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Polychlorinated dibenzo-p-dioxins, dibenzofurans and dioxin-like polychlorinated biphenyls in bivalve molluscs. Risk to Polish consumers?

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Abstract

Introduction: Concentrations of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) and dioxin-like polychlorinated biphenyls (DL-PCBs) were investigated in six species of bivalve mollusc purchased on the Polish retail market. The risk to consumers was calculated as a percentage of the tolerable weekly intake (TWI) (2 pg World Health Organization toxic equivalent (WHO-TEQ) kg^{-1} body weight (b.w.)). **Material and Methods:** Altogether 32 samples were analysed using an isotope dilution technique with high resolution gas chromatography coupled with high resolution mass spectrometry. **Results:** Low levels of all analysed compounds were found. The range of PCDD/Fs was 0.08–0.37 pg WHO-TEQ g^{-1} of wet weight (w.w.) and 0.04–0.41 pg WHO-TEQ g^{-1} w.w. for DL-PCBs. The highest concentrations of all analysed compounds were found in Pacific oysters, at 0.30 pg WHO-TEQ g^{-1} w.w. for the sum of PCDD/Fs and 0.19 pg WHO-TEQ g^{-1} for the sum of DL-PCBs. These concentrations were 2–4 times higher than those detected in the other analysed mollusc species. Different species-dependent congener profiles were observed for PCDD/F concentrations, while PCB congener concentration profiles were species independent. The risk to consumers was assessed relating theoretical intakes of PCDD/Fs and DL-PCBs per 25, 50 and 100 g of consumption of molluscs per week to the TWI. **Conclusion:** Taking into account the low consumption of molluscs in Poland and low concentrations of analysed compounds, neither adults nor children are likely to exceed the TWI by ingestion of food in this category.

Keywords: dioxins, PCBs, bivalve molluscs, risk.

Introduction

Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) and dioxin-like polychlorinated biphenyls (DL-PCBs) are compounds that belong to the group of persistent organic pollutants (POPs). PCDD/Fs have never been produced intentionally but are released into the environment during combustion processes and as by-products of various manufacturing activities (paper whitening; production of pesticides, herbicides, and fungicides; iron smelting; and cement kilning) (2, 15, 19). Also natural release from forest fires and volcanic eruptions can be their sources (8). In contrast, PCBs were manufactured from 1929 to the late 1980s and used in heat exchangers and as hydraulic fluids, lubricants, plasticizers in plastics and paint fillers (34). Air transport is considered the main route for the spread of PCDD/Fs and PCBs, even over long distances, and precipitation causes their deposition on the soil surface and introduces them into water bodies (16, 21). Solid particles suspended in water bind to PCDD/Fs and PCBs because of the hydrophobic nature of the chlorinated compounds and they descend to the bottom sediments (1, 37), becoming a source of these toxic substances for aquatic organisms. Their omnipresence, bioaccumulative ability, persistence and toxicity to humans and wildlife (34) necessitate the constant monitoring of these compounds in the food chain. The possibility of PCDD/F and DL-PCB bioaccumulation in bivalve molluscs has been reported by other authors (14, 20, 32, 35). Bioaccumulation occurs while feeding, when molluscs filter nutrients from seawater and absorb PCDD/Fs and DL-PCBs, which they are unable to metabolise and which they excrete very slowly (14). No studies on the

exposure of bivalve mollusc consumers to toxic PCDD/Fs and DL-PCBs have been conducted in Poland. In 2018, the European Food Safety Authority (EFSA) decided to reassess the tolerable weekly intake (TWI) of PCDD/Fs and DL-PCBs and reduced the tolerable dose sevenfold to 2 pg World Health Organization toxic equivalent (WHO-TEQ) kg^{-1} b.w. (12). Such a low TWI value means that the consumption of products which even meet the acceptable limits may result in exceedance of the TWI. Bearing in mind this, the increased interest of consumers in bivalve molluscs and the lack of data in Poland, the authors were prompted to undertake research to assess PCDD/F and DL-PCB concentrations in food of this type available on the Polish retail market and to conduct an assessment of the potential risk for consumers in relation to the new TWI.

Material and Methods

Sampling and sample collection. Altogether 32 samples of six species of molluscs were collected, comprising five dog cockles (*Glycymeris glycymeris*), five Manila clams (*Ruditapes philippinarum*), five Atlantic jackknife clams (*Ensis directus*), ten blue mussels (*Mytilus edulis*), five Pacific oysters (*Crassostrea gigas*) and two common cockles (*Cardium edule*). Frozen samples were taken randomly from retail markets and immediately shipped to the National Reference Laboratory for Halogenated Compounds at the National Veterinary Research Institute. The molluscs were caught in the North Sea, Atlantic Ocean and Mediterranean Sea.

Analytes of interest. The following analytes were investigated: seven 2,3,7,8-substituted PCDDs (2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), 1,2,3,7,8-pentachlorodibenzo-p-dioxin (PeCDD), 1,2,3,4,7,8-hexachlorodibenzo-p-dioxin (HxCDD), 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin (HpCDD) and octachlorodibenzo-p-dioxin (OCDD)), ten 2,3,7,8-substituted PCDFs (2,3,7,8-tetrachlorodibenzofuran (TCDF), 1,2,3,7,8-pentachlorodibenzofuran (PeCDF), 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-hexachlorodibenzofuran (HxCDF), 1,2,3,6,7,8-HxCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 1,2,3,4,6,7,8-heptachlorodibenzofuran (HpCDF), 1,2,3,4,7,8,9-HpCDF and octachlorodibenzofuran (OCDF), and twelve DL-PCBs (PCB 77, PCB 81, PCB 126, PCB 169, PCB 105, PCB 114, PCB 118, PCB 123, PCB 156, PCB 157, PCB 167 and PCB 189).

Standards and reference materials. The concentrations of $^{13}C_{12}$-labelled internal standards were 25 pg mL^{-1} and 400 pg mL^{-1} for PCDD/F and DL-PCB congeners, respectively. The recovery control $^{13}C_{12}$-labelled standards concentration was 25 pg mL^{-1} for 1,2,3,4-TCDD (PCDD/F fraction) and 400 pg mL^{-1} for PCB 111 (PCB fraction). As a reference material T-0645–fish oil was used (FAPAS, Fera Science, Sand Hutton, UK).

Reagents and chemicals. Dichloromethane, toluene, n-hexane and n-nonane were supplied by LGC Standards (Wesel, Germany). Sodium sulphate and 98% ACS grade sulphuric acid were purchased from Merck (Darmstadt, Germany), and diatomaceous earth from Restek (Bellefonte, PA, USA). Helium (purity 99.9999%) and nitrogen (99.999%) were sourced from Messer (Gumpoldskirchen, Austria). All of the organic solvents were of suitable purity for the residue analysis. All standards were purchased from the Cambridge Isotope Laboratory (Andover, MA, USA) or Wellington Laboratories Inc. (Ontario, Canada). Ready-made columns for sample purification (silica PCB-HCDS-ACD-TFC, silica PCBS-ABN-STD, alumina PCBA-BAS-011 and carbon PCBC-CCE-034) were supplied from Fluid Management Systems (Billerica, MA, USA).

Sample preparation, extraction and purification. After homogenisation, samples were freeze dried. Before pressurised liquid extraction (Fluid Management Systems) samples were spiked with $^{13}C_{12}$-internally labelled standards. A mixture of dichloromethane/hexane (50/50, v/v) was used for extraction under high pressure (10 bar) at 120°C. The next step was purification carried out using an automated Power Prep sample preparation system (Fluid Management Systems). After fat removal with silica gel in the first two columns, the extract was subjected to fractionation in the activated alumina and carbon columns. Two fractions were collected. The first (including the 8 DL-PCB congeners 105, 114, 118, 123, 156, 157, 167 and 189) was eluted from the alumina using hexane/dichloromethane (98:2, v/v) and hexane/dichloromethane (1:1, v/v) and from the carbon with ethyl acetate/toluene (1:1, v/v) and hexane. To elute the second fraction from the carbon column (comprising all 2,3,7,8-PCDD/F and the 4 DL-PCB congeners 77, 81, 126 and 169), toluene was used. Before instrumental analysis, internal recovery standards were added to the fractions.

Instrumental analysis. High-resolution gas chromatography coupled with high-resolution mass spectrometry was used for detection and the apparatus was an Ultra Trace GC gas chromatograph, TriPlus autosampler, and DFS dual-focusing mass spectrometer (Thermo Scientific, Bremen, Germany). Positive electron ionisation operating in selected-ion monitoring mode at a resolution of 10,000 was employed. Chromatographic separation was carried out in a DB-5 MS fused-silica capillary column (60 m × 0.25 mm × 0.1 mm). The limits of quantification (LOQs) were 0.01–0.12 pg g^{-1} w.w. for PCDD/Fs and 0.09–1.16 pg g^{-1} w.w for DL-PCBs. Estimation of the LOQs of individual congeners was performed in accordance with the European Commission Joint Research Centre's Guidance Document on the Estimation of LOD and LOQ for Measurements in the Field of Contaminants in Feed and Food (11).

Quality assurance and quality control. Blank samples and reference material were analysed in every series of samples. The trueness for the reference material analysis ranged between −20% and +20% and the recoveries of the internal standards ranged between 60% and 120% in all samples, which met the criteria set out

in European Commission Regulation 2017/644/EU (10). The method performance was verified by successful participation in the proficiency testing (PT study) organised by the European Union Reference Laboratory for Halogenated Persistent Organic Pollutants in Feed and Food (Freiburg, Germany).

Results presentation. Results are presented as a TEQ, which is calculated using the following equation:

$$TEQ = \sum_{i=1}^{7}(PCDD_i \times TEF_i) + \sum_{j=1}^{10}(PCDF_j \times TEF_j) + \sum_{k=1}^{12}(PCB_k \times TEF_k)$$

World Health Organization toxic equivalency factors (TEF) were established by Van den Berg (41). World Health Organization toxicity equivalents were expressed as upper-bound concentrations (all values of the congeners below LOQ were equal to their LOQ). In accordance with European Commission Regulation 1259/2011/EU results are expressed on a wet weight basis (9).

Dietary intake. Since there are no data regarding average consumption of bivalve molluscs in Poland, three weekly intake levels were assumed: 25 g, 50 g and 100 g. The calculations were performed for an adult of 70 kg body weight and 3–10-year-old children of average 23.1 kg body weight (13). To characterise the potential health risk associated with the intake of dioxins and DL-PCBs, the doses ingested with molluscs were expressed as a percentage of the TWI established by the EFSA (2 pg WHO-TEQ kg^{-1} b.w.).

Results

Levels of PCDD/Fs and PCBs in bivalve molluscs. The content of PCDD/Fs and PCBs in bivalve molluscs is summarised in Table 1. All samples were compliant with Commission Regulation 1259/2011/EU, which sets the maximum levels for PCDD/Fs and DL-PCBs in foodstuffs at 3.5 pg WHO-TEQ g^{-1} w.w. for PCDD/Fs and 6.5 pg WHO-TEQ g^{-1} w.w. for PCDD/Fs/DL-PCBs (9). The highest mean concentrations of all three groups of analysed compounds were found to be in the Pacific oyster. The mean concentration of PCDD/Fs of 0.30 pg WHO-TEQ g^{-1} w.w. was almost twelve times lower than the maximum level but twice as high as in blue mussels and around three times higher than in the remaining species. The mean level of DL-PCBs in Pacific oysters of 0.19 pg WHO-TEQ g^{-1} w.w. was also considerably higher than those in other species. The sum contents of PCDD/Fs and DL-PCBs were severalfold lower than the limit in all samples (Table 1).

Congener profiles in bivalve molluscs. Three different profiles of PCDD/Fs were identified (Fig. 1). In the first type of profile which was observed in dog cockles and Manila clams, OCDD and 2,3,7,8-TCDF dominated, but concentrations were very low at a respective 0.16 pg g^{-1} w.w and 0.07 pg g^{-1} w.w. in dog cockles and 0.23 pg g^{-1-1} w.w and 0.16 pg g^{-1} w.w. in Manila clams. The second congener profile was observed in Atlantic jackknife clams, blue mussels and common cockles. In these species, apart from the dominant congeners (OCDD and 2,3,7,8-TCDF), 1,2,3,4,7,8,9-HpCDF and 1,2,3,4,6,7,8-HpCDD were also present. These congeners were at concentrations many times higher than in dog cockles and Manila clams. Because OCDD, 1,2,3,4,7,8,9-HpCDF and 1,2,3,4,6,7,8-HpCDD have lower TEF values (0.0003, 0.01 and 0.01, respectively) they are less important from a toxicological point of view. The 2,3,7,8-TCDF (TEF 0.1) and 2,3,4,7,8-PeCDF (TEF 0.3) congeners are more important, and these were the dominant congeners in Pacific oysters. The mean level of 2,3,4,7,8-PeCDF in Pacific oysters of 0.28 pg g^{-1} w.w was 2–5-fold higher than in other species except dog cockles, in which it was not detected. The most toxic congeners, with TEF = 1 (2,3,7,8-TCDD and 1,2,3,7,8-PeCDD), were not detected in any samples of dog cockles or Manila clams. The following PCDD/Fs congeners were not found in any of the 32 analysed samples: 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF and 1,2,3,4,7,8,9-HpCDF.

The profiles of DL-PCBs were alike in all species, and PCB 118 were found to be most abundant (Fig. 1). Its concentrations ranged from 7.6 pg g^{-1} w.w. in dog cockles to 664.5 pg g^{-1-1} w.w. in blue mussels. This compound has very low toxic potential and its TEF is 0.00003. The congener with the highest TEF of all DL-PCBs, PCB 126 with 0.1, was detected in all Atlantic jackknife clam, blue mussel, Pacific oyster and common cockle samples. The highest mean concentration in Pacific oysters was 1.68 pg g^{-1} w.w. Polychlorinated biphenyl 169 was not present in any sample.

Dietary intake. Dietary intake of PCDD/Fs and DL-PCBs *via* one assumed weekly serving for adults was from 0.05 to 0.7 pg WHO-TEQ kg^{-1} b.w. Consumption of the 25 g serving led to intake below 4% of the TWI and eating the 100 g serving exposed the individual to below 16% of the TWI (Fig. 2). The maximum PCDD/F and DL-PCB amounts were ingested *via* Pacific oysters.

Higher exposure was noticed for children: from 0.14 to 2.12 pg WHO-TEQ kg^{-1} b.w. This corresponds to intake of 3–48% of the TWI. The highest exposure was from consumption of Pacific oysters; nevertheless, it did not result in the TWI being exceeded. It should be noted that this calculation does not take into account other consumed food commodities which may also contain PCDD/Fs and DL-PCBs, such as fish, eggs, milk or meat (22, 24, 26, 28, 29, 43). However, bearing in mind the low consumption of bivalve molluscs in Poland, especially by children, they should not be of concern as sources of PCDD/F and DL-PCB exposure.

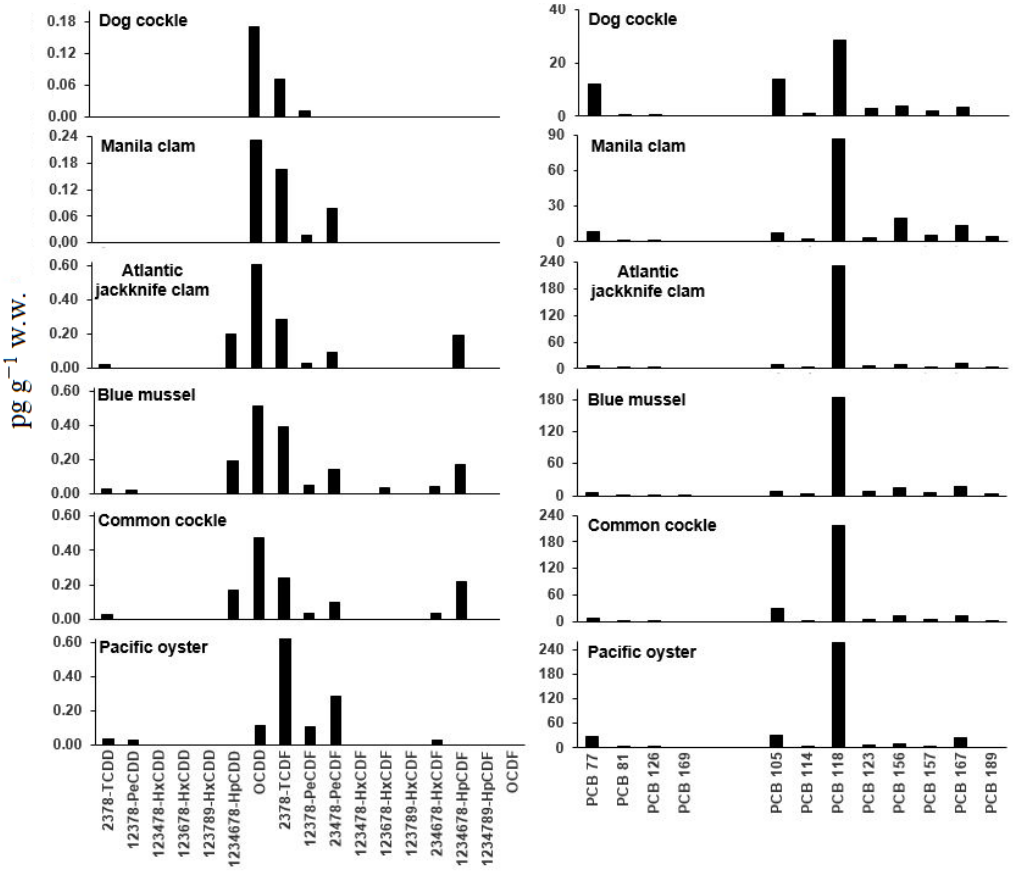

Fig. 1. Comparison of the polychlorinated dibenzo-p-dioxin, polychlorinated dibenzofuran and dioxin-like polychlorinated biphenyl (PCB) congener profiles in different bivalve mollusc species

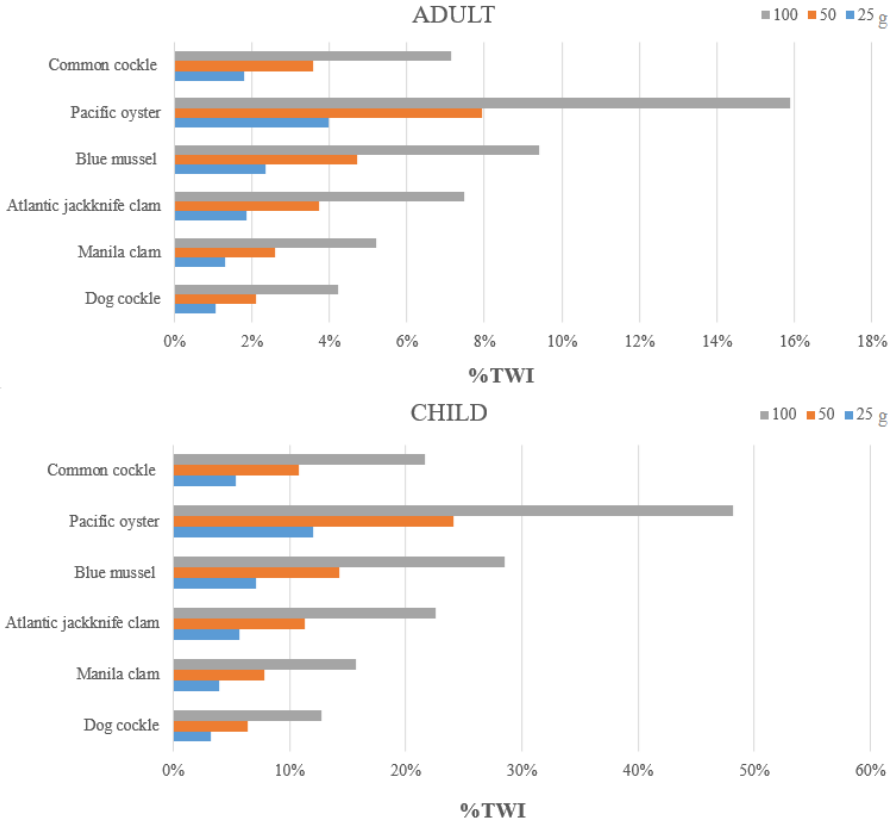

Fig. 2. Estimated intake of polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and dioxin-like polychlorinated biphenyls with weekly consumption of 25 g, 50 g, and 100 g of bivalve molluscs, expressed as % of TWI

Table 1. Concentrations of PCDD/Fs and DL-PCBs (x ± SD and range) in bivalve molluscs

Species	pg WHO-TEQ g^{-1} w.w.		
	PCDD/Fs	DL-PCBs	PCDD/Fs/DL-PCBs
Dog cockle	0.09 ± 0.01	0.05 ± 0.01	0.13 ± 0.01
	0.08–0.10	0.04–0.06	0.13–0.16
Manila clam	0.10 ± 0.01	0.06 ± 0.02	0.16 ± 0.02
	0.09–0.10	0.05–0.09	0.14–0.19
Atlantic jackknife clam	0.12 ± 0.02	0.11 ± 0.01	0.23 ± 0.02
	0.10–0.15	0.10–0.12	0.21–0.26
Blue mussel	0.15 ± 0.08	0.14 ± 0.12	0.29 ± 0.20
	0.09–0.33	0.05–0.41	0.13–0.74
Pacific oyster	0.30 ± 0.07	0.19 ± 0.03	0.49 ± 0.08
	0.23–0.37	0.16–0.21	0.44–0.58
Common cockle	0.12 ± 0.04	0.11 ± 0.08	0.22 ± 0.07
	0.09–0.14	0.08–0.13	0.17–0.27
Maximum levels (under Regulation 1259/2011/EU)	3.50	–	6.50

WHO-TEQ – World Health Organization toxic equivalent; PCDD/Fs – polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans; DL-PCBs – dioxin-like polychlorinated biphenyls

Discussion

Molluscs are a valuable food product because of their properties. They are a source of n-3 polyunsaturated long-chain fatty acids, have high calorie content, and are rich in protein, nutrients and vitamins (A, B12, D and E and taurine (2-aminoethanesulfonic acid)) (25). Unfortunately their propensity to bioaccumulate PCDD/Fs and DL-PCBs make them potential sources of these toxic compounds for consumers. The intensive human activity during the last few decades has had a significant impact on the marine environment and led to the introduction of toxic xenobiotics even into waters distant from emission sources. Since molluscs have the potential for bioaccumulation of POPs, they are commonly used as pollution indicators (14). The bivalve molluscs presented in this paper generally contained low levels of PCDD/Fs and PCBs. Orders of magnitude higher concentrations were reported in molluscs from polluted areas of the Venetian Lagoon (33, 35). Concentrations both similar to those in our results and twice as high were found in molluscs caught along the Scottish coast (14). Severalfold higher levels (up to 2.11 pg WHO-TEQ g^{-1} w.w.) were detected in molluscs from the Spanish Atlantic coast (4).

Analysis of the profiles of dioxins and DL-PCBs provides an opportunity to identify potential sources of contamination (17). Some specific sources may be suspected because of the specific compounds emitted by them. The most abundant congener in all species analysed in this investigation except Pacific oysters, OCDD, is a characteristic emission from incineration of sewage sludge and municipal waste and operation of petrol and diesel engines (5), and was frequently detected in air samples (3, 21). This congener is also connected with dioxin-contaminated pesticides, past use of chlorophenols and atmospheric deposition (3). Octochlorodibenzo-p-dioxin may be causally linked with ship engine emissions and the discharges of urban waste water treatment plants (33). The second most abundant compound, 2,3,7,8-TCDF, might originate from the paper industry (pulp bleaching) and similarly to OCDD, is an indicator of air deposition (38, 42). The profile observed in our samples of Pacific oysters, with 2,3,4,7,8-PeCDF and 2,3,7,8-TCDF as its two dominant congeners, was similar to the pattern in molluscs from the Spanish Atlantic coast (4). The PCB 118 and PCB 105 congeners, which were the predominant DL-PCBs, may be emissions from metallurgical processes, cement kilns, coal-fired power plants and medical waste incineration plants (27, 44). They might also derive from improper disposal of PCB mixtures like Aloclor 1254 and 1248, Clophen A40 and Sovol (18, 39).

In 2018, the EFSA published a new scientific opinion on risk for animal and human health related to the presence of dioxins and dioxin-like PCBs in feed and food (12). Based on new experimental and epidemiological animal data on the toxicity of PCDD/Fs and DL-PCBs and more refined modelling techniques for predicting the fate of these contaminants in the human body over time, EFSA experts decided to reduce sevenfold the then-current TWI. The conclusions to be drawn from this opinion are that the exposure of Europeans to PCDD/Fs and DL-PCBs is too high and that the new TWIs were being exceeded across all age groups. In order to ensure the safety of consumers, constant surveillance of the food chain is essential, which will enable the elimination of hazardous food from the market.

Comparing the exposure data resulting from the consumption of bivalve mussels with the exposure

resulting from the consumption of other products, mussels are not a significant source of PCDD/Fs or DL-PCBs. Much higher exposure is due to the consumption of Baltic fish: ingestion of one 100 g portion resulted in 24- and 8-fold TWI exceedances for children and adults respectively (24). Consumption of not only Baltic fish, but also of freshwater fish from contaminated sites, *e.g.* the Vistula River within Kraków, risks adults exceeding the TWI by a factor of 10 and children doing so by a factor of over 30 (23). Consumers of eggs, particularly free range eggs, might be at a higher level of risk (30, 31), and consumers of game animals, especially game liver are also more exposed to PCDD/Fs and DL-PCBs (43). In Japan (40), Spain (7), Italy (6) and France (36), where seafood is more frequently consumed, molluscs are a much higher contributor to PCDD/F and DL-PCB dietary intake than in Poland. Based on our research, taking into account the low consumption of molluscs *per capita* in Poland and the low concentrations of the analysed congener compounds, molluscs should not be of concern to Polish consumers.

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