

## Distribution of migration (state) forms of microelements in the sediments of the ports of Klaipėda and Gdańsk

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### Abstract

During investigations of the Baltic Sea basin significant differences have become manifest in the distribution of certain chemical elements in different chains of the geo (-eco) system (soils, river, lagoon and marine sediments). This paper presents data on the quantitative relationships of elements resulting from interactions of natural sedimentation processes and the possible human impact on the sediments from two port areas. The total (T), lithogenic (LG; stable) and hydrogenic (HG; mobile, reactive) migration forms of Zn, Cr, Cd, Cu, Pb and Ni were analysed. The HG component comprises that pool of the elements contained in readily degrading minerals;

increases in this form potentially being an indicator of adverse human impacts. The distribution of total forms depends on the quantity of the sediment fraction with grain size  $< 0.063$  mm (fr.  $< 0.063$  mm) and on the concentration of organic content ( $C_{org}$ ).

With increasing sediment depth, the concentration of elements decreases sharply, although HG concentrations were seen to increase on several occasions. One explanation for such findings is the mineralisation and decomposition of metals from the remnants of biological activities of organisms (pellets, globules) into the sediments. Element concentrations in the natural sedimentation zone (NSZ) of the marine-influenced North Port at Gdańsk are less than in the NSZ and technogenic sedimentation zone (TSZ) of the riverine part of the port of Gdańsk. The ratios between HG, LG and T in the two sedimentation zones are different for different elements, but are always higher in the TSZ than in the NSZ. Multi-site analyses of the port basins allowed NSZ and TSZ to be distinguished. The TSZ is typified by anomalous concentrations of elements, the specific distribution of their migration forms, the semi-stagnant conditions prevailing there and the proximity of human impact sources. The data presented in this paper indicate that the concentrations of only some of the elements in the TSZ sediments of the ports of Klaipėda and Gdańsk exceed the permitted norms for spoil dredged from port basins. By no means can the total load of elements contained in the spoil dumped at sea be treated as an indicator of marine pollution. For an objective assessment of the real pollution threat to port environments, detailed investigations of the various migration forms of chemical elements need to be carried out, and previously established levels revised.

## INTRODUCTION

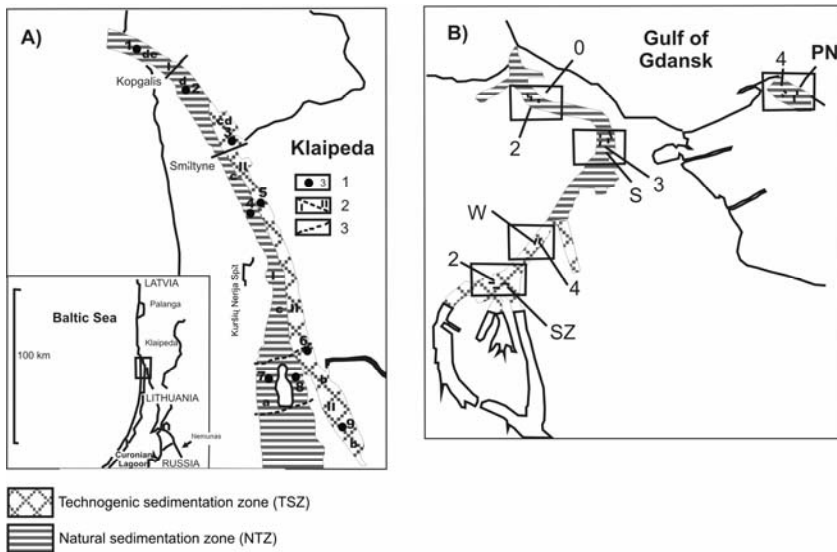
Being interfaces of fresh and saline water the Klaipėda Strait and Martwa Wisła (Dead Vistula) river-areas, in which the ports of Klaipėda and Gdańsk are, respectively, located, act as geochemical barrier zones (GBZ), concentrating numerous hydrological, sedimentological, biological, chemical and artificial factors. The joint action of these factors can complicate the ecology of these boundary areas, and frequently has an adverse effect on the conditions for recreation in the surrounding areas.

The hydrodynamic regime is one of the major factors in the formation of geochemical anomalies at the bottom of the areas under investigation. It governs the migration patterns of sedimentary material, which depend on the velocity and direction of currents. Sediment fluxes are often predetermined by morphometric changes of the bottom during port reconstruction and basin dredging. This activity is reflected in accumulation processes, in the intensification of various chemical processes and silting up of some port areas. These areas thus need to be periodically dredged, with the resulting spoil being dumped at sea or on land. Analysis of mechanical disturbances to the upper layer of sediments (caused by shipping movements), and consequently their aeration, are important in estimating the ratio between the natural and artificial constituents of sediments. At the same time, such analyses make it easier to perceive many aspects of the current state of such ecosystem boundaries, and to

find solutions to contemporary problems of the development of port city areas and their infrastructures.

## MATERIALS AND METHODS

The material for this article was obtained during long-term studies of both Klaipėda and Gdańsk port areas in 1990-2004. Nine monitoring stations were sited in the Klaipėda Strait, which since 1995 have been used for detailed research into a battery of scientific and technological problems (Fig. 1A). These stations reflect the different sedimentation aspects of the Klaipėda Strait GBZ, which is additionally complicated by human activities. Natural sedimentation zones (NSZ) and technogenic sedimentation zones (TSZ) have been distinguished. Other data from these studies have previously been published, e.g. Jokšas et al. (2003), Pustelnikovas (1994, 1996, 1998, 2002, 2003), Pustelnikovas and Bolalek (1995), Trimonis and Gulbinskas (2000).



**Fig. 1.** Situational map of the investigated areas of Klaipėda (A) and Gdańsk (B) ports: A: 1- sampling station, 2- sedimentation zone (I-natural, II-technogenic), 3- migration zone and its boundary: a) input, b) accumulation, c) transit, d) output, e) mixing zone of fresh and marine waters. B: Quays – Shtetin (SZ), Vistula (W), Sulphur (S), Oliwa (O), North port (PN); 2,3,4- sampling stations on the various quays.

Analogous studies were carried out in 1997-2004 in the port of Gdańsk (Fig. 1B) in the vicinity of five quays. Four of these quays are in the Martwa Wisła riverbed and the fifth is in the North Port. This last is located in the Gulf

of Gdańsk about 2.5 km to the northeast of the Martwa Wisła mouth and the main port structures. As in the Klaipėda Strait, NSZ and TSZ were distinguished in the port of Gdańsk. Other data from this region have also previously been published, e.g. Bolałek et al. (1999), Dembska et al. (2001 a, b), Pustelnikovas et al. (2005) and Radke et al. (2004).

Sediments were collected from r/v “Gintaras” (Klaipėda) and “Dr. Lubecki” (Gdańsk) with a van Veen dredger and gravity- (diameter 40 mm) and vibro- (100 mm) corers from the following layers: Klaipėda – 0-2, 2-5, 0-10 cm; Gdańsk – 0-20, 20-40, 40-60, 60-80, 80-100, 100-120, and occasionally 120-140 cm.

Prior to analysis the sediments were stored at 4°C. The dredged and cored material was evaluated macroscopically, divided with a plastic spatula into segments from 1 to 20 cm thick, and packed in marked polyethylene bags. Moisture content and loss on ignition were determined for each sample. After being dried at 110°C, the samples were homogenised in a porcelain mortar, after which each sample was split into two subsamples, one for determining grain size, the other for chemical analysis of heavy metals (microelements).

Grain size was determined by passing the sediments through metal sieves of 2.00, 0.5, 0.125, 0.063 and 0.032 mm mesh size<sup>1</sup>.

The sediments used for chemical analysis were passed through plastic sieves of 2.00 mm, 0.063 and 0.032 mm mesh size.

The contents of Zn, Ni, Cr, Cd, Cu and Pb in hydrogenic forms (HG) and total forms (T) were determined. Lithogenic form is calculated as the remnant between total and hydrogenic forms ( $LG = T - HG$ ). HG were separated by extracting all grain size fractions with 1M HCl (Luoma&Bryan 1981, Lukashev 1986), whereas T were determined after mineralisation of the sediments with conc. HF and HNO<sub>3</sub> in a microwave digestion system.

The content of these forms was determined by the Flame Atomic Absorption Spectrometry (FAAS) technique in a Spectral AA PLUS variant.

### ***Study areas: Hydrological and sedimentation conditions***

#### *The Klaipėda port basin*

The Klaipėda port basin (Klaipėda Strait) covers an area of 6.23 km<sup>2</sup> (Klaipėda port..., 2000). The distance between the port entrance in the north and the Kiaulės Nugara shoal is 12 km, and the width varies from 1.5 km (at the

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<sup>1</sup> In the case of Klaipėda Strait the grain size distribution of the sediments were determined by water-mechanical and pipette analyses, because finely dispersed sediments, silty and silty-clayey muds, occur in this basin (in the TSZ). The fractions were obtained by sieving through 2.00, 1.00, 0.50, 0.25, 0.10, 0.05 and 0.01 mm mesh sizes.

shoal) to 0.4 km at the entrance to the Baltic Sea. The sandy Kiaulės Nugara shoal, which supports an abundant growth of macrophytes, separates the strait from the northern part of the Kuršių Marios lagoon (Curonian Lagoon), dividing it into western (deeper) and eastern (shallower) branches. The Smeltė peninsula lies between the latter and the continental (eastern) coast of the Strait. The eastern part of the peninsula encloses Malkū Bay, 1.6 km long and 300-500 m wide. Not much water from the Klaipėda Strait drains into this Bay. The small River Smeltė flows into the northeastern part of the Bay, and the River Danė discharges into the Strait 5 km from the port entrance. The sewage effluent from Klaipėda, partly biologically purified, drains into the Strait via these rivers.

An 11-14 m deep and 100-110 m wide fairway runs along the western part of the Strait-port area, providing an outflow to the sea for the 26.5 km<sup>3</sup> of water discharged annually into the lagoon from the River Nemunas (Niemen), from other smaller rivers, and from precipitation.

The Klaipėda Strait is a complex hydrological system with pulsating fluxes of energy, sediment migration and biomass exchange between the freshwater Kuršių Marios lagoon and the saline Baltic Sea. Given the extreme conditions in this sedimentation area, a multitude of natural factors are concentrated there: grain size differentiation, variations in the migration forms of sedimentary matter, and the periodic input of sandy material into the sea water strait. Outflowing currents can reach speeds of 0.2-0.25 m s<sup>-1</sup> (and possibly > 2 m s<sup>-1</sup> during spring floods). Similar speeds are also characteristic of the inflowing sea water. According to Gailiusis (Klaipėda port..., 2000) the sea water inflow lasts for about 74 days and can raise the water level in the strait by > 60 cm. The annual sea water input of 5.954 km<sup>3</sup> brings saline water (12-15%) and sandy marine sediments (sandy and silty fractions) into the lagoon.

The sedimentation zones are distributed according to the hydrodynamics of this complex area. The NSZ lies in the main stream of the River Nemunas into the Baltic. This zone includes the fairway and extends from the Ferry Terminal as far as the KLASCO quays, and further north includes the entire strait (Figure 1, A-I). In many cases sediments fail to accumulate at the bottom of this zone because the strong water flow carries the finely dispersed matter out into the Baltic Sea.

The TSZ is situated in the eastern part of the strait and lies quite a long way from the main flow of water and suspended matter. It includes the commercial harbour and fishing port, shipyard, river ferry landing-stage and the mooring berths for the port authority's launches. Stagnation and semi-aeration conditions are prevalent in these areas (Figure 1, A-II), which receive untreated city wastewater and abound in building and shipping wastes. The movement of ships resuspends and redistributes the surface sediments.

### *The port of Gdańsk*

The port of Gdańsk is located in the Gulf of Gdańsk close to the mouth of the Martwa Wisła River. 27 km of this river (which includes 2.5 km of the Śmiała Wisła River) lie between Przegalina and Nowy Port. Mean current speeds range from 2 to 5 cm s<sup>-1</sup>, and the salinity is between 2.48 and 6.13 PSU (with an average of <5 PSU) (Majewski 1990). Salt water influxes from the sea occur in the near-bottom water layer. The Martwa Wisła carries only 0.99% of the total Wisła River outflow into the Gulf of Gdańsk.

The principal factors affecting the water circulation are NNW winds with speeds of 10 m s<sup>-1</sup>, which cause the water level to rise; SE winds have the opposite effect. The outflowing current is extremely sluggish (0-0.1 m s<sup>-1</sup>, mean speed 0.02 m s<sup>-1</sup>), rarely achieving a speed of 0.35 m s<sup>-1</sup>. Storm surges penetrate only as far as the Kanał Portowy, where breakwaters and other hydro-engineering structures dissipate their energy. The river bed in the port can be as much as 12 m deep and quays line both sides of the river.

The Port of Gdańsk is divided into two areas, the inner port and the North Port. The former is located on either bank of the Kanał Portowy and on the eastern bank of the Kanał Kaszubski. The oldest port structures are located along the Martwa Wisła, where until 1947 two small shipyards were located (Mamuszka 1988). At present, different enterprises are located here, e.g. the premises of the company responsible for dredging and underwater operations in the river and its equipment (excavators, tractors), timber storage facilities and the Gdańsk Shipyard. The Szczecin (Timber Terminal) (Sz) and Wiślany (small cargo and grain, coal and ore) (W) Quays (Fig. 1B) are located just beyond Ostrów Island on the main branch of the river. Sulphur is transferred at the Sulphur Quay (S). The Oliwa Quay (small cargo, e.g. fruit and vegetables) (O) is located in the Kanał Portowy. The Kanał Portowy, the final section of the Martwa Wisła, ends at the entrance to the port.

Connected directly with the sea and extending 2.5 km from the shoreline, the North Port (PN) handles coal and liquid fuels (crude oil, gasoline, diesel fuel and heating oil) (Kreft 1996). It is the most recently built part of the port of Gdańsk and has two 19 m deep quays.

According to Szvernowski (1957), the rate of sedimentation in the port of Gdańsk is 7 cm year<sup>-1</sup>. For comparison, sedimentation rates elsewhere in the Baltic are 0.13-2.92 mm year<sup>-1</sup> (Pempkowiak 1992) or 1.0-2.0 mm year<sup>-1</sup> (Winterhalter et al. 1981, Szczepańska&Uściniowicz 1994). Because of the vast amounts of sediments at Gdańsk (and a similar situation at Klaipėda), the ship and port channels have to be dredged to such depths as to allow shipping operations to proceed normally and guarantee the safety of vessels entering the port and manoeuvring in it (Korzeniewski 1998). There is thus a continual need

to remove the bottom sediments from the port channels and to dump them on land or specified sites at sea. For example, in 1994-1995 the 300-400 thousand  $\text{m}^3 \text{ year}^{-1}$  of spoil dredged up from the port of Klaipėda was dumped at depths of 28-32 m (Zaromskis&Gulbinskas 1996). According to HELCOM data (1996) Poland in 1992-1993 dumped ca. 0.3 million tons of different sediments in the Baltic. In order to forestall possible contamination of the marine environment, it is essential to know the granulometric and chemical composition of these bottom sediments.

## RESULTS AND DISCUSSION

### *Grain size distribution and chemical composition (total content) of sediments*

Sedimentation processes in the NSZ and TSZ of both port areas are governed by the input of sedimentary material from the catchment areas and are evidently affected by frequent sea level changes and geochemical changes in the states of the elements caused by saline water inflows.

Both port areas are transition zones for sediment, and the frequent (continual) changes in sea level impact on the hydrodynamics of the sedimentation zones, thereby complicating the accumulation of sediment. The granulometric and chemical composition of the sediments in the Klaipėda and Gdańsk port areas has previously been analysed in detail (Pustelnikovas 2002, Pustelnikovas et. al. 2005, Trimonis&Gulbinskas 2000). Without analysing this material in any greater detail, we may conclude that:

1. Whereas coarse-grained clastic (silty and sandy) material is prevalent (average 84.9%) in the NSZ in the western part of the Klaipėda port, fine sand with patches of medium-grained sand, pebbles and gravel are dominant in the port entrance area. Here the invasion and accumulation of marine sediments is predominant.
2. A distribution zone of fine silty and silty-clayey mud (average 79%) with patches of silty sand is prevalent in the eastern, continental part of this port, where the human impact on sedimentation processes is obvious. The scale of this impact is, however, unknown.
3. Sedimentary matter enters the sedimentation areas from the Kuršių Marios lagoon (suspensions are predominant) and from the Baltic Sea (sediment fluxes)<sup>2</sup>. This matter is heterogeneous, which is reflected by the sediment types, as well as their granulometric and chemical compositions. The former source supplies silty (0.1 – 0.01 mm) and clayey (< 0.01 mm) particles, but during

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<sup>2</sup> That some of this matter derives from technogenic sources cannot be ruled out. Though clearly on a much smaller scale than sources 1 and 2, the exact quantities of this technogenic matter are debatable.

spring floods the proportion of fine sand (0.25 – 0.1 mm) is considerably greater. The latter source yields predominantly fine sand. Technogenic sediments are characterised by a very finely dispersed, even colloidal, composition, which is evidently reflected in the chemical composition of sediment types. The scale of invasion, the amounts of sedimentary matter accumulating, and the technogenic impact are revealed by budget calculations (Pustelnikovas 2003). According to these data 58.3 thousand tons of finely dispersed material are accumulated in the TSZ and 242.9 thousand tons of sandy sediment at the bottom of the NW part of the NSZ.

4. The data in Table 1 show that the total quantities of the analysed microelements in the NSZ are at the same level (or less) as in the northern sedimentation area of the Kuršių Marios lagoon, and do not exceed their values in the Holocene and glacial deposits in the nourishment areas (Pustelnikovas 1998). In the TSZ their concentrations are several times higher than in these latter deposits. The chemical composition of sediment types reflects the dependence of element quantities on the content of finely dispersed material (Emelyanov 1998). It is natural that as a result of human activities in the TSZ extreme geochemical anomalies may occur, where the contents of elements may be 5-50 times greater than in the NSZ, but the actual ratios between the natural and human-influenced forms of elements in the sediments of these two zones has remained unknown. It is only by analysing the sediments from the Port of Gdańsk that some idea of these ratios has been obtained.

**Table 1**

Average total concentrations of elements in the sedimentation zones in the port of Klaipėda (Pustelnikovas 2003)

Elements $10^{-4}$ (mg kg <sup>-1</sup> d.w.)	Sedimentation zone		Sediment types						
	NTZ	TSZ	NSZ			TSZ			
			Sand	Coarse silt	Till	Sand	Coarse silt	Fine silty mud	Till
Zn	31	172	16	38	52	140	171	287	76
Ni	16	25	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.
Cr	42	58	37	46	57	74	88	119	39
Cd	1.3	1.5	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.
Cu	10	105	3	10	16	29	26	757	24
Pb	9	62	8	10	16	n.i.	n.i.	n.i.	n.i.
C <sub>org</sub> [%]	1.5	3.2	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.

n.i. - not identify

5. Coarse-grained (sandy) material was clearly prevalent (76.0-98.6%) (Table 2) in the NSZ of Gdańsk (the Oliwa and Sulphur quays and the North Port quays). Since the coarse fractions were prevalent (85.9-99.7%) (Table 3) in the



**Table 3**

Quantity and ratio of total (T), lithogenic (LG) and hydrogenic (HG) migration (state) forms of elements in the sediments at the Vistula quays in the port Gdańsk (station W-4) in the technogenic sedimentation zone (TSZ)

Thickness [cm]	Grain-size		Content of C <sub>org</sub> , %	Quantity of elements in total sample, mg kg <sup>-1</sup> d.w./percentage of T form																	
	Fractions <0.063 mm, % of total	Type of sediments		Zn			Ni			Cr			Cd			Cu			Pb		
				T	LG	T	HG	LG	T	HG	LG	T	HG	LG	T	HG	LG	T	HG	LG	
0-20	14.1	Sand middle-small	5.0	333.7	215.7	118.0	10.8	3.3	7.5	37.8	9.4	28.4	2.0	1.4	0.6	130.5	85.3	45.2	92.7	55.5	37.2
20-40	11.2	Sand small	3.5	236.1	114.7	121.4	16.1	5.3	10.8	33.3	9.4	23.9	2.1	1.8	0.3	29.9	25.0	4.9	52.0	24.0	28.0
40-60	2.3	Sand small	n.i.	48.6	51.4		32.9	67.1		28.8	71.2		85.7	14.3		83.6	16.4		46.2	53.8	
60-80	0.9	Sand middle-small	0.4	n.i.	5.3	-	n.i.	3.4	-	n.i.	2.8	-	n.i.	0.1	-	n.i.	1.3	-	n.i.	1.2	-
80-100	0.3	Sand small-middle	0.2	3.7	2.7	1.0	1.7	1.7	rare	2.4	2.0	0.4	0.3	0.1	0.2	1.5	1.5	rare	1.25	1.2	0.05
100-120	0.8	Sand small	0.3	63.0	37.0		99.0	1.0	83.3	16.7		33.3	66.6		99.0	1.0		96.0	4.0		
				1.1	1.0	0.1	8.2	2.2	6.0	2.4	1.9	0.5	0.14	0.1	0.04	1.0	0.7	0.3	2.5	1.2	1.3
				2.7	2.6	0.1	1.7	1.7	rare	1.6	1.6	rare	0.14	0.1	0.04	1.2	1.1	0.1	4.4	1.2	3.2
				96.3	3.7		99.0	1.0	99.0	1.0		71.4	28.6		91.7	8.3		27.2	72.7		

n.i. - not identify

TSZ (Szczecin and Vistula quays), the content of finely dispersed material was higher in some layers (3.2-23.1%). This is evidence interactions between invasion of sea water, and hence of Holocene brackish water sediments. In the TSZ we can see how the characteristic features of the GBZ, natural processes and human impact have become interlaced.

6. The data in Table 4 show that the microelement concentrations in the sedimentation zones at Gdańsk Port are more variable than those at Klaipėda Port (Table 1).

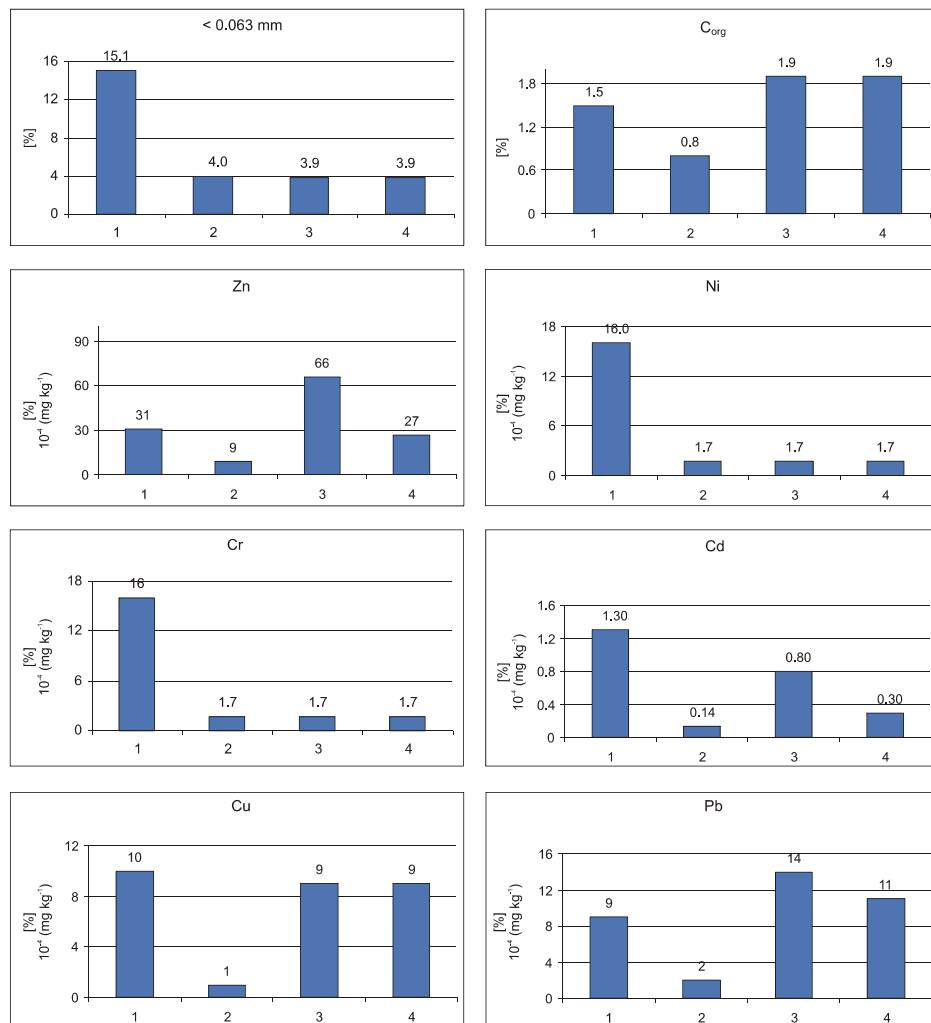
**Table 4**

Average total concentrations of elements in sedimentation zones in the port of Gdansk (Pustelnikovas et al. 2005)

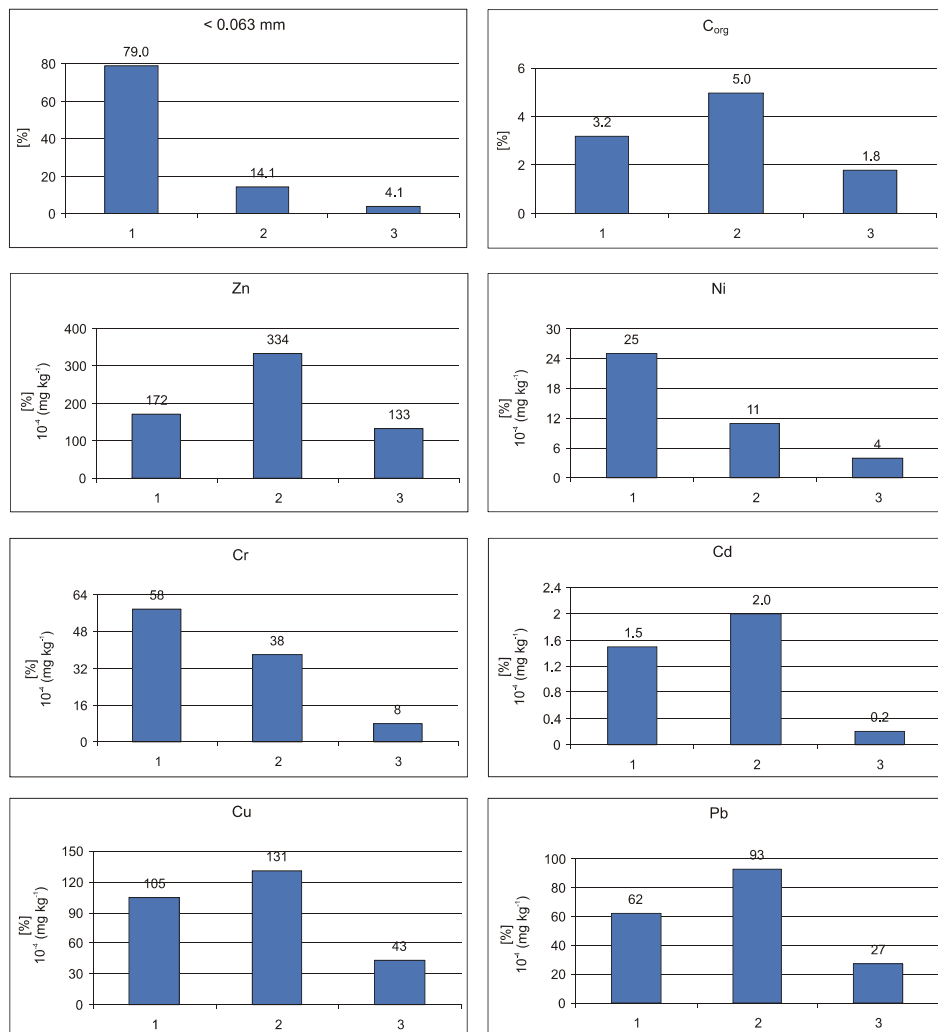
Elements, $10^{-4}$ mg kg <sup>-1</sup> d.w.)	Sedimentation zone				
	NSZ			TSZ	
	Port Północny quay	Oliwa quay	Siarkowe quay	Wiślane quay	Szczecin quay
Zn	27	9	66	334	133
Ni	1.7	1.7	1.7	11	4
Cr	6	5	9	38	8
Cd	0.3	0.14	0.8	2.0	0.2
Cu	9	1	9	131	43
Pb	11	2	14	93	27
C <sub>org</sub> [%]	1.9	0.8	1.9	5.0	1.8

In the vicinities of the North Port and the Oliwa quays, located near the sea shore and the river mouth respectively, the hydrological activity and oxygen content are high, resulting in relatively low quantities of the elements under consideration. Further there is less organic matter (C<sub>org</sub>) and finely dispersed material (in the fraction comprising grain sizes < 0.063 mm (fr. < 0.063 mm)) present than in the NSZ at Klaipėda. At the Sulphur quay, which lies on the inner boundary of the GBZ of the Martwa Wisła, these contents are higher than at the other quays at Gdańsk, and the contents of some elements (Zn, Cu) are even greater than in the NSZ of Klaipėda. Nevertheless, the mean concentrations of the study elements in the NSZ at Klaipėda are higher than in the corresponding area in the Port of Gdańsk (Fig. 2A). The main causes of this variability may be different hydrological conditions (water quantities, sea water inflow and outflow currents), geological structure and relief in the catchment areas of the two ports.

In the GBZ (the mixing zone of fresh and saline waters, where flocculation, enhanced aeration etc. take place), microelement concentrations are from 1.2 to 15 times higher in the TSZ of both ports than in the NSZ. The amounts of Zn, Cd, Cu and Pb (although not Ni or Cr) in the TSZ at Gdańsk Port are 1.5-2 times higher than at Klaipėda, and C<sub>org</sub> content is also higher at Gdańsk Port (Fig. 2B).



**Fig. 2A.** Distribution of comparable characteristics in the surface layer of bottom sediments of NSZ areas of Klaipeda and Gdańsk Port: 1- Klaipeda Port; 2-4 – Gdańsk Port quays: Oliwa (2), Sulphur (3) and North Port (4).



**Fig. 2B.** Distribution of comparable characteristics in the surface layer of bottom sediments of TSZ areas of Klaipeda and Gdańsk Port: 1- Klaipeda Port; 2-3 – Gdańsk Port quays: Wiślane (2) and Szczecińskie (3).

The total concentrations of elements in the sediments reflect human impacts on their chemical composition. Our previous data (Pustelnikovas&Bolalek 1995) have shown that by causing the resuspension of sediments, shipping considerably alters the chemical composition of interstitial waters in surficial sediments (0-5 cm) in the stagnant, accumulation subtype of sedimentation in the Klaipėda TSZ. Such changes can be observed in many other ports. In these cases the technogenic influence plays a positive role in improving the ecological conditions prevailing in water and surficial sediments. Some of the finely dispersed material raised from the bottom of the port basin gradually finds its way into the main stream of the river, which tends to reduce the microelement concentration in the TSZ sediments.

### ***Element migration (state) forms in the sediment layers***

Element migration forms in the top 127 cm of sediment at Gdańsk Port were analysed. The hydrogenic form (HG) and lithogenic form (LG) were determined together with the total form (T) of the elements. The determinations were performed at stations PN-4 (the outer, marine part of the North Port), O-2 (Oliwa) and W-4 (Martwa Wisła, Inner Port). The first two stations are located in the NSZ, the third in the TSZ (Fig. 1B, Tables 4-5).

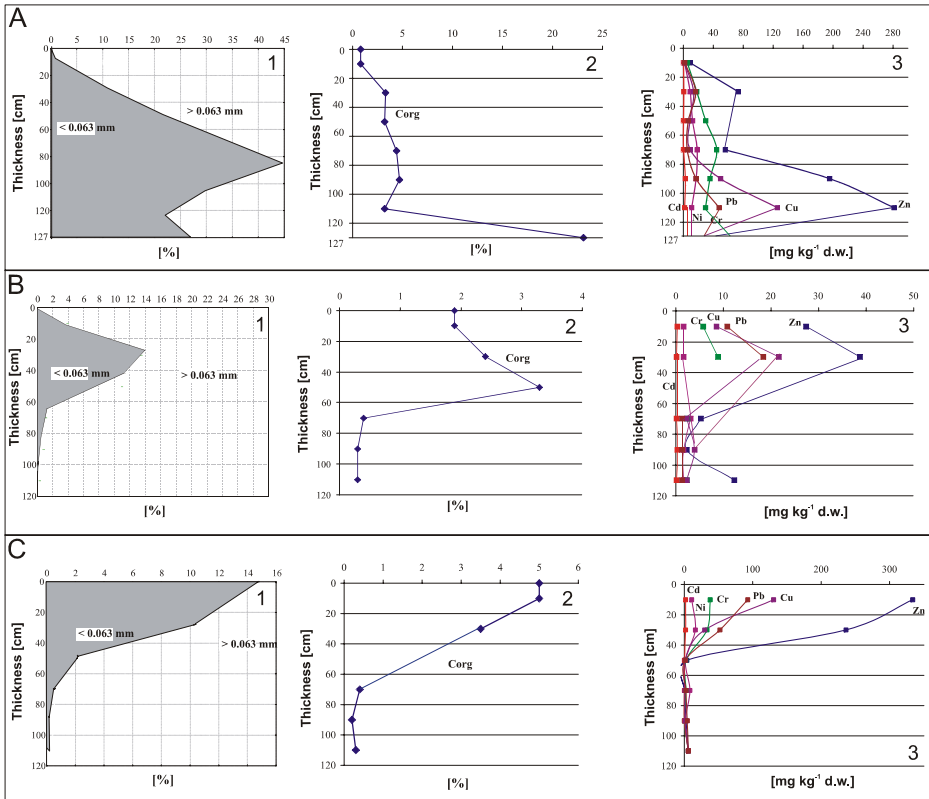
#### ***Inner Port***

A range of grain sizes (from medium- and coarse-grained to silty) comprise in the top 127 cm of sediment of the NSZ at station O-2. The fine-grained fraction is dominant between the depths of 60 and 100 cm, where the content of the finely dispersed fr. < 0.063 mm reaches 29.1-44%, whilst at other depths its content varies from 1.4 to 27.6% (Fig. 3A-1). The quantity of  $C_{org}$  varies accordingly (0.8-4.7%), and is as high as 23.1% in the bottom two cm of the sample (at 125-127 cm deep) (Fig. 3A-2). These two parameters, i.e. fr. < 0.063 mm and the  $C_{org}$  content, are chiefly responsible for the distribution of T, HG and LG forms (Figure 3A-3 to 8).

The stable, non-toxic LG form consists of elements incorporated in the crystal lattice during mineral formation.

The labile, reactive HG form comprises that portion of the elements formed by the degradation of primary minerals and the formation of their diagenetic species, and also by their migration and participation in the biological cycle in aquatic environments. This labile form (ion-exchange, organic-mineral and iron hydroxide species are released) can also be produced as a result of technogenic activity.

In the light of the above, the distribution of these element forms can be analysed by separating them into natural, non-toxic, LG and technogenic,



**Fig. 3.** Depending of chemical elements distribution in the sediments: A) thickness 0 – 127 cm from the quantity of fr.<0.063 mm and content of Corg in the st. O-2 (Oliwa quay) NSZ area of the Gdańsk Port; B) thickness 0 – 120 cm from the quantity of fr.<0.063 mm and content of Corg in the st. Pn-4 (North Port) NSZ area of the Gdańsk Port; C) thickness 0 – 120 cm from the quantity of fr.<0.063 mm and content of Corg in the st. W-4 (Wiślane quay) TSZ area of the Gdańsk Port.

potentially toxic (more or less contaminated) HG compounds. The total quantities of these forms are shown in Tables 4-5 and the changes of these quantities in the sediments thickness are presented in Figure 3A, B, C.

The average concentrations of elements in the lithosphere (clarks) are different, so likewise, their quantities are not the same in the sediments of Gdańsk Port are not equal, being (in decreasing order): Zn, Cr, Cu, Pb, Ni and Cd. In many cases their quantities decrease from the surface to the deeper layers. The exception to this rule is the increase in fr. < 0.063 mm and C<sub>org</sub> together with increasing of sediment depth. In terms of relative distribution in the NSZ, the most natural elements are Cr and Zn, their respective average HG

**Table 5**

Quantity and ratio of total (T), hydrogenic (HG – mobile, reactive) and lithogenic (LG-stable) migration (state) forms of the chemical elements in the sediments of the liquid fuel quay (station PN-4) in the port of Gdańsk

Thickness [cm]	Grain-size Fractions <0.063 mm % of total		Type of sediments	Content of C <sub>org</sub> , %	Quantity of element forms in sample, mg kg <sup>-1</sup> d.w./percentage of T form																																		
					Zn			Ni			Cr			Cd			Cu			Pb																			
					T	HG	LG	T	HG	LG	T	HG	LG	T	HG	LG	T	HG	LG	T	HG	LG																	
0-20	3.9		Sand middle	1.9	27.4	22.2	4.5	1.7	n.i.	n.i.	5.8	1.7	4.1	0.3	0.2	0.1	8.6	7.5	1.1	10.8	7.1	3.7	83.6	16.4		n.i.	n.i.	29.3	70.7		66.7	33.3		87.2	12.8		65.7	34.3	
20-40	13.4		Sand various size	2.4	38.7	33.6	4.5	1.7	n.i.	n.i.	8.9	1.7	7.2	0.14	0.1	0.04	21.7	20.7	1.0	18.4	16.6	1.8	88.2	11.8		n.i.	n.i.	19.1	80.9		71.4	28.6		95.4	4.6		90.2	9.8	
40-60	10.9		Sand various size	3.3	n.i.	67.9	n.i.	n.i.	n.i.	n.i.	4.8	n.i.	n.i.	n.i.	0.5	n.i.	n.i.	n.i.	25.3	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.
60-80	1.1		Sand middle-small	0.4	5.2	2.8	2.4	3.1	n.i.	n.i.	2.4	1.6	0.8	0.2	0.1	0.1	2.34	2.3	0.04	1.25	1.2	0.05	53.8	46.2		-	-	66.7	33.3		50.0	50.0		98.2	1.8		96.0	4.0	
80-100	0.6		Sand middle-small	0.3	2.3	1.4	0.9	1.7	n.i.	n.i.	n.i.	1.6	n.i.	0.3	0.1	0.2	3.9	3.1	0.8	1.25	1.2	0.05	60.9	39.1		-	-	-	-		33.3	66.7		79.5	20.5		96.0	4.0	
100-120	0.2		Sand middle-grab	0.3	12.3	1.5	10.8	1.7	n.i.	n.i.	2.3	1.6	0.7	0.2	0.1	0.1	2.3	2.1	0.2	1.25	1.2	0.05	12.2	87.8		-	-	-	-		50.0	50.0		91.3	8.7		96.0	4.0	

n.i. - not identify

contents from the sediment surface to a depth of 127 cm are 11% and 29%. The corresponding contents of Cu, Cd, Ni and Pb are 45, 50, 52 and 54%. These four elements are anthropogenic and as such exhibit greater mobility.

In the TSZ of the inner Port, medium-small- and small-grained sands prevail, and the contents of fr. < 0.063 mm here are 11.2–14.1% in the layer 40 cm of the sediment, and below that (40-120 cm) only 0.3-2.3% (Figure 3B-1). Correspondingly, the  $C_{org}$  content decreases from 3.5-5% in the upper layer to 0.2-0.4% in the lower one (Table 3).

At NSZ station O-2, where oxidising conditions prevail, the quantities of fr. < 0.063 mm and  $C_{org}$  increase below a depth of 40 cm. The total form concentrations of most of the elements also rise rapidly beneath this point. The HG/T ratio clearly decreases, except in layer (125-127 cm), which contains maximum quantities of  $C_{org}$  (cf. Tables 4 and 6). As a result of the ageing of the

**Table 6**

Ratio of element forms in the sediment layers of different sedimentation zones in the port of Gdańsk

Sedimentation zone	Area	Thickness [cm]	Ratio of element forms/average contents in the thickness											
			Zn		Ni		Cr		Cd		Cu		Pb	
			HG/T	LG/T	HG/T	LG/T	HG/T	LG/T	HG/T	LG/T	HG/T	LG/T	HG/T	LG/T
NSZ	fresh water area	0-127	0.29	0.71	0.52	0.48	0.11	0.89	0.50	0.50	0.45	0.55	0.54	0.46
	marine water area	0-120	0.60	0.40	n.i.	n.i.	0.46	0.54	0.46	0.54	0.90	0.10	0.89	0.11
TSZ	fresh water area	0-120	0.73	0.27	0.60	0.40	0.62	0.38	0.66	0.34	0.82	0.18	0.55	0.45
Ratio: TSZ/NSZ (fresh water) 0-120 / 0-127			2.5	0.4	1.1	0.8	5.6	0.4	1.3	0.7	1.8	0.3	>1	<1
NSZ (marine water area)/NSZ (fresh water area) 0-127/0-120			2.1	0.6	n.i.	n.i.	4.2	0.6	0.9	1.1	2.0	0.2	1.6	0.2
TSZ (fresh water area)/ NSZ (marine water area) 0-120/0-120			1.2	0.7	n.i.	n.i.	1.3	0.7	1.4	0.6	0.9	1.8	0.6	4.1

n.i. - not identify

sedimentary matter, the more mobile HG forms of the elements gradually decompose and rejoin the biochemical cycle in the form of simple, soluble ions. The anomalous quantities of  $C_{org}$  and HG (except Cr) in the deep (125-127 cm) layer (finely dispersed matter) are probably derived from remnants of the biological activities of living organisms (pellets, globules). This is especially evident in the TSZ (station W-4), at a depth of 40 cm along with an abrupt decrease in the proportions of fr. < 0.063 mm,  $C_{org}$  and total form (Table 3), there is a considerable decrease in the quantities of nearly all the elements (cf. Tables 3 and 6). Regardless of the distribution pattern of total form of the elements with regard to sediment depth, comparisons of the mean HG/T and

LG/T in both sedimentation zones indicate that while these ratios for particular elements are very different, they are always higher in the TSZ than in the NSZ (Table 6). In ascending order, these ratios are 1.02 (Pb), 1.1 (Ni), 1.3 (Cd), 1.8 (Cu), 2.5 (Zn) and even 5.6 (Cr). As previously shown, the main reason for this increase can only be the biological activities of organisms, by no means can it be due to technogenic influences.

### *Outer Port*

Analyses of the sediments from station PN-4, and the hydrological data from the inner Port, show that the grain size distribution and chemical composition of the sediments are much the same in both areas (Tables 5 and 6). In the outer Port only the NSZ was analysed. These quantities were much lower than in the NSZ and especially in the TSZ of the inner Port. In contrast, the HG forms were relative higher in the outer than inner port area. While there is a distinct decrease in the quantities of the T form, there is a relative increase in part of the HG form in the outer Port. The mean HG/T ratios for various elements in the sediment are 0.9 (Cd), 1.6 (Pb), 2.0 (Cu), 2.1 (Zn) and 4.2 (Cr).

In this case, the features of marine sedimentation in the river-sea geochemical barrier zone, together with the chemical processes and aeration, undoubtedly affect the conversion of the dissolved forms of elements into hydrogenic, colloidal or sedimentary forms.

## CONCLUSIONS

1. The distribution of the T form of the investigated elements depends on the quantities of fr. < 0.063 mm and  $C_{org}$ .
2. The concentrations of elements below a sediment depth of 40 cm decrease sharply as a result of mineralisation and degradation. The increase in HG at the expense of T in the deeper sediments can be explained by the presence of HG due to the biological activities of organisms (pellets, globules).
3. Natural and technogenic sedimentation zones (Table 7) were distinguished in both ports on the basis of the occurrence of the T forms of the elements under investigation.
4. The ratios of the three migration forms of elements in the sediment thickness are different for different microelements, but are always higher in the TSZ than in the NSZ.
5. Natural sedimentation conditions prevail in most cases. Anomalous T concentrations in sediments only occasionally exceed the permitted norms, while HG concentrations were never seen to be greater than the permitted norms.

**Table 7**

Distribution of the total (T) form of the chemical elements in surficial sediments in the sedimentation zones in the ports of Klaipėda and Gdańsk

Port	Sedimentation zone	Grain-size fractions		C <sub>org</sub>	Elements (mean content), mg·kg <sup>-1</sup> d.w. (C <sub>org</sub> -%)								Remarks
		>0.063 mm	>0.063 mm		Zn	Ni	Cr	Cd	Cu	Pb			
Klaipėda	NSZ	84.9	15.1	1.5	31	16	42	1.3	10	9	Standard 462002 of Lithuanian Environment Ministry N <sup>o</sup> -77 of 2002 year		
	TSZ	21.0	79.0	3.2	131	22	58	1.5	105	62			
Largest allowed concentration norms for the dredged material	Total area of port	-	-	-	300-400	50-100	100-200	2-5	100-200	100-200			
Gdańsk:													
-Oliva quay	NSZ	97.0	3.0	1.3	34	<1.7	7	0.4	6	9	According to norms for the North Sea (Helcom - 1966)		
-Liquid fuels quay (North Port)	TSZ	96.1	3.9	1.9	27	<1.7	6	0.3	9	11			
-Vistula quay		90.9	9.1	3.4	233	8	23	1.1	87	40			
Largest allowed concentration norms for the dredged material	Total area of port	-	-	-	350	50	150	25	40	100			

6. In order to determine actual levels of pollution by chemical substances in port sediments, detailed studies of the migration forms of the elements in these sediments need to be carried out.

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