since 1961

Baltica
http://www.geo.lt/geo/index.php?id=71C

BALTICA Volume 23 Number 2 December 2010 : 77-90

Influence of chemical weapons and warfare agents on the metal contents in sediments in the Bornholm Basin, the Baltic Sea

Emelyan Emelyanov, Victor Kravtsov, Yuri Savin, Vadim Paka, Ildus Khalikov

Emelyanov, E. M., Kravtsov, V. A., Savin, Y. I., Paka, V. T., Khalikov, I. S., 2010. Influence of chemical weapons and warfare agents on the metal contents in sediments in the Bornholm Basin, the Baltic Sea. *Baltica, 23 (2),* 77-90. Vilnius. ISSN 0067-3064.

Abstract Large quantities of German trophy chemical weapons (CW)[1] were dumped after World War II in the Bornholm Deep of the Baltic Sea. Four ships wrecks were found on the bottom of the central part of the Bornholm Deep at depths of 90-100 m. The bottom of the deep is covered by mud with thickness of 1-3 m. The heavy metal contents (iron, manganese, zinc, copper, cobalt, nickel, chromium, cadmium, lead) and arsenic in the bottom sediments of chemical weapons dumpsite area were investigated with 378 samples in order to develop new data assessing the influence of chemical weapons on the environment. The data obtained indicate that an increased concentration of arsenic (111-277 mg/kg) in the mud of the dumpsite area is related to the chemical warfare agents, where the corrosion processes of chemical munitions and leakage of arsenic-containing agents are happening. The arsenic contamination is of local character and is not regarded hazardous for the environment. In most of the sediment samples outside the chemical weapons dumping area the contents of all the studied elements are in levels of background concentrations. Seven maps of the distribution of the toxic metals in the bottom sediments of Bornholm Basin were compiled. The contents of the studied heavy metals decrease in the direction away from the chemical weapons dumpsite area to the border of the Bornholm Deep. Although the release of warfare gases from dumped chemical weapons has persisted for many decades, the specific pollution of sediments is found to be rather small. The prognosis for further degradation from chemical weapons should exclude catastrophic scenarios.

Keywords *Baltic Sea, Bornholm Basin, dumped chemical munitions, heavy metals and arsenic, bottom sediments, contamination.*

Emelyan Emelyanov [ioran@atlas.baltnet.ru], Victor Kravtsov [kravtsov@atlas.baltnet.ru] Vadim Paka [paka@ioran.baltnet.ru], Atlantic Branch of P.P. Shirshov Institute of Oceanology of the Russian Academy of Sciences (AB IO RAS), Prospect Mira 1, RU-236022 Kaliningrad, Russia; Yuri Savin, Ildus Khalikov [khalikov@typhoon.obninsk.ru], TYPHOON Research and Poduction Association, Governmental Institution (RPA Typhoon), Lenin Str. 82, RU-249038 Obninsk, Russia.
Manuscript submitted 24 May 2010; accepted 4 November 2010.

INTRODUCTION

After the Second World War disposal of chemical munitions became one of the urgent tasks facing anti-Hitler alliance. At that time in the same way as after the First World War the sea dumping was seen as a most common and reasonable way of chemical weapons waste disposal. In our research focus is on the Bornholm Basin which was a main dump site in the Baltic where according to Final Report of the Working Group on Dumped Chemical Munitions (HELCOM 1996) 32 000 tonnes of various chemical weapons (CW) containing about 11 000 tonnes of chemical warfare agents were dumped into the sea (Table 1).

[1] ***Abbreviations:*** *CW – chemical weapons; HM – heavy metals; RAS – Russian Academy of Sciences; VSEGEI – All-Russian Geological Institute; MERCW – Modelling of ecological risks related to sea dumped chemical weapons; VERIFIN – Finnish Institute for Verification of the Chemical Weapons Convention; EMERCOM – The Committee (Ministry)of Emergency Situations of Russian Federation.*

Chemical munitions were delivered by ships and dumped overboard at the circular dumps site within a radius of three nautical miles as shown at the navigation maps (Fig. 1). However according to HELCOM (1993, 1994) some munitions were discharged out of the bounds of the prescribed square which resulted in a much wider actual dumping square within 55^0 07'–55^0 26'N and 15^0 25'–15^0 55'E, also shown on the maps. This is the area containing major part of chemical weapons that had been seized by the soviet troops in Germany. Weapons from American and British zones of occupation were dumped outside the Baltic [in Skagerrak (HELCOM 1996)], in which case it was predominantly shipboard dumping. Whereas main environmental threats in Skagerrak are constituted by sunken ships loaded with chemical munitions, which ultimately make a finite number of dangerous objects, in the case of the Bornholm Basin thousands of various chemical munitions are resting at certain depth in the sea mud scattered over a big sea region. It is this specific character of the Bornholm chemical dumpsite that underlies our survey and on which our research methods are based.

Expeditions conducted during 1997–2007 by P. P. Shirshov Institute of Oceanology of the Russian Academy of Sciences revealed three shipwrecks in the dispersed CW dumping area (Gorodnitski, Filin 2002; Paka, Spiridonov 2001, 2002) with one more ship identified at a later stage, when with the support of European Commission explorations stepped up to an international scale. These shipwrecks were repeatedly examined with remotely operated vehicles (Paka, Spiridonov 2002) and high resolution sonar (Missiaen, Feller 2008). Video recording proved the presence of certain warfare items (artillery shell and aircraft bomb) on two of them, but these data were not however sufficient to conclude about the presence of any chemical munitions in the ship holds. In HELCOM documents (HELCOM 1996) dumping of CW-containing ships is only mentioned as unconfirmed evidence. Hence identification of these shipwrecks at the dumping site does not answer the question about their relation to the dumped chemical munitions.

concentration in water is not kept over a long period of time. Due to its accumulation in bottom sediments and concentration in the vicinity of chemical munitions sources, arsenic may be regarded as indicator of leakage of As containing chemical warfare agents to the marine environment (Emelyanov, Kravtsov 2007).

The main objective of this paper was to study chemical contamination of bottom sediments in the Bornholm Basin with toxic agents, i.e. arsenic and heavy metals (Zn, Cu, Ni, Co, Fe, Mn, Cr, Cd, Pb) and to establish their spreading in and outside the dump site which could enable to assess the influence of dumped chemical munitions and shipwrecks on marine contamination and locate "hot spots" where warfare chemical agents are likely to be found for their subsequent direct examination. In line with these tasks

Table 1. Kind of CW and quantities (in tons) in it of poison materials (HELCOM 1996).

Kind of CW	Quantities in it of poison materials					
	Mustard gas	As-containing	Adamsite	CAP*)	Others	Total
Aircraft bombs	5 920	906	591	479	-	7 896
Artillery shells	671	-	61	36	-	768
High–explosive bombs	314	-	-	-	-	314
Mines	42	-	-	-	-	42
Encasements	80	203	693	-	74	1 050
Smoke grenades	-	-	65	-	-	65
Containers	-	924	-	-	-	924
Drums	-	-	18	-	-	18
Total	7 027	2 033	1 428	515	74	11 077

*) CAP – chlorine–acetatephenone.

The main dump site (CW) (Fig. 1) is located in the central part of the Bornholm Basin in water depth ranging between 70 and 100 m, covered with soft mud up to two-to-three metres thick being semi-liquid on top (Emelyanov 2007). Munitions should sink into this mud which fact is confirmed by numerous evidences (Missiaen, Feller 2008).

Can CWs be regarded as the source of toxic agents really hazardous to the marine environment and people? If the answer is "yes"–how far can these agents be spread from their source? And what is their concentration in seabed sediments? Along with many other questions these issues received either general consideration (MEDEA 1997) or were specifically examined for particular dumpsites, which is illustrated in documents from special conferences held in the Moscow region (Kaffka 1996), in Gent (Missiaen, Henriet 2002), in Halifax (2007, no reports published), in Vilnius (2008, no reports published), in Honolulu (2009, reports published in special issue of *Journal of Marine Technology Society, 43, 4*), as well as in a number of published research findings (Paka 2004; Emelyanov 2007; Emelyanov, Kravtsov 2007). However well founded conclusions and forecasts are unfortunately often difficult to make due to having no sufficient reliable data about dumping cases and experimental data about condition of warfare chemical agents and their actual effects on different constituents of the ecosystem. With the support of international project (The European Union Commission Sixth Framework Programme Priority Project: Modelling of Ecological Risks related to Sea–

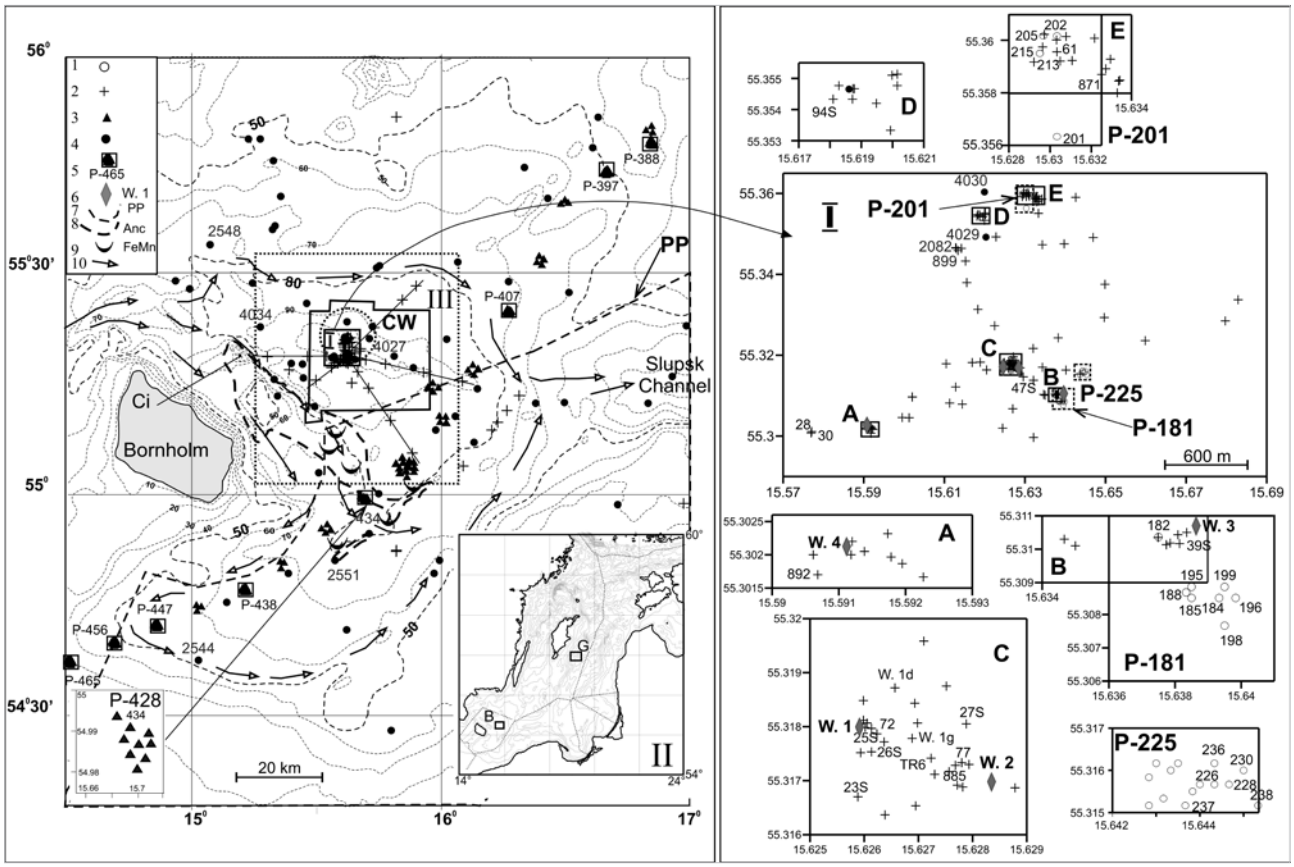

Fig. 1. Map (isobaths in m; after L. Ž. Gelumbauskaitė 1998) of geological stations in the Bornholm Basin, the Baltic Sea. Compiled by E.M. Emelyanov, V.A. Kravtsov, Y.I. Savin, V.T. Paka, I.S. Khalikov.
II – location of the dumpsites; B – Bornholm Basin; G – Gotland Basin; CI – Christiansö Island. CW – conventional area where chemical weapons (CW) are buried. The circle (the length of radius is 3 nautical miles) in the rectangle CW shows the main dumping area of chemical weapons (CW) and where ships were sunken.
I – polygon investigated in detail (sea areas A, B, C, D, others). Symbols 1-10: 1 – stations of R/V *Centaurus* (2003–2007); 2 – stations of R/V *Fritz Reuter* (2008); 3 – stations of other vessels along the track of North Stream; 4 – stations of other vessels; 5 – polygons of detail research along the track of North Stream; 6 – sunken ships (wrecks) on the bottom – W.1; W.2; W.3; W.4; 7 – the northern boundary of Polish (PP) geochemical maps, where P-428 – 9 samples of mud obtained in this polygon (track of North Stream); 8 – area without recent sediments (Ancylus clay and till outcrops); 9 – iron–manganese crusts or nodules; 10 – near-bottom currents (after E.M. Emelyanov 2007).

dumped Chemical Weapons – MERCW, Contract No. 013408) and through cooperation with EMERCOM of Russian Federation and its partners, it became possible for the authors of this article in 2006–2008 to take more samples of water and bottom sediments in the Bornholm CW dumpsite and conduct chemical analyses (Figs 1, 2). During these expeditions on R/Vs *Professor Shtokman*, *Centaurus* and *Fritz Reuter* nearly 400 mud samples have been taken.

Speaking about the analysis of samples presumably contaminated with toxic agents, it should be mentioned that there are specific difficulties in the identification of trace amount of toxic agents and / or their toxic hydrolysates. Even with very high resolution mass–spectrometer identification of toxic agents should be based on their reference samples, which the authors did not have. Main focus hence was made on arsenic (As), which is contained in a number of toxic agents and may be found in sediments at considerably low background level (up to 1 mg/kg). In the South Baltic its average content in sediments is about 5 to 20 mg/kg As.

Arsenic is contained in the following chemical warfare agents: diphenylarsine chloride (Clark I (Ph_2AsCl)), diphenylarsine cyanide (Clark II), phenarsazine chloride (adamsite) ($Ph_2As(NH_2)Cl$), 2-chlorovinyldichloroarsine (lewisite) ($C_2H_2AsCl_3$), diphenylarsine dichloride ($PhAs_2Cl_2$) and arsenic butter, as well as industrial mixture of arsenic (III) chloride 5%, diphenylarsine dichloride 50%, Clark I 35% and triphenylarsine 5%. Arsenic butter was used in mixtures with bis (2-chloroethyl) sulphide (Franke 1976; Kopecz 1996).

As it is commonly known the major part of shells and bombs caught by fishermen in the Bornholm Basin, is heavily corroded (HELCOM 1996). Leakage of bombs and shells on the sea bottom causes continuous supply of toxic agents to marine environment. Behaviour of such toxic agents in marine environment depends on their physical–chemical properties and such environmental conditions as temperature, salinity, Eh and pH values, as well as diffusion rate and advection by bottom currents. Warfare chemical agents are for the most part poorly soluble in water; with time however they start to dissolve and decompose – quicker or slowly. This results in release of toxic components into the marine environment. However their elevated

we provided available data about specific conditions in which leakage of CW casings is happening with subsequent release and decomposition of warfare chemical agents.

GEOLOGICAL SETTINGS

The Bornholm Basin with water depth of about 100 m is located east of the island of Bornholm, in the south–western Baltic Sea. It has its boundaries at $50^0$30'–$55^0$45'N and $14^0$30'–$16^0$30'E. The basin is assumed to be bordered by 50 m isobaths (Fig.1) thus covering the area of 14 000 sq. km. It is surrounded by shallow bottom areas with depth ranging between 25 and 30 m. Saline and dense waters occasionally penetrating to the Baltic from the North Sea, find their way from the Danish passages first to the Arkona Basin with depth of about 46 metres, then entering the Bornholm Basin through the Bornholm Gat channel. The Słupsk Trench is another considerably deep basin to the east of the Bornholm Basin, separated from the latter by a moraine ridge, thus forming Słupsk Sill with its ridge coming at the depth of 56 m.

The Bornholm Basin has smooth slopes what only go steeper in the west. Here on a small plateau Christiansö Island is found. This island is separated from the Bornholm Island by a valley with depth ranging between 60 and 70 m. At the flat bottom of the Bornholm Basin main types of sediments are terrigenous aleuro–pelitic and pelitic mud containing respectively 50-70 and 70-79% of the < 0.01 mm fraction (Emelyanov *et al.* 1995a). Redox potential Ept is normally negative in the mud and reaches –135 mV (Eh=+65 mV).

During the last 40 years no less than five times near-bottom waters in the Bornholm deep were stagnated: 1969, 1971–1972, 1976, 1982 and 1989 (Shpaer, Larionov 1982; Stryuk *et al.* 1995). According to Emelyanov *et al.* (1995b) and Emelyanov (1996) the interface of O_2-H_2S in the water strata lay at the depth about 80 m.

Recent sediments (0-5 cm) found in the Bornholm Basin are terrigenous, including also pelitic mud. Mud contains elevated (3-6%) C_{org} (up to 7.84% max.). According to our previously accepted classification this is either sapropel (5-10% C_{org}) or sapropel–like (3-5% C_{org}) mud.

Among clastic minerals in sediments quartz is prevailing, normally accounting for 80-90% of the 0.1-0.05 mm light sub–fraction. The amount of feldspar is up to 2%, mica up to 5-–6%; in some samples glauconite can also occur. Clastic part of the heavy sub–fraction of 0.1-0.05 mm (specific weight >2.9) is comprised of mica, hornblende, epidote–clinozoisite, ilmenite–hematite and garnet. Terrigenous minerals (quartz in light sub–fraction, ilmenite and magnetite in the heavy one) are more frequently found in the marginal parts of the basin, whereas mica and glauconite are more common in the central area of the basin (Trimonis *et al.* 1995). Illite is the prevailing clay mineral, followed by kaolinite, montmorillonite and chlorite.

Plant remains are plentiful in the upper sediment layer. These are darnel of cereals, grains of pollen and spores, and diatom skeletons. Also sediments reveal some whole shells of *Macoma baltica* mollusc and their fragments.

Authigenous minerals found in the mud are mainly iron sulphides, phosphates, including some phosphates that build on fish bones. Though rather unexpected, limonite and hydrogoethite are also frequently found in the reduced sediments. Also some brown orbicular and black irregular–shaped iron sulphide micro–nodules occur in bottom sediments.

MATERIAL AND METHODS

Material underlying this article is based on samples of bottom sediments taken from the Bornholm CW dumpsite during implementation of MERCW Project: explorations on R/Vs *Professor Shtokman and Centaurus* in 2006 and 2007 and on the chartered German vessel *Fritz Reuter* in 2008. Sampling stations in the Bornholm Deep were chosen on the basis of earlier data about arsenic distribution and location of the shipwrecks that had been obtained during 1997–2005 and subsequently studied in AB IO RAS (Paka 2004; Emelyanov, Kravtsov 2007). 178 samples of sediments from the Bornholm Basin were subject to chemical analysis in AB IO RAS (Emelyanov 2007; Emelyanov, Kravtsov 2007). This included grain size analysis of sediments and determination of the following 18 elements contained in the sediments: C_{org}, N_{total}, P_{total}, Ca, Mg, K, Na, Fe, Mn, Ti, Cu, Zn, Co, Ni, Cr, Cd, Pb, As. The central part of the CW dumps site (encircled area at Fig. 1) was further referred to as "hot spot".

During 2006–2008 expeditions 200 bottom sediment samples were taken at 141 stations in the vicinity of the four shipwrecks and in the "hot spots". Nine short (up to 30-40 cm) mud cores proposed taken in the immediate proximity to the 'hot spots', were frozen at – 18^0 C and given to the Finnish MERCW project partners at Finnish Institute for Verification of the Chemical Weapons Convention (VERIFIN), where they have necessary facilities for micro–determination of certain chemical warfare agents. Traces of chemical warfare agents were found in each sample, which hence proved the relevance of arsenic data. In order to investigate how the content of arsenic and heavy metals in sediments depends on remoteness from presumable source, some of the stations were sampled outside the main chemical munitions dumps site. Stations were positioned at six profiles running in different directions from the point of two closely located shipwrecks, at the intervals of 50; 100; and 500 metres, and 1; 5; 10; 20; and 30 kilometres (Fig. 2).

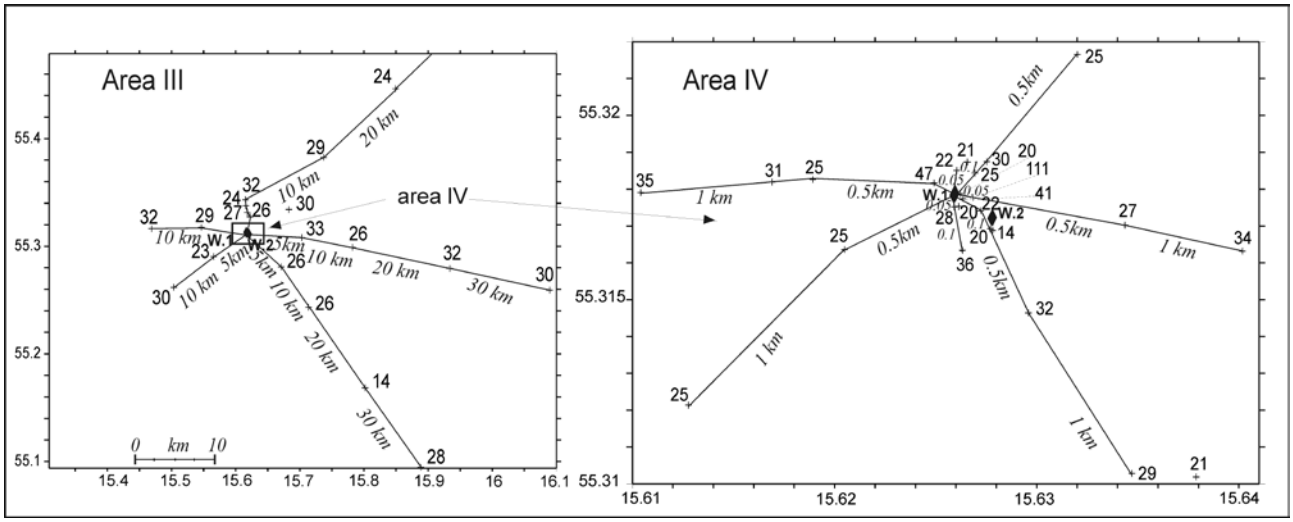

Fig. 2. Distribution of As contents in the upper layer (0-5 cm) of mud near wrecks W.1 and W.2 along the radial profiles at the areas III (see Fig.1) and IV (inside of area III). The numbers near the points are values of As content (in mg/kg); 1 km, 10 km, etc. – distance from the wreck W.1. Location of wrecks W.1 and W.2 see also area C in Fig. 1. Compiled by Y.I. Savin, I.S. Khalikov.

Sampling was made with ODOK box–corer and coring tube (Niemistö corer). From the box–corer the top central part of undisturbed sediment layer (0-5 cm) (i.e. having no contact with box–corer's sides) was sub–sampled. Sediment cores were then cut in layers according to horizons: 0-5; 5-15; 15-25; 25-35; and 35-45 cm. Each sample (black and grey mud) was placed into indexed airproof plastic bag and frozen in deep–freezer at t= – 18^{0}C. The top sediment layer (0-5 cm) was semi-liquid, i.e. with very high content of moisture (70– 80%). After having removed large objects with a tweezers, samples were dried at t=75^{0}C, then mechanically pulverized and homogenized.

Atomic absorption spectrometry (AAS) was used in AB IO RAS for measuring arsenic and heavy metals in 178 samples using *Varian SpectrAA 240FS* spectrometer with air–acetylene flame atomizer and *KWANT.Z–ETA* spectrometer with electro-thermal atomizer and graphite furnace (Emelyanov, Kravtsov 2007). The pulverized sample was subject to digestion using one of the two following techniques: 1) oxidation by acid digestion throughout evaporation, using acid mixture $HNO_3 – H_2SO_4 – H_2O_2$ or $HNO_3 – H_2SO_4 – HClO_4$; or 2) dry digestion using $MgO – MgNO_3$ (Irgolic *et al.* 1995). Main extraction methods were: mixing/shaking, pressurized extraction systems such as microwave heating in special airproof containers (Francesconi, Kuehnelt 2004). There are no universal extraction systems that may be used for all forms of arsenic and heavy metals. AAS findings on arsenic and heavy metals contained in 178 sediment samples may be found in the paper (Emelyanov, Kravtsov 2007); also some findings are presented in this paper (map of arsenic distribution in sediments in chemical munitions dumpsite at P-201, P-181, P-225 polygons, as shown in Fig.1).

In the RPA "Typhoon" for determination of arsenic and heavy metals in 200 sediment samples was used X-ray fluorescence spectrometry (XRF) (CARION NRF 2005). Weighed portions (0.5-1 g) of dried pulverized samples were pressed into pellets 1.5 cm in diameter and 0.5 cm thick. Then total arsenic and heavy metals were measured using X-ray fluorescence spectrometric analysis (XRF). XRF is multi–element analysis; this method shows a number of advantages, as less weighed sample is required (1 g or less) and it does not require prior digestion. XRFS enables to perform both qualitative and quantitative analysis of chemical elements. By determining X-ray peak energy in a sample spectrum and calculating the count–rate for various peak values of elements it becomes possible both to make qualitative elemental analysis of sample and measure concentration of these elements. Detection limits for the tested elements are: 8 mg/kg for As; 9 mg/kg for Pb; 9 mg/kg for Cu, 10 mg/kg for Zn; 10 mg/kg for Ni; 9 mg/kg for Co; 30 mg/kg for Cr; 100 mg/kg for Mn; 7000 mg/kg for Fe.

XRF was used to determine concentration of the following elements in each of the 200 samples: As, Pb, Cu, Zn, Ni, Co, Fe, Mn, Cr. Preparation of all sediment samples and reference samples for XRF was made in permanent fixed–site laboratory equipped with forced clean air ventilation to reduce potential risk of sample contamination ("clean room"). X-ray Fluorescent Analyzer *Spectroscan* was pre–calibrated before measurement. Several standard reference samples with known composition were measured to make calibration graphs. For the purpose of check analysis statutory registered reference samples of seabed sediments and soil were used, approved by Russian Committee for Standardization, Metrology and Certification. Analysis data were received from automatic readouts. Multiple regression equations were used to translate emission line intensity into concentration values. Coefficient of correlation for calibration curves was at any time

exceeding 0.96. This allowed determination of arsenic and heavy metals with inaccuracy never to exceed 20% at 0.95 confidence probability. Certified reference material with known composition was measured together with each batch of samples to ensure accuracy of analysis. Reproducibility of measurements was 85-95% for all tested elements. During analysis variability of blank test results was taken into account for further correction of analysis results.

RESULTS

Sapropel and sapropel–like mud is common not only in the Bornholm Basin but also in many other Baltic Sea basins. In the Bornholm Basin this mud contains up to 7.87% C_{org}, 7.08% Fe, 0.86% Mn (Table 2). Two mud samples taken near the shipwreck (stations 26S and 47) contained 17.7 and 41.5% Fe respectively (Table 3). Apparently these sediments might have some metal scrap corrosion products. Ignoring these outliers, Fe concentration varies in a much narrower range–between 0.05-7.08% (Table 2). Mud containing Fe (above 5%) and Mn (above 0.10%) can normally be found at a depth exceeding 80-90 m, i.e. under reducing conditions. As opposed to sapropel–like mud in Gdansk Basin that is less affected by stagnation (Emelyanov 1986). Bornholm mud shows higher contents of C_{org}, Mn, P, Zn, Cu (Fig. 3) and in some cases of Pb and Cd.

C_{org} occurs predominantly in biogenic components, i.e. darnels of cereals, spores and pollen and fragments of algae. All these particles are commonly 0.05-0.001 mm in size. Hence the elevated C_{org} is not as comparable to the finest pelitic mud, but rather for aleuro–pelitic mud enriched with this fraction. Organic carbon may also be on clayey particles.

Table 2. Minimal, maximal and average contents of fraction <0.01 mm and chemical elements in the surface layer of sediments (0-5 cm) of the Bornholm Basin* (contents of fraction <0.01 mm, C_{org}, Fe and Mn – in %; from Cu to Cd – in 10^{-4}% or mg/kg).

	fr.<0.01 mm	C_{org}	Fe	Mn	Cu	Zn	Cr	Ni	Co	Pb	As	Cd
Sand (18 samples)												
min	0.1	0.02	0.20	0.01	10	10	22	11	4	2	1	0.08
max	17.8	1.13	2.35	0.08	22	52	60	27	15	28	2	0.10
average	10.2	0.28	1.21	0.04	15	28	37	18	13	14	1	0.09
Coarse aleurite (24 samples)												
min	5.9	0.38	0.91	0.01	6	19	16	10	8	7	2	0.10
max	39.8	2.64	3.10	0.04	25	106	54	68	48	11	7	0.40
average	16.4	0.80	1.40	0.02	17	46	35	29	22	8	4	0.18
Fine aleuritic mud (15 samples)												
min	19.2	0.69	1.35	0.01	12	47	20	16	2	13	3	0.10
max	47.8	4.75	4.56	0.05	52	165	84	88	35	17	4	0.30
average	38.6	2.62	2.49	0.02	31	92	40	37	22	15	3	0.20
Aleuro–pelitic mud (113 samples)												
min	46.2	0.98	0.05	0.02	20	76	40	14	14	6	3	0.10
max	69.5	7.84	7.08	0.61	68	671	671	241	64	74	277	1.00
average	60.2	4.87	3.96	0.10	40	157	94	62	34	18	42	0.40
Pelitic mud (205 samples)												
min	25.8	0.30	1.13	0.01	11	11	27	13	9	3	2	0.10
max	87.5	6.94	6.32	0.86	738	703	965	815	237	101	210	0.60
average	63.0	4.05	4.70	0.19	88	238	95	67	24	54	28	0.28
All the types (375 samples)												
min	0.1	0.02	0.05	0.01	6	10	16	10	2	2	1	0.08
max	87.5	7.84	7.08	0.86	738	703	965	815	237	101	277	1.00
average	48.6	3.54	4.16	0.15	67	193	92	64	27	41	31	0.34

* The data are presented for all studied samples (375 samples) taken in the *RVs Professor Shtokman, Centaurus* and *Fritz Reuter* cruises in 1997–2008, except three samples from the stations 47-S-1, 26-S-1 and PSh-4030 (see Table 3).

Table 3. Contents of the chemical elements in aleuro–pelitic (AP) and pelitic (P) mud (layer 0-5 cm) of the Bornholm Deep with the highest contents of Fe, Mn and As; contents from C_{org} to P – in %, from Cu to Cd – in 10^{-4}% (mg/kg).

Station	Depth, m	Sed. type	C_{org}	Fe	Mn	Ti	P	Cu	Zn	Pb	Cr	Ni	Co	As	Cd
As contents 50-100 mg/kg															
C-182	97	AP	5.87	3.88	0.11	0.39	0.05	39	171	19	109	72	30	50	0.6
C-205	97	AP	6.35	4.16	0.06	0.43	-	36	124	11	87	78	28	53	0.2
94-S-1	93	P	-	5.02	0.08	-	-	112	357	65	74	59	9	56	-
C-215	97	AP	6.45	4.41	0.06	0.33	0.09	27	174	24	110	73	53	58	0.2
23-S-1	94	P	-	4.88	0.07	-	-	82	388	47	84	63	9	60	-
C-237	97	AP	7.16	3.51	0.14	0.26	0.08	49	166	14	89	79	40	61	0.7
C-226	97	AP	6.65	4.27	0.07	0.31	0.08	34	120	7	105	74	35	63	0.3
C-201	97	AP	6.16	4.13	0.07	0.38	0.09	30	165	18	89	76	37	64	0.4
C-236	97	AP	6.67	4.00	0.07	0.27	0.08	27	172	19	99	69	35	69	0.5
C-198	97	AP	6.89	4.40	0.11	0.41	0.09	47	143	11	125	49	37	73	0.4
C-196	97	AP	7.09	4.38	0.13	0.39	0.04	45	174	26	102	68	30	75	0.4
C-230	97	AP	7.20	3.55	0.13	0.29	0.08	47	140	8	97	79	44	75	0.6
C-184	97	AP	4.95	3.49	0.10	0.33	-	28	98	7	102	47	35	77	0.4
C-238	97	AP	7.84	4.39	0.11	0.30	0.10	53	214	26	100	73	51	77	0.7
C-228	97	AP	6.88	3.53	0.2	0.31	0.09	38	164	11	125	71	51	100	0.4
As contents >100 mg/kg															
G-434	54	P	3.70	-	-	-	-	-	-	-	-	-	-	101	-
W.1g	88	P	-	4.33	0.35	-	-	95	226	25	76	57	21	111	-
C-188	97	AP	6.84	4.06	0.12	0.34	0.07	36	169	25	82	41	37	114	0.6
C-185	97	AP	-	3.95	0.13	0.30	0.09	47	171	28	104	56	28	122	0.7
C-202	97	AP	-	3.25	0.10	0.32		34	98	9	109	60	32	135	0.4
C-199	97	AP	6.51	3.88	0.17	0.42	0.07	43	153	15	125	48	43	143	0.5
C-213	97	AP	6.04	4.01	0.13	0.41	0.08	41	106	7	109	66	38	169	0.2
25S	90	P	-	6.32	0.47	-	-	738	467	66	965	815	237	210	-
C-195	97	AP	-	4.75	0.48	0.39	0.07	30	94	12	125	66	30	277	0.1
Mn contents 0.5-1.0%															
PSh-4029	95	P	-	4.50	0.61	0.34	0.09	44	200	-	56	60	30	-	
PSh-4034	86	P	-	4.47	0.50	0.38	-	38	198	-	82	106	46	-	-
871-S	93	P	-	5.46	0.52	-	-	70	175	53	74	61	16	31	-
899-S	94	P	-	5.33	0.53	-	-	59	136	49	94	58	17	41	-
2082	86	P	-	4.44	0.53	-	-	112	302	67	76	71	71	21	-
892	95	P	-	5.19	0.56	-	-	74	135	69	128	60	27	16	-
27S	94	P	-	5.11	0.56	-	-	68	299	79	84	59	<9	25	-
39S	90	P	-	5.14	0.62	-	-	65	290	64	65	62	12	25	-
TR6	88	P	-	5.80	0.70	-	-	131	190	52	110	88	34	22	-
W.1d	88	P	-	4.83	0.75	-	-	103	202	31	32	67	43	21	-
885	95	P	-	5.48	0.86	-	-	38	102	23	116	52	22	32	-
Fe >10.0% and Mn >1% contents															
26S	90	P	-	17.67	0.33	-	-	162	433	38	71	68	20	51	-
47S	94	P	-	41.52	2.12	-	-	424	703	83	391	87	9	51	-
PSh-4030	95	AP	-	5.32	3.24	0.32	0.11	36	158	-	56	56	28	-	-

* The stations located near the wrecks see Figure 1.

Content of heavy metals (HM) in sediments varies depending on their grain–size composition (Fig. 3): contents of all components and elements are increasing from sand towards coarse aleurite—fine aleuritic mud—aleuro–pelitic mud—pelitic mud in case of Fe, Zn, Cu, Ni and K.

Based on their average content in the sediments (Fig. 3) the examined elements may be divided into

two groups. Elements in the first group (C_{org}, Cr, Co, As) are mainly confined to the 0.05-0.01 mm and 0.01-0.001 mm fractions, in particular to aleuro–pelitic mud. This means that elements in this group are predominantly concentrated in sediments in central areas of the basin and over its periphery.

Elements in the second group (Fe, Cu, Ni, Pb) are closely related to pelite (mainly clayey and sub–colloidal particles). These elements are distributed in sediments according to the so called "Pelitic Fraction Rule" (Emelyanov 1986, 2002, 2005): the higher the content of the <0.01 mm fraction in the sediments, the higher the content of the second group elements (Fig. 3). The highest values of these elements are confined to central areas of the basin covered with the finest (pelitic) mud (Figs 4, 5, 6, 7, 8).

In some cases, increased concentrations of As and HM in the more shallow bottom sediments of Bornholm Basin peripheral area are explained by the presence of oxyhydroxides of Fe and Mn (micro–nodules, fragments of crusts) there. Such oxyhydroxides actively concentrate certain metals. Crusts and nodules of hydro–oxides of Fe and Mn may contain up to 653 mg/kg As, up to 301 mg/kg Ni and increased amounts of other trace metals (Baturin *et al.* 1995). In the mud of the central area of Bornholm Basin under reducing condition ferric sulphides are formed. Due to their sorption ability such sulphides may contain up to 440 mg/kg As (Emelyanov, Kravtsov 2007).

Marine Holocene mud is sometimes enriched in Pb (up to 101 mg/kg, Table 4). This element is concentrated in the mud from central part of the basin (Fig. 8). Similarly to Mn and Cu (Figs 5, 6) and also Ni, its values are increasing from periphery towards the centre of the basin.

In the Gdańsk and Northern Baltic Basins, where there is also periodically stagnation of near–bottom waters but more weak, than in the Bornholm Deep, distribution of Mn is strictly follows according to the "Pelitic Fraction Rule" (Emelyanov 1986). At the same time its distribution in the Bornholm Basin sediments is different: the average content of Mn in the aleuro–pelitic and pelitic mud is five to ten times higher than in the more coarse sediments (see Table 2, Fig. 3). This may be explained by the fact that major part of Mn in the sediments of the Bornholm Deep is not related to terrigenous pelitic material as was in the case of previously mentioned basins, but rather to authigenous minerals–finest crystals of manganese carbonate–rhodochrosite (Emelyanov *et al.* 1995), which is forming under the influence of the periodical stagnation of the near–bottom waters (Shpaer, Larionov 1983; Stryuk *et al.* 1995).

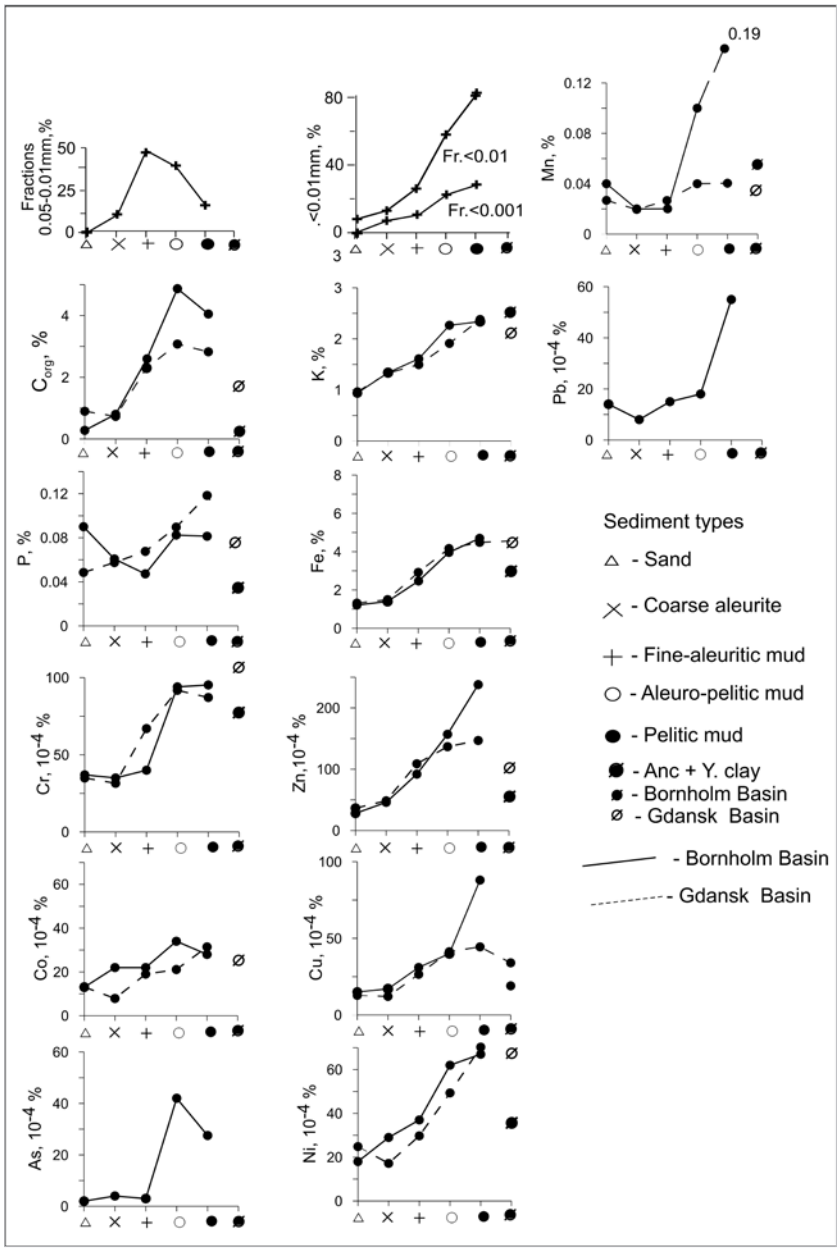

Fig. 3. Average distribution of the grain size fractions (0.05-0.01 and <0.01 mm) and selected chemical components and elements in the sediment (0-3; 0-5 cm) types in the Bornholm (solid line) and Gdansk (dashed line) basins. After E. M. Emelyanov 2002.

Based on their pair correlations Zn, Cu, Cr and Ni fall into the same group – their correlation coefficients (r) are generally above 0.50. All of them however correlate differently with the <0.01mm fraction, C_{org}, and Fe. Zn and Ni are better correlated with Fe (r=0.63), thus making their spatial distribution pattern similar to one of Fe: Cu and Cr have weak (r=0.50-0.30) or bad correlation (r<0.30) with Fe and C_{org}. Ni is largely associated with C_{org}, Cu, Mn and Fe. Co is better correlated with Ni and C_{org}. As only correlates with C_{org}

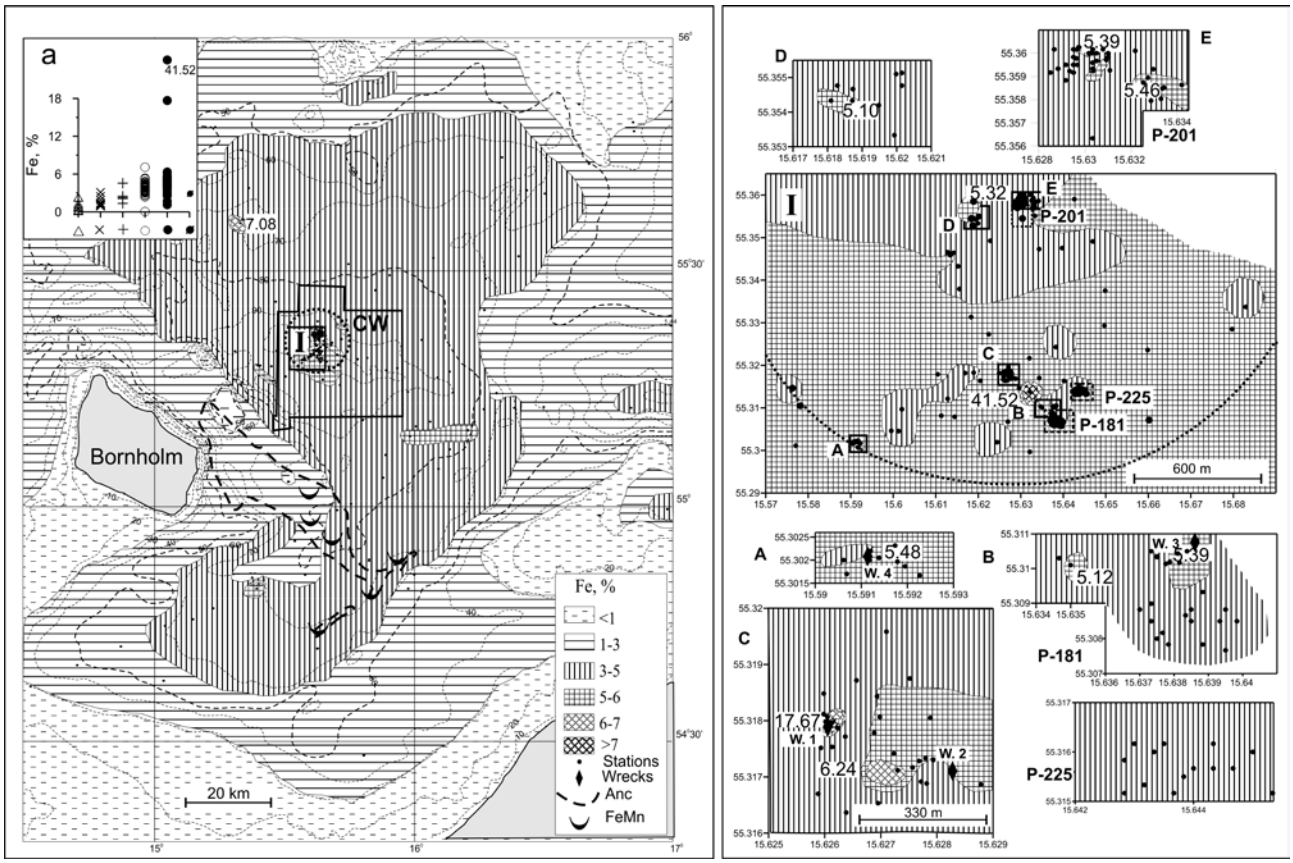

Fig. 4. Isoline plot of Fe content (in %) in the surface (0-3 cm) sediments of the Bornholm Basin. Compiled by E.M. Emelyanov, V.A. Kravtsov, Y.I. Savin, V.T. Paka, I.S. Khalikov.
CW – area, where chemical weapons were sunken. The numbers (5.10; 17.67; others) on the maps of the polygons (A, B, others) mean maximum contents of Fe, points – investigated samples, W.1, W.2 – wrecks, a – distribution of Fe in the different sediment types (from left to right: sand; coarse aleurite (silt); fine aleuritic (silty) mud; aleuro–pelitic mud (or mud); pelitic (clayey) mud; Ancylus+Yoldia clay (see Fig. 3). Circle in the rectangle CW see Fig.1. Number 41.52 – maximal Fe content, %.

Table 4. Contents of toxic elements in the mud of "hot spots", in 10^{-4}% (mg/kg); Fe and Mn in %.

	Station	As	Pb	Zn	Cu	Ni	Co	Fe	Mn	Cr
Area	Wreck-1 (W.1)									
C	W.1g	111	25	226	95	57	21	4.33	0.35	76
	23S	60	47	388	82	63	<9	4.88	0.07	84
	25S	210	66	467	738	815	237	6.32	0.47	965
	26S	51	38	433	162	68	20	17.67	0.33	71
Polygon I										
I	55S	36	58	333	90	60	<9	5.41	0.11	104
E	66S	47	47	268	95	78	17	5.39	0.20	83
D	94S	56	65	357	112	59	<9	5.02	0.08	74
I	2042	46	46	286	110	65	<9	4.63	0.27	120

(r=0.58) and shows weak correlation with Ni, whereas Cd correlates with Zn and weakly (r=0.45) with C_{org}.

Manganese is distributed in sediments very specific. None of the examined elements correlate with this element. Increased concentration of Mn is found in the very centre of the basin. The area of mud containing 0.10-0.20% Mn covers 550 km^2, whereas areas containing >0.20% are only about 2 sq. km in size. Compared to Fe the highest Mn content is more clearly confined to the centre of the basin (Fig. 4, 5). This is apparently largely due to stronger stagnation condition in the near-bottom layer of the central part of the basin. It results in more intensive accumulation of Mn, which in heavily reducing conditions is diagenetically accumulated in the form of composite manganese carbonates or rhodochrosite (Emelyanov 2005).

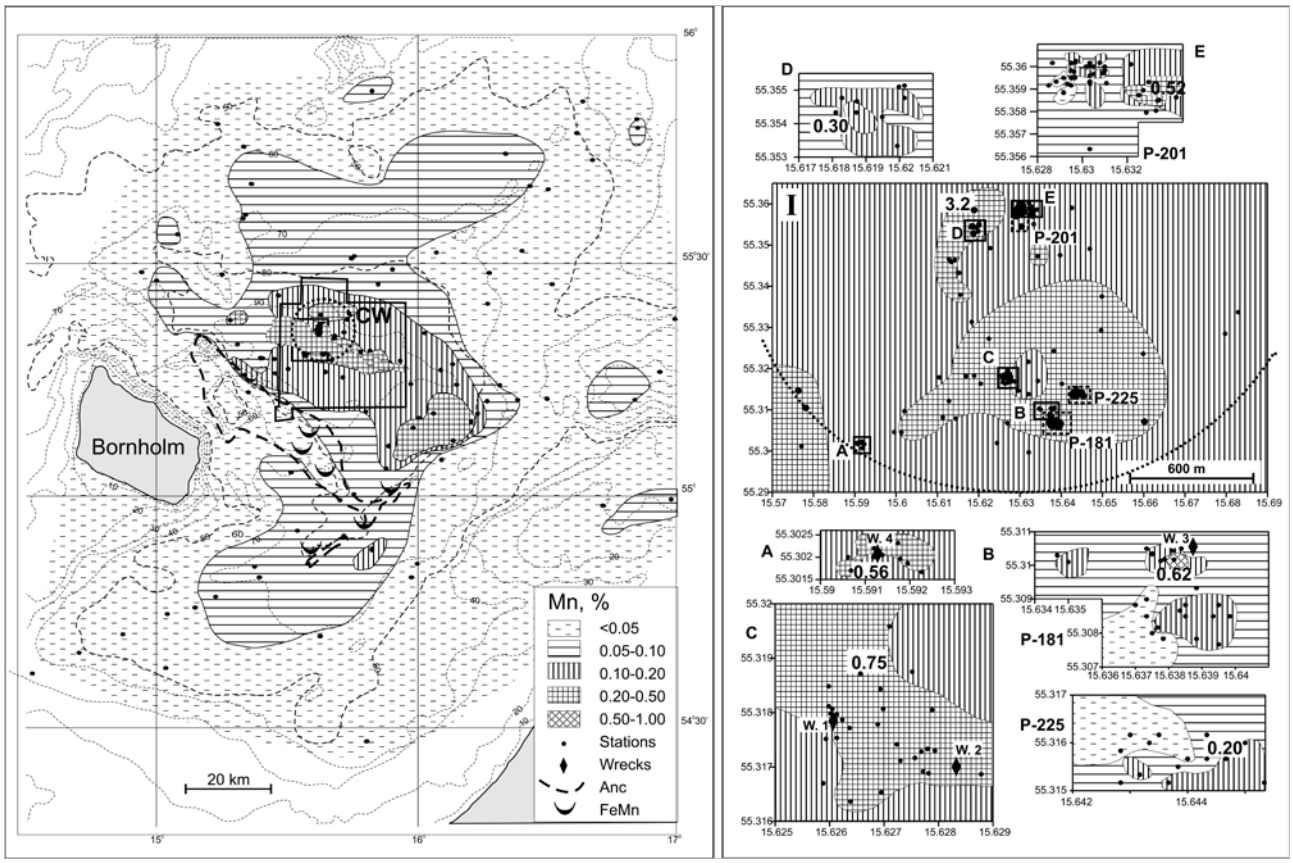

Fig. 5. Isoline plot of Mn content (in %) in the surface (0-3 cm) sediments of the Bornholm Basin. Compiled by E.M. Emelyanov.

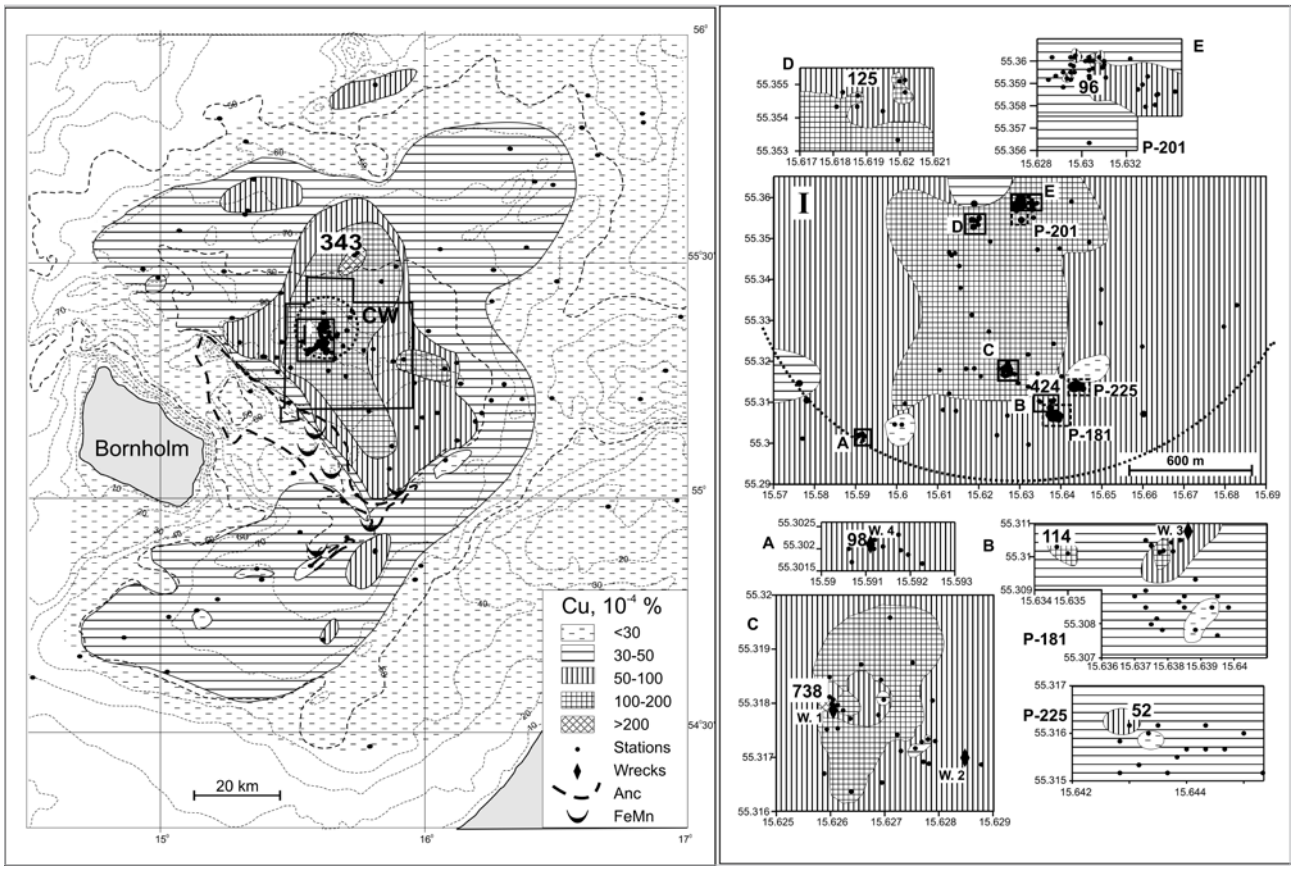

Fig. 6. Isoline plot of Cu content (in 10^{-4}% or mg/kg) in the surface (0-3 cm) sediments of the Bornholm Basin. Compiled by E.M. Emelyanov, V.A. Kravtsov, Y.I. Savin, V.T. Paka, I.S. Khalikov.

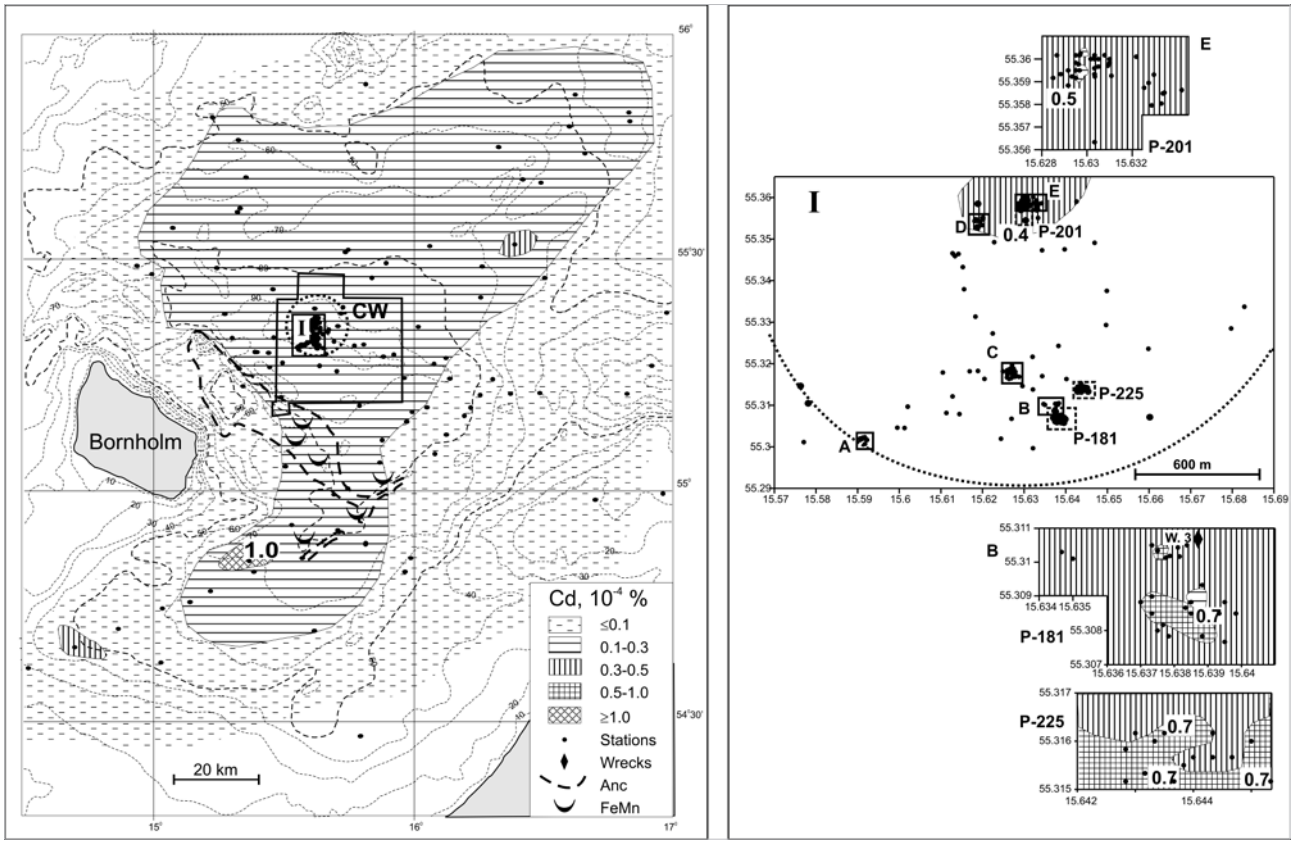

Fig. 7. Isoline plot of Cd content (in 10^{-4}% or mg/kg) in the surface (0-3 cm) sediments of the Bornholm Basin. Compiled by E.M. Emelyanov, V.A. Kravtsov.

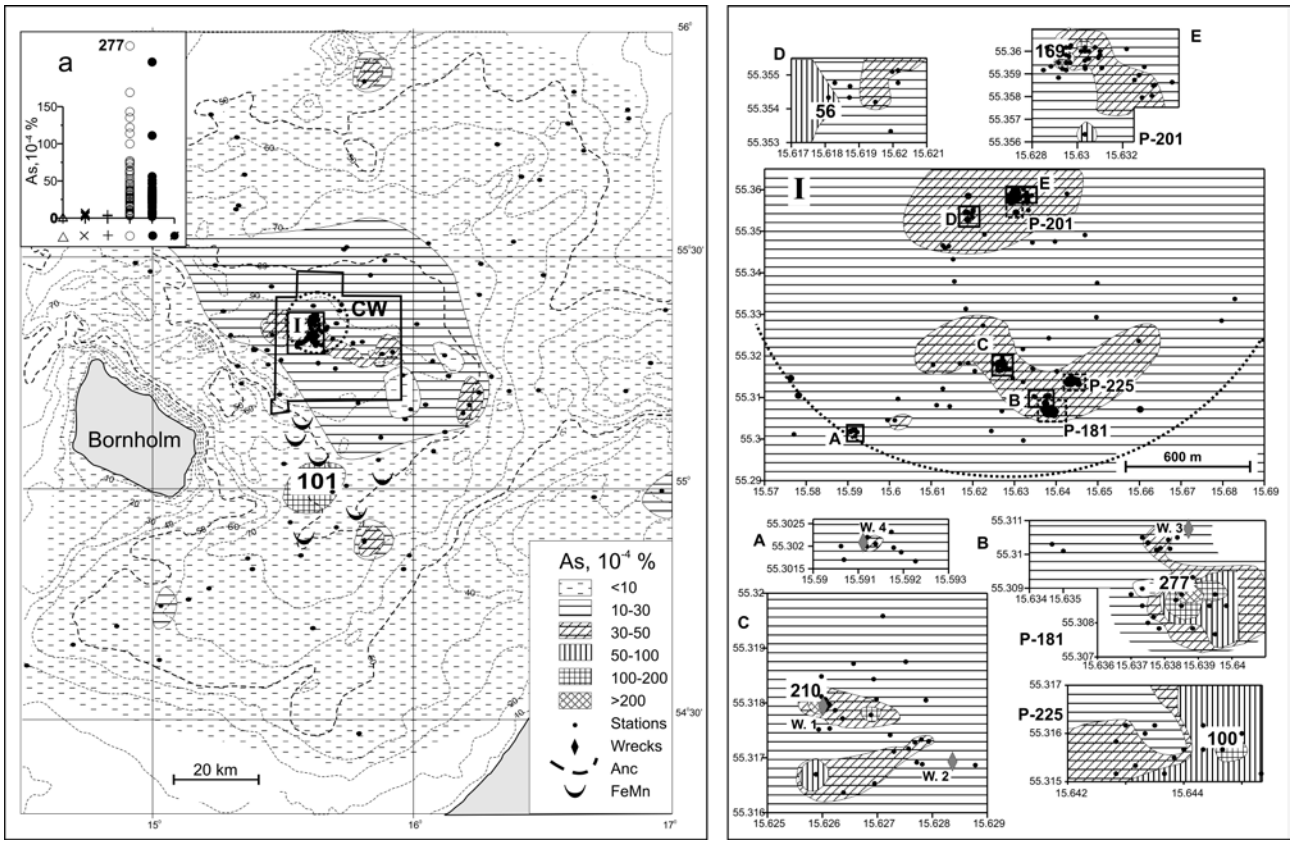

Fig. 8. Isoline plot of As content (in 10^{-4}% or mg/kg) in the surface (0-3 cm) sediments of the Bornholm Basin; a – distribution of As in the separate sediment types (for the legend see Fig. 3). Compiled by E.M. Emelyanov, V.A. Kravtsov, Y.I. Savin, V.T. Paka, I.S. Khalikov.

DISCUSSION

For clay and shale the average background content of As is normally 10 mg/kg. Examined samples from the Bornholm Basin, based also on the data shown by Emelyanov and Kravtsov (2007), contain from 1 to 277 mg/kg As (see Tables 2, 3). The highest As value (277 mg/kg) was found in the mud from "hot spot" of the P-181 area in the Bornholm Basin, located about 500 m to the south from W.3 shipwreck.

The thickness of marine Holocene mud (Hl_{2-3}) is 200-300 cm, exceeding 300 cm in the direction from the centre to the Bornholm Island (near Christiansö Island) (up to 5-6 m; Emelyanov *et al.* 1995). In the mud layer (5-60 cm) the amount of chemical elements and components (Table 5) is the same as in their upper 3 cm layer. However, both Mn and Cu, and also As are found to have their highest content in the upper (0-3; 3-5 cm) mud layer, with slightly lower content in the deeper Litorina mud (5-60 cm).

Samples with increased As contents 25S (210 mg/kg) and 26S (51 mg/kg) were taken in immediate proximity to W.1 shipwreck, samples 23S (60 mg/kg), W.1g (111 mg/kg) and TR (47 mg/kg) were taken in one hundred to several hundred metres away from shipwrecks W.1 and W.2. All these samples are however located in the small area C in the centre of the bigger polygon I within the circle (Fig. 1). At the same time samples 55S (47 mg/kg), 94S (56 mg/kg) and 2042 (46 mg/kg) are taken near "hot spots" within the areas B, D and E (Fig. 1).

In the mud sampled immediately near the W.1 shipwreck As concentration is 210 mg/kg (Table 4) as mentioned above, near W.2 and W.3 shipwrecks it is 10-30 mg/kg; near W.4 shipwreck it reaches 30-50 mg/kg. In total at the area there have been two very small areas identified with elevated As contents (30-50 mg/kg). These areas cover 500x600 and 1000x300 m. Therefore, the leakage of the chemical warfare agents in the location of three shipwrecks is lower than in the region with scattered objects. Nine samples taken at certain distances from the shipwrecks contain >100 mg/kg As, and 15 samples contain 50-100 mg/kg As (Table 3; Fig. 3). Areas with such concentration are not very big they only cover the square between 100x100 m to 100x500 m.

In high As containing samples W.1g (111 mg/kg) and 25S (210 mg/kg) (Table 5) also the highest concentration of As containing chemical warfare agents (triphenylarsine and diphenylchlorarsine, phenyldichloroarsine or adamsite transformation products) were found (Söderström *et al.* 2008). Comparison of total arsenic and As containing chemical warfare agents (triphenylarsine and diphenylchlorarsine, phenyldichloroarsine or adamsite transformation products) in sediments proved good correlation between these two sets of data (r=0.87, n=57).

Concentration of As in sediments in access of 50 mg/kg, i.e. higher than its background values for pelitic mud in this basin (30 mg/kg), served to us as a potential indicator of the presence of As containing chemical warfare agents in the Bornholm Basin. At small areas in close proximity to the shipwrecks

Table 5. Contents of As and other metals (Fe and Mn in %; Cu, Zn, Pb, and As in 10^{-4} % or mg/kg) in the aleuro–pelitic mud of the Bornholm Deep (core PSh-4027, 55°21.48' N, 15°43.07' E; depth 93 m) (after Emelyanov, Kravtsov 2007).

Layer, cm	Fe	Mn	Cu	Zn	Pb	As
3 - 4	4.35	0.15	33	155	43	13
7 - 8	4.08	0.30	30	155	38	22
8 - 9	4.20	0.25	33	155	43	13
9 -10	4.08	0.25	25	105	28	13
10 -12	4.15	0.30	25	100	23	16
12 -14	4.28	0.68	38	120	19	18
14 -16	4.20	0.70	33	95	24	28
16 -18	4.50	0.48	20	120	22	22
18 - 20	4.40	0.68	33	145	22	40
22 - 24	6.00	0.80	25	125	21	34
24 - 26	4.33	0.75	30	85	19	18
26 - 28	4.53	0.30	25	120	22	16
28 - 30	4.20	0.35	25	120	21	12
30 - 32	4.03	0.83	20	125	19	21
32 - 34	4.10	0.60	20	130	18	41
34 - 35	4.08	0.53	33	115	19	17
Average	4.34	0.50	28	123	25	22

or near any unidentified metallic objects in the very centre of the Bornholm Basin (within the circle) the As content is above 50 mg/kg. It most likely depends on the number and the proximity of sunken objects with chemical warfare agents or on the place where any corroded shell, bomb or container might release chemical warfare agents filling.

At the same time, several samples of sediments containing elevated As contents (50-100 mg/kg and higher) were also found outside of CW dumpsite area–in the location with no chemical warfare agents containing objects (Emelyanov, Kravtsov 2007). Assessment of data on As content in the environment of the Bornholm Basin proved insignificant risk for fish and its consumption (Sanderson *et al.* 2008).

CONCLUSIONS

Increased As concentrations (111-277 mg/kg) in the surface layer of the bottom sediments were found near the ships wreck W.1 and W.3 and mostly, and just in areas where the metal objects occur in the mud. The sources of arsenic could be thin–wall containers, shells and bombs with As–containing agents depressurized during they remained at surface of the bottom. Such distribution of arsenic could be reckoned as indicator of leakage of As– containing warfare agents to the marine environment. The state of metal objects (probably, shells, bombs, containers) were buried in the mud at depth 1-2 m from the surface is unknown. It is desirable to conduct special study of these objects in future.

Elevated As concentration (up to 101 mg/kg) was found also and in the Baltic Sea far from the known dumps sites. In such samples, arsenic could be included into Fe and Mn oxyhydroxides, which may contain up to 653 mg/kg As, or included into ferric sulphides, which may contain up to 440 mg/kg As. Both hydro–oxides and sulphides are authigenous formations, which have no relations to CW.

The CW dumps site in the Bornholm Basin at present time is not the immediate threat for the marine environment, as well as not the obstacle for hydro–engineering activity outside of this area. The environmental monitoring in the Bornholm Basin is necessary to continue for detecting the tendency for any changes.

Acknowledgements

Authors are grateful to the crews of the MS *Fritz Reuter* and the RV *Professor Shtokman* and collaborators of Department of Atlantic Geology of AB IO RAS Djuraboy Fidaev, Sergey Isachenko, Tatyana Konovalova, Julia Polosina, Galina Romanova, Anelia Adamovich, Irina Klimentyeva and others who helped us and made sampling, chemical and grain–size analysis and compiled figures, tables and other materials for this article. We express our gratitude to reviewers Drs Helmar Kunzendorf (Copenhagen), Birger Larsen (Copenhagen) and Henry Vallius (Helsinki) for the valuable comments.

References

Baturin G. N., Emelyanov, E. M., Kunzendorf, H., 1995. Authigenous deposits in the sediments. *In* E. M. Emelyanov, Ch. Christiansen, O. Michelsen (eds), Geology of the Bornholm Basin, *Aarhus Geoscience 5,* 189-194.

CARION NPF, 2005. *Technique of performance of measurements of a mass fraction of metals in powder tests of sea bottom sediments by a method X-Ray Fluorescence Spectrometry.* M-002/2005. Certificate of Compliance № 242/57-2005. Mendeleyev Institute for Metrology (VNIIM).

Emelyanov, E. M., 1986. Geochemistry of suspended matter and sediments of Gdańsk basin and sedimentation processes and their role in sedimentogenesis. *In* E. M. Emelyanov and V. N. Lukashin (eds), *Geochemistry of the sedimentary process in the Baltic Sea,* Moscow, Nauka, 67–115. [In Russian].

Emelyanov, E. M., 1996. Chemical components and elements in the suspended matter and sediments of the western Baltic. *Baltica 9*, 5-15.

Emelyanov, E. M. (Ed.), 2002. *Geology of the Gdańsk Basin. Baltic Sea.* Kaliningrad, Yantarny Skaz, 496 pp.

Emelyanov, E.M., 2005. *The barrier zones in the ocean*. Springer, Berlin, Heidelberg, New York, 636 pp.

Emelyanov, E. M., 2007. Geochemical and geoecological situation in the areas of the Skagerrak and the Baltic Sea where chemical munition was dumped. Vilnius, *Geologija 59,* 8–29.

Emelyanov, E. M., Trimonis, E. S., Slobodyanik, V. M., Nielsen, O. B., 1995a. Sediment thickness and accumulation rates. *In* E. M. Emelyanov, Ch. Christiansen, O. Michelsen (eds), Geology of the Bornholm Basin, *Aarhus Geoscience 5,* 81–84.

Emelyanov, E. M., Kravtsov, V. A., Kunzendorf, H., 1995b. Trace metals in sea and pore water from the Bornholm Basin. *In* E. M. Emelyanov, Ch. Christiansen, O. Michelsen (eds), *Aarhus Geoscience 5,* 157-174.

Emelyanov, E. M., Kravtsov, V. A., Paka, V. T., 2000. Danger to life of areas of dumped trophy chemical munitions in the Skagerrak Sea and in the Bornholm Basin, Baltic Sea. *In* T. Ecimovic, E. F. Stuhler , M. Vezjak (eds), *Proceedings of the 16th International Conference on Case Method Research and Case Method Application,* 58–64.

Emelyanov, E. M., Kravtsov, V. A., 2007. Cause of elevated As concentrations in the Baltic Sea and Vistula Lagoon. *Geochemistry International 45, 8,* 798–815.

Gelumbauskaitė, L. Ž., 1998. Bathymetric Map of the Central Baltic Sea. Scale 1:500 000. *LGT Series of Marine Geological Maps / SGU Series Ba, 54, Vilnius–Uppsala.* 2 sheets.

Gorodnitski, A., Filin, A., 2002. Techniques and results of magnetic detection of dumped weapons in Bornholm and Skagerrak dump sites. *In* T. Missiaen, J.-P. Henriet (eds), *Chemical Munition Dump Sites in Coastal Environments,* 53-63.

Francesconi, K.A, Kuehnelt, D., 2004. *Determination of arsenic species: A critical review of methods and applications, 2000–2003*. Analyst 129, 373 pp.

Franke, S. 1976., *Lehrbuch der Militärchemie, Band 1, Militärverlag der Deutschen Demokratishen Republik.*

HELCOM, 1993. Complex analysis of the hazard related to the captured German chemical weapon dumped in the Baltic Sea. CHEMU 2/2/1/Rev.1 (27 September 1993) as amended 11 October 1993 – submitted by Russia.

HELCOM, 1994. Report on chemical munitions dumped in the Baltic Sea. Report to the 15th meeting of the Helsinki Commission from the Ad–Hoc Working Group on Dumped Chemical Munition (HELCOM CHEMU), January 1994. Danish Environmental Protection Agency.

HELCOM, 1996. Third periodic assessment of the state of the marine environment of the Baltic Sea, 1989–1993, Executive summary & background document. Baltic Sea Environment Proceedings 64A; 64B.

Irgolic, K.J., Greschonig, H., Howard, A.G., 1995. Arsenic. *In* A. Science*, Encyclopedia of Analytical*, London, Academic, 168-184.

Kaffka, A. V. (Ed.), 1996. *Sea–dumped chemical weapons: aspects, problems and solutions.* NATO ASI Series 7, 112 pp.

Kopecz, P., 1996. *Review of suspected warfare–related environmental damage in the Federal Republic of Germany. Part 3: Chemical agents dictionary.* UBA-Texte 32/96, Berlin.

Kunzendorf, H., Larsen, B., 2009. Environmental changes in the Bornholm Basin as deduced from the geochemistry of short and long sediment cores. *Baltica 22*, *2,* 101–110.

MEDEA, 1997. *Ocean dumping of chemical munitions: environmental effects in arctic seas.* US Governmental Report, 235 pp.

Missiaen, T., Feller, P., 2008. Very–high–resolution seismic and magnetic investigation of a chemical munitions dumpsite in the Baltic Sea. *Journal of Applied Geophysics 65,* 142–154.

Missiaen, T., Henriet, J.-P. (eds), 2002. *Chemical munitions dump sites in coastal environments.* Federal Ministry of Social Affairs, Public Health and the Environment, Brussels, 167 pp.

Paka, V., 2004. Zatoplennoye chimicheskoye oruzhiye: sostoyaniye problemy. *Russian Chemical Journal XLVIII, 2,* 99–109. [Dumped chemical munitions: the state of the problem]. [In Russian].

Paka, V., Spiridonov, M., 2001. Research of dumped chemical weapons made by R/V "Professor Shtokman" in the Gotland, Bornholm and Skagerrak dumpsites. *In* T. Missiaen, J.-P. Henriet (eds), *Chemical weapons in coast, chemical munitions dump sites in coastal environments,* 27–42.

Paka, V., Spiridonov, M., 2002. An overview of the research of dumped chemical weapons made by the R/V "Professor Shtokman" in the Gotland, Bornholm and Skagerrak dump sites during 1997–2001. *HELCOM MONAS 4/2002*, 21 pp.

Sanderson, H., Frauser, P., Thomsen, M., Sorensen, P., 2008. Screening level fish community risk assessment of chemical warfare agents in the Baltic Sea. *Journal of Hazardous Material 154,* 846-857.

Söderström, M., Vanninen, P., Kuitunen, M.-L., Kostiainen, O., Björk, H., 2008. Chemical analysis. MERCW project, Deliverable D 3.3.2.

Shpaer, I., Larionov, Y., 1983. Oxygen. *In* Problems of research and mathematic simulation for the Baltic Sea, issue 1, Leningrad, 102–113. [In Russian].

Stryuk, V. L., Skyum, P., Christiansen, C., 1995. Sources supply and distribution of suspended matter. *In* E. M. Emelyanov, Ch. Christiansen, O. Michelsen (eds), Geology of the Bornholm Basin, *Aarhus Geoscience 5,* 105–110.

Trimonis, E.S., Isachenko, S.M., Mrazek, J., Nielsen, O.B., 1995. Mineral composition of recent sediments. *In* E. M. Emelyanov, Ch. Christiansen, O. Michelsen (eds), *Aarhus Geoscience 5,* 141–148.