# BALTIC COASTAL ZONE Journal of Ecology and Protection of the Coastline

Vol. 21 pp. 211-224 2017

ISSN 1643-0115

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Original research paper

Received: 25/07/2017 Accepted: 13/10/2017

# HEAVY METALS IN BEACH DEPOSITS, BOTTOM SEDIMENTS OF A BALTIC FISHING PORT AND SURFACE WATER

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#### Abstract

Concentrations of metals, i.e. As, Cd, Cu, Mn, Ni, Pb, Zn were analysed in bottom deposits of a marine port in Ustka and within the adjacent beach sections. Metal concentrations within the port channel may be ordered in terms of increasing values as: Cd < As < Ni < Zn < Cu < Pb < Mn. Heavy metal concentrations detected in port sediments were much higher than those in beach deposits. Samples of surface waters were also collected from the port channel, harbour basins and nearby beaches and selected physico-chemical indexes were determined, including heavy metal concentrations.

Key words: Baltic Sea, port, bottom sediments, beach deposits, heavy metals, arsenic

#### **INTRODUCTION**

The marine port in Ustka is a major port located at the northern boundary of Poland. It is one of the largest among small ports of the Polish coast. It covers an area of over 30 ha, of which approx. 12 ha are sea areas, while land accounts for approx. 18 ha (Palmowski 1994, Pacuk and Michalski 2002). The port is administered by the Maritime Authority in Shupsk (Pacuk and Michalski 2002). The Port in Ustka has limited technical facilities required for cargo handling and as a result its function in this respect is minimal (Palmowski 1994, Nowaczyk 2016). Additionally, the port lacks support facilities, which results in a decline of inshore navigation. Major cargo handling operations are provided by large ports equipped with specialist facilities

(Palmowski 1994). For this reason the primary function of the port in Ustka is connected with fisheries and the growing recreation and tourism services (Pacuk and Michalski 2002). At present the port is gaining in popularity as a marina.

A significant problem observed in ports is connected with the accumulation of heavy metals in bottom deposits in the port channel and harbour basins and its effect on nearby beaches. The amount and type of bottom deposit pollutants in marine ports and waters are connected with the number of ships mooring in the port (Radke et al. 2013). According to international environmental protection standards heavy metals are the most important indicators for the degree of pollution in port sediments. Heavy metals are deposited in bottom sediments, while their sources may be anthropogenic or natural (Bolałek et al. 1999). Anthropogenic sources include domestic wastewater, industrial wastewater, wastewater generated during excavation, refining and processing of mineral resources as well as wastewater from agricultural production processes. A considerable role in pollution is also played by non-point sources, e.g. surface run-off, run-off from farmland and atmospheric deposition (Działoszyńska-Wawrzkiewicz 2008), as well as tourism and industrial processes (Gheskiere et al. 2005, Santhiya et al. 2011).

The aim of study was to determine and compare concentrations of analysed heavy metals and arsenic in port bottom sediments and beach deposits.

# MATERIAL AND METHODS

# Collection of water and bottom sediment samples

Bottom sediments were sampled in 2015 at 21 selected sampling stations as shown in Fig. 1 from the marine port, the port channel (denoted by C), harbour basins (B) in the Ustka port and from the western (W) and eastern beaches (E).



Fig. 1. Location of sampling stations

Samples of bottom sediments were collected using an Eckman grab sampler. Surface waters were sampled from a depth of approx. 10 cm using a dipper equipped with a polyethylene container. Samples were collected at a distance of 2-3 m from the shore at eight sampling stations located in the port channel and three in harbour basins, and ten sampling stations located along beaches of the Baltic Sea (from the western and eastern beaches).

Samples of water and bottom sediments were stored in polyethylene containers washed with diluted nitric acid (V) 5% (soaking for 24 h) and subsequently rinsed with deionised water by Hydrolab (Poland).

# Determination of metal contents in sediments

Contents of heavy metals in bottom sediments were analysed at the Laboratory of Environmental Analyses, the Institute of Plant Protection – NRI, using certified reference materials. Samples of beach deposits, bottom sediments (circa 50 g) were sieved through a sieve. Sediment samples were ground in a Fritsch Pulverisette 7 planetary micro mill. After milling 0.5 g of the sample was weighed. Ground sediment samples were mineralised in a microwave oven (CEM MARS 5) in 10 ml 65% HNO<sub>3</sub> (Merck Suprapur<sup>®</sup>). Total contents of analysed metals were assayed by AAS using F-AAS (Varian AA240FS), ET-AAS (Varian AA240Z). Nitric acid (Merck Suprapur<sup>®</sup>) was used in the blank test. All the analyses were conducted using ultrapure water with conductivity of 0.05  $\mu$ S/cm from a Polwater CDRX-200 deioniser. All laboratory glassware used in analyses was washed in diluted nitric acid (V) (soaking for 24h) and next rinsed with deionised water. Accuracy of the method was confirmed by analyses of reference materials CONTEST 77 (LGC Standards Proficiency Testing, mineral soil) and GM 2014.1.1 (PT-SChR verification test, mineral soil) and the obtained results are presented in Table 1.

Table 1

	Parameter											
Reference material	As	Cd	Pb	Zn	Zn         Cu         Ni           340.49         185.03         51.36           20.10         2.79         2.72           326.96         181.76         54.13           16.83         2.21         2.91							
reference value [µg g <sup>-1</sup> ]												
CONTEST 77	211.75	1.61	931.60	340.49	51.36							
GM2014.1.1	1.33	0.15	6.66	20.10	2.79	2.72						
obtained value [µg g <sup>-1</sup> ]												
CONTEST 77 (AAS-F)	-	-	923.11	326.96	181.76	54.13						
GM2014.1.1 (AAS-GF)	0.98	0.12	7.80	16.83	2.21	2.91						
recovery [%]												
CONTEST 77	-	-	99.09	96.03	98.23	105.40						
GM2014.1.1	73.46	83.56	117.12	83.73	79.21	106.98						

Recovery rates of reference material, reference values and concentrations recorded in the study

## Chemical analyses of water samples

Samples of water for analyses (10 ml) were acidified to pH = 2 with 65% HNO<sub>3</sub> (Merck Suprapur<sup>®</sup>) and subsequently they were mineralised in a microwave oven (CEM MARS 5). Heavy metals in the obtained extracts were assayed by the AAS technique using the F-AAS (Varian AA240FS), ET-AAS (Varian AA240Z). Concentrations of dissolved ions:  $SO_4^{2^-}$ ,  $NO_3^-$ , Cl<sup>-</sup>, Br<sup>-</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup> and NH<sub>4</sub><sup>+</sup> were determined in a Methrom 881 Compact IC Pro ion chromatograph. Water samples were filtered on syringe filters of 0.20 µm in diameter. Standard series were prepared by dilution from standard solutions of 1000 mg L<sup>-1</sup>. Analyses were performed using ultrapure water from a Hydrolab deioniser. Concentration of dissolved oxygen was determined with a portable Martini Instruments Mi 605 oxygen meter. Electrolytic conductivity was determined using a CP-315 Elmetron conductometer. Water reaction was determined using a multiple parameter Martini Instruments Mi 805 meter with a series of buffer solutions.

### Statistical analysis

Statistical analysis was conducted using the Past 3.0 programme calculating the mean, median, minimum, maximum, standard deviation, the normality test, the Mann–Whitney U test as well as the multiple parameter cluster analysis (Ward's method, Euclidean similarity index) according to Hammer (2017).

# RESULTS

#### Heavy metals in bottom sediments

Table 2 presents basic statistical parameter concerning heavy metal concentrations in bottom sediments of the port in Ustka, its harbour basins and beach deposits. Metal concentrations within the area of the port channel produce the following order of increasing values: Cd < As < Ni < Zn < Cu < Pb < Mn. In turn, for beach deposits this series was as follows: Cd < As < Zn < Ni < Pb < Cu < Mn.

Figures 2 and 3 present the distribution of Mn, Ni, Cu, Zn, Cd, Pb and As at the individual sampling stations. Graphs on the left give the distribution of metal concentrations along the port channel, while those on the right present the distribution of heavy metals at the beach sampling stations. Concentrations of all analysed heavy metals in the port channel bottom sediments were statistically higher (Table 3) than those observed in the beach deposits.

At the 1C sampling station (the last section of the Shupia River before the entrance to the port) the concentrations of heavy metals were lower in comparison to those in the farther sections of the channel: 3C-10C. At section 11C the bottom sediments had a similar chemical composition as beach deposits.

Manganese concentrations in bottom sediments of the port channel increased from sampling station 1C to station 5C. In the beach deposits from the western beach the concentration of manganese was almost 1.5-fold higher than at the eastern beach.

Parameter		Mean		Median	L.	US		IIIIIIIIII	Maximum	D	Q	
Location	harbour	sea	harbour	sea	harbour	sea	harbour	sea	harbour	sea	ΓC	ΓC
						μg g <sup>-1</sup>						
Mn	562.35	17.79	553.62	16.02	498.48	4.88	64.41	13.48	1,710.90	25.47	4.000	8.000
Ni	12.87	1.77	16.57	1.64	7.70	0.51	1.82	1.26	22.66	2.96	0.280	0.550
Cu	75.10	2.45	37.42	2.43	90.69	0.22	3.81	2.06	267.13	2.84	0.330	0.660
Zn	42.45	< LOD	32.24	< LOD	31.58	< LOD	2.09	< LOD	113.93	2.18	1.840	3.690
Cd	0.28	< LOD	0.32	< LOD	0.17	< LOD	0.01	< LOD	0.55	0.01	0.006	0.012
Pb	131.32	1.79	157.10	1.78	73.74	0.65	6.23	0.80	249.20	2.85	0.210	0.410
As	5.02	0.34	4.50	0.33	4.88	0.06	0.52	0.26	16.38	0.47	0.110	0.210

Statistical parameters for heavy metal and As concentration in bottom sediments and beach deposits

Explanations: LOD - limit of detection, LOQ - limit of quantitation

The lowest nickel concentration was observed at sampling stations 1C to 3C. Three high Ni levels were recorded at stations 5C, 8B and 10C. Nickel concentration within the port channel was approx. 10.5-fold greater than in the beach deposits. A comparison of the values in beach deposits showed higher concentrations of this metal at the western beach.

In the case of copper the highest concentrations in the port channel sediments were recorded at sampling station 2C. A slightly lower value was found in the harbour basin -9B – and a slight increase of the concentration was observed at sampling station 4B. Mean concentrations in the beach deposits were on average 15-fold higher than in the port channel.

Table 3

Differences in significance between concentrations of heavy metals and As recorded in beach deposits and bottom sediments of the port provided by the Mann–Whitney U-test (after Kolmogorov–Smirnov normality test)

Parameter	Z value	Level of statistical significance
Pb	- 3.84	***
Zn	- 3.77	***
Cu	- 3.84	***
Ni	- 3.63	***
Mn	- 3.84	***
Cd	- 3.85	***
As	- 3.84	***

\*\*\* - p < 0.001

Table 2



Fig. 2. Concentrations of Mn, Ni, Cu and Zn in bottom sediments (left) and beach deposits (right) (for Zn in beach deposits data below LOD except data from sampling station 1W)

The maximum value for zinc was recorded at sampling station 4B, which is within the harbour basin. High values were also found at sampling stations 2C and 9B. Zinc concentration in the beach deposits (LOD value) was over 23 times greater than the mean for the port channel. It should be stressed here that the highest concentration in the beach deposits was observed at the sampling station extending farthest into the Baltic (1W).



Fig. 3. Concentrations of Cd, Pb and As assayed in bottom sediments (left) and beach deposits (right) (for Cd in beach deposits data below LOD)

Cadmium concentration in the bottom sediments of the port channel increased from sampling station 1C to station 5C, where it reached the maximum value. For Cd high concentrations were recorded at sampling stations 5C, 8B and 10C, respectively. In the beach zone higher concentrations were observed at the eastern beach, reaching the highest value at sampling station 2E, whereas LOD value of cadmium concentrations in the beach deposits were approx. 46-fold lower than in the port sediments.

In the case of lead a systematic increase was found for the concentrations from sampling station 1C to station 5C, where it reached the maximum. Another increase in lead concentration was also observed at sampling station 9B. In the beach deposits Pb concentrations were approx. 70-fold lower than the mean recorded for the port channel. In the beach deposits from the eastern beach concentrations of lead were decreasing with an increasing distance from the port entrance, while at the western beach the lowest concentration was found at sampling station 5W, whereas the concentration increased at stations 1W, 3W and 4W.

In the case of As the highest concentrations were also recorded at sampling station 5C. Mean arsenic concentrations in the port channel sediments were almost 15-fold

higher than those observed in the beach deposits. Moreover, higher concentrations were recorded on the western beach in comparison to the eastern beach.

The multiple parameter cluster analysis was applied to group the tested heavy metals in terms of the similarity in their distribution at individual sections of the port channel (left) and the beaches (right) (Fig. 4). In port sediments two main clusters were distinguished, one comprising Pb, Ni, Cd, As and Mn, while the other consisting of Zn and Cu. In the beaches two main clusters were distinguished, one comprising Zn, Ni, Pb, Mn and As and second cluster consisting Cu and Cd.



Fig. 4. Hierarchical diagram of cluster analyses (Ward's method, Euclidean similarity index) for studied metals in harbour bottom sediments (left) and beach deposits (right)

### Chemical compounds contained in water

Table 4 presents basic statistical parameters for concentrations of analysed metals in surface waters of the port channel and in waters sampled along the beaches. Concentrations of heavy metals and arsenic in waters of the port channel and harbour basins as well as samples of water collected along the beaches may be arranged according to the increasing concentrations as follows: Cd < As < Cu < Mn < Ni. Concentrations of zinc and lead were below 5 ppb and Zn 20 ppb.

Table 4

Element	Harbour           mean           An           2.66           Ni           4.50           Cu           3.56           Cn           <20           Cd           0.14           %b	our	Coastal sea water					
Liement	mean	SD	mean	SD				
		μg L <sup>-1</sup>						
Mn	2.66	1.09	3.07	2.16				
Ni	4.50	4.08	10.93	2.87				
Cu	3.56	2.89	5.5	2.43				
Zn	<20	-	<20	-				
Cd	0.14	0.81	0.21	0.08				
Pb	<5	-	<5	-				
As	0.41	0.38	0.62	0.71				

Mean concentrations of heavy metals and arsenic and standard deviations recorded in surface waters of the port and coastal sea water Table 5 presents concentrations of ionic substances, dissolved oxygen as well as pH and EC values, to the greatest degree connected with salinity. These components, such as chlorine ions, were found at the highest concentrations in marine water, with their concentration being approx. 10-fol greater than the mean value obtained in the entire port channel. Concentrations of bromides in marine waters was almost 2-fold greater, those of sulphates 7-fold, sodium 10-fold, magnesium 19-fold, potassium 4-fold and calcium 2-fold, respectively. Electrolytic conductivity in marine waters was approx. 7-fold higher than in water sampled in the port channel. Water reaction in both these areas was comparable, while marine waters contained more dissolved oxygen (mean 6.20 mg L<sup>-1</sup> and 7.32 mg L<sup>-1</sup>). Concentrations of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> were higher in harbor water than in coastal water (about 50% and 30%, respectively).

Table 5

umeter	Jnit		Mean	:	Median	U2			Mumun	Maximum		
Par		harbour	coastal	harbour coastal		harbour	coastal	harbour coastal		harbour	coastal	
Cľ	mg L <sup>-1</sup>	382.32 3,887.76		344.69	4,044.87	92.51	308.56	279.22 3,340.79		531.92	4,109.88	
Br⁻	mg L <sup>-1</sup>	5.78 13.51		5.72	13.71	0.19	0.64	5.56	12.43	6.11	14.06	
NO <sub>3</sub> -	mg L <sup>-1</sup>	1.00	0.67	0.94	0.56	0.39	0.40	0.46	0.25	1.63	1.28	
SO4 <sup>2-</sup>	mg L <sup>-1</sup>	84.83	83 584.22 7		610.76	20.82	49.64	66.13	496.63	127.86	618.37	
NH4 <sup>+</sup>	mg L <sup>-1</sup>	0.28	0.21	0.14	0.14	0.32	0.18	0.09	0.08	1.00	0.54	
K <sup>+</sup>	mg L <sup>-1</sup>	18.60	80.98	11.07	79.12	16.24	8.05	9.00	74.34	54.74	96.65	
Na <sup>+</sup>	mg L <sup>-1</sup>	205.93	2,092.88	181.50	2,077.09	58.46	84.56	149.23	1,989.19	305.01	2,231.45	
Mg <sup>2+</sup>	mg L <sup>-1</sup>	11.73	228.02	4.43	229.76	13.74	8.57	3.80	214.37	36.11	237.72	
Ca <sup>2+</sup>	mg L <sup>-1</sup>	41,62	97.41	24.75	89.79	35.94	25.23	21.84	70.13	121.67	139.83	
EC	mS	1.79	12.39	1.76	12.32	0.37	0.11	1.34	12.32	2.32	12.56	
рН	-	7.79	7.60	7.78	7.66	0.05	0.20	7.75	7.21	7.90	7.78	
<b>O</b> <sub>2</sub>	mg L <sup>-1</sup>	6.20	7.32	6.25	7.60	0.35	0.91	5.40	6.20	6.50	8.10	

Statistical parameters for dissolved ions, oxygen, EC and pH in coastal and harbour waters in Ustka

# DISCUSSION

Bottom sediments and the heavy metals they contained provide information on pollutants deposited occasionally even for decades. Dynamics of changes in heavy metal concentrations in bottom sediments is much lower than observed in water (Protasowicki and Niedźwiecki 2004). The amount and type of deposited metals in the bottom sediments of marine ports are connected with the numbers of ships mooring in the port (Radke et al. 2013) and the type of port infrastructure. The results clearly show dramatic differences between concentrations of analysed heavy metals and arsenic between their contents in the port bottom sediments and the beach deposits sampled at the nearby beaches. These data are confirmed by the results of statistical tests (Table 3). Mean contents in these areas for Mn in the port sediments were by 31.6-fold higher than in the beach deposits, for Ni it was 7.3-fold, Cu 30.6-fold, Zn 32.9-fold, Cd 28.0-fold, Pb 73.4-fold and As 14.8-fold, respectively.

Sources of pollutants in the port sediments may be anthropogenic or natural. Generally heavy metals are bound by solid particles or organic matter and are deposited on the bottoms of water bodies (Szefer and Skwarzec 1988). In this study conducted in the port in Ustka the highest concentrations of analysed metals were found in the central part of the port and not in its entrance (Figs 2-3). Ports such as Ustka situated at the mouth of the Słupia River to a certain extent are contaminated with heavy metals carried from the river catchment towards its mouth. Along the river course concentrations of heavy metals may increase towards its mouth (Nocoń et al. 2013, Barbusiński and Nocoń 2011). In the case of Cd, As, Cu, Mn and Ni concentrations in the bottom sediments at the stretch of the Słupia River upstream of the port were much lower than in the port itself in comparison to the central part of the port. The greatest loads of pollutants in the Ustka port were found for Pb and Cu. According to Szefer and Skwarzec (1988), coastal zones are polluted by Zn, Pb, Cd and Cu due to the impact of large industrial plants and urban areas. Copper and zinc are components of brass alloys, frequently used in ships and to produce gun cartridges. Both components are found in one cluster in the cluster analysis (Fig. 4). In contrast, in the beach settlements, copper and zinc occur in different clusters. According to a study by Santhiya et al. (2011), high contents of Ni, Cu, Pb and Zn in bottom sediments are explained by the presence of a fishing port and industrial pollution.

As a result of the natural water self-purification process heavy metals are deposited on the bottoms of water bodies. As a result of sorption and sedimentation soluble forms of heavy metals penetrate to bottom sediments, which results in an improved quality of surface waters and increased metal concentrations in bottom sediments of water bodies (Barbusiński and Nocoń 2011). Metals sparsely soluble in water (Cd, Hg, As, Cr, Ni, Cu and Zn) are particularly well accumulated in bottom sediments (Działoszyńska-Wawrzkiewicz 2008). At the entrance to ports water from the port channel mixes with marine waters, as a result polluting marine waters and sediments (Trojanowski and Bigus 2013, Gheskiere et al. 2005, Santhiya et al. 2011). Beach deposits contain much lower amounts of organic matter than port sediments, thus metals are much less intensively deposited in beaches than in organic port sediments. Moreover, they are dissolved in much greater volumes of marine waters.

According to the LAWA classification (1998) presented in a study by Bąk et al. (2014), the collected samples (means) of bottom sediments are classified in terms of individual metals as follows: Ni – unpolluted (class I), Cu – moderately polluted (class II) (according to the median classes I-II), Zn – unpolluted (class I), Cd – unpolluted (class I) (according to the median classes I-II), Pb – moderately pollut-

ed / critically polluted (classes II-III). In turn, samples of the beach deposits in terms of Zn, Pb, Cu, Ni and Cd were classified to class I (unpolluted sediments). In Italy geochemical purity classes were developed for sediments extracted from port basin bottoms for use in other environments (Bojakowska and Sokołowska 1998). According to the respective classification proposed by Cariocchla et al. (1992), samples of the bottom sediments in terms of their Ni, Zn, Cd and As contents fell within class I, while for copper and lead – class II. Beach deposits in terms of all the analysed metals were class I. Bojakowska and Sokołowska (1998) presented the classification, sediments from the port of Ustka for Zn and Cd concentrations were within the geochemical background. As concentration was slightly higher than the geochemical background, Ni – class I, Cu i Pb – class II. The concentration of Ni, Cu, Zn, Cd, Pb and As in beach sediments was within the geochemical background.

Table 6 presents information on concentrations of heavy metals in various coastal areas in Poland and Germany and Lithuania. The results are consistent with data for marine ports of Poland and are typically lower than for large marine ports. In turn, results obtained for the beach deposits were comparable to those given by Perkowska and Protasowicki (1996) for bottom sediments of the southern Baltic.

Recorded concentrations of heavy metals and As in surface waters were not high and are comparable to those reported in a study by Bigus et al. (2016) for the upper reaches of the Słupia River. Concentrations of Cl<sup>-</sup>, Br<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> as well as EC values were higher in marine waters than in the port water samples. This is naturally connected with salinity of marine waters. As a rule, the abovementioned ions are found in greater amounts in the marine waters of the Baltic (Dojlido 1995) than in the nearby inland waters of the Pomerania region. Salinity is manifested in terms of EC, providing the total value of dissolved components. Also marine waters in the period of the study contained more dissolved oxygen than waters in the port channel. In turn, waters of the port channel contained greater amounts of nitrogen compounds usually of anthropogenic origin, drainage from catchment area, which are transported to the sea with river waters (Korzeniewski et al. 1989).

#### CONCLUSIONS

In the case of Cd, As, Cu, Mn and Ni concentrations in the analysed bottom sediments at the section of the Słupia River preceding the entrance to the port were lower than those recorded in samples collected from the central part of the port.

Beach deposits contained much lower concentrations of heavy metals and arsenic than those collected from the port channel and harbour basins.

Metal concentrations in the port channel may be arranged in the increasing concentration order as follows: Cd < As < Ni < Zn < Cu < Pb < Mn, while an analogous order for the beach deposits was: Cd < As < Zn < Ni < Pb < Cu < Mn, respectively.

Table 6 huania	Deference	reletence	Szefer and Skwarzec 1988	Protasowicki et al. 1993				Protasowicki and Niedwiecki 2004	Karczewska et al. 2013	Glasby et al. 2004	Perkowska and Protasowicki 1996	Protasowicki and Niedwiecki 1993					Bolaek and Radke 2010		Helios-Rybicka et al. 2005	Bolaek et al. 1999
ıd Lithuan	As		1	ı	1	I	I	I	8.500- 17.200	ı	-	ı	ı	I	I	I	I	I	62.6	I
l, Germany ar	Cd		11.2	9.8+/-6.5	7.4+/-3.5	3.9+/-3.3	0.4+/-0.2	3.0	I	3.8-4.3	0.05-1.4	1.7-4.3	29	15	13	0.8	1.3-1.5	<0.14-2	9.7	0.3-0.8
l areas in Poland	Mn		781.0	190.0 + / -180.6	86.7+/-65.3	68.8+/-41.8	29.3+/-8.4	I	I	1.610-2.200	12.5-129.8	391.3-836.4	I	1	I	35.5	I	I	2,101	I
n various coasta	Ni	1- 8-	29.9	24.8+/-14.3	16.9+/-9.4	16.6+/-13.2	3.66+/-1.2	15.8	I	37-38	ı	6.2-15.9	106	Į	95	7.19	16-22	<1.7-11	52.7	1.8-3.9
y metals and As ii	Cu	. 20	72.4	131.9+/-112.6	52.1+/-46.1	45.1+/-35.8	5.9+/-2.3	45.1	I	64-75	0.5-55.6	9.4-50	410	517	110	3.2	10-105	<1-131	131	5.8-25.0
trations of heavy	Pb		119.8	175.9+/-92.5	112.7+/-57.4	107.9+/-98.8	11.0+/-3.1	119.2	I	108-122	1.6-59.1		560	280	340	23.8	6-62	2-93	153	4.9-3.6
Data on concen	Zn		437.0	896.4+/-516.9	417.4+/-419.5	592.0+/-454.7	41.4+/-11.9	654.6	I	762-832	6.2-206.4	155.5-374.4	1.700	1.760	1.800	63	31-131	9-334	1226	11.6-89.9
	۸ ۳۵۵ م۴ ملیطی	AICA UI SIUUY	Southern Baltic	Szczecin, Poland	Police, Poland	Trzebie, Poland	winoucie, Poland	Szczecin Lagoon, Poland	Zotystok, Poland	Szczecin Lagoon, Poland	Southern Baltic	Odra estuary, Poland	Hamburg, Germany	Hamburg, Germany	Brema, Germany	Cuxhaven, Germany	Klaipeda, Lithuania	Gdask harbour, Poland	Odra, Poland	Gdask harbour, Poland

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#### REFERENCES

- Barbusiński K., Nocoń W., 2011. Zawartość związków metali ciężkich w osadach dennych Kłodnicy. The content of heavy metal compounds in bottom sediments of Kłodnica. *Ochr. Środ.*, 33, 13-17, (in Polish).
- Bąk Ł., Górski J., Szeląg B., 2014. Heavy metal concentrations in water and bottom sediments of small water reservoir at Kaniow. In: Proceedings of Ecopole, 8, 119-125, doi: 10.2429/proc.2014.
- Bigus K., Astel A., Antonowicz J., Nałęcz-Jawecki G., Drobniewska A., 2016. Hydroelectric power plants in the basin of Słupia river – touristic attraction or ecological threat? *Fol. Pom. Univ. Techn. Stet.*, 330 (40), 4, 23-33.
- Bojakowska I., Sokołowska G., 1998. Geochemiczne klasy czystości osadów wodnych. (Geochemical classes of water sediment purity). Przegl. geol., 46 (1), 49-54, (in Polish).
- Bolałek J., Dembska G., Aftanas B., Hofman J., Szefer P., 1999. Przestrzenne i wgłębne rozmieszczenie chromu, cynku, kadmu, miedzi, niklu, ołowiu i rtęci w różnych frakcjach granulometrycznych osadów Portu Gdańskiego. (Spatial and in-depth distribution of chromium, zinc, cadmium, copper, nickel, lead and mercury in various granulometric fractions of Gdańsk harbours sediments). Zesz. Nauk. Inst. Mor., 2, 21-37, (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 Klaipeda harbours. *Pr. i stud. geogr.*, 44, 249-265.
- Cariocchla A., Chiavarini S., Cremisini M., Fantinim R., Moabito R., 1992. Monitoring program for the evaluation of the pollution level of the Italian harbour sediments. In: International Symposium on Environmental Contamination in Central and Eastern Europe. Symposium Proceedings. Chaerse, Budapest, 542-544.
- Dojlido J.R., 1995. Chemia wód powierzchniowych. (Surface water chemistry). Ekonomia i Środowisko, Białystok, (in Polish).
- Działoszyńska-Wawrzkiewicz M., 2008. Metale ciężkie w osadach rzecznych terenów zurbanizowanych zlewni rzeki Kłodnicy. (Heavy metals in the river sediments of urbanized areas of the Kłodnica river basin). http://www.ietu.katowice.pl/klodnica/dokumenty/ Publikacje/osady monografia.pdf., access on 22.05.2017, (in Polish).
- Gheskiere T., Vincx M., Weslawski J.M., Scapini F., Degraer S., 2005. Meiofauna as descriptor of tourism-induced changes at sandy beaches. *Mar. Environ. Res.*, 60, 245-265.
- Glasby G.P., Szefer P., Geldon J., Warzocha J., 2004. Heavy-metal pollution of sediments from Szczecin Lagoon and the Gdańsk Basin, Poland. *Sci. Tot. Environ.*, 330, 249-269.
- Hammer Ø., 2017. PAST. Paleontological Statistics. Reference manual. Natural History Museum, University of Oslo, Oslo, available online: http://folk.uio.no/ohammer/past/ past3manual.pdf., access on 22.09.2017
- Helios-Rybicka E., Adamiec E., Aleksander-Kwaterczak U., 2005. Disposition of trace metals in the Odra River system: Water-suspended matter-sediments. *Limnol.*, 35, 185-198.
- Nocoń W., Barbusiński K., Nocoń K., Kernert J., 2013. Analiza zmian ładunku metali śladowych transportowanych wraz z zawiesinami wzdłuż biegu rzeki. (The analysis of changes in load trace metals transported together with suspended matter along the river). *Ochr. Środ.*, 35, 33-38, (in Polish).
- Karczewska A., Krysiak A., Mokrzycka D., Jezierski P., Szopka K., 2013. Arsenic Distribution in Soils of a Former As Mining Area and Processing. *Pol. J. Environ. Stud.*, 22 (1), 175-181.
- Korzeniewski K., Trojanowska C., Trojanowski J., Zielke R., 1989. Transformation of pollution along the course of Łupawa River in years 1985-1986. *Pol. Arch. Hydrobiol.*, 36 (2), 289-312.
- Nowaczyk P., 2016. Determinanty rozwoju działalności żeglarskiej małych portów morskich w Polsce. (The Determinants of Sailing Activity Development of Small Seaports in Po-

land). Fol. Pom. Univ. Techn. Stet. Oecon., 82, 107-116, doi: 10.21005/oe.2016.82.1.10, (in Polish).

- Pacuk M., Michalski T., 2002. Problemy funkcjonowania małych portów morskich na przykładzie Ustki. W: Wybrane zagadnienia geografii transportu. (Problems in functioning of small seaports on the example of Ustka. In: Selected issues of transport geography). (Ed.) J. Wendt, Wydawnictwo Uniwersytetu Szczecińskiego, Szczecin, 133-140, (in Polish).
- Palmowski T., 1994. Małe porty polskiego Wybrzeża i ich funkcje. W: Ku wspólnocie Europy Bałtyckiej. (Small ports of the Polish Coast and their functions. In: Towards the community of Baltic Europe). (Ed.) C. Ciesielski, Instytut Bałtycki, Gdańsk, 101-115, (in Polish).
- Perkowska A., Protasowicki M., 1996. Heavy metal contents in sediments and blue mussels Mytilus edulis from three regions of the Southern Baltic Sea. *Oceanom. Stud.*, 25 (4), 55-63.
- Protasowicki M., Niedźwiecki E., 1993. Zawartość metali ciężkich w osadach dennych portów ujścia Odry. (Heavy metal content in bottom sediments of ports of the Odra estuary). *Stud. i Mat. MIR*, Ser. S, 117-120, (in Polish).
- Protasowicki M., Niedźwiecki E., Ciereszko W., 1993. Metale ciężkie i substancje chloroorganiczne w rdzeniach osadów z Zalewu Szczecińskiego. W: Substancje toksyczne w środowisku. (Heavy metals and chloroorganic substances in sediment cores from the Szczecin Lagoon. In: Pollutants in Environment). (Eds) A. Smoczyńska et al., ATR, Olsztyn, 155-159, (in Polish).
- Protasowicki M., Niedźwiecki E., 2004. An Attempt of Heavy Metals Load Estimations During Sedimentation of Sludges in the Szczecin Lagoon. Ochr. Środ., 6, 91-97.
- Radke B., Piketh S., Wasik A., Namieśnik J., Dembska G., Bolałek J., 2013. Aspects of pollution in Gdańsk and Gdynia harbours at the coastal zone of the South Baltic Sea. *Internat. J. Mar. Nav. and Safety Sea Trans.*, 7, 11-18, doi: 10.12716/1001.07.01.01.
- Santhiya G, Lakshumanan C., Jonathan M.P., Roy P.D., Navarrete-Lopez M., Srinivasalu S., Uma-Maheswari B., Krishnakumar P., 2011. Metal enrichment in beach sediments from Chennai Metropolis, SE coast of India. *Mar. Poll. Bull.*, 62, 2537-2542.
- Szefer P., Skwarzec B., 1988. Distribution and possible sources of some elements in the sediment cores of the southern balite. *Mar. Chem.*, 23, 109-129.
- Trojanowski J., Bigus K., 2013. The biochemical composition of sedimentary organic matter in sandy beaches of various anthropopressure. *Balt. Coast. Zone*, 17, 5-20.

# METALE CIĘŻKIE W OSADACH PLAŻOWYCH, OSADACH DENNYCH ORAZ W WODZIE POWIERZCHNIOWEJ BAŁTYCKIEGO PORTU RYBACKIEGO

#### Streszczenie

Wykonano analizy stężenia metali As, Cd, Cu, Mn, Ni, Pb, Zn w osadach dennych portu morskiego w Ustce oraz w sąsiadujących odcinkach plaży. Stężenia metali w obszarze kanału portowego tworzyły stężeniowy szereg rosnący: Cd < As < Ni < Zn < Cu < Pb < Mn. Uzyskane stężenia metali ciężkich w osadach portowych były znacznie wyższe niż w osadach plażowych. Z kanału portowego, basenów portowych oraz w pobliżu plaż pobrano również próbki wody powierzchniowej, w których przeanalizowano stężenie wybranych parametrów fizykochemicznych, w tym metali ciężkich.