

# Aspects of Pollution in Gdansk and Gdynia Harbours at the Coastal Zone of the South Baltic Sea

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**ABSTRACT:** Organotin compounds (OTC), as well as metals, are toxic to many organisms. Even at very low concentrations OTC and metals can have several negative effects. The paper discusses key issues relating to the location of harbours in the coastal zone (including near the river mouths and semi-closed access to the sea) and the pollution of harbour sediments with heavy metals (e.g. zinc, copper, nickel and lead) and organotin derivatives (e.g. butyltin, phenyltin, octyltin, and tricyclohexyltin), using the examples of the Gdańsk and Gdynia ports. The authors have described key spatial factors of the two ports which largely determine sedimentation processes. It has been shown that the heavy metals content in the sediments of the Port of Gdańsk does not exceed the concentration values permitted by Polish law, however, the problem with the establishment of standard concentration levels for organotin derivatives remains.

## 1 INTRODUCTION

Once introduced into the marine environment through human activities (i.e. the shipbuilding industry, the chemical industry, the agriculture), metals (i.e. Zn, Ni, Cr, Cu, Cd, Pb), as well as organotin compounds (OTC: tributyltin (TBT), dibutyltin (DBT), monobutyltin (MBT), triphenyltin (TPhT), diphenyltin (DPhT), monophenyltin (MPhT)) present higher persistence in benthic sediments and a hazard to living, marine organisms (Alzieu, 2000).

Because of favourable navigation conditions and easy access to the sea, most harbours are located within the coastal zone of the land. The better developed this section of the coast is, the more efficient the transport and movement of ships in the harbour are. The demersal hydrodynamic regime present in harbours, however, is mostly dictated by the movement of ships and, consequently, differs from the natural hydrological and sedimentation

conditions of the sea. On the other hand, mechanical resuspension of the sediment caused by ships moving in the harbour may lead to repeat pollution of the water basin (due to the release of chemical substances from the harbour sediments). Such a phenomenon may lead to changes occurring near the bottom of port channels, above all: changes to chemical and biological composition of sediments, changes to pH values and oxidation/reduction conditions, bioavailability of old and new pollutants. Furthermore, the unnatural increase in the water flow in the port may give rise to the inflow of sea sediments into port channels and contribute to the increased rate of sedimentation (e.g. in the Port of Gdańsk this amounts to approximately 7 cm per year<sup>-1</sup>, in the Baltic Sea – between 0.13 and 2.92 mm per year<sup>-1</sup> (Szwernowski, 1957; Pempkowiak, 1992)). In the end this provokes the port channels bottom shoal patching and gives rise to the necessity of removing the accumulated sediment in order to ensure safe navigation throughout the harbour. Spoil

dredged from the harbour may be stored, under certain conditions, on the land or in the sea, on areas specially assigned for this purpose. Because of a high risk of polluting the sea regions with chemical substances, however, the port sediment should be tested in order to reduce the inflow of pollutants into the sea. Results presented in these papers have in part already been published by Dembska et al. (2001), Radke et al. (2004, 2008, 2012a,b), Pustelnikovas et al. (2005, 2008). Tests results for samples of sediments collected in years 1998-2010 from the channels of the Port of Gdańsk and the Port of Gdynia are discussed in these articles. A review of the results of many years of tests on the content of trace metals and organotin derivatives at the Port of Gdańsk, as well as organotin derivatives at the Port of Gdynia, will be presented in this article.

### 1.1 Sample area

Port Gdański S.A. is the largest marine port in Poland. The port consists of two major areas, i.e. the inner port located on both sides of the Dead Vistula river (length of 27 km, depth of 10-12 m) and the outer port (the Northern Port) (depth of 10-15 m) lying directly within the coastal zone of the Gulf of Gdańsk (Fig. 1). The mean flow values range from 2 to 5 cm s<sup>-1</sup>, salinity ranges from 6.13 to 2.48 PSU (Majewski, 1990), and the inflow of saline seawater occurs in the near-bottom water layer in the river. The Port of Gdynia is the third largest port in Poland and consists of the West Port (inner port) and the East Port (outer port). The port is protected year-round by a 2.5 km breakwater and never freezes over during winter. The value of water salinity ranges from 7.94 to 8.12 PSU, while pH ranges from 7.48 to 8.35.

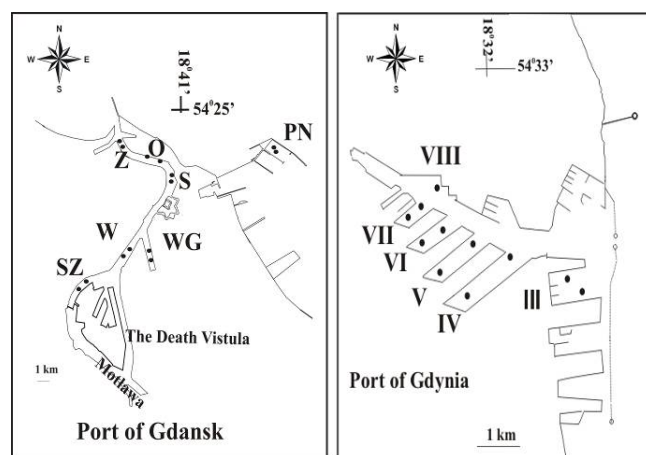


Figure 1. Map of the Port of Gdańsk and the Port of Gdynia where: Z- sampling sites at Ziółkowskiego Quay; W- Wiślane Quay; O- Oliwskie; WG- Węglowe Quay; S- Siarkowe Quay; PN- Northern Port, I,II,III,IV,V,VI,VII,VIII – individual docks

### 1.2 Samples and methods

Sediments (25 cm) for analysis were collected in 1997-2010 onboard r/v Dr Lubecki (the vessel of the Marine Institute) and Oceanograf2 (Institute of Oceanography, University of Gdańsk), respectively. Sediments were collected using a gravity corer

*Niemistö* from the following locations: the Port of Gdańsk (Oliwskie Quay, Siarkowe Quay, Northern Port and Wiślane Quay); the Port of Gdynia (quays III, IV, V, VI, VII and VIII). Two locations were designated for each of the docks (Fig. 1). Granulometric (grain size from 2.00 to 0.0625 mm in mesh diameter), as well as chemical analyses (organotin, metals and organic matter (LOI)), were performed for the samples. The methodologies proposed by Luoma & Bryan (1981) and Loring & Rantal (1992) were used to determine the total content and the labile form content of metals. Organotin derivatives were measured using a procedure developed by Wasik et al. (2007). The total content of metals was measured by means of atomic absorption spectroscopy (AAS) (using SpectrAA 250 PLUS spectrometer by Varian). Inductively coupled plasma atomic emission spectroscopy (ICP-OES) was applied in the case of the labile form of metals (OPTIMA 2000DV spectrometer by Perkin-Elmer). Organotin compounds assay was performed using a gas chromatograph (GC 8000 series by Carlo Erba). The determined limits of detection are shown in Table 1. Reference materials PACS-2, BCR-646 (for organotin derivatives) and PACS-2 (for metals) were used for the method validation (Table 1). The achieved recovery amounted to between 82 and 96%.

Table 1 Determined limits of detection (MDL) of metals (mg kg<sup>-1</sup> d.w.) and organotin derivatives ngSn g<sup>-1</sup> d.w.

Assay method	Metals					
	Zn	Ni	Cr	Cd	Pb	
AAS	0.17	0.56	0.53	0.05	0.42	
ICP-OES	0.08	0.05	0.08	0.01	0.08	
Organotin derivatives						
GC-FPD	MBT	DBT	TBT	MPhT	DPhT	TPhT
	4.5	3.8	6.9	7.0	5.6	4.1

\* Method quantification limit (MQL) was determined as follows: MQL=3xMDL

## 2 RESULTS AND DISCUSSION

### 2.1 Sedimentation

Sedimentation within both harbours may be conditioned, above all, by the sediments grain level, the change of migration forms of the sedimentation material, the effect of near-bottom currents generated by ships, as well as periodical spreading of sediments into the harbour area (Bolalek & Radke, 2010). Based on the results obtained by (Radke et al., 2008, 2012a,b) it was found that there was sand (mostly silty sand and sandy silt) in the entire material collected from the Ports of Gdynia and Gdańsk. Moreover, the lithodynamic analysis of grain size performed for individual samples confirmed that the bottoms of both ports have undergone transformation by shipping activity (mechanical mixing) and dredging works. As a result sediment samples were very poorly sorted. In the case of the Port of Gdańsk the most important factors affecting the hydrological conditions, as well as sedimentation in the bottom were: storm surges, backwater and waves (from the sea side), river flooding (from Motława) (Szczecińskie Quay, Figure 1.) (Bolalek & Radke, 2010). Furthermore, the tendency for clay and silt (<0.063 mm fraction) sediments to flow into the

middle section of the port (5.1- 6.6% Wiślane and Węglowe Quays) was observed, but sediments from Ziółkowskiego, Oliwskiego Quays and Northern Port have been enriched in coarser fractions and depleted of fine ones (Radke et al., 2008) (Fig.1). Sediments originating from the latter location are subjected to spring flooding of Motława which stimulates the washing-out of fine fractions and their transport in the direction of the Wiślane Quay. This phenomenon is the most likely cause of the low content of fine fractions by the Szczecińskie Quay and the high content by the Wiślane Quay (Bołatek et al., 2006; Radke et al., 2008; Pustelnikovas et al., 2005, 2008). On the other hand, the area close to the Vistula river mouth (Ziółkowskiego Quay) is characterized by the influence of marine waters. Such location stimulates the transport of fine-grained fractions from the river mouth towards the gulf. In comparison to the samples from the Port of Gdańsk, samples from the Port of Gdynia presented higher percentage of fine fractions (between 36.8 and 76.9%) (Table 2). This reflects the highly sorptive properties of silt and clay (Langston and Pope, 1995; Hoch, 2001). Moreover, the obtained results of thermogravimetric analysis (TGA) (Radke et al., 2008) indicated the existence of kaolinite and biogenic minerals (carbonates) in the samples from this region. Such sediment compositions give rise to conditions that are favourable to the accumulation of any chemical substances including metals and organotin compounds. Although the Port of Gdynia is protected year-round by the outer breakwater (2.5 km), which prevents mixing from currents or high waves in the port, during sustained strong westerly winds the water level can rise by up to 0.6 m and can decrease during strong easterly winds by as much as 0.6 m. This phenomenon may cause intensive movement of water mass and sediments into the port channel and consequently lead to direct and consistent distribution of sediment materials toward individual docks. In this particular instance the largest percentage of fine fraction (43.2-76.9%) was found in sediment samples from the stations located in the sections of the port furthest from the sea (docks VI, VII and VIII). The sediments from the docks located in the middle section of the port (IV, V) and its immediate vicinity (III) contained less clay and silt (36.8-38.5%) and more sand (61.5-63.2%) (Radke et al., 2010, 2012a,b). It should be mentioned that individual docks of the Port of Gdynia provide easier access to the water mass from the sea, in comparison to the quays from the inner Port of Gdańsk, which are mostly affected by the river. Taking into account the above details it may be assumed that storms and winds may play the main natural role in the formation of sedimentation, as well as the transport of water mass in the Port of Gdynia channel.

## 2.2 Influence of the area subject to the sea influence and the area related with the land on the distribution of chemical substances in harbours

A significant factor conditioning the distribution of chemical substances in sedimentation in harbour areas are the increased erosion phenomena related with ships movement in the harbour and dredging works. In the discussed ports, however, we can differentiate between two areas responsible for the distribution of chemical substances in sedimentation:

the area subject to the influence of the sea and the area that is strictly related with the land and the anthropogenic influence (Table 2). A geochemical barrier (Pustelnikovas et al., 2005, 2008) that is formed as a result of fresh water (from the river) coming into contact with saline water (from the sea), as well as storm surges and the distance from the sea mouth, may have a significant influence on this kind of distribution of chemical substances. A geochemical barrier is especially emphasized in the case of the Port of Gdańsk where there is a strong inflow of fresh water originating from the Motława to the port channel. Majewski (1972) estimated that the inflow of fresh water to the Vistula River basin (the longest river in Poland, introducing the largest amount of water mass to the Gulf of Gdańsk of the Baltic Sea) mostly originates from the Motława River (approximately 87.0%), while the Dead Vistula river on its own contributes very little – approximately 0.99%. In the case of the Port of Gdynia the local inflow of underground fresh water from the Chylonka river is much less significant. Although the watercourse may locally form a geochemical barrier (probably within the area of dock VII) it seems that the zonation in the port is caused by storm surges, whose inflows may even reach basin V (large amounts of clams, shells, coarse-grained material and a smaller share of clay fraction and organic matter were found in the sediment samples in comparison with basins VI, VII and VIII).

Table 2. Division of the Port of Gdynia and the Port of Gdańsk areas into zones of the sea and the land influence, considering the organic matter, as well as the fine and coarse-grained fraction values.

Port	Port area	Coarse fraction (>0.063 mm)	Fine fraction (<0.063 mm)	Organic matter (%)
<b>Port of Gdańsk</b>				
Sea influence	Northern Port	96.2%	3.8	1.9
	Oliwskie Quay	98.1	1.9	0.9
	Siarkowe Quay	96.1	3.9	1.9
	Ziółkowskiego Quay	96.7	3.3	2.0
Land influence	Węglowe Quay	94.9	5.1	4.9
	Wiślane Quay	93.4	6.6	6.8
	Szczecińskie Quay	95.9	4.1	1.8
<b>Port of Gdynia</b>				
Sea influence	Dock III	61.5	38.5	3.1
	IV	63.2	36.8	3.9
	V	62.5	37.5	0.8
Land influence	VI	23.1	76.9	7.4
	VII	56.8	43.2	5.0
	VIII	24.2	75.8	7.6

The regularities presented above can be easily observed in relation to all the results (granulometric analysis, results of metal and organotin derivatives content) obtained for samples collected from the Port of Gdańsk. A similar analysis of sediments samples from the Port of Gdynia does not pose many

difficulties, as it is based on granulometric analysis, thermogravimetric analysis and the analysis of organotin derivatives (Radke et al., 2008, 2010, 2012a). The latter behave in the marine environment similarly to metals (in a similar way they are accumulated in sediments, adsorbed on the surface of clay minerals and organic matter, etc.) (Langston & Pope, 1995; Hoch, 2001). Coarse- and medium-grained fraction (various types of sand and stone, as well as pebbles) prevails in the samples of sediments from zone one over the fine fraction (sludge, clay). This particular fraction of fine sediments (<0.063 mm) is the main element of the marine environment responsible for the accumulation of the largest contamination loads in sediments. A smaller share of organic matter (mostly organic carbon, humic and fulvic acids) (Hoch, 2001) that is the second important factor supporting the share of pollutants in the sediments can be observed in this area. Considering the aspects described above it is not difficult to conclude that this zone is characterised with lower concentrations of chemical substances (the Port of Gdańsk – metals and organotin derivatives, the Port of Gdynia – organotin derivatives), and due to the easy exchange with the sea there are no conditions in this area that would be favourable to the accumulation of high concentrations of pollutants. In the case of both ports this concerns sediments originating from the middle and the outer section of the port: the Port of Gdynia – docks III, IV, V; the Port of Gdańsk – the Northern Port and the following quays: Ziółkowskiego, Siarkowe and Oliwskie. Physical and chemical conditions occurring within the area with the influence of the land differ. Sediments from this zone are characterised with a larger share of the fine fraction and they are enriched with organic matter that increases the sorptive capacity of the sediments. Therefore, the highest concentrations of metals and organotin derivatives in the collected material may be expected in this area of the harbour. Furthermore, a characteristic feature of the region is the prevalence of anthropogenic factors originating both from the land and the port (e.g. high level of industrialization and operation, municipal waste, repair and handling works, removal of waste from ships, release of pollutants from ships hulls, emission from stokeholds and treatment plants, etc.) over natural factors (Bołatek & Radke, 2010). The second zone involves samples of port sediments collected from stations located in the port sections furthest from the sea: docks VI, VII and VIII in the case of the Port of Gdynia, and quays: Wiślane, Węglowe and Szczecińskie in the case of the Port of Gdańsk. A similar dependence was obtained by Pustelnikovas et al. (2005, 2008) when examining the distribution of trace elements in the sediments from the Port of Klaipėda in Lithuania, in the region of the South Baltic Sea.

### 2.3 Metals and organotin derivatives in the sediments from the Port of Gdynia and the Port of Gdańsk

Figures 2-5 provide information on the content of chemical substances examined in the port samples. The highest levels of metals and organotin derivatives content were discovered in samples collected from regions with a high industrialization level and located in the vicinity of a shipyard. In the case of the Port of Gdańsk these are quays Wiślane, Węglowe and

Szczecińskie. An additional factor that could have contributed to the increase of the determined components is the basin dynamics. In this particular case this concerns the Wiślane and the Węglowe Quays (the Szczecińskie Quay is located in the immediate vicinity of a shipyard) located within the area prone to accumulation (Fig.2).

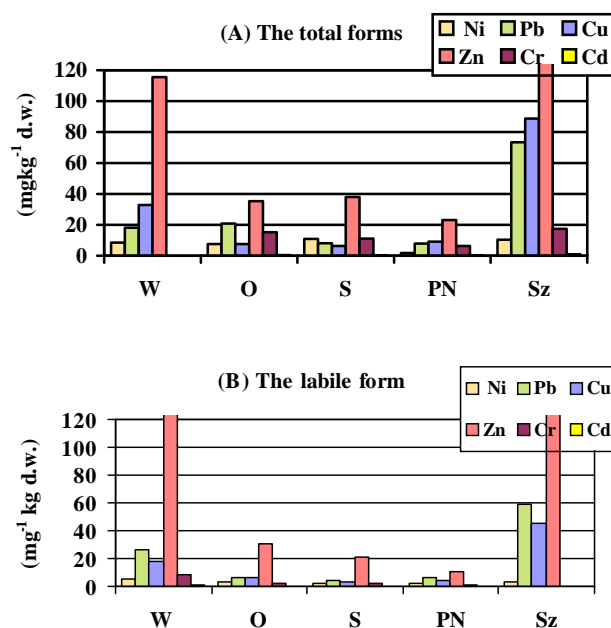


Figure 2. Comparison of average concentrations of metals  $\text{mg.kg}^{-1} \text{ d.w.}$ , total metals content (A) and in the labile form (B), in a fraction below 2.00 mm in sediments of the Port of Gdańsk quays where W – Wiślane, O – Oliwskie, S – Siarkowe, NP –Northern Port, Sz – Szczecińskie

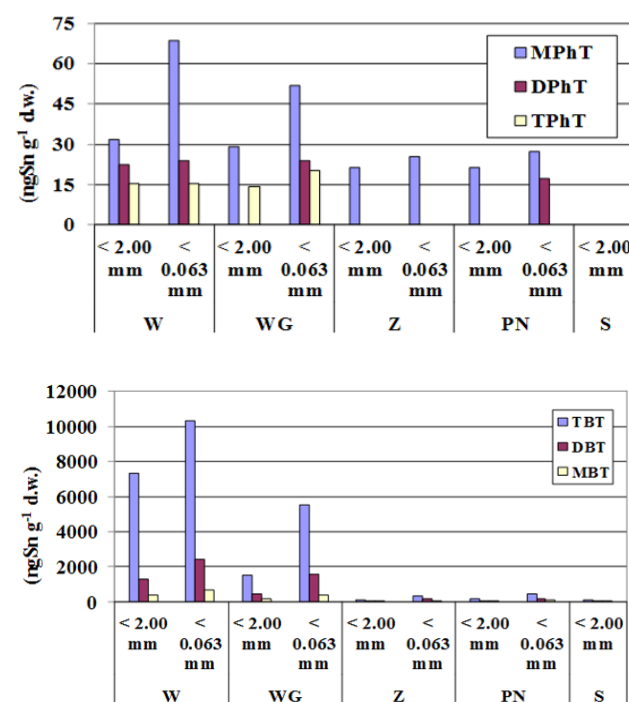


Figure 3. Comparison of average concentrations of organotin derivatives ( $\text{ngSn.g}^{-1} \text{ d.w.}$ ) in the total fraction of sediments below 2.00 mm and in fraction <0.063 mm from the Port of Gdańsk, where W – Wiślane Quay, O – Oliwskie Quay, S – Siarkowe Quay, NP –Northern Port, WG – Węglowe Quay



In samples of sediments from the remaining quays (the Northern Port, the Siarkowe and the Ziółkowskiego Quays) the content of chemical substances was much lower. Close vicinity of the sea (area of fine sediments washing-out) and significant distance from the shipyard are particularly responsible for this phenomenon (Fig. 3 and 4). On the basis of the obtained results it may be concluded that the highest levels of concentration of chemical substances in samples of sediments from the Ports of Gdynia and Gdańsk occurred within the fine fraction sediments (sludge and clay, grain diameter <0.063 mm) (Fig. 4 and 5). Samples of sediments from the Port of Gdańsk contained mostly zinc, lead, copper and tributyltin.

The lowest concentrations were found for nickel, cadmium and triphenyl tin (Radke et al., 2008; Bolałek & Radke, 2010). In the case of the Port of Gdynia, the largest contamination load was found in samples collected from the West Port (docks: VI, VII and VIII, respectively) (Fig. 5).

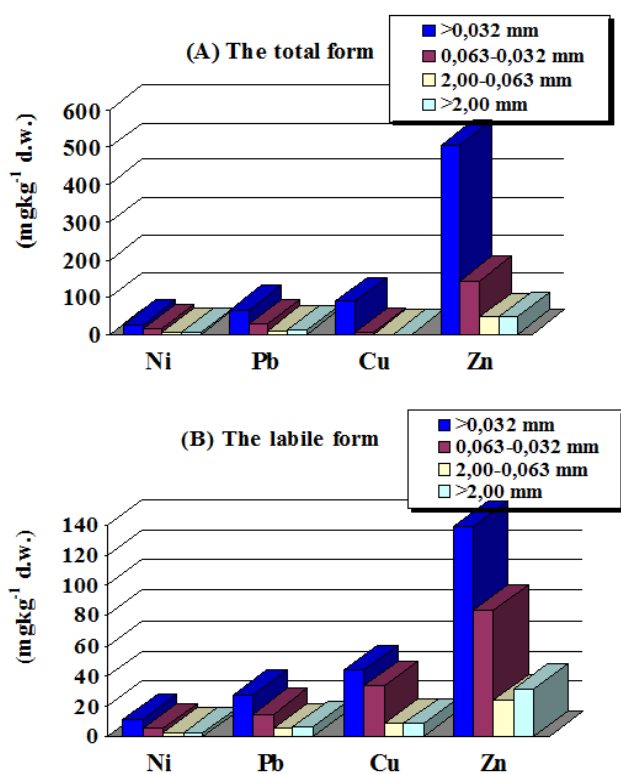


Figure 4. Determined concentrations of metals (a) in the total composition (b) in the labile form in individual grain-size fractions of sediments of the Port of Gdańsk (Bolałek and Radke, 2010)

There are two large shipyards in the vicinity of the West Port (in the region of docks VI and VII) where vessels are built and undergo renovation. In this area (dock VIII) there is also the largest shipping terminal in the Baltic Sea, the *Baltic Container Terminal*, with a current annual handling capacity of up to 750 000 TEU (*The twenty-foot equivalent unit*) (Radke et al., 2012b).

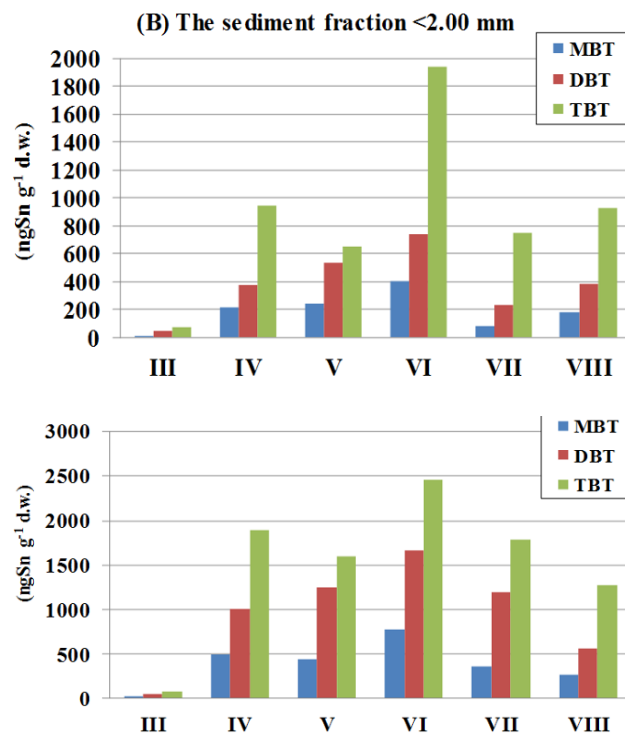


Figure 5. Comparison of average concentrations of organotin derivatives ( $\text{ng Sn g}^{-1} \text{ d.w.}$ ) in the total fraction of sediments below 2.00 mm and fine fraction <0.063 mm from the Port of Gdynia, where I-VIII are the individual docks.

A higher content of butyltin derivatives (TBT, DBT, MBT) than the content of phenyltin derivatives (TPhT, DPhT, MPhT) was discovered in samples of sediments from both ports. Values of phenyl derivatives of tin concentrations were usually below the limit of detection. This may prove that there is no inflow of those derivatives into the two ports or indicate increased decomposition of phenyl derivatives of tin in this region. Tributyltin was the most abundant species in samples from the Port of Gdynia and the Port of Gdańsk, while the monosubstituted forms had the lowest concentrations (i.e.  $\text{TBT} > \text{DBT} > \text{MBT}$ ) (Radke et al., 2008, 2012a,b). This phenomenon may be caused by fresh TBT input into the marine port at a greater rate than the rate of its decomposition. This may also indicate the processes of removing old antifouling paint coats from ships hulls (especially since a ban introduced in 2008 by the IMO regarding the use of tin-based antifouling paints for the protection of ships hulls). A comparison of the values obtained for organotin derivatives in the samples of sediments from both regions shows that the Port of Gdańsk is polluted with OTC to a greater degree than the Port of Gdynia (Table 3).

Table 3 Average content of organotin derivatives ( $\text{ng Sn g}^{-1} \text{ d.w.}$ ) in the samples of sediments of fraction (<2.00 mm) from the Port of Gdynia and the Port of Gdańsk.

Port	MBT	DBT	TBT	MPhT	DPhT	TPhT
Gdańsk	22.1- 411.3	55.1- 1293.3	135.0- 7635.0	<MDL 46.1	<MDL 21.3	<MDL 15.3
Gdynia	12.2- 364.8	50.0- 1806.1	72.0- 2200.8	<MDL	<MDL	<MDL

\*MDL – limit of detection

#### 2.4 Hazards resulting from the coastal zone development

One of the major problems in the coastal area of the sea modified by man are the processes of mechanical coast damaging (above all: sediments washing-out, uncontrolled inflow of water mass to water basins). This fact becomes even more significant if the land/sea area is developed for the purpose of port facilities. Heavy erosion processes (natural processes: storm surges, mechanical processes: rate of near-bottom currents, generated by the moving ships) occurring in this zone may lead directly to: increased rate of processes of mechanical bottom damaging, damaging of port channels and docks structures and damaging of bottom reinforcements and quays stability.

Another important element, very common for harbours, are various breakwaters and other protective structures. On the one hand, they protect the port against heavy waves and an uncontrolled inflow of water to port channels (storm surges). On the other hand, they constitute a form of a barrier for the moving water mass in port channels that, combined with the accumulated contamination load in sediments, leads to the generation of an unnatural environmental situation. For example, samples of sediments from a semi-closed region of the Port of Gdynia contain a large amount of total sulphur (mean value of 0.97% in winter and 0.85% in summer). This suggests that oxygen consumption and mineralization processes of organic matter predominate over oxygenation (Radke et al., 2012). Maksymowska (1998) observed that such processes occur only in the deeper parts of the Gulf of Gdańsk (<0.93%), at a significant distance from the coastal zone.

Another important harbour-related issue are storm surges and backwaters. These involve an increase in the water table in the direction of the upper course of a watercourse (Bołałek & Radke, 2010). For example, in the Port of Gdańsk storm surges in the main port channel reach the Siarkowe Quay (in the examined cores of sediments of the length of 14 m large amounts of sea material were found) while backwater can be found up to the Oliwskie Quay (Pustelnikovas et al., 2005, 2008). Consequently, there is an accumulation of fine material with a contamination load in only one section of the port (in this case – in the region of the Wiślane and the Węglowe Quays). Such a phenomenon may lead to the “overloading” of pollution in one area of the port. Considering processes such as the resuspension of sediments, this may lead to the remobilization of chemical substances from sediments into the sea depths.

Another important factor often occurring in ports is the fast rate of port channels and docks silting. The accumulated sediment contributes to the restriction of ships movement and the reduction of navigational safety. This in turn requires regular removal of the accumulated sediment. It is estimated that the annual amount of sediments classified for removal from the Port of Gdańsk amounts to between 50 and 60 thousand tons m<sup>3</sup> (Eko - Konsult, 1998). Further handling of the excavated material, however, is not that easy. The main reasons behind this are as follows: content of toxic substances in port sediments and restricted capacity of the sea dumping sites for receiving sediments. Furthermore, according to

Pustelnikovas et al. (2005), the evaluation of a possibility for deepening the port and the port channel mouth between 13 and 15 m must be based on the results of specialist tests aimed at evaluating the chemical composition of the process of pollutants accumulation in these sediments.

Table 4. Limit values of selected concentrations of chemical substances (mg kg<sup>-1</sup> d.w.) in dredged spoil (ICES CM, E:03 (2002); Polish Journal of Laws No. 55, Item 498. (2002))

	France <2.0 mm		Germany <20 µm		Sweden <2.0 mm		Poland <2.0 mm (labile form)	
	L1	L2	L1	L2	L1	L2	L1	L2
As	25	50	30	150	30	100	30	30
Cd	1.2	2.4	2.5	12.5	0.9	3	7.5	7.5
Cr	90	180	150	750	60	200	200	200
Cu	45	90	40	200	60	200	150	150
Hg	0.4	0.8	1	5	0.3	1	1	1
Ni	37	74	50	250	15	150	75	75
Pb	100	200	100	500	30	100	200	200
Zn	276	552	350	1750	375	1250	1000	1000

\* L1 – Action level 1, means the lack of the sediment contamination and the possibility of sinking the sediment in the sea, L2 – Action level 2, means a contaminated sediment that cannot be sunk in the sea. A sediment classified for action level 2 must be subjected to cleaning and then can be sunk in the sea or deposited on the land (i.e. used for beaches reinforcement, environmental development, expansion of islands, parks, ports or road pavements).

In Poland, though, until 1990 sediments originating from port channels were stored in the sea and it was not required to conduct any tests whatsoever (Dembska et al., 2001). The current legal status in Poland regulates the issue of sinking excavated material on sea dumping sites in details (Polish Journal of Laws No. 55, Item 498, 2002). Furthermore, particular legal regulation in European countries contain an obligation to remove pollutions from sediments before they are sunk in the sea. In the case of the Baltic Sea detailed rules for handling dredged spoil are regulated by Article 11 and Appendix V to the Helsinki Convention (1992), Recommendation HELCOM 13/1 (1992), Appendix to the Recommendation (2007). Sample criteria for the evaluation of dredged spoil for metals and tributyltin (TBT) are listed in Tables 4 and 5 respectively. Although the issue of metals does not arouse much controversy, the issue of organotin derivatives remains unsolved. Organotin compounds (OTC) have been used for many years as biocides in agriculture, as catalysts and plastic (PCV) stabilizers in industry, for wood treatments, and in antifouling systems to protect ships. It was recognized that antifouling paints are the main source of TBT being introduced into the sea. Since 2008 the International Maritime Organisation (IMO) has been prohibiting the use of organotins in antifouling systems. Although a reduction of OTC contamination has been observed in sediments from around the world, TBT can still be detected in many areas of the world. The most important issue, however, is the establishment of procedures for determining permissible concentrations of organotin derivatives in port sediments. Not all European countries have established such criteria.

Table 5. Classification criteria for dredged spoils containing TBT (Mędrzycka et al., 2006)

Country	Critical value 1 (target value) (ngSn g <sup>-1</sup> )	Critical value 2 (limit value) (ng Sn g <sup>-1</sup> )
Belgium*	3	7
Finland*	3	200
The Netherlands*	7	240
Great Britain**	200	500
Germany**	20	600 (since 2001) 300 (since 2005) 60 (since 2010)

Limit values were established in different ways, however, critical value 1 corresponds to the limit of detection. Critical value 2 was determined from the background values of marine samples and multiplied by 5.\* per dry weight of sediment, \*\* per sediment mass, \*\*\*sum of TBT, DBT and MBT

### 3 CONCLUSION

Chemical substances may be non-uniformly distributed in port sediments. Not all port sediments are polluted enough to pose a threat to living organisms. There are such areas in a harbour where a large accumulation of medium- and coarse-grained material (area of fine-grained sediments washing-out), however, with a small contamination load, as well as areas with a large amount of fine-grained material and with a large contamination load (area of fine-grained sediment accumulation) may be found. That is why dredging works in harbours should involve not only the analyses of locations in which large accumulation of contamination in sediments occurs but also the analysis of the hydrology of the basin and physical processes (e.g. storm surges, backwaters) responsible for the transfer of the contaminated fine-grained material to the accumulation zone.

For many years now HELCOM has been monitoring the issue regarding concentrations of chemical compounds in dredged spoil in the Baltic Sea, thus requiring particular countries of the Baltic Sea to establish proper legal regulations (above all, for the determination of active levels of concentrations above which the sediment is deemed contaminated) regulating the issue of sinking dredged spoil in the sea. It seems, however, that not all has yet been done in this matter. There are still legal regulations to be established that would regulate the process of sinking in the sea sediments with certain chemical compounds (e.g. organotin derivatives).

### REFERENCES

Alzieu, C., 2000. Environmental impact of TBT: the French experience. *Science of the Total Environment* 258: 99-102.

Article 11 of the Helsinki Convention, 1992, on the protection of the marine environment of the Baltic Sea area. Helsinki Convention

Bolałek J., Radke B., 2006. The content of labile and total form of Pb, Ni, Cu, Zn in sediment. *Zeszyty Komunalne* 9:78-80 (in Polish).

Bolałek J., Radke B. 2010. Aspects of pollution in the harbours located near the river mouth using the

example of the Gdańsk and Klaipėda harbours. *Prace i Studia Geograficzne* T.44: 249-265.

Dembska, G., Bolałek, J., Aftanas, B., Guz, W., Wiśniewski, S., 2001. The share of labile and total forms of heavy metals in benthic sediments from the Port of Gdańsk. In J. Siepak (eds.), *Problemy analityczne badań osadów dennych. Sympozjum Naukowe Komitetu Chemii Analitycznej PAN. Conference materials.* 64-97. UAM, Poznań (in Polish).

Dz. U. No. 55, Item 498, 2002. Ordinance of the Minister of Environment of 16 April 2002 on the types and concentrations of substances that cause spoil contamination. *Polish Journal of Laws*

Eko-Konsult, 1998. Ocena realizacji obowiązków wynikających z tytułu wymagań ochrony środowiska Zarządu Portu Gdańsk S.A. w Gdańsku. *Projmors BPBM Sp. z o.o.* 36: 48-54, 60-64.

HELCOM, 1992, Recommendation 13/1, Helsinki: HELCOM

HELCO M, 2007, Guidelines for the Disposal of Dredged material at Sea 2007. Helsinki: HELCOM

Hoch M., 2001. Organotin compounds in the environment – an overview. *Applied Geochemistry* 16: 719 - 743.

ICES CM, E: 03, 2002, Report of the working group on marine sediments in relation to pollution. San Sebastian: AZTI, 11–15 March 2002.

Langston, W.J., Pope, N.D., 1995. Determination of TBT adsorption and desorption in estuarine sediments. *Marine Pollution Bulletin* 31: 32-43.

Luoma, S.N., Bryan, G.W., 1981. A statistical assessment of the forms of trace metals in oxidized estuarine sediments employing chemical extractants. *Science of the Total Environment* 17: 165-196.

Loring, D.H., Rantala, R.T.T., 1992. Manual for the geochemical analysis of marine sediments and suspended particulate matter. *Earth Science Reviews* 32: 235-283.

Majewski A., 1972. Charakterystyka hydrologiczna estuariowych wód u polskiego wybrzeża. Gdańsk: PIHM.

Maksymowska D. 1998. The degradation of organic matter in the water column and sediment samples from the Gulf of Gdańsk. Typescript, Gdańsk: UG (in Polish).

Mędrzycka, K., Dubiella-Jackowska, A., Wasik, A., Namieśnik, J., 2006. The application of GC-FPD method for determining organotin compounds in sediments samples from marine Gdańsk and Gdynia Harbours. *Ekologia i technika* T 14 (85): 62-66 (in Polish).

Pempkowiak J., 1992, Enrichment factors of heavy metals in the South Baltic surface sediment dated with 210Pb, 137Cs and 134Cs. *Environmental International* 17: 421-428

Radke B., Dembska G., Aftanas B., Bolałek J., 2004, The occurrence of total and labile forms of lead and nickel in the sediments of the port of Gdańsk. *Oceanological and Hydrobiological Studies* 33(2): 41-56

Radke B., Łęczyński L., Wasik A., Namieśnik J., Bolałek J., 2008. The content of butyl- and phenyltin derivatives in the sediment from the Port of Gdańsk. *Chemosphere* 73: 407-414.

Radke B., Wasik A., Jewell L., Pączek U., Gałuszka A., Namieśnik J., 2012a. The seasonal changes of organotin compounds in water and sediment samples collected from the area of Port of Gdynia. *Science of the Total Environment* 441: 57-66.

Radke B., Wasik A., Jewell L., Pączek U., Piketh S., Namieśnik J., 2012b. The speciation of organotin compounds in sediment and water samples from the Port of Gdynia – in press in *Soil and Sediment Contamination*

Pustelnikovas O., Dembska G., Radke B, Bolałek J., 2005, Sedimentation and distribution of microelements in ports of the South Baltic Sea (Klaipėda and Gdansk). In W. Florek (eds) *Geologia i geomorfologia pobraża i Południowego Bałtyku*: 6: 67-88, Słupsk: PAN (in Polish)



Pustelnikovas O., Dembska G., Szefer P, Radke B., Bolalek J., 2008. Distribution of the element migration (state) forms of microelements in the sediments of Klaipeda and Gdańsk Ports, *Oceanological and Hydrobiological Studies* 36(4): 129-149.

Szwernowski P., 1957. *Studium gospodarki urobkiem*. Gdańsk: IM: (in Polish)

Wasik, A, Radke, B., Bolalek, J., Namieśnik, J., 2007. Optimisation of pressurised liquid extraction for elimination of sulphur interferences during determination of organotin compounds in sulphur-rich sediments by gas chromatography with flame photometric detection, *Chemosphere* 68: 1-9.