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Original Research

Heavy Metal Contamination of Harbor Bottom Sediments

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Abstract

Samples of surface bottom sediments were taken at 82 stations in Lithuania's Klaipeda harbour in 2008-09. Sediment parameters such as the percentages of particles and the concentrations of organic carbon and heavy metals (Cu, Zn, Ni, Pb, Cr, Cd, and Hg) were determined. The heavy metal contamination of harbor sediments was established by calculating Nemerov's pollution index applied to soil. The spatial structure of the obtained data and the factors responsible for sediment distribution and contamination patterns were analyzed in order to evaluate the changes that have occurred since 1998 in the sedimentation conditions, the level of heavy metal contamination, and the structure of the contaminants.

Keywords: bottom sediments, contaminants, deepening, heavy metals, Klaipeda Harbor

Introduction

Marine ports are always significant sources of environmental pollution due to the fact that their activities are associated with a particular contamination of aquatic areas and bottom sediments [1]. Contaminants get into the aquatic environment through shipping traffic, loading, repairs, and dredging, as well as rainwater runoff, effluent discharge, dust, etc. [2-4]. Heavy metals (i.e. metallic elements with a specific gravity 5 or more times higher than that of water) are regarded as especially dangerous contaminants because of their environmental persistence, toxicity, and ability to be incorporated into food chains [5-7]. The strongest toxic properties are characteristic for inorganic metals compounds, which dissociate well and are easily soluble [8]. Some heavy metals dissolve immediately and tend to accumulate in aquatic organisms [9]. They reach the bottom sediments on the strength of biodetritus. After getting into the water, chunks of heavy metals tend to be sequestered at the bottom [9]. The fluctuation in the spectrum and quantities of heavy metals in bottom sediments is not as rapid as in water and therefore the investigation of heavy metals in a relatively stable state enables the integral specific features of the heavy metal contamination of a water basin to be determined for a specific interval of time [11, 12].

In Lithuania, absolutely all activity related to sea navigation, ship building and repairs, and stevedoring is concentrated in Klaipeda Seaport. The physical and chemical parameters and their dynamics in the harbor water area in every case depend on human economic activity [13]. The harbor is situated in Klaipeda Strait, which connects the freshwater Curonian Lagoon to the Baltic Sea (Fig. 1). The character of the water circulation in the strait depends on the strait's throughput, which increases after every dredging [3, 13]. Freshwater runoff into the sea is dominant; however, a significant inflow of seawater has acquired the character of a permanent process [14]. On the one hand, contaminants collected from a broad catchment area are carried into the harbor basin [3], on the other, pollution also enters from sources in the port itself [13]. The waters of the Baltic Sea in this sense are the most clean and play a positive role

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in diluting the polluted harbor water, thereby reducing its contamination level [13]. A certain percentage of the contaminants that enter the water, including heavy metals, leave the Klaipeda Harbor basin prior to settling to the bottom. Another percentage reaches the bottom in Klaipeda and becomes lodged in the bottom sediments [15]. The heavy metals in Klaipeda bottom sediments were investigated episodically prior to 1998. Only sporadic scientific publications contained some information about their concentrations in the harbour's bottom sediments [15-18]. In 1998 samples of surface bottom sediments were taken throughout the Klaipeda Harbor basin and granulometric [19] and geochemical [3] tests performed on them.

The tests determined what lithological types of surface bottom sediments had existed at that time and the main features of their contamination with heavy metals. After these tests, the Klaipeda harbor basin was intensively cleaned and deepened and therefore virtually none of the former layer of surface bottom sediments remained. It was replaced by a new sediment layer that reflects the current conditions of the heavy metal contamination of the Harbors aquatic environment. In 2008 and 2009, samples of the newly formed sediments were collected and the results of their testing are published in this article. In order to more successfully process and analyze the environmental information, we have made use of environmental quality indices and their spatial visualization. The aim of this article is to examine the Klaipeda Harbor bottom sediments for contamination with the heavy metals: Zn, Cr, Cd, Ni, Cu, Pb, and Hg, and, after comparing them to the situation in 1998, to estimate the contamination levels and trends.

Material and Methods

The present study was conducted at 82 stations in 2008 and 2009 (from July to September). Hydrographic vessels belonging to Klaipeda seaport were used to perform the field work. The sampling station and depth measurement locations were determined (with an accuracy of 1 m) using the positioning equipment aboard the vessels. Water depths in Klaipeda strait cross-sections were measured (with an accuracy of 0.05 m) with a sea gauge every 20 m and recalculated to zero water level in the Baltic elevation system [20]. The surface (0-10 cm) bottom sediment samples were collected in a wide area from the Baltic Sea foreshore at the Klaipeda Harbor gateway to Kiaules Nugara Island on the southern periphery of the harbor area (Fig. 1). The investigation did not include the local small harbors and bays. A Van Veen grab sampler was used for sampling. The minutely described soil samples were preserved and later dried in a laboratory. In accordance with the Lithuanian classification standards [21, 22] and traditional methods [23], the percentages of particles from <0.063 mm to >2 mm were determined in 6 fractions. Muddy sediments with a large quantity of particles <0.063 mm in diameter were analyzed using the pipette method [24].

The metals (Zn, Cr, Cd, Ni, Cu, Pb, and Hg) were analyzed in the bottom sediments using inductively coupled plasma – mass spectrometry (ICP-MS) [25, 26]. The organic carbon concentrations were determined using high-temperature catalytic oxidation (HTCO) [27].

The bottom sediment samples taken in 1998 were also analyzed using the aforementioned methods. In order to evaluate the changes that have occurred in recent years, the data from 71 sediment samples collected in 1998 were analyzed in this work.

The maximum concentration limit (MCL) values were taken as a point of departure in evaluating sediment contamination. While Lithuanian standard LAND 46A-2002 sets MCL values for sand that are 3.3 (Cr) to 10 (Cu) times higher than those for mud, this standard is not suitable for bottom sediments, which are evaluated in a single manner and in large part consist of a sand-mud mixture. Therefore, the Norwegian classification system [28], which is used to evaluate the contamination of marine and harbor sediments and focuses on the toxicity to aquatic organisms as well as the impact on human health, was selected for this work. This classification system's values for the upper limits of Class I (background levels) are called MCL in this article. The other classes (II-V) represent an increasing degree of damage to the ecological communities in the water and sediments [28].

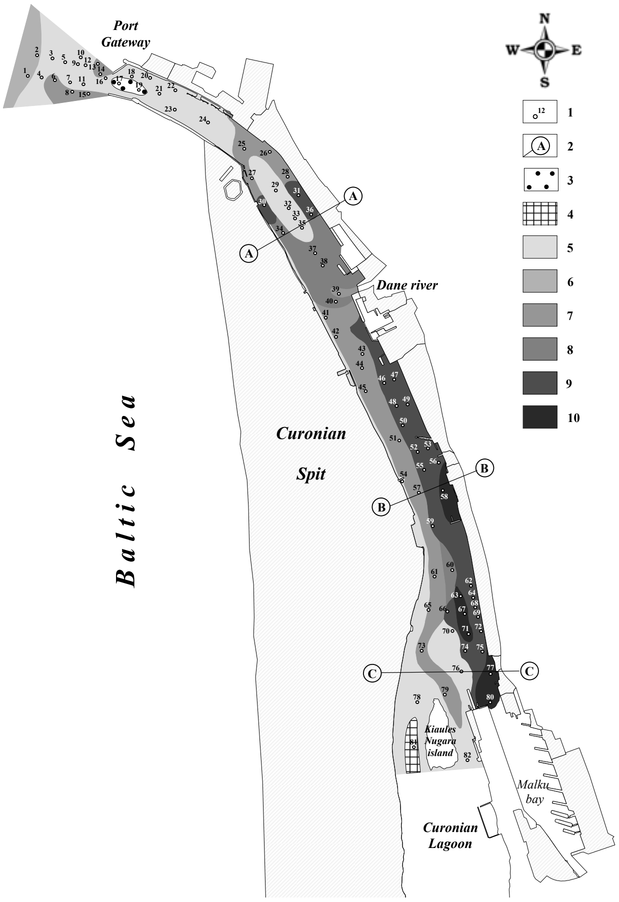


Fig. 1. Sampling station (numbered), cross-sections (A, B, and C) and the types of surface (0–10 cm) bottom sediments: 1 – moraine; 2 – sand, medium-grained; 3 – sand, fine-grained; 4 – sand, extra-fine-grained; 5 – sand, silty; 6 – sand, extra-silty; 7 – mud, sandy; 8 – mud, silty.

The pollution index used in this study was chosen on the basis of the following criteria: all of the contaminants eventually were integrated into a single value. The contamination level was determined by calculating Nemerov's pollution index (*PI*) applied to soil [29], which reflects the effect of each investigated pollutant on the bottom sediments, and also highlights the influence of entire heavy metals on the quality of the environment. The impact of every metal (*i*) (single factor index) on the environment (PI_i) was evaluated by the ratio between its measured (C_i) value and the MCL value (L_i): $PI_i = C_i/L_i$.

The integral pollution index for the bottom sediments of every station's *PI* was derived using the following formula [29]:

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

...where *PI* stands for the synthetic sediment pollution index, $AVG(PI_i)$ represents the average of the various sediment pollution indices, and $MAX(PI_i)$ is the maximum pollution index of a single-factor pollutant. The contamination level was evaluated using a classification analogous to single-factor (PI_i) and multi-factor (*PI*) impacts: $PI(PI_i) \leq 0.7$ are clean sediments (the heavy metal concentration in the sediments is under the warning limit); $0.7 < PI(PI_i) \leq 1$ are sediments in a warning condition (the heavy metal concentration in the sediments is already in a warning condition, but does not exceed the environment quality standard); $1 < PI(PI_i) \leq 2$ are lightly contaminated sediments; $2 < PI(PI_i) \leq 3$ are moderately contaminated sediments; and $PI(PI_i) > 3$ are heavily contaminated sediments [29, 30].

The spatial structure of the obtained data for the bottom sediments in the aquatic area of Klaipeda Harbor was analyzed by creating a map showing the distribution of the obtained parameters. Pearson's correlation coefficient (r) was calculated for the sediments in order to determine the interrelations between the concentrations of heavy metals (Zn, Cr, Cd, Ni, Cu, Pb, and Hg) and total organic carbon, as well as the quantity of the fine-grained fraction in the bottom sediments (<0.063). Each data set was checked for normality using the Kolmogorov-Smirnov test and evaluated according to histogram forms [31]. 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 [31]. The similarity among the harbor stations under consideration for possible inclusion in a specific contamination level zone had to be examined using a cluster analysis of the standardized data (Ward's method, Squared Euclidean distances) [33].

Results

The changes in the bottom relief that occurred due to the deepening of the Klaipeda harbour basin were evaluated by comparing the depths measured in 1998 and 2008-09 at the sampling station locations and at three Klaipeda Strait cross-sections (1998 and 2009) (Fig. 1, A-C). It was determined that the greatest changes in the bottom relief occurred in the segment closest to the sea, where the average depth in the 0.56 km long cross-section (Fig. 1, A) grew from 9.5 m to 12.7 m, and in the 0.3 km wide fairway from 11.3 m to 14.8 m (the greatest difference in depth being 5.3 m) (Fig. 2, A). The average depth in the cross-section further to the south grew from 8.3 m to 10.2 m, and in the 0.16 km wide fairway from 10.1 m to 13.2 m (Fig. 2, B). In the southern part of the harbor, where the basin's width increases to 0.82 km, the average depth grew from 7.3 m to 8.8 m, and in the 0.18 km wide fairway from 8.5 m to 12.8 m. The maximum depth of 13.3 m (the greatest difference in the depths being 5.1 m) occurred only in the northern part of the fairway (Fig. 2, C). A larger or smaller increase in depth was determined at all of the sampling stations from the Baltic Sea to the eastern part of cross-section C (Figs. 1 and 2), as

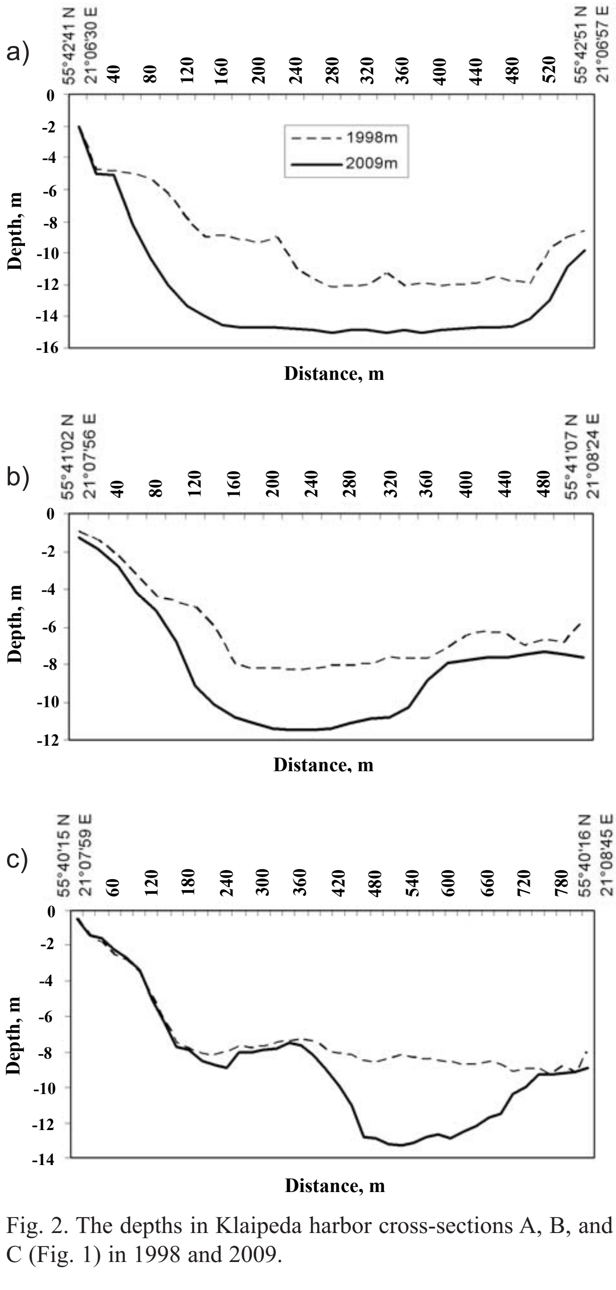


Fig. 2. The depths in Klaipeda harbor cross-sections A, B, and C (Fig. 1) in 1998 and 2009.

well as on the southern periphery of the harbor basin. Only near the edge of the Curonian Spit's shoreline did the depth remain unchanged in many places throughout the decade.

The moraine deposit areas were only defined by their boundaries, whereas the other sediment types were determined on the basis of their granulometric measurements. The following sand and mud types were distinguished (LAND 46A:2002): sand, medium-grained (0.5-0.25 mm >50%); sand, fine-grained (0.25-0.1 mm >50%); sand, extra-fine-grained (0.1-0.063 mm >50%); sand, silty (<0.063 mm 10-30%); sand, extra-silty (<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%). Unlike in 1998, mud, clayey (<0.002 mm 10-30%) was not detected.

The largest bottom sediment areas in the harbor gateway segment were covered with fine-grained sand sediments and in the some sea areas near the harbor gateway even finer grained sand (extra-fine-grained sand and silty sand) sediments (Fig. 1). Much more fine-grained material settled on the bottom deeper in the strait, where the sediments begin to become muddy. To the south of the river Dane's mouth on the eastern side of Klaipeda Strait, a continuous mud zone has formed, which continues throughout the harbour. Sandy mud predominates in this zone, but there are local areas of silty mud (Fig. 1). On the western side of the strait near the shore, fine-grained sand predominates, which changes to silty sand toward the fairway and further south to extra silty sand. In the southern segment of the harbor basin the area of fine-grained sand expands through the entire Klaipeda Strait, and more medium-grained sand appears (Fig. 1). After averaging the data from the granulometric analysis, it was determined that the 'average' Klaipeda Harbor mud sediment type is sandy mud and sand sediment-type silty sand. After performing such calculations with the 1998 data, it was determined that the 'average' mud sediment type had not changed and that the 'average' sand sediment a decade earlier was somewhat less fine-grained: fine-grained sand. In the harbor's central part, a decrease (from west to east) in mud sediment areas and an increase in organic carbon content (on average, from 0.81% to 1.01% in the sand and from 3.33% to 3.97% in the mud) can be seen during the decade.

The heavy metal concentrations are highest in the mud, less in the sand, and minimal in the moraine (Table 1). The average Cu (25.18 mg/kg), Pb (25.87 mg/kg), Zn (134.8 mg/kg), and Ni (13.07 mg/kg) concentrations are greatest in silty mud, but in the case of Cr, Cd, and Hg, greater concentrations were determined in sandy mud: 31.73 mg/kg, 0.87 mg/kg, and 0.08 mg/kg, respectively (Fig. 3). The C_{org} content in both types of mud was practically identical: 3.96% (sandy mud) and 3.99% (silty mud). The concentrations of all the studied heavy metals increased in the sand sediments in a straight progression: medium-grained sand, fine-grained sand, silty sand, and extra-silty sand (Fig. 3). Their average C_{org} content grew from 0.67% to 2.96%. The average Cu concentration increased from 2.30 to 19.06 mg/kg, Pb from 12.50 to 20.56 mg/kg, Zn from 19.00 to 66.32 mg/kg, Ni from 2.60 to 10.62 mg/kg, Cr from 6.70 to 27.78 mg/kg, Cd from 0.30 to 0.76 mg/kg, and Hg from <0.01 to 0.06 mg/kg. Only extra-fine-grained sand, which is found only outside the harbour gateway in the open Baltic Sea, is not included in this sequence (Fig. 1). In the samples from this sand both the C_{org} (0.22%) content and the concentrations of the majority of the heavy metals (except Cr (9.3 mg/kg) and Ni (3.0 mg/kg)) are even lower than in the samples of medium-grained sand from the harbor. In the samples taken from the Baltic Sea of another type of fine-grained sand sediment (silty sand), the average concentrations of all of the studied heavy metals were lower than in the samples of the same sediments taken in Klaipeda Harbor. The average C_{org} concentration in this type of sea sediment is as much as 8× lower, and among the heavy metals, the quantities of Zn and Hg fell the most (2×) in the sea. The smaller scale decrease in heavy metal concentrations (5-10%) outside the harbor gateway is characteristic mostly in the fine-grained sand sediments common there (the C_{org} concentration dropping 3×). Similar results were obtained in studying the dependency of heavy metal concentrations on bottom sediment type using the 1998 data. Only in the muddier medium-grained sand with greater organic content was the average concentration of heavy metals at that time greater than in the fine-grained sand [3]. This is especially clear in looking at the distribution of mercury concentrations (Fig. 3). The results of the investigation of the moraine soil samples taken in 1998 were strongly affected by the fact that this soil had

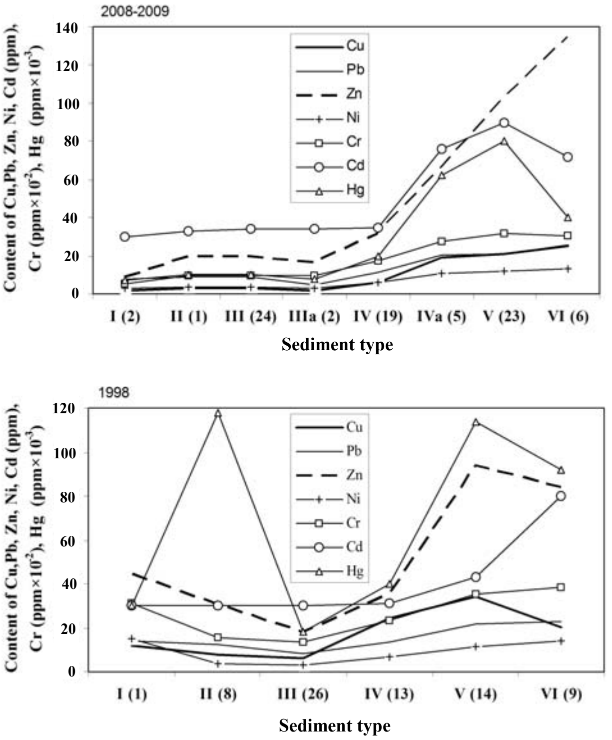


Fig. 3. Average heavy metal content in the different types of surface bottom sediments in 2008-09 and 1998: I – moraine; II – sand, medium-grained; III – sand, fine-grained; IIIa – sand, extra-fine-grained; IV – sand, silty; IVa – sand, extra-silty; V – mud, sandy; VI – mud, silty.
The number of samples is given in parentheses.

Table 1. Indices for the main types of surface bottom sediments and the values for the maximum concentration limits (MCL) for heavy metals in Klaipeda Harbor.

Sediment type	*Parameter	Fraction <0.063 mm, %	C_{org}, %	Heavy metal concentration, mg/kg						
				Cu	Pb	Zn	Ni	Cr	Cd	Hg
2008-09										
Sand (51 samples)	AVG	12.3	1.01	5.49	10.91	28.56	5.26	14.02	<0.40	0.02
	STDV	13.7	0.95	6.04	4.94	18.81	3.08	7.67		
	MIN	0.60	0.04	1.50	5.00	9.00	2.60	5.00	<0.40	<0.01
	MAX	53.0	3.38	23.40	25.10	79.80	12.90	33.20	0.90	0.07
Mud (29 samples)	AVG	56.7	3.97	21.89	21.96	109.43	12.14	31.46	0.84	0.07
	STDV	7.5	0.99	5.81	7.61	40.45	4.18	13.14	0.28	0.04
	MIN	50.9	1.90	10.90	5.00	55.40	3.30	13.40	0.50	0.01
	MAX	71.9	6.19	29.50	32.80	185.20	18.40	67.10	1.40	0.15
Moraine (2 samples)	AVG		0.04	1.50	7.50	9.00	3.00	5.50	<0.40	<0.01
	STDV		0.00	0.00	0.70	0.00	0.00	0.70		
	MIN		0.04	1.50	7.00	9.00	3.00	5.00	<0.40	<0.01
	MAX		0.04	1.50	8.00	9.00	3.00	6.00	<0.40	<0.01
1998										
Sand (46 samples)	AVG	8.47	0.81	10.87	10.48	24.78	4.13	16.26	<0.40	0.04
	STDV	9.59	0.75	23.16	6.85	21.99	2.53	9.51		0.14
	MIN	0.08	0.01	0.60	4.90	5.00	1.6	4.00	<0.40	0.01
	MAX	30.10	3.40	148.0	41.00	109.0	13.00	52.00	0.70	0.96
Mud (21 samples)	AVG	43.20	3.33	28.41	22.41	89.82	12.36	36.45	0.59	0.10
	STDV	18.46	1.64	35.59	11.85	68.96	4.46	15.14		0.10
	MIN	9.74	1.12	6.00	11.00	31.00	6.00	22.00	<0.40	0.02
	MAX	78.49	7.59	154.0	48.00	329.0	22.00	95.00	2.00	0.44
Jumbled Morainic Loam (3 samples)	AVG	42.2	0.60	12.00	14.00	44.70	15.00	31.30	<0.40	0.03
	STDV	12.0	0.60	1.00	3.50	4.70	4.00	5.00		0.01
	MIN	34.6	0.20	11.00	12.00	41.00	11.00	26.00	<0.40	0.02
	MAX	56.1	1.30	13.00	18.00	50.00	19.00	36.00	0.40	0.04
MCL				*35.00*	*30.00*	*150.00*	*30.00*	*70.00*	*0.25*	*0.15*

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

recently been disturbed during dredging, mixed with resuspended mud particles, and resettled on the bottom [3]. Due to this reason, the metal load of the jumbled moraine loam was greater than that of the sand, and the nickel load was even greater than that of mud (Table 1).

After calculating the correlation coefficients, a strong dependency on the quantity of the fraction <0.063 mm and on the C_{org} content was determined for almost all of the heavy metals (except Hg) and a relatively fair dependency for Hg (Table 2). In 1998 a strong dependency was established only for nickel, a relatively fair one for chromium and cadmium (Pb only on C_{org}), and a poor or r value below the significant level for the other elements (Table 2).

The majority of the calculated PIi values increased in the fine-grained mud sediments. The average PI_{Ni}, PI_{Cu}, PI_{Pb}, and PI_{Zn} values mostly grew in silty mud, PI_{Cr}, PI_{Hg}, and PI_{Cd} in sandy mud (Fig. 4). The PI_{Cd} values are the highest and did not fall below 1 for any sediment type. According to the 1998 data, the general tendency for the distribution of the calculated PI_i values according to the sediment types is similar to that for 2008-09, although certain differences can occur in the dynamic of each single factor index (Fig. 4).

Table 2. Pearson's correlation coefficients (r) calculated for the heavy metals concentrations (Cu, Pb, Zn, Ni, Cr, Cd, and Hg), organic carbon (C_{org}), and the amount of fraction <0.063 mm (FR) in Klaipeda Harbour bottom sediments.

2008-09 (significant r>0.29)										1998 (significant r>0.31)									
	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	0.89	1.00								Cu		1.00							
Pb	0.76	0.90	1.00							Pb	0.48	0.65	1.00						
Zn	0.86	0.90	0.81	1.00						Zn	0.44	0.68	0.88	1.00					
Ni	0.77	0.89	0.82	0.81	1.00					Ni	0.86	0.49	0.68	0.69	1.00				
Cr	0.72	0.83	0.79	0.68	0.89	1.00				Cr	0.69	0.59	0.68	0.66	0.86	1.00			
Cd	0.77	0.73	0.59	0.59	0.59	0.68	1.00			Cd	0.58		0.53	0.56	0.55	0.53	1.00		
Hg	0.65	0.63	0.49	0.46	0.51	0.66	0.86	1.00		Hg		0.45	0.72	0.62				1.00	
C_{org}	0.88	0.92	0.83	0.86	0.88	0.83	0.71	0.62	1.00	C_{org}	0.83		0.53	0.48	0.70	0.63	0.54	0.34	1.00

Significance level p<0.01

According to the distribution of *PI* values in the harbor bottom sediments, it is seen that sediments in a warning condition ($0.7<PI\leq1$) cover the bottom on both sides of the harbor gateway, on the harbor's southern periphery at Kiaules Nugara Island, and in a narrow western foreshore strip. From this zone of relatively clean sediments toward the central and eastern zones, the contamination consistently increased from lightly contaminated ($1<PI\leq2$) to moderately contaminated sediments ($2<PI\leq3$), in certain areas reaching the level of heavily contaminated sediments (PI>3) (Fig. 5). In the northern (to sta. 24, Fig. 1) and southern (from sta. 76, Fig. 1) parts of Klaipeda harbor basin, the average *PI* value was 0.87, but 1.90 in the central part of the harbor. There was a trend for the average values of all of the single factor indices to increase: PI_{Cd} 2.2×, PI_{Pb} 2.4×, PI_{Cr} 2.8×, PI_{Ni} 3.0×, PI_{Zn} 5.3×, PI_{Hg} 5.7×, and PI_{Cu} 11.7×. Although the PI_{Cd} value grew the least, it remained extremely high not only in the harbor's central part (2.63), but also high on its edges (1.2).

It is possible to see the same essential 2008-09 tendencies in the distribution scheme for *PI* values created on the basis of the 1998 data, only the moderately and heavily contaminated areas were smaller in 1998, while the maximum *PI* value (5.8) was larger (Fig. 5). The contamination in the central part of the Klaipeda harbor basin was also greater (*PI*=1.49) than in the border zones (*PI*=0.87), the average values of the single factor indices in the central part being from 1.5× to 7.7 × higher: PI_{Cd} 1.5×, PI_{Pb} 2.3×, PI_{Cr} 2.5×, PI_{Ni} 3.7×, PI_{Zn} 4.9×, PI_{Hg} 6.9×, and PI_{Cu} 7.7×. In 1998, the average value of only PI_{Cd} exceeded 1 not only in the harbor's central part (1.77) but also on its edges (1.2).

The cluster analysis of the distribution of the heavy metal and total organic carbon concentrations in bottom sediments in 2008-09 showed that the data are divided into two clearly distinguishable parts, each of which consists of two data groups. The elements in these parts and groups are more similar to one another than to the elements of the other parts and groups (Fig. 6). The first part of the data combines the stations in the central and eastern zones in the central part of Klaipeda Strait from station 31 in the northwest to Malku Bay in the southeast (Fig. 1). Only two stations (sta. 30 and sta. 54, Fig. 1) are at locations locally deepened for harbor purposes on the western shore, where sandy mud sediments occur. Two data groups are distinguishable in this part (Fig. 6):

1 – stations located between bathymetric cross-sections B and C (a *PI* from 1.5 to 3.8) (Fig. 1)

2 – stations extending to the northwest from cross-section B and located between cross-section C and Malku Bay (a *PI* from 1.5 to 4.05)

The second data part combines the stations located further to the northwest and to the southeast of the range of stations in the first part, a narrow zone along the western foreshore, and the mouth of the Dane River. The two groups of stations differ in this part (Fig. 6). Group 3 stations ring the range of part 1 stations in an arc (a *PI* from 0.88 to 1.0), and group 4 stations are arranged on both sides of Klaipeda Harbor's sea gateway and around Kiaules Nugara Island (*PI*=0.87 at all of the stations).

Discussion

During the cleaning and deepening of Klaipeda Harbor, the average quantity of dredged soil during 2000-10 was 1 million m^3 per year [34]. Although the areas where the harbor basin's bottom was deepened and cleaned were divided up unevenly in respect to time and space, over a longer period the general results of constantly dredging the soil become clear. During 1998-2009, a bottom sediment layer that was on average 3.2 m thick was dug up and removed at the investigation's northern cross-section location in the harbor basin. The average size of the layer of soil dredged in the central part of the harbor basin fell to 1.9 m, the central fairway having been deepened the most (a depth difference of up to 3 m), and less at the edges of the strait. The results of dredging the bottom sediments in these two investigation zones manifested themselves practically throughout the entire width of the Klaipeda Strait. A bottom almost untouched by the deepening work ran along the western part of the southern harbor basin, but a layer of up to 5 m of soil was removed from the fairway in the eastern part (Figs. 1 and 2). On the harbor's southern periphery at Kiaules Nugara Island, the depth remained almost unchanged. An analysis of the changes in the bottom relief showed that during the comparison period practically all of the present-day bottom sediments and some of the moraine sediments under them [1] were removed from approximately 80% of the harbor basin. The sediment material collected in it during 2008-09 has been newly deposited and is in no way connected with the sediment material investigated in 1998. Thus the results of each investigation period reflect only the situation at that time, and the comparison of these results allows an objective assessment of the changes that occurred during the last decade to be made.

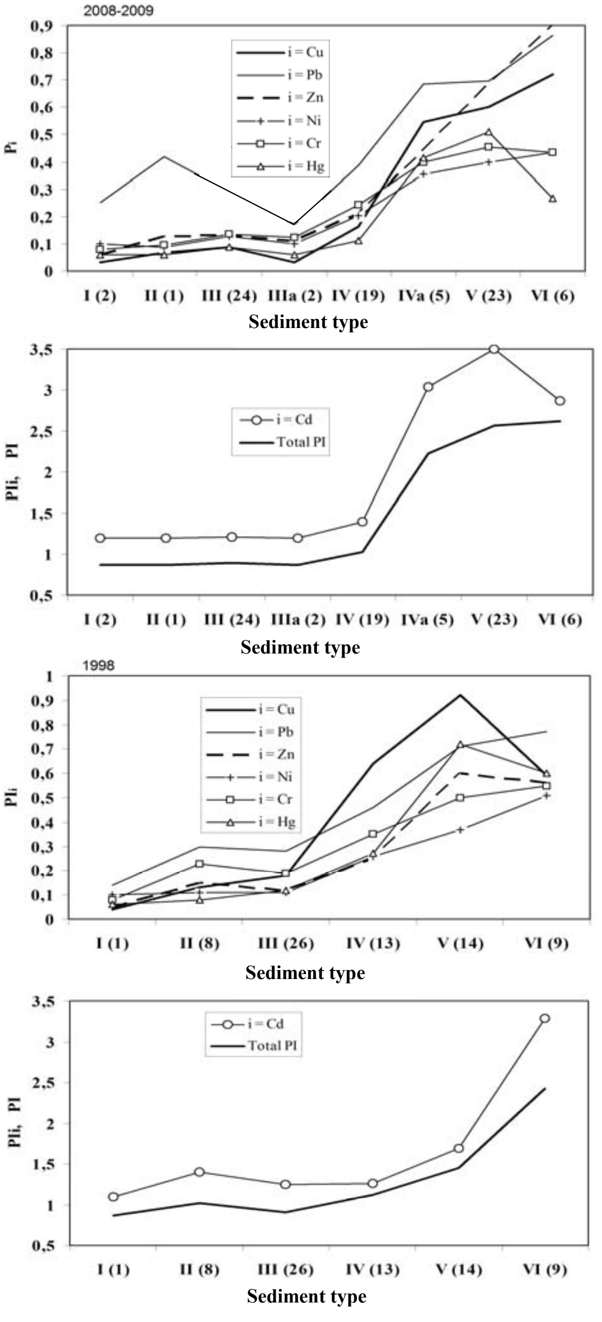


Fig. 4. Average single factor (PI_i) and total (PI) pollution indices in the different types of surface bottom sediments in 2008-09 and 1998: I – moraine; II – sand, medium-grained; III – sand, fine-grained; IIIa – sand, extra-fine-grained; IV – sand, silty; IVa – sand, extra-silty; V – mud, sandy; VI – mud, silty. The number of samples is given in parentheses.

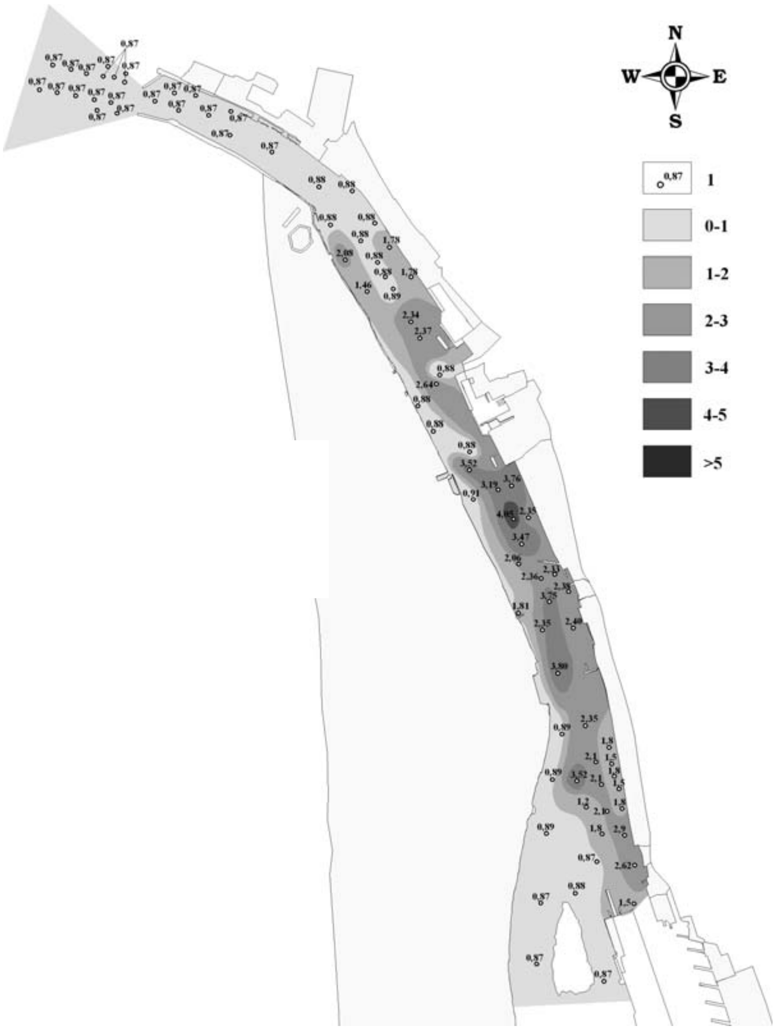
Areas of moraine soil not covered by modern sediments remain for a certain period after the bottom is dredged, but the largest areas are quickly recovered with sand and mud. The increased water current speed and active water circulation between the strait and the sea do not allow finely dispersing materials to lodge in the bottom sediments on the harbour's marginal northern and southern parts [3, 14, 15]. Due to more active hydrodynamics, the finely dispersing material also does not accumulate in the northwestern foreshore strip (except in several deepened locations) [3]. Like in 1998 [3], the largest areas were covered with fine-grained sand there. The appearance of areas of finer sediments (extra-fine-grained sand and silty sand) in the Baltic Sea opposite the harbor gateway and on both sides of the gateway (Fig. 1) can be explained as an inflow of finely dispersing material from Klaipeda Strait, and its accelerated sedimentation due to the sudden drop in the current's speed in the sea [3, 15]. The sedimentation of finely dispersing sediment materials flowing into Klaipeda Harbor with the Curonian Lagoon water currents is mostly accelerated by currents flowing in opposite directions in the very intensive mixing zone between the Baltic Sea and the Curonian Lagoon, especially in its deepest locations, where, due to the reduced current speed (when the cross-section area increases), fine-grained mud sediments are deposited [14, 15]. In other cases, this material becomes the part of sandy sediments that most accumulates contaminants [15]. Almost all of the mud sediments are deposited in the eastern part of Klaipeda Strait, closest to the rows of quays and small semi-closed local harbors, where the highest heavy metal contamination in the harbor water basin has been established [13].

The composition of the 1998 bottom sediments [3] is the most similar to the present-day one on the marginal northern and southern harbor segments. Although the depth increased significantly at the Baltic Sea, it remained similar to the previous depth at the Curonian Lagoon and the sedimentation conditions and the materials forming the bottom sediments (fine-grained sand) practically did not change in these segments. The range of the mud sediments decreased in the central harbor segment during the decade, but the organic carbon quantities increased in both the sand and mud. The newly deposited sand sediments are more finely grained.

The strong correlation between decreasing grain size and increasing heavy metal concentration is well documented [4, 35]. The concentrations of the heavy metals studied in the Klaipeda harbor basin have a tendency to increase as the sediments become muddier and the sediment particles become smaller because small particles have a much larger surface area for adsorption relative to their volume than large particles. Organic matter also plays an important role in metal binding in sediments [36]. The obvious dependency of metal concentrations on sediment composition in Klaipeda harbor is also confirmed by the correlation coefficient values, which show a strong connection between the majority of the metal concentrations and the quantities of fine-grained fractions < 0.063 mm and C_{org} (the dependency on C_{org} being somewhat greater) (Table 2). In 1998 the connections among the aforementioned elements were much weaker. At that time the arrangement of the contamination sources and their impact over a long period affected the spatial dynamics of the sediments laden with heavy metals more than the composition of the bottom sediments [3].

The determined strong dependency among many metal concentrations (which was especially strong between Cu and Pb, Zn, and Ni (r=0.9) and slightly weaker between these metals and Cr) allows us to assert that the sources and migration routes of these contaminants are identical. The same can be said about cadmium and mercury (r=0.86) (Table 2). The mechanism in the formation of the bottom sediments sampled in 1998 was longer and more complex [3]; therefore, no such strong connections were demonstrated. The strongest connections determined by the data from that year were those of Pb and Zn with Ni and Cr (Table 2).

The heavy metal concentrations in the glacial sediments (moraine) exposed at the bottom of Klaipeda Harbor are minimal. Heavy metals recently can get into these sediments only during the excavation of moraine soil and secondary sedimentation processes [3], when the aquatic mixture of suspended moraine clay particles and resuspended mud becomes an especially receptive medium that adsorbs the heavy metals from the water [36-38]. Due to these reasons, the metal load of jumbled moraine loam can be greater than that of sand, and in certain cases, even of mud.



2008-2009

1998

Fig. 5. Spatial distribution of the calculated total pollution index (*PI*) for Klaipeda Harbor surface bottom sediments in 2008-09 and 1998.

Although an acceleration in the sedimentation of the finest sand particles is noticeable in the Baltic Sea immediately outside the harbor gateway and the conditions for accumulating heavy metals are less favorable there, the concentrations of heavy metals and (especially) C_{org} in the seabed sediments are lower there than in the same type of sediments in Klaipeda harbor.

Since 1998 the average concentrations of Cu and Hg in the sand of Klaipeda harbor have dropped twofold, the concentrations of the other studied heavy metals have changed less (the Zn and Ni concentrations having grown somewhat). The quantities of Cu and Hg have decreased in the mud sediments by a quarter, but the quantity of Cd has increased by the same amount, and an increased Zn concentration is also noticeable (Table 1). The drop in copper quantities is connected with changes in the nature of ship repair work and in its technologies [3] during the last couple of decades. The drop in mercury quantities in the waters of the harbor, the nearby Baltic Sea and Curonian Lagoon, in the fish, and in molluscs has been observed for about 20 years and is connected with a reduction in the inflow of this metal from the Curonian Lagoon basin [39]. It is known that the dynamics of metal concentrations in living organisms reflect changes in the bottom sediment concentrations [40]. Although the growth in cadmium concentrations in the mud of Klaipeda Harbor cannot be dissociated from pollution from the port's companies; the increased quantities of this metal not only in the harbor, but also in a wider range in the sea and Curonian Lagoon [39] show that the sources of cadmium contamination are not concentrated in the harbour. However, both previously [15] and now [13, 39], the degree to which the Klaipeda harbor bottom water and bottom sediments are loaded with heavy metals is significantly greater than in the nearby Baltic Sea and Curonian Lagoon basins.

According to some of the authors' data [41, 42], the heavy metal concentrations in the most recent harbor sediments, compared with the older sediments, show a tendency to decrease. The maximum concentrations of some metals (Cu, Hg) in Klaipeda Harbor dropped, while those of other metals (Pb, Zn, Cd) exceed the MCL values (whereas the Cu, Pb, Zn, Cr, Cd, and Hg concentrations all exceeded it in 1998) (Table 1). The heavy metal contamination of Klaipeda Harbor bottom sediments is not conspicuous compared to the contamination of neighboring Gdansk port (Ni – 7.1 mg/kg, Pb – 11.4 mg/kg [43]), Gdansk basin (Cu – 22-71 mg/kg, Cr – 65-107 mg/kg, Ni – 20-46 mg/kg, Pb – 38-83 mg-kg [44]) and Ventspils Harbor (Ni – 5-35 mg/kg, Pb – 3-34 mg/kg, Cr – 12-71 mg/kg, Cu – 3-29 mg/kg [45]) bottom sediments. Compared to more distant harbors, the contamination in Klaipeda is considerably less than that in Norway's Bergen [46], Spain's Ceuta [4], and especially Italy's Naples, where the fluctuation range of heavy metal concentrations is broad and the maximum concentrations are especially high: Cu – 12-5743 mg/kg, Pb – 19-3083 mg/kg, Zn – 17-7234 mg/kg, Ni – 4-362 mg/kg, Cr – 7-1798 mg/kg, Cd – 0.01-3.0 mg/kg, and Hg – 0.01-139 mg/kg [47]. The high heavy metal levels in harbor sedi-

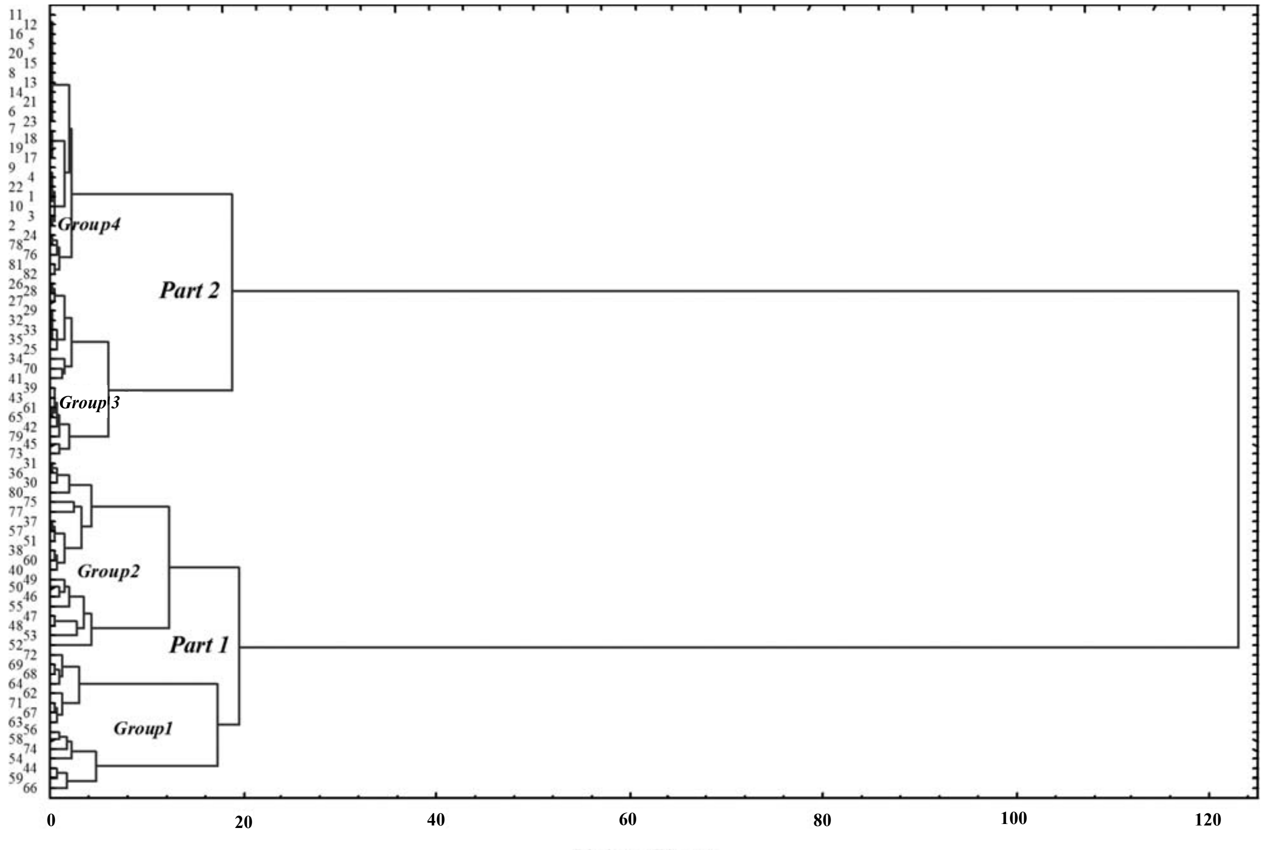


Fig. 6. A tree diagram of the cluster analysis for the 82 sampling stations in Klaipeda Harbor.

ments are chiefly due to the discharge of untreated industrial and domestic wastewater and other spills [12].

The evaluation of bottom sediment contamination on the basis of pollution index *PI* reflects each of the studied heavy metals and their general effect on the quality of the aquatic environment [29]. The average PI_i values, like the heavy metal concentrations, depend on the composition of the bottom sediments and have a tendency to increase in the following order: moraine – sand – mud. On the other hand, the values of these indices have a tendency to increase near the harbor's shoreline and semi-closed small harbors, from which the most polluted water emanates [13]. In the case of Klaipeda, both of the aforementioned factors together mean that the highest total *PI* values were established in the harbor's central part, where large quantities of fine-grained and organic laden materials settled in the deepened areas, and the heavy metals have an opportunity to easily get into them not only from the Curonian Lagoon but also from the most urbanized harbor locations (Fig. 5). The most navigated harbor part, which is closest to the quays, from station 31 in the northwest to Malku Bay in the southeast (Fig. 1), also differs sharply according to the cluster analysis data (Fig. 6). Although there are no completely clean sediments ($PI \leq 0.7$) in Klaipeda Harbor (Fig. 5), the average heavy metal contamination level in the bottom sediments in the harbor basin's marginal segments with the Baltic Sea and Curonian Lagoon and in the northwest foreshore is clearly less (PI=0.87) than in the harbor's central part (PI=1.90), where the average values of the single factor indices grew from 2.2× (PI_{Cd}) to 11.7× (PI_{Cu}). PI_{Cd} is the most important for the total *PI* index of all the single factor indices. The average value of just PI_{Cd} exceeds the clean soil limit not only in the harbor's central part (2.63), but also on its periphery (1.2). According to the single factor index values, the heavy metals for the total *PI* index for the harbor's more contaminated central part follow the order: Cd>Pb>Zn>Cu>Cr>Hg>Ni (in 1998: Cd>Cu>Pb>Hg>Cr>Zn>Ni). In the relatively clean zone surrounding the harbor's central part, this order appears somewhat differently: Cd>Pb>Cr>Ni>Zn>Hg>Cu (in 1998: Cd>Pb>Cr>Ni, Zn, Hg, Cu). Although the place of each of the studied heavy metals in the cleaner part of the harbor practically did not change in the general spectrum of bottom sediment contamination, in the harbor's more contaminated central part the values for copper and mercury declined during the decade while those for zinc increased, as did those for lead (somewhat).

Since 1998 the area of Klaipeda harbor with contaminated (PI>1) surface bottom sediments increased 23%. The ranges of the heavily contaminated (2.5×) and moderately contaminated (2.1×) sediments grew the most. The range of the lightly contaminated sediments shrank 1.8×. In the harbor's central part, the average contamination increased (from PI=1.49 to PI=1.90). In the marginal zones with the Baltic Sea and Curonian Lagoon, sediment contamination did not change (PI=0.87). The essential principles of the heavy metal contamination of the bottom sediments virtually did not change during the decade. According to the scale of the increase in the PI_i values in the harbor's central part (compared to the external marginal zone), the heavy metals are arranged in the same order as in 1998: Cd<Pb<Cr<Ni<Zn<Hg<Cu. Only the current distribution of the PI values is much more even, and their maximum values are much smaller than in 1998. No clear local contamination sources were identified in Klaipeda Harbor on the basis of the heavy metal concentration dynamics in the bottom sediments. All of this allows the assertion to be made that the ranges of the moderately and heavily contaminated bottom sediments (Fig. 5) increased not due to the appearance of strong pollution sources in the harbor, but primarily due to the increased depth of as much as several metres in a large area (Fig. 1, Fig. 2). In such bottom depressions, the sedimentation of finely-dispersing sediment material, which is inclined to adsorb contamination (including heavy metals) and is being abundantly carried in from the Curonian Lagoon [48], accelerated sharply. With the continued deepening of the harbor, this process will become ever more intensive.

Conclusions

The modern sedimentation regime and level of heavy metal contamination in Klaipeda Harbor's sediments have been strongly influenced by the harbor's deepening: on the one hand, the upper sediment layer, which had formed over many years and was contaminated in certain areas with heavy metals, was removed from a large part of the harbor basin, and on the other hand, the sedimentation of the thin mineral particles and organic material, which accelerated in the deepened part of the harbor, intensified the heavy metal accumulation process in the bottom sediments. The essential principles in the formation of bottom sediments remained the same as those a decade before: fine-grained mud sediments gathered in the deeper eastern side of the Klaipeda Strait, closer to the potential pollution sources. The area of mud sediments, which decreased during the dredging, has a tendency to increase.

The spatial distribution of heavy metals in the surface sediments of Klaipeda Harbor was controlled by the association of heavy metals with fine particles (<0.063 mm) and organic carbon content and reflects the impact of anthropogenic input as a source for heavy metals. The area of Klaipeda harbor with contaminated (PI>1) surface bottom sediments increased 23% during the decade. The ranges of the heavily contaminated and moderately contaminated sediments increased the most, while the range of lightly contaminated sediments decreased. The increase in the ranges of the moderately and heavily contaminated bottom sediments is not directly connected with local contamination sources in Klaipeda harbor. The integral heavy metal contamination is having an ever greater effect on the aquatic environment of Klaipeda harbor, primarily due to the acceleration of the sedimentation of finely dispersing sediment materials that are receptive to metals. The cadmium concentrations increased the most among these materials in the mud sediments that formed during the decade. During the same time, the zinc concentrations grew somewhat in all the types of Klaipeda harbor bottom sediments while the copper and mercury quantities decreased considerably. The established strong dependency among the metal concentrations allows two heavy metal groups, the sources and migrations routes of which are identical, to be distinguished: Cu-Pb-Zn-Ni and Cd-Hg. According to the heavy metal value for the total PI index for the most contaminated part of the harbor, the heavy metals are arranged in the following order: Cd>Pb>Zn>Cu>Cr>Hg>Ni.

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