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The geochemical and geoecological situation of the Gotland Basin in the Baltic Sea where chemical munitions were dumped

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The environment of chemical munition (CM) dumpsites in the Skagerrak and in the Bornholm Basin was described in the previous publication (Emelyanov, 2007). The dumpsite of chemical munitions in the Gotland Basin is located in the southern part of the Gotland Deep. This part was named as Słupsk “River’s foredelta”. This “river” discharges suspended particulate matter into this foredelta. As a result, the layer of the Litorina mud here is the thickest in the Gotland Basin (up to 730 cm, sedimentation rate is 0.94 mm/y). From the eastern side of the foredelta there is non deposition or reworking area, where till deposits with a thin cover of sand forms the surface of a hard bottom. Shells and bombs with poisonous matter could have been laid on the hard bottom or in the soft Litorina mud. However, we did not find any bombs or shells during our investigations. All the twenty two chemical elements we studied in the sediments were distributed according to the rule of the pelitic fraction (Emelyanov, 2005): the more the pelite (fraction < 0.01 mm) – the higher the content of the element. The maximal content of Zn (in the pelitic mud) is 39 times higher than its minimal value (in the sand), for Mn it is 416 times, for Fe – 17 times and for As – 77 times. The mean values of the elements in the pelitic mud (or clay in the western terminology) are 1.4–3.1 times higher than in the sand.

The maximal content of As (which is an indicator of the hydrolysis of lewisite and mustard gas (yperite) in the surface (0–5 cm) sediments) is 32 mg/kg (10–20 mg/kg on the average), i. e. similar to the same type of mud far from the dumpsite areas. In some layers of the Litorina mud strata and in the Ancylus clay we obtained us much as 130 mg As / kg. These heightened contents were formed due to the presence of iron sulphides in these layers: the sulphides contained up to 400–450 mg As / kg. The high contents of As and other toxic elements (Cd, Pb, etc.) formed due to natural (diagenetic) processes, but not as a result of the hydrolysis of CM on the bottom. The bottom of the Southern Gotland Deep is sufficiently clean.

Key words: Gotland Deep, chemical munitions, geology, geochemistry, environment, pollution

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INTRODUCTION

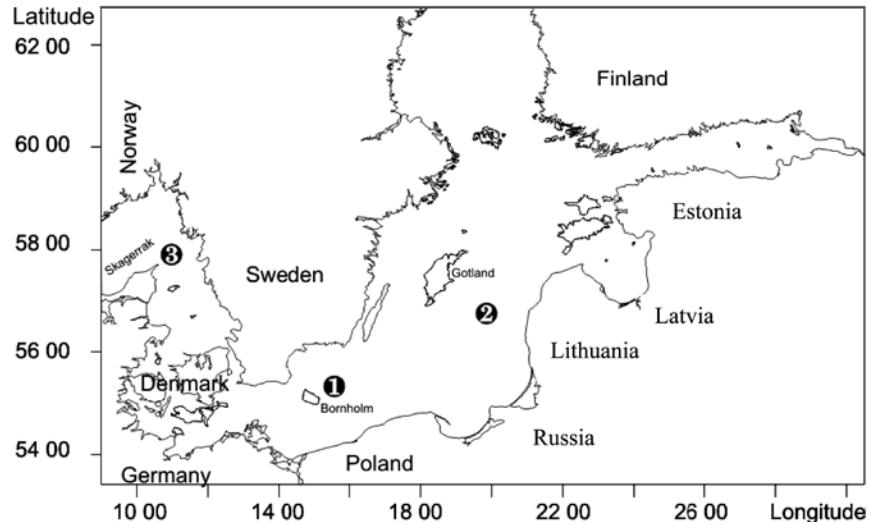
Chemical munitions were deposited after the World War II in three places on the sea bottom of North Europe: in the Skagerrak Sea, in the Bornholm and in the Gotland Deeps (HELCOM, 1994; 1996) (Fig. 1). The deposition of chemical munition in the Skagerrak Sea may be called “concentrated” because it comes from sunken ships with munitions. The depositions in the Bornholm and Gotland Deeps are of “scattered” type because aircraft bombs, artillery shells and special containers (reels) were sunken by the “scatter” method. The “concentrated” and the “scattered” depositions are detected by the strong gradient of the

magnetic field anomaly (Theobald, 2001; Paka, Spiridonov, 2002; Пака, 2004).

During the summer of 1997 and 1998, two expeditions of ABIORAS to the Skagerrak Sea (Пака, 2004) and seven expeditions to the Bornholm and Gotland Basins of the Baltic Sea were undertaken (Emelyanov, Kravtsov, Paka, 2000; Емельянов, Кравцов, Спиридовон, Пака, 2004; Emelyanov, Kravtsov, 2004; Рыбалько и др., 2004).

The report is based on materials of hydrophysical, hydrochemical and geological-geochemical researches carried out aboard on the R/V “Professor Shtokman” during 1997–2007 under the leadership of Dr. V. Paka, as well as on earlier papers

Fig. 1. Location of the studied munition dumpsites in the Baltic Sea and Skagerrak: 1 – Bornholm dumpsite, 2 – Gotland dumpsite, 3 – Måseskär dumpsite
1 pav. Cheminių ginklų palaidojimo vietas Baltijos jūroje ir Skagerake: 1 – Bornholmo, 2 – Gotlando ir 3 – Måseskär savartynas



and reports of other authors (HELCOM Report on Chemical Munition Dumped in the Baltic Sea, 1994; 1996; Хорошев, Ермакова, 1994; Васильев и др., 1994; Юфит, 1994; Борисов, 1997; Paka, Spiridonov, 2002; Пака, 2004; Рыбалко и др., 2004). Swedish, Belgian and Danish scientists also participated in these expeditions (Paka, Spiridonov, 2002).

The results of the geological-geochemical studies in the sites where toxic chemical munition (TCM) was dumped in the Måseskär area (in the Skagerrak Sea), and the Bornholm Basin of the Baltic Sea have been described in part A and published earlier (Emelyanov, 2007). The main goal of this article is to continue part A and describe the geological and geochemical situation in the Gotland Basin (part B).

Additional material for this paper was obtained during some expeditions on the R/V "Professor Shtokman" (cruise 76) and research vessels of AtlantNIRO "Atlantida" and "AtlantNIRO" (2005–2006) in the Central Baltic, especially in the western part of the Gotland Basin (mainly in the Swedish fishery zone) during 2005–2006. Two long sediment cores (303590 and 303610) were found in the German expedition on the R/V "Poseidon" (Psd) under the leadership of Prof. Jan Harff.

PART B. THE GOTLAND BASIN

The Gotland Basin consists of the Gotland Deep, which is limited by the depth contours of 80–90 m, and the surrounding shallow waters (depths of 0–80 m) (Fig. 2). The Deep itself is divided by the Dobrynnin moraine ridge and the Klints Bank into the lesser and larger parts – the western area (or the Klints Deep) and the eastern one (or the Gotland Deep), respectively.

The Gotland Deep, for a better description, was divided by the author into three parts: Central Gotland, Middle Gotland and Southern Gotland Deeps. The Central Gotland Deep located in the north is the deepest area. It is restricted by the 190 m depth contour and has a maximum depth of 248 m: its area in the limits of the 190 m depth contour is equal to 6525 km². The eastern slope of the Deep is relatively steep (the angle of inclination is up to 1°–3°) with transverse tectonic and erosion valleys in places. The western slope is gentler and less interrupted by valleys. The Southern Gotland part of the deep we call the "Slupsk underwater river's foredelta". This part is the shallowest in the Gotland Basin. The depth there is only 90–130 m. In the southern and the south-western parts the Southern Gotland deep verges the Slupsk trough (depths of 60–80 m), which connects it with the Bornholm Deep (Fig. 2). The Slupsk trough is the passage through which the saline waters of the North Sea flow from the Bornholm Deep into the Gotland Deep. The Middle Gotland part (or the Deep) is of intermediate depth – it ranges from 120 to 180 m.

In the north, the Gotland depression is separated by the moraine Fårö Ridge from the Fårö Deep. The depth of the ridge's saddles that join both deeps is 120–126 m.

I. Bottom sediments of the Gotland Deep

Coarse and medium-grained sands with boulders and individual pebbles, as well as fine-grained sands are deposited in the Gotland Deep at depths of 50–80 m (Figs. 3 and 4). In many cases, these types of sediments form a thin layer (within 10 cm) on moraines. Those sediment types are relict, as far as the abrasion processes of the ancient coasts and moraine erosion resulted in their formation during the Litorina transgression. In the western part of the Gotland Basin, sands are deposited bathymetrically higher by 10–30 m (at depths of 0–50 m) than in the eastern part. Moraines are commonly found at the bottom surface at depths of 50–80 m. Occasionally, they are covered by a sand layer of a thickness of no more than 1 cm (Емельянов, Гриценко, 1999; Свиридов, Емельянов, 2000).

Mud and silt (aleurite) are deposited at depths exceeding 80–100 m (Fig. 5), and in the western part of the Gotland Deep – at a depth of more than 50–60 m. Pelitic (clayey) mud is found at depths of more than 120–150 m in the eastern part, and of more than 120–130 m in the western part. One may distinguish a few areas of pelitic clayey mud prevalence: (1) the shallowest southern area (the Southern Gotland Deep, depths 95–130 m), (2) the western area (Klints Deep, depths 105–180 m), (3) the middle area (the Middle Gotland Deep, depths 130–170 m), (4) the wide northern area (Central Gotland depression, depths 170–248 m). All these areas are separated by bands or spots of coarser mud (silts). The boundary between areas (3) and (4) passes approximately at 56°55'N.

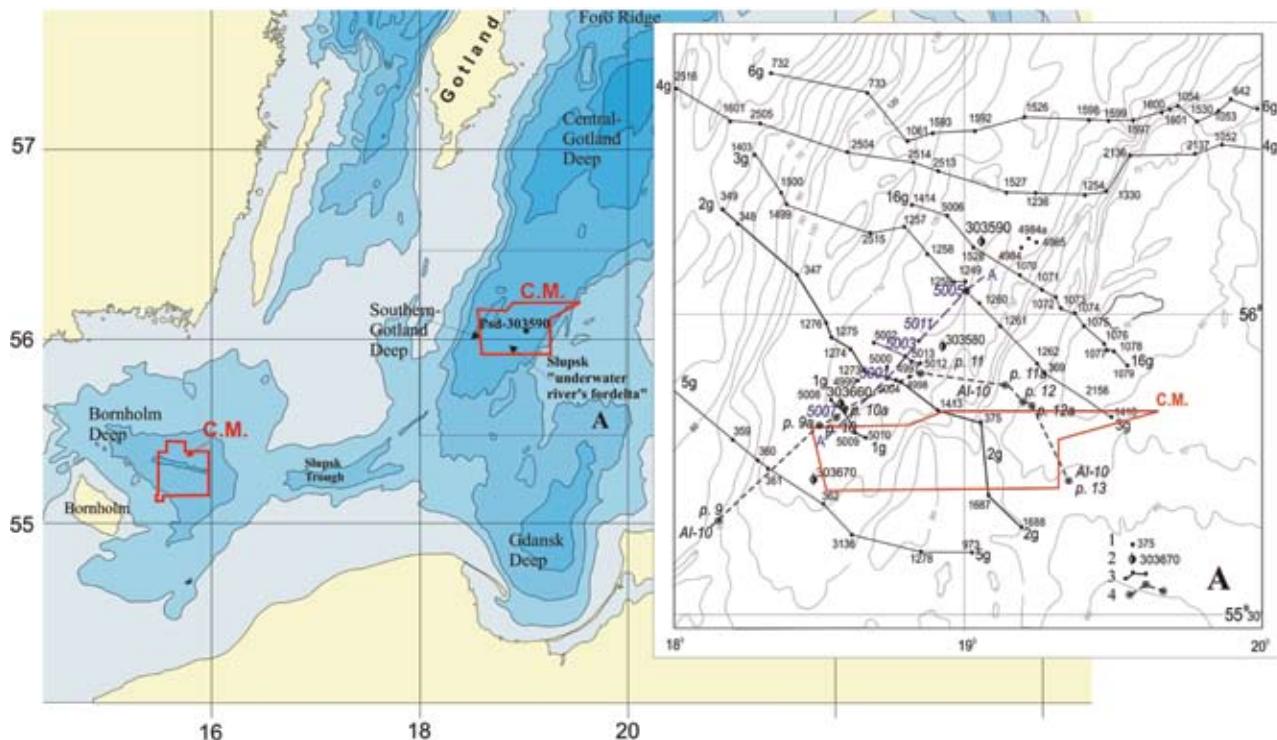


Fig. 2. The bathymetric map of the Southern Baltic, where chemical munitions (CM) were dumped. CM – conventional areas, where CM were dumped. A – detailed bathymetric map of the Southern Gotland Deep. Isobaths each are of 10 m. After Руденко, Ражева, 2006. Legend: 1–2 – geological stations (1 – R/V "Shelf" and "Akademik Kurchatov", 2 – R/V "Poseidon"), 3 – lithological profiles (profiles 2G, 3G, and 16G are published in Емельянов, 2007), 4 – Parasound profile AI-10 (see Fig. 3)

2 pav. Cheminių ginklų laidojimo Pietų Baltijoje arealų batimetrinis žemėlapis. CM – cheminių medžiagų laidojimo sulygininiai plotai, A – Pietų Gotlando jdaubos detalus batimetrinis žemėlapis

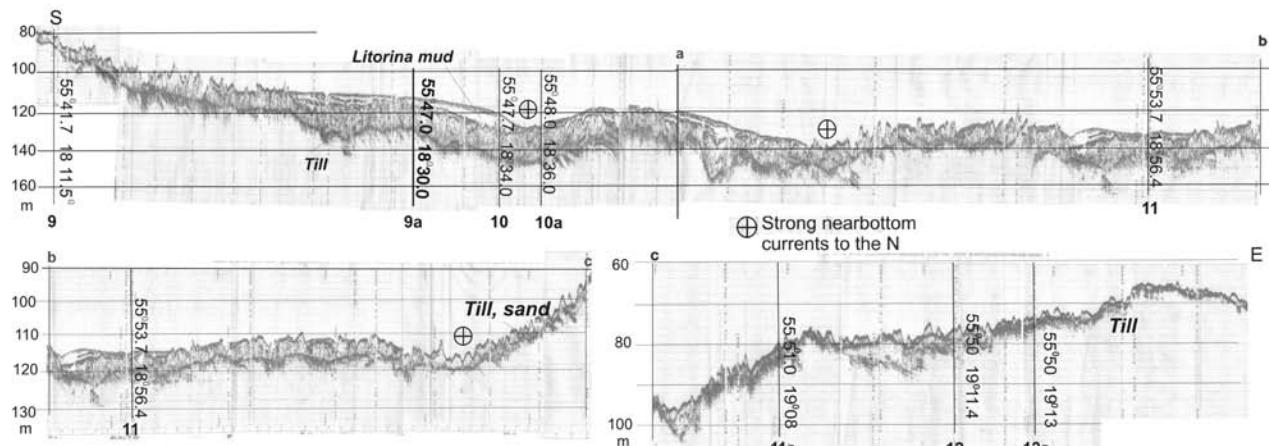


Fig. 3. Parasound profile AI-10 in the Southern Gotland Deep (for the location see Fig. 2, A)

3 pav. Zondavimo profiliai Pietų Baltijos jdauboje (profiliai linijas žr. 2 pav., A)

A general case is the exposure of the moraine deposits and Ancylus clays at the bottom not far from the Dobrynin Ridge. The Grey Ancylus clays are exposed (or overlapped by a thin layer of sands or silts of 1–2 cm) at elevated portions of that ridge and at the Klints bank moraines. Outcrops of grey lacustrine clays are also characteristic of the margins of the Southern and Central Gotland Deeps (mainly, between the depth contours of 180 and 210 m), as well as the exposures of the same clays at the saddles of the Fårö moraine ridge. Silts (usually coarse-grained) are usually deposited in the form of narrow strips a little higher than the halocline or just below it (usually, fine aleuritic (silty) mud).

The thickness of the marine Holocene sediments (7800 years BP) varied within 0–700 cm. The minimum thickness (<1 cm) was found far from the coasts at depths of 10–80 m at moraine banks (Емельянов, Гриценко, 1999; Emelyanov, 2001). At depths of 20–80 m, the sediment thickness is 0–10 cm, and in the eastern coastal zone (depths 0–30 m) usually varied from 10–50 cm. The thickness of the mud in the Deep usually varied within 200–400 cm. In the Southern Gotland Deep (in the Slupsk river's foredelta) the thickness reaches 400–700 cm (Fig. 4), and at one site (Psd-330590) it even exceeded this value. This is the greatest thickness of the marine Holocene mud in the Central Baltic.

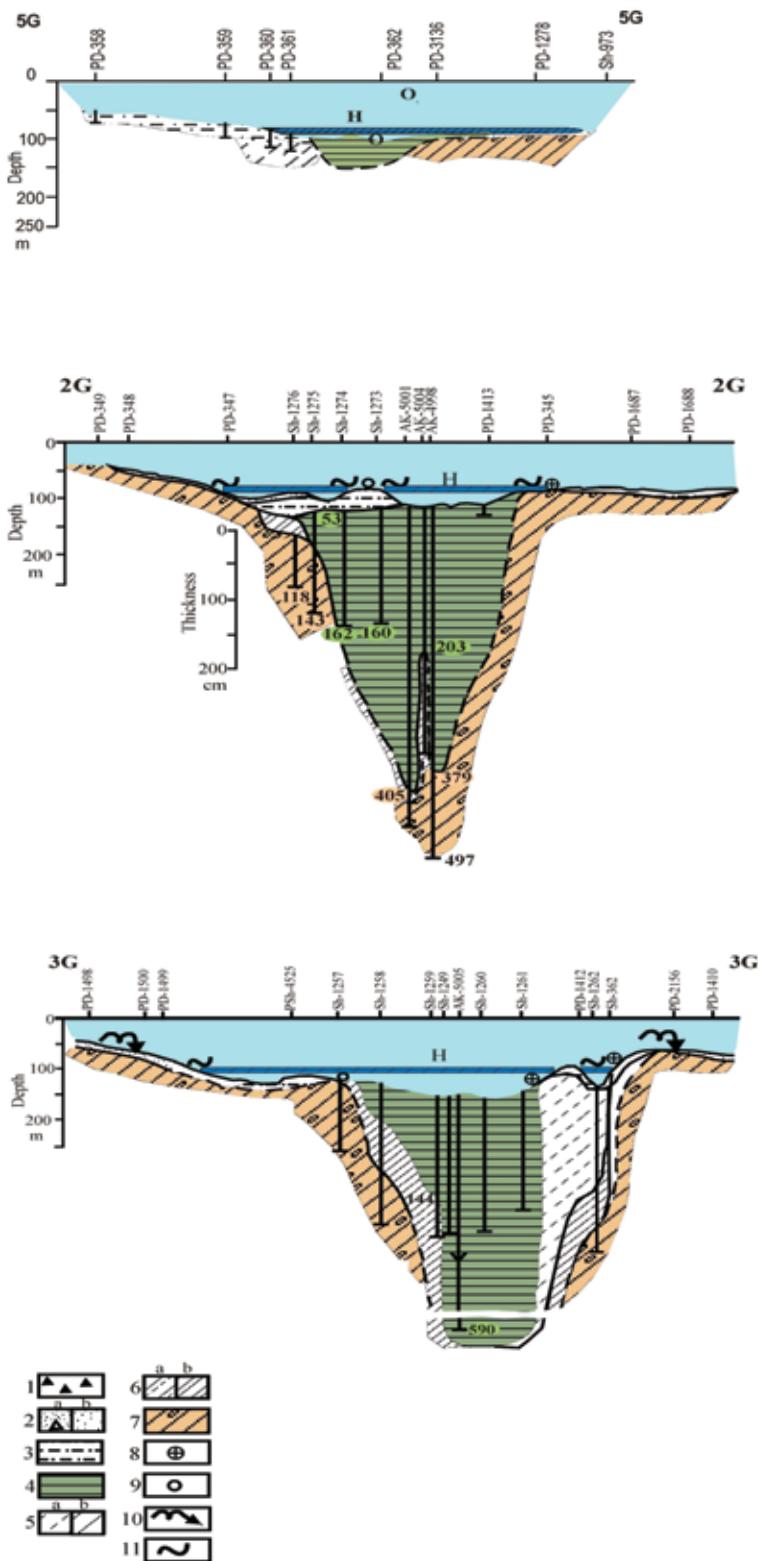


Fig. 4. Lithological profiles (for the location see Fig. 2, A). Legend: 1 – gravel, 2a – sand with gravel, 2b – sand, 3 – fine-aleuritic mud, 4 – pelitic mud, 5a – homogenous clay, greyish, 5b – homogenous clay, gray-brown, 6a – micro-varved clay, 6b – varved clay, 7 – till, 8 – near-bottom currents (to the N), 9 – near-bottom currents (to the S), 10 – resuspension and redeposition, 11 – internal waves
4 pav. Litologiniai profilių linijos žr. 2 pav., A

In the Klints Deep, the sediment thickness reaches from 50 to 258 cm and in the Central Gotland Deep it ranges from 100 to 383 cm. In the Klints Deep, as well as in the Middle Gotland and the Central Gotland ones, small areas with an increased thickness were also observed along their margins (depths 190–100 m): either at the slope's foot or at the upper slope (not far from the saddles of the Fårö moraine ridge and in the lower part of the Klints Deep).

II. The underwaters of the Słupsk “River’s fore-delta”

The Słupsk “river’s foredelta” is the most important area in the Baltic Sea because of the following reasons: 1) there were observed the highest rates of sedimentation in the areas of the open sea and 2) on the bottom of this area shells, bombs and containers with chemical munitions (CM) (about 2000 tons) had been dispersed (Emelyanov, Paka, Kravtsov, 1999).

Hydrography. The saline (transformed) North Sea water enters the Gotland Deep from the Bornholm Basin through the latitudinally oriented Słupsk Trough (Fig. 2). The depth of this trench is 70–80 m, and the height of its banks (slopes) ranges from 20 to 30 m. These slopes are composed either of moraine or of overlying sands. Sand also covers the trench floor, and coarse aleurite occurs in its lows (depressions). This points to periodic bottom currents in the trench with a velocity of 100–150 cm/s.

Therefore, the southern slope of the Słupsk trench composed of moraine with erosion features is washed by currents with a velocity not less than 50–70 cm/s. Judging by the presence of two narrow valleys (with relative depths of 3–10 m) at the eastern end of the floor of the Słupsk trench, saline water flows out of the trench into the Southern Gotland Deep in two streams: strong northwestern and weak southeastern (Емельянов, Гриценко, 1999; Емельянов, Гриценко, Егорихин, 2004). Because of the deep extension, as compared with the Słupsk trench, the current loses its velocity (hydrodynamic barrier) and starts to unload sand, aleurite and, later pelite. This foredelta of the “underwater” Słupsk River is unusual. The pelite-sized material transported via the right (southern) branch of the Słupsk trench is also discharged into this foredelta (settling basin). It reaches the branch from the Polish–Lithuanian side, where the main unloading of the sedimentary material from the currents occurs, including particles of < 0.001 mm.

At a depth of 75–80 m, at the Słupsk “river’s” mouth, there is no mud (Figs. 3 and 4) – it begins to deposit at a depth of 80–90 m on the hard moraine substrate. The thickness of the marine mud here is about 10–100 cm. However, at a distance of 10–20 miles from the mouth of the Słupsk trench, the thickness increases up to 400 cm, and in some small areas it attains 600 cm or even more than 730 cm (Fig. 6).

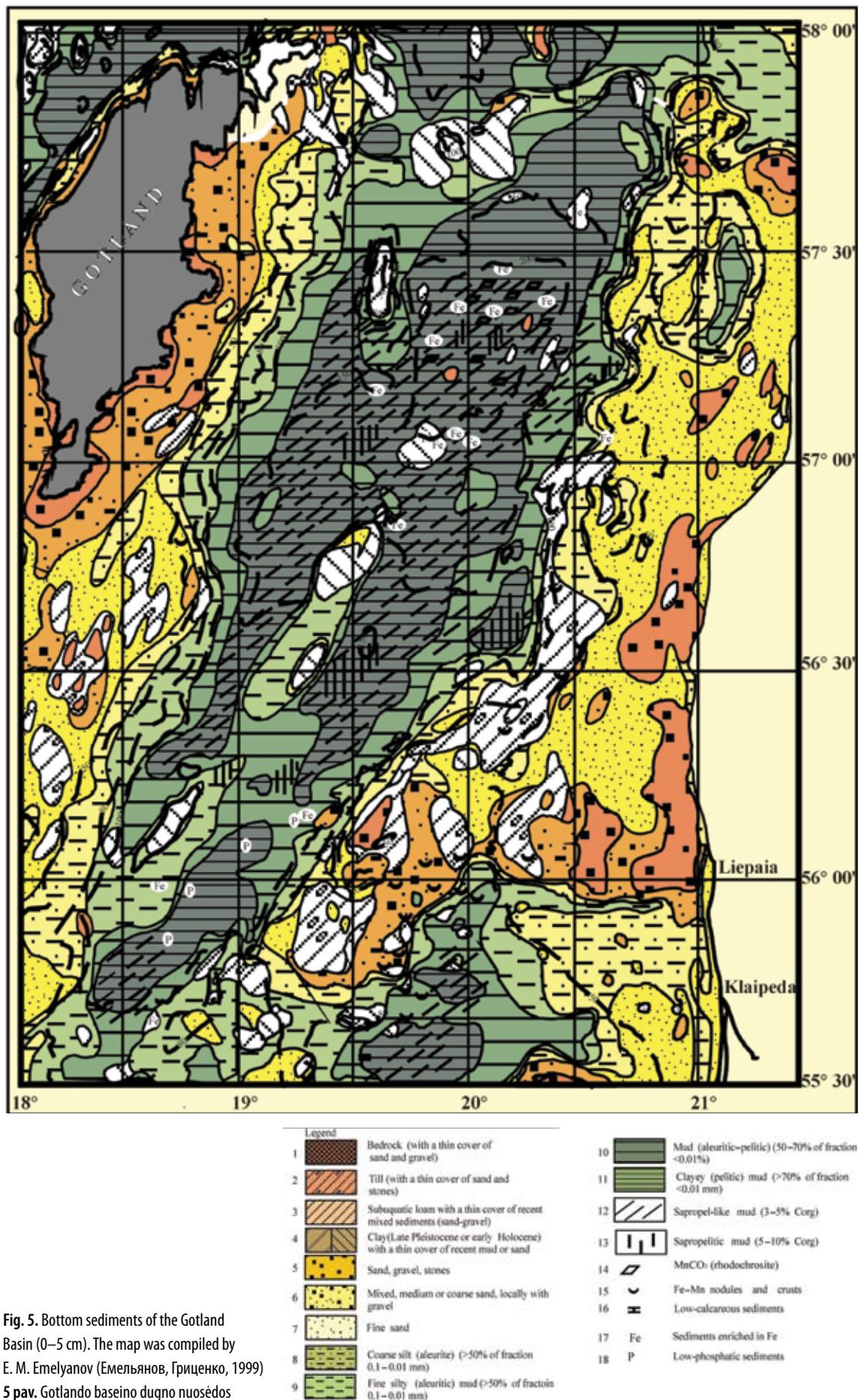


Fig. 5. Bottom sediments of the Gotland Basin (0–5 cm). The map was compiled by E. M. Emelyanov (Емельянов, Гриценко, 1999) 5 pav. Gotlando baseino dugno nuosėdos

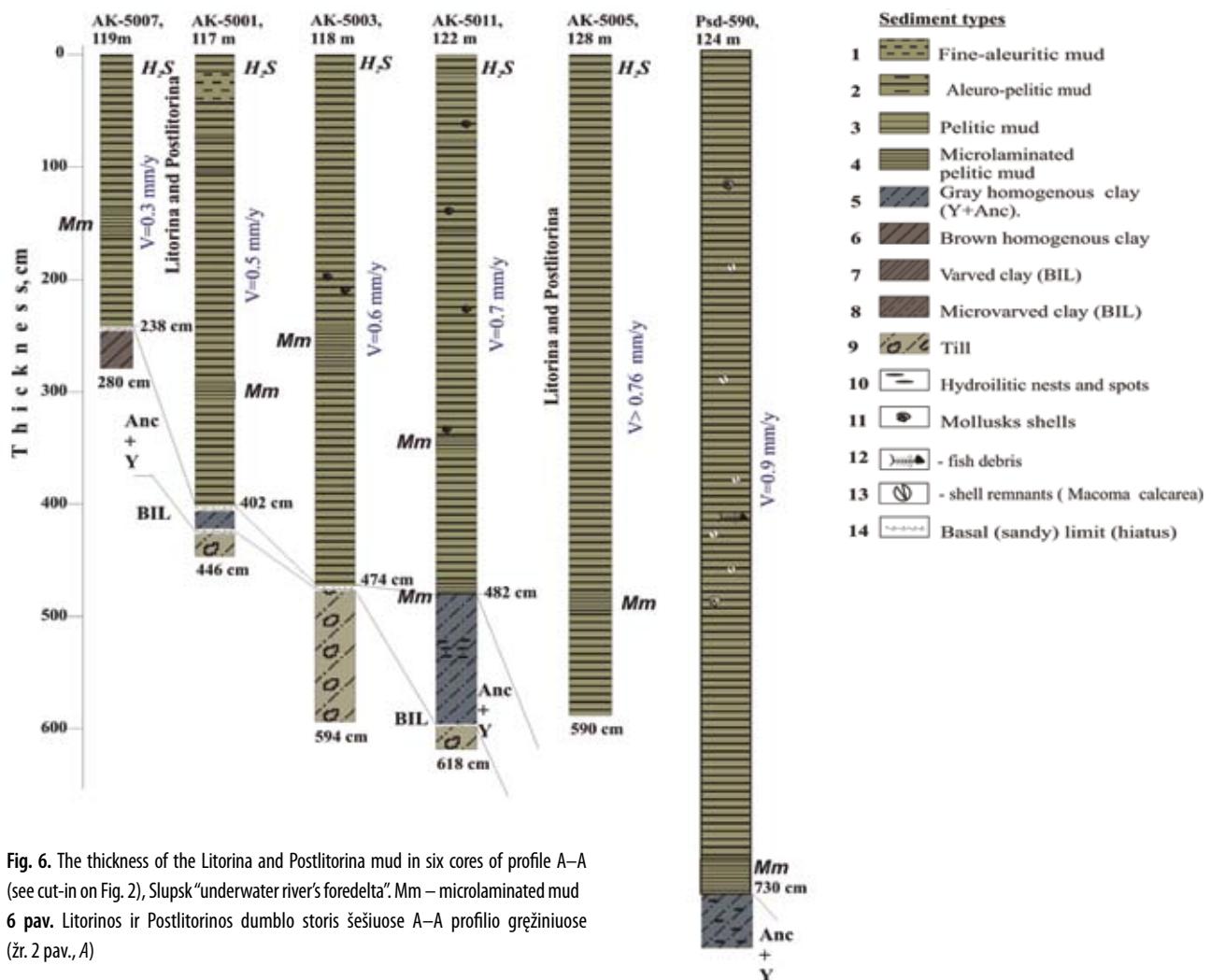


Fig. 6. The thickness of the Litorina and Postlitorina mud in six cores of profile A–A (see cut-in on Fig. 2), Slupsk “underwater river’s foredelta”. Mm – microlaminated mud
6 pav. Litorinos ir Postlitorinos dumbo storis šešiuose A–A profilio grėžiniuose (žr. 2 pav., A)

This is the greatest thickness of the marine Holocene mud (Hl_2) in the entire Gotland Deep.

The upper sediment layer (0–10 cm) in the Gotland Deep is self-represented by semiliquid (water content 70–85%), reduced, dark greenish-grey mud (Tables 1 and 2). Below 10 cm, the water content somewhat decreases (to 60%) and the mud becomes soft and plastic, but the colour remains the same – dark greenish-grey, with black hydrotroilitic spots or interbeds in places. The redox potential Eh is usually negative, up to –200 mV. The mud is well saturated with gas, mainly methane (NH_4), and contains free H_2S (Table 1). Craters of mud volcanoes or pockmarks, appearing as significant hollows in the bottom surface, occur at the sites of gas seepages. Within the mud field of the Slupsk River’s foredelta, the number of those craters is more than 300 (Блажчишин и др., 1990). The pockmarks are valley-like and sinuous in shape. The length of some pockmarks is up to 5–20 km; they are 50–100 m in width and 1–5 m in depth (from the bottom surface). The gas flux from such pockmarks into the bottom water is very high.

The mud contains from 1.60% to 2.96% C_{org} . Moreover, high C_{org} is traced throughout the sequence of the marine mud (Table 2). Along with the organic matter, mud is enriched with N and on the average contains 0.10% P, which is 1.5 times more than the marine mud from the Gdansk basin. The sediments of the southern Gotland deep are characterized by mean (Clarke

concentrations of reduced mud of the Baltic of Fe, Mn, Ti, K, Na and Mg, of trace elements Ba, V, Sn, Cr, Li, Rb, Z, and somewhat by an increased average contents of Zn, Cu, Ni, and Co (Table 2).

However, the presence of sapropel-like laminated mud in many cores of the southern Gotland Deep, usually forming in periodically stagnating deeps, allows us to assume that hydrogen sulfide has been appearing periodically in the bottom water of local depressions within these deeps.

A distinguishing feature for the mud of the underwater Slupsk River’s foredelta are pillow-like forms (clinoforms) composed of mud, that have been caused by the effects of a near-bottom contour current (Fig. 7). To the left of the bottom current stream, suspended matter from the flow occurs; under the current and to the right of it, an erosion of moraine occur, however, no deposition of sediments take place.

For the palaeoreconstruction of the near-bottom currents below the halocline level in the Gotland Deep we used the surficial sediment map (Fig. 5) and the bottom relief (Fig. 2) and lithological profiles (Емельянов, 2007). Therefore, in order to evaluate them near the bottom, one author used a theoretical graph (Postma, 1967). According to this graph, a consolidated clay, here represented by moraine with a water content of less than 50%, is washed away at velocities not less than 80–100 cm/s. Unconsolidated clay, represented by the

Table 1. Lithology of the terrigenous sediments of the “underwater Slupsk river’s foredelta”, the Baltic Sea

1 lentelė. Baltijos Slupsko povandeninės upės priekinės deltos terigeninių nuogulų litologija

| Horizon, cm | Sediment type | W, % | Age | | R. of sed., mm.y ⁻¹ |
|---|---|------|--------------------|-------|-----------------------------------|
| | | | Horizon | Index | |
| Station AK-5000, depth. 119 m, 55°55'2 N, 18°44'1 E | | | | | |
| 0–3 | Pelitic mud dark grey | 77.9 | Hl ₃ | SA | — |
| 50–55 | The same | 75.9 | Hl ₃ | SA | 0.22 |
| Station AK-5001, depth. 117 m, 55°53'9 N, 18°44'4 E | | | | | |
| 0–3 | Pelitic mud, brownish-grey with H ₂ S | 77.9 | Hl ₃ | SA | 0.44 |
| 50–55 | The same, dark grey | 75.9 | “ | SA | 0.44 |
| 100–105 | The same, with weak microlayers | — | “ | SA | 0.44 |
| 200–205 | The same, with patches of hydrotroilite | 69.1 | Hl ₃ | SB | 0.01 |
| 250–255 | The same, weakly microlayered | 64.7 | “ | “ | 0.01 |
| 300–305 | The same, microlayered | 33.1 | Hl ₂ | At | 0.35 |
| 290–298 | The same, light white, with blue shade | — | Hl ₂ | At | 0.35 |
| 400–405 | Pelitic mud | — | Hl ₂ | — | 0.35 |
| 421–425 | Till | — | Plt | — | — |
| Station AK-5002, depth. 118 m, 55°57'2 N, 18°40'7 E. | | | | | |
| 0–5 | Pelitic mud, black, with H ₂ S | >75 | Hl ₂₋₃ | — | 0.68 |
| 300–305 | The same, greenish-grey | 58.9 | Hl ₂₋₃ | — | 0.68 |
| 530–535 | Aleuro-pelitic mud, microlayered | 56.5 | Hl ₂₋₃ | — | 0.68 |
| 650–655 | Homogenous clay, with sulphides | 58.4 | Hl ₁ | — | — |
| Station AK-5002-2, depth. 118 m, 55°53'9 N, 18°44'4 E | | | | | |
| 0–3 | Pelitic mud, darky-grey, with the brownish shade, with H ₂ S | 75.6 | Hl ₃ | SA | 0.47 |
| 80–85 | Aleuro-pelitic mud, microlayered, grey, with H ₂ S | 70.1 | Hl ₂₋₃₋ | — | 0.47 |
| 245–250 | The same | 67.4 | “ | — | 0.47 |
| 260–265 | Aleuro-pelitic mud, microlayered, with H ₂ S | 57.1 | “ | — | 0.47 |
| 355–370 | Pelitic mud, grey | — | — | — | 0.47 |
| 395–400 | Clay, grey, with hydrotroilite | 60.8 | Hl ₁ | — | — |
| 498–570 | Till, with pebble and gravel | 37.4 | Plt | — | — |

W – moisture, R. of sed. – rate of sedimentation.

Ancylus and Yoldia clays, with a water content of about 70%, is washed away at a velocity of 60–70 cm/s. However, loose clays with a water content of about 80% represented by the Litorina mud, are washed away at velocities of approximately 50 cm/s. Likewise, the transportation of particles of a size of about 1 µm occurs when the velocity is about 10–15 cm/s; for particles of 5 µm (the velocity is 15–20 cm/s and for those of 10 µm it is 25–30 cm/s) (Емельянов, Гриценко, 1999).

The hydrodynamic conditions in the muddy part of the Slupsk River’s foredelta are rather active. Numerous erosion channels occur on the mud field surface. Many mud volcanic craters are oriented southwest to northeast, i. e. in the direction of the bottom current (Блажчишин и др, 1990). At the bottom of the foredelta, there is an almost constant, well-expressed light dispersion layer related to an increased suspended matter content near the bottom. At test area III AK-44 (depth 110–130 m) located in the eastern part of the foredelta of the Shupsk River, stagnation phenomena at the bottom was not observed in July–August of 1986 and 1994 (Fig. 8). The bottom water commonly contained oxygen. The evidence for this is a brown (oxidized) film on the mud surface, despite the fact that under the film (likely several millimeters thick), black mud contain free H₂S. Intense fluxes (Романкевич, Емельянов, Бобылева, 1990), of methane, hydrogen sulfide, and, likely, phosphorus, manganese (Mn²⁺) iron (Fe²⁺) and trace elements from fresh and porous,

organic-rich mud of the foredelta (of pockmarks craters) are dispersed into the bottom water and transported by the bottom current further down, firstly, to the Mid-Gotland Deep, then, to the Central Gotland Deep. Since the reducing conditions are constantly preserved in the mud of foredelta, the flux of gas, biogenic components and metals from the interstitial waters of the mud into the bottom water does not cease. Therefore, the mud of the foredelta constantly depletes in elements unable to form authigenic minerals in the given physicochemical situation. First of all, this concerns nitrogen, manganese and to a lesser degree, Ba, Ni, Mo and some other trace elements.

It is significant that the conditions of sedimentation in the foredelta have changed during the Litorina stage (7800 years BP), as evidenced by the presence of thinly laminated mud, although the lamination is not distinct in some cases. Thin laminae consist of brown sapropelic material and clayey mud. This diffusely laminated mud contains up to 1.20% Mn! As mobile Mn⁴⁺ is practically absent in the mud, we can draw a conclusion that all mobile manganese is present in the form of Mn²⁺ and forms amorphous manganese carbonate, transforming into rhodochrosite (Емельянов, 1981). The reason for the formation of the laminated mud most probably is that it is due to the periodic inflow of the water of the saline North Sea into the Gotland Deep. Some micro-layers, obviously, have annual cyclic recurrence.

Table 2. The content of the chemical composition of the terrigenous sediment of the "underwater Słupsk river's" foredelta, Baltic Sea (CaCO_3 – Na – in %, Rb – Zr in 10^{-4})
2 lentėlė. Baltijos jūros Słupsko povandeninės upės prikinės deltos terigeninių nuosėdų cheminė sudėtis

| Horizon, cm | $\text{H}_2\text{S},$ ml/l | CaCO_3 | C_{org} | P | Fe | | Mn | | Ti | Ca | Mg | K | Na | Rb | Li | Cr | Ni | Co | Cu | Zn | Zr | Sed. type ^{a2} | | |
|--------------------------|-------------------------------|-----------------|-------------------------|------|------------------|------------------|----------------------------|------------------|------|------|------|------|------|------|-----|----|-----|-----|----|----|-----|----------------------------|-------|------|
| | | | | | Fe^{2+} | Fe^{3+} | Fe_{total} | Mn^{++} | | | | | | | | | | | | | | | | |
| Station AK-5000, 119 m | | | | | | | | | | | | | | | | | | | | | | | | |
| 0–3 | nd | 17.01 | 2.70 | 0.20 | 1.13 | nd | 5.02 | nd | 0.05 | 0.42 | 0.40 | 1.68 | 2.54 | 1.84 | 76 | 44 | 78 | 96 | 40 | 54 | 178 | – | Mud | |
| 100–105 | nd | 15.01 | 2.39 | 0.10 | 1.83 | nd | 5.22 | nd | 0.26 | 0.45 | 0.16 | – | 2.60 | 1.54 | 128 | 54 | 63 | 186 | 82 | 62 | 110 | – | " | |
| 200–205 | nd | 15.26 | 2.20 | 0.12 | 1.73 | nd | 6.02 | nd | 0.19 | 0.44 | 0.45 | – | 3.31 | 1.61 | 138 | 57 | 76 | 62 | 39 | 40 | 90 | – | " | |
| 300–305 | nd | 12.26 | 2.61 | 0.10 | 0.57 | 0.14 | 6.02 | 0.007 | 0.12 | 0.44 | 0.45 | – | 2.45 | 1.91 | 144 | 60 | 70 | 74 | 38 | 40 | 90 | – | " | |
| 400–405 | nd | 13.26 | 2.55 | 0.10 | 0.59 | 0.07 | 6.8 | nd | 0.06 | 0.45 | 0.57 | – | 2.50 | 1.14 | 141 | 60 | 50 | 68 | 35 | 37 | 96 | – | " | |
| Station AK-5002, 118 m | | | | | | | | | | | | | | | | | | | | | | | | |
| 300–305 | 0.27 | 11.51 | 2.84 | 0.10 | 0.49 | 0.07 | 6.60 | nd | 0.13 | 0.44 | 0.43 | 1.82 | 2.54 | 1.29 | 152 | 63 | 63 | 60 | 39 | 40 | 106 | – | Mud | |
| 530–535 | nd | 10.01 | 2.87 | 0.09 | 1.63 | nd | 6.08 | 0.02 | 0.63 | 0.44 | 0.72 | 1.64 | 2.74 | 1.47 | 158 | 62 | 63 | 68 | 44 | 44 | 120 | – | " | |
| 650–655 | nd | 10.76 | 2.48 | 0.10 | 2.33 | 0.1 | 6.02 | 0.01 | 0.04 | 0.43 | 0.62 | 1.98 | 3.20 | 1.69 | 200 | 75 | 75 | 63 | 96 | 45 | 48 | 134 | – | Clay |
| Station AK-5002-2, 118 m | | | | | | | | | | | | | | | | | | | | | | | | |
| 0–3 | 1.98 | 12.76 | 2.96 | 0.10 | 1.93 | nd | 5.58 | nd | 0.48 | 0.42 | 0.62 | – | 2.64 | 2.00 | 80 | 48 | 82 | 94 | 40 | 50 | 176 | – | Mud | |
| 80–85 | 1.88 | 12.51 | 2.82 | 0.10 | 0.70 | 0.13 | 5.46 | 0.10 | 0.01 | 0.45 | 0.53 | – | 2.70 | 1.53 | 155 | 76 | 96 | 62 | 50 | 50 | 120 | – | " | |
| 245–250 | 1.23 | 9.78 | 2.61 | 0.09 | 0.95 | 0.06 | 5.28 | nd | 0.06 | 0.50 | 0.66 | – | 2.93 | 1.27 | 130 | 58 | 28 | 85 | 60 | 41 | 102 | – | " | |
| 260–265 | 0.86 | 10.31 | 2.89 | 0.09 | 0.86 | nd | 5.12 | 0.07 | 0.09 | 0.53 | 0.80 | – | 2.96 | 1.18 | 116 | 50 | 102 | 80 | 40 | 44 | 92 | – | " | |
| 395–400 | 1.08 | 9.01 | 2.79 | 0.09 | 1.68 | nd | 5.32 | 0.2 | 0.35 | 0.51 | 0.62 | 1.60 | 2.96 | 1.34 | 110 | 50 | 96 | 120 | 32 | 58 | 114 | – | –Clay | |
| 565–570 | – | 10.10 | 2.61 | 0.08 | 0.97 | nd | 4.88 | 0.02 | 0.07 | 0.47 | 4.20 | 1.90 | 3.00 | 0.92 | 106 | 50 | 108 | 60 | 46 | 32 | 76 | – | Till | |

* nd – not determined. In the horizons 0–3 and 50–55 cm (core AK-5000) were measured: V – 1120 and 120; Ba – 370 and 370/Zr – 240 and 450.

^{a2} For the sediment types and coordinates see Table 1.

The underwater Słupsk River is the main mechanism of sedimentary material delivery to the Southern Gotland Deep, bringing suspended material from the Bornholm Deep and, in addition, material derived from Polish and southern Swedish shores, as well as products from bottom erosion of the Słupsk Trench floor and slopes. All these materials (including possible pollution components) precipitate in the foredelta of the underwater Słupsk River. Thus, the underwater Słupsk River, together with its foredelta, is unique in the entire Baltic sedimentary system. In terms of the volume of the supplied and accumulated material, it is comparable to the sedimentary system of the Neman River.

THE DISTRIBUTION OF BIOGENIC COMPONENTS AND ELEMENTS IN THE SURFACE SEDIMENTS (0–5 cm)

In the sediments of the Central Baltic and its gulf and bays the following maximum contents of components and elements are found: C_{org} 13.03% (in the Puck Bay, Gdansk Basin – up to 20–25%), N 1.24%; P 0.67%, $\text{SiO}_{2\text{am}}$ 8.92%, CaCO_3 52.8%, Fe 12.70%, and Mn 12.86% (Emelyanov, 1995). In some cases, these maxima occur in the upper sediment layer (0–5 cm) and sometimes in other sediment strata. However, practically in all the cases studied, the content of C_{org} , N and P, sometimes $\text{SiO}_{2\text{am}}$, biogenic CaCO_3 as well as Fe and Mn in the bottom sediments in the Baltic Sea¹ are enriched as compared with their average contents in clays and shale of the contents or hemi-pelagic mud of the margins of the Atlantic Ocean (Емельянов, 1982; Emelyanov, 1995).

The distribution of biogenic components (CaCO_3 , C_{org} , P and N) and chemical major (Fe, Mn) and minor (toxic) elements in the sediments are usually largely determined by their grain-sized composition (Emelyanov, 1995; 2001). The contents of all the studied components and elements increase in the succession of sand – coarse silt – fine silty mud – mud – pelitic mud (Table 3). This means that the elements in the sediments are distributed according to fractions rules (Figs. 9 and 10) (Емельянов, 1982; Emelyanov, 1995). While passing from the coarse silt to the fine silty mud, or from the fine silty mud to mud, the contents drastically changes. This jump results from a sharp growth of pelitic fraction (< 0.01 mm) in the

¹ The maps of the distribution of all the mentioned components and elements are given in Emelyanov, 1995 (The Baltic Sea).

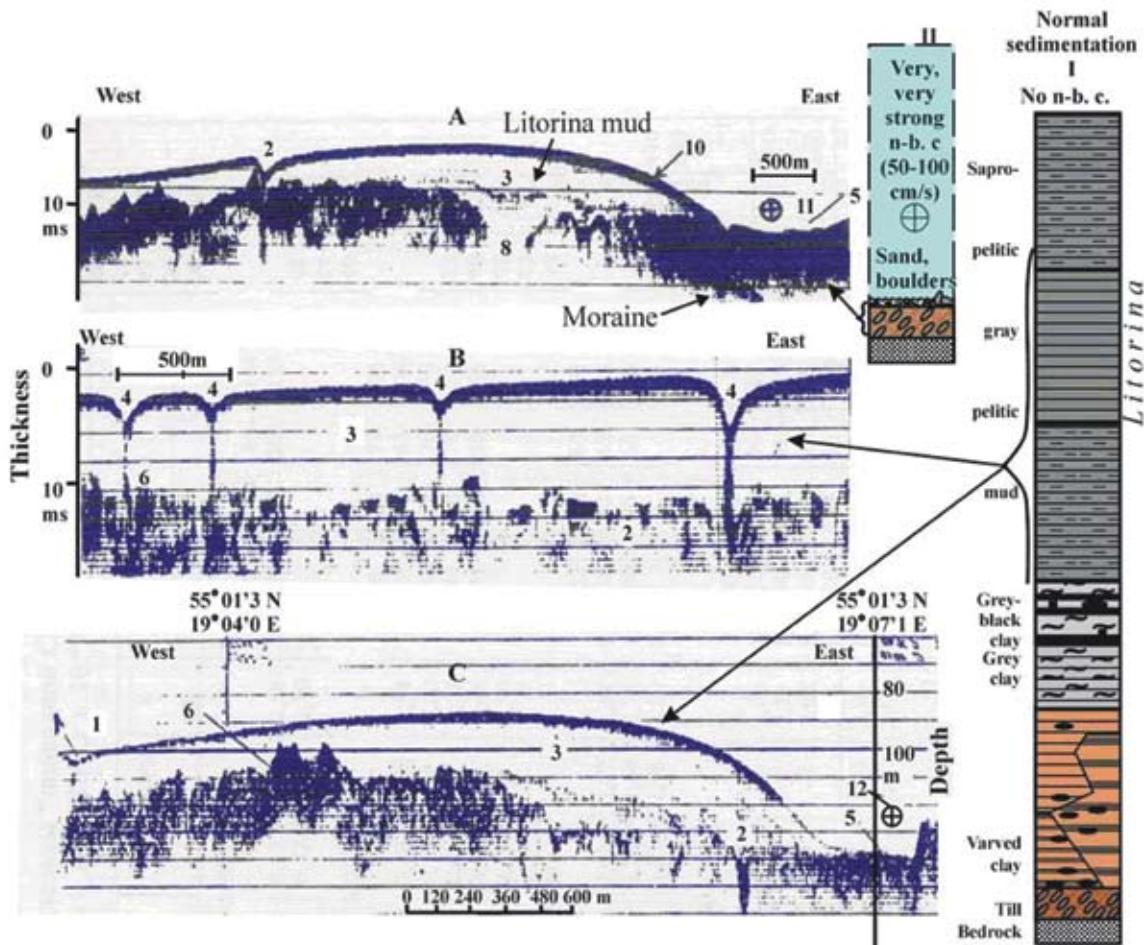


Fig. 7. Acoustical profiles of sediment strata in the region of the “underwater Slupsk river’s” foredelta in the Southern Gotland Basin (acoustic profiles after Блажчишин и др., 1990; interpretation after Emelyanov, 2005). A – eastern part of the muddy field; B – western part of the muddy field; C – eastern part of the muddy field.

1, 2 and 4 – muddy craters (pockmarks); 3 – muddy bodies; 5 – the surface of the nondeposition of the marine Holocene mud and erosion of the bottom; 6 and 8 – the till relief; 10 – the slope of the muddy body; 11 and 12 – near-bottom contour currents (n-b. c.). I – normal sedimentation (full stratigraphic section); II – reduced sedimentation (Holocene sediments and BIL clay are reworked and redeposited)

7 pav. Pietų Gotlando baseino „Slupsko povandeninės upės“ priekinės deltos nuosėdų sluoksnių akustiniai profilai (Блажчишин и др., 1990; interpretacija pagal Emeljanovą, 2005). A – dumblo laukai rytinėje dalyje, B – dumblo laukai vakarinėje dalyje, C – dumblo laukai rytinėje dalyje

same succession. The contents of $\text{SiO}_{2\text{am}}$ and C_{org} in the Gotland Basin increase from sand to aleuro-pelitic mud, and then their contents in the pelitic mud come to somewhat lower values. Such distribution of biogenic components and chemical elements in the sediments of the lagoon and open sea is explained by a mechanical differentiation of sedimentary material in the sea. Evidence from microscopic studies in smears slides indicate that $\text{SiO}_{2\text{am}}$ is represented mainly by siliceous particles of 0.05–0.005 mm in diameter, while a considerable part of C_{org} – by organic detritus, spores and pollen grains of 0.05–0.003 mm in diameter (Емельянов, Романкевич, 1979). It should be noted that such particles are commonly concentrated in aleuro-pelitic (silty) mud, rather than in pelitic (clayey) mud. This is why the maximum average content of $\text{SiO}_{2\text{am}}$ and C_{org} in the Gdansk and Gotland Basins occurs in aleuro-pelitic mud, instead of pelitic mud.

The high factor of enrichment (7.4) of the organic matter (C_{org}) in pelitic mud relative to sand causes the distribution of a very low contents (< 0.5%) in the near-shore (shallow) areas of the Gotland Basin, and a high content (3–5%) in the central

(deepest) part of the Deep. The highest contents of C_{org} (5–7%) are located in some peripheral small areas (near the facts of the deep slopes), where aleuro-pelitic mud is located. The highest content of C_{org} (7%) was found in one small area between the Klins Bank and the Dobrynin morainic ridge (Fig. 2). High contents (3–5%) of C_{org} were found in the mud of the Slupsk “river’s foredelta” as well (Emelyanov, 2001).

The enrichment factor of phosphorous (P) in the pelitic mud relative to sand (1.8, see Table 3) is not so high as compared to that of C_{org} , but it causes low contents of P (< 0.05%) in the shallow area, and normal contents (0.05–0.07%) below the isobath 100 m, and heightened contents (0.07–0.10%) in the Central Gotland Deep (at a depth of 150–220 m). High contents (0.10–0.20%) of P occur in two areas at the deepest part of the Central Gotland Deep (a depth of 220–248 m) and at the Slupsk “river’s foredelta” (or depth of 110–130 m).

The refluxes of P from the sediments to the bottom water were estimated by applying Fick’s Law of Diffusion (Hille et al., 2005). A fairly good positive correlation between the sedimentary P deposition and P release was obtained. P re-

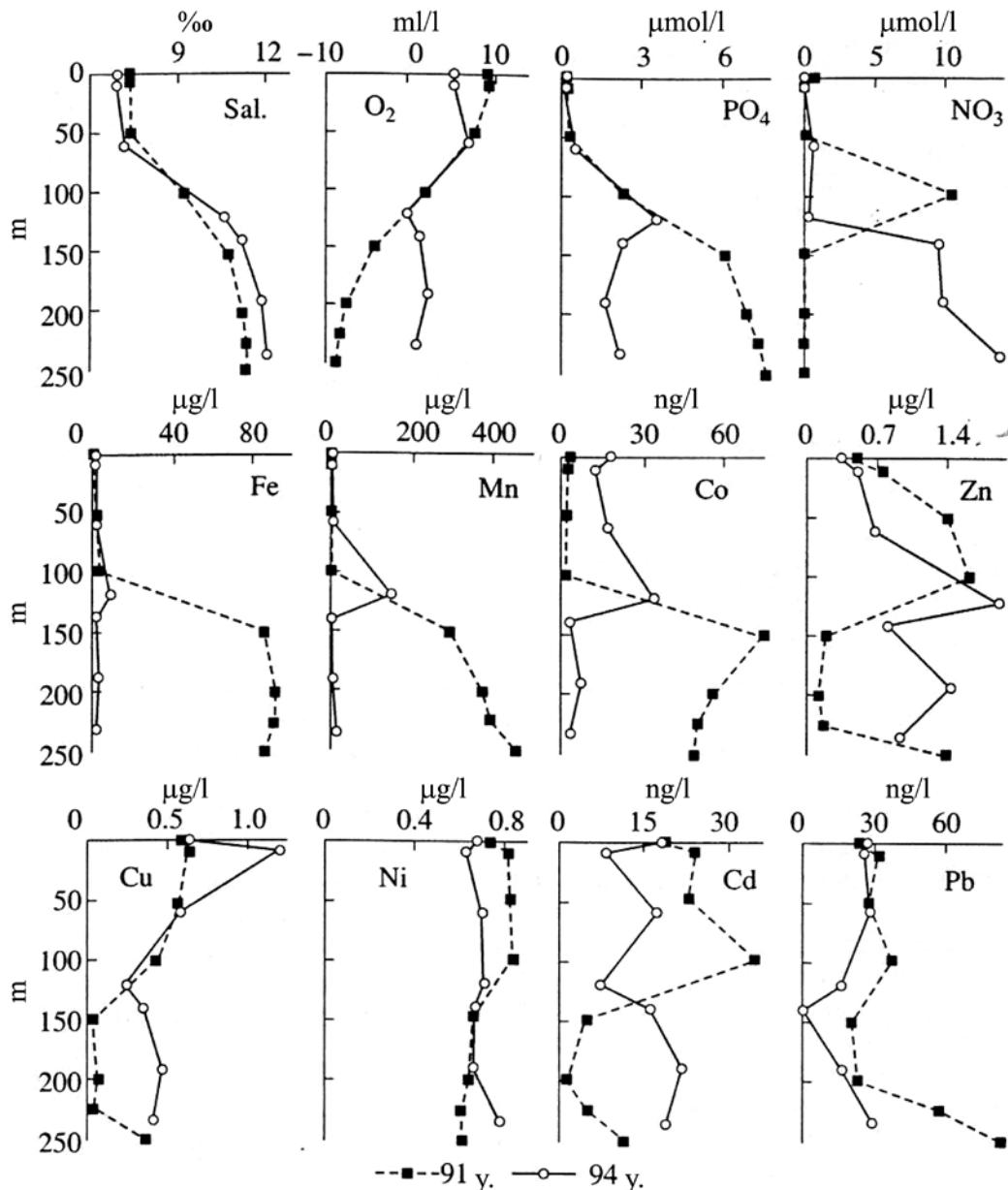


Fig. 8. Vertical distribution of the hydrochemical parameters and dissolved forms of the transition and heavy metals on station BY in the Gotland Deep in May, 1991 (during hydrogen sulphide contamination of near-bottom waters) and in August, 1994 (after the inflow of the saline North Sea waters) (Brügmann, Hallberg, Larsson et. al., 1997; Емельянов, Кравцов, 2002)

8 pav. Tranzitinių bei sunkiųjų metalų išstirpintų formų ir hidrocheminių parametrų vertikalus pasiskirstymas Gotlando jėdaubos stotyje BY 1991 m. gegužę ir 1994 m. rugpjūtį

lease from the sediments by diffusion exceeds the net P deposition by a factor of 2. This suggests that 2 / 3 of the deposited gross P is recycled in the sediments and released back into the water column; only 1 / 3 remains in the sediment permanents (Hille et al., 2005).

The content of the most toxic elements (Pb, As, Cd and Hg) in the sediments of the Gotland Basin is common for the Baltic Sea (Emelyanov, 1995) (Table 3): the maximal contents of toxic microelements are: Pb – up to 39, As – up to 77, Cd – up to 4.0 and Hg – up to 0.21 mg/kg.

As it can be seen from Table 3, the factor of the enrichment of the studied components and elements in the pelitic mud relative to sand are 1.5–7.4 times as large as that in the sands. The awareness of the factors governing the distribution of the average

contents in granulometrically different types of sediments made it noticeably easier to draw maps showing the distribution of the components and elements over the bottom area even in the regions of insufficient sampling network (Fig. 10).

The maximal content of As is characteristic of those samples of the mud, in which there are authigenic iron sulphides. These minerals are good concentrators of As – sulphides contain 270–440 mg/kg of As (Емельянов, Кравцов, 2007). As does not correlate with Fe or with microelements. It does not correlate with the pelitic fraction (Table 4). There is a weak correlation with Mn ($r = 0.22$, Table 4). Other toxic microelements (Zn, Cu and Cd) are in good positive correlation with the fraction of < 0.01 mm, and also with C_{org} , Fe, and Mn (Table 4).

The reason of the maximal contents of As (up to 130 ppm) in some Litorina mud samples of the core Psd-330590 (Table 5), taken in the conventional area where chemical munitions were dumped (Fig. 11), is not chemical munition (lewsite or yperite), but iron sulphides. The iron sulphides are the reason of a very high content of As in the Ancylus clay, which was deposited 8–9 thousands years ago, when there were no chemical munition in the bottom.

CONCLUSIONS

There are places in the Southern Gotland Deep (a depth of 90–130 m) where there are no Holocene sediments. They are re-washed and redeposited by strong near-bottom flows of saline water, which comes to the Gotland Deep from the Słupsk Trough. There are outcrops of till with a thin cover of sand in these places. Bombs and shells with poison that have been thrown into the

sea, should be on the hard bottom, and strong bottom currents should roll them. Outside the re-washed bottom areas there are active depositions of soft mud, particles of which were brought and deposited from the Słupsk near-bottom current. The thickness of the Litorina mud here is the biggest in whole Gotland Basin – up to 730 cm (the sedimentation rate is 0.94 mm/y). Bombs and shells with chemical munition, if they have been thrown here, should be in the soft muddy strata. However, we did not find any chemical munitions in the Southern Gotland Deep. We did neither find any influence of the products of the hydrolysis of yperite, or other kinds of CM on the concentration of toxic elements in the sediments. The chemical composition of the mud from the dumpsite areas and from other regions is similar.

The main chemical elements in the sediments of the Southern Gotland Deep are distributed according to the pelitic fraction (< 0.01 mm) rule: the larger the fraction, the higher the content of chemical elements. The exception is only As, Hg and sometimes Cd.

Table 3. Extreme and average contents of chemical elements in the bottom sediments of the Central Baltic
3 lentelė. Centrinės Baltijos dugno nuosėdų cheminių elementų kiekių kraštutinės ir vidurkinių reikšmės

| | Content, g/kg | | | | | | Content, mg/kg | | | | | | |
|----------------------------------|------------------|------|------|-----|-----|-----|----------------|----|----|-----|----|-----|------|
| | C _{org} | Fe | Mn | Cu | Zn | Ni | Cr | Co | As | Cd | Pb | Sn | Hg |
| Gravel | | | | | | | | | | | | | |
| Min | 0.6 | 5.0 | 0.2 | 10 | 17 | 16 | 17 | 15 | 1 | 0.1 | 5 | 1.2 | 0.02 |
| Max | 9.2 | 59.1 | 1.2 | 127 | 99 | 131 | 68 | 46 | 9 | 0.5 | 16 | 7.2 | 0.03 |
| Average | 2.2 | 21.2 | 0.5 | 34 | 53 | 39 | 37 | 23 | 5 | 0.2 | 8 | 3.2 | 0.02 |
| Sand | | | | | | | | | | | | | |
| Min | 0.5 | 3.5 | 0.1 | 7 | 10 | 10 | 15 | 10 | 1 | 0.1 | 2 | 1.7 | 0.01 |
| Max | 10.4 | 20.5 | 0.6 | 67 | 87 | 68 | 59 | 40 | 21 | 0.3 | 21 | 3.0 | 0.18 |
| Average | 2.2 | 8.7 | 0.2 | 15 | 28 | 25 | 31 | 19 | 3 | 0.1 | 8 | 2.8 | 0.07 |
| Coarse aleurite | | | | | | | | | | | | | |
| Min | 2.7 | 4.5 | 0.1 | 10 | 20 | 15 | 15 | 10 | 1 | 0.1 | 3 | 1.0 | 0.01 |
| Max | 25.2 | 14.5 | 0.6 | 25 | 67 | 41 | 56 | 35 | 53 | 0.5 | 19 | 3.8 | 0.12 |
| Average | 7.8 | 9.5 | 0.2 | 17 | 39 | 26 | 34 | 22 | 8 | 0.2 | 9 | 2.6 | 0.04 |
| Fine-aleuritic mud | | | | | | | | | | | | | |
| Min | 5.3 | 9.1 | 0.1 | 8 | 25 | 16 | 15 | 15 | 1 | 0.1 | 5 | 1.8 | 0.01 |
| Max | 22.5 | 24.4 | 0.5 | 40 | 118 | 68 | 78 | 43 | 60 | 1.0 | 21 | 4.3 | 0.14 |
| Average | 11.7 | 14.8 | 0.2 | 21 | 59 | 32 | 35 | 25 | 10 | 0.2 | 10 | 2.9 | 0.04 |
| Aleo-pelitic mud | | | | | | | | | | | | | |
| Min | 1.7 | 8.3 | 0.1 | 11 | 50 | 23 | 22 | 16 | 3 | 0.1 | 7 | 2.0 | 0.02 |
| Max | 38.6 | 43.2 | 0.8 | 64 | 265 | 73 | 86 | 43 | 42 | 0.7 | 39 | 6.3 | 0.14 |
| Average | 17.0 | 30.3 | 0.3 | 38 | 124 | 43 | 61 | 30 | 9 | 0.3 | 15 | 3.5 | 0.07 |
| Pelitic mud | | | | | | | | | | | | | |
| Min | 11.1 | 12.3 | 0.2 | 14 | 42 | 26 | 20 | 15 | 3 | 0.2 | 6 | 3.7 | 0.02 |
| Max | 37.5 | 66.0 | 48.0 | 91 | 580 | 105 | 134 | 71 | 77 | 4.0 | 32 | 6.3 | 0.21 |
| Average | 21.8 | 46.9 | 4.2 | 49 | 219 | 65 | 89 | 42 | 14 | 0.7 | 20 | 4.3 | 0.07 |
| Mixt sediments | | | | | | | | | | | | | |
| Min | 1.8 | 5.0 | 0.1 | 11 | 24 | 16 | 15 | 15 | 1 | 0.1 | 3 | – | 0.02 |
| Max | 14.0 | 39.1 | 0.5 | 28 | 102 | 39 | 64 | 30 | 15 | 0.3 | 14 | – | 0.19 |
| Average | 6.5 | 18.1 | 0.3 | 19 | 51 | 26 | 35 | 22 | 5 | 0.2 | 9 | – | 0.10 |
| Lakes clay | | | | | | | | | | | | | |
| Min | 0.6 | 9.8 | 0.3 | 10 | 47 | 25 | 27 | 20 | 2 | 0.1 | 5 | 3.0 | 0.02 |
| Max | 8.9 | 67.2 | 0.9 | 68 | 183 | 94 | 118 | 51 | 47 | 0.7 | 29 | 4.4 | 0.05 |
| Average | 4.3 | 39.6 | 0.5 | 35 | 110 | 48 | 65 | 33 | 19 | 0.4 | 18 | 3.9 | 0.03 |
| All sediment types (297 samples) | | | | | | | | | | | | | |
| Min | 0.5 | 3.5 | 0.1 | 7 | 10 | 10 | 15 | 10 | 1 | 0.1 | 2 | 1.0 | 0.01 |
| Max | 38.6 | 67.2 | 48.0 | 127 | 580 | 131 | 134 | 71 | 77 | 4.0 | 39 | 7.2 | 0.21 |
| Average | 9.9 | 24.1 | 1.3 | 29 | 100 | 40 | 52 | 28 | 9 | 0.3 | 13 | 3.5 | 0.06 |

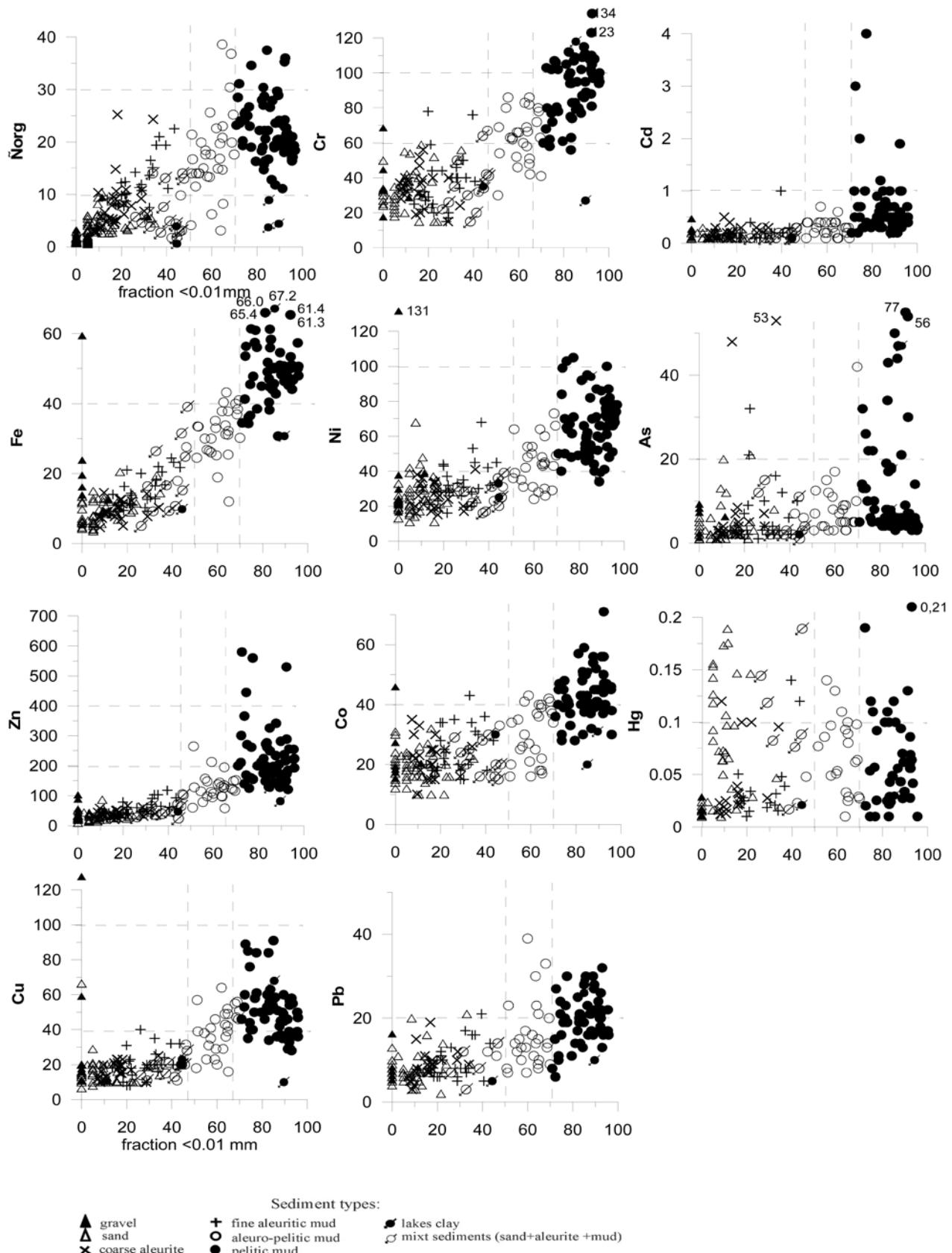


Fig. 9. The distribution of chemical elements (C_{org} , Fe, Mn – in $10^{-1} \%$, Zn – Hg in $10^{-4} \%$) in the bottom sediments (0–5 cm) of the Central 9 pav. Vidurio Baltijos cheminių elementų (C_{org} , Fe, Mn – in $10^{-1} \%$, Zn – Hg in $10^{-4} \%$) pasiskirstymas 0–5 cm dugno nuosėdose

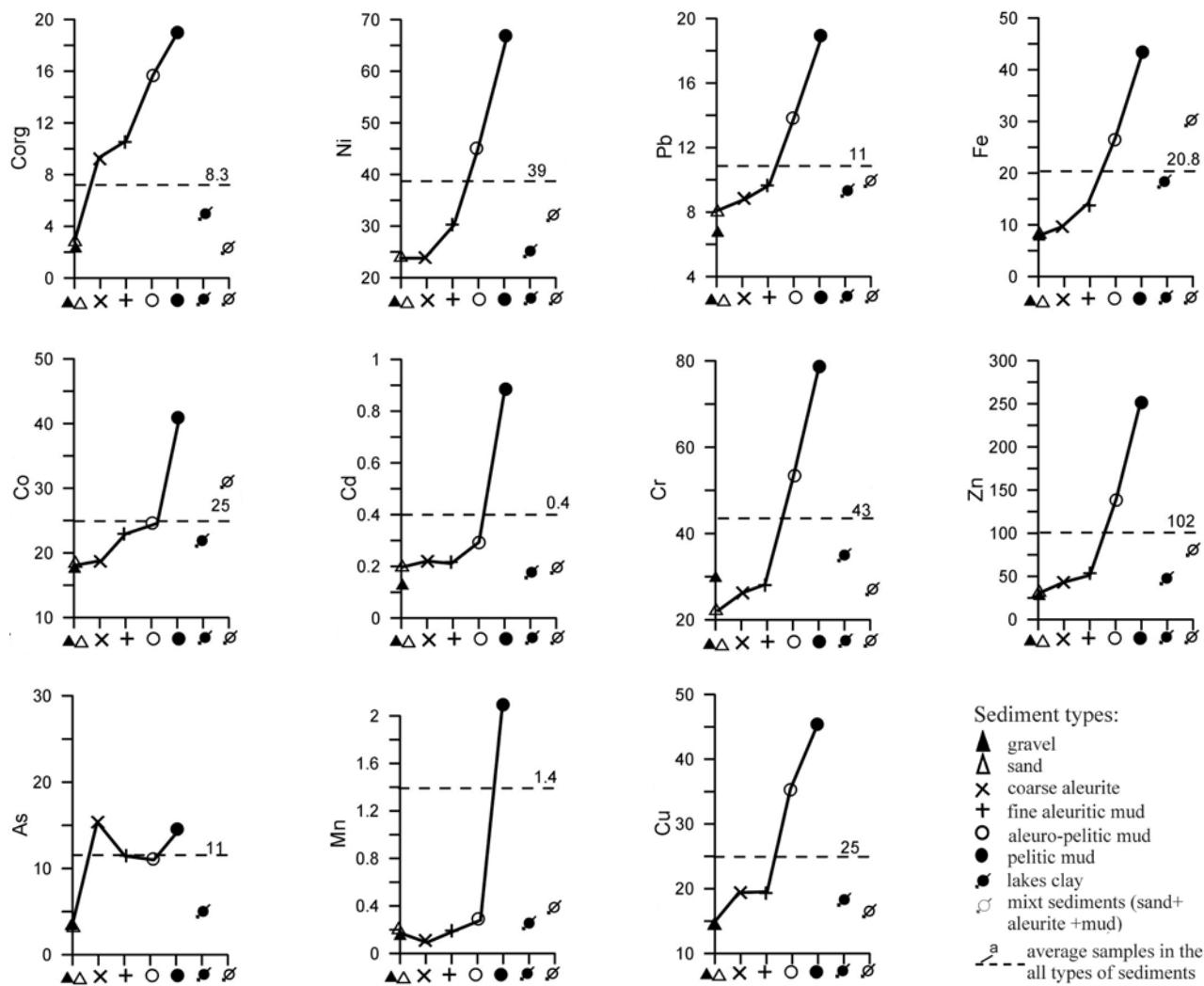


Fig. 10. The distribution of the average contents of elements in different types of the bottom sediments (0–5 cm) of the Central Baltic (the rule of peletic fraction). C_{org} – Mn – in g/kg or 10⁻⁴ %, Zn – As in mg/kg or 10⁻⁴%

10 pav. Cheminių elementų (C_{org}, Fe, Mn – in 10⁻¹ %, Zn – Hg in 10⁻⁴) vidutinių reikšmių pasiskirstymas Vidurio Baltijos skirtingų tipų dugno nuosėdose (0–5 cm) (pelitinės frakcijos taisyklė)

Table 4. The pair correlation of chemical elements and fraction < 0.01 mm in the sediments (0–5 cm) of the Central Baltic

4 lentelė. Vidurio Baltijos nuosėdų (0–5 cm) cheminių elementų ir granuliometrinės frakcijos, smulkesnės už 0,01 mm, porinė koreliacija

| Element | C _{org} | Fe | Mn | Cu | Zn | Ni | Cr | Co | As | Cd | Pb | Sn | Hg | Fraction <0.01 mm |
|-------------------|------------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|-------------------|
| C _{org} | 1 | 0.72 | 0.23 | 0.69 | 0.67 | 0.64 | 0.73 | 0.69 | 0.18 | 0.40 | 0.58 | 0.53 | 0.21 | 0.73 |
| Fe | 233 | 1 | 0.38 | 0.79 | 0.82 | 0.83 | 0.89 | 0.81 | 0.31 | 0.51 | 0.69 | 0.58 | 0.12 | 0.92 |
| Mn | 233 | 233 | 1 | 0.36 | 0.56 | 0.40 | 0.29 | 0.29 | 0.22 | 0.61 | 0.22 | 0.19 | 0.07 | 0.24 |
| Cu | 242 | 233 | 233 | 1 | 0.77 | 0.74 | 0.72 | 0.65 | 0.20 | 0.58 | 0.60 | 0.44 | 0.05 | 0.78 |
| Zn | 233 | 233 | 233 | 233 | 1 | 0.81 | 0.73 | 0.73 | 0.31 | 0.80 | 0.64 | 0.58 | 0.02 | 0.75 |
| Ni | 251 | 233 | 233 | 242 | 233 | 1 | 0.76 | 0.75 | 0.29 | 0.58 | 0.54 | 0.39 | 0.09 | 0.76 |
| Cr | 233 | 233 | 233 | 233 | 233 | 233 | 1 | 0.79 | 0.20 | 0.44 | 0.67 | 0.61 | 0.16 | 0.84 |
| Co | 233 | 233 | 233 | 233 | 233 | 233 | 233 | 1 | 0.31 | 0.45 | 0.61 | 0.53 | 0.07 | 0.77 |
| As | 241 | 232 | 232 | 232 | 232 | 241 | 232 | 232 | 1 | 0.26 | 0.32 | 0.19 | 0.04 | 0.28 |
| Cd | 227 | 227 | 227 | 227 | 227 | 227 | 227 | 227 | 226 | 1 | 0.58 | 0.35 | -0.05 | 0.45 |
| Pb | 233 | 233 | 233 | 233 | 233 | 233 | 233 | 233 | 232 | 227 | 1 | 0.43 | 0.01 | 0.71 |
| Sn | 97 | 97 | 97 | 97 | 97 | 97 | 97 | 97 | 97 | 91 | 97 | 1 | 0.32 | 0.68 |
| Hg | 151 | 151 | 151 | 151 | 151 | 151 | 151 | 151 | 150 | 149 | 151 | 80 | 1 | 0.10 |
| Fraction <0.01 mm | 214 | 182 | 182 | 183 | 182 | 192 | 182 | 182 | 191 | 182 | 182 | 77 | 127 | 1 |

Table 5. The minimal, maximal and average contents of chemical components and elements in the sediments of core Psd-303590, the Stupsk "river's foredelta" (Corg - Na - in %, Li - As - in ppm)
Slentelė. Slupsko upės delta nuoseidū Psd-303590 gėrynyje dherinių komponentų ir elementų minimalūs, maksimalūs vidurkiniai kiekiai

| | C | CO _{2atm} | CaCO ₃ | MgCO ₃ | SiO ₂ | Al | Fe | Mn | Ti | N | Ca | Mg | K | P | Na | Li | Cu | Zn | Cr | Ni | Co | Pb | Cd | As |
|---|------|--------------------|-------------------|-------------------|------------------|------|-------|------|------|------|------|------|------|------|------|------|------|----|----|-----|----|-----|----|----|
| Psd-303590, hor. 0–625 cm, Litorina and Post – Litorina mud | | | | | | | | | | | | | | | | | | | | | | | | |
| min | 2.22 | 2.24 | 0.75 | 4.03 | 0.21 | 0.89 | 46.80 | 7.52 | 4.55 | 0.04 | 0.37 | 0.21 | 0.30 | 1.16 | 2.15 | 0.06 | 1.48 | 62 | 34 | 104 | 50 | 47 | 32 | 8 |
| max | 3.58 | 5.21 | 2.50 | 5.69 | 0.31 | 4.0 | 61.00 | 8.57 | 5.94 | 0.15 | 0.49 | 0.44 | 1.00 | 1.64 | 3.22 | 0.10 | 2.68 | 77 | 59 | 215 | 94 | 220 | 52 | 42 |
| average | 3.02 | 3.61 | 1.65 | 4.88 | 0.24 | 1.66 | 53.98 | 8.13 | 5.21 | 0.10 | 0.42 | 0.33 | 0.66 | 1.41 | 2.73 | 0.08 | 1.95 | 68 | 45 | 130 | 80 | 78 | 40 | 14 |
| Psd-303590, hor. 625–741 cm, Litorina microlaminated mud | | | | | | | | | | | | | | | | | | | | | | | | |
| min | 1.90 | 0.95 | 0.55 | 4.55 | 0.21 | 0.60 | 47.5 | 7.62 | 4.48 | 0.08 | 0.30 | 0.22 | 0.22 | 0.92 | 2.40 | 0.06 | 1.60 | 42 | 16 | 62 | 20 | 34 | 21 | 6 |
| max | 4.01 | 4.62 | 3.08 | 6.52 | 1.88 | 1.10 | 54.00 | 8.73 | 7.57 | 0.90 | 0.50 | 0.46 | 1.23 | 1.88 | 2.97 | 0.07 | 3.39 | 75 | 79 | 137 | 92 | 93 | 52 | 13 |
| average | 2.69 | 2.66 | 1.88 | 5.34 | 0.48 | 0.84 | 51.38 | 8.20 | 5.27 | 0.21 | 0.44 | 0.34 | 0.75 | 1.52 | 2.69 | 0.07 | 2.01 | 65 | 55 | 115 | 76 | 65 | 41 | 9 |
| Psd-303590, hor. 741–947 cm, Ancylus clay | | | | | | | | | | | | | | | | | | | | | | | | |
| min | 0.40 | 0.40 | 0.88 | 5.48 | – | 0.55 | 51.00 | 7.94 | 4.53 | 0.06 | 0.43 | 0.08 | 0.35 | 1.58 | 2.33 | 0.06 | 1.55 | 71 | 38 | 114 | 65 | 47 | 35 | 10 |
| max | 2.52 | 2.24 | 4.03 | 8.81 | – | 1.15 | 58.00 | 9.52 | 6.51 | 0.23 | 0.50 | 0.43 | 1.61 | 2.54 | 3.20 | 0.07 | 3.13 | 96 | 69 | 175 | 88 | 95 | 49 | 21 |
| average | 1.25 | 1.15 | 2.02 | 6.69 | – | 0.78 | 54.63 | 8.84 | 5.54 | 0.12 | 0.47 | 0.20 | 0.81 | 1.93 | 2.81 | 0.06 | 2.13 | 83 | 55 | 138 | 81 | 72 | 44 | 14 |

The content of it depends on the presence of authigenic minerals in the sediments – iron sulphides or iron–manganese nodules or crusts, which are good concentrators of the toxic elements (up to 450 mg As / kg). Due to the presence of sulphides in some layers of the Litorina mud and Ancylus clay, the content of As is the highest – up to 130–131 mg/kg.

The sediments of the Gotland Deep are not contaminated with toxic elements (As, Cd, Pb and others).

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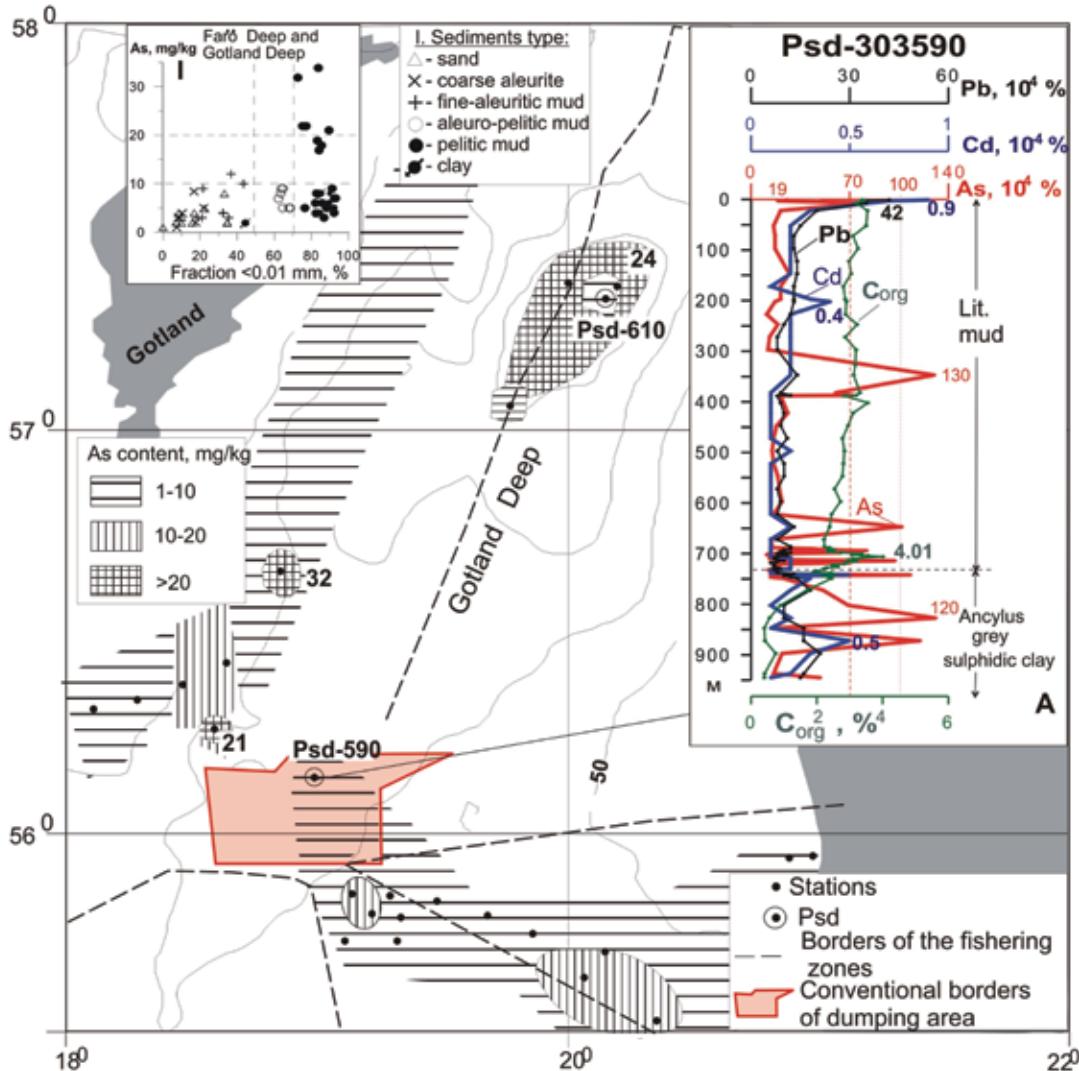


Fig. 11. The content of As (mg/kg) in the sediments (0–5 cm) of the Central Baltic. The samples from the south–eastern corner of the map after Garnaga, Stankevičius, 2005. The numbers on the map – maximal contents of As, %. In the cut-in A: the distribution of toxic elements (Pb, Cd, As) and C_{org} in the mud of the core Psd-303590 (Psd-590), obtained in the conventional area, where chemical munitions were dumped
11 pav. As (mg/kg) kiekis Vidurio Baltijos nuosėdoje (0–5 cm). Pavyzdžiai paimti iš žemėlapio pietrytinio kampo (pagal Garnaga, Stankevičius, 2005). Skaičiai žemėlapyje – As maksimalus kiekiai (10^{-4}). A įkarpoję: toksinių elementų (Pb, Cd, As) ir C_{org} pasiskirstymas Psd-303590 (Psd-590) grėžinio dumble, cheminio ginklo nuskandinimo vietoje

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GOTLANDO BASEINO BALTIJOS JŪROJE, KURIAME PASKANDINTAS CHEMINIS GINKLAS, GEOCHEMINĖ IR GEOEKOLOGINĖ APLINKA

Santauka

Skagerako jūros ir Bornholmo įdaubos rajonų aplinka buvo aprašyta šio straipsnio pirmojoje (A) dalyje (Emelyanov, 2007).

Sviediniai, bombos ir konteineriai su nuodingomis medžiagomis buvo išbarstyti didelėje Gotlando baseino teritorijoje ties Liepojos uostu (Latvia).

Ginklai buvo išmesti pietinėje Gotlando įdubos dalyje (90–130 m gylyje), netoli Slupsko kanalo, iš kurio sūrūs Šiaurės jūros vanduo patenka į Gotlando įdubą. Dėl sumažėjusio srovės greičio iš vandens ant dugno nusėda suspensija, kuri Pietų Gotlando įduboje formuoja stambų išnašų kūgi; maksimalus jo storis Gotlando įduboje siekia 730 cm. Šią teigiamą nuosėdų formą (kūgi) autorius pavadino „povandeninės Slupsko upės“ priekine delta.

Prieinės deltos nuosėdos, jų granuliometrinė ir cheminė sudėtys buvo išnagrinėtos daugelyje ēminiu iš paviršinio sluoksnio (0–5 cm) ir nuosėdų (9,5 m) kolonelių. Šiuo metu ginklų su nuodingomis medžiagomis ant dugno neaptikta.

Cheminiai elementų koncentracijų Gotlando įdubos nuosėdose gana įvairi, maksimalios koncentracijos viršija minimalias: Zn – 39 kartus, Mn – 416 kartų, Fe – 17 kartų, As – 77 kartus, kitų elementų – 10–20 kartų. Vidutinių cheminių elementų koncentracijų pasiskirstymas įvairiuose nuosėdų tipuose atitinka pelitinės (<0,01 mm) frakcijos taisyklikę: koncentracijos didėja nuo smėlio (žvyrždo) iki pelitinio dumblo. Pelitinis dumblas turtingesnis už smėlį 3–8 kartus. Ši taisykla netinka tik arsenui ir gyvsidabriui.

Gotlando įdubos dumbblas redukuotas, jo sudėtyje apstū hidrotröilito ir laisvo sieros vandenilio (H_2S). Tokia redukcinė aplinka neleidžia formuotis oksidiniam autogeniniams mineralams: geležies-mangano konkrecijoms (GMK) ir plutelėms, t. y. mikroelementų koncentratams. Pagal mineralinę sudėtį Gotlando įdubos smėlis daugiausia yra kvarcinis, tame yra mažai Fe ir Mn, kur kas mažiau mikroelementų, lyginant jų vidutinį kiekį visos Gotlando įdubos nuosėdų tipuose.

Ir maksimalūs, ir minimalūs cheminių elementų kiekiai Pietų Gotlando įdubos nuosėdose maži, praktiškai tokie pat, kaip ir visos Baltijos jūros nuosėdose. Taigi nuosėdos yra švarios, jos neužterštos mūsų tyrinėtais elementais. Cheminio ginklo (daugiausia liuizito, iprito, Klarko I, Klarko II ir kt.) hidrolizės produktai, kaip rodo mūsų tyrinėjimai, neatsispindi cheminių elementų (visų pirmą As) koncentracijų nuosėdose.

Didesnis arseno kiekis dumbble priklauso nuo autogeninių elementų kiekiių šiose nuogulose – geležies sulfidų, autogeninių mangano mineralų: oksidineje aplinkoje – tai geležies ir mangano konkrecijos bei plutelės, redukcineje – mangano karbonatai ir geležies sulfidai. Kuo daugiau šių autogeninių mineralų yra nuosėdose, tuo daugiau yra arseno.

Емельян М. Емельянов

ГЕОХИМИЧЕСКАЯ И ГЕОЭКОЛОГИЧЕСКАЯ ОЦЕНКИ МЕСТ ЗАХОРОНЕНИЯ ХИМИЧЕСКОГО ОРУЖИЯ В ГОТЛАНДСКОМ БАССЕЙНЕ БАЛТИЙСКОГО МОРЯ

Резюме

Обстановка мест захоронения в море Скагеррак и в Борнхольмской впадине была рассмотрена в предыдущей статье (Emelyanov, 2007). Химическое оружие (ХО) в Готландском бассейне было выброшено на глубинах более 100 м примерно на траперзее порта

Лиепая, Латвия. Снаряды, бомбы и контейнеры с отравляющими веществами выбрасывались „вручную“, поэтому они рассеяны по большой площади и в настоящее время пока не обнаружены (цит. Fig. 11). Местом выбросов ХО явилась южная часть Готландской впадины (глубины 90–130 м), которая находится под влиянием сильного придонного течения соленых североморских вод, выходящих в Готландскую впадину из Слупского желоба. Здесь происходит разгрузка от несомого этим течением осадочного материала и накапливается крупное осадочное тело литориновых илов с максимальной для Готландской впадины мощностью – 730 см. Из-за этого южная часть Готландской впадины названа автором авандельтой „подводной Слупской реки“.

Донные осадки и их гранулометрический и химический составы данной авандельты, а также всей Готландской впадины были изучены на многих станциях, в т. ч. и в длинных колонках (9,5 м) экспедиции на судне „Poseidon“ (Германия).

В осадках Готландского бассейна разброс значений элементов в разных типах осадков очень велик, и максимальные содержания превышают минимальные для Zn – в 39 раз, для Mn – в 416 раз, для Fe – в 17 раз, для As – в 77 раз, для всех остальных элементов – в 10–20 раз. Распределение же средних содержаний большинства элементов в осадках разных типов соответствует правилу пелитовой фракции, т. е. они повышаются от песков (и гравия) к пелитовым илам. Обогащение илов по сравнению с песками достигает 3–8 раз. Не подчиняется правилу пелитовой фракции лишь As и Hg. Следовательно, пелитовые илы в отличие от всех других гранулометрических типов осадков Центральной Балтики обогащены по отношению к пескам всеми изученными элементами: фактор их обогащения в среднем колеблется в пределах 1,4 (As) = 3,1 (Mn). Все другие типы осадков, за исключением алевритово-пелитовых илов, содержат значительно меньшие количества элементов, чем их средние содержания в осадках всей Центральной Балтики.

Илы Готландской впадины обычно сильно восстановлены, они содержат гидротроилит и свободный H_2S , что не позволяет окисным аутигенным минералам (ЖМК и др.) – концентраторам микроэлементов здесь накапливаться. Пески Готландской впадины по минеральному составу являются полевошпатово-кварцевыми, они содержат мало Fe и Mn и, следовательно, сопутствующих микроэлементов.

В целом, как экстремальные, так и средние содержания химических элементов в осадках Южно-Готландской впадины довольно низкие, практически такие же, как и в осадках всей Балтики. Все это говорит о чистоте донных осадков Балтики: изученными элементами они практически не загрязнены. Второй вывод касается влияния химического оружия. Продукты его гидролиза, в основном, люизит², по имеющимся у нас данным, не оказывают ощутимого влияния на концентрацию и распределение токсичных элементов (в первую очередь, As) в осадках. Повышенные концентрации As в илах обусловлены нахождением в этих илах сульфидов железа и, частично, аутигенных минералов Mn: в окислительной зоне это железомарганцевые конкреции и корки (содержащие до 800–1020 As/кг), в стагнированной – карбонаты марганца.

² В заключительном отчете [Helcom 64B] в списке произведенных ОВ Люизит упомянут в последней строке с примечанием: Production small, but unknown. Бесспорными источниками мышьяка следует указывать Clark I, Clark II, Adamsite, Arsinic oil (смесь Pffificus (phenyldichloroarsine), Clark I, arsenic trichloride and triphenyl-arsine) – всего 13 тыс. тонн. Иприта произведено 25 тыс. тонн.