Deployment, toxicity and influence on the environment and other issues connected with sea-dumped chemical weapons

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1. Introduction

Dumping of chemical warfare in the Baltic Sea after WW II
After World War II some 300,000 tons of chemical weapons (CW) were captured on German territory. The largest part of these weapons was dumped in the Baltic Sea and Skagerrak Strait on the orders of the British, Soviet, and American Military Administrations in Germany. At least 170,000 tons of CW was dumped in the Skagerrak, mainly in the Norwegian trench and in the south-eastern Skagerrak. In most of the dumping operations in the Skagerrak complete ships were sunk with their cargo [HELCOM 1994, 1996].

In the Baltic Sea at least 50,000 tons of CW were dumped. The declared dumpsites here are located near the island of Bornholm (32,000 t), in the Little Belt (5,000 t), and in the Gotland basin (2,000 t); witnesses also reported about additional amount of CW dumped near the Bornholm - 23,000 t, however this information was not verified. In most cases the warfare was thrown over board, either loose (bombs, shells) or in containers, but some ships were also sunk [HELCOM 1996]. There are strong indications that part of the warfare was thrown overboard during transport to the Baltic dumpsites; how many tons were thus dumped is not known [Andrulewicz 1996, Schultz-Ohlberg 2001].

In the beginning of the 90's expert groups in Denmark, Russia, Sweden, Germany and other States prepared several national reports on dumped chemical munitions in the Baltic Sea [HELCOM 1993a-i]. An *ad-hoc* working group was set up by the HELCOM, which deals with the protection of the marine environment of the Baltic area. All these activities had the purpose to compile the information on the locations, quantities and types of chemical munitions dumped in the Baltic Sea, and to assess the situation and make recommendations for further action [HELCOM 1993c, Theobald & Rühl 1994, Theobald 2001].

A lot of the field research had focused on tracing and inventorying dump areas, and screening of seabed sediments and water samples. In many cases the measurement sites were more or less picked at random, and screening was often done for merely one, occasionally two, chemical warfare agents, thereby overlooking the fact that the presence of other toxic substances. Laboratory studies, on the other hand, had mainly paid attention to the stability of toxic warfare agents. Still, the marine ecosystem is not comparable with the laboratory environment, and little is still known about the dynamic behaviour of pollutants under actual marine conditions, their environmental impact and possible bioaccumulation in fauna and flora.

During recent years, however, different countries have carried out an increasing number of detailed investigations, including ecotoxicity studies and detailed geophysical and hydrodynamical monitoring. Nevertheless, the information available on the different munition dumpsites up to this very day remains very scattered and incomplete. Large gaps remain in our understanding of these dumpsites, and the reliability of the assessment is often not sufficient. According to Theobald (2001), the main recommendations for further research include (1) examination of known and suspected dumping areas using state appropriate techniques, (2) examination of the condition of the munitions, (3) chemical and biological investigations in the dumping areas, (4) investigations into the ecotoxicology of slowly degradable warfare agents, and (5) investigations into how the warfare agents are degraded.

The planned construction of North European gas pipeline (North Stream project) in the Baltic Sea heightened the community interest to sea-dumped chemical weapons: will the new project increase risks to the marine environment and hence to the population of Baltic States or the situation will not sufficiently change?

In this presentation grounded on the position of FP6 research and development project “Modeling of ecological risks related to sea-dumped chemical weapons” (INCO-CT2005-013408 MERCW) the available initial and recently acquired data will be summarized for better awareness of the community which plays an important role since it will reduce uncertainties and doubts on the status of marine dump sites, avoid over-reactions (having possible effects on the social-economical situation), and spur the political response.

2. Dump sites in the Baltic Sea

In figure 1 there are shown all known (1-5) and not verified (6) dump sites of captured CW. The dump site 5, contained 5,000 t of tabun and phosgene bombs and shells, is clear after successful recovery operations made by Germany. Dumpsites 3 and 4 are located far from the North Stream project area. The reality dump site 6 is doubtful, because here could be only vessels loaded with CW, which could be easily found in shallow sea. Actual for our objectives now are dump sites 1 and 2. Tables 1 and 2 present types and quantities of munitions and warfare agents for these two areas. Besides the declared 32,000 t of CW, dumped to east from Bornholm under the Soviet supervision, some witnesses reported about the additional 8,000 t of CW dumped here by British supervision, and respectively small amount of residual CW dumped by GDR. The declared boundaries of this dump site are shown in figure 1 by scaled polygon (1).

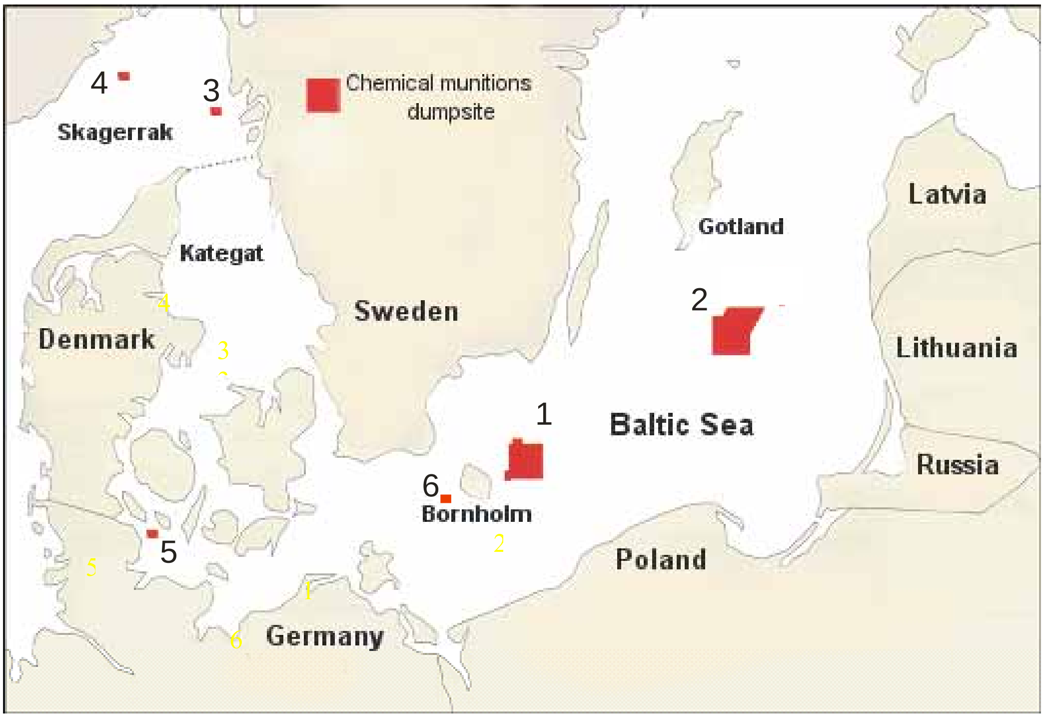


Figure 1. Location of the chemical munition dumpsites in the Baltic Sea and Skagerrak.

(1)East Bornholm dumpsite	*(4) Arendal Dumpsite*
(2) Gotland dumpsite	*(5) Little Belt dumpsite*
(3) Måseskär dumpsite	*(6) SW Bornholm dumpsite (not verified)*

The smaller CW content in the Gotland dump site was scattered within much wider area, its boundaries were also showed in figure 1 by scaled polygon (2).

Table 1. Quantities of chemical munitions (CMs) and types and quantities of chemical warfare agents (WAs), [t], dumped in the Bornholm dump site [HELCOM. 1996b]

WAs→ ↓CMs	Mustard gas	As-cont.	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

Table 2. Quantities of chemical munitions (CMs) and types and quantities of chemical warfare agents (WAs) dumped in the Gotland dump site [HELCOM. 1996b]

WAs→ ↓CWs	Mustard gas	As-cont.	Adamsite	CAP	Others	Total
Aircraft bombs	512	78	51	41	-	682
Artillery shells	58	-	5	3	-	66
High-explosive bombs	27	-	-	-	-	27
Mines	4	-	-	-	-	4
Encasements	7	18	60	-	6	91
Smoke grenades	-	-	6	-	-	6
Containers	-	80	-	-	-	80
Drums	-	-	2	-	-	2
Total	608	176	124	44	6	958

3. Properties of warfare agents

The necessary appropriate information is presented in Appendix. The analysis was made by Dr. Tine Missiaen, the member of MERCW project, representative of Renard Centre of marine geology of University of Gent, Belgium.

Actual conclusions derived from properties of CM and WA

3.1. According to Tables 1,2, thin-wall containers (bombs *et al.*) were used for encapsulating of 80% of all types of WA, so, after a 60 years residence time in seawater, release of WA from corroded munitions as well as destruction of WA due to hydrolysis should began. WA with high

rate of hydrolysis - Tabun, Phosgene, Lewisite, Clark II - should be fully destructed, and only arsenic containing remainders pose some threat to environment. WA with low hydrolysis rate also got contacts with seawater, and consequences of these basin-scale events should be the main task of present and future investigations.
3.2. Mechanical disturbances of both released and encapsulated WA with low rate of hydrolysis do not lead to significant acute influence to the environment, because the radius of toxic action for such WA is small enough [MEDEA, 1997]; having a density higher than that of seawater, the re-suspended toxicants will settle down and sink into muds. Most dangerous can be direct human contacts with CM and lumps containing active toxicants, but this can occur only if munitions will be recovered.
3.3. Risks related to mutagenic and carcinogenic will increase proportionally to increasing of contacting of WA with marine habitants. To estimate the treat, one should take into account that dump sites are located at great distances from the rout of the pipeline, so the probability of crossing of large amount of WA is low. Anyway, any contacts with CW should avoid. To minimize risks, designers must assimilate the present knowledge of distribution of CW in the Baltic Sea and hold the necessary equipment for search of potentially dangerous objects located on the bottom or beneath its surface.

The next paragraph describes main results of researches of Baltic dump sites and following conclusions.

4. Dump site research in the Bornholm Basin

Over the past years a number of different investigations were carried out in the dumping site area east of Bornholm.

4.1. German hydrographic investigations (1987)

In 1987 the German Hydrographic Institute investigated the seawater in the dumping site area east of Bornholm, including near-bottom water. Results showed that the arsenic content does not exceed 1 µg/l (0,001 ppm). Concentrations of CW agents in the dumping area were not higher than elsewhere [Helcom 1993c].

4.2. Danish sediment sampling investigations (1992)

In 1992 sediment sampling and video recordings were carried out east of Bornholm by the Danish authorities. Two samples close to one another were taken from the middle of the dumping area. Mustard gas was found in one sample and the by-product 1,4-dithiane in both samples. In addition, increased arsenic concentrations were observed (Helcom 1993e). The samples were also analyzed for Arsenic, and an increased content was found (185 and 210 mg/kg) compared to samples taken from other parts of the Baltic Sea. No other traces of chemical warfare agents or chemical compounds related to such agents were found in the sediment samples [Helcom 1993e].

4.3. German sediment sampling investigations (1992)

In 1992 18 sediment samples were collected by the German authorities at 6 different positions, 5 of them in the Bornholm dumping area. The Norddeutscher Rundfunk had the sediment samples analysed. In one sample a concentration of 10 ppm was found; nothing was found in the other samples. No increased arsenic concentrations were observed [Helcom 1993c].

4.4. Russian geophysical/hydrographical/sedimentological investigations (1997-2006)

Between 1997 and 2006, a number of monitoring cruises were undertaken in the dumpsite area east of Bornholm in the framework of the Russian Federal Programme “World Ocean”. Instrumentation used included a.o. water and sediment samplers, sidescan sonar, magnetometer, multibeam, current meters, current profiler, and microstructure probe; in addition ROV's were used for inspection of sunken vessels [Paka & Spridonov 2001, Paka 2004]. Chemical analysis mainly concentrated on arsenic, phosphorus, and major products of hydrolysis able to change the seawater chemistry.

Arsenic data

The As levels measured at the Bornholm dumpsite are characterised by high dispersion and sharp anomalies reaching up to 300 mg/kg; minimum and typical background As levels are resp. 18 and 25 mg/kg [Paka & Spridonov, 2001]. These values differ from those presented in other reports [Helcom 1993c; Helcom 1994]. Experts have previously proposed a value of 100 mg/kg as a typical background for As contents in the Baltic [Emelyanov 1998]. Consideration must be given to the fact that there are natural mechanisms of accumulation of As from its uniform background distribution due to processes typical for redox or sorption barrier zones (Emelyanov 1998). Still there is good reason to believe that the highest observed contents of As are related to a localized source, especially if it is accompanied by low Fe and Mn values. However, samples containing large amounts of Fe and Mn also show signs of deflection from the pattern typical for natural accumulation [Paka & Spridonov 2001, Paka 2004].

Figures 2 and 3 demonstrate present results of investigations of *As* distribution in the Baltic Sea and Skagerrak. Comparison of maximum *As* content in the CW dump sites and regions with different sedimentation processes leads to conclusion that the arsenic pollution of dump sites is overestimated: it is far below some natural maximums.

pH values

Only the 1997 field data showed anomalies of pH values presumably linked with dumped CW [Emelyanov et al. 2000]. At the Bornholm dumpsite, abnormally low pH values (6.36 - 6.78) were also detected at two sampling points [Paka & Spridonov 2001].

Phosphorus data

In a few sampling points within the Bornholm dumpsite the total phosphorus (P_{tot}) and organic phosphorus (P_{org}) concentrations in the near-bottom water were 2 to 5 times higher than the background values. Maximum measured phosphorus concentrations exceeded 10 µg-at/l, where the detecting threshold was 0.1 µg-at/l. Natural increase of P_{tot} concentration with depth is generally connected with an oxidation of organic suspended matter. This oxidation moves the phosphorus into the dissolved form, where the P_{org} concentration sharply decreases by sinking from the photosynthesis layer down to the bottom and an inorganic phosphorus (P_{in}), as the final oxidation product, increases and finally dominates. Thus an increase of P over P_{in} in the near-bottom water could be explained by the presence of an additional source of P_{org} (e.g. phosphorus containing gases) [Paka & Spridonov 2001, Paka 2004].

Microbiological data

Samples of upper sediment and near-bottom and porous water were subjected to microbiological studies for the presence of organisms being tolerant to mustard and its decay products, as well as for organisms capable of destruction of mustard and products of its hydrolysis.

Searching of shipwrecks

Magnetic gradiometry surveys were carried out in 1999-2000 using a proton gradiometer. Two magnetic anomalies were observed with sources located at a depth of 90-100 m, indicating objects on the sea floor or buried by sediments. In 2001 The rented r/v “Doctor Lubecki” confirmed by the multibeam echosounder and ROV that these anomalies were related to two shipwrecks, and discovered one more wreck; an artillery shell an a bomb were found on decks. Chemical analyses did not indicate any increasing of As concentration in sediments in vicinity of these wrecks, but similar “calming” results followed from investigations of sunken vessels loaded with CW in the Arendal dump site [Tørnes, et al. 2002.]

4.5. Recent researches

In 2006 there were two cruises in the Bornholm dumping area:

1) r/v Professor Stokman cruise was organized by Shirshov institute of oceanology in collaboration with EMERCOM of Russia in May-June 2006 (fig.4); the task was to continue the monitoring of “hot spots” within the Bornholm dump site and to make a search of shipwrecks in the Bornholm segment of the planned North Stream route. In addition to 3 previously discovered

wrecks, the 4th wreck was found in the "hot spot" area, and two more wrecks (one is a vessel and another one is a boat) - were found in North Stream area at 30 n.m. from the Bornholm dumpsite.

Figure 2. Investigations of *As* in sediments (mg/kg).
Black figures – typical background content, red figures – scatter in dumpsites. [Garnaga and Stankevičius, 2005]

A lump of *chloracetophenon (CAP)* was taken by bottom grabber in the "hot spot" area. The toxic sample was rapidly encapsulated for careful study in stationary conditions. Other samples taken in 19 points did not change the present concept on the dump site contamination: the background concentration of *As* remains a little bit increased with respect to similar reference areas, but of the same or even weaker level with respect to regions with different geological conditions, where *As* could be supplied and absorbed by natural mechanisms, for instance, in regions reach with iron sulfides and Fe-Mn corks and concretions. Samples taken nearby the *chloracetophenon* finding showed nothing distinguished; this confirms the conclusion that the polluted area nearby the lumps with active WA is localized.

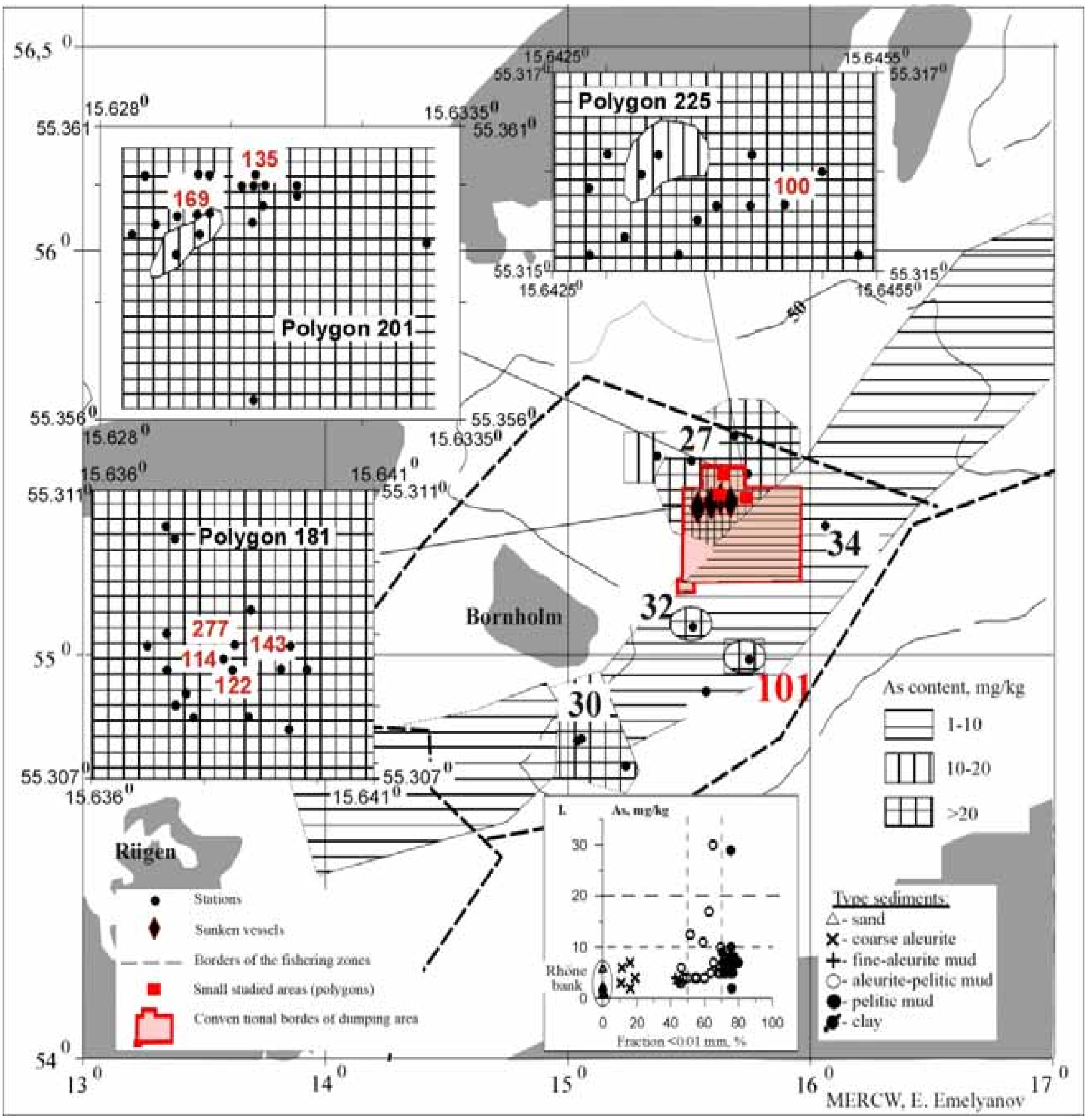


Fig.3 Distribution of As in the surficial (0-5 cm) bottom sediments of the Bornholm Basin. Big red numbers the maximal content of As in the area. Polygons 181, 201 and 225 are regions of dense grid sampling. Rombuses mark wrecks. The graph shows the As content in the different sediment types versus pelitic (<0.01 mm) fraction, the samples with the As >100 mg/kg not shown.

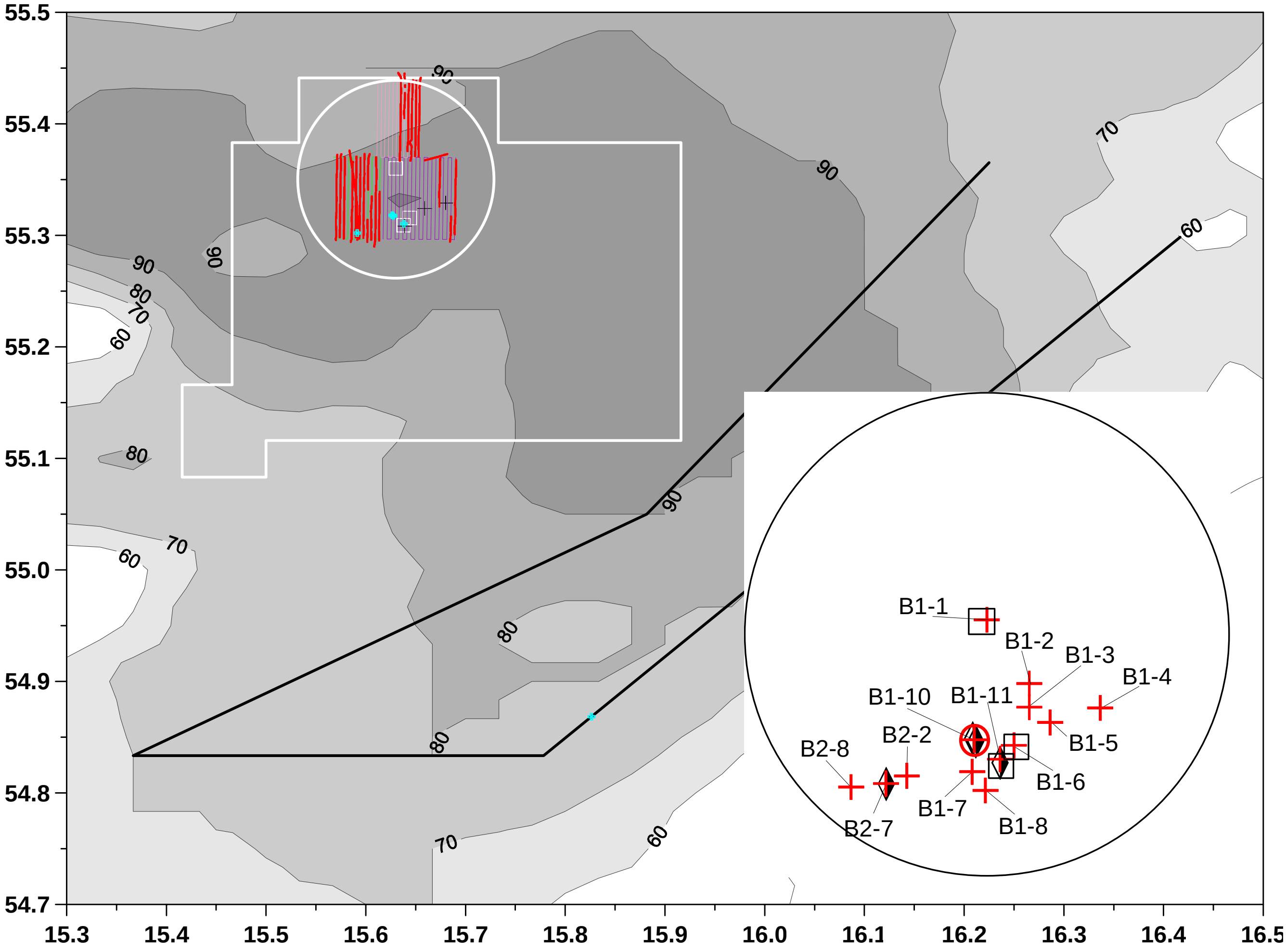


Figure 4. Research area of the "Shtokman" cruise in May-June 2006. Grid lines correspond to Side-scan and acoustical nearbottom current profiler surveying, a zoomed circle shows the respective position of shipwrecks (diamonds), "hot spots" (squares), and sampling points accompanied with high resolution hydrographic measurements (crosses). C*hloracetophenon* was found in point B1-1.

2) r/v Shelf cruise (fig.5) was organized by Shirshov institute of oceanology under frames of MERCW project in the "hot spot" area focused on development of seismic investigations of bottom sediments storing the scattered CW, as well as searching the buried CW and new shipwrecks as potentially dangerous objects. Results of high resolution seismic profiling give confidence to real perspective to find meters-size buried bodies. Figures 6, 7 demonstrate some typical seismic profiles. It is clear now that buried bodies will be found if the surveying grid will be dense enough. This task was postponed to the next cruise, which should operate with proper magnetic and seismic instruments.

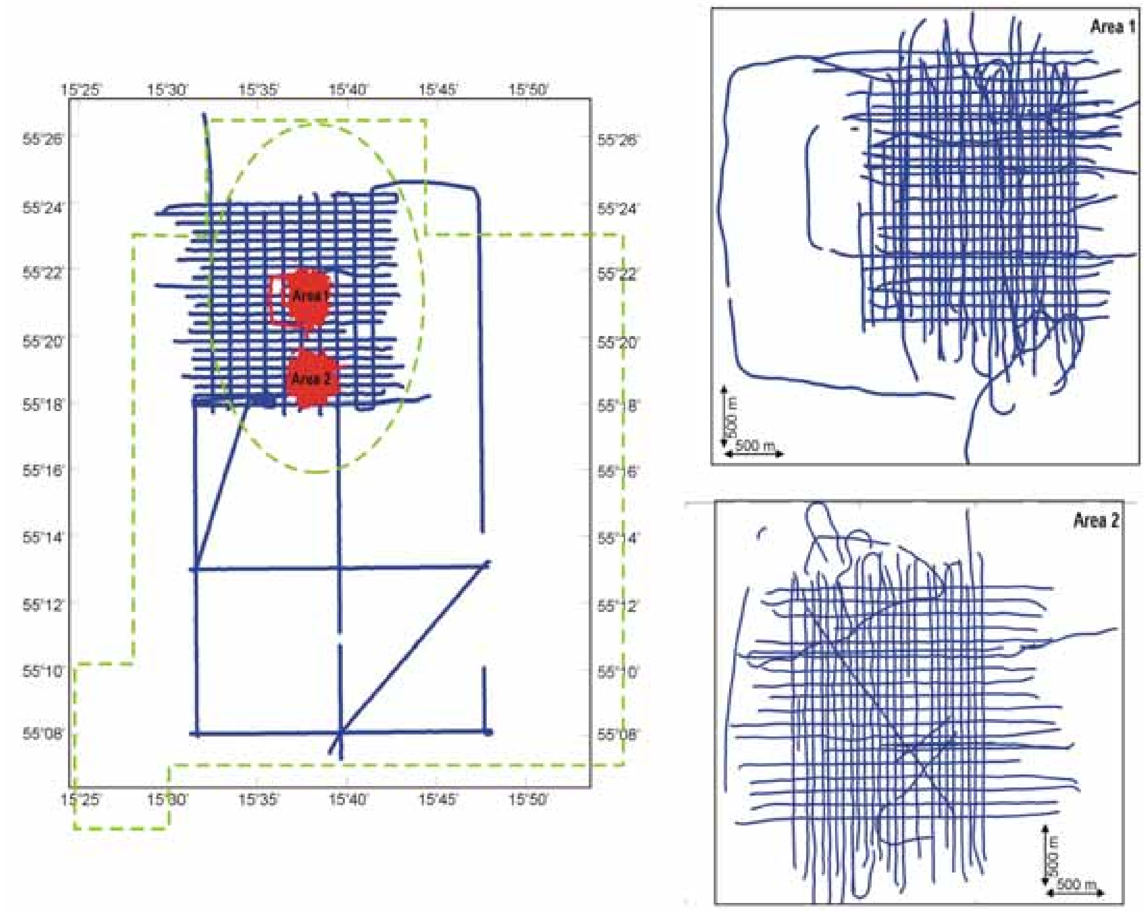
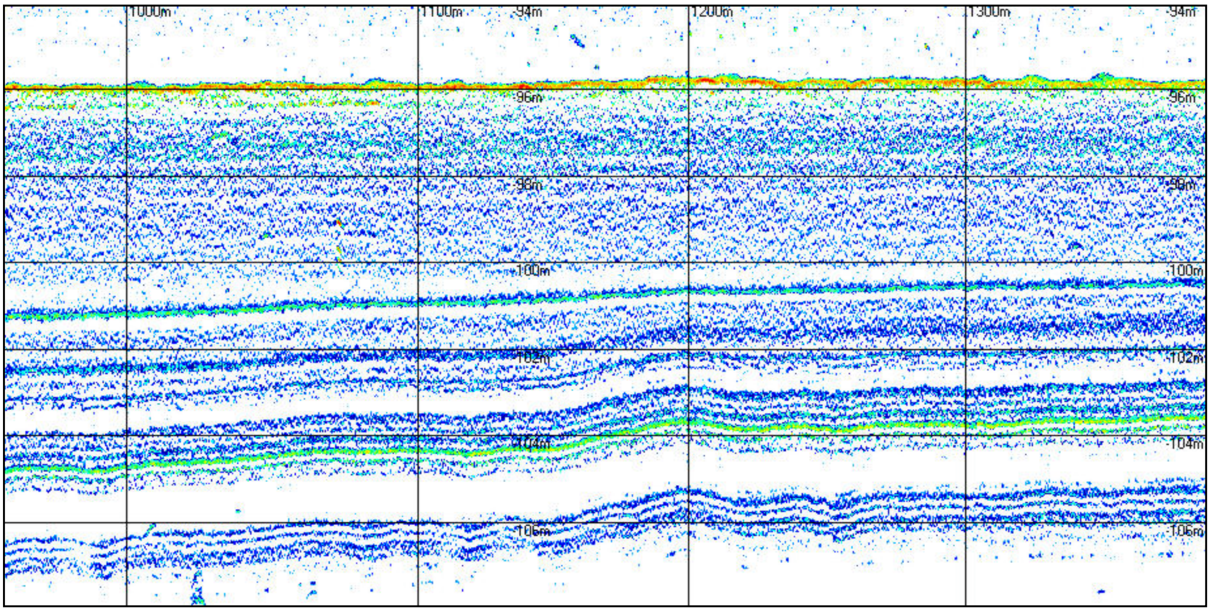


Fig. 5. Research area of "Shelf" cruise in July 2006. The polygon drawn by green dashed line corresponds to that drawn by white line in the figure 4. Three seismic networks recorded in the Bornholm Basin are presented. Blue: large-scale 2D network. Red: small-scale pseudo 3D networks. Right: Close-ups of the two small-scale pseudo 3D networks (Area 1 & Area 2).



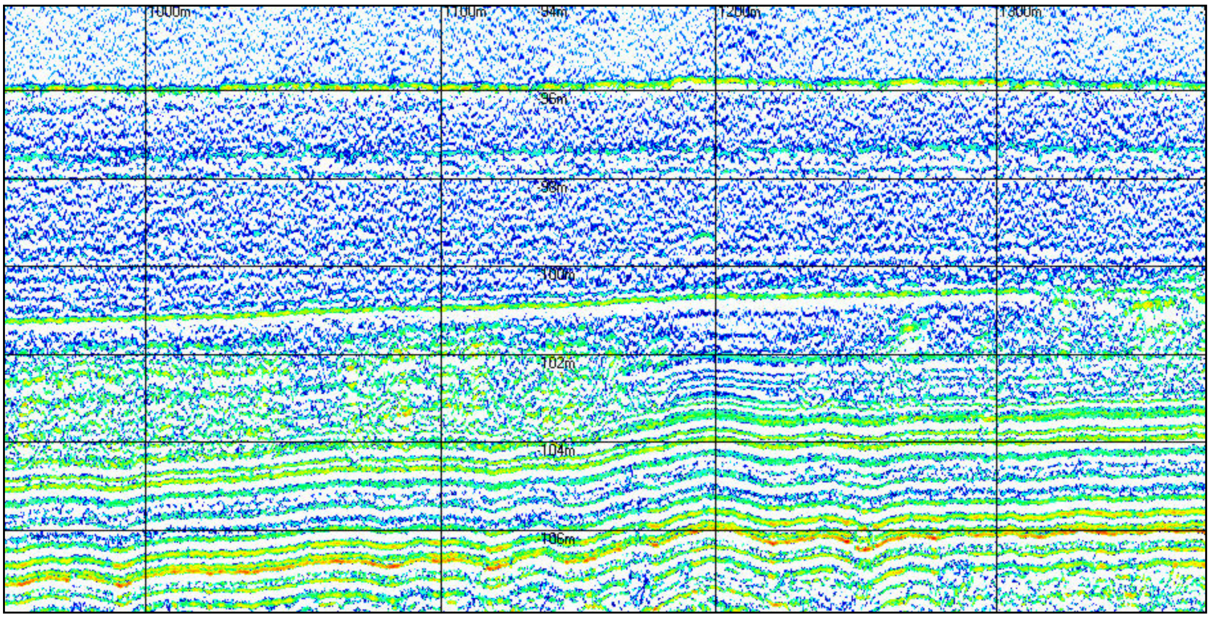


Figure 6. Typical parametric echosounder profiles (Area 1). Top: high frequency signal (100 kHz). Bottom: low frequency signal (10 kHz). Remark the deep penetration of the HF data. Vertical interval 2m. Horizontal spacing 100 m.

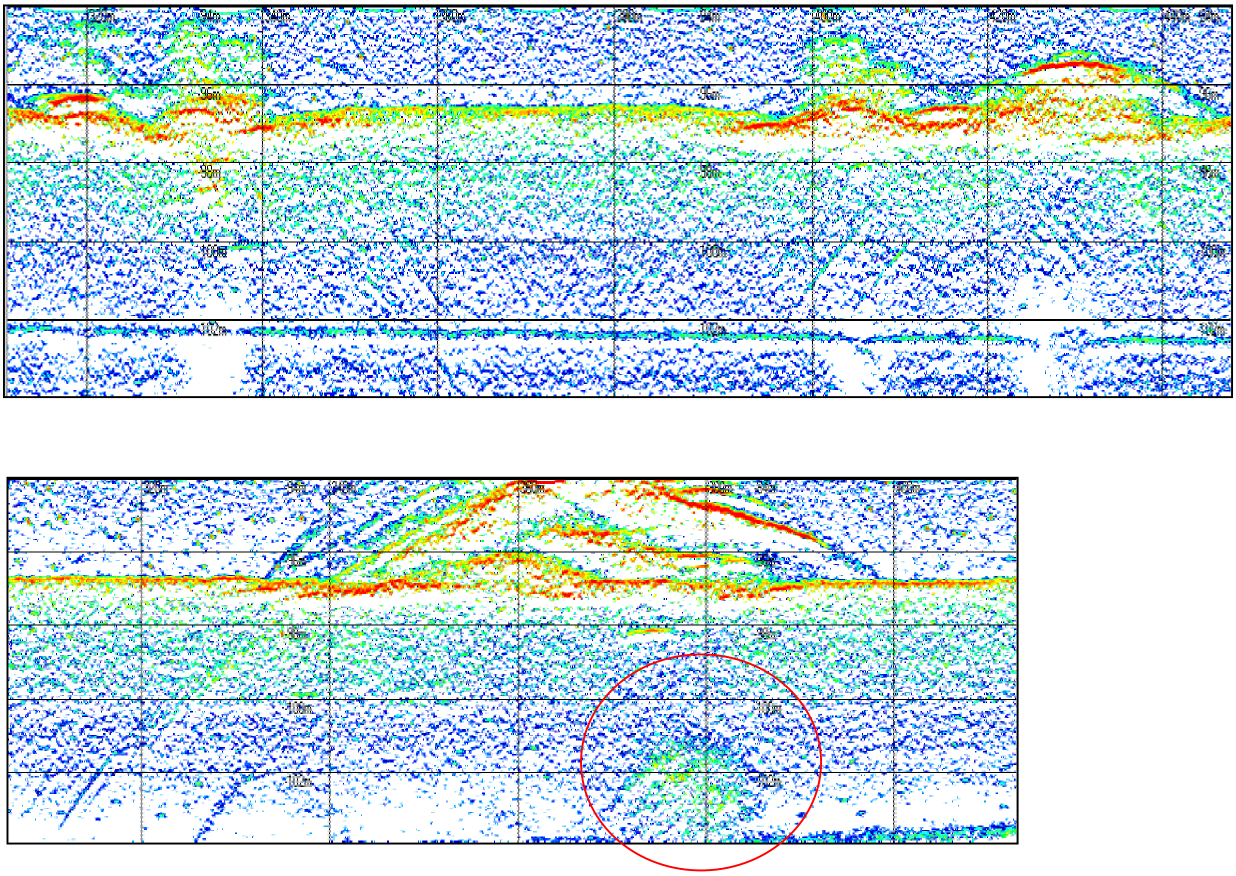


Figure 7. Top panel: HF echosounder profile across wreck 1 (left) and wreck 2 (right). Remark that both wrecks consist of several parts. Vertical interval 2m. Horizontal spacing 20 m. Bottom panel: HF echosounder profile across wreck 3. Remark a buried mass 5 m below the botton surface.Vertical interval 2m. Horizontal spacing 20 m.

5. Dump site research in the Gotland Basin

The only confirmation of the presence of sunken CW in the Gotland dump site was a warfare caught by fishery trawls [HELCOM 1993f]. Environmental researches discovered very weak manifestations of probable destruction products [Garnaga and Stankevičius, 2005] and microbial changes [Paka and Spridonov, 2001].

6. Treats and Incidents [HELCOM. 1996b]

6.1 Based on present knowledge, a widespread risk to the marine environment from dissolved warfare agents can be ruled out. Elevated levels of sparingly soluble Clark, Adamsite or viscous mustard gas may, however, occur in the sediment in the immediate vicinity of dumped munitions. Because of the very limited extent of the agents, however, no threat is posed to marine flora and fauna according to current information. No harmful effects on the marine environment due to warfare agents have so far been observed. According to the existing knowledge, no content of mustard gas or other chemical warfare agents have been found in edible fish or other types of seafood. Given the present knowledge, the chemical warfare agents do not constitute a problem in terms of food toxicology.

6.2 Insufficient ecotoxicological data is available for most of the chemical warfare agents. Further investigations should be carried out with a special emphasis on mustard gas, chlorinated additives and arsenic compounds.

6.3 Spreading of dumped chemical warfare material is to some degree caused by fishermen re-dumping chemical warfare equipment which had been caught in fishing nets, possibly a long way from the position where it was dumped originally.

6.4 The dumping areas are pronounced as foul with an "anchoring and fishing not recommended" on nautical charts. However, since fishing in these areas is not prohibited, commercial fishing can occur.
6.5 It is generally accepted that since Denmark compensates its fishermen if they destroy contaminated catches, fairly reliable Danish statistics exist about reported finds of warfare agents. Fishermen from other nations bordering the Helsinki Convention Area are not obliged to notify the authorities of such findings. Accordingly, only incomplete figures exist on warfare agent finds by fishermen from other countries. Information has been provided by Germany, Latvia, Lithuania, Poland and Sweden.
Denmark data: number of "catches" from 1985 to 1992: 342; mass of CW, kg: 17,072; landed CW, kg: 1,917.
Germany has reported 13 incidents in which crews were injured, all incidents occurred east of Bornholm.
Sweden has reported 4 incidents with mustard gas from Bornholm area and 4 incidents south-east of Gotland since 1980.
Latvia and Lithuania have reported fishermen's contacts from the 1950s to the 1970s, and in some cases later (1986), within the dumping area south-east of Gotland.
In the Polish exclusive economic zone, there have been 16 identified findings of outdated ammunition and weapons. Chemical munitions have occurred on the route which the ships used to the dumping area south-east of Gotland.

Comments to HELCOM statements and conclusions

1) All the reported incidents were located in or nearby the declared dump sites. However fishing is not limited by these areas. So, the probability of presence of CW out of these areas is low.
2) Fishing trawls causes permanent disturbance upon the upper sediment layer. Ecologists protest against this barbarous influence on the benthic biota, but without success, even for dump sites. Hydroengineering projects (cable- and pipeline construction) act summarily much shorter and disturb much smaller areas than the fishery. Hydroengineering projects are easily subjected to national and international supervision, including realizing of special safety measures related to sea-dumped CW. Nobody reported that the earlier performed projects [Andrulewicz et al., 2003] caused a sizeable treat to the ecosystem and human health. Thus, no objective arguments exist against realizing of hydroengineering projects, which economical meaning is comparable with that of marine fishery.
3) Hydroengineering projects as well as any other economic activity do not improve the state of marine ecosystem. Nevertheless, such activity provides money for researches, which are necessary for understanding of all ecological problems and performing the necessary measures for decreasing of ecological risks in proper priority.

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