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ASSESSING BOTTOM SEDIMENT CONTAMINATION WITH HEAVY METALS IN THE KLAIPĖDA PORT SEMI-CLOSED BAYS

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Abstract. The present paper reports the results obtained by investigation of surface bottom sediment contamination with Cu, Zn, Ni, Pb, Cr, Cd, Hg in three largest semi-closed bays of Klaipėda Port in 2008 and 2009. The concentrations of heavy metals and organic carbon same as the percentages of 6 granular fractions were determined at 41 stations. The contamination level was established by calculating the Nemerov's pollution index. The major factors responsible for sediment contamination with heavy metals and distribution patterns of discrete pollutants and different pollution areas were determined. By comparison of the obtained results with the results of 1998, the changes of sediment contamination with heavy metals in the last ten years were evaluated. It was determined that bottom sediments not contaminated with heavy metals are dominant in the semi-closed bays of Klaipėda port. Heavy contamination with nickel, and moderate contamination with zinc and copper only occur in small areas.

Keywords: pollution of geoenvironment, bottom sediments, heavy metals, Klaipėda Port, mud, sand.

1. Introduction

The activities of any sea port are unavoidably associated with contamination of coasts, bodies of water and bottom sediments (Denton *et al.* 2005). Contaminants get into the environment during ship loading, building and repairs, bottom dredging, with dust, etc. (Jokšas *et al.* 2003; Baltrėnas *et al.* 2007). A significant proportion of the contaminant load is introduced in solution, including urban storm-water runoff and effluent discharge (Stull *et al*. 1996; Schiff 1997).

Toxic metallic elements with the specific gravity 5 or even more times as high as that of the water (heavy metals), such as zinc (specific gravity 7.1), chromium, cadmium, nickel, copper, lead and mercury (specific gravity 13.5) are regarded as serious pollutants of aquatic ecosystems because of their environmental persistence, toxicity and ability to be incorporated into food chains (Herut *et al.* 1994; Kishe, Machiwa 2003; Andrews, Sutherland 2004; Idzelis *et al. 2008*). Many heavy metals tend to be sequestered at the bottom (Katz, Kaplan 1981), but some dissolve and tend to accumulate in aquatic organisms (Salomons, Förstner 1984; Saad *et al.* 2003). On the other hand, biodetritus tend to accumulate in the bottom sediments whereas biosorption is one of the techniques to remove the heavy metals from the water. In their turn, fine biodetritus and clay particles are perfect sorbents of heavy metals (Lavelle *et al.* 1991; Galkus, Jokšas 1997). If a sufficiently stable sediments sink can be located and studied, it will allow the investigators evaluating the geochemical changes over time and possibly establishing the baseline levels with which current conditions can be compared (Nasr *et al.* 2006). Bottom sediments can be sensitive indicators for monitoring and investigation of heavy metals in aquatic environments (Pekey *et al*. 2004; Nasr *et al.* 2006).

The only Lithuanian Seaport is situated in the Klaipėda Strait connecting the Curonian Lagoon with the Baltic Sea. The quays and semi-closed water areas are concentrated at the eastern bank of the strait. It was established that anthrophogenic pollution in Klaipėda is most appreciable in the areas neighbouring the seaport (Taraškevičius 2008). Moreover, the levels of water and bottom contamination with pollutants are highest in the semi-closed bays because they are located in the neighbourhood of coastal industrial objects (Jokšas *et al.* 2003). Furthemore, the fluctuation patterns of salinity demonstrate slower renewal of the water in the bays than in the open areas of Klaipėda Strait (Galkus 2007). These are the substantial causes of higher concentrations of heavy metals in semi-closed water areas (Jokšas *et al*. 2003).

Notwithstanding that technogenic contamination is intrinsic to sea ports, it has not been sufficiently well investigated in the bottom sediments of Klaipėda port. Just a few scientific sources contain scanty information about heavy metal concentrations and distribution patterns in the port bottom sediments (Gudelis, Pustelnikov 1983; Jokšas 1996; Galkus, Jokšas 1997; Jokšas, Galkus 2000). The most explicit granulometric (Trimonis, Gulbinskas 2000) and geochemical (Jokšas *et al.* 2003) investigations of bottom sediments in the Klaipėda port were carried out based on the samples collected in 1998. Then the semi-closed bays of the port were also investigated. In the following ten years, the water circulation and sedimentation conditions in the port water

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area were continually changing. The navigation intensity grew together with the increasing cargo turnover. The changing sedimentary environment and contamination sources inevitably have changed the concentration patterns of heavy metals in the bottom sediments. The present article introduces the yet unpublished analysis results of the bottom sediment contamination with heavy metals Zn, Cr, Cd, Ni, Cu, Pb and Hg. The aim of the present study is to investigate the distribution of heavy metals in the bottom sediments of semi-closed water areas of Klaipėda port, and to estimate the levels and trends of contamination with heavy metals.

2. Materials and methods

The present study was carried out at 41 stations in 2008 (from August to September) and 2009 (from July to September). The surface (0–10 cm) bottom sediment samples were collected in the largest semi-closed water areas of the Klaipėda Port: Malkų Bay (area 0.85 km^2, depth 10–11 m) and local ports of Baltija Shipbuilding Yard (Baltija SY, 0.09 km^2, 5–7 m) and Winter Port (0.08 km^2, 8–9 m) (Fig. 1). A Van Veen grab sampler was used for sampling. The minutely described soil samples were preserved and later dried in a stationary laboratory. Taking into account

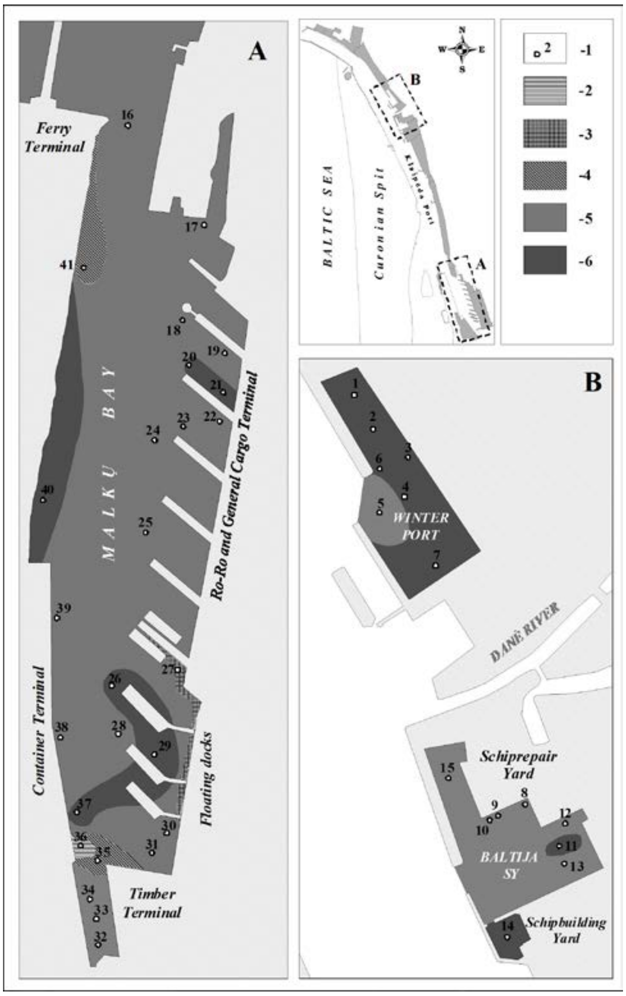

Fig. 1. Sampling stations and types of surface (0–10 cm) bottom sediments: 1 – sampling station; 2 – coarse-grained sand; 3 – medium-grained sand; 4 – silty sand; 5 – mud sandy; 6 – mud silty

the composition of heterogeneous bottom sediments and following the Lithuanian standards of classification (Gaigalas 1995; LAND 46A:2002), the percentages of the particles from < 0.063 mm to > 2 mm were determined in 6 fractions (Petelin 1967). The mud sediments with a high amount of particles < 0.063 mm in diameter were analysed by the pipette method (Folk 1974).

The metals Zn, Cr, Cd, Ni, Cu, Pb and Hg in the bottom sediments were analysed by ICP-MS (Inductively Coupled Plasma Mass Spectrometry) method (Loring, Rantala 1992; Montaser 1998). As the sorption potential of soils depends on the amount of organic material the concentrations of organic carbon was also determined using a High-temperature Catalytic Oxidation technique (Tiessen, Moir 1993).

The values of maximal concentration limit (MCL) of investigated heavy metals set in the Lithuanian standard LAND 46A: 2002 were taken as a point of departure for evaluation of sediment contamination. The contamination level was determined by calculating Nemerov's pollution index (PI) applied to soil (Guozhang *et al*. 2006), which reflects the effect of each investigated pollutant on the bottom sediments, and also highlights the influence of heavy metals on the quality of environment. The impact of every metal (i) (single factor index) on the environment PI_i was evaluated by the ratio between its measured value (C_i) and maximal concentration limit value (L_i): $PI_i = C_i/L_i$.

The integral contamination index for bottom sediments of every station PI was derived using the formula (Gouzhang *et al.* 2006):

$$PI = PI = \sqrt{\frac{[AVG(PI_i)]^2 + [MAX(PI_i)]^2}{2}}, \qquad (1)$$

where PI stands for the synthetic contamination index of soil, $AVG(PI_i)$ represents the mean of various pollutant indices in the soil, and the $MAX(PI_i)$ is the maximum pollution index of single-factor pollutant in the soil. The level of contamination was evaluated using classification analogous to single-factor (PI_i) and multi-factor (PI) impacts: $PI(PI_i) \leq 0.7$ – clean sediments (the content of heavy metals in sediments stands under the warning limit); $0.7 < PI(PI_i) \leq 1$ – sediments in the warning condition (the concentration of heavy metals in the sediments has already been in the warning condition, but it does not exceed the environment quality standard); $1 < PI(PI_i) \leq 2$ – lightly contaminated sediments; $2 < PI(PI_i) \leq 3$ – moderately contaminated sediments; $PI(PI_i) > 3$ – heavily contaminated sediments (Fang *et al.* 2003; Guozhang *et al.* 2006).

For evaluation of the changes that took place in the last ten years, the data of 39 sediment samples collected in 1998 were analysed. Some of the data (of chemical and granulometric analysis) already have been published (Jokšas *et al.* 2003). The areal structure of bottom sediments in the semi-closed water areas of Klaipėda Port was analysed by GIS methods. Based on the analysis of data obtained in 1998 and 2008–2009, the sediments were grouped into 2 basic types (mud and sand) with different MCL. For finding out the interrelations between the concentrations of heavy metals Zn, Cr, Cd, Ni, Cu, Pb, Hg and total organic carbon and also between these parameters and the content of fine-grained fraction in bottom sediments (< 0.063), Pearson's correlation coefficient (r) was calculated for sediments (without distinguishing sand sediments due to the small number of samples and absence of significant r values). Each data set was checked for normality using Kolmogorov-Smirnov test and evaluated according to the form of the histograms (Kruopis 1993). The linkage of significant correlation coefficients (significance level $p < 0.01$) between two variables was estimated using the commonly accepted gradation: when $r \leq 0.5$, the link between the variables is poor, when $0.5 < r < 0.7$, it is relatively fair and when $r \geq 0.7$, it is strong (Chertko 1987). The similarity among the considered port stations for possible zonation according to the level of contamination had to be examined. For this purpose, the cluster analysis (Ward's method Squared Euclidean distances) was used to decide witch stations were similar to each other, considering all of the contamination properties simultaneously (Čekanavičius, Murauskas 2004). The data for cluster analysis were standardized.

3. Results and discussion

In 2008–2009, as in 1998, the bottom of Klaipėda port semi-closed bays was almost completely covered with mud sediments. There were only a few sand areas in the bottom surface of Malkų Bay. The following types of bottom sediments were distinguished (LAND 46A:2002): coarse-grained sand (1–0.5 mm > 50%), medium-grained sand (0.5–0.25 mm > 50%), silty sand (< 0.063 mm 30–50%), mud sandy (2–0.063 mm 30–50%) and mud silty (0.063–0.002 mm 50–70%; < 0.063 mm > 70%) (Fig. 1). As distinct from 1998, mud silty-clayey (< 0.05 mm) was not identified. The largest areas of semi-closed bays were covered with mud sandy. The coarsening of grains in the lithogenic framework of bottom sediments presumably was predetermined by bottom dredging, active resuspension and elimination of fine-grained sediments into the Klaipėda Strait waters as a result of intensifying navigation. The sand areas uncovered with mud in the Malkų Bay episodically occur in the places where the bottom, according to our knowledge, has been recently cleaned or deepened (Fig. 1).

The concentrations of investigated heavy metals are in direct dependence on the lithological type of sediments. In most cases, the ratio of mean concentrations in mud and sand sediments exceeded 2: Cr – 2.1 (2.4 in 1998); Cd – 2.6 (2.1); Ni – 3.2 (2.7); Pb – 2.4 (1.1); Hg – 2.1 (2.4), so Zn – 2.85 and Cu – 3.2 (Table 1). Only in 1998, due to anomalous concentrations of Zn (791 mg/kg) and Cu (425 mg/kg) in the silty sand taken in the floating docks area, the mean values of the metals were slightly (1.1–1.3) higher in sand than in mud. The mean concentrations of heavy metals consistently increase from coarse-grained through to silty sand (in 2008–2009): Zn from 48.6 mg/kg to 116 mg/kg, Cu from 15.6 mg/kg to 20.2 mg/kg, Pb from < 5 mg/kg to 23.4 mg/kg, Ni from < 2 mg/kg to 9.55 mg/kg, and Cd from < 0.4 mg/kg to 0.45 mg/kg. Only the concentrations of chromium and mercury distribute unevenly in this direction. In 1998, the average value of all metals in silt sand was 1.3 to 7 times as high as in the coarse-grained sediments. Mud silty with finer lithological framework is distinguished for higher mean concentrations of heavy metals in comparison with mud sandy: Zn respectively 300 mg/kg and 202 mg/kg, Cu 74.2 mg/kg and 57.2 mg/kg, Pb 46.5 mg/kg and 40.5 mg/kg, Ni 35.4 mg/kg and 15.2 mg/kg, Cd 1.1 mg/kg and 0.98 mg/kg, Cr 44.6 mg/kg and 26.5 mg/kg, and Hg 0.18 mg/kg and 0.14 mg/kg. The maximal concentrations of heavy metals were determined in mud silty: Cu, Pb (St. 29 at the floating docks) and Cd (St. 21) in the Malkų Bay; Zn, Ni, Cr and Hg in Baltija SY (St. 11 in the area of floating docks in the past (Fig. 1). Comparison of results obtained for bottom sediments of different bays shows that the highest mean concentrations of all heavy metals occur near the Baltija SY (in 1998, the highest concentrations of Cu and Pb were characteristic of Malkų Bay). The lowest concentrations of most heavy metals (except Cr and Pb) were established in the sediments of Winter Port. In 1998, this Port was only distinguished for the lowest mean concentrations of Cu, Zn and Hg (Table 1).

Comparison of heavy metal concentrations in the sediments of Klaipėda port bays against the analogous concentrations in the sediments of other ports shows that heavy metal concentrations, even in mud sediments obtained during the present investigation, are not high in the context of contamination of bottom sediments with heavy metals in other ports (Table 2). The concentrations of copper and zinc are slightly higher than in some other ports (Ventspils, Aden, Xiamen) (Table 2) whereas the lower concentrations of nickel and lead in the Port of Gdansk can be explained by that they were determined in sand sediments (Radke *et al*. 2004).

There is a rather obvious dependence of metal concentration on the type of sediments. Yet the dependence is not so obvious in relation to the amount of fine-grained fraction < 0.063 mm. The calculated correlation coefficients between the concentrations of heavy metals and amount of this fraction showed that the interdependence between these elements is tenuous. Meanwhile in 1998, when the amount of fine-grained fraction was higher (Table 1), the dependence of Ni and Cr on the amount of fraction < 0.063 mm was strong and the dependence of Cd was fair (Table 3). The results of newest investigations show that in the not as fine-grained recent bottom sediments the concentrations of heavy metals rather depend on the amount of C_{org}: fair dependence was determined for Cu, Pb and Zn. In 1998, this dependence was even more obvious: strong dependence on C_{org} for Ni, Cr and Cd and fair for Hg (Table 3). The amount of C_{org} in the dominant bottom sediments of bays was 1.23 times as high in 1998 as at the time of the last investigation (Table 1).

As MCL values for sand are from 3.3 (Cr) to 10 (Cu) times as high as those for clay (Table 1), the calculated mean PI_i values for sand in the Malkų Bay (sand was found only in this bay) can be qualified as rather high: PI value for lead (PI_{Pb} = 0.91) approaches the threshold of light contamination ($PI_i \geq 1$) whereas PI values for Cu and Zn (PI_{Cu} = 1.89, PI_{Zn} = 1.40) can be classified as light contamination. Only the values for mercury and chromium are within the limits for the category of clean sediments (PI_{Hg} = 0.70, PI_{Cr} = 0.53) (Fig. 2).

The highest PI value (2.25) was calculated for muddy sand at a depth of 10 m in the area between the Klaipėda container terminal and timber terminal not far from the region of floating docks in the southern part of Malkų Bay (St. 35; Fig. 1, Fig. 3). There is a high probability that due to permanent impact of intensive navigation and setups–backwashes the mud from the terminal part of the bay is washed out yet the remaining sand still contains a large portion of fine-grained fraction < 0.063 mm (21%) and much C_{org} (3.2%) what means that it also contains a rather high concentrations of heavy metals.

Table 1. Indices of surface bottom sediments and values of maximal concentration limit (MCL) for heavy metals in the Klaipėda port semi-closed bays (LAND 46A: 2002)

Sediments type	*Parameter	Fraction < 0.063 mm,%	C_{org},%	Heavy metal concentration, mg/kg						
				Cu	Pb	Zn	Ni	Cr	Cd	Hg
				2008–2009						
Sand 4 samples	AVG	13.3	1.95	19.9	18.1	83.8	7.15	15.8	0.40	0.07
	STDV	15.3	0.90	7.02	11.6	53.2	4.59	7.41	0.15	0.02
	MIN	0.1	1.19	12.1	< 5	48.6	< 2	11.2	<0.4	0.05
	MAX	31.2	3.24	28.4	31.8	162	12.0	26.9	0.60	0.09
				1998						
Sand 5 samples	AVG	17.5	1.06	116	51.2	234	7.20	19.4	0.40	0.125
	STDV	8.9	0.28	78.1	23.7	143	1.39	4.66	0.06	0.050
	MIN	6.8	0.33	20.0	11.0	25.0	4.00	9.00	< 0.4	0.030
	MAX	29.6	1.93	425	138	791	11.0	35.0	0.60	0.335
	MCL			*10*	*20*	*60*	*10*	*30*	*0.50*	*0.100*
				2008–2009						
Mud 37 samples	AVG	59.8	3.77	63.7	42.7	239	22.8	33.3	1.03	0.15
	STDV	10.4	0.75	52.8	21.9	139	39.7	31.4	0.68	0.08
	MIN	42.8	1.90	18.7	17.0	61.5	< 2	8.70	< 0.4	0.06
	MAX	75.2	5.05	287	99.5	810	189	167	2.80	0.40
	AVG in semiclosed bays:									
	Winter Port	70.4	3.69	33.8	35.6	168	5.83	28.8	0.71	0.12
	Baltija SY	57.4	4.38	99.7	69.0	332	47.2	63.4	1.35	0.25
	Malkų Bay	57.2	3.57	60.0	35.5	227	19.4	23.9	1.01	0.13
				1998						
Mud 34 samples	AVG	69.1	4.65	87.5	56.9	219	19.4	46,0	0.85	0.30
	STDV	3.0	2.10	84.7	45.1	132	5.10	13.9	0.40	0.30
	MIN	27.5	0.99	11.0	11.0	39.0	7.00	17.0	< 0.4	0.015
	MAX	91.4	8.39	430	251	620	26.0	75.0	1.60	1.61
	AVG in semiclosed bays:									
	Winter Port	69.2	4.57	48.8	54.4	172	19.2	48.6	0.82	0.21
	Baltija SY	68.8	6.46	86.4	82.6	277	22.4	57.0	1.23	0.31
	Malkų Bay	69.1	4.10	96.6	49.4	210	18.5	41.9	0.74	0.37
	MCL			*100*	*100*	*300*	*50*	*100*	*2*	*0.50*

* Parameters: AVG – average value; STDV – standard deviation; MIN – minimal value; MAX – maximal value

Table 2. Comparison between heavy metal concentrations (mg/kg) in bottom sediments of the different port

Heavy metal	*Port of Klaipeda semiclosed bays, Lithuania (Present study). Mud.	*Port of Gdansk, Poland (Radke *et al.*, 2004). Fraction < 2 mm.	Ventspils harbour, Latvia (Muller-Karulis *et al.* 2003).	Harbour of Ceuta, Spain (Guerra-Garcia, Garcia-Gomez 2005).	Bergen harbour, Norway	Naples harbour, Italy (Adamo *et al*, 2005).	*Aden harbour, Yemen (Nasr *et al.* 2006)	Xiamen Bay, China (Zhang *et al.* 2007)
Cr	33	–	12–71	13–381	–	7–1798	82	37–134
Cu	64	-	3–29	5–865	25–1090	12–5743	20	19–97
Ni	23	7.1	5–35	8–671	–	4–362	35	25–65
Pb	43	11.4	3–44	10–516	24–1920	19–3083	77	45–60
Zn	239	–	17–254	29–695	46–2900	17–7234	129	65–223
Cd	1.0	–	–	–	–	0.01–3	–	0.11–1.01
Hg	0.15	–	–	–	–	0.01–139	–	–

* Mean values

Table 3. Pearson's correlation coefficients (r) calculated for concentrations of heavy metals, C_{org} and amount of fraction < 0.063 mm (FR) in bottom sediments of the semi-closed bays of Klaipeda Port

2008–2009 (significant r > 0.42)										1998 (significant r > 0.44)									
	FR	Cu	Pb	Zn	Ni	Cr	Cd	Hg	C_{org}		FR	Cu	Pb	Zn	Ni	Cr	Cd	Hg	C_{org}
FR	1.00									FR	1.00								
Cu		1.00								Cu		1.00							
Pb		0.80	1.00							Pb		0.81	1.00						
Zn	0.43	0.78	0.64	1.00						Zn		0.88	0.84	1.00					
Ni		0.87	0.66	0.76	1.00					Ni	0.85				1.00				
Cr		0.79	0.76	0.72	0.87	1.00				Cr	0.77		0.57	0.55	0.94	1.00			
Cd			0.46				1.00			Cd	0.66		0.46	0.44	0.85	0.90	1.00		
Hg		0.74	0.83	0.72	0.67	0.76		1.00		Hg		0.58		0.50	0.55	0.60	0.53	1.00	
C_{org}	0.60	0.56	0.56	0.60					1.00	C_{org}	0.71				0.76	0.82	0.88	0.53	1.00

Significance level $p < 0.01$

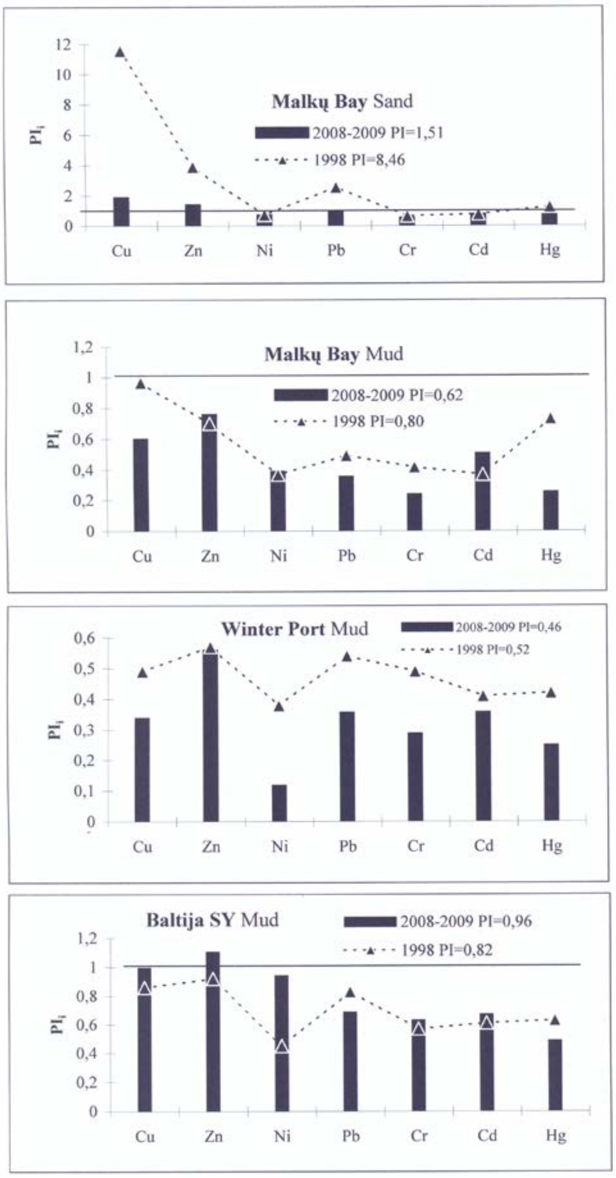

Fig. 2. Single factor index (PI_i) values for investigated heavy metals in 2008–2009 and 1998

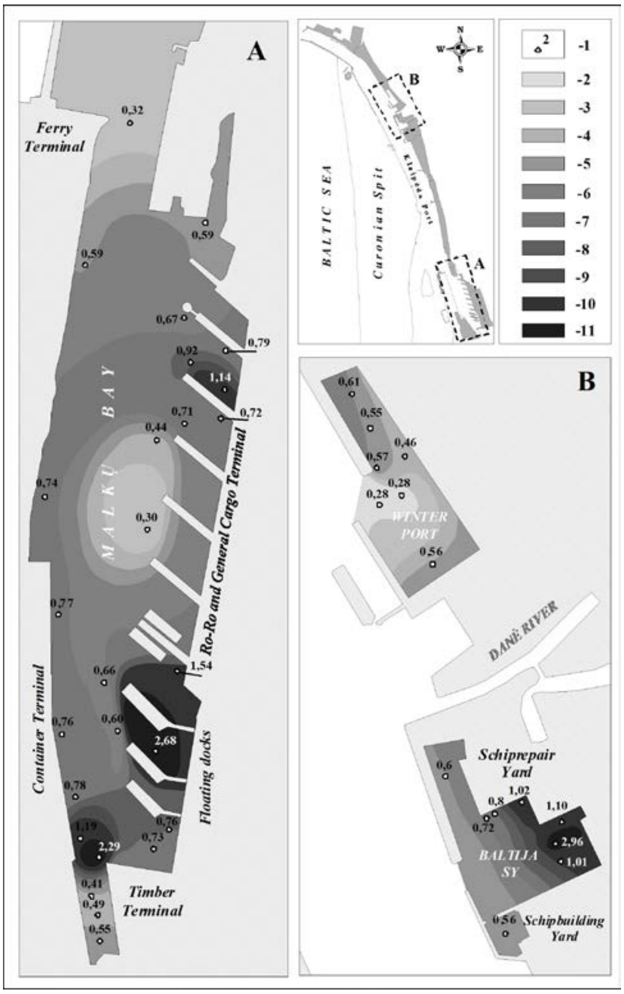

Fig. 3. Spatial distribution of calculated synthetic contamination index (PI) for surface bottom sediments in the semi-closed bays of Klaipėda port

The calculated mean PI_i values for sand compared against the values obtained in 1998 show appreciable decrease of average contamination of sandy sediments with lead, zinc and, in particular, copper (6.1×) (Fig. 2). In 1998, the maximal contamination with these heavy metals (PI_{Cu} = 42.5, PI_{Zn} = 13.2, PI_{Pb} = 6.90) was established for the silty sand near the floating docks not far from St. 29 (Fig. 1) and slightly lower contamination south of the docks and at the western coast of Malkų Bay. The floating docks, where ship carcasses were cleaned and repaired, then undoubtedly were the long-lasting source of heavy metals (Jokšas *et al*. 2003). After ten years, sand was found only at the eastern coast of the bay (Fig. 1) and PI_i values exceeded 1 only for copper. From 1998 till 2008–2009, the synthetic contamination index of sand decreased from 8.46 to 1.51 and only accounts for 18% of former pollution.

The indices of prevailing mud sediments in the bottom of investigated water areas are most important for assessment of heavy metal loads. Neither in the Malkų Bay nor in Winter Port, had the mean PI_i values for mud exceeded 1. Only in the Baltija SY the mean PI_i value for mud reached 1.1 due to high Zn concentrations in St. 11 (810 mg/kg) and St. 12 (350 mg/kg) (Fig. 1). In the mud of Winter Port, the average amount of fraction < 0.063 mm is highest and reaches 0.4% (69% in 1998) whereas the mud of Baltija SY is distinguished for the highest mean amount of C_{org}: 4.38% (6.46% in 1998). Judging from the material and granular composition, the mud of the Malkų Bay is the least potential of absorbing heavy metals. Despite this, the lowest concentrations of heavy metals are characteristic of Winter Port with fine sediments and rather high amount of C_{org} (the 2 place after the Baltija SY) (Table 1, Fig. 2).

The bottom sediments of Winter Port with synthetic PI = 0.46 (from PI_{Zn} = 0.56 to PI_{Ni} = 0.12) can be attributed to the class of clean sediments. The calculations made based on the data of 1998 showed that the situation in that year was slightly worse: PI = 0.52 (from PI_{Zn} = 0.57 to PI_{Ni} = 0.38). Thus recent contamination of bottom sediments with heavy metals only accounts for 88.5% of the contamination in 1998. In the spectrum of contamination, Zn is followed by Pb, Cd and Cu (in 1998 Zn, Pb, Cu and Cr) (Fig. 2). The PI values tend to decrease towards the gateway of this semi-closed water area (Fig. 3). The good results obtained for the sediments of Winter Port can be accounted for by the circumstance that there are no important industrial objects and potentially dangerous cargo loading does not take place in the environs.

Shipbuilding Yard, Shiprepair Yard and Cruise and Naval Vessel Quay are situated around the water area of Baltija SY and two floating docks have, for some time, been dislocated within the area. This area surpasses the Winter Port in the number of potential pollution sources. After general assessment, its bottom sediments with synthetic PI = 0.96 (from PI_{Zn} = 1.11 to PI_{Hg} = 0.49) can be classified as being in warning condition and is very close to the category of lightly polluted sediments (PI > 1) (Fang *et al.* 2003; Guozhang *et al.* 2006). Contaminated sediments were identified only in St. 11 (PI = 2.96; the limit value is between moderate and strong pollution) and the surrounding area (Fig. 1).

Namely in this point, the floating docks, where ship building and repairs took place, have been dislocated for a long time. Towards the gateway of Baltija SY water area, PI values for bottom sediments gradually decrease (Fig. 3). In 1998, bottom sediments of this area were slightly cleaner than in the other two: PI = 0.82 (from PI_{Zn} = 0.92 to PI_{Ni} = 0.45) (Table 1, Fig. 2). The recent level of contamination with heavy metals accounts for 117% of the level in 1998. In the contamination spectrum of Baltija SY, zinc is followed by copper and nickel (as distinct from the Winter Port) (Fig. 2). Cooper was in the same position in 1998. Meanwhile, the elevated values of nickel (to PI_{Ni} = 0.94) are a new phenomenon in the Klaipėda port not characteristic even of Gdansk Port (Radke *et al.* 2004). As distinct from Cu, Ni is bound to the layer of lithogenic material and is an easily released metal (Radke *et al*. 2004). Therefore its introduction and persistence among the main elements in the PI spectrum for mud can be explained by a repeated technogenic contamination.

After general assessment, the mud of the Malkų Bay (Fig. 1) with PI = 0.62 (from PI_{Zn} = 0.76 to PI_{Cr} = 0.24) can be classified as a clean sediment (in 1998 – a sediment in the warning condition: PI = 0.80, from PI_{Cu} = 0.97 to $PI_{Ni;Cd}$ = 0.37). The leading position in the contamination spectrum belongs to zinc. It is followed by copper, cadmium, nickel and lead. Mercury, which in 1998 was in the second position, and chromium are pollutants of least importance (Fig. 2). The synthetic PI values indicate polluted sediments at the quays of Ro-Ro and General Cargo Terminal (light contaminated sediments) and at the floating docks (lightly and moderately contaminated sediments) (Fig. 3). In the first region, sediment contamination is predetermined by elevated values of Zn and Cd (PI_{Zn} = 1.49; PI_{Cd} = 1.40 in St. 21) and in the second one by the elevated values of Ni, Cr and Zn (PI_{Ni} = 3.42; PI_{Cu} = 2.87; PI_{Zn} = 1.66 in st. 29). High levels of sediment contamination with heavy metals were also established in 1998 (Jokšas *et al.* 2003). Then, the copper was the dominant heavy metal also in the mud of Malkų Bay (Fig. 2). The emergence of PI_{Ni} values classified in the category of strong pollution in the contamination spectrum of Malkų Bay sediments is a new phenomenon. In comparison with 1998, the synthetic pollution of bay bottom sediments only accounts for 77.5%. The decrease of contamination levels in this area is most appreciable among the studied areas.

In general, after the average PI calculation, sediments contamination factors of heavy metals, could be arranged as following: Zn > Cu > Cd > Ni > Pb > Cr > Hg (Cu > Zn > Hg > Pb > Cr > Cd > Ni in 1998) – for mud of all investigated areas and Cu > Zn > Pb > Cd > Ni > Hg > Cr (Cu > Zn > Pb > Hg > Cd > Ni > Cr in 1998) for sand of Malkų Bay. By measuring the area of different contamination categories (Fig. 2), it was determined that the levels of pollution have not exceeded the limits (PI ≤ 1) in 100% of the Winter Port area, 90% of the Malkų Bay area and 79% of the Baltija SY area.

Cluster analysis of distribution patterns of heavy metals in the Klaipėda port bottom sediments in 2008–2009 showed that the data can be divided into three groups within which the objects are more comparable among themselves than with the objects from other groups (Fig. 4).

A group of only two stations (11 and 29) in the points of past and present dislocation of floating docks stands out among other groups (Fig. 1). Namely in these stations, the highest synthetic PI values were recorded (Fig. 3) predetermined by elevated values of nickel (PI_{Ni} = 3.78 in St. 11 and PI_{Ni} = 3.42 in St. 29), zinc (PI_{Zn} respectively 2.70 and 1.66) and copper (PI_{Cu} respectively 1.99 and 2.87). The stations of the following group (1.10 > PI > 0.72) are located in the Baltija SY (St. 8–10, 12, 13), where the total

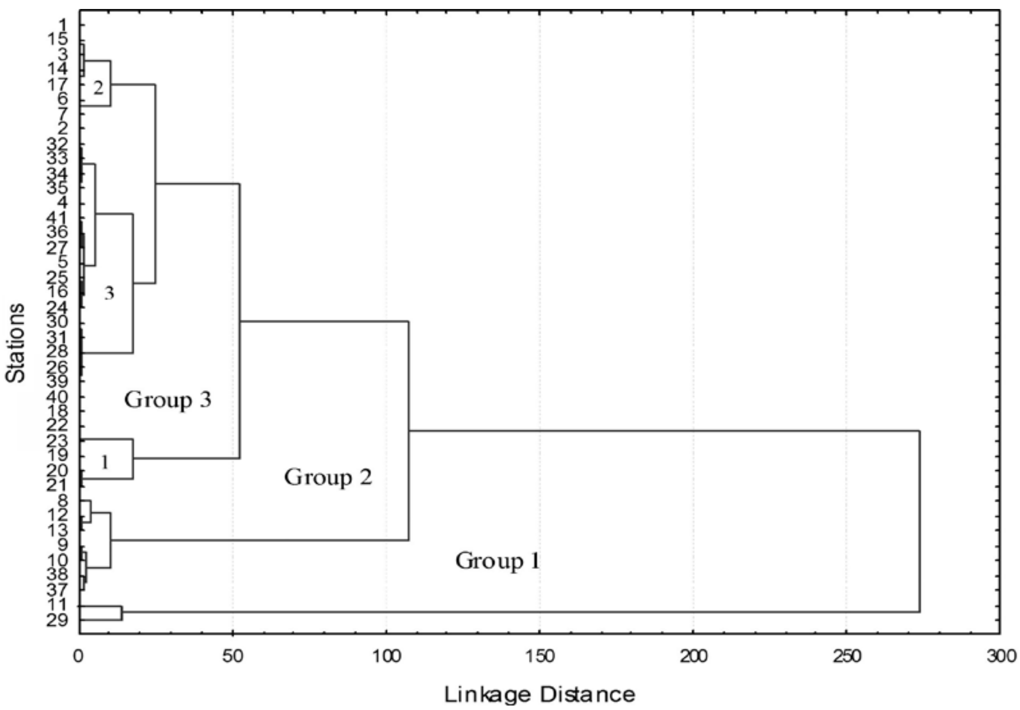

Fig. 4. Tree diagram of cluster analysis for the 41 sampling stations of Klaipėda port semi-closed bays

bottom sediment contamination is highest among the studied semi-closed water areas, and at the quay of intensively exploited container terminal in the Malkų Bay (St. 37 and St. 38) (Fig. 1).

The third group includes the Winter Port, the greater part of Malkų Bay and St. 14 and St. 15 located at the peripheries of Baltija SY (Fig. 1). This large group is subdivided into three sub-groups. The stations of one of the sub-groups (19–23) are located in and around the Malkų Bay water area where 1.14 > PI > 0.71 and elevated concentrations of zinc and cadmium in the central part are responsible for light pollution of sediments (Fig. 1, Fig. 3). The second sub-group encompassing stations of clean sediments (0.59 > PI > 0.46) include the greater part of Winter Port (Sts 1, 3, 6, and 7), the peripheral zones of Baltija SY (St. 14 and St. 15) and mouth region of Smeltelė River in the Malkų Bay (St. 17) (Fig. 1). The third sub-group includes most of the stations in the Malkų Bay (except the above mentioned) and stations 3, 4 and 5 in the Winter Port (Fig. 1). This sub-group includes stations with mud sediments (0.78 > PI > 0.28) and stations with sediments where PI exceeds 1 (St. 27 and St. 36) and even 2 (St. 35). Inclusion of stations with very different PI values in one cluster sub-group shows that sediment pollution levels in the stations of this sub-group actually are more comparable among themselves than is demonstrated by PI values calculated separately for sand and mud. This allows stating that the MCL values of heavy metal concentrations for sand and mud sediments indicated in the normative documentation (LAND 46A: 2002) should be corrected and better matched up. At present, the use of these values as datum-line in the studies of bottom sediment contamination with heavy metals is relevant only for soils of the same type.

4. Conclusions

1. The surface bottom sediments contamination with heavy metals in the semi-closed bays of Klaipėda port is mainly predetermined by the distance from pollution sources and sediments capacity to absorb and retain metals.

2. The mean concentrations of metals in sand sediments increase with decreasing grain size of sediments: from coarse-grained sand to silty sand. In general, the mean concentrations in the mud are higher than in the sand. The fine-grained mud silty is distinguished for higher mean concentrations of heavy metals than those of coarser mud sandy. The levels and patterns of surface bottom sediments contamination with heavy metals Zn, Cr, Cd, Ni, Cu, Pb and Hg in the semi-closed bays are predetermined by the concentrations of these metals in the dominant mud sediments.

3. Smaller amounts of fine-grained matter and organic matter in the semi-closed bays of Klaipėda port reduce sediment capacity to absorb heavy metals. This is why the concentrations of heavy metals tend to lower values even when contamination level is the same. The role of zinc, cadmium and nickel as contaminant heavy metals has increased whereas contamination with copper, mercury, chromium and lead has decreased from 1998 to 2008–2009.

4. Cluster analysis showed that the character of pollution rather than sedimentary environment and belonging to different semi-closed basins is responsible for similarities and differences of bottom sediments contamination with heavy metals.

5. The semi-closed bays of Klaipėda port are predominated by bottom sediments not contaminated with heavy metals: the levels of contamination do not exceeded the limits of 100% of the Winter Port area, 90% of the Malkų Bay area and 79% of the Baltija SY area. The

maximal levels of contamination with heavy metals are established (as also in 1998) in the areas where technological processes take place in the body of water: dislocation points of floating docks. In these areas, the saturation of mud silty with nickel reaches the level of heavy pollution and the level of moderate pollution with zinc (in the Baltija SY) and with copper (Malkų Bay).

6. The situation calls for necessity to review and match up the MCL values of heavy metals for sand and mud indicated in the Lithuanian normative documentation and to implement regular monitoring so the safe limits are not exceeded due to increased activities of the port.

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KLAIPĖDOS UOSTO PUSIAU UŽDARŲ ĮLANKŲ DUGNO NUOSĖDŲ UŽTERŠTUMO SUNKIAISIAIS METALAIS VERTINIMAS

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S a n t r a u k a

Nagrinėjami trijų didžiausių Klaipėdos uosto pusiau uždarų įlankų paviršinių dugno nuosėdų užterštumo sunkiaisiais metalais 2008–2009 m. ypatumai. Tyrimų tikslas – įvertinti nuosėdų užterštumo sunkiaisiais metalais Cu, Zn, Ni, Pb, Cr, Cd, Hg lygį ir nustatyti taršos tendencijas. Tikslui įgyvendinti 41 stotyje nustatytos metalų ir organinės anglies koncentracijos bei nuosėdų šešių granulinių frakcijų procentiniai kiekiai. Užterštumo lygiui nustatyti apskaičiuotas Nemerovo užterštumo indeksas, atlikta jo reikšmių erdvinio pasiskirstymo analizė. Nustatyti svarbiausi nuosėdų užterštumą sunkiaisiais metalais lemiantys veiksniai, skirtingo užterštumo nuosėdų arealų ir įvairių taršos elementų pasiskirstymo ypatumai. Gautus rezultatus palyginus su analogiškais 1998 m. tyrimų rezultatais, įvertinti nuosėdų užterštumo sunkiaisiais metalais pokyčiai per dešimtmetį. Įrodyta, kad Klaipėdos uosto pusiau uždarose įlankose vyrauja sunkiaisiais metalais neužterštos dugno nuosėdos. Tik nedideliuose arealuose yra dugno nuosėdų, labai užterštų nikeliu, vidutiniškai užterštų cinku ir variu.

Reikšminiai žodžiai: dugno nuosėdos, užterštumas, sunkieji metalai, Klaipėdos uostas, dumblas, smėlis.

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