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The geochemical and geoecological situation in the areas of the Skagerrak and the Baltic Sea where chemical munition was dumped

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Kravtsov, Paka, 2000; Paka, Spiridonov, 2002; Paka, 2004; Emelyanov, Kravtsov, 2007 investigated the geological structure and geoecological situation in all three areas of chemical munition (CM) dumping. In this paper, we shortly describe the first two sites. The results of geochemical, hydrochemical and geoecological research are presented.

The geological structure of the sites where chemical munition (CM) had been dumped is more or less simple, glaciomarine, the bottom is somewhat inclined, with some steps on the bottom in the Skagerrak (depth 180–220 m), and flat (horizontal) in the Bornholm Deep. The bottom is covered mainly by mud (thickness about 1–3 m) in both areas. However, in both sites there are places where the thickness of the Holocene mud is strongly reduced or the mud cover is fully absent. The strong near-bottom currents in these places are able to resuspende the mud and redeposit it. In those places in the Bornholm Deep (depth 80–105 m), on the bottom surface hard moraine or lake clay is lying. The shells and bombs at these places are rolling and are able to move very far from the dumped areas.

The upper layer (0–5 cm) of the mud contains up to 6.29% of $C_{org.}$, 0.35% of P, 0.72% of Mn and up to 227 ppm of As. The contents of all the other toxic elements studied (Pb, Cd, Hg, Cu, Zn) are in the Clarke (mean) concentrations (see Tables 1–8).

Arsenic, as one of the most toxic elements, is released during hydrolysis of CM and disperses in the mud up to average contents of 10–30 ppm. Overclarke contents of this element are concentrated in iron sulphides (up to 440 ppm of As) in the stagnant environment or in the iron–manganese nodules or crusts (up to 1021 ppm of As) in the oxic zone. No signs of the distribution of dispersed arsenic from dumped CM areas over the whole Bornholm Deep were detected. This element is concentrated in some places near sunken warships with CM. According to our data (Emelyanov, Kravtsov, 2007), the background concentrations of As in the mud and its over-concentrations in sulphide and iron-manganese nodules are not ecologically dangerous to man. They are not dangerous for building in the future cable lines and pipelines on the bottom outside of the conventional areas of dumped CM, and these lines will not stimulate CM hydrolysis and the distribution of arsenic over the Bornholm Deep.

Key words: Baltic Sea, Skagerrak, Bornholm, buried chemical munition, geochemistry of sediments, geoecology

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INTRODUCTION

Chemical munition was deposited after 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 (Fig. 1). The deposition of chemical munition in the Skagerrak Sea may be called "concentrated" because it comes from sunken ships with munition. The depositions in the Bornholm and Gotland Deeps are of "scatter" type because aircraft bombs, artillery shells and special containers (reels) were sunken by the "scatter" method. The "concentrated" and "scattered" depositions are detected by the strong gradient of the magnetic field anomaly (Theobald, 2001; Paka, Spiridonov, 2002; Paka, 2004).

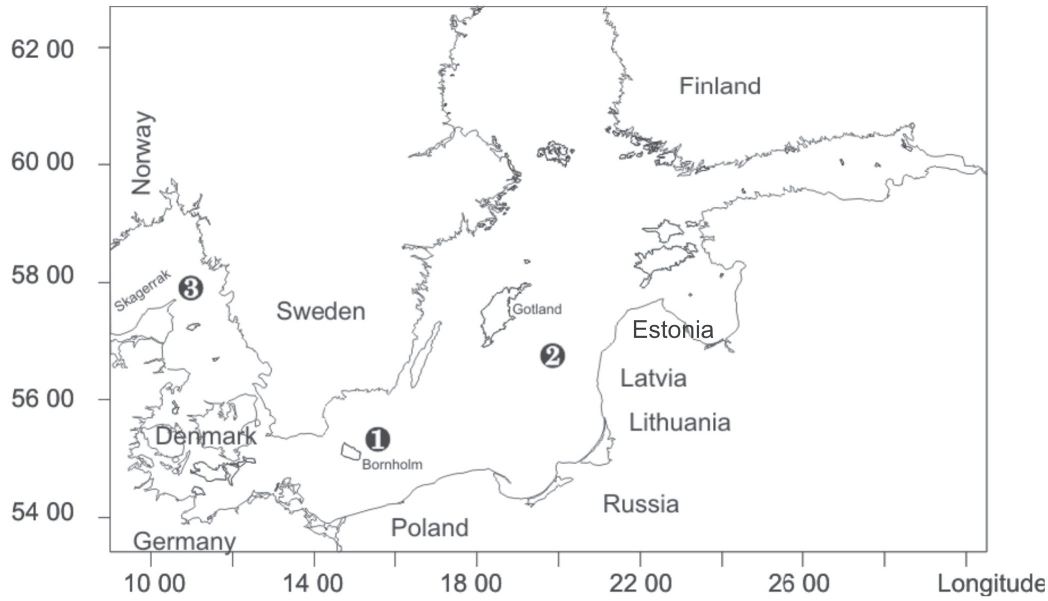

Fig. 1. Location of the munition dumpsites studied in the Baltic Sea and Skagerrak: *1* – Bornholm dumpsite, *2* – Gotland dumpsite, *3* – Måseskär dumpsite

1 pav. Cheminių ginklų paskandinimo vietos Baltijos jūroje ir Skagerake: *1* – Bornholmo, *2* – Gotlando, *3* – Måseskär sąvartynai

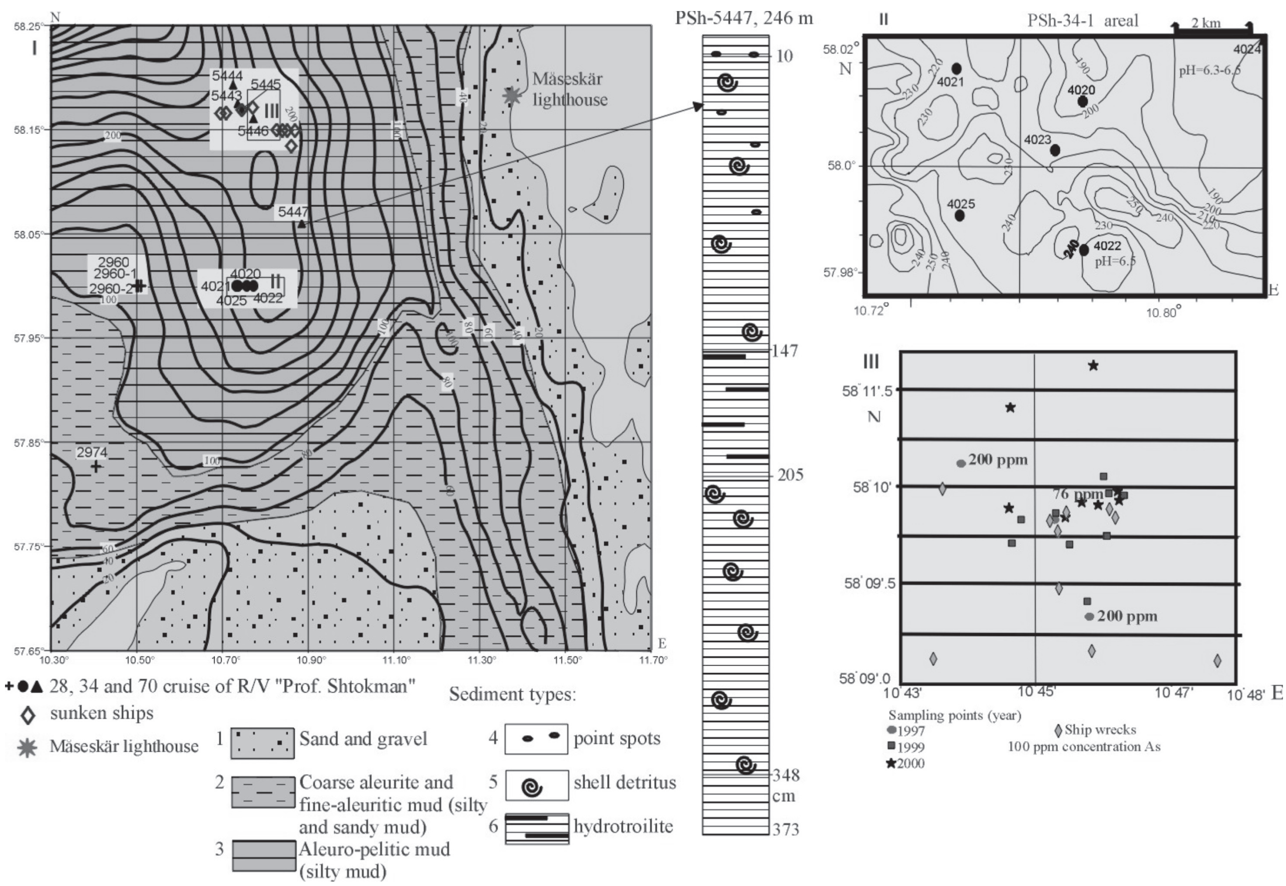

Fig. 2. Bathymetric and sediment map of Måseskär area in the Skagerrak Sea, where ships with chemical munition were sunken. Map I: *1* – location of sampling bottom sediments, *2* – sites of sunken ships, *3* – bathymetry (after Руденко, Ражева, 2004), *4* – sediment types. The lithology of the core PSh-5447 taken in the Skagerrak is shown. II – location of sampling points on the small area (PSh-34-1). pH numbers for the bottom water area after Paka and Spiridonov, 2002. Area III – sampling points, ship wrecks and As content in the surface mud. After Paka and Spiridonov, 2002

2 pav. Skagerako sąsiaurio Måseskär ploto nuosėdų (I) ir batimetrinis (II) žemėlapiai. I žemėlapyje: *1* – dugno nuosėdų ėminių vietos, *2* – paskandintų laivų vietos, *3* – batimetrija (Rudenko ir Razheva, 2005), *4* – nuosėdų tipai. PSh-5447 nuosėdų kolonėlės Skagerako sąsiauryje litologija. II – ėminių vietos PSh-34-1 poligone. Dugno vandens pH dydžiai (pagal Paka ir Spiridonov, 2002). III – ėminių poligonas, paskandinti laivai ir As kiekis paviršiniame dumble (pagal Paka ir Spiridonov, 2002)

Table 1. Content of fraction <0.01 mm and chemical elements in the mud of stations 4022 and 4025 in the Måseskär area, the Skagerrak Sea
1 lentelė. <0,01 mm granuliometrinės frakcijos ir cheminių elementų kiekis Skagerako sąsiaurio Måseskär ploto dumble (4022 ir 4025 stotys)

Horizon, cm	<0.01 mm, %	W, %	%										10^{-4}%						
			SiO_2 total	Al	N	Fe	Mn	Ti	Ca	Mg	K	Na	Rb	Li	Cu	Zn	Cr	Ni	Co
Station PSh-4022, depth 211 m, 58° 09 08' N, 10° 46 34' E																			
0–5	64.	Apm*	–	–	0.21	3.38	0.02	0.48	3.86	1.24	2.14	2.40	82	38	10	122	110	66	32
15–20	–	"	52.00	8.60	–	3.60	0.03	0.45	3.48	1.42	2.02	1.82	94	40	12	122	118	120	32
Station PSh-4025, depth 219 m, 58° 3 42' N, 10° 44 21' E																			
0–5	64.2	Apm	–	–	0.24	3.38	0.02	0.45	5.28	1.64	2.16	2.42	95	40	14	190	126	94	32
15–20	–	"	47.80	7.20	–	3.64	0.03	0.44	4.68	1.74	2.04	1.62	100	42	12	136	84	106	30

* – Apm – aleuro-pelitic (silty) mud.; W – moisture, %.

During the summer of 1997 and 1998, two expeditions of ABIORAS to the Skagerrak Sea (Paka, 2004) and seven expeditions to the Bornholm Basin of the Baltic Sea were undertaken (Emelyanov, Kravtsov, Paka, 2000, 2004; Emelyanov, Kravtsov, 2004; Rybalko et al., 2004).

The report is based on materials of hydrophysical, hydrochemical and geological-geochemical researches carried out aboard R/V "Professor Shtokman" during 1997–2004, as well as on earlier papers 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, 1998; Paka, Spiridonov, 2002; Paka, 2004; Рыбалков и др., 2004).

Studies of the geochemical, hydrochemical, geoecological situation in sites where toxic chemical munition (CM) had been dumped in the Skagerrak Sea (Måseskär area), the Bornholm and Gotland Basins of the Baltic Sea have been carried out by researchers of P. P. Shirshov Institute of Oceanology of RAS, Atlantic Branch (ABIORAS), Kaliningrad, jointly with scientists from All-Russian Geological Institute (VSEGEI), St. Petersburg, in the course of some cruises of R / V "Professor Shtokman" in 1997–2004 within the frames of the programs "Marine Ecological Patrol", "The Baltic" and "World Ocean". Also Swedish and Danish scientists participated in these expeditions (Paka, Spiridonov, 2002).

THE MÅSESKÄR AREA AND THE BORNHOLM DEEPS

I. Måseskär area in the Skagerrak Sea

Chemical munition (CM) is sunken in the area with a depth close to 200 m. The bottom of this area is flat, somewhat inclined, with some steps on the bottom (Fig. 2). The Norwegian Trench served as a border of the study area from W and NW. From the east side, the Måseskär CM cemetery is bordered by the Luisikill small depression which stretches from SSW to NNE (Granbom, 1996; Paka, Spiridonov, 2002).

The primary topography is formed by the glaciomarine processes. On the flat plateau there are morainic hills with the height of up to 15 m. These make rather big slopes on the inclined plateau (the inclination reaches 1.5°) (Paka, Spiridonov, 2002). Typical glaciomarine bottom forms occur on the slope of the Norwegian trench: there are steps and ridges with troughs between them. This means that the CM was buried in the area of a rather contrasting bottom topography. This topography serves as a hydrodynamical area with well expressed sedimentological (resuspension and redeposition) processes. These hydrodynamical processes promote accumulation of sediments from the "shadow" sides of the sunken warships and rewashing of sediments from the opposite side of them.

Bottom sediments. Recent sediments in the Måseskär area are represented by aleuro-pelitic (silty-clayey) mud and in some places by sand. In area II studied the detail (Fig. 2, Tables 1, 2) mud has a gray color; fraction <0.01 mm accounts for 61–66% of mud (Tables 1, 2), while fraction <0.001 mm accounts for 8.4–16.9%. In the surface layer (0–10 cm), mud is represented by a semi-liquid substance; in the layer below mud is soft and contains 50–70% of water.

Table 2. **Content of fraction <0.01 mm, W (moisture) and chemical elements in the aleuro-pelitic mud of st. PSh-4021, depth 192 m, 58°10 75'' N, 10° 43 93'' E, station PSh-34-1, in the Skagerrak Sea, where CM is buried. Mud thickness at this station is 150 cm**

2 lentelė. **<0,01 mm granuliometrinės sudėties, W (drėgmės) ir cheminių elementų kiekis Skagerako sąsiaurio (PSh-4021 stotis, gylis 192 m, (58° 10',75'' N, 10° 43,93 E), PSh-34-1 poligonas) aleuritiniame-pelitiniame dumble, cheminių medžiagų palaidojimo vietoje. Šioje stotyje dumblo storis yra 150 cm**

Horizon, cm	<0.01 mm, %	%										10^{-4} %						
		SiO_2 total	Al	N	Fe	Mn	Ti	Ca	Mg	K	Na	Rb	Li	Cu	Zn	Cr	Ni	Co
0–1	–	–	–	0.05	3.50	0.02	0.45	6.10	1.82	2.18	6.32	88	36	11	112	116	80	40
0–5	61.6	46.30	7.60	–	3.50	0.03	0.38	3.12	1.86	2.12	2.10	74	42	16	122	114	132	40
1–2	–	43.50	6.90	–	3.56	0.03	0.42	4.78	1.58	4.22	4.56	84	36	12	108	122	76	40
3–4	62.2	–	–	0.21	3.38	0.02	0.45	4.72	1.26	2.68	3.14	96	44	12	106	116	140	40
4–5	–	44.70	7.40	–	3.64	0.03	0.44	3.96	1.32	2.16	3.04	82	42	12	108	108	78	50
5–6	–	45.70	7.50	–	3.72	0.03	0.44	3.64	1.32	2.18	2.66	82	40	12	108	108	72	38
7–8	61.4	–	–	0.22	4.04	0.02	0.45	3.52	1.20	2.20	2.98	84	42	12	119	116	74	32
8–9	–	–	–	0.20	3.50	0.02	0.45	3.04	1.60	2.18	2.44	106	36	12	116	116	74	40
10–12	63.3	42.00	7.20	–	3.72	0.03	0.44	3.16	1.66	2.12	2.22	88	40	14	108	116	78	40
12–14	–	–	–	0.34	3.70	0.02	0.46	3.44	1.48	2.18	3.38	84	40	12	119	126	74	42
14–16	64.8	48.00	7.30	–	4.02	0.03	0.44	3.12	1.52	2.24	2.50	80	42	12	100	116	76	38
15–20	–	47.30	7.70	–	3.60	0.03	0.39	1.86	1.92	2.00	1.88	58	45	20	122	174	68	38
16–18	–	49.00	7.90	–	4.12	0.02	0.44	3.10	1.52	2.30	2.22	96	44	12	118	122	70	38
18–20	–	–	–	0.47	3.20	0.03	0.46	3.22	1.24	2.40	6.20	96	40	13	140	126	66	42
20–22	62.9	48.00	7.80	–	4.00	0.03	0.44	3.36	1.36	2.38	2.26	94	40	12	120	116	72	40
22–24	–	46.10	7.40	–0	3.70	0.02	0.44	4.44	1.56	2.42	2.28	90	40	12	120	128	62	32
24–26	–	–	–	0.20	3.50	0.03	0.45	5.42	1.68	2.40	2.86	88	38	12	116	144	54	32
26–28	64.2	47.00	7.60	–	3.58	0.03	0.44	4.06	1.70	2.38	2.42	96	42	12	108	116	50	40
28–30	–	–	–	–	3.60	0.02	0.44	4.02	1.72	2.36	2.48	100	42	10	90	116	50	42
30–32	–	–	–	0.18	2.90	0.03	0.45	4.40	1.44	2.40	6.32	106	40	8	92	116	46	42
32–34	65.9	45.10	7.50	–	3.38	0.03	0.45	4.30	1.48	2.30	3.00	106	42	12	92	92	90	36
34–36	–	46.30	7.80	–	3.64	0.03	0.46	3.76	1.40	2.22	1.74	100	44	12	90	112	66	38
36–38	–	52.00	7.80	–	3.68	0.03	0.46	3.70	1.38	2.16	1.82	104	44	12	90	100	76	36
38–40	–	49.00	7.80	–	3.70	0.03	0.46	3.70	1.36	2.14	1.92	106	42	12	92	92	90	36
40–42	–	–	–	0.18	3.70	0.02	0.47	3.72	1.26	1.18	2.52	102	40	8	100	80	104	32
42–44	63.6	51.00	8.30	–	3.78	0.04	0.47	3.68	1.30	2.18	1.98	96	40	12	108	100	98	32

There were observed numerous 0.1–0.7 mm long ellipsoid pellets in the uppermost part of the mud, especially in more sheltered bottoms. The pellets are formed by pelagic or benthic animals, chiefly bivalves and copepods (Paka, Spiridonov, 2002). Judging from the amount of pellets on the mud bottom surfaces, the sedimentation of sediment pellets dominates in sheltered bays and is possibly also of importance in the more open Kattegat. The pellets are comparatively physically resistant (Paka, Spiridonov, 2002). Thus, redeposition does not seems to cause a significant sorting not of the components of the mud bottom, but of sand grains that are not built into pellets. A few centimeters down to the bottom, the pellets gradually combine into a coherent gel structure. It is considerably more resistant to erosion than the pellets.

The upper layer of the mud (0–50 cm) is mixed by bioturbation. There are numerous *pelecypods*, *polychaetes*, *urchinus*, worms and crabs in the mud (Paka, Spiridonov, 2002).

The surface layer of the mud (5–7 cm, sometimes-more) is oxidized. Deeper, under this oxidized layer, mud is grey. The oxidized layer serves as a good cover – gechemical redox barrier, which does not allow any exchange of chemical elements between the upper (oxidized) and the lower (reduced) layers of the mud.

Arsenic as a toxic element in sediments of the Måseskär area was indicated in 1997. The maximum content of As reaches 95 mg/kg. These maximal concentrations occurred in the lower part of the upper oxidized layer (redox-barrier) at a level of 2–4 cm (at the lower part of the redox barrier Eh). Paka and Spiridonov (2002) supposed that As moved towards the redox-barrier Eh from the lower, reduced layer of the mud.

Abnormally low values of the hydrogen index pH (from 6.52 to 6.31) (Емельянов, Пака, Кравцов, 2000) were observed in the near-bottom waters in the Skagerrak Sea in July 1997 at sites of TCM burials. These anomalies were characteristic of two of the five study sites (stations), with depths 235 and 180 m. It should be noted that one station (PSh-4024) lay some hundreds of meters from a sunken ship loaded with CM (depth 180 m), while other stations were located 4–10 km away from it (Емельянов и др., 2000) (Fig. 2).

Hydrolysis of poisonous matter leads to formation of secondary acids (HCl, HF, HCN, etc.) (Юфит, 1994) that result in a decrease of pH in bottom water to a weakly acid reaction (pH < 7); this is an anomalous phenomenon for marine environment. Most of poisonous substances undergo a rapid and complete hydrolysis in sea water, while only HCN from the whole list of se-condary acids shows a well pronounced toxic effect upon marine organisms (Юфит, 1994). However, the weakly acid reaction in bottom water influences unfavorably the near-bottom life (microorganisms, benthos) and may lead to irreversible changes of their species composition (e. g., development of microorganisms tolerant to yperite) and break the functioning of feed chains and of the ecological system as a whole. Our observations revealed an unusually strong enrichment of near-bottom suspended particulate matter (SPM) with iron (22.5%) (Emelyanov, Kravtsov, 2004; Paka, Spiridonov, 2000), which is comparable to iron contents in the iron–manganese crusts and nodules. It may be associated with corrosion of ships and containers with munitions and distribution of iron hydroxide (rust) throughout the water column.

Current velocities measured by current meters at the station PSh-34-1 at a height of 5 m above sea bottom come up to 10–15 cm.s^{-1} (Емельянов, Пака, Кравцов, 2000). Such currents can transport silt particles, as well as contaminants. It should be stressed that measurements were carried out in calm weather.

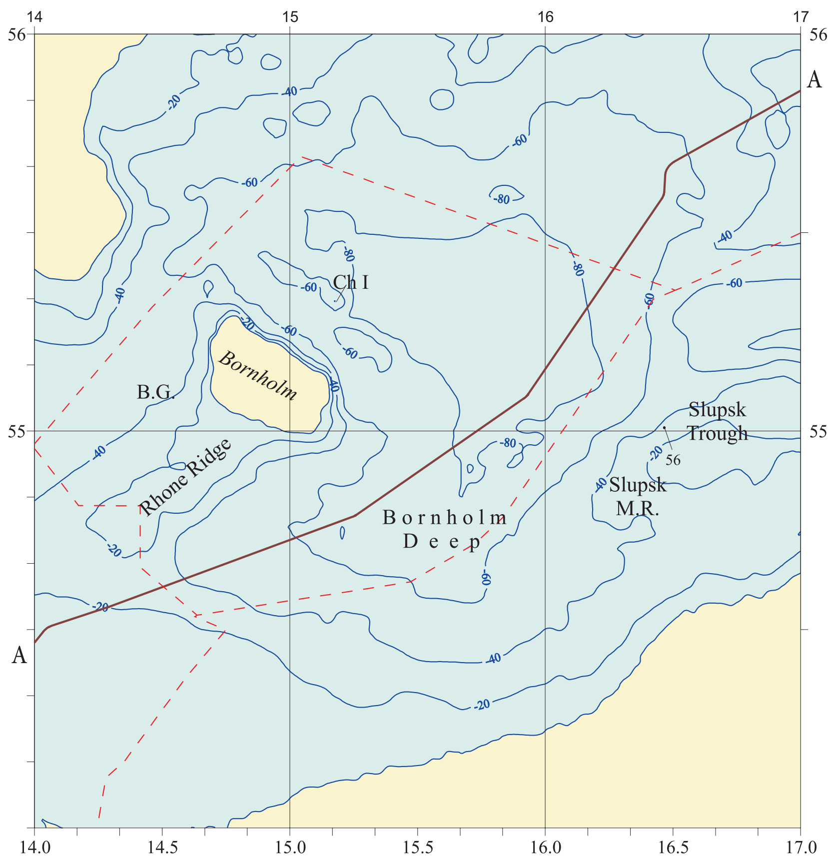

Fig. 3. The bathymetry of the Bornholm Basin. After Руденко, Ражева, 2004. B. G. – Bornholmgat; Ch. I. – Christiansø island; Slupsk M. R. – Slupsk morainic ridge; A – A-approximate position of NE gas pipeline

3 pav. Bornholmo įdaubos batimetrija (pagal Rudenko, Razheva, 2006). BG – Bornholmgat Ch. I. – Christiansø sala; Slupsk M. R. – Slupsko moreninis kalvagūbris; A – A – dujotiekio apytikrė linija

Table 3. Content of fraction <0.01 mm, W (moisture) and chemical elements in the mud of Bornholm Basin where CM is buried
3 lentelė. <0,01 mm frakcijos, W (drėgmės) ir cheminių elementų kiekiai Bornholmo įdubos dumble, cheminio ginklo palaidojimo vietoje

Horizon, cm	<0.01 mm	Sed. type	%									10^{-4}%						
			N	Fe	Mn	Ti	Ca	Mg	K	Na	P	Rb	Li	Cu	Zn	Cr	Ni	Co
St. PSh-4026, depth 93 m																		
0–5	57.9	Apm	0.95	4.02	0.28	0.37	2.42	1.82	2.86	2.22	0.10	174	46	50	200	50	62	30
15–20	69.5	"	0.65	3.92	0.21	0.37	0.88	1.74	2.68	2.80	0.09	158	46	36	194	56	78	30
St. PSh-4028, depth 92 m																		
0–5	71.3	Pm	0.80	4.08	0.22	0.35	0.62	1.49	2.12	1.56	0.09	167	46	44	200	56	60	30
15–20	66.5	Apm	0.60	4.90	0.29	0.33	0.60	0.72	2.00	1.38	0.08	160	48	40	226	56	56	30
St. PSh-4029, depth 95 m																		
0–5	70.5	Pm	0.80	4.50	0.61	0.34	0.72	1.57	1.90	1.44	0.09	167	46	44	200	56	60	30
15–20	67.9	Apm	0.75	4.66	0.43	0.33	0.75	1.57	2.12	1.46	0.08	160	48	40	226	56	56	30
St. PSh-4031, depth 95 m																		
0–5	79.2	Pm	0.81	5.20	0.14	0.42	0.66	1.58	3.14	2.68	0.07	112	34	48	232	68	94	46
15–20	74.6	Pm	0.69	5.78	0.21	0.39	0.42	1.52	2.92	1.62	0.09	114	34	36	152	92	70	40
St. PSh-4032, depth 96 m																		
0–5	75.8	Pm	0.83	5.34	0.28	0.40	0.42	0.46	2.78	1.84	0.10	111	32	52	220	68	91	30
15–20	74.0	Pm	0.90	5.30	0.30	0.41	0.42	1.54	2.74	1.62	0.09	111	30	50	206	66	80	26
St. PSh-4033, depth 96 m																		
0–5	75.1	Pm	0.88	5.30	0.20	0.40	0.58	1.54	2.80	1.6\52	0.09	114	32	62	214	96	64	32
			0.83	4.50	0.20	0.39	0.42	1.58	3.00	1.14	0.10	101	32	64	190	88	94	32

It is evident that under conditions of strong autumn and spring storms, the velocities of bottom currents could be several times as high as before.

II. Bornholm Basin

II.1. Bottom relief

The Bornholm Deep is located east of Bornholm Island in the southwestern part of the Baltic Sea. The margins of the Deep are bordered between 54° 30' and 55° 45' N and 14° 50' and 16° 30' E. The Deep itself is defined as an area inside the 50 m isobath (Fig. 3). The Bornholm Deep has an area of about 14000 km^2. The depth of the Deep reaches 90 m, maximum 110 m (Руденко, Ражева, 2004). The Bornholm Deep is surrounded by shallow areas 25–50 m deep. The Deep is connected with the Arkona Deep by the Bornholm Gate Ridge (depth 46 m) in the northwest and by a morainic ridge in the Slupsk Channel (Trough) in the southeast (the maximum depth 56 m).

The slopes of the Bornholm Deep are gently inclined. Only in the west they are steep. In the small plateau there is Christiansö Island. This island is separated from Bornholm Island by a valley about 60–70 m deep.

According to Folk's classification (Folk, 1974), ten grain-size types of bottom sediments are distinguished (Emelyanov, Nielsen, 1995). The most widespread sediment types are sand and mud, followed by silty sand, muddy sand, sandy silt, sandy mud and silt. Silt is characteristic mainly of the southern, most shallow area of the basin. Silt usually corresponds to either fine-aleuritic or aleuro-pelitic mud according to the IORAS classification. The northern deep-sea area of the Bornholm Deep is covered by mud. This mud corresponds to pelitic mud in the IORAS classification (Fig. 4). According to Folk's triangle, clay is distinguished in two small areas only – at stations PD-2439 (water depth 70 m) and PSh-2554 (water depth 93 m). Samples from these stations contain 78.0 and 82.1% of the <0.01 mm fraction and 49.4 and 45.7% of the <0.001 mm fraction, respectively.

According to IORAS classification (Bezrukov, Lisitzin, 1960; Emelyanov, Nielsen, 1995), sediments on the flat bottom in the Bornholm Deep are represented by aleuro-pelitic (silty-clayey) and pelitic (clayey) mud which contains 50–70 and 70–79% of fraction <0.01 mm, respectively (Emelyanov, Neumann et al., 1994) (Tables 3, 4a, 4b, 5).

All types of the Bornholm Deep muds are deposited under slightly reduced conditions (Fig. 4). The Eh values in the mud are usually negative and reach –135 mV.

Recent sediments (0–5 cm) of the Bornholm Deep, including pelitic (clayey) mud (Fig. 4) are terrigenous. Among clastic minerals, quartz is prevailing and usually constitutes 80–90% of the 0.05 mm fraction. Feldspar comprises up to 2%, mica up to 5–6%, and clastic glauconite is present. The clastic part of the fraction 0.1–0.05 mm is represented mainly by mica, common hornblende, epidote-clinozoisite, ilmenite-hematite and garnet. Moreover, the heaviest minerals (quartz in the

Table 4. Sediment type and content of fraction <0.01 mm and chemical elements in mud at the area of Bornholm Deep where CM is buried. After Emelyanov, Kravtsov, Paka, 1999 (st. PSh-4030, 55°21', 63 N, 95°37', 13 E)
4 lentelė. Sedimentų pobūdis (Apm – aleuritinis-pelitinis dumblas, Pm – pelitinis dumblas (molis) <0,01 mm frakcijos ir cheminių elementų kiekis Bornholmo įdubos dumble, cheminio ginklo palaidojimo vietoje

Horizon, cm	Sed. type, Se	%											ppm or 10^{-4} %							Moisture W, %	Fraction < 0.01 mm, %
		$SiO_{2tot.}$	Al	Fe	Mn	Ti	N	Ca	Mg	P	K	Na	Rb	Li	Cu	Zn	Cr	Ni	Co		
PSh-4030, Grab, depth 95 m																					
0–5	Pm	–	–	5.32	3.24	0.32	0.64	1.04	1.55	0.11	2.08	1.88	154	44	36	158	56	56	28	75.9	70.6
15–20	Apm	–	–	3.52	2.76	0.31	0.77	1.28	1.53	0.11	1.96	1.30	137	44	36	128	44	60	24	75.5	66.7
PSh-4030, NC, depth 95 m																					
0–1	Apm	–	–	3.52	0.25	0.34	0.85	0.86	1.46	0.10	2.12	1.34	152	44	44	214	44	60	30	82.6	67.5
2–3	Apm	–	–	3.52	0.33	0.38	0.93	0.62	1.42	0.09	2.12	1.14	156	46	44	192	56	56	28	–	–
4–5	Apm	47.20	7.60	3.70	0.49	0.38	1.10	0.50	1.36	0.09	2.30	1.28	148	46	36	204	44	60	26	82.2	67.0
6–7	Apm	–	–	3.62	0.22	0.38	0.88	0.66	1.36	0.09	2.34	1.16	146	46	32	192	56	56	28	–	–
8–9	Apm	51.00	8.00	4.02	0.38	0.36	1.10	0.68	1.44	0.09	2.64	2.00	167	44	44	212	56	60	30	–	–
9–10	Apm	–	–	3.26	0.32	0.34	1.08	0.86	1.44	0.10	2.60	1.88	160	46	58	226	56	56	32	78.4	68.2
12–14	Apm	50.00	8.00	2.88	0.37	0.35	1.05	0.80	1.42	0.09	2.50	1.92	152	46	40	204	56	54	28	–	–
16–18	Apm	51.00	7.90	3.70	1.03	0.35	1.10	1.10	1.35	0.25	2.50	1.72	148	46	32	180	64	52	26	–	–
18–20	Apm	–	–	4.08	0.70	0.37	0.80	1.22	1.46	0.10	2.46	1.70	152	46	32	158	64	54	24	77.3	64.1
22–24	Apm	51.00	8.00	5.58	0.47	0.38	0.72	1.14	1.54	0.10	2.64	1.84	136	46	32	120	56	54	26	–	–
26–28	Apm	51.00	8.30	5.00	0.28	0.37	0.71	0.94	1.50	0.09	2.54	1.74	158	46	30	132	56	66	28	–	–
32–34	Apm	51.00	8.10	4.02	0.32	0.36	0.88	0.98	1.57	0.10	2.60	1.66	168	46	30	122	56	56	28	73.1	66.2
34–36	Apm	49.00	7.80	5.16	0.40	0.36	0.80	0.94	1.49	0.09	2.50	1.82	164	46	30	106	56	52	28	74.4	67.7

Note. G – grab; NC – Niemisto Corer. Sediment type: Apm – aleuro-pelitic (silty) mud; Pm – pelitic mud (clay).

light subtraction and ilmenite, magnetite and garnet in the heavy one) are more frequent in the marginal areas, while mica and glauconite are more frequent in the deeper areas of the basin. Illite is the prevailing clay mineral, followed by kaolinite, montmorillonite and chlorite.

Vegetal remains are abundant in the upper layer of sediments, including darnel of cereals, pollen grains, spores and diatom skeletons. Shells of the mollusk *Macoma baltica* and their fragments were also found.

Authigenic minerals are frequently represented by phosphates, including phosphates developed on fish bones, and Fe-sulphides. It seems to be a characteristic feature that despite of reduction of sediments, limonite and hydrogoethite are found in many cases. These hydrous oxides are apparently supplied from the surrounding land area, while sulphides are authigenic / diagenetic. At stations PSh-2545 and PSh-2554 (Figs. 5, 6), brown spheroidal and black sulphide microconcretions are found.

At stations PSh-2555 and PSh-2560, carbonate spherulites in amounts of 15.3% and 10.7% respectively occur. These spherulites are probably authigenic. Previously, siderite, barite and Mn-calcite were found in the Bornholm Deep sediments (Blazhchishin, 1976).

Some samples of aleuro-pelitic muds at three stations contain much calcium carbonate – up to 15.80% of clastic calcite and dolomite. This sediment type had the highest content of C_{org} in the upper layer in the Bornholm Deep – up to 6.28%. The content of SiO_{2am} was also increased (up to 3.53%), and at one station the content of Fe was increased up to 7.08% (Emelyanov, Christiansen, 1995).

For the rest of the elements, the contents are normal for Baltic Sea muds (Emelyanov, 1981, 1986, 1995).

The bulk SiO_2 makes up 46.92–53.63% in pelitic muds, $A1_2O_3$ 12.51 – 16.67%, K_2O up to 4.01%.

The contents of organic remains in the pelitic mud are high and the SiO_{2am} content is slightly increased (Emelyanov, Christiansen, 1995). The content of $CaCO_3$ is also increased (in one case even up to 16.75%, apparently the highest value for the Bornholm Deep). At some stations a high content of Mn was observed (up to 0.40%). It is apparently present as Mn-carbonates of complex composition.

Individual mud samples are enriched in one of the trace elements (Zn, Zr or Ba). The content of Ni is high for almost all mud samples studied (Baturin, Emelyanov, Kunzendorf, 1995).

New data on some sediment samples and on the short cores are shown in Tables 3, 4 and 5 and the content of trace metals and REE in Table 6.

II. 2. Sediment thickness

Mud in the Bornholm Basin accumulates below the 50 m isobath (Emelyanov, Trimonis, Slobodyanik and Nielsen, 19951). Thicknesses covered by cores

Table 5. **Content of fraction <0.01 mm, W (moisture) and chemical elements in the mud of st. Sh-4027, depth 93 m (55° 21, 43' N, 15° 43' 09'' E) Borhholm Basin where CM is buried**
5 lentelė. **<0,01 mm frakcijos, W (drėgmės) ir cheminių elementų kiekiai Bornholmo įdubos dumble (PSh-4027 stotis, gylis 93 m (55° 21', 43'' N, 15° 43' 09'' E), cheminio ginklo palaidojimo vietoje**

Horizon, cm	< 0.01 mm	Sed. type	%										ppm or 10^{-4} %							
			$SiO_{2tot.}$	Al	N	Fe	Mn	Ti	Ca	Mg	K	Na	Rb	Li	Cu	Zn	Cr	Ni	Co	As
0–1	68.6	Apm	–	–	1.43	4.28	0.44	0.31	0.52	1.49	2.46	3.36	142	44	54	208	56	60	26	–
0–5	67.2	"	–	–	0.60	4.12	0.45	0.44	2.42	1.62	2.68	2.14	138	40	46	250	60	52	40	–
2–3	61.8	"	–	–	1.10	4.66	0.18	0.34	0.62	1.55	2.30	2.80	144	44	36	200	74	64	24	–
3–4	–	"	49.00	7.60	–	4.22	0.19	0.34	0.98	1.62	2.58	2.02	140	44	38	182	72	70	28	13
4–5	66.5	"	–	–	1.30	4.66	0.29	0.33	1.08	1.64	2.54	3.72	133	46	30	168	74	74	28	–
6–7	–	"	–	–	1.28	3.66	0.28	0.34	0.62	1.51	2.24	2.40	154	46	30	162	56	68	30	–
7–8	–	"	49.00	7.90	–	4.28	0.29	0.34	0.52	1.50	2.32	2.12	162	44	30	146	72	64	30	32
8–9	–	"	–	–	0.75	4.08	0.24	0.34	0.50	1.49	2.32	2.10	167	46	24	132	56	62	26	13
9–10	–	"	50.00	8.00	–	4.16	0.23	0.34	0.48	1.52	2.40	2.02	150	44	30	122	64	58	28	13
10–12	63.0	"	45.30	7.20	–	4.24	0.27	0.34	0.48	1.50	2.40	2.08	154	44	30	106	52	64	28	16
10–15	68.4	"	46.10	7.40	–	4.38	0.30	0.40	0.98	1.50	2.86	1.90	132	42	42	164	78	52	42	–
12–14	–	"	–	–	0.79	4.28	0.66	0.32	0.68	1.42	2.06	1.75	158	46	30	80	44	64	26	18
14–16	–	"	44.70	7.20	–	4.36	0.57	0.33	0.52	1.42	2.36	2.02	156	46	32	92	52	68	30	28
15–20	–	"	–	–	0.88	4.29	0.29	0.39	0.36	1.42	2.58	2.66	144	42	33	199	84	54	28	–
16–18	–	"	–	–	1.18	4.34	0.46	0.33	0.50	1.33	2.22	1.94	156	46	32	92	44	64	28	22
18–20	–	"	46.50	7.40	–	4.54	0.57	0.33	0.64	1.58	2.32	2.04	164	46	30	100	48	64	28	40
20–22	68.8	"	–	–	–	4.72	0.42	0.37	1.02	2.64	2.62	1.88	136	46	30	132	60	56	24	–
20–25	64.5	"	–	–	0.60	4.40	0.32	0.37	0.96	1.66	2.68	1.92	130	42	36	150	84	52	44	–
22–24	–	"	–	–	0.49	6.22	0.72	0.31	0.94	1.60	2.30	2.80	170	46	32	120	44	60	28	34
24–26	–	"	42.80	6.90	–	4.72	0.68	0.32	0.64	1.52	2.24	2.04	158	44	32	114	52	62	26	18
26–28	–	"	–	–	0.40	4.50	0.34	0.33	0.62	1.44	2.32	2.08	152	44	32	126	56	64	26	16
28–30	–	"	45.60	7.20	–	4.36	0.40	0.33	0.72	1.50	2.36	2.16	152	44	32	116	44	64	26	12
30–32	–	"	–	–	–	4.02	0.28	0.37	0.94	1.52	2.58	1.76	160	46	30	120	58	62	28	21
30–35	67.3	"	–	–	0.56	4.22	0.14	0.37	0.96	1.60	2.96	1.72	133	44	28	140	102	114	40	–
32–34	–	"	–	–	0.70	3.99	0.58	0.33	0.76	1.44	1.98	2.75	148	46	28	156	36	60	26	41
34–35	64.7	"	44.00	7.50	–	4.02	0.28	0.38	0.70	1.38	2.28	2.18	140	42	34	116	58	56	28	17
36–38	–	"	–	–	–	4.72	0.24	0.37	0.90	1.50	2.48	1.84	142	46	30	98	62	66	28	–
40–45	62.2	"	–	–	1.00	4.35	0.17	0.38	0.94	1.56	2.80	2.20	114	42	34	124	84	52	28	–
50–55	63.0	"	49.00	7.90	0.45	4.40	0.34	0.39	0.84	1.60	2.82	2.02	112	40	34	122	60	74	24	–
60–65	70.1	Pm	–	–	0.45	4.11	0.60	0.39	0.96	1.84	2.94	2.10	112	40	26	120	60	106	24	–
70–75	64.9	Apm	44.60	7.40	–	4.96	0.38	0.43	0.80	1.62	2.96	2.00	122	42	30	116	62	88	24	–
80–85	67.4	"	–	–	0.40	4.83	0.44	0.34	0.74	1.74	3.02	2.50	120	46	30	120	84	106	20	–
90–95	67.2	"	53.00	9.10	–	4.64	0.34	0.34	0.80	1.74	3.02	2.16	126	46	30	116	78	90	24	–
100–105	68.7	"	–	–	0.48	4.29	0.21	0.37	0.96	1.74	3.08	2.68	133	47	28	114	102	72	20	–
110–15	65.1	"	–	–	0.53	4.03	0.11	0.38	1.02	1.74	1.98	2.46	139	40	28	124	102	72	23	–

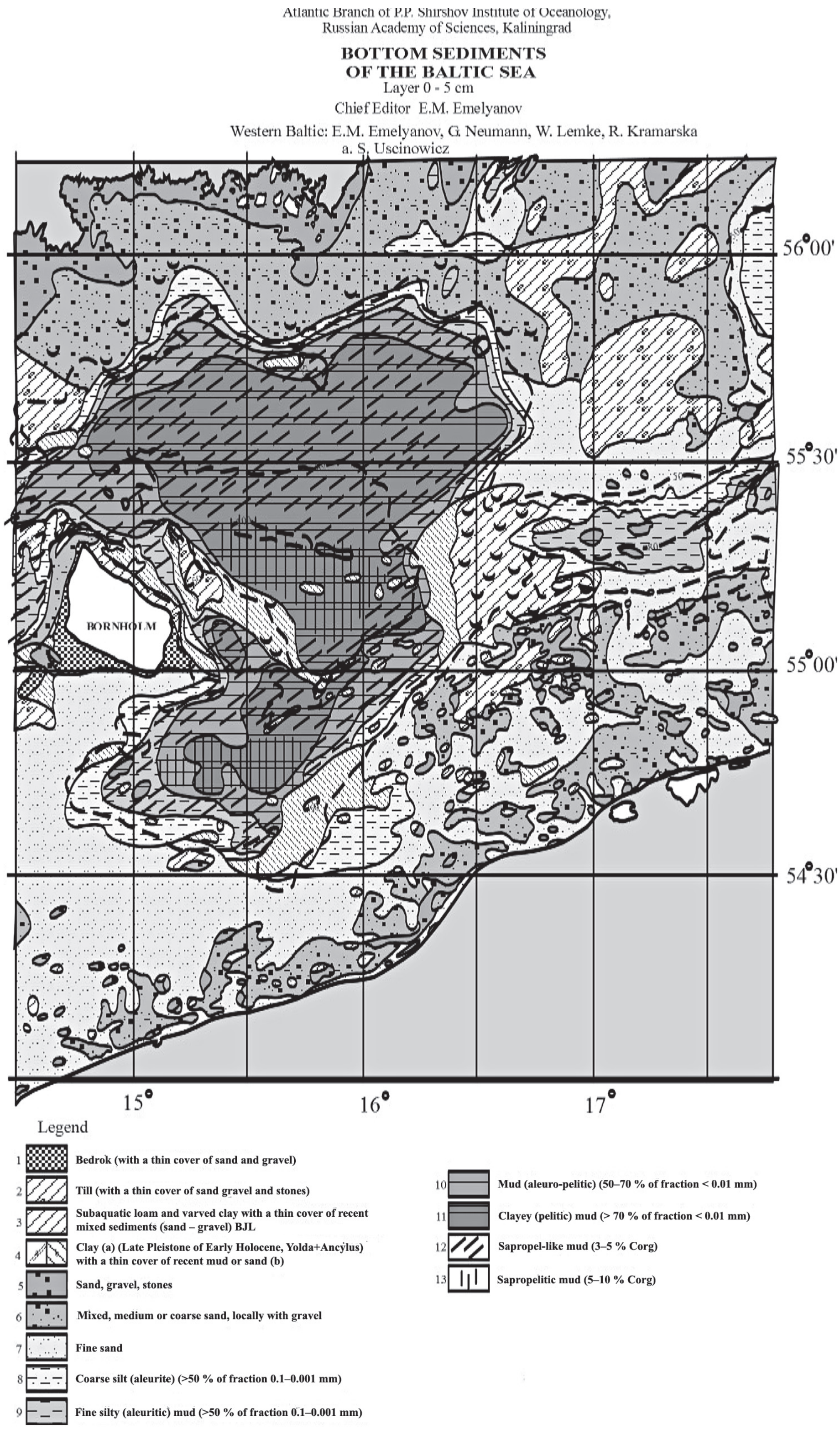

Fig. 4. Bottom sediments of the Western Baltic (after Emelyanov, Neumann, Lemke, Kramarska and Uscinowicz, 1994) with changes by E. Emelyanov (2005). The map was digitized by Y. E. Olkhova (2005)

4 pav. Vakarų Baltijos dalies dugno dabartinės nuosėdos (pagal Emelyanov, Neumann, Lemke, Kramarska, Uscinowicz, 1994) su E. M. Emelyanovo papildymais, (2005). Žemėlapį sudarė Y. E. Olkhova (2005)

reach 280–300 cm (Figs. 6, 7). In accordance with CSP data and Parasound echosounder, these thicknesses can reach even 8–12 m. However, the Parasound echosounder did not allow differentiating between Litorina mud, Ancylus clay and Yoldia clay. The echograms, however, showed a distinct boundary between Holocene muds and clays and the underlying varved clays (Figs. 6, 7). Marine Holocene mud (Hl_{2-3}) reaches the greatest thicknesses in the central area of the Bornholm Basin close to

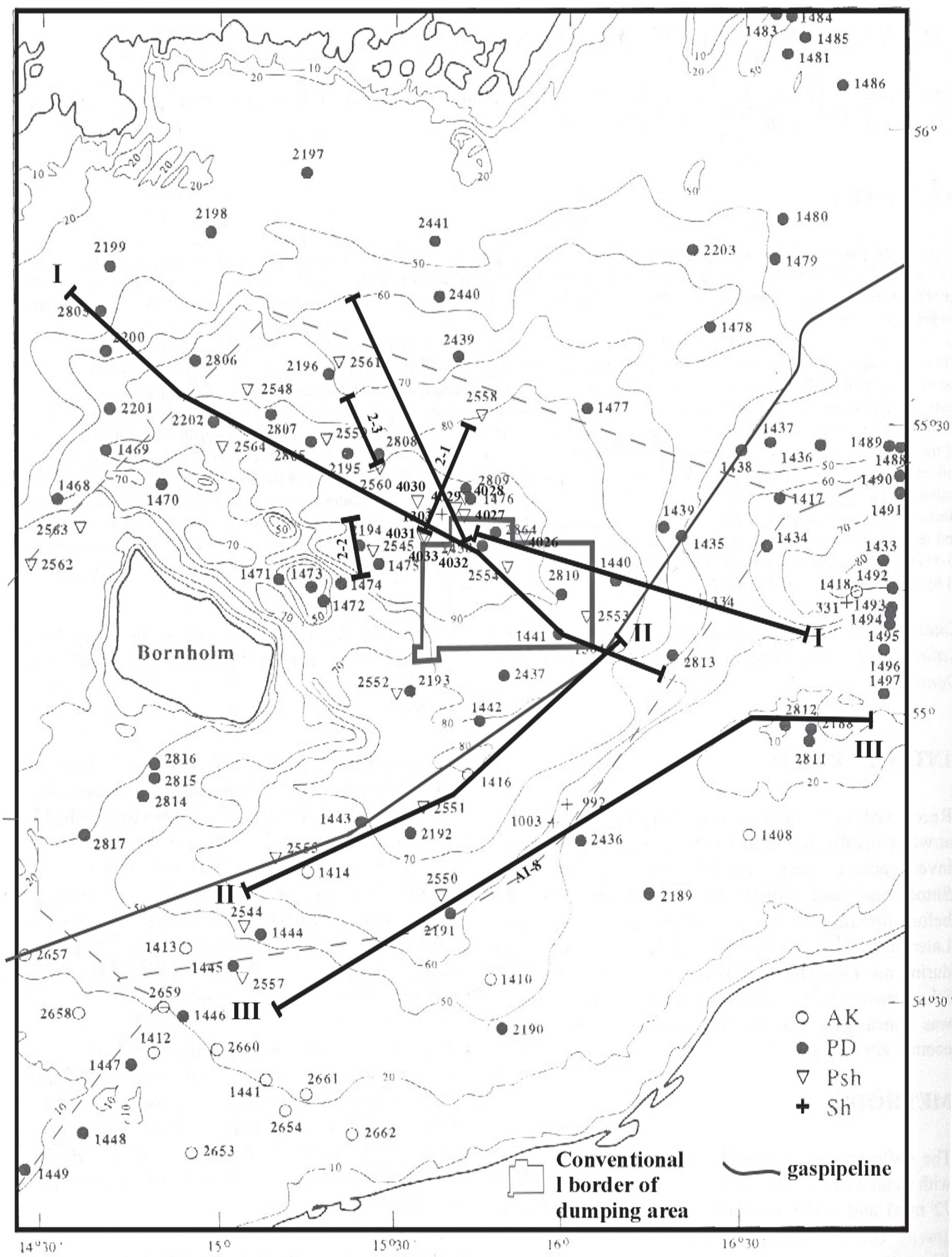

Fig. 5. Map of geological stations on board the Soviet scientific-research vessels: AK – "Akademik Kurchatov"; PD – "Professor Dobrynin", PSh – "Professor Shtockman", Sh – "Shelf". Thin lines – isobaths in m, thick lines – Parasound (2–3 and 2–1) and lithological profiles (I–I, II–II) and Parasound profiles 2–1; 2–2; 2–3 and AI–8

5 pav. Tarybinių tyrimo laivų geologinių stočių žemėlapis: AK – „Akademikas Kurčiatovas", PD – „Profesorius Dobryninas", PSh – „Profesorius Štokmanas", SH – „Šelfas". Plonos linijos – izobatos m; storos linijos – parazondai (2–3 ir 2–1), litologiniai profiliai (I–I ir II–II) ir parazondiniai profiliai (2–1, 2–2, 2–3 ir AI-8)

stations PSh-2545 and Sh-1303 (Figs. 5, 8). There are four small areas in which the thickness of $H1_{2-3}$ (Middle-Upper Holocene) exceeds 200 cm. In these places the sedimentation rate of mud is more than 0.3 mm and at station PSh-2564 even more than 0.4 mm per year. The young age of mud from the above stations is confirmed by ^{14}C dating as well. It is a characteristic feature that there are some areas in the deeper parts of the basin (below the halocline level, see Fig. 9) where the mud is either absent (stations PSh-2551, PD-2202, Figs. 6, 7) or is considerably decreased in thickness. In these regions intensive near-bottom currents are present, apparently preventing accumulation of large masses of muddy material (Sviridov et al., 1995).

Table 6. Sediment type and content of fraction <0.01 mm and chemical elements in mud in the area of the Bornholm Deep (station PSh-4033, 96 m, 55° 18 74' N, 15° 34 68' E) where CM is buried. After Emelyanov, Paka, Kravtsov, 1999
6 lentelė. Sedimentų pobūdis (Apm – aeuritinis-pelitinis dumblas; Pm – pelitinis dumblas (molis)) Bornholmo įdubos dumble (PSh-4033 stotis, 96 m, 55° 18 74' N, 15° 34 68' E), cheminio ginklo palaidojimo vietoje

Horizon, cm	Sed. type	%									ppm 10^{-4} %							Moisture W, %	Fraction <0.01 mm, %
		Fe	Mn	Ti	N	Ca	Mg	P	K	Na	Rb	Li	Cu	Zn	Cr	Ni	Co		
0–1	Pm	4.10	0.20	0.41	1.28	0.42	1.35	0.11	2.60	1.80	110	31	56	240	68	70	46	88.0	72.7
2–3	Pm	4.70	0.05	0.41	0.83	0.52	1.54	0.09	2.63	2.36	110	31	56	278	96	90	46	–	–
4–5	Pm	4.74	0.06	0.42	1.03	0.52	1.46	0.08	2.50	2.24	92	31	54	278	92	102	32	80.0	73.6
6–7	Pm	5.58	0.06	0.40	0.85	0.48	1.46	0.08	2.92	2.14	88	31	52	278	92	78	38	–	–
8–9	Pm	5.00	0.06	0.42	1.23	0.48	1.44	0.08	2.78	1.44	84	32	62	286	68	94	30	–	–
9–10	Pm	4.10	0.07	0.38	0.63	0.42	1.38	0.07	2.74	1.46	77	30	50	286	66	94	32	77.1	74.7
12–14	Pm	4.50	0.18	0.38	0.93	0.56	1.52	0.08	2.72	2.06	80	30	46	210	78	94	26	–	–
16–18	Pm	4.74	0.25	0.40	0.59	0.48	1.54	0.09	1.72	1.72	80	30	42	200	88	94	32	–	–
22–24	Pm	4.60	0.40	0.38	0.73	0.76	1.54	–	2.06	2.14	86	30	40	186	68	94	26	77.7	71.9
26–28	Pm	4.46	0.48	0.40	0.74	0.52	1.50	–	2.74	1.46	91	30	40	164	88	138	32	–	–
30–32	Apm	4.11	0.39	0.39	0.71	0.66	1.70	–	2.80	2.12	103	30	36	144	61	98	40	52.0	67.9
34–36	Apm	4.20	0.32	0.38	0.78	0.76	1.64	–	2.80	2.52	120	30	42	148	68	80	40	–	–
38–40	Apm	4.51	1.48	0.36	0.63	0.78	1.42	–	2.67	2.33	111	34	45	138	68	74	32	43.7	66.0
Minimal, maximal and average contents																			
0–40	min	2.88	0.05	0.31	0.59	0.42	1.35	0.07	1.72	1.14	77	30	30	106	44	52	24	43.7	64.1
0–40	max	5.78	3.24	0.42	1.28	1.28	1.70	0.25	3.14	2.68	168	46	64	286	96	138	46	88.0	79.2
0–40	mean	4.46	0.50	0.38	0.86	0.70	1.49	0.10	2.56	1.78	123	38	44	194	68	75	32	–	–

Note. NC – Niemisto Corer. Sediment type: Apm – aleuro-pelitic (silty-clayey) mud; Pm – pelitic mud (clay).

II. 3. Distribution of elements in sediments from the marine Holocene (Hl_{2-3})

Chemical elements and components in the upper sediment layer (0–3 cm) are distributed in different ways as regards granulometric sediment type: sand (s), coarse aleurite (Ca), fine aleuritic (Fam), aleuritic-pelitic (Apm), and pelitic mud (Pm). According to their average elemental contents (Table 7 and Fig. 10) they may be grouped into the following element combinations:

– SiO_2(total) and Sn
– $CaCO_3$, Zr and W
– Cr, Zn, Cu, Mo and SiO_{2am}
– Al, P, K, Na, Fe, Ti, Rb, Ba, V, B, (Co, Li)
– Mn, Ni and Cu.

The elements of the first (1) group are representative of minerals in the sand fraction (1–0.1 mm grain size), quartz (prevails among clastic minerals in the >0.01 mm fraction), feldspar and cassiterite. That explains why their distribution according to gra-nulometric sediment types is similar to quartz distribution in the bulk samples, i. e. is maximum in sand (shallow areas of the basin, see map) and minimum in pelitic mud (deep areas of the basin).

Calcium carbonate, Zr and W (not compiled) are also associated with clastic minerals but rest probably in the aleuritic (0.1–0.01 mm grain size) and not in the sandy fraction. This means that their maximum average contents are confined to the aleurites or sand (Table 7) which are found at the slopes of the basin and in depressions, above isobaths of 50–60 m. Zirconium as a typical element of the hydrolysate fraction is present in the minerals ilmenite, titanomagnetite, biotite and amphiboles (e. g., Лукашин, Лисицын, Емельянов, 1986). Tungsten in the sediments has a clear correlation with clastic Fe, i. e. the part which occurs in the crystalline lattice of minerals (e. g., Пилипчук, Емельянов, 1979). Positively charged colloids of ferric hydrate adsorb anions very well. In the Bornholm Deep this process should occur in sediments above the O_2–H_2S boundary, i. e. within the oxic zone where aleuro-pelitic mud is replaced by fine aleuritic mud. This explains why W is generally confined to the periphery of the basin and to aleuritic sediments.

Elements of the third (3) group are generally confined to the aleuro-pelitic muds (Fig. 10). This means that they preferably occur in sediments of the peripheral and central parts of the Bornholm Basin (e. g., Cr and Zn). Chromium, which generally as one of the less mobile chemical elements, is connected with the finely dispersed clastic minerals (0.01–0.001 mm grain sizes). Its higher contents are found in aleuro-pelitic muds. Zn, Cu and Mo are often found in the same minerals as Cr, but they may also occur in authigenic minerals (e. g., ferric oxides, sulfides) and in organic detritus, the latter component often concentrating in the 0.05–0.001 mm grain size fraction.

Amorphous silica and C_{org} being grouped together with Cr, Zn, Cu and Mo are genetically not connected with these elements. They are both confined to the biogenic components, e. g., diatom skeletons (SiO_{2am}), spore and

Table 7. **Average content of chemical components and elements in the top layer (0–3 cm) of sediments, %. After Emelyanov and Christiansen, 1995**
7 lentelė. **Cheminių komponenčių ir elementų kiekiai paviršiniame sedimentų sluoksnyje (0–30 cm) (pagal Emelyanov, Christiansen, 1995)**

Components, elements	Sand(s)	Coarsealeurite silt	Fine-silty mud	Silty mud	Pelitic (clayey) mud (m) (Pm)	Pm / S*
			1. Bornholm Basin			
$CaCO_3$	1.28	3.10	8.74	4.97	5.42	4.2
SiO_{2am}	1.21	1.14	0.75	2.09	1.77	1.5
C_{org}	0.56	0.91	1.91	4.11	4.15	7.4
P	0.05	0.03	0.05	0.15	0.08	1.6
			2. Gdansk Basin			
$CaCO_3$	1.30	4.02	3.20	2.14	5.64	4.3
SiO_{2am}	1.32	1.11	3.83	3.95	3.11	2.4
C_{org}	0.38	0.73	2.25	2.89	2.62	6.9
N	0.03	–	0.17	–	0.64	21.3
P	0.05	0.06	0.07	0.10	0.10	2.0
Fe	1.47	1.45	2.82	4.19	4.67	3.2
Mn	0.03	0.02	0.02	0.03	0.04	1.3
N. of samples	35	21	25	17	61	
			3. Gotland Basin			
$CaCO_3$	2.82	3.31	2.88	2.25	4.32	1.5
SiO_{2am}	1.09	1.30	1.34	1.78	1.73	1.6
C_{org}	0.44	1.10	2.03	2.74	3.61	7.4
P	0.05	0.05	0.05	0.08	0.09	1.8
Fe	1.45	1.96	2.99	3.64	4.65	3.2
Mn	0.03	0.03	0.03	0.04	0.06	2.0
N. of samples	20	27	16	26	126	

* – Pm/S ratio of average content in pelitic mud (Pm) and sand (S) (enrichment factor).

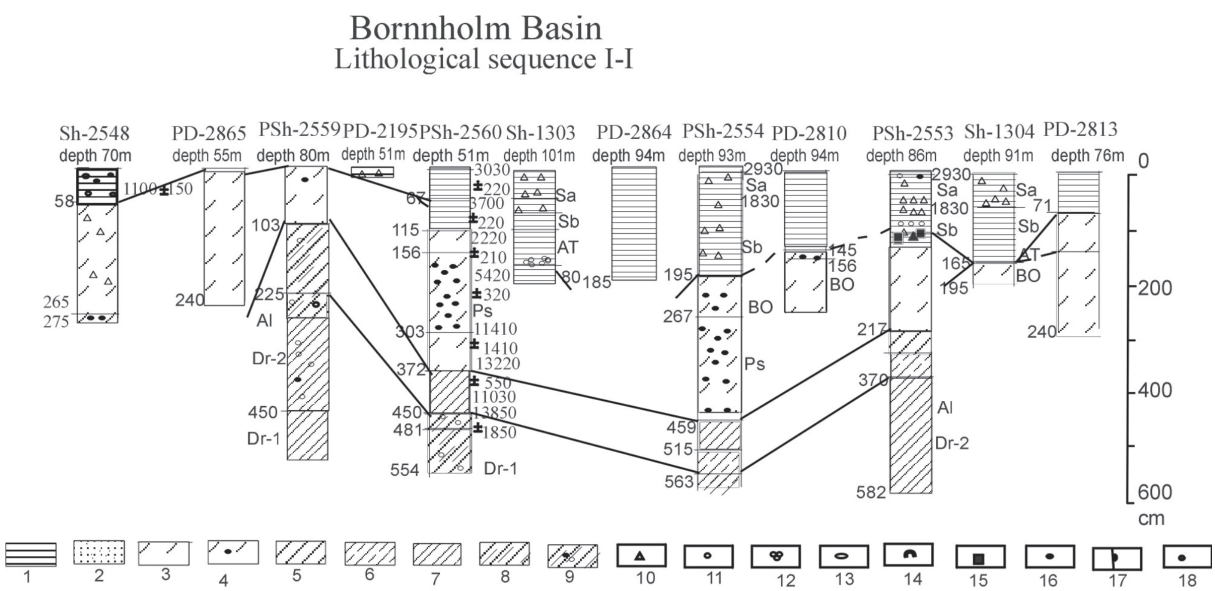

Fig. 6. Lithological profile I–I across the Bornholm Deep. *1* – Litorina mud (Lt), *2* – Litorina sands and aleurites (Lt), *3* – grey homogenic clay (Anc), *4* – sulphidic (hydrotrothic) clay (Anc), *5* – grey-brown clay (Y), *6* – clay with indistinct layers (microvarves) (BIL), *7* – varved clay (BIL), *8* – clay of near glacial lakes with indistinct varves (BIL), *9* – grey-brown clay of near glacial lakes or moranic clay with indistinct layers (varves) and with lenses of sand and aleurite; *10* – mollusk fragments, 11 – benthic foraminifera, *12* – planctonic foraminifera, *13* – coprolite, *14* – remmants of cereals, *15* – iron sulphides, *16* – pebbles and gravel, *17* – absolute age (^{14}C), *18* – absolute age (^{14}C, grab samples)

6 pav. I–I litologinis profilis per Bornholmo įdaubą. *1* – Litorinos dumblas (Lt), *2* – Litorinos smėlis ir aleuritas (Lt), *3* – pilkas homogeniškas molis (Anc), *4* – sulfidinis (hidrotrolitis) molis (Anc), *5* – pilkai rudas molis, *6* – neryškiai sluoksniuotas molis (mikrovarvos) (BIL), *7* – varvinis molis (BIL), *8* – periglacialinio ežero molis su neryškiomis juostomis (varvomis) (BIL), *9* – periglacialinio ežero pilkai rusvas molis arba moreninis molis su smėlio ir aleurito lęšiais, *10* – moliuskų fragmentai, *11* – bentoso foraminiferos, *12* – planktoninės foraminiferos, *13* – kaprolitai, *14* – grūdų likučiai, *15* – geležies sulfidai, *16* – gargždas ir žvirgždas, *17* – absoliutus amžius (^{14}C), *18* – absoliutus amžius (^{14}C, dragos mėginiai)

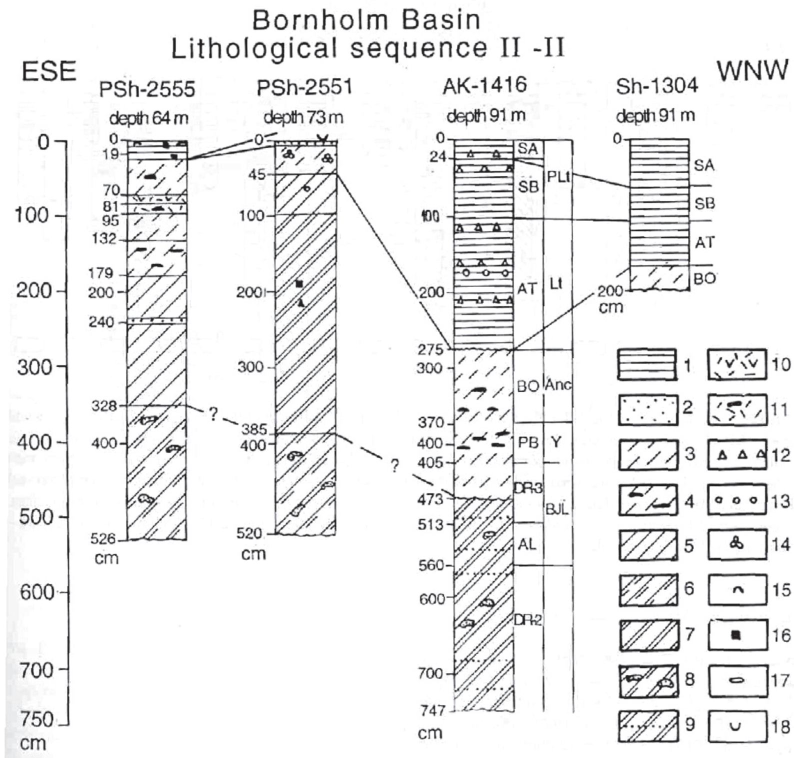

Fig. 7. Lithological profile II–II across the Bornholm Deep: *1* – Litorina mud (Lt), *2* – Litorina sands and aleurites (Lt), *3* – grey homogenic clay (Anc), *4* – sulphidic (hydrotroilithic) clay (Anc), *5* – grey-brown clay (Y), *6* – clay with indistinct layers (microvarves) (BIL), *7* – varved clay (BIL), *8* – grey-brown clay of nearglacial lakes and morainic clay with indistinct layers (varves) (BIL) and lenses of sand and aleurites; *9* – layers of sand and aleurites, *10* – sediments with remnants of wood, terrestrial plants and red algae (peat), *11* – hydrotroilithic clay with organic remnants, *12* – mollusk fragments; *13* – benthic foraminifera, *14* – planktic foraminifera, *15* – remnants of cereals, *16* – iron sulphides (at PSh-2551 – chains of small balls), *17* – coprolite, *18* – iron-manganese crusts and nodules.

Stratigraphy after Emelyanov, Lukashina, 1995; lithology after Emelyanov (1995)

7 pav. II–II litologinis profilis per Bornholmo įdaubą: *1* – Litorinos dumblas (Lt), *2* – Litorinos smėlis ir aleuritas (Lt), *3* – pilkas homogeniškas molis (Anc), *4* – sulfidinis molis (hidrotrolitis), *5* – pilkai rudas molis (Y), *6* – neryškiai sluoksniuotas molis (mikrovarvos), *7* – varvinis molis (BIL), *8* – periglacialinio ežero pilkai rusvas molis arba moreninis molis su neryškiais tarpsluoksniais (varvomis) (BIL) ir su smėlio bei aleurito lęšiais, *9* – smėlio ir aleurito sluoksniai, *10* – nuogulos su medienos likučiais, sausumos augalais ir vandens augalais (durpė), *11* – hidrotrolitinis molis su organinėmis liekanomis, *12* – moliuskų likučiai, *13* – bentoso foraminiferos, *14* – planktoninės foraminiferos, *15* – grūdų likučiai, *16* – geležies sulfidai (PSh-2551 – grandinėlės iš smulkių rutuliukų), *17* – kaprolitai, *18* – geležies-mangano plutelės ir gniutuliukai.

Stratigrafija pagal Emelyanov ir Lukašin, 1995, litologija pagal Emelyanov, 1995

pollen grains, and fragments of algae tissue. All these particles have usually a grain size of 0.05–0.001 mm, which concentrates in the aleuro-pelitic mud (Table 7, Fig. 10). Organic carbon may also be sorbed onto clayey particles.

The fourth (4) group of elements is closely related to pelites (mainly with clayey and subcolloidal particles). These elements are distributed according to rules valid for pelitic sediment fractions (e. g., Emelyanov, 1982, 2005): the higher the contents of the <0.01 mm fraction in the sediments the higher is the content of these elements (see Fig. 10). The maxima of these elements are confined to sediments of the central areas of the basin.

Mud from the marine Holocene (Hl_{2-3}) sometimes enriched in Ba, V, Mo, Pb, Cr and Ce (Blazhchishin, Emelyanov, 1977). One can see that maximum Ba contents are found in the peripheral areas of the Bornholm Deep, i. e. transitional between the stagnant and the oxic depositional environments. Barium usually occurs in the mineral baryte ($BaSO_4$), (e. g., Emelyanov, Blazhchishin, 1976). On the contrary, V, Mo and probably Pb levels are high in sediments towards the central area of the basin, suggesting a closer affinity to Mn.

While Mn and Ni strictly follow the rules for pelitic fractions in other parts of the Baltic Sea (Emelyanov, 1986), they behave differently in the Bornholm Basin. This could be explained by the fact that the major part of Mn in sediments is connected not with clastic but with authigeneous minerals. Authigeneous minerals are either hydrous oxides of Fe and Mn (micronodules, large flakes and hydroxide particles of irregular forms) leading to increased Mn contents in the sediments (Fig. 10), or they are finely dispersed. Mn-containing carbonates (rhodochrosite) (e. g., Emelyanov, 1981) are often en found in higher amounts in pelitic mud of the deep sea; Ni is generally associated with Mn. Being generally sorbed onto Fe and Mn hydroxides, Cu is distributed in a similar way as Mn. This fact explains the higher Cu, As, Pb, Cd (and Mn) contents in sediments of the peripheral areas of the Bornholm Deep where weakly oxidised sands with considerable amounts of Fe–Mn and Mn concretions occur; these concretions (and crusts) contain up to 25.75% of Mn, up to 153 ppm of Cu and up to 1021 ppm of As (Tables 8, 9). It explains also the occurrence of higher Mn in the central area of the basin where finely dispersed authigeneous Mn carbonates are widely present.

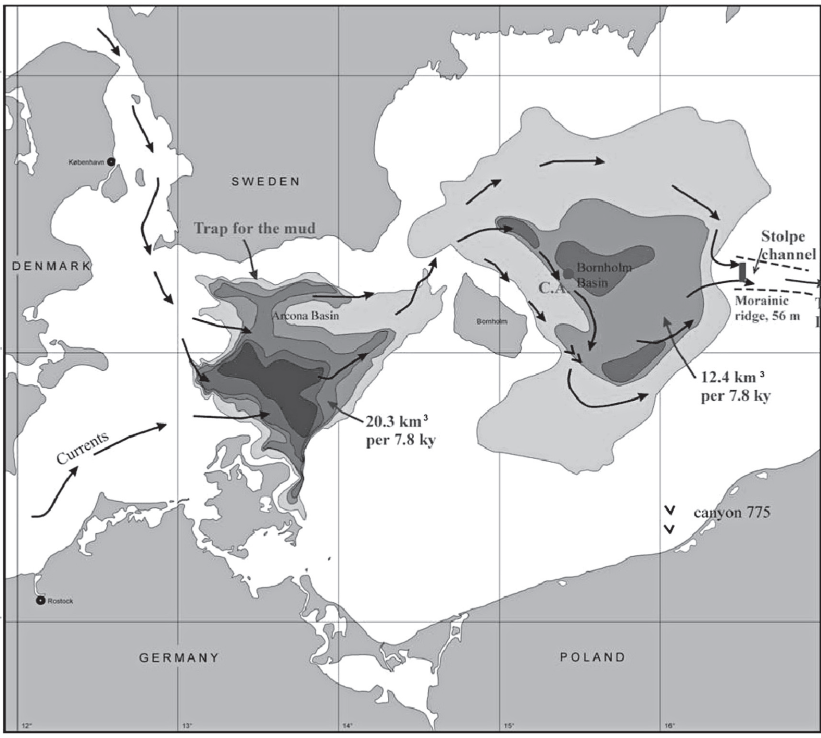

Fig. 8. Thickness of Hl_{2-3} mud, near-bottom currents and location of sunken chemical munition. After Emelyanov, Trimonis et al., 1995

8 pav. Holoceno (Hl_{2-3}) dumblo storis, priedugnio srovės ir nuskandinto cheminio ginklo vietos (pagal Emelyanov, Trimonis ir kt., 1995)

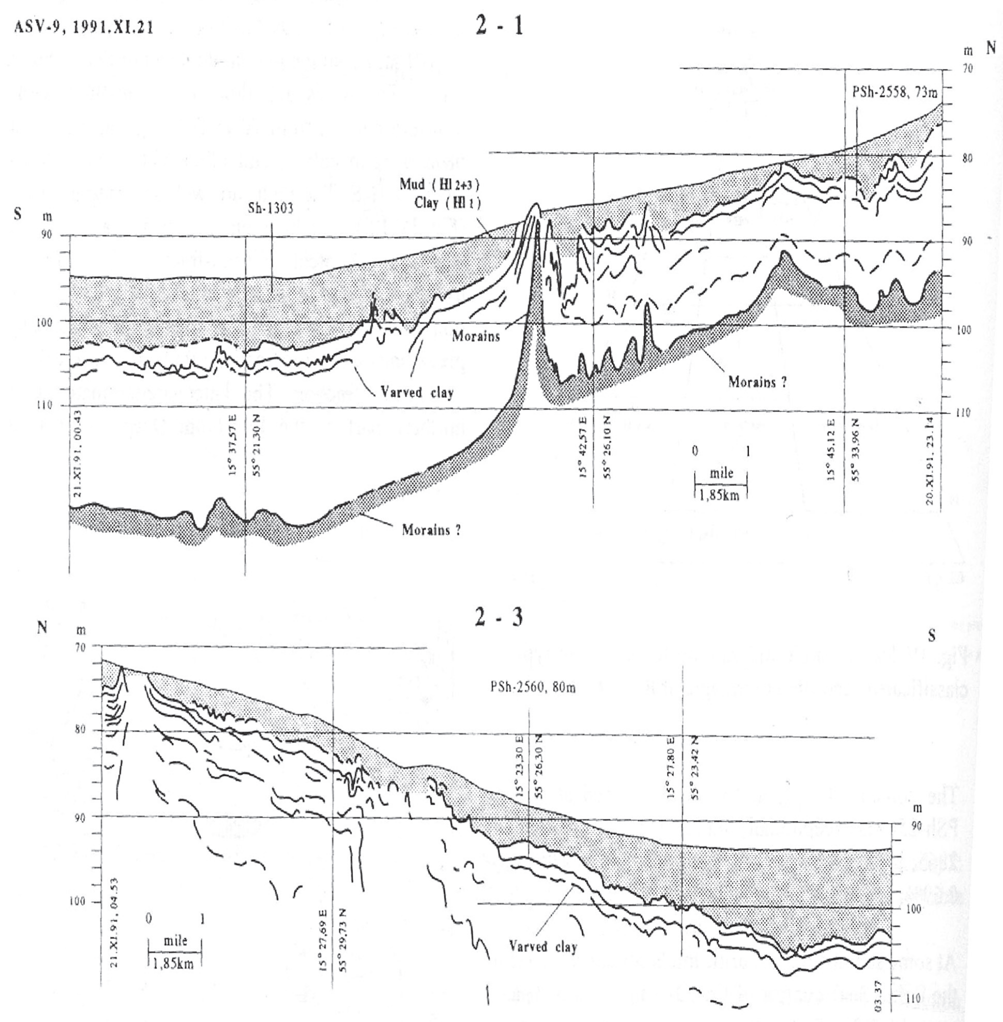

Fig. 9. Structure of the Late Pleistocene sedimentary cover of the Northern Bornholm Basin. Parasound profiles 2–1 and 2–3 (for location, see Fig. 5)

9 pav. Bornholmo įdaubos šiaurinės dalies vėlyvojo pleistoceno nuosėdų dangos struktūra. 2–1 ir 2–3 parazondų profiliai (padėtį žr. 4 pav.)

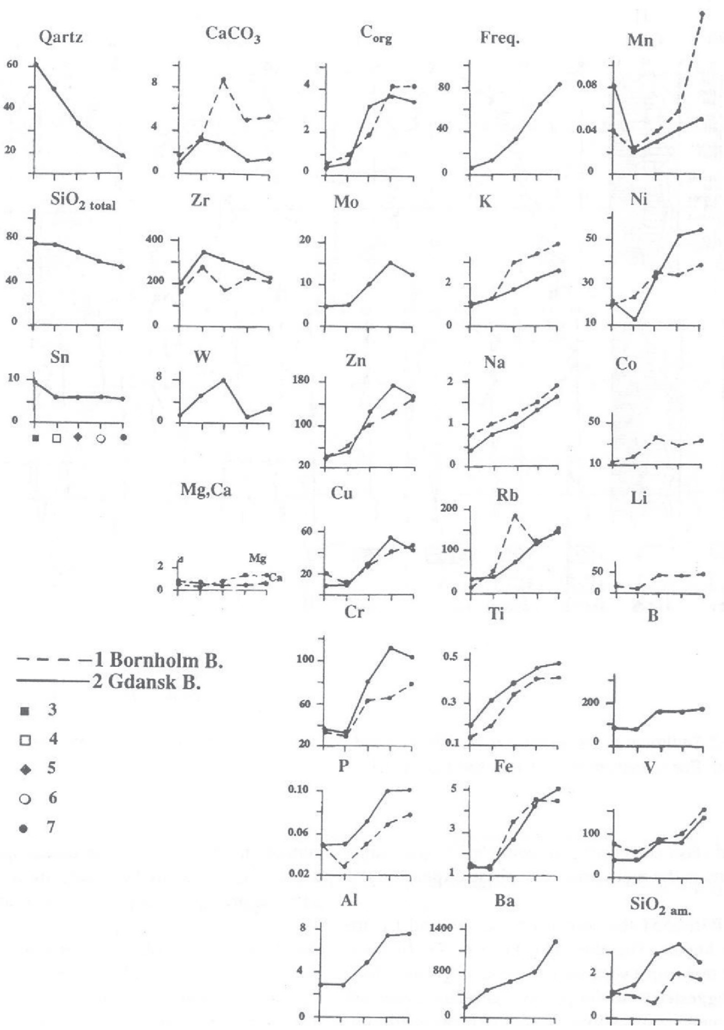

Fig. 10. Distribution of average quartz contents, fraction <0.01 mm (Fr), and selected chemical components and elements according to fraction rule by Emelyanov (1982, 1986, 2005) in surface sediments (0–30 mm depth) in the Bornholm Basin (stippled line) and the Gdansk Basin (solid line). Legend: *3* – sand, *4* – coarse aleurites, *5* – fine aleurites, *6* – aleuro-pelitic mud (clay). After Emelyanov, Baturin, Kunzendorf, 1995

10 pav. Kvarco vidutinio kiekio, <0,01 mm frakcijos ir kai kurių cheminių komponenčių bei elementų pasiskirstymas pagal frakcijų taisyklę (1982) Gdansko (ištisinė linija) ir Bornholmo įdaubų (punktyrinė linija) dugno paviršinėse nuosėdose 0–30 mm gylyje (Emelyanov, 1982; 1986; 2005). *3* – smėlis, *4* – stambus aleuritas, *5* – smulkus aleuritas, *6* – aleuritinis-pelitinis dumblas (molis) (pagal Emelyanov, Baturin, Kunzendorf, 1995)

In comparison to Fe, the maximum Mn values occur closer to towards the centre of the basin. This is most likely caused by a stagnant water condition frequent in the central parts of the Deep. The result is an increased accumulation of Mn, which in strongly reduced conditions accumulates diagenetically in the form of complex Mn carbonates.

It should also be mentioned that sediments of the Bornholm Deep contain elevated $CaCO_3$, C_{org}, K, Na and Mn levels (e. g., Baturin, Emelyanov, Kunzendorf, 1995; Emelyanov, 1986). This may be explained by: 1) the frequent occurrence of carbonate rocks on land adjacent to the Bornholm Basin (island of Rügen; coast of Sweden), 2) higher salinities in water and pore water (explains high Na, and partially K), and 3) longer periods of stagnation of near-bottom waters (could explain the high Mn), but other processes may also be considered.

It is noticeable that P contents in aleurites and muds from the Bornholm Deep are considerably lower than those found in analogous sediments of the Gdansk Deep (Fig. 9, Emelyanov (ed.), 2002). This is easily explained by the agricultural activities on land. The Bornholm Basin is relatively remote from these activities, while the large river Vistula transports large amounts of phosphates into the Gdansk Basin.

The marine Holocene (Hl_{2-3}) sedimentary layer (0–4 m) contains approximately the same amounts (concentrations) of chemical components and elements than the upper 3 cm of other sediment types (Emelyanov, 1995). However, the maxima of Mn and Cu within the sedimentary column are somewhat displaced.

Lithogenic elements (Al, K, Ti) in marine Holocene mud correlate well. A good correlation exists between Fe and Ti, Mn, P, Rb, Ni and Mo, and between K and Al, Ti, Na and Li. There is only a very weak correlation between CO_2 and $CaCO_3$, the latter content being calculated according to measured CO_2. Apparently this is due to the fact that in stagnant muds a considerable part of CO_2 is present not in the form of $CaCO_3$ but occurs as $MgCO_3$ and $MnCO_3$. This is why $CaCO_3$ calculation according to CO_2 contents is not correct (Emelyanov, 1995). They should be calculated from their Ca, Mg or Mn contents directly.

II. 4. Areal distribution of organic carbon, phosphorous and arsenic

II.4.1. *Organic carbon*

The content of C_{org} in sediments makes up 0.02–6.26%. Its areal distribution depends on the depth and through it on the content of the <0.01 mm grain size. The average content of C_{org} in the sands is 0.1% and in the pelitic muds 3.5% (Emelyanov, Christiansen, 1995). A sharp increase in the content occurs at water depths below 60–65 m. This depth coincides with the pycnocline position and with the border between clastic sediments (coarse aleurites, see Fig. 10) and mud.

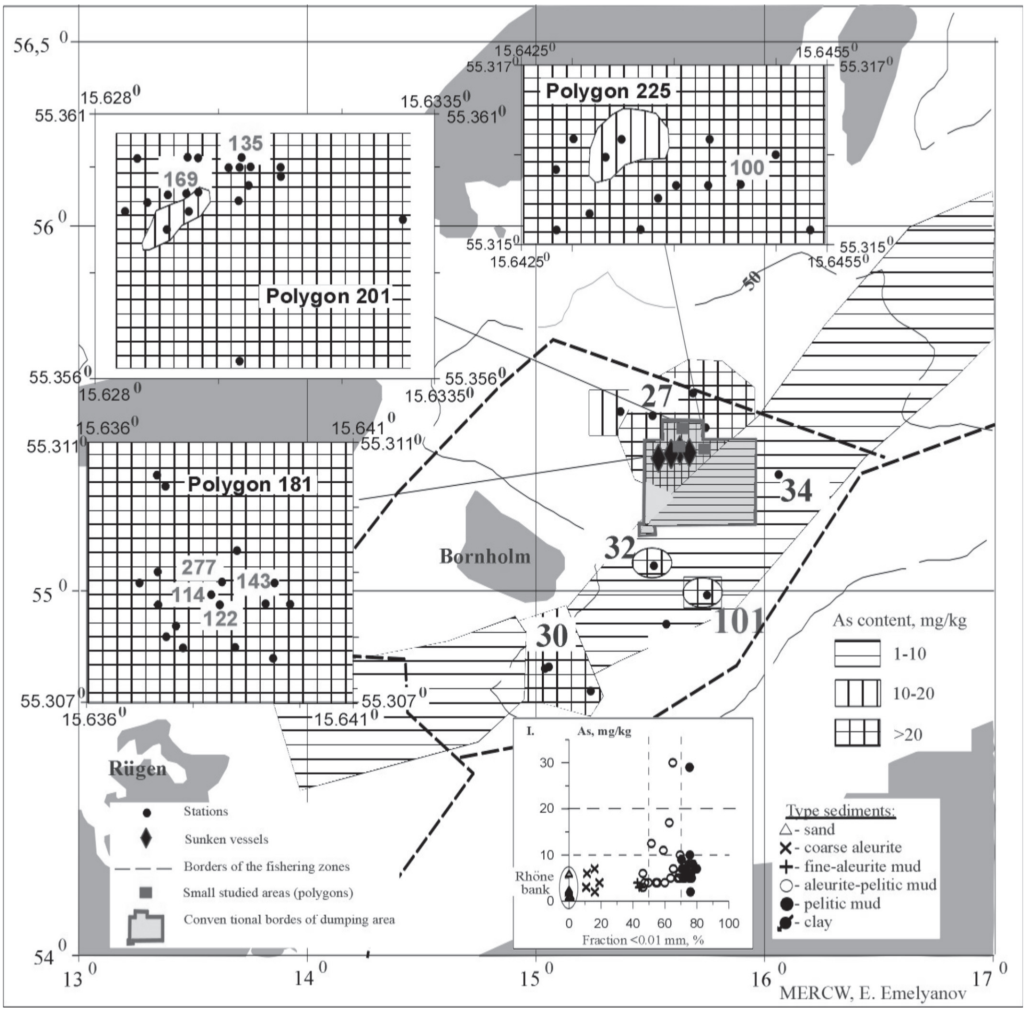

Fig. 11. Distribution of As in the surface (0–5 cm) bottom sediments of the Bornholm Basin. Big numbers show the maximum content of As in the area. Areas 181, 201 and 225 are located near ship wrecks. After Емельянов, Кравцов (2007) with some additions. I. The graph showing As content in different granulometric sediment types of the Bornholm Basin *versus* pelitic (<0.01 mm) fraction. Samples with As >100 mg/kg are not shown in this graph

11 pav. As pasiskirstymas Bornholmo įdaubos dugno paviršinėse (0–5 cm) nuosėdose. Dideli skaičiai rodo maksimalų As kiekį tirtame plote. 181, 201 ir 225 poligonai yra netoli paskandintų laivų (pagal Emelyanov, Kravtsov, 2007 su papildymais). I diagramoje matyti As kiekis skirtinguose Bornholmo įdaubos nuosėdų granuliometriniuose tipuose. Grafike neparodytos *versus* pavyzdžių pelitinės frakcijos (<0,01 mm) su As >100 mg/kg

There are two areas in the deeper part of the Bornholm Basin with high concentrations of C_{org}. In the southern part the high concentrations are found in the aleuro- pelitic muds and in the northern and central part in the pelitic mud. It seems possible that the division between these two areas is determined by near-bottom currents as the division shows signs of sediment erosion.

The content of C_{org} in the cores increases upwards from 0.35–0.63% in the varved clays of the periglacial lakes to 3.5–4.0% in the Holocene muds. An especially sharp increase in C_{org} content is observed in the transition from lacustrine (Ancylus) clays to Litorina mud (Emelyanov, Christiansen, 1995). Sometimes, however, a relative high content (1–3%) can be observed in the Ancylus (sulphide) clays. Thus, as found earlier (Emelyanov, 1995; Емельянов, Кемпиньска, 1987), a sharp increase in C_{org} content is one of the most obvious geochemical evidences indicating sea water inflow into the Bornholm Basin.

II. 4.2. ***Phosphorus***

The content of P ranges from 0.02% to 0.35% (Tables 3, 4). Excluding, however, one sample from station PSh-2551 the range will narrow to 0.02–0.10%. The highest content is found in recent sediments. Generally, P content increases from sands or aleurites towards aleuro-pelitic and pelitic mud. This is why the areal distribution has a maximum in the central part of the Bornholm Basin. Here the content is 0.07–0.08% which can be considered normal for the entire Baltic (Emelyanov, 1986; 1995). Only mud from the deepest part of the basin contains 0.09 – 0.11% and one sample (horizon 6–9, Table 4)) 0.25%. These stations have also a high content of Mn (0.1 –0.5%).

Phosphorus is generally dispersed in sediments. However, in samples where the content exceds 0.07–0.08% it can be found as authigenous phosphate. Vivianite has also been observed in the Bornholm Basin sediments (Blazhchishin and Emelyanov, 1977).

Table 8. **Content of Fe and Mn (g/kg) and toxic elements (Zn, As, Cd and Pb, ppm) in the iron-manganese crusts and flat nodules of the Baltic Sea**
8 lentelė. **Fe ir Mn (g/kg) ir toksinių elementų (Zn, As, Cd ir Pb (ppm)) kiekiai Baltijos jūros plokščiuose geležies mangano gniutuluose ir plutelėse**

	%		Ppm or 10^{-4}%				
	Fe	Mn	Zn	As	Cd	Pb	Cu
Gulf of Finland (15 samples)							
Limits	7.35–25.0	1.83–25.75	165–625	242–1021	0.9–3.8	9.0–23.0	28–153
Average	15.4	16.2	356	583	2.0	15.9	83
Bornholm Basin							
St. PSh-2551	24.9	9.75	210	653	–	30	50

Table 9. **Chemical elements in bottom sediment samples which contain > 100 ppm (10^{-4}%) of As**
9 lentelė. **Cheminių elementų kiekiai dugno nuosėdų mėginiuose, kuriuose > 100 ppm · 10^{-4}% As**

Vessel	Station	Depth, m	Horizon, cm	Sediment type	%			10^{-4} %		
					C_{corg}	Fe	Mn	As	Cd	Pb
Bornholm Basin										
C	185	97	0–2	Apm	–	3.95	0.13	122	0.7	27.8
C	188	97	0–2	Apm	6.84	4.06	0.12	114	0.6	25.1
C	195	97	0–2	Apm	–	4.75	0.48	277	0.1	12.4
C	199	97	0–2	Apm	6.51	3.88	0.17	143	0.5	14.9
C	202	97	0–2	Apm	–	3.25	0.1	135	0.4	8.5
C	213	97	0–2	Apm	6.04	4.01	0.13	169	0.2	7.1
C	228	97	0–2	Apm	6.88	3.53	0.2	100	0.4	10.9
PSh	2551	73	0–3	Fe–Mn.n	1.30	3.00	0.06	709	–	–
Atl	434	80	0–5	Pm	–	–	–	101	–	–
Gotland Basin										
Psd	303590–4	124	345–350	Lit. Apm	3.12	5.21	0.09	130	0.2	14
			645–650	Lit. Apm	2.39	4.65	0.07	107	0.2	13
			713–715	Lit. Apm	3.22	4.88	0.12	102	0.2	10
			825–830	Anc. sulphidic Grey clay	0.56	6.08	0.07	131	0.2	10.1
			870–875	Anc. sulphidic Grey clay	0.42	5.97	0.12	120	0.5	16
Gdansk Basin										
PSh	4810	9	0–3	Gravel + Sand	0.18	2.01	0.06	180	0.1	8
	4L	29	0–5	Gravel	0.12	1.09	0.02	122	0.1	7
	10L	29	0–5	Sand	0.18	1.44	0.03	107	0.1	7

Vessels: C – "Centaurus"; PSh – "Professor Shtokman"; Psd – "Poseidon"; Atl – "Atlantida".
Sediment type: Apm – aleuro-pelitic mud; Pm – pelitic mud; Fam – fine-aleuritic (fine-silty) mud; Fe–Mn. n.– iron–manganese nodules and crusts; G – glauconite.

II. 4.3. ***Arsenic in the bottom sediments***

Arsenic (As) is one of the most dangerous pollutant. By the degree of toxicity, arsenic occupies the 7th place, following such elements as Hg, Cd, Pb, Se, Zn, Cu. Arsenic was determined in the same samples where C_{org}., N, P, CO_2 and other components and elements were measured also. Eight short cores and about 80 samples of the upper layer of bottom sediments were studied.

In the regions of dumped chemical munitions (CM) we have found high contents of As (from 100 to 708 ppm) in nine samples (out of 80 samples from the surface 0–5 cm layer of pelitic mud in which As was determined). These values are approximately 5–10 times more than the background levels of As (10–30 ppm) characteristic of pelitic mud from the Bornholm Basin. The largest number of "anomalies" in As concentrations was found near ships dumped on the bottom and probably loaded with chemical munitions (Fig. 11). Contents of As in the deeper layers of bottom sediments (5–50 cm) were within the limits of background values of this element (10–30 ppm), characteristic of pelitic mud of the Bornholm Basin. Thus, the surface layer of sediments is contaminated with As, indicating its additional sources. The other elements (Cu, Pb, Cd, Sb, Ag, Cr, Fe, Mn, Ca, Mg, Li, Co, Ni, Na, K, Al, Si, P, N, C) in the mud in the layer 5–50 cm showed no anomalous contents. C, N and P are contained by poisonous matter (PM) also, but they seemingly oxidize to nitrates, phosphates and carbon dioxides which are evacuated from dump sites in a dissolved form.

Increased values of As (50–122 ppm) were found not only in the Bornholm Deep, but also in shallow surface samples of sand, pelitic and aleuro-pelitic mud (Емельянов, Кравцов, 2007), indicating that these sediments are either contaminated by technogenic arsenic or contain Fe-sulfides (or Fe–Mn nodules). It is well known that As is concentrated by Fe-sulfides and Fe–Mn nodules. Fe-sulfides contain up to 440 ppm of As (Emelyanov, Baturin, Kunzendorf, 1995), and Fe–Mn crusts up to 1021 ppm (Table 8).

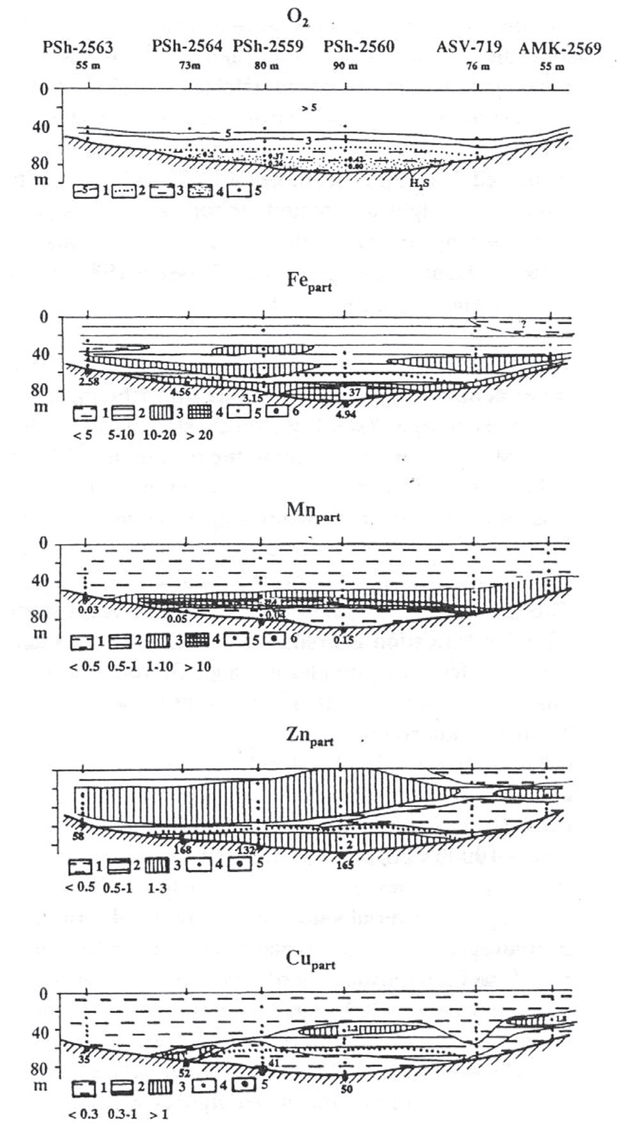

Fig. 12. Distribution of oxygen and particular late forms of Fe, Mn, Zn and Cu along profile II. O_2 in ml/l: *1* – concentration of oxygen, *2* – isoline 1 ml/l oxygen, *3* – less than 1 ml/l, *4* – H_2S in water, *5* – water samples.

Fe_{part}, µg/l: *1* – <5 µg/l; *2* – 5–10; *3* – 10–20; *4* – > 20.5; *5* – water samples; *6* – Fe content in upper sediment layer (%).

Mn_{part}, µg/l: *1* – <0.5 µg/l; *2* – 0.5–1; *3* – 1–10; *4* – >10; *5* – water samples; *6* – Mn content in the upper sediment layer (%).

Zn_{part}, µg/l: *1* – <0.5 µg/l; *2* – 0.5–1; *3* – 1–3; *4* – water samples; *5* – Zn content in the upper sediment layer (ppm).

Cu_{part}, µg/l: *1* – <0.3; *2* – 0.3–1; *3* – >1; *4* – water samples; *5* – Cu content in the upper sediment layer (in ppm). After Emelyanov, Kravtsov, Kunzendorf, 1995

12 pav. Deguonies ir Fe, Mn, Zn bei Cu tam tikrų formų pasiskirstymas išilgai II profilio. O_2 ml/l: *1* – deguonies koncentracija, *2* – 1 ml/l deguonies izolinija, *3* – mažiau negu 1 ml/l, *4* – H_2S vandenyje, *5* – vandens ėminiai.

Fe_{dalis} (µg/l): *1* – < 5µg/l, *2* – 5–10, *3* – 10–20, *4* – > 20,5, *5* – vandens ėminiai, *6* – Fe kiekis viršutiniame nuosėdų sluoksnyje (%).

Mn_{dalis} (µg/l): *1* – 0,5 µg/l, *2* – 0,5–1, *3* – 1–10, *4* – >10, *5* – vandens ėminiai, *6* – Mn kiekis viršutiniame nuosėdų sluoksnyje (%).

Zn_{dalis} (µg/l): *1* – <0,5 µg/l, *2* – 05–1, *3* – 1–3, *4* – vandens ėminiai, *5* – Zn kiekis viršutiniame nuosėdų sluoksnyje (ppm).

Cu_{dalis} (µg/l): *1* – <0,3, *2* – 0,3–1, *3* – >1, *4* – vandens ėminiai, *5* – Cu kiekis viršutiniame nuosėdų sluoksnyje (PPM) (pagal Emelyanov, Kravtsov, Kunzendorf, 1995)

The occurrence of these authigenic formations (and rhodochrosite also) in the sediments is the main reason for the over-clarke contents of As in the sediments.

The river load and aerosols are the main sources of almost all chemical elements in the Baltic Sea. The additional sources of arsenic in the Baltic Sea obviously are:

1) chemical munition (CM) dumped in some Baltic deeps; 2) pesticides (As-containing pesticides) and mineral fertilizers used in agricultural lands, as well as incineration of coal and other fuels.

Arsenic is contained in some types of poisonous matter (luisite, adamsite). It is one of the main indicators of erosion of dumped chemical munition when PM escapes into the environment. Arsenic is different from other products of PM hydrolysis (for example, secondary acids HC1, HF, HCN) (Юфит, 1994). Instead of gradual dissolution in the water column and evacuation beyond the limits of the burial zone, arsenic is deposited in the bottom sediments not far from the dumping site. As a result of corrosion of chemical munitions, PM undergo the following transformation during hydrolysis: luisite (2-chlorvinyldichlorarsin) – chlorvinyl arsenic acid – inorganic forms of As (Юфит, 1994).

Dissolved forms of Mn(II) diffuse into the bottom water layer from the interstitial water through the sea water – bottom barrier through the near-bottom water layer containing H_2S, terminating in the O_2-H_2S layer (Emelyanov, Kravtsov, Kunzendorf, 1995). There, dissolved Mn(II) is oxidised, precipitated in the water column turbidity layer just above the O_2–H_2S coexistence layer (at 72 m of water depth) where concentrations of particulate Mn may reach up to 15 µgm (Fig. 12) and Mn values in SPM reach up to 35.5%. In the near-bottom water, the concentration of particulate Mn and the content of Mn in SPM decreases to values close to the detection limit of the analytical method because of the reduction of Mn (IV) and the dissolution of MnO_2 in this water layer.

The geochemical profiles displayed through the water stratification in the Bornholm Deep (Fig. 12) show that Mn accumulates in suspended particulate matter in the depth interval with oxygen concentrations in seawater 1 and 3 ml/l, usually several meters above the upper part of the boundary of the redox barrier Eh in sea water (O_2–H_2S coexistence layer), i. e. already in the oxic zone. Such a Mn distribution was also observed in the Gotland and Forö Deeps (Емельянов, 1979; Emelyanov, 2005). The behavior of these anoxic systems is controlled by the easy reduction of Mn(IV) to Mn(II) (Emelyanov, Kravtsov, Kunzendorf, 1995).

Trace metal distribution in the redox barrier Eh in water (O_2–H_2S coexistence water layer) is similar for all the stations, although, in the bottom water of station PSh-2545 it was found to be slightly more reduced, what probably also has some influence on the surface sediments of this station. This behaviour in general must influence the upper sediment layers and their pore waters because considerable amounts of reaction-active Fe in the form of $Fe(OH)_3$ occur in the upper sediment layer. Thus, the physical-chemical state of the near-bottom water and the position of the redox barrier in the water column exert a significant influence on the chemical composition (e. g., trace metals) of the upper sediment layer and pore waters.

III. Chemical munition and its influence on geoecology

The burial area we have inspected in the Bornholm Basin is 8 miles (15–18 km) east of Christiansö Island at a depth of about

95–105 m. The sea bottom here is made up of terrigenous sapropelic semi-liquid and soft mud with 60–85% of moisture and 3–5% of organic carbon. Mud had a grayish-black and blackish-gray color with interlayers of hydrotroillite FeS. The thickness of mud at the burial sites ranges from 1.4 to 10 m or, together with lacustrine clay underlying mud, from 5 to 20 m. Evidently this is the reason why single bombs, shells, tanks and other metallic objects do not lie on the surface of semi-liquid and soft mud and clay and are submerged in sediments. At the same time there are outcrops of hard bottom surfaces made up of consolidated clay or moraine deposits (Emelyanov, Booström et al., 1995). Metal objects (including those filled with poisonous matter) are chemically affected after getting into such a hard surface, by near-bottom water, so the process of corrosion here must run much faster than in mud. Besides, in parts of bottom characterized by absence of bottom mud (at a depth 90–110 m as well) occurrence of regular or periodical currents with velocities up to 50–80 cm.s^{-1} take place. Such currents not only prevent accumulation of clayey or fine silt particles on the bottom, but also erode the older (clayey or moraine) bottom. Metallic objects (first of all cigar-like bombs and shells) can be rolled over bottom by currents to a large distance and can be caught by trawls (HELCOM, 1993 a, b). Periodic papers have given many evidences of such dangerous catches. The Bornholm Basin is a zone of active commercial fishery. There were reports about many incidents when munitions were caught by trawls and fishermen got chemical burn (HELCOM, 1993 a, b; Васильев и др., 1994; Рыбалко и др., 2004).

On the other hand, metal objects (or remains of decomposed bombs, tanks and shells) can be caught accidentally by a bottom grab or piston corer and delivered to a ship's deck in the course of oceanographic researches. During investigation in the Bornholm Basin, our bottom grab got accidentally to the surface a sample of unknown material – a small piece of crust (coat without metallic cover). After heating the substance started to emanate a harmful gas and was immediately isolated from the environment. Later the substance was identified as sulphuric yperite. This means that a certain part of dumped CM, not hermetically sealed and beyond metal tanks, is presently situated on the bottom. Nevertheless, in the mud sampled from CM dumps there is no evidence of abnormally high content of elements. In 1989, increased concentrations (relative to background values) of dissolved and suspended forms of Fe, Mn, Zn, Pb and Cd were found in the upper layers of water column in the central part of the Bornholm Basin (Emelyanov, Booström et al., 1995). It was concluded that the anomalies might have resulted from transportation of metals to the surface layer of water column by deep-sea upwelling (Emelyanov, Kravtsov, Kunzendorf, 1995).

In August 1997, abnormally low values of pH in near-bottom waters (6.36 to 6.76) were observed in the Bornholm Basin at two stations located at a depth of 97–99 m. Besides, maximum concentrations of organic phosphorus and phosphates, 5.9 µg-at/l and 5.3 µg-at/l, respectively, i. e. on average 2–5 times higher in comparison with their background values in the near-bottom waters, were found here. Supposedly they were associated with the delivery of supplementary portions of phosphorus, together with products of PM hydrolysis, into the near-bottom layer.

In sites of CM dumps, in addition to changed pH, phosphorus and iron concentrations, a sharp increase of sulphur, chloride and fluoride ion concentrations (2–3 times higher in comparison with the background values) were observed earlier (Ермаков, Хорошева, 1994).

The products of PM hydrolysis have been proved to affect the hereditary structure of living organisms – genes and chromosomes (Tarasov V. A., personal communication). In 1997, it was found that the intensity of PM effect on the environment (Емельянов, Кравцов, 2007) decreased according to the following trend: Skagerrak Sea – Bornholm Basin – Gotland Basin. The number of microflora species tolerant PM (yperite) fellen too within the same trend (Medvedeva, Spiridonov, et al., 1998). A more intensive development of such microflora was registered in the Skagerrak Sea in the vicinities of dumped ships loaded with CM.

According to research of Vasilyev et al. (1994), the present ecological state of the Baltic Sea is not related to dumped CM and depends mainly on the supply of man-made pollutants, industrial and domestic wastes. In their opinion, the only real hazard would come from this chemical weapon if it would be caught by deep-sea trawls of fishery boats.

When observing the intensive trawling of the Bornholm Basin by a great many of fishery boats one may easily agree with the conclusions of our colleagues. Nevertheless, we (Emelyanov, Kravtsov, Kunzendorf, 1995) believe that there is the hazard that the near-bottom saline waters, with their composition having been changed due to PM hydrolysis and supposedly containing single molecules of PM could penetrate into the upper active layer of the sea in shallow water sounds – Danish and Bornholmgat – and in sills (entrance to Slupsk Through, the Baltic Sea).

CONCLUSIONS

The geological and geoecological environment of two important dumpsites the Mäsesskär area in the Skagerrak Sea (depth 180–220 m) and the Bornholm Deep (depth 90–105 m) where thousands of tons of chemical munition (CM) are lying on the bottom were studied. The sunken warships, supposedly with CM, in both dumpsites lie on the muddy bottom. The thickness of the soft Litorina mud in the Mäsesskär area is 1–3 m and in the Bornholm Deep 2–3 m. There is a good aeration of near-bottom water in the Skagerrak Sea and a periodical stagnation in the Baltic Sea. Sometimes strong near-bottom currents are ventilating the waters in the Bornholm Deep also. The reduced thickness or complete absence of Litorina mud occur in both dumpsites: in the Skagerrak and the Baltic Seas.

Abnormally low values of the hydrogen index pH (6.52 to 6.31) were observed in the near-bottom waters in the Skagerrak Sea in July 1997 at sites of CM burials. Hydrolysis of poisonous matter leads to formation of secondary acids (HCl, HF, HCN, etc.), resulting in a decrease of pH in bottom water. Enhanced levels of the toxic element As were found in the mud of the Måsesskär area (Paka, Spiridonov, 2002).

Hydrogen sulfide episodically (each 7–10 years) appears in the Bornholm Deep.

The upper layer (0–5 cm) of the mud contains up to 6.29% of $C_{org.}$, 0.35% of P, 0.72% of Mn, 5.78% of Fe and up to 227 ppm of

As. The contents of all other studied toxic elements (Pb, Cd, Hg, Cu, Zn) are within the Clarke (mean) limits (Tables 1–8).

Arsenic, one of the most toxic elements, is released during hydrolysis of CM and disperses in the mud at average contents of 10–30 ppm. Overclarke contents of this element are concentrated in iron sulphides (up to 440 ppm of As) in a stagnant environment or in iron-manganese nodules or crusts (up to 1021 ppm of As) in a oxic zone. No signs of the distribution of dispersed arsenic from areas of dumped CM over the whole Bornholm Deep were detected. This element is concentrating locally near sunken warships with CM. According to our data (Emelyanov, Kravtsov, 2007), the background concentrations of As in the mud and its hyper concentrations in the sulphides and iron-manganese nodules are not ecologically dangerous to man. They are not dangerous for building in the future cable lines and pipelines on the bottom outside of the conventional areas of dumped CM, and these lines will not stimulate CM hydrolysis and the distribution of arsenic over all Bornholm Deep.

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CHEMINIO GINKLO PALAIDOJIMO VIETŲ SKAGERAKE IR BALTIJOS JŪROJE GEOCHEMINĖ IR GEOEKOLOGINĖ APLINKA

S a n t r a u k a

Cheminio ginklo palaidojimo vietų geologinė sandara yra nesudėtinga. Skagerako sąsiauryje jūros dugnas santykinai lygus, glacialinis, su keliomis pakopomis, o Bornholmo įduboje – lygus (horizontalus). Abiejuose rajonuose dugnas padengtas daugiausia dumblu (sluoksnio storis apie 1–3 m), tačiau atskirose vietose dumblo sluoksnis smarkiai suplonėja arba jo visai nėra. Tose vietose pasireiškia stiprios dugno srovės, arba dugninių vandenų judėjimas, kuris sudrumsčia ir perklosto dumblingą medžiagą. Bornholmo įduboje (80–105 m gylyje) tokiose dugno vietose atsidengia morenos arba ežerinis molis. Sviediniai ir bombos su nuodingomis medžiagomis minėtose vietose gali būti ridenamos dugno srovių.

Bornholmo įdubos viršutiniame dumblo sluoksnyje yra iki 6,29% $C_{org.}$, iki 0,35% P, iki 0,72% Mn ir iki 277,10^{-4}% As. Visi kiti cheminiai elementai yra vidutinių (Klarko) koncentracijų.

Arsenas, kaip vienas toksiškiausių elementų, patenkantis į nuosėdas dėl nuodingųjų cheminių medžiagų (NChM) hidrolizės, neutralizuojasi kaupdamasis arba geležies sulfiduose (redukcinėje aplinkoje), arba mangano ir geležies hidrooksiduose (konkrecijose, oksidacinėje aplinkoje).

Bornholmo įdubos dumble aplink NChM palaidojimo vietas po visą įdubą arseno paplitimo pėdsakų nesurasta. Šis elementas kaupiasi šalia NChM. Foninės As sankaupos dumble (10–30 ppm), geležies mangano konkrecijose bei plutelėse (iki 1021,10^{-4}%) ir geležies sulfiduose (iki 440,10^{-4}%), mūsų nuomone, nekelia žmonėms ekologinės grėsmės. Manome (Emelyanov, Kravtsov, 2007), kad NChM netrukdo Baltijos jūroje tiesti kabelį ir kloti vamzdžius. Kabelio linijos ir dujotiekis nespartina NChM irimo ir jų hidrolizės produktų paplitimo jūros akvatorijoje.

Емельян М. Емельянов

ГЕОХИМИЧЕСКАЯ И ГЕОЭКОЛОГИЧЕСКАЯ ОЦЕНКИ МЕСТ ЗАХОРОНЕНИЯ ХИМИЧЕСКОГО ОРУЖИЯ В СКАГЕРРАКЕ И В БАЛТИЙСКОМ МОРЕ

Р е з ю м е

Геологическое строение районов захоронения химического оружия является сравнительно простым, ледниково-гляциальным, слабо наклоненным, с несколькими ступенями в море Скагеррак (глубины 180–220 м) и ровным (горизонтальным) – в Борнхольмской впадине (глубины 80–105 м). В обоих районах дно покрыто в основном илами (слой мощностью около 1–3 м). Однако в отдельных участках обоих районов имеются либо сильно сокращенные мощности голоценовых илов, либо они полностью отсутствуют. В таких местах иногда проявляются сильные придонные течения, способные взмучивать и переотлагать илистый материал. В Борнхольмской впадине в таких участках на поверхности дна обнажаются либо морены, либо озерные глины. Снаряды и бомбы с ядовитыми веществами в таких участках могут перекатываться под действием придонных течений и вылавливаться рыбацкими донными тралами.

В иле содержится до 6,26% $C_{орг}$, до 0,35% P, до 0,72% Mn, до 277 · 10^{-4}% As. Все остальные изученные химические элементы находятся в кларковых содержаниях.

Мышьяк, как один из наиболее токсичных элементов, поступающий в осадки в результате гидролиза отравляющего химического вещества (ОХВ), нейтрализуется, накапливаясь либо в сульфидах железа (до 440 · 10^{-4}%) (в восстановительной обстановке), либо в гидроокисях (конкрециях) марганца и железа (до 1021 · 10^{-4}%) в окислительной обстановке. Путей распространения рассеянного в илах мышьяка, а также других токсичных (Pb, Cd, Hg, Cu, Zn) элементов в Борнхольмской впадине нами не выявлено. Мышьяк скапливается в непосредственной близости от залегания ОХВ. Как фоновые концентрации As в илах (10–30 · 10^{-4}%), так и сконцентрировавшиеся в железо-марганцевых конкрециях, корках и сульфидах железа, по нашему мнению (Емельянов, Кравцов, 2007), экологической опасности для человечества не представляют. Не представляют ОХВ и помех для прокладки по дну Балтийского моря за пределами мест непосредственного захоронения ОХВ и различных инженерных сетей, и, наоборот, проложенные по дну эти сети (кабель, трубы, буровые вышки и т. д.), по нашему мнению, не будут стимулировать ускорение разложения ОХВ и распространение продуктов его гидролиза на обширных акваториях моря (Емельянов, Кравцов, 2007).

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