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Presence, concentrations and risk assessment of dioxins in bottom sediments of Port of Gdynia

Keywords

Port of Gdynia, bottom sediments, dioxins, toxic equivalency factor, total toxic equivalent

Abstract

The risk associated with the exposure of humans and the environment to the impact of toxic compounds such as dioxins is associated with a number of factors such as: the level of contamination, environmental conditions and the dynamics of the food chain. The aim of the study is to provide a primary understanding of the risk of dioxins pollution in bottom sediments of the Port of Gdynia. The research was conducted to obtain data on the presence, concentration and risk assessment of PCDD/Fs in the bottom sediments of the Port of Gdynia. Sediments from five port basins were analyzed by GC-MS/MS and all PCDD/Fs congeners, capable of accumulating in fat cells of organisms, were detected in them. PCDD congeners dominated in the sediments. The highest concentration (902 ng/kg d.w.) was obtained for OCDD, dioxin with the lowest toxicity factor. The concentration of all 17 dioxin congeners (WHO-TEQ) ranged from 0.9 to 9.5 ngTEQ/kg d.w. Thus, bottom sediments from examined zones of port basins do not have a negative impact on the environment.

1. Introduction

Dioxins belong to the so-called persistent organic pollutants (POPs) and are known as one of the most toxic groups of chemicals, listed in the Stockholm Convention. As the name suggests, dioxins are compounds that are difficult to degrade, in particular they are resistant to biodegradation, i.e. decomposition by living organisms. From a chemical structure point of view, the term *dioxins* is used to refer to toxic chemicals with a similar chemical structure and a common mechanism of toxic action.

This group includes 75 of the polychlorinated dibenzo-p-dioxins (PCDDs) and 135 of the polychlorinated dibenzofurans (PCDFs) (Ogura et al., 2001). Both of these groups (PCDDs and PCDFs) pose a serious threat to the environment due to their ubiquity, toxicity and strong resistance to biodegradation. The name *dioxins* also includes the so-called dl-polychlorinated biphenyls (PCBs). Although there are 210 unique dioxin/furan congeners, only 17 of these are typically evaluated.

Dioxin contamination of marine waters usually refers to the most toxic and persistent 17 polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and 12 dioxin-like polychlorinated biphenyls (dl-PCB), which have the ability to accumulate in the fatty tissue of organisms (Nevalainen et al., 2021).

The toxic equivalency factor (TEF) values for the individual PCDD/Fs congeners are presented in Table 1.

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Table 1. Dioxin/furan homologue groups and 17 congeners of greatest concern

Congener	Abbreviation	Toxic equivalency factor (TEF)
tetrachlorodibenzo-p-dioxins	**TCDD**	
2,3,7,8-tetrachlorodibenzo-p-dioxin	2,3,7,8-TCDD	1
pentachlorodibenzo-p-dioxins	**PeCDD**	
1,2,3,7,8-pentachlorodibenzo-p-dioxin	1,2,3,7,8-PeCDD	1
hexachlorodibenzo-p-dioxins	**HxCDD**	
1,2,3,4,7,8-hexachlorodi-benzo-p-dioxin	1,2,3,4,7,8-HxCDD	0.1
1,2,3,6,7,8-hexachlorodi-benzo-p-dioxin	1,2,3,6,7,8-HxCDD	0.1
1,2,3,7,8,9-hexachlorodi-benzo-p-dioxin	1,2,3,7,8,9-HxCDD	0.1
heptachlorodibenzo-p-dioxins	**HpCDD**	
1,2,3,4,6,7,8-heptachlorodi-benzo-p-dioxin	1,2,3,4,6,7,8-HpCDD	0.01
octachlorodibenzo-p-dioxin	**OCDD**	
octachlorodibenzo-p-dioxin	OCDD	0.003
tetrachlorodibenzofurans	**TCDF**	
2,3,7,8-tetrachlorodibenzofuran	2,3,7,8-TCDF	0.01
pentachlorodibenzofurans	**PeCDF**	
1,2,3,7,8-pentachlorodibenzo-furan	1,2,3,7,8-PeCDF	0.03
2,3,4,7,8-pentachlorodibenzo-furan	2,3,4,7,8-PeCDF	0.3
hexachlorodibenzofurans	**HxCDF**	
1,2,3,4,7,8-hexachlorodiben-zofuran	1,2,3,4,7,8-HxCDF	0.1
1,2,3,6,7,8-hexachlorodiben-zofuran	1,2,3,6,7,8-HxCDF	0.1
1,2,3,7,8,9-hexachlorodiben-zofuran	1,2,3,7,8,9-HxCDF	0.1
2,3,4,6,7,8-hexachlorodiben-zofuran	2,3,4,6,7,8-HxCDF	0.1
heptachlorodibenzofurans	**HpCDF**	
1,2,3,4,6,7,8-heptachlorodi-benzofuran	1,2,3,4,6,7,8-HpCDF	0.01
1,2,3,4,7,8,9-heptachlorodi-benzofuran	1,2,3,4,7,8,9-HpCDF	0.01
octachlorodibenzofurans	**OCDF**	
octachlorodibenzofuran	OCDF	0.003

In practice, we usually deal not with just one congener, such as pure TCDD, but with mixtures of various compounds in the dioxin group. Since different compounds in this group exhibit different toxicity, in order to estimate the risk associated with exposure to such mixtures, individual congeners belonging to PCDD/Fs or dioxin-like PCBs are assigned a number called a toxic equivalency factor. TEF is used to convert the concentrations of each of the dioxin congeners into an equivalent total amount of 2,3,7,8-TCDD for use in risk assessment. There are TEFs for people, birds, and fish with those for fish being used for ecological risk assessment (Manning & Batley, 2023). The values of TEF for dioxins are regulated in the Commission Regulation (EU) No 277/2012 of 28 March 2012 (Commission Regulation, 2012). For 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD a TEF of one is assumed, the other congeners have TEFs less than unity (Table 1). The total toxic equivalent (TEQ), the parameter proposed by the World Health Organization (WHO), is defined by the sum of the products of the concentration of each compound multiplied by its TEF value. TEQ-WHO is the equivalent of 2,3,7,8-TCDD-like activity for the total mixture of PCDD/Fs congeners (Van den Berg et al., 2006).

Dioxins enter the sea from the atmosphere due to interactions with the air, flow in from the land along with river waters, and can also end up there due to accidents and spills in the maritime transport of raw materials (HELCOM, 2010). Industrial disasters are also a source of dioxin in the environment; the most notorious is an accident that occurred in 1976 in Seveso, Italy (Eskenazi et al., 2018). Fortunately, industrial accidents involving PCDDs/PCDFs have not been reported in Poland (Zieliński et al., 2014). Dioxin emissions into the environment have both: natural (volcanic, erosion, fires) and anthropogenic sources (Dobrzycka-Krahel & Bogalecka, 2022). The latter are associated with leaks in technological processes, especially that use chlorine or other chlorinating agents (Kawamoto & Weber, 2021; Masunaga et al., 2001). Dioxins are released from the venting of production processes, in transportation, from plant leaks, and in combustion processes (Lewandowski et al., 2014; Vikelsøe & Johansen, 2000). Uncontrolled waste incineration processes (e.g., in landfills) and household coal burning also contribute to these emissions (Rappe, 1994). Dioxin emissions increase very significantly when waste is burned along with coal or biomass, particularly plastics, even those that do not contain chlorine, as well as waste treated, varnished or glued wood. In particular, burning wood treated with organochlorine compounds or copper compounds can result in significant emissions of PCDD/Fs (Pitea et al. 1989; Schatowitz et al., 1994). The most important source of dioxin is open combustion processes. Global dioxin emission is about 100 kg TEQ/year. The most dioxin emitting countries are Asia and Africa. One of the countries emitting the largest amounts of dioxin is China. The country emits about 9 kg of toxic equivalent (TEQ) among countries. Dioxin emissions in developed countries remain low and stable, while emissions in developing countries have remained relatively high or continue to increase (Wang et al., 2016; Lei et al., 2021).

Having a low solubility in water dioxins adhere to particles suspended in water and sink to the bottom with them. Therefore, it is very important to analyze the level of contamination of bottom sediments of water bodies. Adsorbed sediment particles are part of the food chain in which dioxins bioaccumulate (Zielinski et al., 2014). Dioxins accumulate in sediments near their major sources, such as chemical plants, especially those producing paper, vinyl chloride or biocides, and in the port area. In port areas, dioxins can run off with grease and oil as rain washes over concrete surfaces and steel structures. Port sediments have a varied and variable composition. This is due to the dredging of the bottom of the port channels to maintain their proper depth and activities to modernize port infrastructure. Dredged material is deposited in neighbouring ecosystems. If the limits for the measured concentrations of substances (including dioxin) are not exceeded, the dredged sludge from the port basin is stored in specially designated land or sea areas. Therefore, the quality of the sediment of the port bottom has a significant impact on the ecosystem of the neighbouring areas of the Baltic Sea (Sapota et al., 2012).

Like many other harmful substances (e.g. heavy metals, or other POPs) dioxins accumulate in living organisms (bioaccumulation), and usually the higher up the food chain an organism is, the more harmful substances it contains (biomagnification). Therefore (and also because of the good solubility of these compounds in fats), the most dioxins per unit weight of food will be found, for example, in egg yolks, fatty dairy and meat, fish (McLachlan & Undemann, 2020). In the marine environment, dioxins can penetrate organisms through the digestive or respiratory tracts, or accumulate on their surfaces through sorption processes. A significant amount of dioxin is adsorbed by phytoplankton. For example, DLC accumulates in herring and moose populations (mainly in fat and eggs). As a result – anthropogenic harmful substances, accumulated in marine organisms through the food chain, negatively affect human health due to the consumption of seafood contaminated with toxic substances (Copat et al., 2012).

Consumption of dioxin-contaminated food contributes to more than 90% of total human exposure, with fish and seafood considered to be one of the main contributors to exposure. In the South-West Baltic Sea region, no risk to human health from fish consumption has been demonstrated, because it is at a low level. However, excessive consumption of certain species may have a significant impact on the health of different subgroups of consumers. To assess the risk of exposure to dioxins in the general population and to identify time trends, it is recommended to regularly test levels of PCDD/Fs in the environmental food chain and in sediments (Piskorska-Pliszczynska et al., 2012).

The PCDD/PCDF levels in the fish are relatively stable. WHO and FAO have jointly established a maximum tolerable human intake level of dioxins via food, and within the EU there are maximum allowable levels of dioxins in food and feed stuff. The European limit for dioxin concentration in the muscle tissue of fish is 3.5 ng/kg wet weight (w.w.) WHO-TEQ. PCDD/Fs levels in fat fish, mainly herring and salmon, from the Baltic Sea often exceed this limit (Bignert et al., 2017; Kawamoto & Weber, 2021).

Dioxin accumulation is also affected by the degree of eutrophication of a water body. A decrease in nutrient concentration lowers the density of DLC carriers thereby reducing its accumulation in fish. The Baltic Sea is an inland sea with low water exchange, a large influx of anthropogenic pollution and a high level of water eutrophication. For this reason, it is also heavily polluted with PCDD/Fs and dl-PCB dioxins (Kowalewska et al., 2003).

HELCOM has listed PCDD/Fs and dl-PCBs as priority hazardous substances of specific concern for the Baltic Sea (HELCOM, 2010). Risk assessment of dioxin and related compounds is based on the concept of TEF factor (Safe, 1990). The use of TEFs represents the overall toxicity of a sample in terms of a single number. TEFs are weighting factors by which the toxicity of a mixture of congeners is compared to that of 2,3,7,8-TCDD. For calculation of Toxic Equivalent (TEQ), the concentrations of the individual substances in a given sample shall be multiplied by their respective Toxic Equivalency Factor (TEF) and subsequently summed to give the total concentration of dioxin-like compounds expressed as TEQs (Eljarrat et al., 2005).

Dioxin's concentrations in sediments examined in the Polish costal area allows us to evaluate this zone as relatively less contaminated. About 60% of the concentrations of the sum of PCDD/PCDF congeners in the bottom sediments of the southern Baltic Sea do not exceed the TEQ value of 5 ng/kg d.m. (Niemirycz & Jankowska, 2011). This value is considered by many researchers to be the limit value for areas considered uncontaminated with dioxins (Rappe, 1993). Studies of bottom sediments show that elevated levels of PCDD/Fs are present in both coastal and offshore areas of the Baltic Sea. The main points of high pollution are close to the shore, indicating that the main causes of pollution are, or were, local emissions (Sundqvist et al., 2009; Verta et al.2007).

Port sediments should be continuously analysed for dioxin contamination. Primary sources, occurrence, predominant mechanisms of formation and factors influencing their formation in port environment can provide informative and practical directions for better understand them and control in the environment (NewFields et al., 2013). Near-surface aquatic sediments represent the recent deposition of dioxin-like chemicals, and provide information on the present concentrations of these chemicals in the benthos and adjacent aquatic layer. These chemicals can be dispersed extensively and presented in port basins. Theirs the exact accumulation period is difficult to determine since the deposition rates and source of dioxins is highly variable in the port area (Müeller et al., 2004). Therefore, the quality of the port bottom sediments has a significant impact on the Baltic Sea ecosystem adjacent to the port.

The Port of Gdynia is the third largest port in Poland. It consists of the Western Port (inner port) and the Eastern Port (outer port). The Port of Gdynia conducts both industrial and commercial activities. The main sources of pollution come from municipal and port activities. The different origins of pollution significantly affect their concentrations, which do not change at the same rate at the same time. Even though the Port of Gdynia is protected by an external breakwater, the intense water movement occurring during high winds or storms still leads to mixing of port waters and bottom sediments with the waters of the Gulf of Gdansk and, as a result, to the movement of pollutants accumulated in the port basins (Radtke et al., 2012; Dereszewska et al., 2023).

The air over the area of high northern Poland is significantly contaminated with dioxins (Bartnicki et al., 2013). High concentrations of them are also reported in the bottom sediments of the Gulf of Gdansk (Niemirycz & Jankowska 2011; Nevalainenet et al., 2021). However, there is little data on the presence of dioxins in harbour basins. For this reason, a study was undertaken to find out whether and to what extent the port sediments of the Port of Gdynia are contaminated with dioxins.

2. Experimental

Dioxins were collected from surface bottom sediments at seven measurement points in the five port basins (No. I, III, IV, V, VI). The location of selected basins and points of sediment collection (1–7) in the Port of Gdynia is presented in Figure 1.

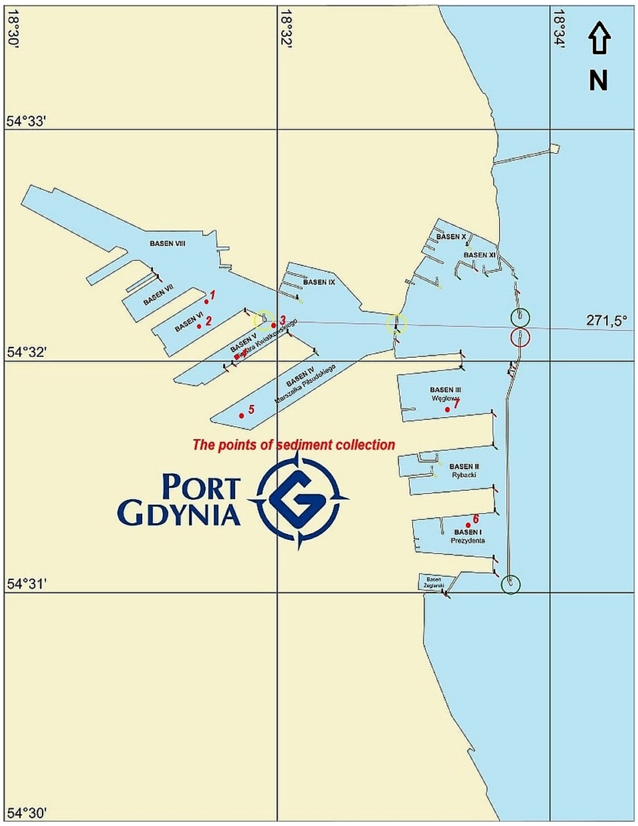

Figure 1. Location the harbour basins and points of sediment collection (1–7) in the Port of Gdynia. The map provided by the Port of Gdynia Authorities.

The surface bottom sediments at the investigated measurement points were collected in accordance with PN-EN ISO 5667-19:2006 Water quality. Sampling. Part 19: Guidelines for sampling marine sediments, using a Vanveen scoop.

The sediments were analysed in a standardized external laboratory. The analyses for dioxins/furans are made according to Good Manufacturing Practice quality standards, secured by governmental inspections according to § 64 German Pharmaceuticals Act. Determination of dioxin content in sediments was performed using gas chromatography coupled to mass spectrometer (GC-MS/MS) technique, according to DIN EN ISO/IEC 17025:2005.

The analysis included 17 congeners considered by the WHO to be the most toxic. These congeners have chlorine atoms in the 2, 3, 7, and 8 positions. A formula showing the position of chlorine atoms in dioxin is shown in Figure 2.

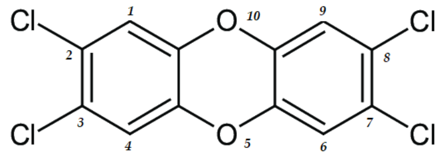

Figure 2. Structure of 2,3,7,8-tetrachlorodibenzo para dioxin (TCDD).

3. Results

The bottom sediments in Gdynia Port were tested three times, at different seasons of a year (October, May and July). The results are presented in Tables 2–4. The dominant congeners for each family of compounds were: OCDD and 1,2,3,4,6,7,8-HpCDD for dioxins, OCDF for furans. Similar dominance also exists in the Spanish port of Tarragona. However, OCDD concentrations detected there are lower, while furan concentrations are many times higher than in the Port of Gdynia (Eljarrat et al., 2005).

Table 2. Concentration (ng/kg d.w.) of 17 PCDD/Fs congeners in sediment samples collected from the Port of Gdynia in October

Congener	Basin of the Port of Gdynia / collection point						
	VI		V		IV	I	III
	1	2	3	4	5	6	7
2,3,7,8-TCDD	0.235	–	–	–	0.274	–	–
1,2,3,7,8-PeCDD	0.981	0.297	–	–	0.968	–	–
1,2,3,4,7,8-HxCDD	1.65	0.547	–	–	1.81	–	–
1,2,3,6,7,8-HxCDD	8.56	2.42	0.895	0.973	8.50	9.37	–
1,2,3,7,8,9-HxCDD	3.32	1.27	0.523	0.612	2.85	–	–
1,2,3,4,6,7,8-HpCDD	191	66.4	35.2	38.5	199	185	6.61
OCDD	902	328	164	144	962	882	36.6
2,3,7,8-TpCDF	8.47	2.44	1.68	2.02	9.11	7.21	0.508
1,2,3,7,8-PeCDF	3.07	0.645	–	–	3.00	-	–
2,3,4,7,8-PeCDF	6.40	1.94	1.02	1.14	6.91	5.95	–
1,2,3,4,7,8-HxCDF	9.25	3.20	1.19	1.08	9.89	13.3	–
1,2,3,6,7,8-HxCDF	4.91	1.66	0.476	0.512	3.05	5.21	–
1,2,3,7,8,9-HxCDF	–	–	–	–	–	–	–
2,3,4,6,7,8-HxCDF	2.13	0.792	–	–	2.05	–	–
1,2,3,4,6,7,8-HpCDF	31.7	10.8	4.29	4.10	32.1	39.2	1.29
1,2,3,4,7,8,9-HpCDF	2.73	0.999	0.520	0.494	2.39	–	–
OCDF	33.1	12.3	3.49	3.36	30.4	–	–

(–) below the range of quantification.

Table 3. Concentration (ng/kg d.w.) of 17 PCDD/Fs congeners in sediment samples collected from the Port of Gdynia in May

Congener	Basin of the Port of Gdynia / collection point						
	VI		V		IV	I	III
	1	2	3	4	5	6	7
2,3,7,8-TCDD	–	–	–	-	0.202	0.321	–
1,2,3,7,8-PeCDD	0.437	0.687	–	-	0.746	1.11	–
1,2,3,4,7,8-HxCDD	0.737	1.26	–	0.447	1.35	1.65	–
1,2,3,6,7,8-HxCDD	3.09	6.05	–	1.31	6.83	8.41	0.453
1,2,3,7,8,9-HxCDD	1.94	3.38	–	1.04	3.13	4.56	–
1,2,3,4,6,7,8-HpCDD	69.8	152	0.912	39.5	132	136	9.78
OCDD	351	839	5.54	167	691	761	58.0
2,3,7,8-TpCDF	2.85	4.05	–	1.25	4.41	6.52	0.523
1,2,3,7,8-PeCDF	0.896	1.22	–	-	1.60	2.78	–
2,3,4,7,8-PeCDF	2.86	3.52	–	1.08	4.06	5.93	0.497
1,2,3,4,7,8-HxCDF	4.12	7.24	–	1.32	7.87	11.0	0.571
1,2,3,6,7,8-HxCDF	1.58	2.00	–	0.428	1.98	3.53	–
1,2,3,7,8,9-HxCDF	–	–	–	–	–	–	–
2,3,4,6,7,8-HxCDF	1.77	2.01	–	–	1.15	2.87	–
1,2,3,4,6,7,8-HpCDF	13.1	24.6	–	3.69	22.8	30.5	2.19
1,2,3,4,7,8,9-HpCDF	1.37	1.98	–	0.401	2.03	2.24	–
OCDF	13.8	26.7	–	3.59	21.8	23.8	–

(–) below the range of quantification.

Table 4. Concentration (ng/kg d.w.) of 17 PCDD/Fs congeners in sediment samples collected from the Port of Gdynia in July

Congener	Basin of the Port of Gdynia / collection point						
	VI		V		IV	I	III
	1	2	3	4	5	6	7
2,3,7,8-TCDD	0.191	–	–	–	0.249	–	–
1,2,3,7,8-PeCDD	0.768	0.264	–	–	1.15	1.03	–
1,2,3,4,7,8-HxCDD	1.18	0.652	–	–	1.87	1.21	–
1,2,3,6,7,8-HxCDD	4.52	2.50	1.09	0.469	9.75	5.08	–
1,2,3,7,8,9-HxCDD	2.48	1.31	0.567	-	5.25	2.70	–
1,2,3,4,6,7,8-HpCDD	89.0	44.7	29.1	10.6	172	88.9	7.39
OCDD	438	197	115	52.5	869	518	41.7
2,3,7,8-TpCDF	5.20	2.83	1.04	0.445	7.48	3.97	0.428
1,2,3,7,8-PeCDF	1.76	1.04	–	–	2.35	1.95	-
2,3,4,7,8-PeCDF	4.63	2.20	0.915	–	5.93	3.59	-
1,2,3,4,7,8-HxCDF	5.51	2.74	1.65	0.467	9.52	6.79	0.432
1,2,3,6,7,8-HxCDF	1.82	0.933	0.428	–	2.90	2.33	–
1,2,3,7,8,9-HxCDF	–	–	–	–	–	–	–
2,3,4,6,7,8-HxCDF	1.47	0.763	–	–	2.02	1.97	–
1,2,3,4,6,7,8-HpCDF	15.6	7.21	3.30	1.25	28.4	19.8	1.36
1,2,3,4,7,8,9-HpCDF	1.58	0.725	0.470	–	2.55	1.54	–
OCDF	14.5	7.88	3.24	–	26.8	15.5	–

(–) below the range of quantification.

The content of OCDD and HpCDD dominates in most samples, however, these 2 congeners are not significant in terms of the risk they pose to human health, as they have a very low TEF (see Table 1). Therefore, the real risk posed by PCDD/Fs present in tested samples is expressed as WHO-TEQ parameter (see Table 5). Total WHO-TEQ values were calculated using TEFs proposed by WHO for dioxin-like PCDDs and PCDFs.

Table 5. Toxicity of Port of Gdynia bottom sediments, expressed as the total toxic equivalent WHO-TEQ (ng/kg sample dry weight)

Basin	Point	Month		
		May	July	October
VI	1	3.88	5.82	9.59
	2	6.43	2.72	3.02
V	3	0.01	1.12	1.23
	4	1.39	0.27	1.34
IV	5	6.67	9.42	9.77
I	6	9.07	5.83	7.80
III	7	0.44	0.19	0.14

The obtained values ranged from 0.19 to 9.59 ng TEQ/kg d.w. The limit value describing uncontaminated regions for Baltic Sea is 5 ng TEQ/kg d.w. (Zieliński et al., 2014; Rappe, 1993). The highest toxicity equivalents was determined for the sediments from Basin IV. The lowest values was reported in the sediments from the Basin III. The reported lower values for sediments from Basin III may be related to their location (Figure 1). The more open space probably facilitated the mixing of port waters and sediments with the waters of the Gulf of Gdansk and the migration of pollutants accumulated in this port basin. In comparison, WHO-TEQ values recorded in the Port of Tarragona range from 10 to 75 ng TEQ/kg d.w. The high contamination of Tarragona samples is related to the area's intensive industrialization (Eljarrat et al., 2005). In contrast, lower toxic equivalent values than in the Port of Gdynia were shown by a 2012 study in the nearby Port of Gdansk (from 2.4 to 2.9 ng TEQ/kg d.w. (Lewandowski et al., 2014). According to the Canadian Council of Ministers of the Environment (Canadian Council of Ministers of the Environment, 2001), adverse biological effects may occur more frequently when the concentration of the sum of 17 dioxin congeners is above the probable effect level 21.5 TEQ ng/kg d.w. The results demonstrate the low level of dioxin contamination of sediments in the Port of Gdynia (Table 5). Congener profiles are used to facilitate the determination of dioxin sources. The profile characterizes the percentage share of congeners with the same number of chlorine substituents (e.g. octa CDD) in relation to the mass of all 17 congeners (Niemirycz & Jankowska, 2011). Previous studies have shown that the increased share of PCDF is associated with industrial emissions (especially in papermaking and metallurgy), emissions from diesel engines (e.g. on busy streets). A clear advantage of PCDF congeners is also noted in the case of municipal waste incineration. OCDD dominates natural processes, but also total emissions from the mass incineration of municipal solid waste (Rappe, 1994; Zieliński, 2014).

The percentage of each PCDD and PCDF congener in sum of all analysed PCDD/Fs determined from collected bottom sediments of the five port basins in October, May and July are presented respectively in Figures 3–5.

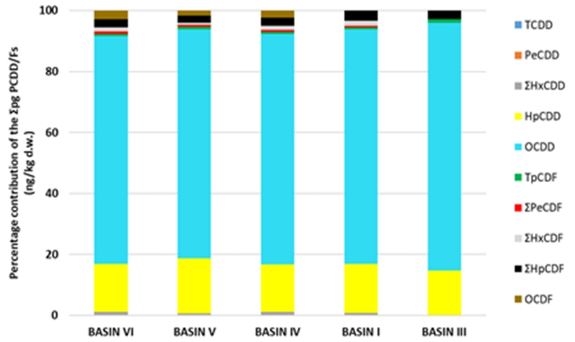

Figure 3. Percentage of each PCDD and PCDF congener in Σ pg PCDD/Fs ng/kg d.w. from collected in October bottom sediments of the five basins of the Port of Gdynia.

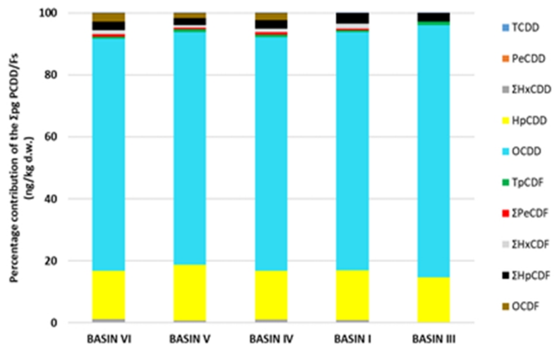

Figure 4. Percentage of each PCDD and PCDF congener in Σ pg PCDD/Fs ng/kg d.w. from collected in May bottom sediments of the five basins of the Port of Gdynia.

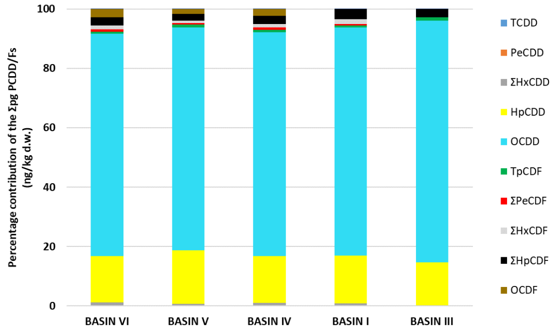

Figure 5. Percentage of each PCDD and PCDF congener in Σ pg PCDD/Fs ng/kg d.w. from collected in July bottom sediments of the five basins of the Port of Gdynia.

ΣOCDDs (75–81%) and HpCDD (13–18%) have the highest percentage contribution to the total WHO-TEQ value of PCDD/Fs in sediments from the Port of Gdynia. The congener profiles for individual basins differ only slightly. They are also practically constant throughout the seasons. What is more, the content of OCDD varies while the content of HpCDD is very close to those obtained in Port of Gdansk (nearest to Port of Gdynia) by Lewandowski et al. in 2014 year (Lewandowski et al., 2014).

OCDD is also the dominant congener in the sediments of terrestrial waters in Poland and accounts for about 70–75% of all PCDD/Fs, regardless of whether the studies were performed in industrialized or rural areas (Zieliński et al., 2014). Therefore, its sources can be considered natural processes and absorption from the atmosphere. Studies conducted in Australia have also led to similar conclusions (Manning & Batley, 2023).

4. Conclusion

To understand the risk of dioxin/furan pollution of sediments in the Port of Gdynia, it is necessary to:

- identify the various signatures of source congeners of dioxins/furans present in port sediments,
- estimate the relative contribution of identified dioxin/furan sources to port-wide contamination,
- characterize neighboring facilities in the Port of Gdynia area to identify potential point source locations on land.

Bottom sediments from 7 points located in five basins of the Port of Gdynia were analyzed. Measurements were conducted at different times of the year.

Of all congeners of PCDD and PCDF, identified by the World Health Organization as the most dangerous ones, only 1,2,3,7,8,9-HxCDF was not detected in the bottom sediments from the Port of Gdynia.

The highest concentrations were recorded for 2 compounds. In the surface layer of bottom sediments, high concentrations were obtained for two polychlorinated dibenzo-p-dioxins of low toxicity: OCDD (5.54–869 ng/kg d.w.) and 1,2,3,4,6,7,8-HpCDD (0.9–172 ng/kg d.w.). The content of dioxins with the highest toxic equivalency factor (2,3,7,8-TCDD and 1,2,3,7,8-PeCDD), ranged from 0.19 to 1.11 ng/kg d.w.

According to the determined TEQ value, in the tested zones of port basins, bottom sediments do not have a negative impact on the environment.

Congener and homologue profiles are useful tools for the determination of source and fate processes of dioxin-like chemicals, which may lead to accumulation in humans. These profiles can be compared to a *fingerprint*, where the focus is not on the concentration but on the ratio of different dioxin-like chemicals to each other.

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