intake (pg TEQ kg^{-1} bw $week^{-1}$).

	UB		LB	
	Adults	Young people	Adults	Young people
Minimum	0.0	0.1	0.0	0.03
P25	0.5	1.0	0.1	0.3
Median	0.9	1.7	0.3	0.5
Mean	1.8	3.4	1.1	1.7
P75	1.6	3.4	0.6	1.0
Maximum	30.4	32.5	29.1	28.0
P90	3.2	7.4	1.8	3.5
P95	6.7	11.4	4.8	8.7
P99	16.2	27.2	14.7	23.8
SD	3.1	4.9	2.9	4.1

On the other hand, the contribution of the different foodstuffs for adults and children can be found in Fig. 2 and Table SD-4. As can be seen, the consumption of fish and sea products accounted for half of the dietary exposure in adults, while the other food groups together (meat and meat products (24 %), fats and oils (13 %), milk and dairy products (9 %) and eggs (3 %)) contributed the other half. In contrast, children exposure was mainly caused by fish and sea products (37 %) and meat and meat products (35 %), contributing more than 70 % of the total dietary exposure. Fats and oils, milk and dairy products and eggs contributed with 13, 12 and 3 % of the total dietary exposure, respectively.

The EWI for adults in this study was ten times lower than those reported by Marin et al. (2011) in the same assessed population. Furthermore, the EWI was significantly lower than the obtained by EFSA around Europe (EFSA, 2012), four times lower than the obtained exposure in other Mediterranean territory like Catalonia in 2008 and Hong-Kong (EDT Catalunya, 2008; Xu and Cai, 2015) and almost three times lower than the obtained in France by Sirot et al. (2012). On the other hand, the estimated dietary intake in our study was slightly higher than the calculated in Italy by Barone et al. (2019) (only for meet food) and China by Sun et al. (2021).

Regarding children intake, the estimated intake was two times lower than the calculated in Europe (EFSA, 2012) and in France by Sirot et al. (2012). Furthermore, the calculated exposure was ten times lower than the calculated exposure for the same assessed population by Marin et al. (2011) (see Table SD-5).

Comparing the exposure in this study using GC-HRMS with the obtained exposure in the analysis of the same assessed samples by Quijano et al. (2018) using CALUX, the calculated EWI was 6 times lower than the previously reported, showing the overestimation of the CALUX procedure.

3.5. Risk assessment

Table 4 shows the percentage of the population exceeding the guide value in two cases, considering as reference values: a) 14 pg kg^{-1} bw per week (established value by SCF during sampling campaign) and b) 2 pg kg^{-1} bw per week (updated value in 2018 by EFSA), respectively. A clear difference can be observed between the two cases, where the percentage of population exceeding the most restrictive guideline value (EFSA et al., 2018) is noticeably higher, being 19 % in adults and 43 % in children in the UB approach. The percentage of the population exceeding the value of 14 pg kg^{-1} bw per week in the study by Quijano et al. (2018) was 22 % and 59 % in adults and young people, respectively. These values are much higher than those reported in the present study, considering that the same samples were analysed. This raises doubts about the reliability of the CALUX method for the quantitative analysis of PCDD/Fs and dl-PCBs and its overestimation of the results, probably caused by the potential detection of other compounds with aryl hydrocarbon receptor

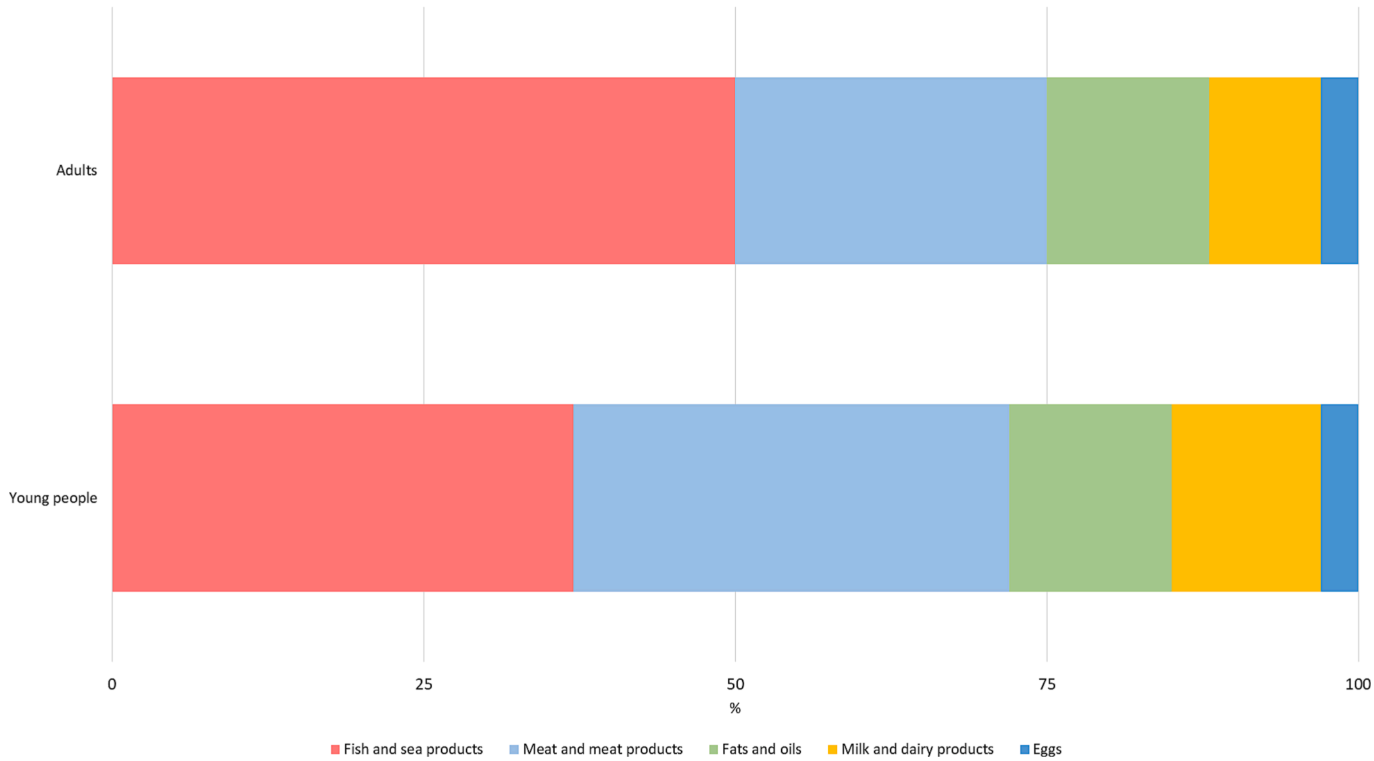

Fig. 2. Percentage of PCDD/Fs + dl-PCBs exposure due to each food group considering the UB approach.

Table 4
Percentage of population exceeding the health-based guideline value set by EFSA.

(a) Using 14 pg kg^{-1} bw per week (Imposed in 2001)		
	Adults (%)	Children (%)
UB	2	4
LB	1	3

(b) Using 2 pg kg^{-1} bw per week (Imposed in 2018)		
	Adults (%)	Children (%)
UB	19	43
LB	9	17

(AhR) affinity.

4. Conclusions

The use of the GC-HRMS has allowed to obtain the most abundant congeners in each group of food samples and to obtain precise levels of PCDD/Fs and dl-PCBs comparing to the previous results reported in the same assessed samples and to observe the congener profiles for PCDD/Fs and dl-PCBs in each type of food. Additionally, this study provides information about a possible overestimation of the results when CALUX bioassay is employed.

In the present study, meat and meat products and fish and sea products presented the highest content of ∑PCDD/Fs + dl-PCBs (mean values 0.6 pg TEQ g^{-1} lipid and 0.5 pg TEQ g^{-1} ww, respectively), been 12378-PeCDD and PCB-126 the largest contributors.

Fish and sea products were the main contributors to adults' intake, taking into account that half of the PCDD/Fs and dl-PCBs exposure is related to the intake of this group of food. However, meat and meat products and fish and sea products contributed more than 70 % of the PCDD/Fs and dl-PCBs exposure in children.

Likewise, the mean of the EWI for children (3.4 pg TEQ kg^{-1} bw w^{-1}) was higher than the guideline value set by EFSA in 2018 (2 pg TEQ kg^{-1} bw w^{-1}), in view of these results it is possible that the 43 % of the assessed children population may exceed the guideline value. In the case of adults, 19 % could be exceeding the guideline value.

Taking into account the reported results and considering risk characterisation, it would be interesting to continue investigating the temporal trends of PCDD/Fs and dl-PCBs exposure in the studied population considering the updates of the health-based guideline values.

CRediT authorship contribution statement

Iñaki Lacomba: Methodology, Validation, Resources, Writing – original draft. **Cristina Socas-Hernández:** Methodology, Validation, Resources, Writing – original draft. **Antonio López:** Supervision, Writing – review & editing. **Olga Pardo:** Conceptualization, Supervision, Writing – review & editing. **Vicent Yusà:** Conceptualization, Writing – review & editing. **María Isabel Beser:** Validation, Resources, Supervision, Writing – review & editing. **Silvia Marín:** Writing – review & editing. **Pilar Villalba:** Writing – review & editing. **Clara Coscollà:** Conceptualization, Supervision, Writing – review & editing.

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.foodres.2023.113839.

References

Barone, G., Storelli, A., Quaglia, N. C., Dambrosio, A., Garofalo, R., Chiumarulo, R., & Storelli, M. M. (2019). Dioxin and PCB residues in meats from Italy: Consumer dietary exposure. *Food and Chemical Toxicology: An International Journal Published for the British Industrial Biological Research Association, 133*(110717), Article 110717. https://doi.org/10.1016/j.fct.2019.110717

Canlı, O., Guzel, B., & Karademır, A. (2022). Determination of PCDD/F and DL-PCB pollution levels, source appointment and risk assessment of surface sediments in dam lakes in Istanbul, Türkiye. *Environmental Science and Pollution Research International, 29*(60), 90923–90935. https://doi.org/10.1007/s11356-022-22244-0

Castells V, Vicente E, Gómez J, Llobet J, Perelló G, Domingo JL. (2012). *Contaminantes químicos. Estudio de dieta total en Cataluña 2008; (Accessed 18 september 2023), from* https://acsa.gencat.cat/web/.content/_Publicacions/Estudis_de_dieta_total/contaminants_quimics/EDT_Contaminants_2008/EDT_Contaminants-2008_Castella.pdf.

EFSA Panel on Contaminants in the Food Chain (CONTAM), Knutsen, H. K., Alexander, J., Barregård, L., Bignami, M., Brüschweiler, B., Ceccatelli, S., Cottrill, B., Dinovi, M., Edler, L., Grasl-Kraupp, B., Hogstrand, C., Nebbia, C. S., Oswald, I. P., Petersen, A., Rose, M., Roudot, A.-C., Schwerdtle, T., Vleminckx, C., … Hoogenboom, L. (ron). (2018). Risk for animal and human health related to the presence of dioxins and dioxin-like PCBs in feed and food. *EFSA Journal*, *16*(11). Doi: 10.2903/j.efsa.2018.5333.

European Commission. (2017). *Commission Regulation (EU) N° 2017/644 of 5 April 2017 laying down methods of sampling and analysis for the control of levels of dioxins, dioxin-like PCBs and non-dioxin-like PCBs in certain foodstuffs and repealing Regulation (EU) No 589/2014*. Off. J. Eur. Union L 92/9.

European Food Safety Authority. (2012). Update of the monitoring of levels of dioxins and PCBs in food and feed. *EFSA Journal*, *10*(7). Doi: 10.2903/j.efsa.2012.2832.

Fullana AM, Jimenez R, Marín S, Ramón R, Quiles J, Rizk J,Zubeldia L. (2010). General Directorate of Public Health. Nutrition survey in the Valencia region 2010-2011. 1ª ed. Valencia: Generalitat Valenciana. Conselleria de Sanitat. ISBN 978-84-482-5866-5.

Grešner, P., Zieliński, M., Ligocka, D., Polańska, K., Wąsowicz, W., & Gromadzińska, J. (2021). Environmental exposure to persistent organic pollutants measured in breast milk of lactating women from an urban area in central Poland. *Environmental Science and Pollution Research International, 28*(4), 4549–4557. https://doi.org/10.1007/s11356-020-10767-3

Güzel, B., Canli, O., Dede, Ş., & Karademir, A. (2020). Assessment of PCDD/F and dioxin-like PCB levels in environmental and food samples in the vicinity of IZAYDAS waste incinerator plant (WIP): From past to present. *Environmental Science and Pollution Research International, 27*(12), 13902–13914. https://doi.org/10.1007/s11356-020-07995-y

Güzel, B., Canlı, O., & Çelebi, A. (2022). Characterization, source and risk assessments of sediment contaminants (PCDD/Fs, DL-PCBs, PAHs, PCBs, OCPs, metals) in the urban water supply area. *Applied Geochemistry: Journal of the International Association of Geochemistry and Cosmochemistry, 143*(105394), Article 105394. https://doi.org/10.1016/j.apgeochem.2022.105394

Hernández, C. S., Pardo, O., Corpas-Burgos, F., Fernández, S. F., López, A., Coscollà, C., Vento, M., & Yusà, V. (2020). Biomonitoring of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (dl-PCBs) in human milk: Exposure and risk assessment for lactating mothers and breastfed children from Spain. *The Science of the Total Environment, 744* (140710), Article 140710. https://doi.org/10.1016/j.scitotenv.2020.140710

IARC. (2012). *A review of human carcinogens. F. Chemical agents and related occupations: IARC Monographs on the Evaluation of Carcinogenic Risks to Humans*. 100, 9-562. International Agency for Research on Cancer.

IARC. (2016). Polychlorinated biphenyls and polybrominated biphenyls. *Monographs on the Carcinogenic Risk of Chemicals to Humans*. 107, 9-500. International Agency for Research on Cancer.

Kanan, S., & Samara, F. (2018). Dioxins and furans: A review from chemical and environmental perspectives. *Trends in Environmental Analytical Chemistry*, *17*, 1–13. Doi: 10.1016/j.teac.2017.12.001.

López, A., Coscollà, C., Hernández, C. S., Pardo, O., & Yusà, V. (2021). Dioxins and dioxin-like PCBs in the ambient air of the Valencian Region (Spain): Levels, human exposure, and risk assessment. *Chemosphere, 267*(128902), Article 128902. https://doi.org/10.1016/j.chemosphere.2020.128902

Marin, S., Villalba, P., Diaz-Ferrero, J., Font, G., & Yusà, V. (2011). Congener profile, occurrence and estimated dietary intake of dioxins and dioxin-like PCBs in foods marketed in the Region of Valencia (Spain). *Chemosphere, 82*(9), 1253–1261. https://doi.org/10.1016/j.chemosphere.2010.12.033

Quijano, L., Marín, S., Millan, E., Yusà, V., Font, G., & Pardo, O. (2018). Dietary exposure and risk assessment of polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and dioxin-like polychlorinated biphenyls of the population in the Region of Valencia (Spain). Food Additives & Contaminants. Part A, Chemistry, Analysis, Control, Exposure & Risk. *Assessment, 35*(4), 741–750. https://doi.org/10.1080/19440049.2017.1414960

Reiner, E. J. (2016). Analysis of dioxin and dioxin-like compounds. In *The Handbook of Environmental Chemistry* (pp. 51–94). Springer International Publishing.

SCF, Scientific Committee on Food. (2001). *Opinion of the Scientific Committee on Food on the risk assessment of dioxins and dioxin-like PCBs in food. Update based on new scientific information available since the adoption of the SCF opinion of 22nd November 2000 (adopted on 30 May 2001)*. http://ec.europa.eu/food/fs/sc/scf/out90_en.pdf.

Shen, H., Guan, R., Ding, G., Chen, Q., Lou, X., Chen, Z., Zhang, L., Xing, M., Han, J., & Wu, Y. (2017). Polychlorinated dibenzo-p-dioxins/furans (PCDD/Fs) and polychlorinated biphenyls (PCBs) in Zhejiang foods (2006–2015): Market basket and polluted areas. *The Science of the Total Environment, 574*, 120–127. https://doi.org/10.1016/j.scitotenv.2016.09.038

Sirot, V., Tard, A., Venisseau, A., Brosseaud, A., Marchand, P., Le Bizec, B., & Leblanc, J.-C. (2012). Dietary exposure to polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and polychlorinated biphenyls of the French population: Results of the second French Total Diet Study. *Chemosphere, 88*(4), 492–500. https://doi.org/10.1016/j.chemosphere.2012.03.004

Ssebugere, P., Sillanpää, M., Matovu, H., & Mubiru, E. (2019). Human and environmental exposure to PCDD/Fs and dioxin-like PCBs in Africa: A review. *Chemosphere, 223*, 483–493. https://doi.org/10.1016/j.chemosphere.2019.02.065

Stadion, M., Hackethal, C., Blume, K., Wobst, B., Abraham, K., Fechner, C., Lindtner, O., & Sarvan, I. (2022). The first German total diet study (BfR MEAL Study) confirms highest levels of dioxins and dioxin-like polychlorinated biphenyls in foods of animal origin. *Food Chemistry: X, 16*(100459), Article 100459. https://doi.org/10.1016/j.fochx.2022.100459

Sun, S., Cao, R., Lu, X., Zhang, Y., Gao, Y., Chen, J., & Zhang, H. (2021). Levels and patterns of polychlorinated dibenzo-p-dioxins and dibenzofurans and polychlorinated biphenyls in foodstuffs of animal origin from Chinese markets and implications of dietary exposure. *Environmental Pollution (Barking, Essex: 1987)*, *273* (116344), 116344. Doi: 10.1016/j.envpol.2020.116344.

United Nations Environment Programme. (2009). *Stockholm Convention on Persistent Organic Pollutants (POPs) as amended in 2009: Text and annexes*. https://wedocs.unep.org/20.500.11822/27568.

Xu, W., & Cai, Z. (2015). Risk assessment of dietary exposure to PCDD/Fs, DL-PCBs and NDL-PCBs of Hong Kong resident. *Science China. Chemistry, 58*(6), 1082–1088. https://doi.org/10.1007/s11426-014-5309-2