





# Bulletin of the Maritime Institute in Gdańsk

# The influence of processes occurring during deposition of port's sediments in the on the Gulf of Gdansk way of bounding metals in the sediments

Wpływ procesów, zachodzących podczas deponowania osadów portowych w Zatoce Gdanskiej, na sposób wiązania metali z osadem

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Abstract: The aim of the work was to investigate the influence of processes occurring during deposition of port sediments in dump sites on the bonding of metals in the sediment.

About toxicity of polluted sediments are deciding not only concentration of macro-and micro-elements but, also the chemical forms in which they exist. These forms have considerable influence on their assimilation of different trophic levels (including human).

The results of the carried out investigations indicated that the concentration of the trace metals ware decreasing in sediments deposited on the dumping sites.

Grain size analysis demonstrated a significant decrease of clay fraction in sediments from the dumping site by comparison with the depositing sediments. The sequential analysis proved that the percentage of the particular forms of the metals (especially Pb and Cd) was changing in the sediments deposited in the dumping site. The changes of salinity, mechanical mixing during excavation, oxygen concentration may result in freeing the labile forms into the water column, especially the exchangeable and carbonate forms, which are loosely connected with the sediment, and these conditions may be sufficient to release these forms.

**Keywords:** Trace metals, sequence analysis, dumping site, pollutions, port sediments

Streszczenie: Celem pracy było zbadanie jaki wpływ na wiązanie metali w osadzie mają procesy, które zachodzą podczas deponowania osadów portowych na klapowiskach. O toksyczności i zagrożeniu jakie może stanowić zanieczyszczony osad decyduje bowiem nie tylko stężenie makro- i mikro- pierwiastków lecz również postać chemiczna, w jakiej występują. Postać ta wpływa w znaczącym stopniu na ich przyswajalność w odniesieniu do kolejnych poziomów piramidy troficznej nie wyłączając człowieka. Znajomość ilościowego składu pierwiastkowego osadów dennych z uwzględnieniem specjacji chemicznej jest bardzo istotnym elementem w prognozowaniu potencjalnego zagrożenia ze strony metali śladowych w stosunku do żywych, tak ważnych dla człowieka zasobów morza.

> W wyniku przeprowadzonych badań stwierdzono, że osady zdeponowane na klapowiskach charakteryzują się znacznie niższymi stężeniami metali niż osady portowe (które są tam deponowane). Analiza granulometryczna wykazała znaczny spadek frakcji ilastych w osadach na klapowiskach w stosunku do osadów portowych tam deponowanych. Analiza sekwencyjna dowiodła, że zmienia się procentowy udział poszczególnych form metali (szczególnie Pb i Cd) w osadzie zdeponowanym na klapowisku.

Słowa kluczowe: Metale, analiza sekwencyjna, klapowisko, zanieczyszczenia, osady portowe



## INTRODUCTION

The dredging of port basins is a very common practice, i.e. annually in Europe about 200 mln  $\rm m^3$  is dredged out of port channels in order to keep the ports accessible and to ensure safety of navigation [1-9]

The EU Directive on waste management (2006/12/EC) [10] indicates that it is most important firstly to reduce the amount of produced waste, and secondly to use effectively the spoil, and only the remaining volume of waste may be stored. A large part of the spoil is still stored at sea in specially designated dumping sites. This is mainly due to economic considerations (storage of so large amounts of spoil at sea is much cheaper than its neutralisation or storage on land).

Nevertheless, we should be conscious of the negative impacts of the process. Conditions during dredging of the sediments from port channels and during their dumping at sea (in designated dumping sites) are very dynamic and facilitate freeing of some of the contaminants. The sediments are first extracted from the bottom with a scoop, then placed in a dump barge, transported to the dumping site, and finally dumped at the site [6]. During these operations the spoil is oxygenated, mixed and washed (it passes two times through the water layer: once during dredging and the second time during the dumping). There is also a change in salinity (as a rule, salinity at the dumping site at sea, is higher than in port channels, which in most cases are located in river outlets).

These processes may cause disturbances of the natural flora and fauna, and they may also contaminate the dumping site area. Incorrect location of the dumping site can negatively impact fishing, recreation and navigation [14].

Among the many contaminants, occurring in the sediments, special attention should be given to the metals. They do not decompose, and in spite of temporary immobilisation in the sediment, they remain a potential threat to biological life in a water basin, because in favourable conditions they can be freed into the water column and penetrate into trophic chain of the ecosystem and in effect the metals once more start to circulate in the environment.

The aim of the work was to investigate the influence of processes occurring during deposition of port sediments in dump sites on the bonding of metals in the sediment.

### MATERIALS AND METHODS

There are two dump sites for dumping dredged spoil in the Gulf of Gdansk region: the Gdynia Dump Site and the Gdansk Dump Site. The Gdansk Dump Site is a circle of 5 cable (926.1 m) radius and centre in position 54° 30,0′ N 018°50,0′ E. The investigated material were sediment samples taken from the Gdansk Dump Site in 2005. At each point a 1.6-2.8 long core was taken by the research vessel "Dr Lubecki" with the use of a 10 cm diameter vibration probe. Location

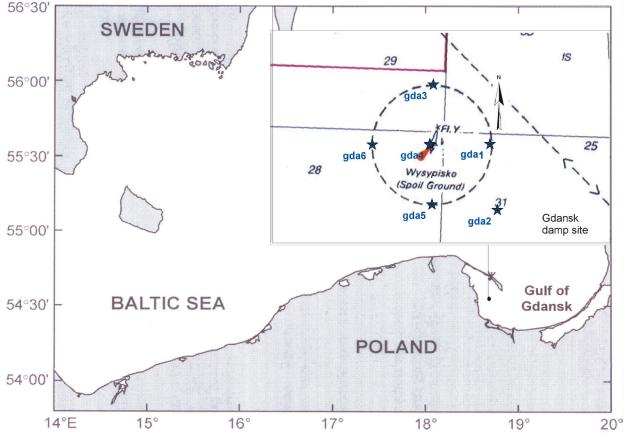


Fig. 1. Location of the sampling stations on Gdansk dumping site



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Tab. I. Macroscopic description and results of physical analysis of bottom sediments from the Gdansk dumping site

CORE	NO. OF ANALYTIC SAMPLE	DEPTH	DENSITY	LOSS ON IGNITION	MACROSCOPIC DESCRIPTION		
		[CM]	[G/CM3]	[%]			
GDA-1 1499	1499/1	0-10	3,83	0,49	Light beige fine sand		
	1499/2	10-30	3,83	0,49	Light beige fine sand		
	1499/3	30-50	3,77	0,15	Dark beige fine sand		
	1499/4	50-100	3,85	0,16	Beige fine sand		
	1499/5	100-150	3,81	0,21	Beige fine sand		
	1499/6	150-200	3,81	0,21	Beige fine sand		
	1499/7	200-230	4,33	0,28	Beige fine sand		
GDA-2 1500	1500/1	0-10	3,83	0,19	Dark beige fine sand		
	1500/2	10-30	3,83	0,19	Dark beige fine sand		
	1500/3	30-40	3,92	0,16	Beige fine sand		
	1500/4	40-58	3,92	0,16	Beige fine sand		
	1500/5	58-100	3,54	0,20	Dark grey fine sand		
	1500/6	100-143	3,67	0,56	Dark grey fine sand		
	1500/7	143-163	3,72	1,05	Grey fine sand with inter-beds of medium sand		
	1500/8	163-200	-	1,35	Dark grey fine sand Inter-bed of soft-plastic grey till		
	1500/9	200-210	3,90	1,17	Dark grey fine sand		
	1501/1	0-10	3,63	0,22	Beige - gray fine sand		
GDA-3 1501	1501/2	10-20	3,63	0,22	Beige - gray fine sand		
	1501/3	20-49	3,90	0,23	Beige fine sand		
	1501/4	49-71	3,68	0,24	Dark grey fine sand		
	1501/5	71-100	3,68	3,92	Soft-plastic grey till		
	1501/6	100-150	3,92	1,61	Dark grey fine sand		
	1501/7	150-200	3,60	0,49	Dark grey fine sand		
	1502/1	0-10	3,76	0,23	Beige fine sand		
GDA-4 1502	1502/2	10-18	3,76	0,23	Beige fine sand		
1502	150/32	18-28	3,93	1,64	Beige fine sand with inter-beds of soft-plastic grey till		
	1502/4	28-38	3,55	0,25	Beige fine sand		
	1502/5	38-46	3,78	0,20	Dark grey fine sand		
	1502/6	46-100	3,49	0,21	Beige fine sand		
	1502/7	100-140	3,68	0,19	Beige fine sand		
	1502/8	140-174	3,68	0,19	Beige fine sand		
	1502/9	174-200	3,42	0,16	Dark grey fine sand		
	1502/10	200-210	3,63	4,30	Soft-plastic grey till		
	1502/11	210-250	4,18	0,25	Dark grey fine sand		
GDA-5 1503	1503/1	0-13	3,89	0,23	Light beige fine sand		
	1503/2	13-25	3,87	0,22	Gray-beige fine sand		
	1503/3	25-49	3,60	0,25	Ginger-beige fine sand		
	1503/4	39-100	3,80	0,28	Beige fine sand		
	1503/5	100-125	3,83	0,19	Beige fine sand		
	1503/6	125-189	3,79	0,30	Dark grey fine sand		
	1503/7	189-200	3,71	0,25	Dark grey fine sand		
GDA-6 1504	1504/1	0-10	3,62	0,22	Dark grey fine sand		
	1504/2	10-23	3,62	0,22	Dark grey fine sand		
	1504/3	23-38	3,62	0,22	Dark grey fine sand		
	1504/4	38-60	4,07	0,28	Ginger-grey fine sand		
	1504/5	60-100	3,92	0,31	Dark grey fine sand		
	1.	100-150	4,11	0,19	Dark grey fine sand		
	1504/6	100-130	т, : :	0,19	Burk grey fine suria		
	1504/6 1504/7	150-200	3,68	0,42	Dark grey fine sand		



of the points of sampling is shown on Fig. 1. The cores were cut into segments in which the following parameters were determined: density, grain size, loss of ignition. 49 samples of sediments from the segments of the investigated cores were selected for chemical analysis. In each core, the surface layer (between depth 0 and 10 cm) was separates. The separation of the next segments was based on the macroscopic description of the cores. After averaging each of the obtained segments, the below 2 mm fraction was separated and chemically analysed. The separation of the analytic samples and results of chemical analysis are shown in Table 1.

The total metal content (Pb, Cu, Zn, Ni, Cd, Cr, As, Fe, Li, Al) after mineralisation in concentrated acids [11] and labile form (Pb, Cu, Zn, Ni, Cd, Cr, As, Hg) after extraction with 1M HCl [2] were determined in the prepared samples. In selected samples, sequential analysis of the mentioned above metals was carried out using the Tessier method [13].

In effect, 5 forms of bonding of metals with the sediment were distinguished: I – exchangeable (adsorbed on the surface of sediment), II – bonded with carbonates, III – bonded with hydrated iron and manganese oxides, IV – bonded with organic matter, V – bonded with aluminosilicates.

Metals in forms I-IV are labile (mobile) forms, which are able to pass into the water column in natural conditions. Form V of metals are built into the crystal lattice of both secondary and primary minerals, and are permanently immobilised (in foreseeable time they will not pass into the water column) [14,15].

The metals, except mercury, were determined using optic emission spectrometry with inductively excitated plasma (ICP-OES) on an PERKIN-ELMER OPTIMA 2000DV spectrometer. Mercury was determined by atomic absorption spectrometry (AAS), using the cold vapour method (CV), on a SpektAA 250 PLUS spectrometer with a VRIAN VGA-77 attachment.

The determined detection limits (DL) are as follows:

- ◆ For ICP-OES: Zn-o.o5; Ni-o.o5; Cr-o.o5; Cd-o.o1; Cu-o.o5; Pb-o.o5, As-o.25 mg/kg s.m.
- ♦ For AAS-CV: Hg-0.002 mg/kg s.m.
  The limit of determination (LoD) is: LoD=5xDL.

The correctness of the analyses was checked by analysing, in parallel with the tested samples, the certified reference materials PACS-2 (Canadian port bottom sediment — National Research Council Canada) and SEDIMNT-31 (Dutch port bottom sediment — obtained by inter-lab comparisons organised by the Wageningen University, in which the Laboratory of the Maritime Institute systematically participates). The satisfactory results of analysis of both materials were obtained (recovery of the metals was between 82 and 98%).

The obtained results were compared with the results of analysis of sediments from the Gdansk dump site, carried out in the Laboratory of the Maritime Institute in 2002 [16] and with port sediments sampled in the Port of Gdansk in the period 1998 – 2005 [17-19].

## **RESULTS AND DISCUSSION**

The investigations showed that the analysed sediments from the Gdansk Dump Site consist of medium sand with small addition of organic matter (maximum loss at roasting was 4%). The grain size analysis showed that most of the sediment was within the 0.50-0.25 mm and 1.0-0,50 mm fractions. The rest of the fractions occurred in small amounts – Fig. 2. The grain size distribution was similar to the result obtained in 2002 for the same area [16]. However, this distribution is significantly different from the grain size distribution for the Port of Gdansk sediments, which are mainly deposited on the Gdansk Dumping Site. About 80,000 m³ of spoil from the Gdansk port channels was deposited in the period 2000 – 2005 on the Gdansk Dump Site [20]. According to earlier investigations, deposits from the Port of Gdansk are characterised by highest percentages of the 0.50 - 0.25 mm and 0.25 - 0.125 mm fractions [14]. This difference may be due to the significantly longer fall time of the fines grained than of the thick grained fractions during the dumping, and in effect the fine fractions can be transported by currents and deposited some distance from the location of the dumping operation.

The deposits from the dumping site were characterised by a low total content of the investigated metals (Table 2) and by low concentrations of the labile form (Fig. 3). In all samples values were below the permitted levels [21]: Pb-200 mg/kg d.m., Cu-150 mg/kg d.m., Cd-7,5 mg/kg d.m., Zn-1000 mg/kg d.m., Ni-75 mg/kg d.m., Cr-200 mg/kg d.m., As-30 mg/kg d.m., Hg-1 mg/kg d.m.)

Analysis of the horizontal distribution of concentrations indicated that the highest concentration of both the total and labile form content of the investigated metals occurred in samples taken from the centre of the dump site GDA - 4 (1502). Metal concentrations in the rest of the cores were significantly lower, and practically did not differ from the typical metal content in sandy sediments of the Southern Baltic [31]. As for the vertical distribution of concentration of the total metal content, generally a small decrease of concentration with depth was observed. In most cases metal concentration was higher in the upper (shallower) layers than in the lower layers. An exception are cores: GDA 2 (1500) (taken outside of the dump site) and GDA-3 (15001), where metal concentration remained at similar levels. In the core GDA-3 (15001), at depth 71 – 100 cm, a strong increase of concentration of the metals was observed. This is because at that depth there is a 30 cm thick interlayer of muddy sand with a high mud fraction content (ca. 30%) and higher organic matter content (loss at roasting ca. 4.0 %), which facilitate the accumulation of metals. A similar 10 cm interlayer (loss at roasting ca. 4.0 %, but lower mud fraction -17 %) was found in core GDA -4 (1502) from the centre of the dump site, at depth 200 -210cm. These inter-beddings were local (they were not found in the other four investigated cores, which due to the grain size aspect were relatively uniform). The inter-beddings may be an indication that at some previous time contaminated deposits were dumped in these places. However, natural origin of the interbeddings cannot be completely excluded.

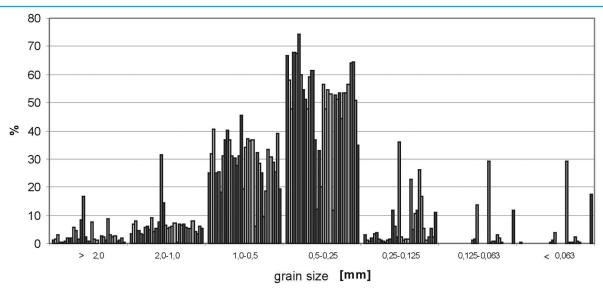


Fig. 2. Percentage of grain size distribution in slices of sediments from the damping site Gdansk.

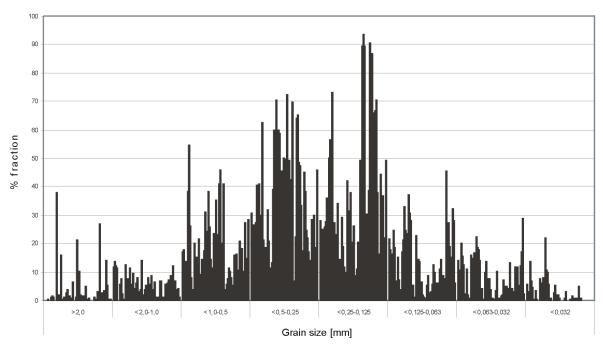


Fig. 3. Percentage of grain size distribution in slices of sediments from the Port of Gdansk.

In the case of the labile form, a distinct decrease of concentration with depth was observed in the core GDA-4 (1502) taken from the centre of the dump site (Fig. 3). At the other places no clear correlation between depth and metal concentration was found. In core GDA-3 (15001), at 71–100 cm depth, similarly to the total metal content, a significant increase of concentration of all investigated analytes was observed. However, for core GDA-4 (1502) there was no considerable increase of metal concentration at the 200-210 cm depth. The reason for this could be related to the lower fine fraction content than in the inter-bedding in core GDA-3 (1501), since the fines are responsible for bonding the labile form of metals.

Percentage of the labile form in the total metal content was very diverse. The highest content was observed for Cu-80%

and Zn – 60%. This means that such a percentage of metals contained in the investigated sediments from the Gdansk Dump Site may pass in favourable conditions into the water column. The other elements (Pb, Cr, Ni, As) were characterised by a low percentage of the labile form. This suggests that they are bonded mainly with aluminosilicates, and only in a small degree can pass into the water column and become a threat to live organisms. Since at the Gdansk Dump Site is deposited spoil from dredging of port channels in the Port of Gdansk, mean concentrations of metal content in port sediments were compared with concentrations of sediments deposited in the dump site. Analysis showed that sediments from the dump site are characterised by significantly lower concentrations of all investigated metals than the port sedi-



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 $\textbf{Tab. II.} \ Results \ of analysis \ of total \ metal \ content \ [mg/kg \ s.m.] \ in \ sediments \ from \ the \ Gdansk \ dumping \ site$ 

			ir content [mg/kg 3.	,			,			
No. of sam	ple Pb	Cu	Cd	Zn	Ni	Cr	As	Fe	Li	Al
GDA-1										
1499/1	1,62	0,47	< 0,05	1,85	0,60	2,35	<1,25	1857	0,12	841
1499/2	14,41	0,30	< 0,05	3,24	< 0,25	1,63	<1,25	2023	0,14	721
1499/3	2,35	0,11	< 0,05	1,85	< 0,25	1,44	<1,25	2041	0,07	599
1499/4	1,13	0,12	< 0,05	0,12	< 0,25	1,45	<1,25	1219	0,07	632
1499/5	1,27	0,13	< 0,05	0,89	< 0,25	1,65	<1,25	1515	0,22	661
1499/6	1,09	-	-	0,54	< 0,25	1,30	<1,25	1667	0,07	709
GDA-2										
1500/1	1,20	0,31	< 0,05	0,92	0,13	1,16	<1,25	1219	0,06	-
1500/2	2,47	0,12	< 0,05	1,73	< 0,25	1,46	<1,25	1889	0,05	573
1500/3	1,33	0,86	< 0,05	4,36	2,51	2,19	<1,25	2753	0,12	1227
1500/4	1,08	< 0,25	< 0,05	0,66	< 0,25	1,23	<1,25	1244	-	477
1500/5	1,05	0,08	< 0,05	0,23	< 0,25	1,34	<1,25	1450	0,08	558,4
1500/6	1,13	0,16	< 0,05	1,27	0,26	3,61	<1,25	2331	0,19	830
1500/7	0,33	0,38	< 0,05	4,75	0,62	0,33	1,54	4999	0,4	1280
GDA-3										
1501/1	1,40	0,34	< 0,05	1,94	< 0,25	1,50	<1,25	1565	0,07	671
1501/2	2,86	0,52	< 0,05	5,49	< 0,25	1,87	<1,25	2539	0,27	751
1501/3	1,14	0,28	< 0,05	2,77	0,10	1,39	<1,25	1728	0,2	622
1501/4	1,38	0,32	< 0,05	3,52	0,27	20,90	1,54	2148	0,39	746
1501/5	5,73	7,18	0,22	23,86	9,58	15,73	5,62	15334	2,71	7817
1501/6	1,46	0,41	< 0,05	2,60	4,16	1,68	2,41	1650	0,36	836
1501/7	1,61	0,35	< 0,05	3,69	0,82	2,75	1,68	2185	0,35	10667
GDA-4										
1502/1	40,68	5,76	0,12	18,07	5,88	10,00	<1,25	7029	1,44	4441
1502/2	10,88	10,73	0,14	17,95	1,23	4,46	1,28	3323	0,41	1406
1502/3	5,21	5,23	0,23	41,72	4,43	10,71	1,27	7586	1,27	3615
1502/4	4,69	2,29	0,05	9,26	1,49	5,20	1,46	3850	0,61	1863
1502/5	3,83	1,40	0,05	7,01	2,18	2,30	<1,25	2399	0,31	838
1502/7	1,25	0,49	< 0,05	2,78	1,00	1,69	<1,25	1863	0,18	536
1502/8	0,83	0,51	< 0,05	1,85	0,55	1,24	<1,25	1215	0,19	529
1502/9	1,10	0,41	< 0,05	2,63	0,71	1,25	<1,25	1492	0,24	654
1502/10	6,49	8,62	< 0,05	29,5	12,61	19,22	2,52	15372	3,62	10951
1502/11	1,05	0,60	< 0,05	3,05	2,90	1,50	<1,25	-	-	-
GDA-5			, 5		,,	,5	, ,			
1503/1	1,82	0,76	0,05	5,21	1,37	2,01	< 1,25	1986	0,19	676
1503/2	2,52	0,95	0,05	5,26	0,71	1,93	<1,25	1724	0,18	548
1503/2	2,01	0,39	< 0,05	2,72	0,56	1,95	<1,25	2256	0,19	631
1503/4	1,41	0,46	< 0,05	3,19	0,50	1,58	<1,25	1426	0,17	567
1503/5	1,23	0,24	< 0,05	2,01	0,66	1,06	<1,25	1203	0,14	477
1503/6	0,93	0,30	< 0,05	2,62	0,51	1,30	<1,25	1087	0,16	444
GDA-6		.5	,,,,		.,,,	,,,	-,-5	-,	-,	
1504/1	1,42	1,07	0,05	3,91	1,33	1,84	< 1,25	1788	0,23	714
1504/2	1,45	0,24	0,04	3,36	1,24	1,56	<1,25	1590	0,15	596
1504/3	1,87	0,38	0,05	3,65	0,26	1,41	<1,25	1869	0,16	5202
1504/4	1,04	0,29	< 0,05	2,26	0,53	1,44	<1,25	1122	0,15	481
1504/5	1,03	0,24	< 0,05	2,54	0,33	1,36	<1,25	1245	0,19	561
1504/6	1,25	0,16	< 0,05	2,96	0,42	1,72	<1,25	1567	0,19	691
1504/7	1,20	0,10	< 0,05	3,27	1,06	1,64	<1,25	1722	0,21	679
1504/8	1,31	0,12	< 0,05	2,83	0,51	0,75	<1,25	1542	0,21	567
1504/0	۱ ر ,۱	0,15	- 0,03	۷,05	0,51	0,/5	~ 1,45	1344	0,21	30/

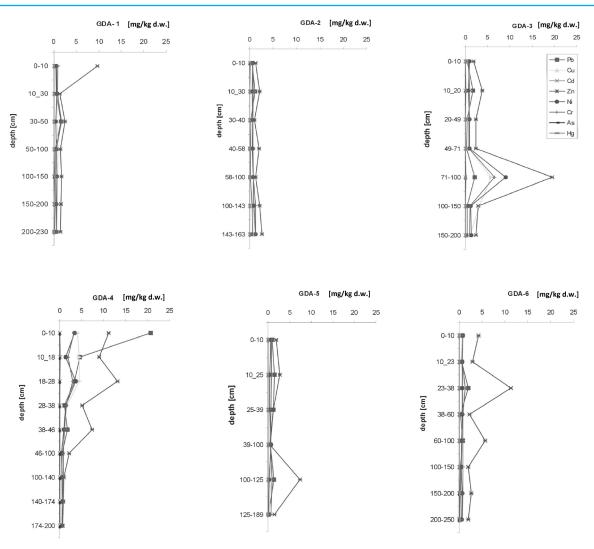


Fig. 4. Content of labile metal forms [mg/kg s.m.] in sediments from the Gdansk dumping site

ments (Fig. 4). Comparing the percentage of the labile form of investigated metals in the bottom sediments from the Port of Gdansk and from sediments deposited in the Gdansk Dump Site, it was determined that, in spite of the much lower content of Cu, Zn, Ni and Cr in the Gdansk dump site sediments, the percentage of the labile form of these elements in both sediments was at a similar level. The labile form was for Cu – about 80%, for Zn – about 60%, Ni –35 - 40%, and for Cr-12-19%.

On the other hand, a significant decrease of the content of the labile forms of Pb and Cd was observed in the Gdansk Dumping Site sediments. Pb decreased from 60% in port sediments to 35% in the dumping site, while Cd decreased from 60% to 2.5%. (Fig. 5).

A similar trend in sediments staying in contact with sea water was observed by Powell. He found that mixing of sediments significantly facilitates mobilisation of the metals from the sediments. In effect of these changes Cd and Pb desorb quickest, and Cr and Ni slowest [22].

Sequential analysis showed that in the sediment from the Gdansk Dumping Site (Fig. 6) Pb occurred mainly bonded with aluminosilicates (about 70%). 19% were bonded with organic matter, 3% with Fe and Mn oxides and 3% with carbonates.

When these results were compared with the results of sequential analysis for lead in port sediments (Fig. 7), a large decrease of Form II, i.e. bonding with carbonates, becomes visible (from 45% in the port sediments to 3% in the dumping site sediments).

Sequential analysis of port sediments showed that Cd was permanently bonded in about 40% with aluminosilicates. Among the labile forms, the largest percentage was of Form III (oxides of Fe and Mn) -30% and Form IV (organic matter) -20%. Also several percent of exchangeable form and of the bonded with carbonates form were found. In the case of sediments from the dumping site, the total of labile forms of Cd decreased to 2.5%.

In the case of the rest of the elements, in spite of the decrease of concentration of the total metal content, no significant change in the percentage of the bonded with aluminosilicates form was

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observed. A similar way of bonding metals (Cu, Cr, Zn) in marine sediments (at river outlets) was observed by Savvides et al, 1995; Parkman et al, 1996 [23, 24]. On the other hand, for these elements (Cu, Cr, Zn, Ni) a marked decrease of participation of the bonded with carbonates form and of the exchangeable form and a significant increase of the organic matter bonded form was observed in the deposited sediments from the dumping site.

Obtained data suggest that during dumping labile forms of these elements (especially forms I and II) may have passed into the water column.

The behaviour of river sediments coming into contact with marine sediments was discussed by many researchers [25 - 28], and they pointed out that the enrichment of the water with metals may be the result of increased concentration of sodium cations (ion exchange in presence of clay material).

Another important factor, which should not be omitted and which may influence the freeing of metals from the investigated sediments, is bioturbation caused by organisms living in the sea bottom. These organisms penetrate the deposits to a depth of several dozen centimetres. By digging in (e.g. *Cardium glaucum*) or building burrows (e.g. *Nereis diversicolor*) they introduce oxygenated water into the sediment, and therefore change reduction conditions. Animals moving on the seafloor or filtering water facilitate diffusion of metals from the near-bottom water layer [29].

The freed CO<sub>2</sub>, appearing during oxygenation of remnants of vegetation, and organic acids, can additionally cause a reduction of the sediment's pH. At pH equal to 5.6 carbonates, which may contain adsorbed heavy metals begin to dissolve [30].

#### SUMMARY AND CONCLUSIONS

The following was found in result of the carried out investigations:

- Concentrations of metals in sediments deposited on dumping sites are lower than in port sediments before dumping.
- Grain size analysis indicated a significant decrease of clay fractions in dumping site sediments by comparison with the sediments before dumping. This may be caused by water current transport of fine grained fractions, which fall to the bottom much slower than the thick grained fractions, and their deposition at a distance from the dumping site.
- Sequential analysis proved that the percentage of the particular forms of the metals (especially Pb and Cd) changes in the sediments deposited in the dumping site. Changes of salinity, mechanical mixing during excavation, oxygenation may result in freeing the labile forms into the water column, especially the exchangeable and carbonate forms, which are loosely connected with the sediment, and these conditions may be sufficient to free these forms.

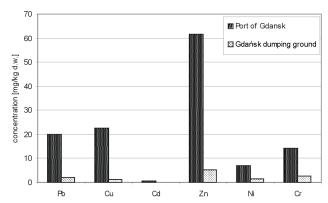


Fig. 5. Comparison of mean concentration of total heavy metal content in the Gdansk dumping site and Gdansk Port sediments.

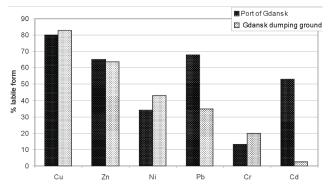


Fig. 6. Percentage of labile form of metals in sediments from the Port of Gdansk and from the Gdansk dumping site.

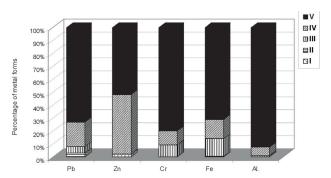


Fig. 7. Percentage of metal forms in bottom sediments of the Gdansk dumping site; Form I - exchangeable, Form II - bonded with carbonates, Form III - bonded with hydrated oxides of Fe and Mn, Form IV - bonded with organic matter. Form V - bonded with aluminosilicates

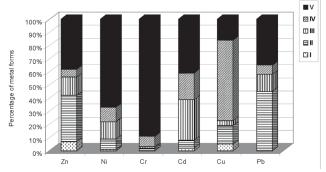


Fig. 8. Percentage of metal forms in bottom sediments of the Port of Gdansk; Form I - exchangeable, Form II - bonded with carbonates, Form III - bonded with hydrated oxides of Fe and Mn, Form IV - bonded with organic matter, Form V - bonded with aluminosilicates



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