

Article

Accumulation Patterns of Polychlorinated Dibenzo-*p*-Dioxins, Dibenzofurans and Dioxin-like Polychlorinated Biphenyls in Sediments of the South-Eastern Baltic Sea

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Abstract: The current research paper presents the results of the first regional assessment of sediment contamination by dioxins (polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (dl-PCBs)) in the south-eastern part of the Baltic Sea (Lithuanian and Polish marine areas) during the periods of 2014 and 2019–2020. In total, 143 surface and core sediment samples were taken of existing offshore dredged-soil-disposal sites in the area of the former shipyard in the Port of Gdynia (Poland), as well as in a profile from the nearshore to the deeps of the Gdansk basin, following the natural pattern of sediment migration in the region. The obtained results indicated wide variation in both the total content of the investigated compounds as well as the profiles of congeners, indicating the likely sources of their origin. Based on the obtained concentration characteristic profiles of the congeners, we determined the amount of dioxins and the likely sources of their origin in the Gdansk Basin. The profiles showed elevated contents of *octa*- and *hepta*-chlorodibenzodioxins (OCDD and HpCDD) in the sediments, while the fractions of most other toxic congeners were considerably lower. The domination of OCDF in the spectrum of the studied PCDFs suggests the possible contribution of industrial processes. The obtained results have filled the gaps in our knowledge while providing a perfect background for more detailed discussions concerning the accumulation of dioxins in surface sediments from the south-eastern part of the Baltic Sea.

Keywords: polychlorinated dibenzo-*p*-dioxins; dibenzofurans; sediments; the Baltic Sea; marine disposal sites

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) are highly toxic persistent organic compounds, regulated under the Stockholm Convention, and are thus a global human health concern [1]. PCDD/Fs are released into the air from combustion processes, such as commercial or municipal waste incineration and the burning of fuels. Another group of hydrophobic compounds is represented by polychlorinated biphenyls (PCBs), of which 12 congeners are chemically and toxicologically similar to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) and are referred to as dioxin-like PCBs (dl-PCBs) [2]. PCBs have been used commercially since 1929 as dielectric and heat exchange fluids, as well as in a variety of other applications. Due to the potential negative impacts on the environment and human health, PCDD/Fs and dl-PCBs are listed as prioritized

hazardous substances of specific concern for the Baltic Sea by the Helsinki Commission [3]. Dioxins are regarded as priority substances in Directive 2008/105/EC on environmental quality standards in the field of water policy. Although their production and trade have been banned, the problem has not been eliminated. The extremely weak water solubility and very low vapor pressure of PCDD/Fs and dl-PCBs results in very strong adsorption on the surfaces of fine-grained particles, transported in the atmosphere or in waters. More than 90% of these substances in the environment are located in sediments and soils [4].

Over the past few years, many studies focusing on PCDD/F or dl-PCB accumulation in surface sediments have been conducted in different coastal sea areas and estuaries suffering from intense anthropogenic turbulence and contamination [5–9].

The Baltic Sea region, regarded as one of the most contaminated by persistent organic pollutants, has been studied for the presence of dioxin-like compounds as well; however, only a small number of the analytical results have been published in the scientific literature [1,10–19].

Episodic investigations of the sediments in the Baltic Sea revealed major dioxin contamination in the Gulf of Finland [13,14] close to the estuary of the Kymijoki River. Local dioxin contamination was also observed on the Swedish coast of the Gulf of Bothnia [7] in the estuary of the Warnow River [12].

The south-eastern part of the Baltic Sea catchment area is characterized by the highest population density, the highest percentage of arable lands, intensive shipping activities, petroleum refineries, paper industries, the operation of ports and industrial as well as municipal wastewater discharge from the coastal cities. Additional pressure on the marine environment is posed by the deposition of dredged port sediments in the designated offshore disposal areas, often regarded as a secondary pollution source with persistent organic pollutants.

The available unitary studies of dioxin accumulation in sediments have mostly addressed the southern part of the Gdansk Basin [1,20], including the estuary areas of the Vistula and Odra Rivers, the Gulf of Gdansk and the Wloclawek Reservoir. Unfortunately, there are no scientific data available regarding the eastern coastal regions of the Baltic Proper and the offshore disposal areas where dredging material from the port areas is deposited.

The current study presents the results of first regional assessment of surface sediment PCDD/F and dl-PCB contamination in the south-eastern part of the Baltic Sea (Polish and Lithuanian marine areas), identifies toxic equivalents of PCDD/Fs and dl-PCBs (WHO-TEQs) and their toxic biological effects, and performs an analysis of the percentage of individual PCDD/F congeners in the investigated sediment samples to identify likely emission/pollution sources. The data were collected in 2014 and 2019–2020, and the study was (1) conducted in the framework of the international ECODUMP project focused on the impact of offshore disposal sites in the Baltic Sea environment, and (2) commissioned by the Ministry of Maritime Economy and Inland Navigation of Poland, under contract number BBF.III.320U.60.2019/93. The results of these studies are crucial for assessing the effects of anthropogenic activities on the marine environment. The obtained results provided the first insights on dioxin occurrence in marine areas of south-eastern Baltic Sea and enable to close the geographical data gaps declared during previous studies.

2. Materials and Methods

Investigations of sediment contamination with dioxins were carried out in the south-eastern sector of the Baltic Sea, namely in the southern and northern parts of the Gdansk Basin (Polish and Lithuanian marine areas). The Gdansk Basin is often treated as a separate sedimentary environment of the Baltic Sea, with the Gdansk Deep (max. depth 118 m) acting as a sink for the suspended matter carried by the Vistula and Nemunas Rivers, the largest ones draining the Baltic Proper [21]. Before entering the sea, both rivers collect wastewater discharge from land-based sources.

The sampling sites in 2014 were distributed as follows: (i) in the areas of the existing offshore disposal sites, used for the deposition of dredged material from port areas and

navigational channels; (ii) in a profile from the shore to the deeps of the Gdansk Basin, following the natural pattern of sediment migration in the region. The sampling sites in the Polish sector covered the areas of the Gdynia disposal site I ($n = 10$), Gdansk disposal site II ($n = 3$), DCT disposal site III ($n = 5$) and Vistula River profile in the Gulf of Gdansk ($n = 10$). Additionally, surface sediment samples ($n = 10$) were taken from the former shipyard area in the Port of Gdynia, in order to evaluate the possible contribution of shipbuilding activities to sediment enrichment with dioxin compounds (Figure 1). Sediments from this area are usually deposited at Gdynia disposal site I.

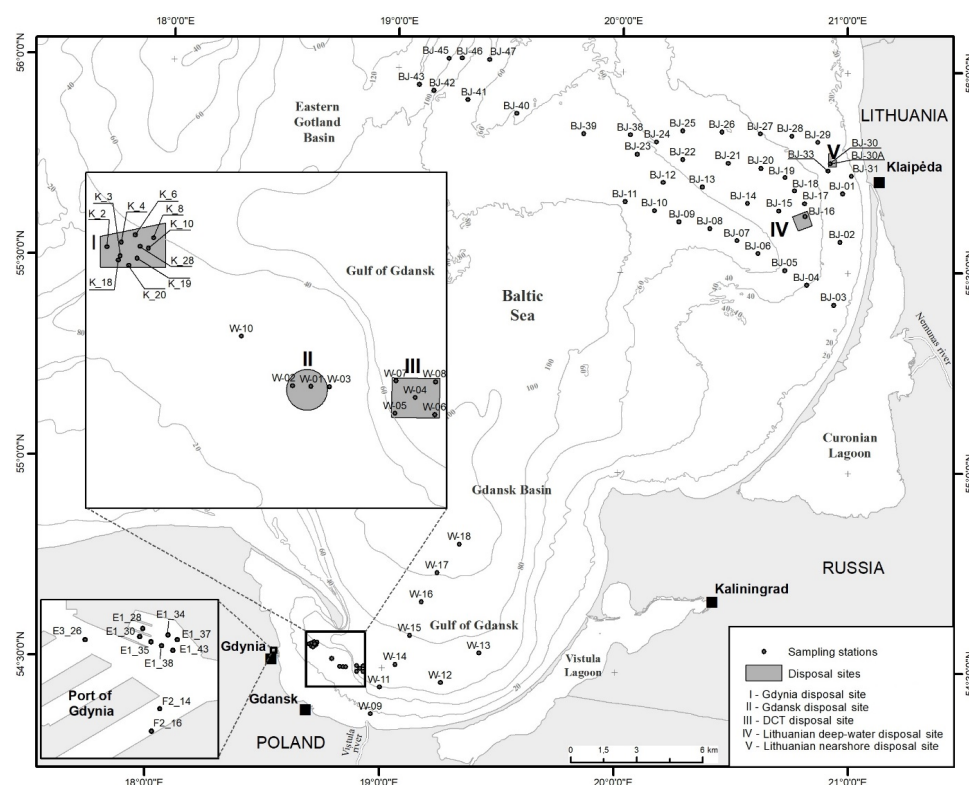


Figure 1. Locations of sampling stations in 2014.

In the Lithuanian sector, all sampling sites were distributed in the profile from the shore towards the deeps of the Gdansk Basin ($n = 35$), including the areas of deep-water disposal site IV ($n = 3$) and nearshore disposal site V ($n = 4$).

In 2019–2020, repeated studies were carried out on the content of dioxins in bottom sediments from selected areas of deposited dredged material in the Polish sector. Investigations of dioxin and furan concentrations were carried out in surface bottom sediments sampled in the individual disposal area and at designated reference points located approximately 1 Mm from the boundaries of the disposal areas. In addition, core sediments collected from the area of the individual disposal sites were also analyzed.

Sampling sites from the Polish sector selected during the period of 2019–2020 were located at Gdynia disposal site I ($n = 14$), Gdansk disposal site II ($n = 2$) and DCT disposal site III ($n = 11$) (Figure 2).

Sample collection. Samples of surface sediments (0–10 cm upper layer) from the study area were collected in 2014 and 2019–2020 during the cruises of R/V “Darius” in Lithuania and R/V “IMOR” in Poland. Samples were taken in accordance with PN-EN ISO 5667-19:2006, Water quality—Sampling—Part 19: Guidelines for marine sediment sampling [22], using a Van Veen grab sampler to obtain surface sediment samples and a VK 3–6 vibro probe to core the samples.

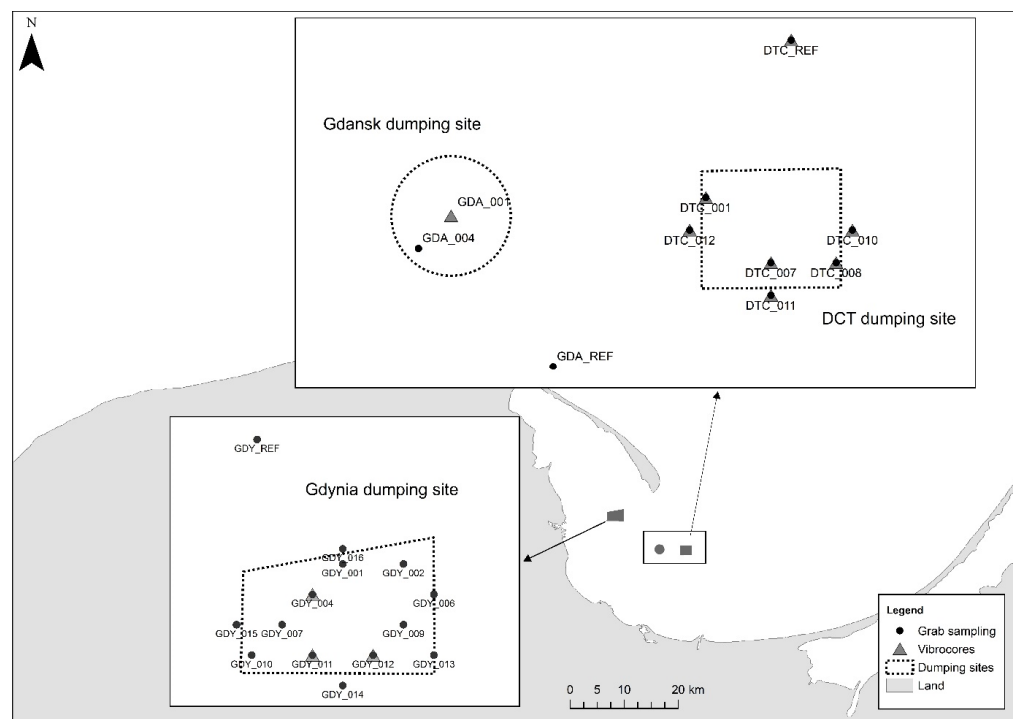


Figure 2. Locations of sampling stations in 2019–2020.

The total concentrations of PCDDs, PCDFs and dl-PCBs were determined in the Laboratory for Trace Organic Analyses at Krakow University of Technology, accredited by Polish Centre for Accreditation (accreditation certificate No. AB 749), according to procedure P/01/03 of 11 May 2010 based on the methodology EPA 1613 [23].

Analyses. The general procedure of the analysis was as follows: after homogenization and freeze-drying of the sediment (approximately 5 g of sediment) the internal standard ^{13}C -PCDD/PCDF was added. The analytes were extracted with toluene for 16 h using Soxhlet apparatus, followed by transfer to n-hexane and extraction in a 250 mL separatory funnel. Stepwise purification was carried out in specially designed columns. The hexane phase was evaporated to a small volume and loaded into a 10 mm diameter column with activated carbon with a bed height of approximately 2 cm. The following purification procedure included washing the column with 3 mL dichloromethane, 3 mL methanol and a small amount of toluene (1 mL) at room temperature. The eluate contained dl-PCB. Then, the carbon column was extracted with toluene after inversion at a fixed point for at least 10 h, and the resulting phase contained PCDDs and PCDFs. Further purification of both fractions was carried out using polyethylene membranes and a column containing, successively, 1 g of silica gel, 4 g of silica gel modified with sodium hydroxide (NaOH), 1 g of silica gel, 8 g of silica gel modified with sulfuric acid (H_2SO_4) and 2 g of silica gel. This system of sorbents was used to remove polar and nonpolar interfering compounds. The analytes were eluted with 100 mL hexane. The resulting eluate was concentrated and subjected to further purification by a column containing 5 g of basic and 5 g acidic aluminum oxide (Al_2O_3). PCDDs and PCDFs were collected in a fraction of 50% dichloromethane/50% n-hexane. Dioxin-like PCBs were collected in the fraction eluted with 2% dichloromethane in hexane. The calibration internal standards of the selected ^{13}C -PCDD/PCDF and ^{13}C -PCB were introduced to the final extracts. The separation of PCDD, PCDF and dl-PCBs was performed using a DB-5MS capillary column with a length of 60 m, an internal diameter of 0.25 mm and a stationary phase thickness of 0.25 μm , and a DB-17 column with a length of 30 m, an internal diameter of 0.25 mm and a stationary phase thickness of 0.25 μm .

The quantification of dioxins in sediment samples was completed by gas chromatography–mass spectrometry (GC-MS/MS) using a Thermo Scientific Finnigan ITQ 1100 analytical system (Thermo Fisher Scientific, Waltham, MA, USA) equipped with a Trace CE 2000 gas

chromatograph (Thermo Fisher Scientific, Waltham, MA, USA). The PCDD/Fs determined included all 17 toxic (2,3,7,8-substituted) congeners. The dl-PCBs included 12 congeners (PCB 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189). The concentrations of congeners were expressed per dry weight (d.w.) of the analyzed sediment.

The limit of quantification for PCDD/Fs and dl-PCBs was determined on the basis of the current measurement. The expanded uncertainty of determination of the PCDD/F congeners was estimated to be 26% and of the dl-PCBs to be 22%, with an expansion factor of $k = 2$ and a 95% probability. The results are presented in accordance with the “Toolkit for Identification and Quantification of Releases of Dioxins, Furans and Other Unintentional POPs under Article 5 of the Stockholm Convention on Persistent Organic Pollutants” and presented as an upper limit.

In order to better interpret the results of the PCDD/Fs and dl-PCBs, an additional loss-on-ignition (LOI) analysis was performed in the collected bottom sediment samples. The LOI analysis was performed at 550 degrees Celsius using a weight-based method in accordance with PN-EN 15935:2022-01 [24].

3. Results

3.1. Characteristics of Studied Sediments

The bottom sediments from the Lithuanian part of the Gdansk Basin are mainly silty sands and pelitic mud with LOIs of 0.27–9.98%, while the bottom sediments deposited at nearshore disposal sites IV and V are mainly silty sands with LOIs of 1.15–6.63%. The detailed data are presented in Table 1.

Table 1. Characteristics of sediments collected from Lithuanian part of Gdansk basin.

Lithuanian Marine Area					
Sampling Station	LOI [%]	Type of Sediment	Sampling Station	LOI [%]	Type of Sediment
BJ01	1.36	silty sand	BJ22	3.04	pelitic mud
BJ02	1.32	silty sand	BJ23	7.86	pelitic mud
BJ03	0.27	fine sand	BJ24	3.81	pelitic mud
BJ04	0.50	medium sand	BJ25	2.96	silt
BJ05	1.38	silty sand	BJ26	1.92	silty sand
BJ06	3.73	sandy mud	BJ27	1.33	silty sand
BJ07	7.23	pelitic mud	BJ28	2.18	silty sand
BJ08	7.69	pelitic mud	BJ31	2.1	Silty sand
BJ09	8.38	pelitic mud	BJ38	6.57	silty sand
BJ10	8.90	pelitic mud	BJ39	3.53	sandy mud
BJ11	9.98	silty–pelitic mud	BJ40	3.83	sandy mud
BJ12	8.07	silty–pelitic mud	BJ 41	2.08	clayey mud
BJ13	4.84	sandy mud	BJ42	3.44	silty mud
BJ14	1.21	sandy mud	BJ43	3.71	clayey mud
BJ18	2.67	silty sand	BJ45	2.50	clayey mud
BJ19	1.29	silty sand	BJ46	1.68	sandy mud
BJ20	1.58	silt	BJ47	2.76	silty mud
BJ21	2.04	silt			
Nearshore disposal site V			Nearshore disposal site IV		
Sampling station	LOI [%]	Type of sediment	Sampling station	LOI [%]	Type of sediment
BJ29	2.13	silty sand	BJ15	1.15	silty sand
BJ30	2.31	till (moraine)	BJ16	2.15	sandy mud
BJ30A	6.63	silty sand	BJ17	1.18	fine sand
BJ33	1.51	silty sand			

The sediments selected from the Gulf of Gdansk, in the profile of the Vistula River, are fine-grained sands with organic matter expressed as LOIs of 0.13–6.90%, while the surface

sediments at the disposal sites Gdynia I, Gdansk II and DCT III (both in 2014 and in the period of 2019–2020) are silts and silty strips with organic matter expressed as LOIs of 0.5–10.3%. The most abundant fine-grained fraction is observed in the area of the Gdynia and DCT disposal sites. Sediments from these regions are also characterized by a higher proportion of organic matter. The detailed data are presented in Table 2.

Table 2. Characteristics of sediments collected from Polish part of Gdansk basin.

Vistula River Profile in the Gulf of Gdansk			Gdynia Disposal Site I		
Sampling Station	LOI [%]	Type of Sediment	Sampling Station	LOI [%]	Type of Sediment
W9	6.90	loam	K2	6.73	dark grey silt
W10	1.22	fine-grained sand	K3	4.97	dark grey silt
W11	7.34	loam	K4	6.20	grey silt
W12	2.18	fine-grained sand	K6	7.19	brown silt
W13	2.74	plastic soft clay	K8	3.05	brown silt
W14	5.23	black loam with sand	K10	6.85	brown clay
W15	1.66	silty sand	K18	8.74	brown silt
W16	6.15	fine-grained sand	K19	10.3	brown silt
W17	0.13	fine-grained sand	K20	5.99	fine-grained sand
W18	1.09	fine-grained sand with shells	K28	8.34	silt

Gdansk disposal site II			DCT disposal site III		
Sampling station	LOI [%]	Type of sediment	Sampling station	LOI [%]	Type of sediment
W1	1.27	dark grey silt	W4	3.78	fine-grained sand
W2	1.52	fine-grained sand with silt	W5	3.18	clay, silt
W3	3.59	silty fine-grained sand	W6	3.21	black silt
			W7	8.06	fine sand, mussel living forms
			W8	0.50	medium-grained sand

Port of Gdynia					
Sampling station	LOI [%]	Type of sediment	Sampling station	LOI [%]	Type of sediment
E3_26	2.82	silt	E1_37	1.14	medium- and fine-grained sand, silt
E1_28	1.53	silt	E1_38	1.85	medium- and fine-grained sand, silt
E1_30	1.64	silt	E1_43	1.13	medium- and fine-grained sand, silt
E1_34	1.15	silt	F2_14	0.69	medium- and fine-grained sand
E1_35	1.96	medium- and fine-grained sand, silt	F2_16	3.46	silt

The core samples, after macroscopic description, were divided into geologically uniform layers on which PCDD/F analyses were performed.

About three to six homogeneous layers were identified in the core samples of bottom sediments collected from the area of Gdynia disposal site I. These were mainly fine-grained sands and silty sands. The detailed data are presented in Table 3.

Table 3. Characteristics of core sediments collected from Gdynia disposal site I in 2019–2020.

Sampling Station	Layer [cm]	Type of Sediment/Macroscopic Description
GDY_004	0–66	very soft plastic silt with admixture of fine sand, large amount of organic matter
	66–100	medium sand, average amount of organic matter
	100–155	soft silt, large amount of organic matter
	155–200	fine sand, grey
	200–222	medium sand, grey
	222–300	fine sand, grey

Table 3. Cont.

Sampling Station	Layer [cm]	Type of Sediment/Macroscopic Description
GDY_011	0–76	soft plastic silt with fine sand, large amount of organic matter
	76–120	fine-grained sand, large amount of organic matter
	120–15	medium sand, large amount of organic matter
	215–265	soft silt
	265–290	fine sand, grey
GDY_012	0–140	very soft plastic silt
	140–175	medium sand, small amount of organic matter
	175–230	fine-grained sand, grey

In a core sample taken from the area of the Gdansk disposal site I, four single-soil layers were identified. These were mainly coarse- and fine-grained sands. A silty fraction was found in the layer at a depth of 22–78 cm. A macroscopic description of the core sample taken is shown in Table 4.

Table 4. Characteristics of core sediments collected from Gdansk disposal site I in 2019–2020.

Sampling Station	Layer [cm]	Type of Sediment/Macroscopic Description
GDA_001	0–22	medium sand with silt, large amount of organic matter, single large stones
	22–78	soft plastic silt, single shells, oil smell
	78–130	fine-grained sand with silt, large amount of organic matter
	130–200	coarse sand, large amount of organic matter

About two to four homogeneous layers were identified in all the core samples of bottom sediments collected from DCT disposal site III. These were mainly fine-grained sands with a high admixture of silty fractions. A macroscopic description of the collected core samples is presented in Table 5.

Table 5. Characteristics of core sediments collected from DCT disposal site III in 2019–2020.

Sampling Station	Layer [cm]	Type of Sediment/Macroscopic Description	Sampling Station	Layer [cm]	Type of Sediment/Macroscopic Description
DTC_002	0–190	fine-grained sand, medium amount of organic matter	DTC_005	0–25	semi-fluid silt with sand
	190–290	soft plastic silt, olive-grey, large amount of organic matter		25–230	soft plastic silt
DTC_004	0–30	fine sand	DTC_006	0–52	fine sand with a lot of organic matter
	30–70	fine sand, small amount of silt and clay, large amount of organic matter		50–100	very soft plastic silt with a lot of organic matter
	70–145	soft silt with fine sand, large amount of organic matter		100–150	soft plastic silt with admixture of fine sand
	145–230	soft plastic silt, large amount of organic matter		150–250	very soft plastic silt, grey
DTC_007	0–68	fine-grained olive-grey sand			
	68–180	very soft plastic silt with a lot of organic matter			
	180–250	soft plastic silt with olive grey admixture			

3.2. Concentrations of PCDD/Fs and dl-PCBs

The Σ PCDD/F concentrations (the sum of the 17 PCDD/F congeners) in the surface sediments of the Lithuanian marine area varied from 2.6 to 430.2 $\text{pg}\cdot\text{g}^{-1}$ d.w., with an

average value of $113.5 \text{ pg}\cdot\text{g}^{-1} \text{ d.w.}$ The highest sum concentration ($430.2 \text{ pg}\cdot\text{g}^{-1} \text{ d.w.}$) was identified on the slopes of Gdansk Deep, where fine laminated sediments prevail (BJ-10 station). The dominant dioxin congeners were octa-CDD, followed by 1,2,3,4,6,7,8-hepta-CDD and furan congener octa-CDF. The fractions of the most toxic congeners (hexa-, penta- and tetra- chlorodibenzo-*p*-dioxins (HxCDD, PeCDD and TeCDD)) were considerably lower if the inflow of dioxins from anthropogenic sources was insignificant.

The $\Sigma\text{dl-PCB}$ concentrations ranged from 18.3 to $1053.3 \text{ pg}\cdot\text{g}^{-1} \text{ d.w.}$ and the average value was $231.9 \text{ pg}\cdot\text{g}^{-1} \text{ d.w.}$, with the dominant congeners in the whole investigated area being PCB 118 followed by PCB 105. The highest sum concentration of dl-PCBs ($1053.3 \text{ pg}\cdot\text{g}^{-1} \text{ d.w.}$) was recorded in the central part of the Lithuanian marine area (BJ-12 station).

Generally, both the $\Sigma\text{PCDD/F}$ and $\Sigma\text{dl-PCB}$ concentrations tended to increase from the coastal areas towards the deepest places, characterized by the accumulation of the finest sedimentary material. There were no increases in $\Sigma\text{PCDD/F}$ concentrations close to the offshore disposal areas, used for depositing sediments that are glaciogenic and recently sedimented and those that have been dredged in the Klaipėda Port (Lithuania). Relatively higher concentrations of $\Sigma\text{dl-PCBs}$ in the sediments were typical for deep-water disposal site IV and the adjacent areas (stations BJ-15, BJ-16 and BJ-17), while several stations located in the nearshore zone (BJ-29, BJ-30) close to nearshore disposal area V had considerably higher concentrations of $\Sigma\text{PCDD/Fs}$ (153.8 and $196.8 \text{ pg}\cdot\text{g}^{-1}$, respectively) compared to the deep-water site. Considering that the nearshore zone of the Lithuanian sector is under the constant impact of the Nemunas River water inflow, as well as the operation of the Klaipėda multipurpose port, the relatively higher level of PCDD/Fs in the sediments may be related to the additional input of those substances from the mentioned sources. The lowest levels of the investigated contaminants were observed in the areas of sand accumulation, suggesting that coarse-grained sedimentary matter may have lower sorption capacity to accumulate PCDD/Fs and dl-PCBs [8,25].

Summarized information on the mean values of dioxin concentrations and toxic equivalents of $\Sigma\text{PCDD/Fs}$ and $\Sigma\text{dl-PCB}$ in the Lithuanian and Polish parts of the studied basin is presented in Table 6.

The $\Sigma\text{PCDD/F}$ concentrations in the sediments taken from the Polish part of the southern Baltic Sea varied from 3.3 to $2329 \text{ pg}\cdot\text{g}^{-1} \text{ d.w.}$ The higher variation in PCDD/F concentrations in the Polish part compared to the Lithuanian part is explained by the presence of port samples in the collected data. The highest content of PCDD/Fs ($2329 \text{ pg}\cdot\text{g}^{-1} \text{ d.w.}$), which is more than five times higher than the maximum concentration recorded in the Lithuanian marine area, was observed in the sediments collected from the part of the Port of Gdynia adjacent to the area of the former naval shipyard. Samples from the same area were characterized by the highest amounts of dl-PCBs ($15,598$ – $113,505 \text{ pg}\cdot\text{g}^{-1} \text{ d.w.}$), with an average value of $729 \text{ pg}\cdot\text{g}^{-1} \text{ d.w.}$ Such large amounts of dioxin compounds in the sediments accumulating in the former shipyard basin provide clear evidence of historic pollution, induced by the presence of the industrial activity on the site.

Table 6. The mean values of the dioxin concentrations and toxic equivalents of Σ PCDD/Fs and Σ dl-PCB in the Lithuanian and Polish parts of the studied basin.

Congener	Lithuanian Part of the Gdansk Basin				Polish part of the Gdansk basin			
	Lithuanian Marine Area (Dredged-Soil-Disposal Areas Excluded), <i>n</i> = 35	Nearshore Disposal Site V, <i>n</i> = 4	Deepwater Disposal Site IV, <i>n</i> = 3	Vistula River Profile in the Gulf of Gdansk (Disposal Areas Excluded), <i>n</i> = 10	Gdynia Disposal Site I, <i>n</i> = 10	Gdansk Disposal Site II, <i>n</i> = 3	DCT Disposal Site III, <i>n</i> = 5	Port of Gdynia, <i>n</i> = 10
<i>Total concentrations [average values] [pg·g⁻¹ d.w.]</i>								
2,3,7,8-tetra-CDD	0.1	0.2	0.1	0.1	0.1	n.d.	0.1	0.2
1,2,3,7,8-penta-CDD	0.3	0.1	0.1	0.2	0.1	0.07	0.2	0.6
1,2,3,4,7,8-hexa-CDD	0.6	2.4	0.1	0.3	0.8	0.01	0.5	0.8
1,2,3,6,7,8-hexa-CDD	0.8	0.7	n.d.	0.5	0.7	0.03	1.0	3.8
1,2,3,7,8,9-hexa-CDD	0.9	1.7	0.1	0.8	0.5	0.2	1.3	2.7
1,2,3,4,6,7,8-hepta-CDD	8.7	3	1.1	9.3	21.4	3.2	12.6	87
octa-CDD	66.2	86.8	6.6	107	127	31.4	103	576
2,3,7,8-tetra-CDF	1.4	0.6	0.1	0.3	0.7	0.1	1.5	3.7
1,2,3,7,8-penta-CDF	1.2	0.3	0.1	0.15	0.4	0.09	1.2	2.6
2,3,4,7,8-penta-CDF	1.6	0.4	0.4	0.13	0.6	0.07	1.4	3.8
1,2,3,4,7,8-hexa-CDF	2.5	0.4	0.3	0.18	1.3	0.1	2.1	7.5
1,2,3,6,7,8-hexa-CDF	1.9	0.5	0.2	0.09	0.4	0.1	1.2	2.2
1,2,3,7,8,9-hexa-CDF	0.4	n.d.	0.1	n.d.	0.1	n.d.	0.1	1.1
2,3,4,6,7,8-hexa-CDF	1.2	0.2	0.1	0.11	0.3	n.d.	0.9	1.4
1,2,3,4,6,7,8-hepta-CDF	9.1	0.4	0.4	0.6	0.3	0.6	10.9	16.7
1,2,3,4,7,8,9-hepta-CDF	1.2	0.3	n.d.	0.05	4.3	n.d.	0.7	2.1
octa-CDF	18.4	1	0.5	0.8	1.3	0.2	9.3	16.9
Σ PCDD/Fs, [pg·g ⁻¹]	113.5	96	10	120	161	36.2	149	729
PCB 77	8	2.6	2.5	3.4	20.9	2.3	11.0	285.2
PCB 126	1.5	0.2	0.2	0.2	5.8	0.2	1.6	47.7
PCB169	0.5	n.d.	0.1	0.5	0.4	0.03	0.3	2.16
PCB 81	0.2	n.d.	n.d.	n.d.	0.6	0.1	0.3	5.4
PCB105	33.9	9.1	34.1	12.0	438	11.6	37.7	9 697
PCB114	1.5	0.7	1.9	0.9	32.8	2.1	2.3	573.6
PCB118	139.2	26	102.7	50	1494	37.5	62.4	17 344
PCB123	11.9	1.8	5.7	1.8	131.7	3.5	8.7	3 186
PCB156	18.8	2.7	36.1	23.1	408	8.2	18.2	3 965
PCB157	4.4	0.6	6	3.2	56.5	1.4	3.1	1 336
PCB167	9.3	1.2	14.8	9.8	151	4.1	9.1	2 859
PCB189	2.8	0.1	4.6	4.1	51.8	0.6	3.4	818.4
Σ dl-PCB, [pg·g ⁻¹]	231.9	45.1	208.6	107.4	2792	71.4	158	40 119
<i>Toxic equivalents [average values]</i>								
PCDD/Fs, pg·g ⁻¹ , TEQ	2.26	0.86	0.43	0.87	1.4	0.34	3.1	6.6
dl-PCB, pg·g ⁻¹ , TEQ	0.17	0.05	0.05	0.05	0.68	0.03	0.24	6.03

n.d.—not detected.

Among the investigated Polish offshore disposal sites, a higher content of Σ PCDD/Fs was identified at Gdynia disposal site I, historically used for the assimilation of sedimentary material dredged at the Port of Gdynia. The determined Σ PCDD/F concentrations ranged from 24 to 539 $\text{pg}\cdot\text{g}^{-1}$ d.w., with an average value of 161 $\text{pg}\cdot\text{g}^{-1}$ d.w. The highest amounts of dl-PCBs (131–8804 $\text{pg}\cdot\text{g}^{-1}$ d.w.) were also recorded at Gdynia disposal site I. The most contaminated areas at the Gdynia disposal site were located on the slopes of the uplift of the bottom in this region. The sedimentary material represented by fine fractions better accumulated impurities. The analyses of bottom sediments from this disposal site carried out in the period of 2019–2020 indicated an approximately twofold increase in dioxin concentrations compared to 2014. In the analyzed sediment cores collected from stations GDY_004, GDY_011 and GDY_012, the highest dioxin concentrations were found in the first sediment layers. The concentrations of total PCDD/Fs were as follows: at station GDY_004 (layer 0–66 cm), 115 $\text{pg}\cdot\text{g}^{-1}$ d.w.; at station GDY_011 (layer 0–76 cm), 258 $\text{pg}\cdot\text{g}^{-1}$ d.w.; and at station GDY_012 (layer 0–140 cm), 147 $\text{pg}\cdot\text{g}^{-1}$ d.w. Similarly to the surface sediments of this area, the highest concentrations were reached by the congeners OctaCDF, HeptaCDD, HexaCDF and HeptaCDF.

The Σ PCDD/Fs concentrations in the areas of Gdansk disposal site II and DCT disposal site III varied from 4.2 to 91 and from 33 to 193 $\text{pg}\cdot\text{g}^{-1}$ d.w., respectively. The obtained concentrations of dl-PCBs were 6–196 $\text{pg}\cdot\text{g}^{-1}$ d.w. in sediments from the Gdansk disposal site and 21–469 $\text{pg}\cdot\text{g}^{-1}$ d.w. in the DCT disposal site area.

The analyses of bottom sediments from the Gdansk and DCT disposal sites carried out in the period 2019–2020 indicated higher levels of dioxin concentrations compared to 2014. In the sediment sample from the Gdansk disposal site, the highest concentrations were reached by the congeners OctaCDD (119 $\text{pg}\cdot\text{g}^{-1}$ d.w.) and HeptaCDD (19.1 $\text{pg}\cdot\text{g}^{-1}$ d.w.), while the fractions of the other most toxic congeners were much lower. In the bottom-sediment core from this area, the concentrations of total PCDD/Fs ranged from 20.3 $\text{pg}\cdot\text{g}^{-1}$ d.w. in the deepest 130–200 cm layer to 897 $\text{pg}\cdot\text{g}^{-1}$ d.w. in the 22–78 cm layer. The organic matter content (expressed in terms of loss on ignition—LOI) in the 22–78 cm layer was 6.01% and was higher than in the other layers. The higher chlorinated PCDD/F congeners (hepta and aceta) predominated in the analyzed samples. The presence of the most toxic congener, TetraCDD, was found only in the 22–78 cm layer at a concentration of 0.418 $\text{pg}\cdot\text{g}^{-1}$ d.w.

The surface sediment samples from the DCT disposal site contained the highest concentrations of the congeners OctaCDD (70–274 $\text{pg}\cdot\text{g}^{-1}$ d.w.) and HeptaCDD (13.2–58 $\text{pg}\cdot\text{g}^{-1}$ d.w.), while the fractions of other more toxic congeners were much lower. The presence of the most toxic congener, TCDD, was only found in the sample from station DCT_012 (0.24 $\text{pg}\cdot\text{g}^{-1}$ d.w.). This station also showed a slightly different percentage of PCDD/Fs than the other samples (). In the studied bottom-sediment cores, the concentrations of total PCDDs were very similar and ranged from 28 to 53 $\text{pg}\cdot\text{g}^{-1}$ d.w. The highest concentration of total PCDDs (154 $\text{pg}\cdot\text{g}^{-1}$ d.w.) was found in the deepest layer of 150–250 cm at station DCT_006. The organic matter content (expressed as loss on ignition—LOI) was 4.13% in this layer. The higher chlorinated PCDD congeners (hepta and aceta) predominated strongly in these samples. The presence of furans (PCDF) was found only in the deepest layer (145–230 cm) of the sediment at DCT_004 (8.6 $\text{pg}\cdot\text{g}^{-1}$ d.w.) and in the surface layer of the sediment (0–52 cm) at DCT_006 (4.2 $\text{pg}\cdot\text{g}^{-1}$ d.w.).

The concentrations of Σ PCDD/Fs identified in sediments taken along the Vistula River profile varied from 116 to 173 $\text{pg}\cdot\text{g}^{-1}$ d.w. (average value: 120 $\text{pg}\cdot\text{g}^{-1}$ d.w.), except the W-09 station, where concentrations reached 3.3 $\text{pg}\cdot\text{g}^{-1}$ d.w. This station located in the coastal zone, which is characterized by the prevalence of sandy fractions, resulting in considerably lower accumulation of organic substances. The concentrations of dl-PCBs showed a constant increase from the mouth of the Vistula River (nearshore zone) towards the Gdansk Deep (10–288 $\text{pg}\cdot\text{g}^{-1}$ d.w.).

It is obvious that the average total concentrations of the studied PCDD/Fs in the Lithuanian and Polish marine areas (with the disposal areas and Port of Gdynia excluded)

are on the same level. Among the offshore disposal areas, Gdynia disposal site I was characterized by the highest average values of Σ PCDD/Fs, followed by DCT disposal area III and Lithuanian nearshore disposal site V. However, by far the highest concentrations of dioxins and furans were found in sediments collected from the Port of Gdynia area.

A slightly different situation was observed for the dl-PCBs. Clear dominance of dl-PCBs ($40,119 \text{ pg}\cdot\text{g}^{-1}$) was found in the sediments from the Port of Gdynia, and the second highest average value was typical for Gdynia disposal site I ($2792 \text{ pg}\cdot\text{g}^{-1}$). The other studied areas were characterized by rather similar average concentrations of dl-PCBs.

Summarized information about the mean values of the dioxin concentrations and toxic equivalents of Σ PCDD/Fs in the Polish part of the studied basin in 2019–2020 is presented in Table 7.

Table 7. The mean values of the dioxin concentrations and toxic equivalents of Σ PCDD/Fs in the Polish part of the studied basin in 2019–2020.

Congener	Polish Part of the Gdansk Basin 2019–2020					
	Gdynia Disposal Site I <i>n</i> = 14	GDY_REF	Gdansk Disposal Site II, <i>n</i> = 1	GDA_REF	DCT Disposal Site III, <i>n</i> = 12	DCT_REF
<i>Total concentrations (average values) [$\text{pg}\cdot\text{g}^{-1}$ d.w.]</i>						
2,3,7,8-tetra-CDD	0.08	0.20	n.d.	n.d.	0.11	n.d.
1,2,3,7,8-penta-CDD	0.30	0.58	n.d.	n.d.	1.41	1.24
1,2,3,4,7,8-hexa-CDD	0.41	0.72	n.d.	n.d.	1.53	1.25
1,2,3,6,7,8-hexa-CDD	1.27	1.99	1.28	n.d.	3.20	2.96
1,2,3,7,8,9-hexa-CDD	0.88	1.75	0.65	n.d.	3.09	2.52
1,2,3,4,6,7,8-hepta-CDD	32.4	24.8	19.1	n.d.	26.6	35.0
octa-CDD	206	181	119	n.d.	130	275
2,3,7,8-tetra-CDF	1.01	0.20	n.d.	n.d.	1.71	3.75
1,2,3,7,8-penta-CDF	0.64	1.81	n.d.	n.d.	3.20	2.15
2,3,4,7,8-penta-CDF	0.97	2.86	0.79	n.d.	1.71	4.01
1,2,3,4,7,8-hexa-CDF	1.46	3.02	0.61	n.d.	8.17	3.6
1,2,3,6,7,8-hexa-CDF	0.74	1.90	0.5	n.d.	3.65	2.48
1,2,3,7,8,9-hexa-CDF	0.17	n.d.	n.d.	n.d.	n.d.	0.87
2,3,4,6,7,8-hexa-CDF	0.67	1.82	0.46	n.d.	1.66	3.07
1,2,3,4,6,7,8-hepta-CDF	4.94	12.4	4.86	n.d.	10.16	13.9
1,2,3,4,7,8,9-hepta-CDF	0.63	1.27	0.61	n.d.	1.61	1.40
octa-CDF	6.90	21.6	6.27	n.d.	10.05	20.0
Σ PCDD/Fs, [$\text{pg}\cdot\text{g}^{-1}$]	259.3	257.9	154.1	n.d.	207.8	373.2
<i>Toxic equivalents [average values]</i>						
PCDD/Fs $\text{pg}\cdot\text{g}^{-1}$ ·TEQ	2.03	4.09	1.70	0.77	4.54	5.77

n.d.—not detected.

Although the average value of Σ PCDD/Fs in bottom sediments collected from offshore disposal sites in the Polish part of the Gdansk basin in 2019–2020, was approximately twice as high as the Σ PCDD/Fs for these areas in 2014; the results obtained were close to or lower than those for the Σ PCDD/Fs at the designated reference points located approximately 1 Mm from the boundaries of the individual disposal areas. The exception to this was the Σ PCDD/Fs ($154 \text{ pg}\cdot\text{g}^{-1}$ d.w.) at Gdansk disposal site II, the concentrations of which were significantly higher than at the designated reference point. At the GDA_REF station, Σ PCDD/Fs was below the lower detection limit.

3.3. Toxic Equivalents of PCDD/Fs and dl-PCBs

The total WHO-TEQ values were calculated by multiplying the absolute concentration of each isomer by a toxicity equivalency factor (TEF) proposed by the WHO in 2005 to represent the toxic or biological effects [8]. The TEQ values in the Lithuanian sector of

the Gdansk Basin ranged from 0.16 to 9.5 $\text{pg}\cdot\text{g}^{-1}$ d.w. for PCDD/Fs and from 0.01 to 1.1 $\text{pg}\cdot\text{g}^{-1}$ for dl-PCBs. The highest toxicity equivalents were found on the north-eastern slopes of the Gdansk Deep (BJ-9–BJ12, BJ-23), characterized by the finest sediments. A TEQ value of 7.1 $\text{pg}\cdot\text{g}^{-1}$ was also observed at station BJ-42 (water depth 100 m) in the Eastern Gotland Basin.

The TEQ values in the Polish part of the Gdansk Basin varied from 0.12 to 4.5 $\text{pg}\cdot\text{g}^{-1}$ d.w. for PCDD/Fs and from <0.01 to 0.42 $\text{pg}\cdot\text{g}^{-1}$ for dl-PCBs. The highest toxicity equivalents were found in the area of DCT disposal site III (4.5 $\text{pg}\cdot\text{g}^{-1}$ at the W-08 station) and Gdynia disposal site I (2.7 $\text{pg}\cdot\text{g}^{-1}$ at the K-20 station). This trend was also observed during the study period of 2019–2020. The highest TEQ values were observed at the DCT disposal site at the stations DCT_012 (TEQ 13.5 $\text{pg}\cdot\text{g}^{-1}$), DCT_008 (TEQ 5.28 $\text{pg}\cdot\text{g}^{-1}$) and reference station DCT_REF (TEQ 5.77 $\text{pg}\cdot\text{g}^{-1}$). The average TEQ values for PCDD/Fs were 1.7 $\text{pg}\cdot\text{g}^{-1}$ d.w. for Gdansk disposal site II, 2.03 $\text{pg}\cdot\text{g}^{-1}$ d.w. for Gdynia disposal site I and 4.54 $\text{pg}\cdot\text{g}^{-1}$ d.w. for DCT disposal site III. Considerably higher TEQ values (up to 16 $\text{pg}\cdot\text{g}^{-1}$ d.w. for PCDD/Fs and 11 $\text{pg}\cdot\text{g}^{-1}$ for dl-PCBs) are typical for the sediments from the Port of Gdynia.

Many scientists assume a TEQ value of 5 $\text{pg}\cdot\text{g}^{-1}$ d.w. to be characteristic of “ecologically clean” territories [14,26]. In 86% of the investigated samples from the Lithuanian part, the TEQ values for PCDD/Fs were lower than the ecologically allowable threshold. Sediments accumulating in the Port of Gdynia and in DCT_REF in this sense can be regarded as strongly contaminated by dioxins, as most of the observed TEQ values were higher than available threshold value. Summarized information on the mean values of the toxic equivalents of $\Sigma\text{PCDD/Fs}$ and $\Sigma\text{dl-PCB}$ in the Lithuanian and Polish parts of the studied basin is presented in Tables 6 and 7.

3.4. Congener Profiles of PCDD/Fs and dl-PCBs

The congener profile term introduced by Rappe [26] indicates the separation of congener groups with the same number of chlorine atoms in a molecule, which often characterizes a certain type of emission source.

The specific composition of congeners is reflected by the source of pollution: 2,3,7,8-TCDF and OCDF are indicators of paper pulp bleaching and the production of vinyl chloride, and the congener 1,2,3,4,6,7,8-HpCDF is an indicator of the production of chlorophenols. OCDD is the main congener in atmospheric dusts and the processing contamination of pentachlorophenols and is produced photochemically and thermally.

Congener pattern analysis showed clear dominance of OCDD in most of the sediment samples collected in both the Lithuanian and Polish marine sectors. However, the distribution of the other congeners varies throughout the study areas. The presence of HpCDF (1,2,3,4,6,7,8-H7CDF–chlorophenols) and HpCDD (1,2,3,4,6,7,8-H7CDD–pentachlorophenol) in the sediments from both study areas indicated that pentachlorophenol or currently used pesticides may be important sources of dioxins. However, due to the lack of significant point source emissions in this region, presence of the mentioned congener is possibly related to the natural properties of sediments (e.g., high contents of organic substances).

The profile patterns of both the PCDD and PCDF congeners and dl-PCBs in surface sediments collected in the Lithuanian and Polish parts of the studied basin are presented in Figure 3.

Analyzing the profiles patterns of PCDD/PCDF congeners and dl-PCBs revealed a similarity between the percentage of individual congeners in samples taken from the Port of Gdynia and Gdynia disposal site. Among the analyzed PCDDs, the most abundant was OCDD, then HpCDD (80% and above 10%, respectively). Similarly, in sediments collected from the Gulf of Gdansk, we found the most abundant was OCDD, followed by HpCDD. However, in the sediments of the Gulf of Gdansk, OCDD participation was much higher (>90%) compared to HpCDD (<10%). In the case of PCDF in surface sediments from the Port of Gdynia and Gdynia disposal site, the difference in the percentages of OCDF and HpCDF was negligible. However, in the sediments of the Gulf of Gdansk, we found a slight

increase in HpCDF in relation to OCDF. Considering the congener profile of the studied dl-PCB, we found the highest percentage of PCB congener 118 in the surface sediments of the entire study area. The differences between the sediments from the Port of Gdynia and Gdynia disposal site and the sediments taken from the Gulf of Gdansk are visible in the case of congeners PCB 105 and PCB 77. In sediments from the Port of Gdynia and Gdynia disposal site, we found a higher percentage of PCB 105 and a lower percentage of PCB 77. In contrast, the opposite situation was observed in sediments of the Gulf of Gdansk. In all examined sediments, a higher content of PCDD in relation to the PCDF was indicated.

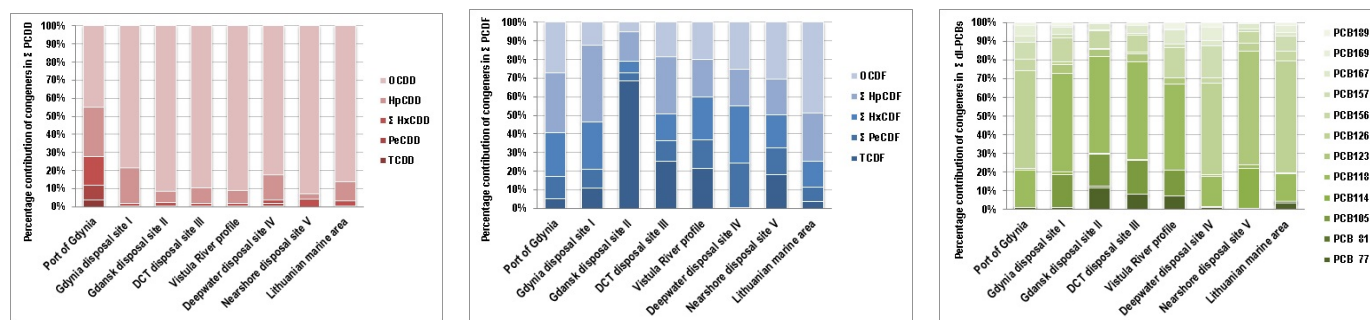


Figure 3. Profile patterns of both PCDD and PCDF congeners and dl-PCBs in surface sediments collected in Lithuanian and Polish parts of studied basin in 2014.

This trend was also observed during the studied period of 2019–2020. The profile patterns of both PCDD and PCDF congeners in surface sediments collected from disposal sites in Gdynia and DCT in 2019–2020 are presented in Figure 4.

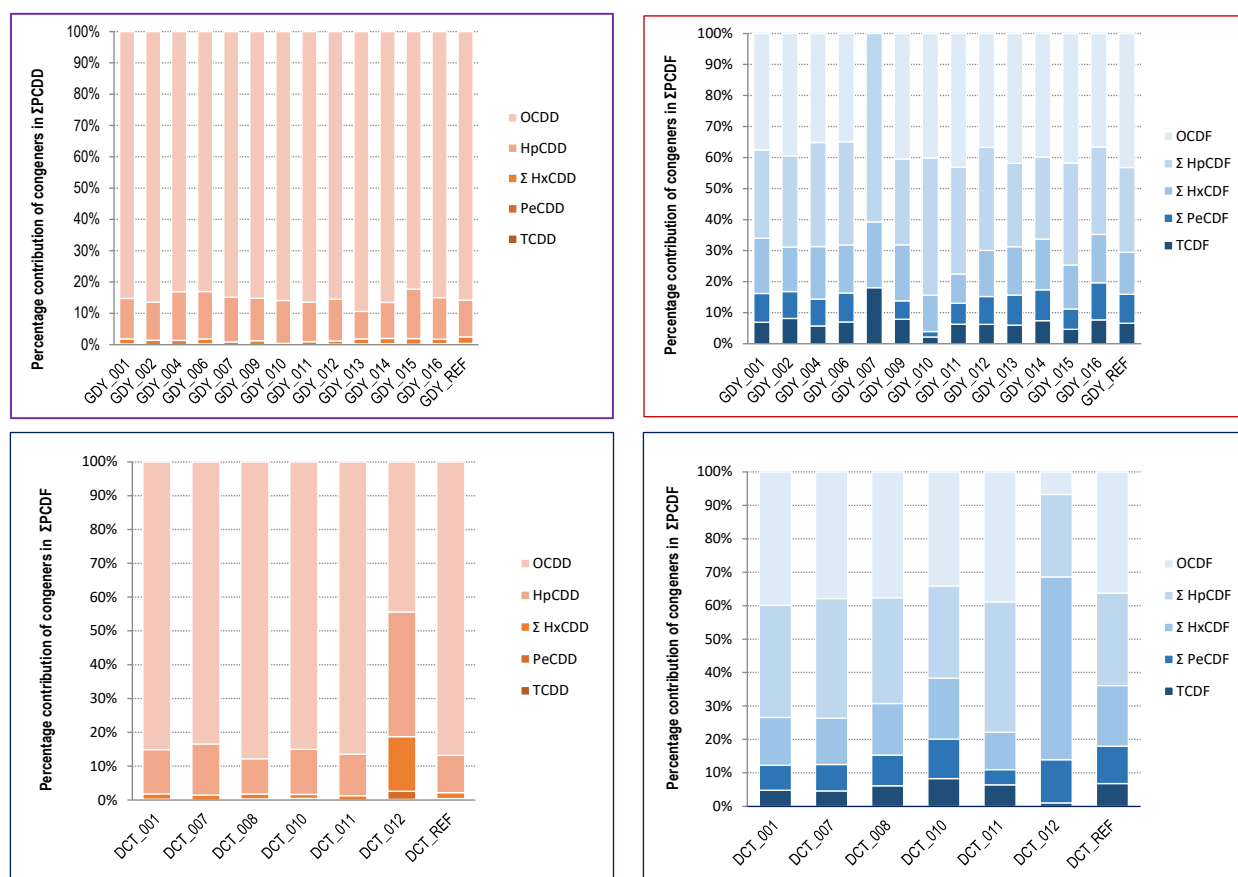


Figure 4. Profile patterns of both PCDD and PCDF congeners in surface sediments collected from disposal sites in Gdynia and DCT in 2019–2020.

Among the PCDDs analyzed, OCDD showed the highest proportion, followed by HpCDD (80% and more than 10%, respectively). The exception was the sediment collected from the DCT disposal site III at DCT_12. At this station, approximately 42% OCDD, 35% HpCDD and 20% Σ HxCDD were found. For PCDFs in the surface sediments of the disposal sites, the difference in the percentage of OCDFs and HpCDFs was not significant. Only at DCT disposal site III at DCT_12 was a different percentage of PCDD/Fs found than in the other samples studied. The highest contribution was shown by Σ HxCDF.

As in the case of surface sediments, the analysis of congener patterns in the core samples showed the dominance of OCDD, as well as OCDF and HpCDF, in the majority of sediment samples collected at the disposal sites. Examples of the patterns of the PCDD and PCDF congener profiles in the core sediments collected at the Gdansk disposal sites are shown in Figure 5.

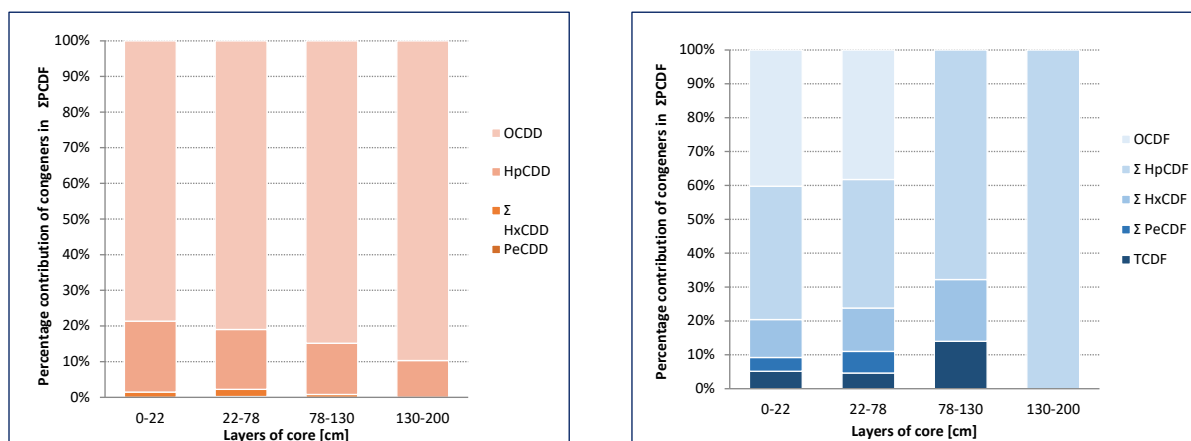


Figure 5. Profiles patterns of PCDD and PCDF congeners in core sediments collected from disposal sites in Gdansk in 2019–2020.

3.5. Principal Component Analysis (PCA)

Details of the application of principal component analysis (PCA) to environmental samples can be found in Johnson and Ehrlich [27]. Twenty-nine congeners were used in the PCA for the south-eastern part of the Baltic Sea (Lithuanian and Polish marine areas): ten dioxins (polychlorinated dibenzo-*p*-dioxins (PCDDs)), seven dibenzofurans (PCDFs) and twelve dioxin-like polychlorinated biphenyls (dl-PCBs)). PCA was conducted using STATISTICA (Version 10). Several exploratory PCAs were conducted to examine the relationships between PCDD, PCDF and dl-PCB congener patterns in different areas of the south-eastern part of the Baltic Sea (Lithuanian and Polish marine areas). A total of 143 surface and core sediment samples were included in this analysis. The statistical analysis showed pollution of polychlorinated dibenzo-*p*-dioxins, dibenzofurans and dioxin-like polychlorinated biphenyls in sediments of the south-eastern Baltic Sea, with a cumulative variance contribution of 78.30%. PC1 had larger loadings on Σ PeCDF, Σ HxCDF and Σ HpCDF, which was able to explain 63.68% of the total variance. PC2 had a large loading on PCB, accounting for 14.62% of the total variance. The PCA score plot confirms that the samples shared similar emission sources. PCA also confirms the domination of OCDF in the spectrum of the investigated PCDFs (Figure 6).

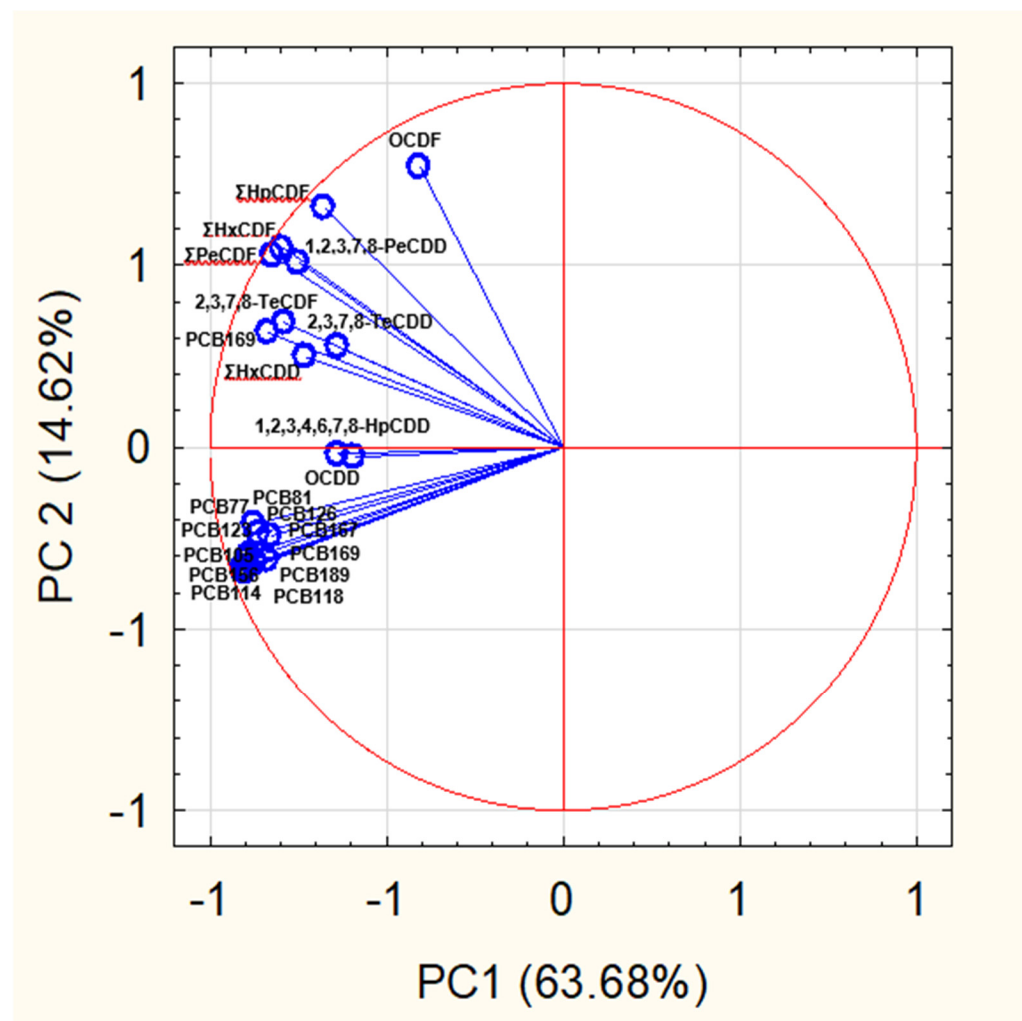


Figure 6. Results of principal component analysis.

4. Discussion

Previous studies of the Baltic Sea environment have shown that PCDD/Fs and dl-PCBs have different sources and source areas [1,28–30]. Although the highest concentrations of congeners are typically found in the vicinities of their direct sources (industrial and non-industrial combustion activities; wastewater discharge areas), air emissions are regarded as the most important external sources, especially for the offshore areas [30].

In [1], the total concentration of PCDD/Fs in the bottom sediments of the rivers studied (lower Oder, Vistula River) were within the range of 146–1424 pg g^{-1} d.w., while the toxicity equivalent ranged from 1.05 to 18.27 pg I-TEQ g^{-1} d.w. The highest concentration was recorded at the site of wastewater discharge.

In [20], the total concentration of PCDD/Fs in marine bottom sediments was in the range of 11–181 pg g^{-1} d.w., while the toxicity equivalent remained in the range of 0.29–9.3 pg I-TEQ g^{-1} d.w. Cato et al. [31] noted that in sediment cores taken from the northern Bornholm basin, the concentrations of PCDD/Fs were, respectively, 18 and 28 pg g^{-1} d.w. at 0–3 cm and 6–9 cm sediment depths.

In [32], the total concentration of Σ PCDD/Fs in the surface layer of bottom sediments from the Port of Gdansk ranged from 281 to 358.5 pg g^{-1} d.w. The authors also found the highest concentrations of OCDD and HpCDD congeners.

Dioxins entering the marine environment have a negative impact on the marine ecosystem as they are particularly toxic substances. The bioavailability of PCDD/Fs and dl-PCBs is influenced by many factors. As hydrophobic substances, these compounds tend to move from the water to the bottom sediments through adsorption on suspended solids and

bottom sediments. In this process, the sedimentation rate, the content of fine granulometric fractions and the size and type of organic matter in the bottom sediments are very important. Most PCDD/Fs and dl-PCBs accumulate in bottom sediment with a high content of fine fractions and organic matter of autochthonous origin. The bioavailability of dioxins and furans is also favored by high primary production in the area and the occurrence of fish with high fat content (e.g., salmon, herring), in which the highest accumulation of dioxins and furans takes place, which have a high affinity for fats [33,34].

Generally, there are no legal regulations regarding the limit values of PCDD/F concentrations in bottom sediments. However, Hemming et al. [35] consider a concentration of $<10 \text{ pg} \cdot \text{g}^{-1}$ to represent no risk, whereas a threshold equal to $0.85 \text{ pg} \cdot \text{g}^{-1} \text{ d.w.}$ is recommended by the European Commission.

Our analysis of the occurrence of correlations between PCDD, PCDF and dl-PCB concentrations in bottom sediments and organic matter (LOI) content showed a significant correlation of the mentioned compounds with organic matter in the Lithuanian marine area (dredged-soil-disposal areas excluded). The correlations in this area were as follows: for ΣPCDD and LOI— $r^2 = 0.72$, $p < 0.05$, $n = 35$; for ΣPCDF and LOI— $r^2 = 0.67$, $p < 0.05$, $n = 35$; for dl-PCBs and LOI— $r^2 = 0.45$, $p < 0.05$, $n = 35$. In contrast, PCDD/Fs and dl-PCBs present in sediments from the other research areas showed no significant correlation with LOI. For these areas, the correlation coefficient (r^2) was ≤ 0.1 , $p < 0.05$. This may be due to the type of organic matter present in the sediment of the Lithuanian marine area (dredged-soil-disposal areas excluded) being characterised by a higher content of autochthonous organic matter, which has a higher affinity for PCDD/Fs and dl-PCBs [34].

Congener pattern analysis showed that higher chlorinated CDDs (octa, hepta) dominated in all the sediment samples.

The distribution of the PCDD/Fs and dl-PCBs in the surface sediments of the Gdansk Basin revealed that the inflow of the mentioned substances from the anthropogenic sources is insignificant. This confirms the earlier findings made by Polish researchers [20,32] regarding the PCDD/F pollution in the coastal zone of the southern part of the Baltic Sea.

The concentrations of the investigated contaminants in sediments of the offshore disposal sites showed a lack of secondary dioxin pollution in the study area. In general, the degree of surface sediment enrichment with PCDD/Fs and dl-PCBs in the investigated areas is considerably lower than that observed in the north-western Baltic Sea coastal areas of Finland, Sweden and Denmark [14,15]. Most likely, this fact can be explained by the absence of major point sources or combined sources related to specific industries (thermal processes, pulp bleaching or vinyl chloride production) both along the Polish and Lithuanian coasts of the Gdansk Basin. The domination of higher-chlorinated PCDDs (octa, hepta) in all of the investigated samples of surface sediments suggests that atmospheric deposition is the main contributor of dioxin occurrence in this part of the Baltic Sea [18–20,26,36,37].

Nevertheless, the recorded PCDD/F values are still well ahead of the existing quantitative targets for these sediments recommended by the European Commission (threshold equals to $0.85 \text{ pg} \cdot \text{g}^{-1} \text{ d.w.}$). In this sense, even the south-eastern part of the Baltic Sea can be characterized as not representing good environmental status.

PCB118 was found to be dominant in the sediments collected from different areas of the Baltic Sea (Southern Baltic Proper, Bothnian Bay, Bothnian Sea, Gotland Deep, Baltic Proper) [38,39].

5. Conclusions

This research paper presents the first regional assessment of sediment contamination by dioxins (PCDDs), dibenzofurans (PCDFs) and dioxin-like PCBs (dl-PCBs) in the southeastern Baltic Sea (Lithuanian and Polish marine areas) during 2014 and 2019–2020. A total of 143 sediment samples were collected from offshore dredged-soil-disposal sites in a former shipyard in Gdynia, and along the natural sediment migration patterns in the Gdansk Basin. The study revealed a wide range of total dioxin content and congener profiles, indicating probable sources. The characteristic congener profiles showed high

levels of OCDD and HpCDD, while the other toxic congeners were less abundant. The dominance of higher-chlorinated PCDDs (octa, hepta) in all of the investigated surface sediment samples suggests that atmospheric deposition is the main cause of dioxin occurrence in this part of the Baltic Sea.

Although the enrichment of surface sediments in PCDD/Fs and dl-PCBs in the study areas is considerably lower than that observed in the north-western coastal areas of the Baltic Sea in Finland, Sweden and Denmark, they are well above the existing quantitative sediment targets recommended by the European Commission. In this sense, the south-eastern part of the Baltic Sea can be characterised as not representing good environmental status.

The results obtained fill previous data gaps and provide a solid basis for further discussion on dioxin accumulation in surface sediments of the south-eastern Baltic Sea.

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References

1. Niemirycz, E. *Halogenowane Związki Organiczne w Ekosystemach Rzecznych i Odpyływ Tych Związków do Morza Bałtyckiego*; IMGW: Warsaw, Poland, 2006; p. 121. (In Polish)
2. Nunes, M.; Marchand, P.; Vernisseau, A.; Le Bizec, B.; Ramos, F.; Pardal, M.A. PCDD/Fs and dioxin-like PCBs in sediment and biota from the Mondego estuary (Portugal). *Chemosphere* **2011**, *83*, 1345–1352. [[CrossRef](#)] [[PubMed](#)]
3. HELCOM. *Hazardous Substances in the Baltic Sea. An Integrated Thematic Assessment in the Baltic Sea*; Baltic Sea Environment Proceeding No. 120; Baltic Marine Environment Protection Commission: Helsinki, Finland, 2010.
4. WHO. *Health Risks of Persistent Organic Pollutants from Long-Range Transboundary Air*; WHO: Copenhagen, Denmark, 2003.
5. Birch, G.F.; Harrington, C.; Symons, R.K.; Hunt, J.W. The source and distribution of polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzofurans in sediments of Port Jackson. *Australia. Mar. Pollut. Bull.* **2007**, *54*, 295–308. [[CrossRef](#)] [[PubMed](#)]
6. Salo, S.; Verta, M.; Malve, O.; Korhonen, M.; Lehtoranta, J.; Kiviranta, H.; Isosaari, P.; Ruokojärvi, P.; Koistinen, J.; Vartiainen, T. Contamination of River Kymijoki sediments with polychlorinated dibenzo-*p*-dioxins, dibenzofurans and mercury and their transport to the Gulf of Finland in the Baltic Sea. *Chemosphere* **2008**, *73*, 1675–1683. [[CrossRef](#)] [[PubMed](#)]
7. Sundqvist, K.L.; Tysklind, M.; Cato, I.; Bignert, A.; Wiberg, K. Levels and homologue profiles of PCDD/Fs in sediments along the Swedish coast of the Baltic Sea. *Environ. Sci. Pollut. Res.* **2009**, *16*, 396–409. [[CrossRef](#)] [[PubMed](#)]
8. Cai, M.; Hong, Q.; Sun, J.; Sundqvist, K.; Wiberg, K.; Chen, K.; Wang, Y.; Qiu, C.; Huang, S. Concentrations, distribution and sources of polychlorinated dibenzo-*p*-dioxins and dibenzofurans and dioxin-like polychlorinated biphenyls in coastal sediments from Xiamen. *China Mar. Chem.* **2016**, *185*, 74–81. [[CrossRef](#)]
9. Prakash, B.O. Persistent organic compounds in the environment their impact on human health: A review. *GSC Biol. Pharm. Sci.* **2019**, *8*, 81–88.
10. Jonsson, P.; Rappe, C.; Kjeller, L.O.; Kierkegaard, A.; Haakanson, L.; Jonsson, B. Pulp-mill related polychlorinated organic compounds in Baltic Sea sediments. *Ambio* **1993**, *22*, 37–43.
11. Koistinen, J.; Stenman, O.; Haahti, H.; Suonperä, M.; Paasivirta, J. Polychlorinated diphenyl ethers, dibenzo-*p*-dioxins, dibenzofurans and biphenyls in seals and sediment from the Gulf of Finland. *Chemosphere* **1997**, *35*, 1249–1269. [[CrossRef](#)] [[PubMed](#)]
12. Witt, G.; Schramm, K.W.; Henkelman, B. Occurrence and distribution of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in sediments of the Western Baltic Sea. *Chemosphere* **1997**, *35*, 1465–1473. [[CrossRef](#)]
13. Isosaari, P.; Kankaanpää, H.; Mattila, J.; Kiviranta, H.; Verta, M.; Salo, S.; Vartiainen, T. Spatial distribution and temporal accumulation of polychlorinated dibenzo-*p*-dioxins, dibenzofurans and biphenyls in the Gulf of Finland. *Environ. Sci. Technol.* **2002**, *36*, 2560–2565. [[CrossRef](#)]

14. Verta, M.; Salo, S.; Korhonen, M.; Assmuth, T.; Kiviranta, H.; Koistinen, J.; Ruokojärvi, P.; Isosaari, P.; Bergqvist, P.A.; Tysklind, M.; et al. Dioxin concentrations in sediments of the Baltic Sea—A survey of existing data. *Chemosphere* **2007**, *67*, 1762–1775. [[CrossRef](#)] [[PubMed](#)]
15. Sundqvist, K.L.; Tysklind, M.; Geladi, P.; Hopke, P.K.; Wiberg, K. PCDD/F source apportionment in the baltic sea using positive matrix factorization. *Environ. Sci. Technol.* **2010**, *44*, 16901697. [[CrossRef](#)] [[PubMed](#)]
16. Assefa, A.T.; Sundqvist, K.L.; Cato, I.; Jonsson, P.; Sobek, A.; Tysklind, M.; Wiberg, K. Trends of PCDD/Fs in costal and offshore Baltic Sea sediment cores covering the 20th century. *Organohalogen Compd.* **2012**, *74*, 328–331.
17. Baran, A.; Mierzwa-Hersztek, M.; Urbaniak, M.; Gondek, K.; Tarnawski, M.; Szara, M.; Zieliński, M. An assessment of the concentrations of PCDDs/Fs in contaminated bottom sediments and their sources and ecological risk. *J. Soils Sediments* **2020**, *20*, 2588–2597. [[CrossRef](#)]
18. McLachlan, M.; Undeman, E. *Dioxins and PCBs in the Baltic Sea*; Helcom Baltic Sea Environment Proceedings n°171; Baltic Marine Environment Protection Commission: Helsinki, Finland, 2020.
19. Dereszewska, A.; Krasowska, K.; Popek, M. Presence, concentrations and risk assessment of dioxins in bottom sediments of Port of Gdynia. In Proceedings of the 17th Summer Safety & Reliability Seminars—SSARS 2023, Kraków, Poland, 9–14 July 2023; pp. 59–68.
20. Niemirycz, E.; Jankowska, D. Concentrations and profiles of PCDD/Fs in sediments of major Polish rivers and the Gdansk Basin—Baltic Sea. *Chemosphere* **2011**, *85*, 525–532. [[CrossRef](#)] [[PubMed](#)]
21. Falandysz, J.; Trzosinska, A.; Szefer, P.; Warzocha, J.; Draganik, B. The Baltic Sea. especially southern and eastern regions. In *Seas at the Millennium: An Environmental Evaluation*; 1. Regional Chapters: Europe. The Americas and West Africa; Sheppard, C.R.C., Ed.; Elsevier Science: Amsterdam, The Netherlands, 2000; pp. 99–120.
22. PN-EN ISO 5667-19:2006; Water quality—Sampling—Part 19: Guidelines for Marine Sediment Sampling. ISO: Geneva, Switzerland, 2006.
23. Method 1613, Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS; U.S. Environmental Protection Agency Office of Water Engineering and Analysis Division (4303), Oktober: Grand Rapids, MI, USA, 1994.
24. PN-EN 15935:2022-01; Soil, Waste, Treated Bio-Waste and Sewage Sludge—Determination of losses on ignition. Polish Committee for Standardization: Warsaw, Poland, 2022.
25. Hung, C.C.; Gong, G.C.; Ko, F.C.; Santschi, P.H. Relationships between persistent organic pollutants and carbonaceous materials in aquatic sediments of Taiwan. *Mar. Pollut. Bull.* **2010**, *60*, 1010–1017. [[CrossRef](#)]
26. Rappe, C. Sources of PCDDs and PCDFs. Introduction. Reactions, levels, patterns, profiles and trends. *Chemosphere* **1992**, *25*, 41–44. [[CrossRef](#)]
27. Johnson, G.W.; Ehrlich, R. State of the art report on multivariate chemometric methods in environmental forensics. *Environ. Forensics* **2002**, *3*, 59–79.
28. Sellström, U.; Egeback, A.L.; McLachlan, M.S. Identifying source regions for the atmospheric input of PCDD/Fs to the Baltic Sea. *Atmos. Environ.* **2009**, *43*, 1730–1736. [[CrossRef](#)]
29. Shatalov, V.; Johansson, J.H.; Wiberg, K.; Cousins, I.T. Tracing the origin of dioxins in Baltic air using an atmospheric modeling approach. *Atmos. Pollut. Res.* **2012**, *3*, 408–416. [[CrossRef](#)]
30. Wiberg, K.; Assefa, A.T.; Sundqvist, K.L.; Cousins, I.T.; Johansson, J.; McLachlan, M.S.; Sobek, A.; Cornelissen, G.; Miller, A.; Hedman, J.; et al. *Managing the Dioxin Problem in the Baltic Region with Focus on Sources to Air and Fish*; Swedish Environmental Protection Agency: Stockholm, Sweden, 2013; ISBN 978-91-620-8652-7. ISSN 0282-7298.
31. Cato, I.; Assefa, A.; Wiberg, K. Background paper on concentrations of polychlorinated dibenzop-dioxins and polychlorinated dibenzofurans (PCDD/Fs) in postglacial clays of the Baltic Sea. Annex 6: 29–35. In Proceedings of the ICES Lisbon, Lisbon, Portugal, 12–16 March 2012. Report of the Working Group on Marine Sediments in Relation to Pollution (WGMS); ICES CM 2012/SSGHIE:06.
32. Lewandowski, K.; Witt, M.; Kobusińska, M.; Niemirycz, E. Polychlorinated dibenzi-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and pentachlorophenol (PCP) in bottom sediments of the Port of Gdansk. *Oceanol. Hydrobiol. Stud.* **2014**, *43*, 312–323. [[CrossRef](#)]
33. Piskorska-Pliszczynska, J.; Maszewski, S.; Warenik-Bany, M.; Mikolajczyk, S.; Goraj, L. Survey of persistent organochlorine contaminants (PCDD, PCDF, and PCB) in fish collected from the Polish Baltic fishing areas. *Sci. J.* **2012**, *2012*, 973292. [[CrossRef](#)] [[PubMed](#)]
34. Nevalainen, L.; Tuomisto, J.; Haapasaari, P.; Lehtikoinen, A. Spatial aspects of the dioxin risk formation in the Baltic Sea: A systematic Review. *Sci. Total Environ.* **2021**, *753*, 142–185. [[CrossRef](#)] [[PubMed](#)]
35. Hemming, J.M.; Brim, M.S.; Jarvis, R.B. A survey of dioxin and furan compounds in sediments of Florida Panhandle Bay systems. *Mar. Pollut. Bull.* **2003**, *46*, 512–521. [[CrossRef](#)] [[PubMed](#)]
36. Lohmann, R.; Jones, K.C. Dioxins and furans in air and deposition: A review of levels. behaviour and processes. *Sci. Total Environ.* **1998**, *219*, 53–81. [[CrossRef](#)] [[PubMed](#)]
37. Hites, R. (Ed.) *Persistent Organic Pollutants in the Great Lakes*; Springer: Berlin/Heidelberg, Germany; New York, NY, USA, 2006.

38. Bandh, C.; Bjorklund, E.; Mathiasson, L.; Naf, C.; Zebuhr, Y. Comparison of Accelerated Solvent Extraction and Soxhlet Extraction for the Determination of PCBs in Baltic Sea Sediments. *Environ. Sci. Technol.* **2000**, *34*, 4995–5000. [[CrossRef](#)]
39. Pikkarainen, A.L. Polychlorinated biphenyls and organochlorine pesticides in Baltic Sea sediments and bivalves. *Chemosphere* **2007**, *68*, 17–24. [[CrossRef](#)]

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