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Geoecological estimation of sedimentation peculiarities of chemical element genetic forms in some basins of the South Baltic

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This work, from the geoecological positions, presents quantitative relation data on elements formed by the interaction of natural sedimentation processes and human impact on the sediments from the study areas – the Gulf of Finland, the Gdansk Bay, Klaipėda and Gdansk ports.

The total (T), lithogenic (stable – LG) and hydrogenic (mobile, reaction capable – HG) migration (state) forms of Zn, Cr, Cd, Cu, Pb, Ni, etc. were analysed. Among the latter genetic forms, ionic exchange (IE), organic–mineral (OM) and hydroxidic (HO) species were analysed as different but most reaction-capable forms. All these forms reflect the regularities of different course of sedimentation processes during the last 10 (and more) thousand years in the history of the Baltic Sea possibly affected by anthropogenic influence in the last two centuries.

A detailed analysis of these forms in the stratum of bottom deposits has revealed that the distribution of elements and formation of their anomalous quantities in the Gdansk Bay and the Gulf of Finland were determined by natural processes: geological structure, rock composition, peculiarities of geochemical barrier zones, changes of hydrological conditions.

During the many-sided investigation of Klaipėda and Gdansk port sediments, the areas of natural (NSZ) and technogenic (TSZ) sedimentation zones were distinguished. Anomalous quantities of elements, specific distribution of their migration forms, hemistagnation conditions and the nearness of technogenical sources are typical of the latter zone. The quantities of elements in the NSZ of marine influence are smaller than those in both sedimentation zones of the river part of the Gdansk Port. The balance of HG, LG and T forms in the port sediments of both zones is different for the various elements, but in the TSZ it is always greater than in the NTZ. The distribution of T form depends on the quantity of fraction <0.063 mm and on the concentration of C_{org}. Going deeper into the sediments, their quantities sharply decreased, but the part of HG form evidently increased. Their presence after mineralisation and destruction of sedimentary matter can be explained only by their concentration in the remnants of biological activity.

The data presented in this work indicate that some geochemical anomalies in the TSZ of both ports and in the Sea Basin only in rare cases exceeded the maximum permissible concentrations (MPCs) for the dredged and dumped material and for the biological conditions. This is not enough to prove the popular conception of global pollution. To determine the more actual (toxic) level of pollution, more detailed investigations of element state forms (especially their HG species) are necessary. The analysis of element forms indicates the necessity of adjusting the existing MPCs.

Key words: migration forms, sedimentation zones, elements distribution, the Baltic Sea

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INTRODUCTION

On a global scale, human activities, the level of technologies and the use of resources have no significant effect on the exogenous processes. Chemical elements and compounds are naturally washed out of minerals, rocks and soil and then, during migration and sedimentogenesis, turn into new formations. The products washed out in different land and water media come in contact with life and cause no negative impact on it, even at anomalous concentrations. These are often at the same level or even higher than in apparentley polluted areas (Emelyanov, 1995). This is not pollution in fact, since the sum of different element forms is not an indicator of anthropogenic pollution. Why? It is rather common that media come in contact with life and cause no negative impact on it, even at anomalous concentrations. These are often at the same level or even higher than in apparently among the migration (state) forms of the same element there are some that cause no risk to life, i. e. the natural (lithogenic) variety present in the crystal lattice of minerals. The hydrogenic (mobile) element species are regarded as indicators of potential human impact, but they do not reveal the role of technogenesis, since this is the prevailing migration form for the major part of elements. Thus, while performing investigations of these forms (species) the most toxic species should be identified, and these forms should be regarded as factual pollution (Pustelnikovas, 2000).

Geochemical trend works generalising heavy metal distribution (Ferguson, 1990; Ebbing et al., 2002; Radzevičius, 2002; Jokšas, 1999; Jokšas et al., 2003; Protasowicki, Niedzwiecki, 1993; etc.) in different basins deal only with the total quantities (T) of elements. These quantities, exceeding the maximum permissible concentrations (MPCs) (HELCOM, 1986), are most often regarded as indicators of pollution complicating the environmental state.

The initial estimations done by us on the basis of comprehensive sedimento-geochemical distribution of T quantities in the bottom sediments of the Kuršių Marios (Curonian) Lagoon and Klaipėda Port area already showed the natural processes to prevail (Pustelnikovas, 1996, 1998, 2002, 2003). An exceptional role of these processes was shown in the estimation of the hydrogenic (HG) element form distribution in the Gdansk Port bottom sediments (Bolalek et al., 1999; Dembska et al., 2001; Pustelnikovas et al., 2005; Radke et al., 2004). Analyses of five forms (species) of Zn, Cu, Cr, and Ni elements in the bottom sediments of different genesis and age in the Gdansk Bay and the Gulf of Finland (Pustelnikovas, Zabukas, Jašan, 2004) confirmed a low influence of technogenesis on heavy metal distribution during sedimentogenesis and further diagenesis. We relate the start of investigations of this trend to the studies of the abovementioned forms in rocks, as well as in the areas of element dispersion and technogenic anomalies (Лукашев, Симуткина, 1976; Лукашев, 1986, Симуткина, 1992).

The aim of the present investigation was to determine the migration (state) forms of some elements, which could be related to both anthropogenic influence and natural factors, as well as to show their distribution in the recent sedimentation media (geochemical-technogenical barriers – ports, bottom surface of the Baltic bays) and the geological evolution of the Baltic Sea (at different layers of sediments). The areas and stations of the research are shown in Fig. 1 A, B, C, D.

The objective of the present paper was to solve the problem by applying the method of consequential analysis.

1. MATERIALS AND METHODS

The material was obtained in the Gdansk Bay (2 stations) and the Gulf of Finland (5 stations) areas during several cruises of r/v *Ayou-Dag* (Estonia) and *Academic Kurcha-*

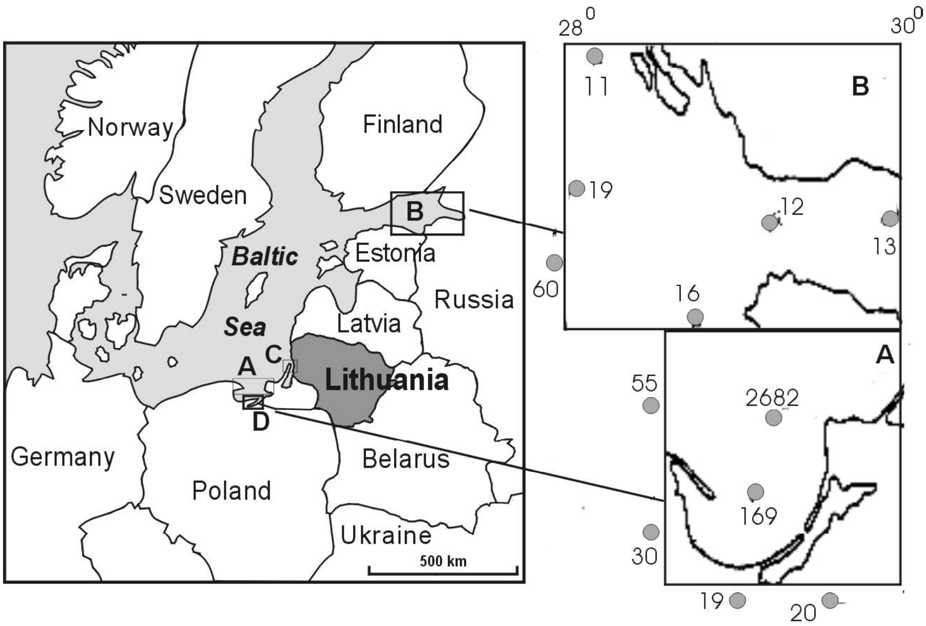

Fig. 1. Study areas of various Baltic Sea basins: *A* – Gdansk Bay, *B* – Gulf of Finland, *C* – Klaipėda Port (Klaipėda strait area, see Fig. 2), *D* – Gdansk Port (see Fig. 3)

1 pav. Įvairių Baltijos jūros baseinų tyrimų arealai: *A* – Gdansko įlanka, *B* – Suomių įlanka, *C* – Klaipėdos uostas (Klaipėdos sąsiauris, žr. 2 pav.), *D* – Gdansko uostas (žr. 3 pav.)

tov (Russia) in 1991–1995. In the Gdansk Bay (St. 2682), a 13.75-m sediment stratum formed in nearly all the Baltic Sea existence time (more than 10 thous. years) was analysed. The sediment thickness at Station 169 (38 cm), according to the sedimentation rate 1.4 mm·y^{-1} (Pustelnikov, 1982), could be formed during the last 250–270 years (see Fig. 1, A). The distribution of heavy metals in the Gulf of Finland was determined at stations 11, 12, 13, 16 and 19 (Fig. 1, B). Samples were taken for various sediment types and from different surficial layers, also from geochemical areas of this bay. At the sedimentation rate about 1 mm y^{-1}, this sediment stratum was formed in no more than 60–70 years.

In the Klaipėda and Gdansk Ports, this material was obtained during long-term investigations of both areas in 1990–2004. In the Klaipėda Port (strait), nine monitoring stations were distinguished, which since 1995 have been used for comprehensive research aimed at solving scientific-technological problems (Fig. 1, C, Fig. 2). These stations reflect different sedimentation aspects of the Klaipėda Strait as a geochemical barrier zone (GBZ) affected by human activity. On this basis, the natural (NSZ) and technogenic (TSZ) sedimentation zones were distinguished.

Similar studies were carried out also in the Gdansk Port (Fig. 1, D, Fig. 3), in the areas of five quays, four of which are located in the Martwa Wisła riverbed and one, the most seaward Northern Port, is located in the Gdansk Bay about 2.5 km to the northeast from the mouth of this river and of the main port structures. In the Gdansk Port, the NSZ and TSZ zones were also distinguished.

The consequential analysis was based on the field improvements from different horizons of the thickness studied (in Klaipėda Port – initially 0–2, 2–5, 0–10 cm, in Gdansk Port – 0–20, 20–40, 40–60, 60–80, 80–100, 100–120 cm, virtually 0–140 cm). Sediments were taken from aboard r/v *Gintaras* (Klaipėda) and *Dr. Lubecki* (Gdansk) with a Van Veen type dredger and gravity (diameter 40 mm) and vibro (100 mm) corers.

The sediments until analysis were stored at 4 °C. The dredger and corer material was evaluated macroscopically and then divided with a plastic spatula into some (1–2) segments up to 20 cm, which were packed in marked polyethylene bags. The water content and loss of ignition were determined for each sample. After drying at 110° C, these samples were homogenised in a porcelain mortar, then each sample was split into two subsamples used for grain-size and chemical analyses of heavy metals (microelements).

The grain-size characteristic was determined by sieving the sediments through metal sieves with 2, 0.5, 0.125, 0.063 and 0.032 mm mesh size[1].

The sediments used for chemical analysis were sieved through plastic sieves with 2, 0.063 and 0.032 mm mesh size.

The determination of the contents of Zn, Ni, Cr, Cd, Cu and Pb in hydrogenic (HG) and total (T) forms were performed using the prepared samples. The first one was separated by applying the extraction procedure with 1N HCl to all grain size fractions of the sediments (Luoma and Bryan, 1981; Лукашев, 1986), whereas the total form was determined after sediment mineralisation in a microwave with the use of concentrated HF and HNO_3. The undissolved remnants after determination of HG form were LG.

The HG species were determined after dissolution of sediments in these solutions: IE – 1N CH_3COONa, OM – 30% H_2O_2, and HO – 3% HCl (Симуткина, 1992).

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

2. DESCRIPTION OF THE STUDY AREA

The total catchment area of the Gdansk Bay measures up to 220 thous. km^2. Its largest part (88%) belongs to the Vistula River basin. The mean annual river runoff into the Gdansk Bay is estimated at 34.4 km^3, with the Vistula River accounting thus for 87% of the total land runoff into this bay (Mikulski, 1970). The deepest part of the bay accumulates sediments brought in by the rivers and entering from the shore and sea bottom as a product of abrasion and erosion. Besides, sedimentary matter is being produced in sea water by the biological processes. In the Gdansk Bay, there are exclusively terrigenous sediments with a low content of $CaCO_3$ (<3–5%) and a higher content of C_{org} (up to 5%, occasionally even to 6.1%). In the deepest parts of this bay (Gdansk Basin) occur recent sediments (mud silty-clayey, hor. 0–30 cm aged about 100–200 years, and Lower Holocene (0.3–13.75 m) sediments (clay) whose age reaches the last 10 (and more) thousand years (Emelyanow (ed.), 2002).

The general characteristic of the Gulf of Finland is given in (Пустельников, 1992). The catchment area of this bay makes 421 thous. km^2 and the annual river runoff from it reaches 114.1 km^3 (25% of all fresh water input into the Baltic Sea). The main arteries of nourishment by the sedimentary material are the rivers Neva, Narva and Kemijoki. The average depth of the bay is 38 m, the maximum being 123 m. Strength west winds form the head of marine water up to 2–4 m. Every year 1.2 mill. t of suspended matter (0.8 mill. t from the river output and 0.5 mill. t from the Neva River) is accumulated mostly in the near-mouth shallow water area. The dissolved flow of sedimentary matter into the Gulf of Finland makes up 5.8 mill. t y^{-1}. Geologically, this bay

[1] In the case of the Klaipėda Port, analysis of sediments was carried out using the so-called water-mechanical and pipette techniques, because in this basin (in TSZ area) thin-dispersed sediments – silty and silty-clayey muds – are located. The following fractions were obtained: 2, 1, 0.5, 0.25, 0.1, 0.05 and 0.01 mm mesh size.

is a depression on a crystal basement, the rocks of which in the north part are old archaic and in the south part younger sedimentary rocks (Cambrian sand, sandstone and Ordovician limestone). The basement in the south direction is sunken under the sedimentary rocks by the line Saint-Petersburg – Chankowiemi Peninsula. On the surface layer of the bottom there are glacial and postglacial deposits (clay, till, sand, gravel, silt and mud). During the latest stages of the Bay development, the chemogenic formation of Fe–Mn nodules enriched by various microelements took place.

Being an interface of fresh and salty water (the Klaipėda Strait and the Martwa Wisła River), the areas in which the Klaipėda and Gdansk Ports are located, perform the functions of a so-called geochemical barrier zone (GBZ) where many hydrological, sedimentological, biological, technogenical and other factors and compounds are concentrated. The joint action of these factors can complicate the ecological situation in these boundary areas and frequently produces a potential negative effect on the recreational conditions in the surrounding areas.

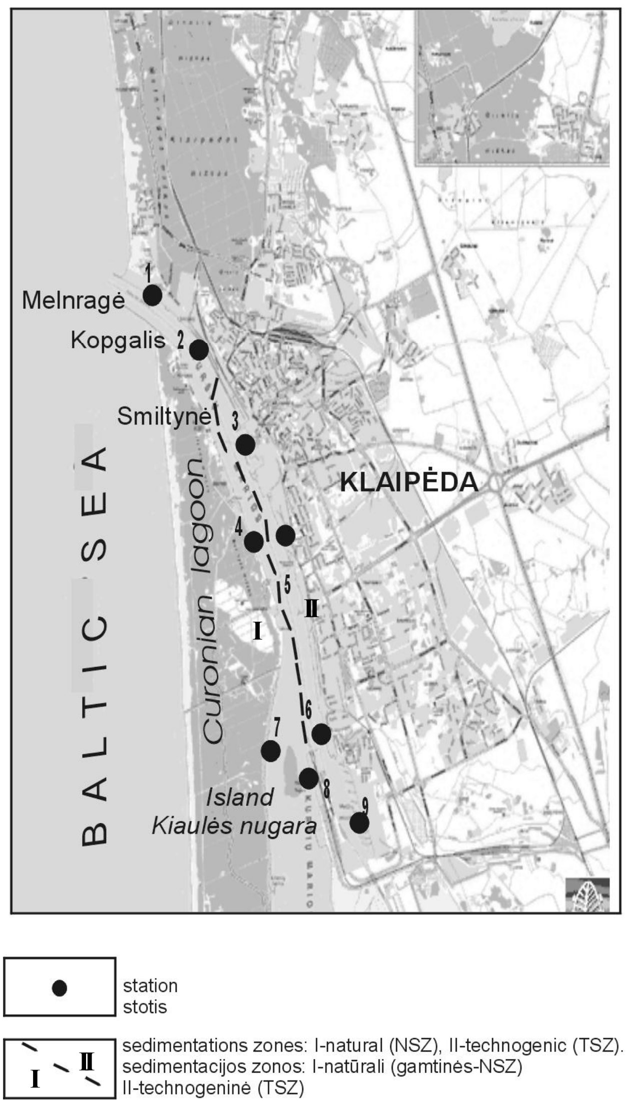

Fig. 2. Study area of Klaipėda Port (see Fig. 1, *C*)
2 pav. Klaipėdos uosto tyrimų arealas (žr. 1 pav., *C*)

The hydrodynamic regime is one of the major factors in the formation of geochemical anomalies in the bottom of the study areas. It results in the migration patterns of sedimentary material, which depend on the velocity and direction of currents. In these cases, sediment fluxes are often predetermined by morphometric changes of the bottom during reconstruction of ports and dredging their aquatories. This activity is reflected in accumulation processes, intensification of various chemical processes and silting up of some port areas. These factors in turn affect the dredging and soil dumping possibilities in the sea or on the land. Analysis of the navigation factors, i. e. of the mechanical disturbance of the upper layer of sediments and, consequently, its aeration, is rather important in estimating the ratio between natural and technogenic constituents of sedimentation. At the same time, it makes easier to perceive many aspects of the actual state of such boundary ecosystem and the topical problems of the development of both port city areas and their infrastructure.

A comprehensive characteristic of the Klaipėda Port (strait) is given in (Pustelnikovas, 2002). Here we want to underline that it is a complicated zone of a geochemical barrier, i. e. a hydrosystem with pulsating fluxes of energy, sediment migration and biomass exchange

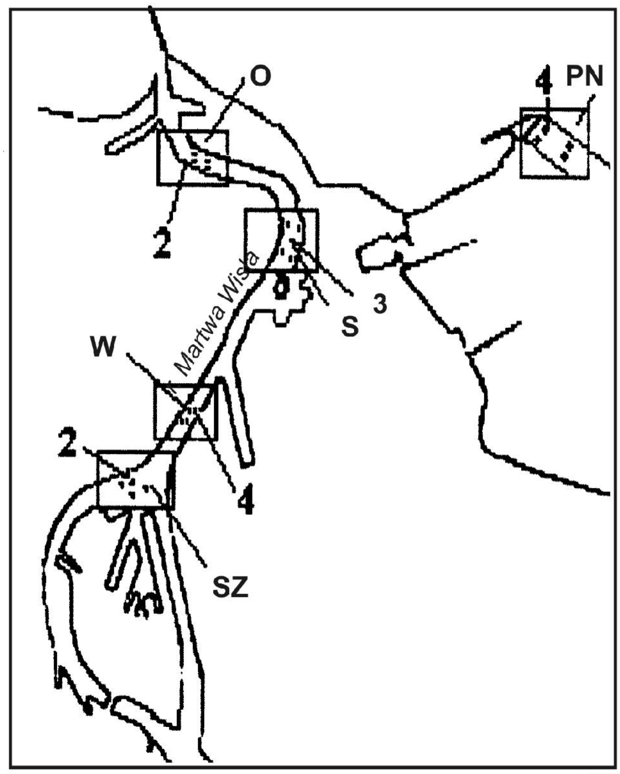

Fig. 3. Study areas of Gdansk Port (Fig. 1, *D*).
Inner Port, quais: SZ – Szczecin, W – Vistula, S – Sulfhur, O – Oliwa. *Outer Port*, quay: PN – Northern Port; 2, 3, 4 – numbers of stations on the quays

3 pav. Gdansko uosto tyrimų arealai (žr. 1 pav., *D*).
Vidaus (upinio) uosto krantinės: SZ – Šcecino, W – Vyslos, S – Lieros, O – Olivos. Išorinio (jūrinio) uosto krantinės: PN – Šiaurės uostas; 2, 3, 4 – tyrimo stočių numeriai atitinkamose krantinėse

between the freshwater Kuršių Marios (Curonian) Lagoon and the salty Baltic Sea. This sedimentation area of extreme conditions concentrates various natural factors (grain-size differentiation, variations of sedimentary matter migration forms) and a periodic input into the strait of marine water containing sedimentary matter.

In this area, the distinguished sedimentation zones are distributed according to the hydrodynamic conditions. The natural sedimentation zone is the main water artery into the sea. This zone includes the navigation channel and extends from the sea ferry station to the KLASCO quays. Further in the north it includes the entire strait (Fig. 2-I). In many cases, sediments fail to accumulate in the bottom of this zone, because strong water flows carry the matter into the Baltic Sea.

The technogenical sedimentation zone is situated in the eastern part of the strait. It is far away from the main flow of water and sedimentary matter. It includes the areas of trade and fishing ports, shipbuilding yards, landing stages and back creaks. Stagnant and semi-aeration conditions prevail in these areas (Fig. 2-II). These areas receive uncleaned city wastewater as well as building and navigation wastes. Navigation resuspends and redistributes the sedimentary matter.

The port of Gdansk is located in the Gulf of Gdansk close to the mouth of the Martwa Wisła River. The length of the Martwa Wisła between Przegalina and the Northern Port is 27 km (2.5 km of the Śmiała Wisła River should be included). The mean values of current speed range from 2 to 5 cm $\cdot$ s^{-1}, while salinity ranges from 2.48 to 6.13 (average <5) ‰ (Majewski, 1990). Influxes of saltwater from the sea occur in the near-bottom water layer in the riverbed. The Martwa Wisła brings into the Gdansk Bay only 0.99% of the total Wisła (Vistula) River output.

The principal factors affecting the water circulation are NNW winds with a speed of 10 m·s^{-1}, which cause the water level to rise, but SE winds exert on opposite effect. The outflowing current is extremely sluggish (0–0.1 m·s^{-1}, mean speed 0.02 m·s^{-1}), rarely achieving 0.35 m·s^{-1}. Storm surges penetrate only as far as the Port Canal, where their energy is dissipated by breakwaters and other hydroengineering structures. The river bed in the port can be as much as 12 m deep. Quaysides line both sides of the river.

The port of Gdansk is divided into two areas – the inner and the northern ports. The former is located on either bank of the Port Canal and on the eastern bank of the Canal Kaszubski.

The oldest port structures are located in the Martwa Wisła riverbed. On the main branch of the river, just beyond the Ostrów Island, are located the Szczecin (Wood Terminal) (Sz) and Wistula (small cargo and grain, coal and ore) (W) quays (Fig. 3). Sulphur is transferred at the Sulphur Quay. In the Port Canal, the Oliwa quay (O) (small cargo, e. g., vegetables and fruit) is located. This canal ends in the sea at the entry to the Port Gate harbour.

The most seaward, 2.5 km from the shoreline, is the Northern Port (PN) area. The handling of coal, liquid fuels, i. e., crude oil, gasoline, diesel fuel and heating oil, takes place in this port (Kreft, 1996), which is the youngest part of the Gdansk Port; there are two 19-m deep quays.

According to P. Szwernowski (1957), the rate of sedimentation in the port of Gdansk is 7 cm·y^{-1}. For comparison, sedimentation rates elsewhere in the Baltic Sea are 0.13–2.92 mm·y^{-1} (Pemkowiak, 1992) or 1-2 mm·y^{-1} (Winterhalter et al., 1992; Szczepanska, Uscinowicz, 1994). Because of these huge amounts of sediments entering the port (the same applies to Klaipėda), the ship and port channels have to be dredged to the depths enough 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 bottom sediments from the port channels and to dump them on land or at specified sites in the sea (Žaromskis, Gulbinskas, 2000; HELKOM, 1996). In order to forestall a possible contamination of the marine environment, it is essential to know the grain-size distribution peculiarities and chemical composition of these bottom sediments.

3. GRAIN-SIZE DISTRIBUTION PECULIARITIES AND CHEMICAL COMPOSITION OF SEDIMENT THICKNESS OF THE STUDY AREAS

Oligomictic conglomerates (sand and silt) lie in the Gdansk Bay at the water depths of 30–50 m and in the area of the Northern Port in Gdansk. Silty-clayey and clayey mud with a significant admixture of C_{org} (up to 2.5–3%) prevail deeper. These sediments are half-liquid at the surface and become soft at a depth of 30–40 cm. Going deeper, due to pressing and diagenesis, the sediments turn into plastic clay met in all Holocene beds in the Gdansk Basin. According to E. Emelyanov (2002), at these water depths the surficial sediments contain fine sand, sandy silt, clayey silt and silty clay. The share of fraction <0.01 mm, which strongly accumulates microelements, increases from 4% in sand to 29.6% in fine-silty mud, to 61.8% in silty-clayey mud and even to 79.7% in clayey mud in the central part of the Gdansk Basin.

In the Gdansk Bay (St. 2682, 111 m, Fig. 1, A), five state forms and species of Zn, Cu, Cr and Ni elements have been analysed (Table 1). The investigation covered both recent and practically all Holocene sediments of the Baltic Sea as a whole. Only recent sediments were studied at Station 169 (0–38 cm, water depth 85 m), however, only T form and hydrogenic species of OM were studied here. A detailed analysis of these investigations is given in (Pustelnikovas, Zabukas and Jašan, 2004), while the present paper presents only brief comments on the regularities in the distribution of the forms (species) of the elements studied.

Comparative results of Table 1 and Table 2 (compiled from Table 1 data) show a rather high content of the

Table 1. **Distribution of total (T), lithogenic (LG) and hydrogenic (HG) migration forms of elements (Zn, Ni, Cr, Cu) in the sediment thickness (st. 2682) of the Gdansk Bay**
1 lentelė. **Suminės (T), litogeninės (LG) ir hidrogeninės (HG) elementų (Zn, Ni, Cr, Cu) migracijos formų pasiskirstymas Gdansko įlankos (st. 2682) nuosėdų storymėje**

Horizon, m	Type of sediments	Zn, ppm /% of T form						Ni, ppm /% of T form						Cr, ppm /% of T form						Cu, ppm /% of T form					
		T	Migration forms					T	Migration forms					T	Migration forms					T	Migration forms				
			LG	HG	Species of HG form				LG	HG	Species of HG form				LG	HG	Species of HG form				LG	HG	Species of HG form		
					IE	OM	HO				IE	OM	HO				IE	OM	HO				IE	OM	HO
0.3–0.4	Mud silty-clayey	120/100	52/43.3	68/56.7	14/11.7	33/27.5	21/17.5	78.6/100	63/80.2	15.6/19.8	rare	8.6/10.9	7/8.9	116/100	83/71.5	33/28.5	14/12.1	11/9.5	8/6.9	46.2/100	16/34.6	30.2/65.4	1.2/2.6	2.0/4.3	27/58.5
3.5–3.6	Clay Holocenic, marine	92/100	45/48.9	47/51.1	3/3.3	4/4.3	40/43.5	104.9/100	80/76.3	24.9/23.7	2.6/2.5	3.3/3.1	19/18.1	96/100	83/86.5	13/13.5	2/2.1	5/5.2	6/6.2	39.6/100	8.3/21	31.3/79	2.3/5.8	13.2/32.8	16/40.4
10.76–10.82	Clay Holocenic, marine	94/100	46/48.9	48/51.1	rare	3/3.2	45/47.9	77/100	69/89.6	8/10.4	rare	rare	8/10.4	92/100	78/84.8	14/15.2	1.6/1.7	1.4/1.5	11/12	41/100	11/26.9	30/73.1	3/7.3	6/14.6	21/51.2
13.65–13.75	Clay Holocenic, marine	98/100	55/56.1	43/43.9	rare	1/1	42/42.9	85/100	61/71.8	24/28.2	4/4.7	2/2.4	18/21.2	110.8/100	96/86.6	14.8/13.4	2.1/1.9	0.7/0.6	12/10.9	42/100	14/33.3	28/66.7	6/14.3	6/14.3	16/38.1
Average 0.3–13.75		101/100	49.5/49.3	51.5/50.7	4.3/3.7	10.2/9	37/38	86.4/100	68/79.4	18.1/20.6	1.6/1.8	3.5/4.1	13/14.7	103.7/100	85/82.4	18.7/17.6	4.9/4.4	4.5/4.2	9.3/9	42.2/100	12.3/28.9	29.9/71.1	3.1/7.5	6.8/16.5	20/47.1

elements studied in all sediment layers and not very pronounced changes of them in different sedimentation stages. At the same time, one can see that T form content is only slightly higher in recent sediments (0–40 cm) potentially affected by technogenesis than in the earlier Baltic Sea stages. A bit sharper differences at the 0.3–0.4 m horizons and 0–1 cm surface layer in Table 2 are seen only for Zn (1.2 (1.4)) and Cu (1.1 (1.2)), while for Ni (0.9 (0.7)) and Cr (1.1 (0.8)) the T form content is even lower in the surface layer (0–1 cm). All this reflects, first of all, changes in sedimentation conditions and the rates as well as peculiarities in element migration for different forms even in the lower part of recent sediment layers (0.3–0.4 m). Similar conclusions arise while comparing the distribution of LG and HG forms. In this case, different migration features of elements, i. e. mobility and participation in metabolism, are manifested better. This is obvious: (1) according to a similar LG form content in all layers (with a slight increase with the depth for Cr (0.9) and a decrease for Cu (1.1), and (2) due to a higher content of Zn, Cr and Cu and a lower content of Ni (0.65) in the HG form in the recent sediments.

Estimation of the relationship between the percentage of these forms and the total (T) content in the sediments shows that migrating Zn and Cr (their lithogenic form) content in the surface sediments is lower than in the deeper horizons notable for pressed Holocene clay, while Cu content is at the same level and Ni content is slightly higher at the surface. Such distribution for HG form of the same elements is inverted (Table 2).

On the whole, the results show the obviously natural origin of the elements studied. Which geochemical features (and at what scale) could be indicators of human (technogenical) impact on the distribution of these elements? We try to answer these questions by studying IE, OM and HO species of the hydrogenic form, since they are very important quantitatively for the surface sediments (0–1 cm). Their potential formation under technogenesis conditions could be explained by the "freshness" of these species and their absence among the stable compounds found in the early stages of sedimentogenesis. To do this, analytical extraction by common chemical reagents is used (see Part 1). The species most closely related to technogenic impact are thought to be ion exchange and organic-mineral species. Beside technogenic impact, hydroxidic species might be formed during various sedimentogenesis stages in the geochemical barrier zones, as well as during the diagenesis when organic metal compounds are formed (Emelyanov, 1998).

The IE species content in the sediments for all elements studied ranges from traces to 14 ppm (0.0–14.3% of the HG form content) (Table 1). It should be noted that the maximum content of Ni, Cr and Cu elements is determined at the lower boundary of the strata, i. e. 13.65–13.75 m horizon, and only for Zn it is found at the basis of the surface layer (0.3–0.4 m) – 14 ppm (11.7%). The surface of this layer (0–1 cm) should contain higher IE element quantities as is for OM species at station 169

Table 2. **Relationship of element forms and species between their contents (ppm and % of T form) in recent (0–40 cm) and early Holocene (13.65–13.75 m) sediments in the Gdansk Bay**

2 lentelė. **Elementų formų ir atmainų koncentracijos santykis dabartinėse (0–40 cm) ir ankstyvojo holoceno (13,65–13,75 m) nuosėdose Gdansko įlankoje**

Element forms (species)	Ratio between 0.3–0.4 m (0–1 cm): 13.65–13.75 m layers							
	Zn		Ni		Cr		Cu	
	ppm	%	ppm	%	ppm	%	ppm	%
T	1.2(1.4)	-	0.9(0.7)	-	1.1(0.8)	-	1.1(1.2)	-
LG	0.9	0.8	1.0	1.1	0.9	0.8	1.1	1.0
HG	1.6	1.3	0.65	0.7	2.2	2.1	1.1	1.0
(IE)	>14	>11.7	<0.02	<0.01	6.7	6.4	0.2	0.2
(OM)	33(100)	27.5(71)	4.3(10)	4.5(14)	15.7(28.6)	1.6(38.3)	0.3(3.3)	0.3(2.8)
(HO)	0.5	0.4	0.5	0.4	0.9	0.6	1.7	1.5

(100 ppm or even 71% of the hydrogenic Zn form), whereas the content of other three elements in the 0–1 cm layer reaches only 20 ppm (23–39% of HG element form) (Pustelnikovas, Zabukas, Jašan, 2001).

Comparing OM species distribution in the sediments, we can see an obvious decrease in Zn and Ni content and an obvious increase in Cr and Cu content towards the base of the strata. The OM copper species shows an especially significant increase (up to 13.2 ppm and 38%) in the interstitial bed of Holocene clay (3.5–3.6 m) (Table 1).

There is a 2–4-fold increase in the content of HO species towards the base of the strata for Zn, Ni and Cr, but in the case of Cu there is a 1.5–1.7-fold decrease.

Such changes in IE, OM and HO species of the HG form and a potential technogenical impact on element distribution in all strata are also shown by the ratio of IE and OM species. In case of Zn and Cr, their content is strongly decreasing towards the base of the strata, whereas that for Ni is not so expressive, and, on the contrary, the content of Cu (also partly Ni) species increases with the depth. The content of HO species in this direction for Zn, Ni and Cr increases 1.1–1.2 times and decreases 1.7 times for Cu (Table 2).

A detailed analysis of the above-mentioned Zn, Cu and Cd element forms and species in the surface sediments (0–5 cm) in the shallow part (eastern) of the Gulf of Finland might be a more obvious indicator of the potential technogenous impact (Table 3). Firstly, these fine-dispersed sediments contain considerably higher T form quantities for the elements studied; HG form content is especially high, as it is that for IE and OM species which might experience the most intensive technogenical impact. This would correspond to the contemporary conception of bioenvironmental contamination – the input of these elements and the pollution of the gulf with Saint-Petersburg wastes brought in by the Neva River. However, the significantly higher content of the study element forms in the remote stations far away from the pollution sources (Stations 11, 16, 19 – see Fig. 1, B) and especially in Fe–Mn concretions which did not depend on the potential technogenesis impact, cast doubt on the above assumption. The doubts are confirmed by a complicated setup of the geochemical barrier zone in the water area (Emelyanov, 1998; Пустельников, 1992).

The especially high content of HG form in Fe–Mn concretions and the low content of its IE and OM parts, in the obvious prevalence of HO species, confirm the importance of geochemical (natural) processes for the quantitative and qualitative distribution of elements. Having in mind that the sediments in this water area are enriched by "fresh" HG form species launching a long concretion-forming stage in the early diagenesis, the domination of these elements of natural-geochemical origin raises no doubts. This is obvious in the distribution of Cd (considered to be the most dangerous pollution indicator) forms (species) (Table 3).

Let us discuss the regularities in the distribution of chemical element forms in Klaipėda and Gdansk Ports which are considered to be areas really affected by technogenic impact in the East Baltic (Figs. 2 and 3), where T, HG and LG forms of six elements (Zn, Ni, Cr, Cd, Cu, Pb) have been studied. These investigations enabled to determine areas in the 0–127 cm sediment layer with the prevailing natural sedimentation (NTZ) or a potential technogenical impact (TSZ) processes.

The sedimentation processes in NSZ and TSZ of both investigated areas are conditioned by sedimentary matter input from the catchment basins and are obviously affected by its input during frequent marine water rises and geochemical changes of element migration forms predetermined by salty water invasion.

Both areas are in the transit zone of sedimentary matter, and the marine water level rise often changes hydrodynamics in sedimentation zones and complicates the accumulation of this matter. The grain-size and chemical composition in Klaipėda and Gdansk Port areas were summarised elsewhere (Pustelnikovas et al., 2005; Trimonis, Gulbinskas, 2000). Without additional deeper analysis of this material, we can conclude that:

1. In the NSZ of Klaipėda Port (western part) coarse-grained clastic (silty and sandy) material prevails (on the

Table 3. **Distribution of Zn, Cu and Cd total (T), lithogenic (LG) and hydrogenic (HG) migration forms and its species (IE – ionic exchange, OM – organic-mineral, HO – hydroxide) in the Gulf of Finland sediment surface (0–5 cm) layer**

3 lentelė. **Suminės (T), litogeninės (LG) ir hidrogeninės (HG) Zn, Cu ir Cd migracijos formų bei pastarosios atmainų (IE – joninių mainų, OM – organinės-mineralinės, HO – hidroksidinės) pasiskirstymas Suomijos įlankos paviršiniame (0–5 cm) nuosėdų sluoksnyje**

Station	Horizoint, cm	Type of sediments	Zn, ppm / % from T						Cu, ppm / % from T						Cd, ppm / % from T					
			T	LG	HG	Species of the HG form			T	LG	HG	Species of the HG form			T	LG	HG	Species of the HG form		
						IE	OM	HO				IE	OM	HO				IE	OM	HO
11	0–3	Mud silty-clayey	193.6 / 100	63.9 / 33	129.7 / 67	68.6 / 35.4	20.8 / 10.8	40.3 / 20.8	52.4 / 100	14.9 / 28.4	37.5 / 71.6	7.4 / 14.2	16.5 / 31.5	13.6 / 25.9	8.1 / 100	4.9 / 61.2	3.2 / 38.8	2.7 / 33.2	0.3 / 3.1	0.2 / 2.5
11	0–3	Fe-Mn nodules	256.4 / 100	49.8 / 19.4	206.6 / 80.6	46.2 / 18	24.9 / 9.7	135.5 / 52.9	19.2 / 100	6.5 / 33.9	12.7 / 66.1	2.8 / 14.5	2.3 / 12.2	7.6 / 39.4	8.5 / 100	3.8 / 44.9	4.7 / 55.1	2.5 / 29.7	0.3 / 3.1	1.9 / 22.3
12	0–1	Mud small-silty	165 / 100	53 / 32.1	112 / 67.9	59.7 / 36.2	12.7 / 7.7	39.6 / 24	42 / 100	13.1 / 31.2	28.9 / 68.8	5.4 / 12.9	11.8 / 28	11.7 / 27.9	7.5 / 100	5.7 / 76.6	1.8 / 23.4	1.2 / 16.1	0.2 / 2.1	0.4 / 5.2
13	0–1	Mud silty-clayey	129.9 / 100	46 / 35.4	83.9 / 64.6	41.7 / 32.1	14.1 / 10.9	28.1 / 21.6	50.3 / 100	11.5 / 22.8	38.8 / 77.2	11.2 / 22.4	17.7 / 35.2	9.9 / 19.6	7.1 / 100	4.5 / 63.8	2.6 / 36.2	2 / 27.5	0.4 / 5.8	0.2 / 2.9
16	0–2	Small silt	148.8 / 100	32.7 / 22	116.1 / 78	60.1 / 40.4	21.3 / 14.3	34.7 / 23.3	41.9 / 100	12.3 / 29.5	29.6 / 70.5	5.9 / 14.1	12.5 / 29.8	11.2 / 26.6	5.6 / 100	3.8 / 68.4	1.8 / 31.6	1.4 / 24.8	0.1 / 2.5	0.3 / 4.3
19	0–5	Mud silty-clayey	107 / 100	40.3 / 37.7	66.7 / 62.3	38.0 / 35.5	11.8 / 11	16.9 / 15.8	27.3 / 100	9.6 / 35.2	17.7 / 64.8	3.4 / 12.5	8.6 / 31.5	5.7 / 20.8	5.7 / 100	4.2 / 73.8	1.5 / 26.2	1.0 / 17.8	0.1 / 1.4	0.4 / 7

average 84.9%). In the port gate region, fine sand with patches of medium sand, pebble and gravel of marine sediments invasion prevail.

In the eastern (continental) part of this ports, the distribution zone of fine silty and silty-clayey mud (average 79% fr. <0.1 mm) with patches of silty sand prevail. In this area, the human impact on sedimentation processes is obvious. The TSZ is differentiated in this port area. The scale of marine sediment invasion, amounts of accumulating sedimentary matter as well as the technogenic impact, according to the data of its balance, have caused that 58.3×10^3 t of inputting highly dispersed material has accumulated previously in the TSZ area and 242.9×10^3 t of sandy sediment fluxes has left on the bottom of the northwest part of the NSZ area (Pustelnikovas, 2003).

2. The data of Table 4 show that the total contents of the study microelements in the NSZ are of the same level (or smaller) than those in the northern sedimentation area of the Kuršių Marios Lagoon, and they do not exceed their values in Holocene and glacial deposits of the catchment area (Pustelnikovas, 1998) and even in the surface soil layer of the northern part of the Klaipėda city (Baltrėnas, Vaišis, 2006).

In the TSZ area they are several times higher than in latter part. The chemical composition of sediment types reflects the dependence of element quantities on the content of highly dispersed material (Emelyanov, 1998). It is natural that, partly as a result of human activities, the TSZ includes extremely high geochemical anomalies where heavy metal contents are from a few to even tens of times higher than in the NTZ. However, we do not know the ratio of the natural and human-influenced element forms in the sediments of these zones. This ratio has been analysed in the sediments of the Gdansk Port.

3. In the NSZ of the Gdansk Port (O, S and PN quays) also evidently prevailed coarse (sandy) material (66.0–98.6%) and in the TSZ (Sz and W quays), in the case of prevailing coarse fractions (85.9–99.7%), the contents of highly dispersed material in some layers increased (3.2–23.1%). It is a result of the evident influence of marine water and the invasion of Holocene brackish marine sediments. In the TSZ, we can see also mixing peculiarities of a geochemical barrier between the natural and human impact (Pustelnikovas et al., 2005).

4. The data of Table 5 show more variable contents of the study microelements in sedimentation zones of the Gdansk Port and especially in more highly dispersed fractions in comparison with those of the Klaipėda Port (Table 4).

In the area of the Northern Port (PN) and the Oliwa (O) Quays which are located on the seaside and near the river mouth where conditions are more active hydrologically and oxidative, the content of the study elements is relatively small. On the other hand, there are smaller contents of C_{org} and highly dispersed (fr. <0.063 mm) material as compared to those in the NSZ of the Klaipėda

Table 4. **Average content of T form elements in sedimentation zones and various sediment types of Klaipėda port area**
4 lentelė. **Elementų T formos vidurkinis kiekis Klaipėdos uosto sedimentacinėse zonose ir įvairiuose nuosėdų tipuose**

Elements, $10^{-4\%}$ (ppm)	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.	
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_{org},%	1.5	3.2	n. i.	n. i.	n. i.	n. i.	n. i.	n. i.	n. i.

Table 5. **Average content of T form elements in sedimentation zones of Gdansk Port (by Pustelnikovas et al., 2005)**
5 lentelė. **Elementų T formos vidurkinis kiekis Gdansko uosto sedimentacinėse zonose (pagal Pustelnikovas ir kt., 2005)**

Elements, $10^{-4\%}$ (ppm)	Sedimentation zone				
	NSZ			TSZ	
	Northern Port quay	Oliwa quay	Sulphur quay	Wistula 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	0.2
Cu	9	1	9	131	43
Pb	11	2	14	93	27
C_{org},%	1.9	0.8	1.9	5	1.8

Table 6. **Ratio of element forms in the sediment thickness of different sedimentation zones and areas of the Gdansk Port**
6 lentelė. **Elementų formų santykiai įvairių Gdansko uosto sedimentacijos zonų ir dalių nuosėdų storymėje**

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	Inner Port	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
	Outer (marine) Port	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	Inner Port	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 (Inner Port) 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 (Outer (marine) Port)/ NSZ (Inner Port) 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 (Inner Port)/ NSZ (Outer (marine) Port) 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

Port. In the Sulphur quay, which is on the inside boundary of GBZ of the Martwa Wisła river, the contents of microelements, C_{org} and fine-grained fractions are higher than those in the other quays of the Gdansk Port and (in the case of Zn and Cu) than in the NSZ of the Klaipėda Port. However, the average contents of the study elements in the latter are higher as compared to those in the Gdansk Port. The main reason of this variability can be various hydrological conditions (water quantities, marine water inflow and outflow currents) and differences in the geological structure and relief of the catchment areas of both ports.

On the contrary, more evident conditions of GBZ (mixing zone of fresh and salty waters, flocculation processes, quantities of the dissolved material, aeration scale, etc.) are determined, i. e. 1.2–15 times higher concentrations of microelements in the TSZ areas of both ports in comparison with their quantities in the NSZ areas. The contents of Zn, Cd, Cu, Pb and C_{org} (except Ni and Cr) are 1.5–2 times higher in the TSZ of the Gdansk Port than in those of the Klaipėda Port.

The obtained data on the total forms of the study elements suggest also a potential human impact on the formation of the chemical composition of sediments. Our previous data on the influence of navigation on this process (Pustelnikovas, Bolalek, 1995) showed that navigation actually dramatically redistributes sediments and elements (i. e. contaminants) and changes the macrocomponent composition of interstitial water in the surface (0–5 cm) layer. Such changes can be observed also in many other ports. In these cases, the technogenic impact plays a positive role in improving the ecological conditions of water and sediments.

To which extent the obtained data may be treated as the factor of contamination? In Conclusions we shall try to answer this question.

5. The analysis of migration forms in the 0–127 cm sediment thickness has been performed by us for the Gdansk Port. Determination of T, LG and HG forms was carried out at the quays (stations): PN-4 of the outside-marine (outer) port and O-2, W-4 of the inner (Martwa Wisła River) port. The first two stations are located in the NSZ and the third one in the TSZ area (Fig. 2 B). A comparison of the distribution of the determined element forms in the investigated thickness of both sedimentation zones of the Gdansk Port is given in Table 6.

Inner Port. The quantities of fr. <0.063 mm and C_{org} are indicative of the distribution of total (T), hydrogenic (HG) and lithogenic (LG) migration forms of the study elements. Therefore the distribution of these element forms was analysed by separating them into natural (not toxic) or possibly toxic (more or less anthropogenic) compounds.

Firstly, as the average concentrations of elements are different in the various sedimentary rocks of the lithosphere (clarks), their quantities vary in the sediments of the Gdansk Port (decreasing in the order Zn > Cr > Cu > Pb > Ni > Cd). Secondly, these quantities in many cases decrease from the surface to the deeper layers. An exception from this peculiarity is an increase of fraction <0.063 mm and C_{org} contents towards the deeper layers. According to the distribution pattern, in the NSZ to the most natural elements belong Cr and Zn whose average HG contents in the 0–127 cm thickness correspond to 11% and 29% of the T content, respectively. The percentage of the HG form for Cu, Cd, Ni and Pb is 45, 50, 52 and 54% of their T form, respectively. These four elements are characterised by a greater geochemical mobility as well as potential technogenic effects.

In the TSZ of the inner port, middle-small and small-grained sand prevails and the content of fr. <0.063 mm is small (11.2–14.1%), ranging from 11.2–14.1 to 0.3–2.3% in the layers of 0–40 and 40–120 cm, respectively). Correspondingly, the content of C_{org} decreases from 3.5–5% in the upper layers to 0.2–0.4% in the lower ones.

How can we explain this contradictory phenomenon? In the NSZ (St. O-2), in the evident presence of oxidation conditions, the content of fraction <0.063 mm and C_{org} below 40 cm depth are rapidly increasing, similarly to the total form contents of most of the study elements. The HG / T ratio evidently decreases along the core depth, except the 125–127 cm layer, in which the maximum content of C_{org} is observed (Table 6). Here, the more mobile HG form of elements is gradually destroyed, probably by the "olden" sedimentary matter, and goes over the dissolved state to the participation in the turnover cycle.

The anomalously high contents of this form (except Cr) in the layer of 125–127 cm are related to the analogous data of C_{org} and possibly to the concentration of highly dispersed material in the pellets – globules, which had passed through the digestive tract of the organisms and were covered by a chitin or some other film. This explanation concerns the TSZ (St. W-4), where below the depth of 40 cm there is a sharp decrease of concentrations of fr. <0.063 mm, C_{org} and T form, while the contents HG forms of elements in general are considerably increased (Table 6). Independently of the distribution peculiarities of T form in the bottom layers and a comparison of the ratio of the mean HG and LG forms with the T form contents in both zones, one can see that the HG / T ratio is very different for the various elements, but is always greater for the TSZ than the NSZ (Table 6). The ratios increase in the following order: Pb < Ni < Cd < Cu < Zn < Cr. As has been already shown, this relationship may be responsible not for the anthropogenic impact, but for the biological activities in the past.

Outer Port. According to the investigation of the sediment thickness (St. PN-4) and the different hydrological conditions than in the Inner Port, the peculiarities of both the grain-size and chemical composition distribution are analogous to those in the Inner Port (Table 6). In the Outer Port only the NSZ is different. The content of T element form is evidently smaller than that in the

NSZ and especially in the TSZ of the Inner Port. In the evident decrease of the total content, its HG form relatively increases. The mean HG / T ratio for the elements studied ranges in the following order: Cd < Pb < Cu < Zn < Cr. In this case, the peculiarities of marine sedimentation in the zone of the river–sea geochemical barrier and especially the effects of chemical processes transferring the dissolved forms of elements into hydrogenic–colloidal–sedimentary forms, as well as aeration processes are postulated.

CONCLUSIONS

1. From geoecological positions, summarised are the quantitative and qualitative data on element forms whose formation and distribution is related to the interaction of natural sedimentation processes and a possible human impact in four areas of the Baltic Sea – the Gdansk Bay, the Gulf of Finland, Klaipėda and Gdansk Ports.

2. A detailed analysis of T, LG and HG forms, together with IE, OM and HO species of the latter, of Zn, Ni, Cr, Cu, Cd in the sediments show the dependence of their distribution on the factors of natural processes, such as geological structure, the composition of the rocks, peculiarities of the sedimentation conditions in geochemical barriers, changes of hydrodynamic conditions.

3. According to the grain-size and chemical composition of elements in sediments depending on natural factors and human impact, two sedimentation zones – NSZ and TSZ – in the Klaipėda and Gdansk Ports were distinguished.

4. The obvious anthropogenic influence on the may be only potentially local in the neighbourhood of human activity objects – in the TSZ of ports, where anomalous quantities of elements, a specific distribution of their migration forms, hemistagnation conditions are fixed.

5. The quantities of elements in the NSZ of marine influence (Northern Port) are smaller than those in the NSZ and TSZ of the river part of the Gdansk Port. The balance of the forms in the port sediments in both sedimentation zones is different for the various elements, but in the TSZ it is always greater than in the NTZ.

6. With the sharp decrease of the total quantities of elements downwards in the port sediments, the part of HG form evidently increases. This fact can by explained only by their concentration in the biological remains (pellets or globules).

7. The obtained data indicate some anomalies in the sediments of the Gulf of Finland and the Gdansk Bay, whereas in the TSZ of the ports only in rare cases the maximum permissible concentrations are exceeded for the dredged and dumped material and for the biological conditions. This is not enough to prove the conception of global pollution.

8. The level of contamination should be determined by investigating element state forms. The existing maximum permissible concentrations must be revised.

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CHEMINIŲ ELEMENTŲ GENETINIŲ FORMŲ SEDIMENTACINIŲ YPATYBIŲ GEOEKOLOGINIS ĮVERTINIMAS KAI KURIUOSE PIETŲ BALTIJOS BASEINUOSE

Santrauka

Šiame darbe iš geoekologinių pozicijų pateikiami kiekybiniai palyginamieji duomenys elementų, susiformavusių dėl natūralių procesų ir galimos žmogaus įtakos sąveikos Suomijos ir Gdansko įlankų bei Klaipėdos ir Gdansko uostų dugno nuosėdose.

Buvo analizuotos suminė (T), litogeninė (stabili – LG) ir hidrogeninė (judri – HG) Zn, Cr, Cd, Cu, Pb, Ni ir kt. elementų migracijos (būsenos) formos. Pastarojoje ištirtos joninių mainų (IE), organinė-mineralinė (OM) ir hidroksidinė (HO) atmainos. Šios formos ir atmainos atspindi įvairius sedimentacinio proceso raidos Baltijos jūros istorijoje dėsningumus per paskutinius 10 (ir daugiau) tūkstančių metų, XIX–XX šimtmečiuose galimai paveiktus technogenezės.

Detali šių formų analizė dugno nuosėdų storymėje rodo, kad elementų pasiskirstymas ir jų anomalijų formavimasis Gdansko ir Suomijos įlankose buvo nulemtas gamtinių procesų: geologinės sandaros, uolienų sudėties, geocheminio barjero zonų ypatybių, hidrodinaminių sąlygų pokyčių.

Kompleksinių Klaipėdos ir Gdansko uostų nuosėdų tyrimų metu buvo išskirtos natūralios (gamtinės – NSZ) ir technogeninės (TSZ) sedimentacijos zonos. Anomalūs elementų kiekiai, jų migracijos formų specifinis pasiskirstymas, pusiauredukcinės sąlygos ir technogeninių šaltinių artumas yra tipiški pastarajai. Elementų kiekiai Gdansko uosto jūrinės dalies NSZ yra mažesni nei abiejose vidinės (upinės) dalies sedimentacijos zonose. Įvairių elementų T, LG ir HG formų pasiskirstymas abiejose zonose skirtingas, bet TSZ jų kiekis visuomet didesnis nei NSZ. T formos pasiskirstymas priklauso nuo <0,063 mm frakcijos ir C_{org} kiekio. Gilėjant nuosėdų storymei, jos kiekis staiga mažėja, bet HG formos dalis akivaizdžiai padidėja. Jos išlikimas mineralizuojantis ir irstant nuosėdinei medžiagai aiškintinas judrios formos kaupimusi bioveiklos atliekose.

Pateikti duomenys rodo, kad kai kurios geocheminės anomalijos abiejų uostų TSZ ir jūros baseinuose tik retkarčiais viršija didžiausias leistinas medžiagos ir biotos gilinimo ir deponavimo normas, bet to negalima sieti su visiško užterštumo samprata. Faktinio (toksinio) užterštumo lygio nustatymui būtina elementų migracijos (būsenos) formų analizė, o kartu ir dabartinių leistinų normų revizija.

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ГЕОЭКОЛОГИЧЕСКАЯ ОЦЕНКА СЕДИМЕНТАЦИОННЫХ ОСОБЕННОСТЕЙ ГЕНЕТИЧЕСКИХ ФОРМ ХИМИЧЕСКИХ ЭЛЕМЕНТОВ В НЕКОТОРЫХ ВОДОЁМАХ ЮЖНОЙ БАЛТИКИ

Резюме

В настоящей работе с геоэкологической точки зрения представлены количественные сравнительные данные элементов, при взаимодействии природных процессов и возможного влияния человека образовавшихся в донных осадках Финского и Гданьского заливов, Клайпедского и Гданьского портов.

Проанализированы общая (Т), литогенная (стабильная – LG) и гидрогенная (подвижная – HG) формы миграции (нахождения) Zn, Cr, Cd, Cu, Pb, Ni и др. элементов. Среди последней изучены ионно-обменная (IE), органико-минеральная (OM) и гидроксидная (ГО) отдельности. Эти формы и отдельности отражают различные особенности развития осадочного процесса в течение последних 10 (и более) тысяч лет истории Балтийского моря с возможным воздействием техногенеза в XIX–XX вв.

Детальный анализ названных форм в толще донных осадков показывает, что распределение элементов и формирование их аномалий в Гданьском и Финском заливах были обусловлены природными процессами: геологическим строением, составом горных пород, особенностями геохимических барьерных зон, изменениями гидрологических условий.

В результате комплексных исследований донных осадков в портах Клайпеды и Гданьска выделены зоны природной (NSZ) и техногенной (TSZ) седиментации. Аномальные количества элементов, специфическое распределение форм их миграции, полузастойные условия и близость техногенных источников типичны для зоны TSZ. Количество элементов в зоне NSZ морской части Гданьского порта меньше, нежели в обеих седимен-тационных зонах внутренней (речной) его части. Распределение форм T, LG и HG для различных элементов неодинаковое, но в зоне TSZ их количество всегда больше, нежели в зоне NSZ. Распределение форм T обусловлено содержанием фр.<0,063 мм и C орг. Внутри толщи осадков её количество резко сокращается, однако часть формы HG явно увеличивается. Сохранность этой формы при минерализации и разложении осадочного материала объяснима накоплением подвижных форм в остатках биологической деятельности.

Представленные данные свидетельствуют о том, что некоторые геохимические аномалии в зонах TSZ обоих портов либо в морских водоёмах лишь в редких случаях превышают предельно допустимые концентрации для материала драгирования и депонирования и для биоты. Этого, однако, нельзя связывать с понятием глобального загрязнения. Для определения уровня истинного загрязнения (токсичности) необходим анализ форм миграции (нахождения). В то же время необходима и ревизия действующих ныне допустимых норм.