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Determination of Selected Organic Contaminants in the Port of Gdynia Sediments: Towards Cleaner Baltic Ports

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Abstract: Seaports affect the environment through various functions related to cargo handling, connectivity to the sea and land transport networks, and industrial, logistics, and distribution activities. The purpose of this study was to perform a preliminary assessment of the contents of dioxins and microplastics in the bottom sediments of the Port of Gdynia. The identification of plastic particles was carried out on the basis of visual and microscopic observations, as well as spectroscopy analysis. Fragments and fibres were dominant when categorised by particle shape, while transparent, white, and black particles dominated when categorised by colour. The predominant polymer types identified polyolefins and their derivatives. These findings suggest that low-density plastics are present in seabed sediments, probably as a result of biofouling. Samples were also tested for the presence of dioxins. In the sediment surface layer, the highest concentrations were obtained for octachlorodibenzo-p-dioxin (5.54–962 ng/kg d.m.), which has low toxicity. The most toxic congener (2,3,7,8-tetrachlorodibenzo-p-dioxin) was present in very low concentrations (0.19–0.32 ng/kg s.m.). The values of the toxicity coefficient ranged from 0.01 to 9.77 ng/kg s.m. The results showed that in the studied bottom zones in Gdynia Port, the analysed pollutants do not cause a high ecological risk and do not require permanent monitoring.

Keywords: marine environment; port; contaminants; port bottom sediments; dioxins; microplastics; Port of Gdynia

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1. Introduction

Economic growth and commercial activities have contributed to significant port development over the past few decades. Nonetheless, increasing environmental consciousness has introduced new challenges for the development and management of ports [1]. The nature of activities and services carried out in the port area can be the reason for many environmental aspects contributing to the port's environmental footprint [2,3]. Seaports impact the environment through their diverse roles in cargo handling, connections to sea and land transport systems, and industrial, logistical, and distribution operations. Several sources of pollution arise from port operations, such as air pollution, sewage pollution, water pollution, and solid waste pollution [4]. It is important to emphasise that the cumulative environmental impact of contemporary port operations across Europe is likely relatively minor when compared to other human activities, including urban development, industrial processes, and tourism [5].

The environmental impact will vary from place to place due to differences in geography, hydrology, geology, shipping intensity, and port industrialisation. Therefore, regular monitoring and evaluation of the port environment is necessary to determine pollution levels, identify the sources of pollution, and predict future pollution levels. With the growing role of ports in the operational processes of global economies, there has been a need to develop a green concept for pollution prevention. The term "green" includes three aspects:

energy efficiency and management, environmental protection, and ecological sustainability [6]. Green is a trend in seaports around the world, and environmental management, which is of utmost importance, is starting to play a key role in port operations. The advantages of environmental management are primarily environmental protection but also cost savings, improved corporate image, and customer satisfaction [7]. European nations have emphasised enhancing port operations through a comprehensive and institutional strategy. They have also concentrated on fostering environmental awareness within ports as part of their green port policies, aligning with European Union directives and international conventions and regulations. The green port concept includes six basic criteria: natural life, air, water, soil and sediments, training, and sustainability [8].

Research on sustainable port development has been growing rapidly, and it has focused on environmental aspects. Various conventions, standards, and frameworks exist around the world to support the implementation of the Sustainable Development Goals in various economic sectors. Over the past few decades, international institutions and organisations have put forward various environmental concepts and regulations. The European Seaport Organization (ESPO) and the World Port Climate Initiative (WPCI) have proposed guidelines for environmental activities: the ESPO Environmental Code and the ESPO Green Guide [9]. Thus, political and economic actions by countries that enhance the implementation of global sustainability efforts affect port standards and regulations. In addition, there are important international and national maritime regulations that ports use to implement sustainability measures. Maritime administrations and port authorities play a significant role in shaping environmental policies aimed at minimising the environmental impact of ports [10]. Port authority policies and priorities are driven by international and local environmental regulations. Most major European ports employ at least one environmental manager, whose job is to ensure the port's compliance with external environmental standards, as well as the environmental requirements set by the port [3]. It is recognised that monitoring the current status of the elements of air, water, soil, sediment, etc., is essential for assessing environmental quality. Under European governance, the level of environmental legislation has been steadily increasing and influencing maritime environmental protection patterns and port operations and development [11]. Such activities include the ISO 14001:2015; Environmental management system Requirements with guidance for use ([12]), the European Union Eco-Management and Audit Scheme (EMAS), and the Port Environmental Review System (PERS), which cover the general requirements of environmental management standards [13].

Given that port activities can degrade the quality of the marine environment in adjacent areas, it is essential to regularly monitor and assess pollution levels. This process should include the identification of pollution sources, the control and disposal of waste from various origins, and continuous evaluation throughout port operations [14]. Port measures and activities to minimise environmental impacts are implemented within environmental management systems [15,16]. Recommendations for dredged material management in the Baltic Sea coastal countries, formulated by the Baltic Marine Environment Protection Commission, as described Ref. [17], recognise the need to control the content of environmentally hazardous chemical compounds. The routine monitoring of the contents of polycyclic aromatic hydrocarbons and petroleum hydrocarbons, polychlorinated biphenyls (PCBs), heavy metals, and tributyltin should be carried out in port-dredged sediments. In the same document, it was recommended that polychlorinated dibenzo-p-dioxins/furans (PCDD/Fs), organochlorines, and pesticides be monitored at suspected locations. PCDD/Fs and PCBs were qualified by HELCOM as priority hazardous substances of major relevance to the Baltic Sea [18]. In the coastal region of the Baltic Sea, due to local sources and the occurrence of high concentrations in bottom sediments, PCDD/F concentrations are monitored in the ports of Finland and Sweden [19,20]. Dioxin control in coastal sediments and fjords is also being carried out by Norway [21,22].

The appropriate use of sediment extracted from the bottom (dredged material) depends on its physicochemical properties, the contamination level, and the existing natural

and anthropogenic conditions of the coast, as well as economic aspects [23,24]. The extracted dredged material, when it is uncontaminated, is most frequently stored either at sea or on land in specially designated areas. In Poland, port sediments are stored mainly in marine landfills. Storage of the dredged material at sea is economically advantageous; however, it can pose a real threat to the environment, especially if the landfill is rarely monitored [25].

Bottom sediments play an important ecological role: among other things, they provide habitats and substrates for benthic organisms and determine the biodiversity of aquatic ecosystems. They are also a natural collector and store of anthropogenic pollutants released into the environment from multiple sources [26,27]. Lying on the bottom of water bodies, sediments store minerals and organic matter, including toxic substances. The structure and composition of sediments make them a natural sorbent on which the adsorption and absorption of various pollutants take place. Thus, the condition of bottom sediments largely reflects the degree of pollution of the entire water body, constituting a sensitive indicator of anthropopression. Studies of their composition are a valuable source of information on harmful anthropogenic activities undertaken within the reservoir [18,28].

The risks associated with human and environmental exposure to hard-to-degrade toxic compounds that accumulate in bottom sediments are connected to various factors, including the degree of contamination, environmental conditions, and the dynamics of the food chain [29]. The monitoring of marine areas, including port bottom sediments, includes a range of toxic compounds, among them heavy metals and persistent organic pollutants (POPs), such as pesticides, PCBs, and PCDD/Fs [26]. Dioxins are non-biodegradable and generally hardly degradable compounds. They are recognised in the Stockholm Convention as one of the most toxic groups of substances. The term "dioxins" refers to chemicals that share a similar chemical structure and have a common mechanism of toxic action (congeners). This grouping encompasses the following: 75 polychlorinated dibenzo-p-dioxins (PCDDs) and 135 polychlorinated dibenzofurans (PCDFs) [30]. Dioxin contamination of marine waters typically involves the most toxic and persistent 17 polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), which accumulate in the tissues of organisms. Congeners do not occur individually but occur as combinations of different compounds within the dioxin group [31]. Dioxins most often penetrate marine waters through atmospheric deposition and inflows from polluted rivers. Since they have poor solubility in water, they fall and accumulate on the bottom. Sediment particles, together with adsorbed dioxins, become part of the food chain, in which dioxins bioaccumulate [32]. In the marine environment, dioxins can infiltrate organisms via ingestion or respiration or adhere to their surfaces through sorption. A considerable portion of dioxins are absorbed by phytoplankton. Because these compounds are highly soluble in lipids, there is a biomagnification of dioxins in higher organisms (fish, birds, mammals) [33].

Also, microplastics (MPs) present in the aquatic environment can act as carriers of harmful substances, including many POPs, heavy metals, and other chemicals or microorganisms, owing to their high sorption capacity [34,35]. MP particles can also be carriers of inorganic and organic contaminants present in the water and can cause increased exposure to them [36].

Plastics, due to their widespread use in all sectors of human activity, are contributing to increasing environmental pollution. Their identification requires complex procedures and advanced analytical techniques, and thus, they are not included in systematic monitoring. Currently, plastic pollution is a major problem for terrestrial, air, and aquatic environments, causing damage at all levels (macro, micro, and nano), and there is no known ecosystem that is not subject to this type of contamination.

The marine and coastal ecosystems of the Baltic Sea are threatened by numerous anthropogenic activities that have serious impacts on marine biota and human health. Due to their small size, microplastics are consumed by organisms throughout the trophic network. The composition and structure of microplastics are giving rise to new environmental threats. Microplastics can accumulate other toxic organic pollutants present in the water on their

surface, causing a local concentration of these compounds. In addition, microplastics often secrete compounds added during production to modify their properties, called plasticisers, which are also considered toxic. Thus, microplastics provide a pathway for the introduction of toxins, increasing the potential for the accumulation (bioaccumulation) of increasing amounts of these compounds in animal bodies, ultimately causing disease or even death. It should also be mentioned that the consumption of smaller organisms containing microplastics causes these compounds to be transported up the food chain (in the process of biomagnification) and, by this route, can, for example, reach fish and other seafood consumed by humans. Thus, these risks extend not only to the environment but also to human health and life [37–39]. Accordingly, the state of the environment in the waters around the Baltic Sea coast is currently the subject of research, monitoring, and national and international regulatory policies [40,41].

Plastics are conveyed into the marine ecosystem from terrestrial sources through the action of rivers, drainage systems, sewage infrastructure, or atmospheric winds. In general, a large number of these plastics consist of synthetic water-insoluble particles smaller than 5 mm, referred to as MPs [29,34]. There are two types of MPs that enter the marine environment: primary and secondary microplastics [42]. Due to the extensive utilisation of plastic items in daily life, increasing quantities of plastic particles are infiltrating the marine ecosystem as primary microplastics, including pellets and fibres, which come from materials that are produced by diverse industries. Apart from the primary MPs, which are used as raw materials in the manufacture of plastic products, secondary MPs are also found. These particles occur with the disintegration of macroplastics [43]. The combination of plastics with other pollutants is probably a category of combined pollution. Among the chemicals present in MPs, including monomers and/or oligomers, there are various additives incorporated into plastics during their production. They can also be released into the environment from plastics, which means that plastics can also be considered sources of some toxic chemicals [44–46]. The fragmentation of plastics is influenced by environmental parameters such as wave activity, turbulence, flow, temperature, solar radiation, and the physicochemical characteristics of the plastics themselves [43,47]. All of these chemical, physical, mechanical, and biological factors may result in the accumulation of fragments of secondary microplastics in the marine environment.

The pollution of the marine ecosystem by MPs represents a significant concern that has garnered international scrutiny, prompting increased scholarly investigation into the issue and resulting in the identification of microplastics across various regions worldwide. The problem of microplastic pollution has increased significantly over the last decade. Research has shown that MPs accumulate in beaches, surface waters, and seafloor sediments [46–52]. A growing number of scientific studies show that microplastic particles can have a very negative impact on the marine environment and its ecosystem [42,53,54]. Its particles can reduce the ability of animals to forage. They can also damage internal organs, cause inflammation, and reduce energy storage and reproduction. It is likely that numerous marine organisms, including clams, fish, and oysters, mistake MPs for food and take them up from the water column or sediments [55]. By consuming microplastic particles, higher cells also consume substances associated with these particles, deposited on their surface through adsorption. This can lead to the accumulation of various adsorbed or leached pollutants, including microorganisms, pharmaceuticals, and toxins, throughout the food web [56,57]. The smaller the particles, the greater the risk that they will penetrate the cells and tissues of the animals and exert adverse effects on their immune cells and organs. MP particles accumulated in the organs of aquatic organisms (i.e., intestines, gills, and liver muscles) are characterised by variability in size and shape and can ultimately reach human organisms by direct and indirect routes [58]. Today, MPs, due to their widespread occurrence in the marine environment, are one of the dominant forms of anthropogenic pollution. They have rapidly evolved from an emerging to a chronic contaminant [51]. MPs are of increasing interest due to their presence in the food chain. Despite ongoing scientific research, the impact of plastic particles on ecosystems is still unclear.

With the growing production and increased awareness of the accumulation of plastic pollutants in the environment, MPs have been identified as a potential contributor to biodiversity loss in the oceans and seas [59]. This has prompted the development of international regulations and the implementation of marine conservation projects. The Marine Strategy Framework Directive (MSFD) mandates that member states implement actions aimed at attaining and sustaining a state of good environmental condition [46]. It underscores the necessity of acquiring precise data concerning the monitoring, identification, and distribution of MPs, as stipulated in priority descriptor 10.1.3. [60]. Populated and industrialised coastal areas and ports are considered potential hotspots for MP emission to the marine environment. The primary origins of MP particles found in aquatic ecosystems and sedimentary deposits are the degradation of plastics originating from industrial activities, uncontrolled waste disposal, sewage discharges, and urban runoff [61]. Ports represent an additional source of MPs in local waters and the open sea due to their intensive industrial and transport activities. Currently, despite evidence indicating a substantial impact of MP pollution on port ecosystems, its level remains inadequately characterised [62,63].

Over the past few years, scientists worldwide have contributed to the progress in the study of marine pollution. China has published the majority of articles concerning microplastic contamination in marine environments, accounting for 41% of the 2000 publications analysed from 2000 to 2023 [51]. These studies show that the region prioritises addressing environmental issues caused by seawater contamination. Research on water pollution in ports and coasts has increased annually since 2010. The studies aim to establish the link between human activity in ports and harbours and marine pollution. Belioka and Achilias conducted an analysis that revealed that China, Brazil, Italy, and the UK have had the highest number of review articles published on microplastic pollution in harbours in recent years [51]. Regrettably, there is limited published information on the contamination of bottom sediments with dioxins and microplastics in Polish ports. Bottom sediments in the area of the Polish economic zone of the Baltic Sea are relatively unpolluted. When evaluating the dredged material, it is rare to find sediments contaminated in terms of HELCOM-selected compounds. PCDD/Fs, due to the lack of significant sources off the Polish coast and low concentrations, were considered not to require continuous monitoring. However, due to their high toxicity and persistence, it is necessary to monitor compounds that, even in low concentrations, can be dangerous to living organisms. Seabed sediments are defined as sinks for compounds such as dioxins and microplastics, and therefore, as reservoirs for contaminants from adjacent industrial activities, urbanisation, and ports, they may pose a serious threat to the environment. At the same time, through the long-term accumulation of the above-mentioned particles, they can constitute appropriate matrices for their long-term monitoring.

Ports around the world use maintenance dredging to maintain safe operating depths of quays and waterways. Due to the high levels of contaminants in the port environment, there is a need to test dredged sediments for the presence of various pollutants, including MPs. Marine sediment is a significant parameter in pollution surveillance, as it functions as both a reservoir for pollutants and a secondary origin of contamination within the aquatic environment [64]. The condition of the marine environment can be assessed by determining the degree of contamination of coastal sediments with heavy metals, chemical compounds such as dioxins, and microplastic particles [65–67]. Bottom sediments are considered a major sink with a high potential for collecting MP and dioxin particles [68]. A comprehensive understanding of the abundance, spatial distribution, and accumulation of MPs in harbour sediments is needed to reduce future risks. However, it involves coping with many difficulties while doing so, because ports have a variety of activities that favour different sources of pollution, the concentration of which does not change at the same rate at a particular time. There may also be technological limitations and difficulties in detecting MPs in harbour sediments. Many different detection techniques are used; so, in consequence, the results are sometimes not comparable [51,69]. Due to this

fact, information on the presence, distribution, and ecotoxicological effects of MPs in the harbour environment is very rarely provided.

The purpose of this study is to provide a preliminary assessment of the contents of dioxins and microplastics in the bottom sediments of the Port of Gdynia. This research is conducted in order to estimate whether there are areas in the bottom zone of port basins with particularly high ecological risk, which should be covered by permanent monitoring. The specific goals are (1) to determine the presence and extent of dioxin contamination in port sediments and (2) to evaluate the occurrence, concentration, and composition of microplastics within the sediments of the Port of Gdynia. This research could also make it possible to identify the potential threat of marine environment contamination resulting from increasing human activities and to point to the need to undertake systematic environmental research.

2. Materials and Methods

2.1. Sampling of Surface Sediments in the Port of Gdynia

Sediment sampling was carried out during four seasons in 2022. The study areas for sediment analysis included seven locations in the Port of Gdynia (in Basin Nos. I, III, IV, V, VI). Three sampling basins were located in the more anthropised and closed part of the port, and two were located in the area where the port waters are easily subjected to the waters of the Baltic Sea.

A grab sampler was used for surface sediment sampling. Grab samplers are characterised by a relatively shallow penetration depth (3–30 cm) and the ability to collect a large sample volume (0.5–70 dm^3), making them particularly suitable for surface sediment sampling [70]. Sediment samples in the Port of Gdynia were collected using a Van Veen grab sampler according to the Polish Standard [71]. The basic sampling data and organoleptic description of sediments are presented in Tables 1–4. The collected sediment samples were individually packed in airtight glass jars and stored at +4 °C for further laboratory analysis.

Table 1. The basic data for winter sampling in the Port of Gdynia.

Sampling Point	Location in the Port of Gdynia	Coordinates		Depth of Sampling (m)	Description of Sediment
1	Basin VI	54.321591	18.313102	11.6	gravelly muddy
2	Basin VI	54.320827	18.312607	11.3	gravelly muddy
3	Basin V	54.320882	18.310144	15.2	slightly gravelly
4	Basin V	54.320128	18.314160	12.2	slightly gravelly muddy
5	Basin IV	54.314723	18.314536	12.9	slightly gravelly muddy
6	Basin I	54.314812	18.331066	9.6	slightly gravelly muddy
7	Basin III	54.311497	18.332384	14.5	slightly gravelly muddy

Table 2. The basic data for spring sampling in the Port of Gdynia.

Sampling Point	Location in the Port of Gdynia	Coordinates		Depth of Sampling (m)	Description of Sediment
1	Basin VI	54.321559	18.313191	11.1	slightly gravelly muddy
2	Basin VI	54.320857	18.312534	10.8	slightly gravelly muddy
3	Basin V	54.320877	18.310040	14.7	slightly gravelly muddy
4	Basin V	54.320099	18.314127	11.6	slightly gravelly muddy
5	Basin IV	54.314682	18.314412	12.3	gravelly muddy
6	Basin I	54.311568	18.332266	9.0	slightly gravelly muddy
7	Basin III	54.314802	18.331187	13.7	slightly gravelly muddy

Table 3. The basic data for summer sampling in the Port of Gdynia.

Sampling Point	Location in the Port of Gdynia	Coordinates		Depth of Sampling (m)	Description of Sediment
1	Basin VI	54.321563	18.313227	11.2	slightly gravelly muddy
2	Basin VI	54.320888	18.312582	11.1	slightly gravelly muddy
3	Basin V	54.320880	18.310066	14.6	slightly gravelly muddy
4	Basin V	54.320106	18.314179	11.7	slightly gravelly
5	Basin IV	54.314675	18.314408	12.3	gravelly muddy
6	Basin I	54.311586	18.332268	9.0	slightly gravelly muddy
7	Basin III	54.314802	18.331265	13.7	gravelly muddy

Table 4. The basic data for autumn sampling in the Port of Gdynia.

Sampling Point	Location in the Port of Gdynia	Coordinates		Depth of Sampling (m)	Description of Sediment
1	Basin VI	54.321596	18.313061	11.0	slightly gravelly muddy
2	Basin VI	54.320861	18.312545	10.7	slightly gravelly muddy
3	Basin V	54.320883	18.310072	14.8	slightly gravelly
4	Basin V	54.320082	18.314132	11.7	gravelly muddy
5	Basin IV	54.314699	18.314527	12.8	slightly gravelly muddy
6	Basin I	54.311550	18.332299	9.1	slightly gravelly muddy
7	Basin III	54.314815	18.331348	13.6	gravelly muddy

2.2. Laboratory Analysis of Surface Sediments from the Port of Gdynia

2.2.1. Analysis of MPs

A significant issue in assessing pollution by MPs in port environments is a lack of standardised methodologies for the collection, preparation, and identification of MP samples. The methodology presented in this work is based on a literature review and the authors' laboratory experience. The process for identifying MPs involved the following main steps: (1) sample collection and initial disaggregation, (2) density separation, (3) wet peroxide oxidation, (4) filtration and visual sorting, and (5) MP identification.

To analyse MPs in sediments, the dried sediments were initially disaggregated using potassium metaphosphate. In the next step, the sediments were separated by sieves with mesh sizes of 5 mm and 0.3 mm, and all sediments were collected for separation in a solution with a density of 1.6 g/cm^3 (zinc chloride) to isolate the plastic debris through flotation. Floating particles were used for further testing after being sieved through a 0.3 mm sieve and oxidised using 30% hydrogen peroxide and an Fe(II) catalyst to remove labile organic matter. This process was continued until no visible natural organic material was present. The plastic debris exhibited no alterations. Next, sodium chloride was added to increase the density of the solution to 1.2 g/cm^3. The mixture was shifted to a glass density separator for the purpose of segregating the plastic fragments via flotation. The solution was then filtered through a 0.3 mm nylon filter using vacuum filtration to retain microplastic particles. Subsequently, MP particles from sediment samples were transferred to a Petri dish, covered with aluminium foil, and allowed to air dry (for further analysis) [72]. Microscopic and spectroscopic methods were used to identify plastic particles ranging in size from 0.3 mm to 5 mm, which were collected from seven sampling sites in five different port basins.

This study analysed plastic particles at both the macro- and microscales. Macroscopic observations were made using a FujiFilm S2500 HD camera (FujiFilm, Tokyo, Japan), while microscopic observations were conducted with a metallographic microscope ALPHAPHOT-2YS2-HNikon (Polish Optical Companies, Warsaw, Poland) connected to a Delta Optical DLT-Cam PRO 6.3MP USB 3.0 photo camera (Delta Optical, Gdańsk, Poland). The micrographs were taken using reflected light [39,72].

The collected plastic particles were chemically identified using Attenuated Total Reflectance–Fourier Transform Infrared spectroscopy (ATR-FTIR) and the OMNIC™ Specta Software. FTIR spectra were recorded using an ATR Smart Orbit Accessory (ATR

Smart Orbit Accessory, Thermo Scientific, Madison, WI, USA) on a Nicolet 380 FTIR spectrometer (Thermo Scientific, Madison, WI, USA) with a diamond cell. The particles were fixed manually onto the diamond crystal and scanned 32 times with a resolution of 4 cm^{-1} and an IR range of 4000 to 600 cm^{-1}. Due to size limitations, only particles larger than 500 µm could be analysed using ATR-FTIR [39,73]. The obtained spectra were compared with the reference spectra held within 20 spectral libraries, which collectively encompass more than 11,300 spectra of synthetic and natural materials and compounds. In accordance with the process of identifying plastic particles, a match was considered credible if the polymer type exhibited compatibility exceeding 60% and critically evaluated if it was lower [39,74–76].

The bottom sediments were tested for the presence of particles with sizes ranging from 0.027 mm to 1 mm (mini-microplastics) in an external standardised laboratory. The polymer types and the number of microplastics were identified using spectroscopy (FTIR and LDIR), while the total mass of particles was determined using thermoanalytical methods (TD-GC/MS and Pyrolysis–GC/MS). The range of analytical tests in this laboratory enables the detection of the following polymers: polyethylene (PE), polyamide 6 (PA 6), polystyrene (PS), polyethylene terephthalate (PET), polypropylene (PP), polymethyl methacrylate (PMMA), polyvinyl chloride (PVC), and polycarbonate (PC).

2.2.2. Analysis of Dioxins and Furans

Sediment testing for PCDD/Fs was performed by a standardised external laboratory. The content of PCDD/Fs in sediments was determined using gas chromatography coupled with mass spectrometry (GC-MS/MS) in accordance with the DIN EN ISO/IEC 17025:2005 standard [77]. The 17 most toxic WHO congeners were selected for analysis. The evaluation of the toxicity of dioxins is based on the TEF (toxic equivalency factor) value. The use of the TEF provides a comprehensive assessment of the overall toxicity of a sample through a singular numerical value. TEFs are weighting factors by which the toxicity of a mixture of congeners is compared with the toxicity of 2,3,7,8-TCDD [78]. The values of TEF for dioxins are stipulated in Commission Regulation (EU) No 277/2012 of 28 March 2012 [79]. There are various TEFs for the different species present in the food chain. The values defined for fish are used for ecological risk assessment [80]. The names of the most toxic PCDD/F congeners and their assigned TEF values are summarised in Table 5.

Table 5. Toxic PCDD/F congeners and their assigned TEF values.

Congener/Abbreviation	Toxic Equivalency Factor (TEF)
Dioxins	
2,3,7,8-Tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD)	1
1,2,3,7,8-Pentachlorodibenzo-p-dioxin (1,2,3,7,8-PeCDD)	1
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin (1,2,3,4,7,8-HxCDD)	0.1
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin (1,2,3,6,7,8-HxCDD)	0.1
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin (1,2,3,7,8,9-HxCDD)	0.1
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin (1,2,3,4,6,7,8-HpCDD)	0.01
Octachlorodibenzo-p-dioxin (OCDD)	0.003

Table 5. *Cont.*

Congener/Abbreviation	Toxic Equivalency Factor (TEF)
Furans	
2,3,7,8-Tetrachlorodibenzofuran (2,3,7,8-TCDF)	0.01
1,2,3,7,8-Pentachlorodibenzofuran (1,2,3,7,8-PeCDF)	0.03
2,3,4,7,8-Pentachlorodibenzofuran (2,3,4,7,8-PeCDF)	0.3
1,2,3,4,7,8-Hexachlorodibenzofuran (1,2,3,4,7,8-HxCDF)	0.1
1,2,3,6,7,8-Hexachlorodibenzofuran (1,2,3,6,7,8-HxCDF)	0.1
1,2,3,7,8,9-Hexachlorodibenzofuran (1,2,3,7,8,9-HxCDF)	0.1
2,3,4,6,7,8-Hexachlorodibenzofuran (2,3,4,6,7,8-HxCDF)	0.1
1,2,3,4,6,7,8-Heptachlorodibenzofuran (1,2,3,4,6,7,8-HpCDF)	0.01
1,2,3,4,7,8,9-Heptachlorodibenzofuran (1,2,3,4,7,8,9-HpCDF)	0.01
Octachlorodibenzofuran (OCDF)	0.003

3. Results and Discussion

3.1. Microplastics

It is known that several factors could be associated with the presence and dispersion of MP contamination in seafloor sediments. These factors encompass both natural aspects, such as plastic characteristics, meteorological conditions, and the hydrodynamics of the aquatic environment, as well as anthropogenic factors like densely populated areas, tourism, fishing practices, sewage discharges, solid waste, passenger ships, and harbour activity. Urbanised water bodies, such as harbours, with high levels of anthropogenic activity may be more contaminated with microplastics and provide a pathway for microplastics to enter seas and oceans. Although much research has been conducted on microplastics in marine and ocean sediments, much less attention has been paid to research on the microplastic contamination of harbour sediments.

MPs ranging in size from 0.3 mm to 5 mm were discovered in the surface and bottom sediments at all the locations analysed in the Port of Gdynia. Firstly, all the particles of MPs collected in the surface sediments at all the sites were analysed visually and by direct light microscopy. MPs appeared in different shapes, sizes, and colours. Examples of images of the MPs collected in sediments at seven points in five port basins are shown in Figures 1 and 2.

Figure 1. Macroscopic image of all MPs collected from five basins in the Port of Gdynia.

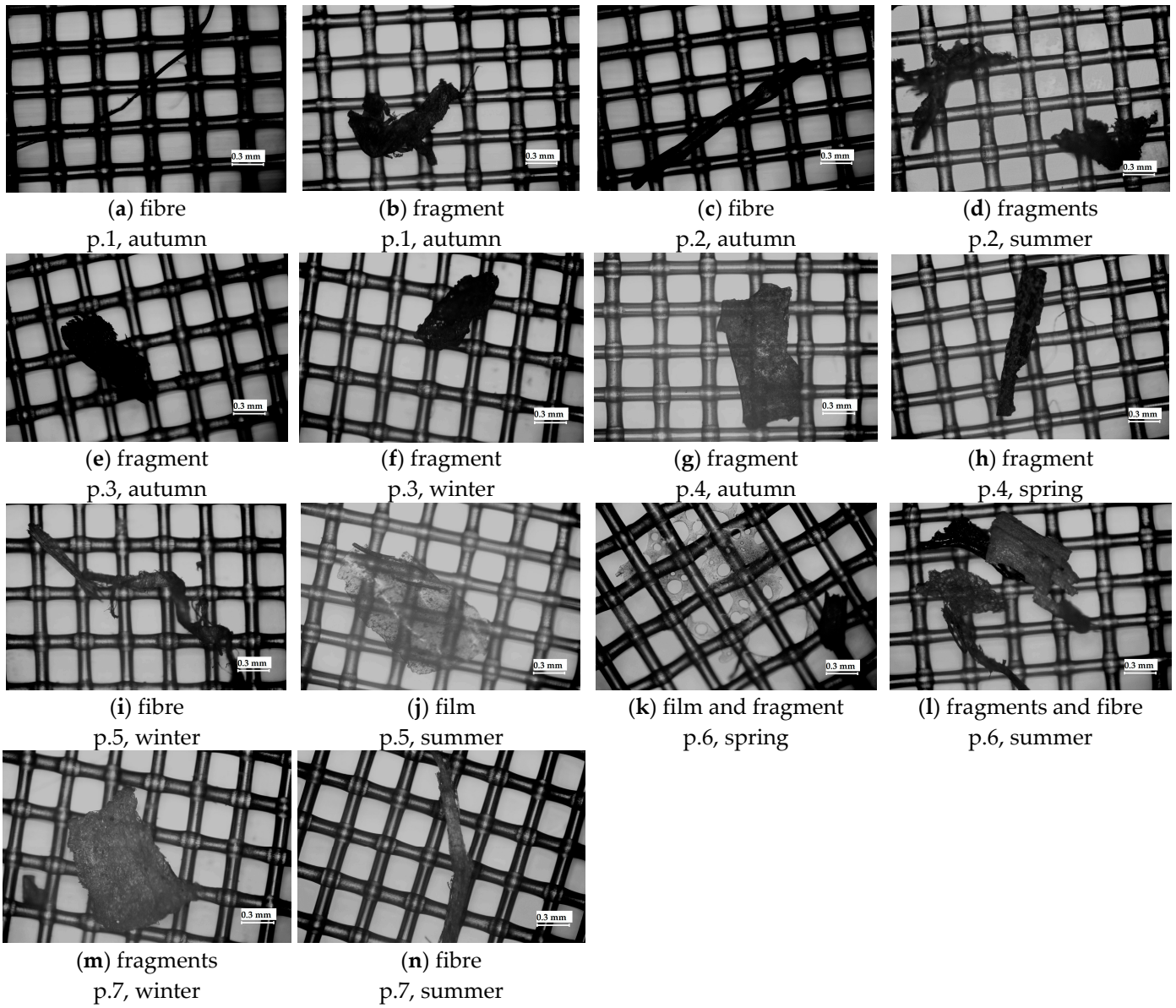

Figure 2. Examples of MPs, observed under a microscope, collected from port sediments at different sampling points: Basin VI (**a**–**d**), Basin V (**e**–**h**), Basin IV (**i**,**j**), Basin I (**k**,**l**), and Basin III (**m**,**n**).

The potential risk posed by small plastic particles is related to their ingestion by organisms at all trophic levels. They can be transferred through the marine food web [81]. The main factors influencing the ingestion or assimilation of MPs by marine organisms comprise particle dimensions (smaller particles are more bioavailable), density (higher densities increase the likelihood of ingestion and/or adsorption), abundance (greater abundance correlates with increased attraction of organisms), and colouration (certain colours tend to attract specific organism groups). These factors lead to the increased bioavailability of microplastics to organisms compared with other anthropogenic wastes [82–84].

Irrespective of the diverse sampling locations, the categorisation of MPs is determined by their shape, including fibres, fragments, spheres, and films [51,85]. The investigated basins of the Port of Gdynia contained all of the plastic particles mentioned above. Fragments and fibres were the most common type of microplastic particles and were found at all the sampling locations. Boats and ships are the primary sources of paint fragments in port waters and sediments. Synthetic polymers, including alkyds, epoxy resins, and polyurethanes, are commonly used in protective coatings for ship hulls and superstructures,

contributing to the plastic particle content in this environment. The other sources of fragments and fibres in the port environment originated from pipes, ropes, and packaging used during various activities. This research indicates that non-spherical microplastics, such as fragments and fibres, are more toxic than spherical microplastics [42,86]. Earlier research has indicated that fibres were the predominant form of MPs identified in the sediments of different seaports, such as the Harbour of Stenungsund, Port Philip, Western Port Bays, Port Melbourne, Sydney Harbour (Middle Harbour), the Port of Suva, and the fishing Port of Dumai and Marinas of Montenegro [49,87–91]. The origin of these fragments is linked to the deterioration of larger plastic debris. Fragments were the most abundant form type recovered from the Baseco Port sediments [92]. Sources of films are likely to be mainly from the degradation, weathering, and breakage of packaging/bags or plastic wrapping.

The classification of MPs by colour is crucial for identifying the source of the most prevalent plastic particles in the marine environment. Blue and green fibres, for instance, are typically derived from clothes, ropes, and nets. Black, blue, white, yellow, red, green, grey, brown, and transparent MPs are the most frequently encountered. Brightly coloured and pigmented microplastics are more easily visible and identifiable. Marine species may recognise coloured microplastics more easily than transparent ones [51,84,93].

In the analysed sediments, black, white, yellow, and transparent plastic particles were often found (Figure 1). Identifying the colour of plastic particles can be challenging due to the loss of their original colour caused by their exposure to aquatic conditions, such as biofilm development and weathering. Additionally, human colour identification is subjective and can be hindered by visual impairments [85,94,95].

Particles larger than 500 µm were selected from sediment samples taken from the port for spectroscopy polymer identification [39,73]. A spectrum was obtained for each particle using ATR-FTIR analysis and compared with the reference library of over 11,300 spectra to determine the polymer composition. This technique enables the clear identification of plastic particles. The results of the identification of plastic particles and the MP concentrations at all sampling locations are presented in Table 6. In contrast, Figure 3 shows the combined content of mini-MPs, with sizes of 0.027 mm–1 mm, collected from sediments at all the sampling sites, together with the identified plastic particle types.

Of all the plastic particles extracted with sizes from 0.3 mm to 5 mm and visually detected at seven locations, only 50 could be identified using ATR-FTIR spectroscopy. Polymer identification by FTIR spectroscopy identified different polymer types, such as PP, PE, LDPPE, PS, PA 6, PU, and some copolymers (e.g., PP-PE). However, identifying these plastic polymers does not necessarily mean that there are no other polymers present in the port environment. The contribution of other, unidentified polymers was limited due to the particle size [73,96–98]. In addition, some particles that have been identified as polymers are difficult to categorise as polymers due to their distribution over time (ageing plastic). The scope of commercial libraries is insufficiently extensive due to insufficient data regarding spectra obtained from plastics subjected to environmental degradation [46,98,99]. The relationship between the bands related to oxygenated moieties in polyolefin particles can indicate the degree of sample degradation [100]. Oxidised PE and PS were found in some sediment sampling locations of the Port of Gdynia (Table 6). The use of pooled plastic particles can also cause analytical issues because of the presence of mixtures of synthetic and non-synthetic particles, which are typically found in fibre components [101]. To sum up, future assessments of microplastic pollution in the port environment should include all analytical challenges and the standardisation of sampling/extraction methodologies to produce more reliable data for decision-making [39,98,102]. The results revealed that Basin VI of the Port of Gdynia has the highest concentration of MPs in both the <0.027 mm–1 mm> and <0.3 mm–5 mm> fractions of bottom sediments (Table 6, Figure 3). The chemical identification of mini-MPs (0.027 mm–1 mm) and MPs (0.3 mm–5 mm) showed that polyolefins (PE, PP, PS) and their derivatives were predominant. These results demonstrate the presence of low-density plastics in marine bottom sediments, likely due to biofouling—the overgrowth of these plastics with organic matter and subsequent sedimentation. The

predominant polymers identified in the surface waters of the Port of Gdynia were polyolefins [39]. This suggests that these items sank and deposited from the surface water to the sediment. PP and PE are two commonly used polymers with high demand and production rates. They are frequently found in marine environments worldwide [46,49–52,103–105]. For example, plastic particles isolated from sediments from the Port of Durban (South Africa) also consisted of polyolefins [73], while in the sediments of New South Wales (Australia), polyethylene terephthalate and nylon were predominant [106].

Table 6. Concentration and identification of MPs (ranging in size from 0.3 mm to 5 mm) collected in different port basins.

Sampling Points	Basins of the Port of Gdynia	Concentration [µg MPs/kg d.w.]	Spectroscopy Identification of Polymer Type *
1	Basin VI	13,734.24	PP, PS, PS/PVC
2		9591.06	PS, PS/PVC, PA6
3	Basin V	9191.34	LDPE, PE
4		8812.0	PP, PE, oxidised PS
5	Basin IV	12,564.27	PS, PE, oxidised PE
6	Basin I	15,571.55	PU, PE, oxidised PE
7	Basin III	21,103.77	PS, PS/PVC, LDPE, PE-PP

* Identified plastic particles with a match higher than 60%.

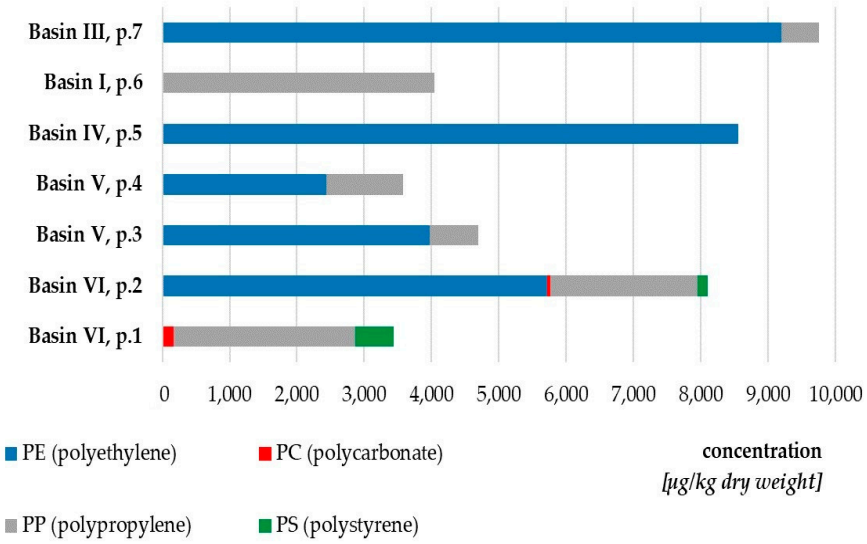

Figure 3. Concentration of mini-MPs (ranging in size from 0.27 mm to 1 mm) collected in sediments of port basins.

It should be mentioned that most published studies on microplastics in sediments have focused on surface sediments (sediments to a depth of 5.5 cm). In contrast, it is estimated that MP storage in bottom sediments may be as much as 5 times higher than in surface samples, which should be taken into account when assessing port sediment contamination with these particles [107,108].

3.2. Dioxins

Port sediments need regular analysis for dioxin contamination. Understanding the main sources, occurrences, key formation mechanisms, and contributing factors in the port environment can offer valuable and practical insights for better comprehension and management of dioxins in these settings [109]. The analyses of bottom sediments collected from the Port of Gdynia in different seasons of 2022 are presented in Table 7.

Table 7. Higher values of PCDD/F congener concentration (ng/kg d.w.) in sediment samples collected from the Port of Gdynia in different seasons of 2022.

Congener	Basins of the Port of Gdynia/Sampling Points						
	VI		V		IV	I	III
	1	2	3	4	5	6	7
2,3,7,8-TCDD	0.235	-	-	-	0.274	0.321	-
1,2,3,7,8-PeCDD	0.981	0.687	-	-	0.968	1.11	-
1,2,3,4,7,8-HxCDD	1.65	1.26	-	0.447	1.81	1.65	-
1,2,3,6,7,8-HxCDD	8.56	6.05	0.895	1.31	8.50	9.37	0.453
1,2,3,7,8,9-HxCDD	3.32	3.38	0.523	1.04	2.85	4.56	-
1,2,3,4,6,7,8-HpCDD	191	152	35.2	39.5	199	185	9.78
OCDD	902	839	164	167	962	882	58.0
2,3,7,8-TpCDF	8.47	4.05	1.68	2.02	9.11	7.21	0.523
1,2,3,7,8-PeCDF	3.07	1.22	-	-	3.00	2.78	-
2,3,4,7,8-PeCDF	6.40	3.52	1.02	1.14	6.91	5.95	0.497
1,2,3,4,7,8-HxCDF	9.25	7.24	1.19	1.08	9.89	13.3	0.571
1,2,3,6,7,8-HxCDF	4.91	2.00	0.476	0.512	3.05	5.21	-
1,2,3,7,8,9-HxCDF	-	-	-	-	-	-	-
2,3,4,6,7,8-HxCDF	2.13	2.01	-	-	2.05	2.87	-
1,2,3,4,6,7,8-HpCDF	31.7	24.6	4.29	4.10	32.1	39.2	2.19
1,2,3,4,7,8,9-HpCDF	2.73	1.98	0.520	0.494	2.39	2.24	-
OCDF	33.1	26.7	3.49	3.36	30.4	23.8	-

(-) Below the range of quantification.

The analyses showed that, regardless of the season, most of the samples are dominated by the contents of OCDD and HpCDD congeners. These congeners have a very low TEF and therefore do not pose a risk to human health (Table 5). The content of 2,3,7,8-TCDD, which has the highest toxic equivalency factor, does not exceed the value 0.3 ng/kg d.w. To facilitate the determination of dioxin sources, congener profiles were determined. These profiles characterise the percentage of congeners with the same number of chlorine substituents (e.g., OCDD) relative to the weight of all 17 congeners.

The proportion of each PCDD and PCDF congener in the total of all analysed PCDD/Fs identified from the gathered sediments at port bottoms is delineated in Table 8. The congener profiles for individual basins differ only slightly. It was also observed that their value is practically unaffected by the seasons.

Table 8. Percentage contributions of individual congeners to the total of all analysed PCDD/Fs in sediments collected in the Port of Gdynia basins.

Congener	Basins of the Port of Gdynia				
	VI	V	IV	I	III
TCDD	0.01	0.00	0.02	0.00	0.00
PeCDD	0.08	0.00	0.08	0.00	0.00
ΣHxCDD	1.08	0.73	1.03	0.82	0.00
HpCDD	15.66	17.97	15.62	16.13	14.69
OCDD	74.85	75.11	75.49	76.88	81.32
TpCDF	0.66	0.90	0.71	0.63	1.13
ΣPeCDF	0.73	0.53	0.78	0.52	0.00
ΣHxCDF	1.34	0.79	1.18	1.61	0.00
ΣHpCDF	2.81	2.29	2.71	3.42	2.87
OCDF	2.76	1.67	2.39	0.00	0.00
Σ	100.00	100.00	100.00	100.00	100.00

Based on the data presented in Table 8, it was found that the OCDD congener, the highest amounts of which were detected in the sediments, accounts for about 75% among the 17 congeners identified in samples.

The World Health Organization (WHO) recommends the use of the Total Toxicity Equivalent (TEQ-WHO) to assess dioxin toxicity. This parameter is calculated by summing the products of the concentration of each compound and its TEF value [110]. It is equivalent to 2,3,7,8-TCDD-like activity for a total mixture of PCDD/F congeners [111]. In Figure 4, the TEQ-WHO parameter illustrates the environmental risk associated with the presence of PCDD/F congeners in the samples.

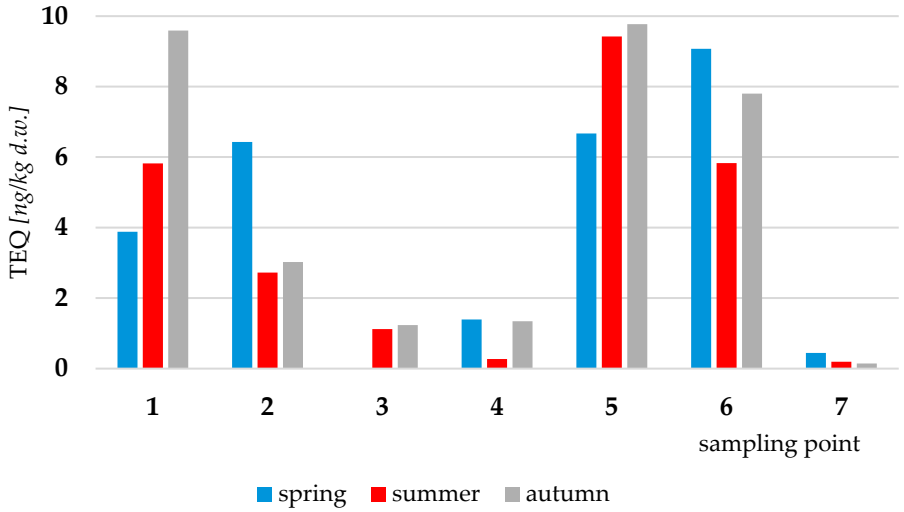

Figure 4. The toxicity of the bottom sediments in the Port of Gdynia, expressed as the total toxic equivalent WHO-TEQ (ng/kg sample dry weight).

The toxic equivalent values obtained ranged from 0.19 to 9.59 ng TEQ/kg d.m. The highest values were determined for sediments from Basin IV (sampling point 5), and the lowest values were recorded for sediments from Basin III (sampling point 7). According to the Canadian Council of Ministers of the Environment [112], negative biological effects are more likely to occur when the concentration of the sum of 17 dioxin congeners exceeds the value 21.5 TEQ ng/kg d.w. On the other hand, 5 ng TEQ/kg s.m. was adopted as the highest value, indicating unpolluted areas of the Baltic Sea [32,113]. Thus, the results obtained for the sediments taken at the Port of Gdynia indicate a low level of dioxin contamination.

4. Conclusions and Suggestions

Marine sediments are an important indicator for monitoring the state of the environment. They have a high potential for accumulating compounds that are difficult to dissolve in water, including those with toxic properties. Once released from the sediment, they are a secondary source of pollutants present in the aquatic environment. For this reason, the study of surface port sediments makes it possible to estimate the chemical pollution status of not only the bottom but also the water depths. Research on port sustainability is rapidly expanding, with a predominant focus on environmental aspects. By adjusting the state of water cleanliness not only to the applicable requirements but also to the recommendations that flow from scientific reports, which characterise the trends of changes in the marine environment, ports can set targets for reducing anthropogenic pollution flowing into the Baltic Sea.

The results revealed negligible amounts of microplastic particles and low concentrations of dioxins in the sediments of the Port of Gdynia. No areas of particularly high ecological risk were detected in any of the basins studied, which should be subjected to continuous monitoring. This shows that, currently, the Port of Gdynia is not a pathway for dioxins and microplastics to enter the sea. However, taking into account that dioxins have been recognised as hazardous substances of particular importance for the Baltic Sea, while, for microplastics, a very dynamic annual increase is observed, it is advisable to extend

studies of the bottom of the Port of Gdynia basins to include these pollutants. Conducting periodic surveys would also positively influence the assessment of the suitability of these sediments for further use when dredging the port's waterways.

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