

Environmental Hazards of Sea-Dumped Chemical Weapons

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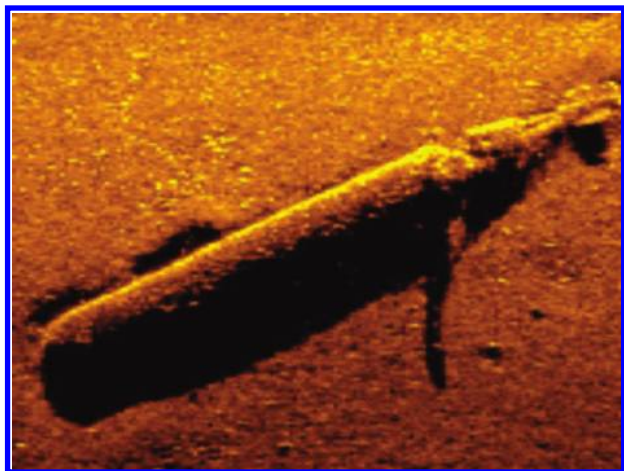
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Does the post-WWII burial at sea of chemical weapons still pose a human and environmental risk?

Brewer and Nakayama (2008) (1) pleaded for complete information concerning the whereabouts of thousands of tonnes of chemical weapons disposed in the ocean starting in 1946. Currently, however, there appears to be the inverted policy of “don’t ask, don’t tell” on this issue. Scientists have not asked for the information about the dumping and the responsible agencies feel no pressure to provide the information. Together with the distasteful nature of the subject matter this has led to a lack of awareness of the issue (1).



NOAA

Chemical warfare agents (CWA) represent environmental legacy contaminants as production and subsequent dumping of CWA typically occurred decades ago. Despite being legacy contaminants it is not only the location and amounts of ocean dumped CWA that is unknown due to their status as illicit compounds, but their inherent properties with regard to physicochemical, fate, long-term human and environmental toxicity properties have not been characterized comprehensively (2). CWA dissipation has been described under laboratory conditions (3, 4), but little is known about the dissipation of CWA at deep sea (>100 m). In lieu of reliable measured property data, these may be modeled, e.g., by using (Q)SAR ([Quantitative] Structure–Activity Relationship) and by default approaches from the European Technical Guidance Document (TGD) (2).

After World War II (WWII) approximately 32,000 t of chemical weapons, containing about 11,000 t of highly toxic agents, were dumped in the Bornholm Basin, east of the island of Bornholm in the southern Baltic Sea (Figure 1) (5). The main chemical agents dumped were blistering agents mustard gas and arsenic-containing compounds Clark I and adamsite. The safe oral dose (reference dose (RfD)) for humans of yperite (sulfur mustard gas) is as low as 0.000007 mg/kg body weight/day. Longer term effects of organoarsenic CWA have been investigated to a lesser degree; therefore inorganic arsenic (As) is often used as a surrogate, with an oral RfD of 0.0003 mg/kg BW/d. Inorganic As is both mutagenic and carcinogenic. The nerve gases are generally expected to be less chronically toxic toward mammals, with RfDs around 0.002 mg/kg BW/d, but significantly more acutely toxic.

Additionally, some 200–300 t of chemical weapons were dumped on the orders of the East German Authorities between 1952 and 1965 (6, 7). The primary dumpsite area is marked by a circle with a radius of 3 nautical miles (3 nmi) with water depths ranging from 70 to >96 m, but it is likely that the chemical munitions were spread over a larger area during dumping (8). The extended dumpsite is marked by a rectangular area roughly ranging between 55°07'N–55°26'N and 15°25'E–15°55'E (Figure 1).

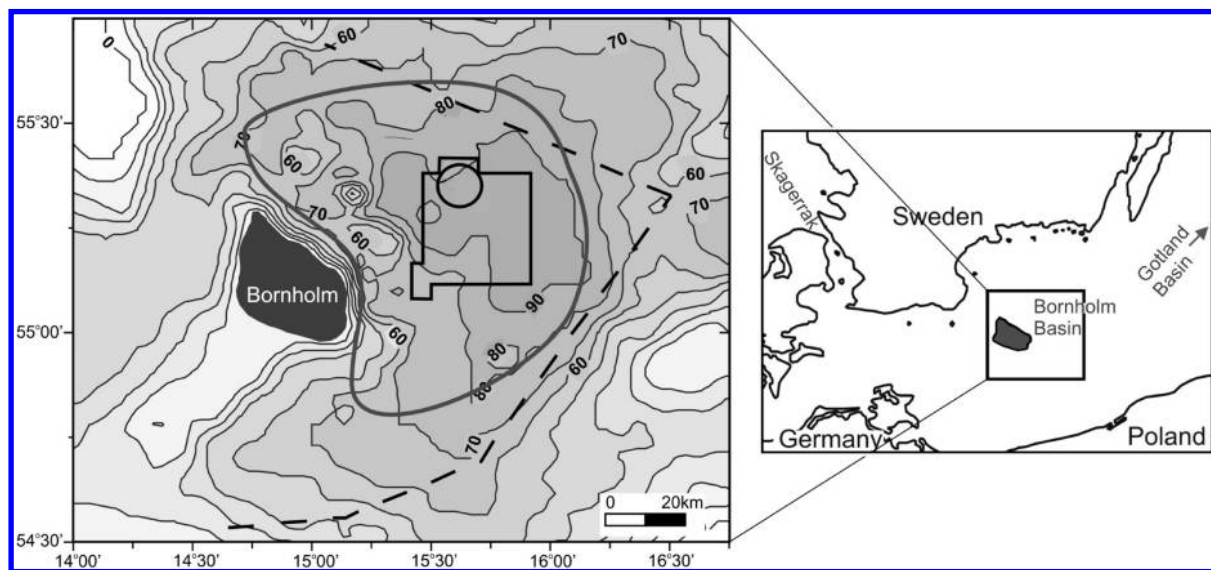


FIGURE 1. Overview map showing the location of the chemical munition dumpsite in the Bornholm Basin. The black circle marks the primary dumpsite area. The black rectangle marks the larger secondary dumpsite boundary. The thick gray line marks the zone where fishing incidents related to chemical weapons have been reported (modified after (9)).

Modeling of Ecological Risks Related to Sea-Dumped Chemical Weapons (MERCW)

There are a number of reasons for the decades of delay in addressing this problem in the U.S., the EU, and elsewhere. Many dumping operations were carried out secretly and it is not always clear who can be held responsible. Moreover, at the time there were no international conventions that prohibited dumping, hence assigning legal liability and responsibility is questionable. The governmental bodies of both the states that carried out the operations and those bordering the dumping areas were reluctant to tackle this sensitive problem. Further, there is a lack of official records of the dumping operations, which often took place under chaotic circumstances right after WWII (1). In 1992 the European Parliament decided that CWA levels and potential risks in the Baltic Sea should be investigated. It was recognized that the problem posed by sea-dumped chemical weapons deserves considerable international attention; the amount dumped in the North European seas alone since the end of WWI runs into hundreds of thousand of tonnes (10, 11). The toxic war material, often dumped in relatively shallow waters in Europe and areas of active fishing, not only represents a serious potential threat to the marine environment but also to the often densely populated coastlines (5, 12–14). In 2005 the European Commission awarded the Sixth Framework Programme project: Modeling of Ecological Risks Related to Sea-dumped Chemical Weapons (Contract 013408) (MERCW) to a consortium consisting of two Finnish research institutions (VERIFIN and SYKE/FIMR); three Russian organizations (RPA TYPHOON, Shirshov Institute of Oceanology, and SRCES); a research institution in Belgium (University of Ghent) and a Belgian company (G-Tec); University of Bonn (Germany); and Aarhus University (Denmark). The project focused on the Bornholm Deep in the Baltic Sea, as this was the site that received the largest amounts of CWA after WWII.

MERCW Study Summary and Results

Due to the complexity and size of the marine risk assessment of CWA in the Bornholm deep, the study design of the MERCW project is centered around a drivers pressure state impact response (DPSIR) weight-of-evidence (WoE) approach, with an emphasis on the PSI parameters (15).

The principle risk-related lines of evidence covered are as follows (letters in parentheses are different DPSIR parameters):

- (1) Desk-based model risk screening of CWA in relation to the fish community; food-web modeling propagation of CWA; and indirect human health risk screening (I).
- (2) Geological and hydrographical survey to detect potential worst-case dumping locations to guide sampling (S).
- (3) Sampling at identified hotspots for chemical analysis of traces of CWA and dissipation products in sediment, porewater, and near-bottom water (S).
- (4) Identification of yperite-tolerant microbes and microbial community impacts (S–I).
- (5) Interviews with local experts (local authorities, fishermen, navy) regarding their assessment of the CWA exposure and effects (S–I).

The MERCW project also contained modeling of dispersion and visualization of CWA propagation in the Baltic Sea as well as other aspects not directly covered in the following, for further details please visit the project Web site (16). This is to our knowledge the first large-scale ecosystem risk assessment of sea-dumped CWA.

1. Screening Level Fish Community Risk Assessment.

The desk-based assessment is founded on worst-case assumptions and will not give a definite evaluation of risk but rather serve as an indication, which can support a more in-depth investigation. The screening provides estimates of the predicted water and sediment concentrations of dumped CWAs in the Bornholm basin, as well as the calculated fate and transport of the CWAs from the dumpsite. The exposure concentrations are compared to calculated CWA fish no observed effect concentrations (NOECs). The NOECs were based on measured or modeled effect concentrations, which were extrapolated to the relevant fish community using ICE web (17). The ratio between the exposure concentration and NOEC is expressed as toxic units (TU). Risk is present when $TU > 1$. Eight active CWAs and one additive compound have been reported dumped in the Bornholm basin (Table 1); additivity is assumed to generate a total CWA mixture TU (18).

The following CWA-specific parameters are used to assess the risk: dumped amounts, degradation half-lives, sorption

TABLE 1. Confirmed Dumped Chemical Warfare Agents East of Bornholm (2, 5, 16)

compound	dumped (tons)	Log K_{ow}	water sol. (mg/L)	vapor pressure (mm HG)	molecular weight
chloroacetophenone (CAP) ^a	515	1.93	1635	0.0436	154.60
sulfur mustard gas (yperite) ^b	7027	2.41	605	0.217	159.07
adamsite ^c	1428	4.05	0.4	2×10^{-13}	277.59
Clark I ^d	711.5	4.52	3	1.8×10^{-4}	264.59
triphenylarsine ^d	101.5	5.97	0.089	4.96×10^{-5}	306.24
phenyldichloroarsine ^d	1017	3.06	639	0.113	222.93
trichloroarsine ^d	101.5	1.61	2291	9.91	181.28
Zyklon B ^e	74	-0.69	95,000	308	27.03
monochlorobenzene ^f	1405	2.64	400	6.46	112.56

^a Riot control agent. ^b Blistering agent. ^c Organoarsenic blistering agent. ^d Arsine oil constituents - organoarsenic blistering agent. ^e Blood agent. ^f Additive.

coefficients, molecular diffusivities, and NOECs. Site-specific parameters are area of dumpsite, current and vertical depth of bottom layer, total water depth, sediment accumulation rate, porosity, and organic carbon content in sediment (19). We assume turbulent mixing of bulk water, advective transport of CWAs, and continuous release of CWAs from buried shell in the sediment to bottom boundary layer water over 60 years. Furthermore, the bulk water is divided into two strata: an upper layer (50–70 m below surface) primarily consisting of brackish water flowing in from the northern and eastern parts of the Baltic Sea toward the North Sea, and a bottom layer (<20 m above sediment surface) originating from the North Sea. It is assumed that all the dumped CWAs are dispersed in both the primary and the secondary dumpsite. In this situation the total mixture TU immediately above the sediment surface, calculated as a sum of TU for all CWAs, is 0.62. Triphenylarsine is the CWA with the highest risk profile at 0.2 TU, followed by adamsite at 0.17, Clark I at 0.086, and yperite at 0.083 TU. This assessment does not include an assessment factor, which is typically in the range 1–5 for assessments based on species sensitivity distributions. Hence, the relative low margin of safety between exposure and effect concentrations would suggest that further assessments are warranted (18).

Temporal 2D Ecopath with Ecosim contaminant tracing (Ecotracer) models with advection fields (20) were employed to describe the potential CWA biomagnification and dispersal within the Baltic Sea food web described by 27 functional groups from primary producers to top predators and trophic flows between them. The potential CWA dispersal was described with a 2D map (11 × 11 km grid size) that takes into account habitat preferences of different species, as well as incorporating surface advection fields. The most important Baltic commercial fish were included: cod (*Gadus morhua*), herring (*Clupea harengus*), and sprat (*Sprattus sprattus*) (21). The contaminant concentration in each functional group as a function of time and space was calculated from direct contaminant uptake from the environment and uptake from food as well as contaminant losses by decay of the contaminant, metabolism, predation, other mortality, and fishery (20). Initially calculated environmental CWA concentrations were introduced into the model (18) and the simulation length was 60 y. The basis for the parametrization of the food-web model lies in the following two simple mass-balance equations (eqs 1 and 2):

$$\text{Production} = \text{predation} + \text{catch} + \text{other mortality} + \text{migration} + \text{biomass accumulation} + \text{standing biomass} \quad (1)$$

$$\text{Consumption} = \text{production} + \text{respiration} + \text{unassimilated food} \quad (2)$$

Lipophilic and persistent adamsite was most likely to biomagnify out of the CWAs studied. Cod was the fish with

highest modeled end concentration of adamsite. The modeled biomagnification (0.613 ppm bioconcentration factor (BCF) 175) and spatial dispersal (up to central Baltic Proper) of adamsite in cod was clearly higher in the case of the total mixing of the water column than in the stratification scenario (2). In the more likely scenario, of limited mixing due to stratification, adamsite concentrations in cod and herring were predicted to be 0.485 mg/kg (BCF 39) and 0.167 mg/kg (BCF 14), respectively, and the spatial dispersal of adamsite was limited to the Southern Baltic Proper. Pelagic-only feeding sprat did not contain any CWA in this scenario. The only other CWAs theoretically to biomagnify in top predator cod were Clark I and triphenylarsine, but the model results did not support this. All maximum concentrations were reached within 2 years after contaminant exposure (22). It was concluded based on EU TGD methods that the indirect human health risk from consuming fish muscle would be negligible (23). See the Supporting Information (SI) for more data.

2. Geophysical Survey of the Location and Characteristics of Objects in Sediment. The initial historical survey provided a framework for the subsequent experimental analysis of a location closer to the dumped munitions, including establishment of hotspots for further chemical investigation. Detailed seismic and magnetic measurements were carried out at the Bornholm dumpsite to obtain information on the precise location and distribution of the dumped weapons (including the burial depth), to obtain information on the sedimentary environment, and to guide sampling at hotspots (24). During the surveys different acoustic sources (boomer, sparker, parametric echosounder) were deployed simultaneously and combined with magnetic measurements. In total three large seismic grids were recorded in the primary dumpsite area in addition to two small and dense seismic-magnetic grids in the dump site (Figure 1). Four shipwrecks (19) were identified in the primary dumpsite area. The wrecks are 20–50 m long and 5–10 m wide with a height above the seafloor of 1–2 m (24). A large number of buried objects were observed in the two seismic-magnetic grids. These objects are interpreted to be indications of CWA. The size of the objects varies between 1 and 5 m (exceptionally up to 10 m). All objects are buried <2 m below the seafloor. The low sedimentation rates in the Bornholm Basin can probably not account for this burial depth so most likely the sediment cover is largely due to the objects sinking into the soft muddy sediments. The difference in object density (460 objects/km² in the northern grid, and 60 objects/km² in the southern part of the dump site) indicates that their distribution is very heterogeneous (Figure 2).

The difference in object density between the two surveyed areas is striking. This may partly be explained by the location. Indeed, grid SM2 is located in the center of the primary dumpsite which was the prime dumping target, whereas grid SM1 is located closer to the boundary of the primary dumpsite. Even so, the results suggest that the distribution

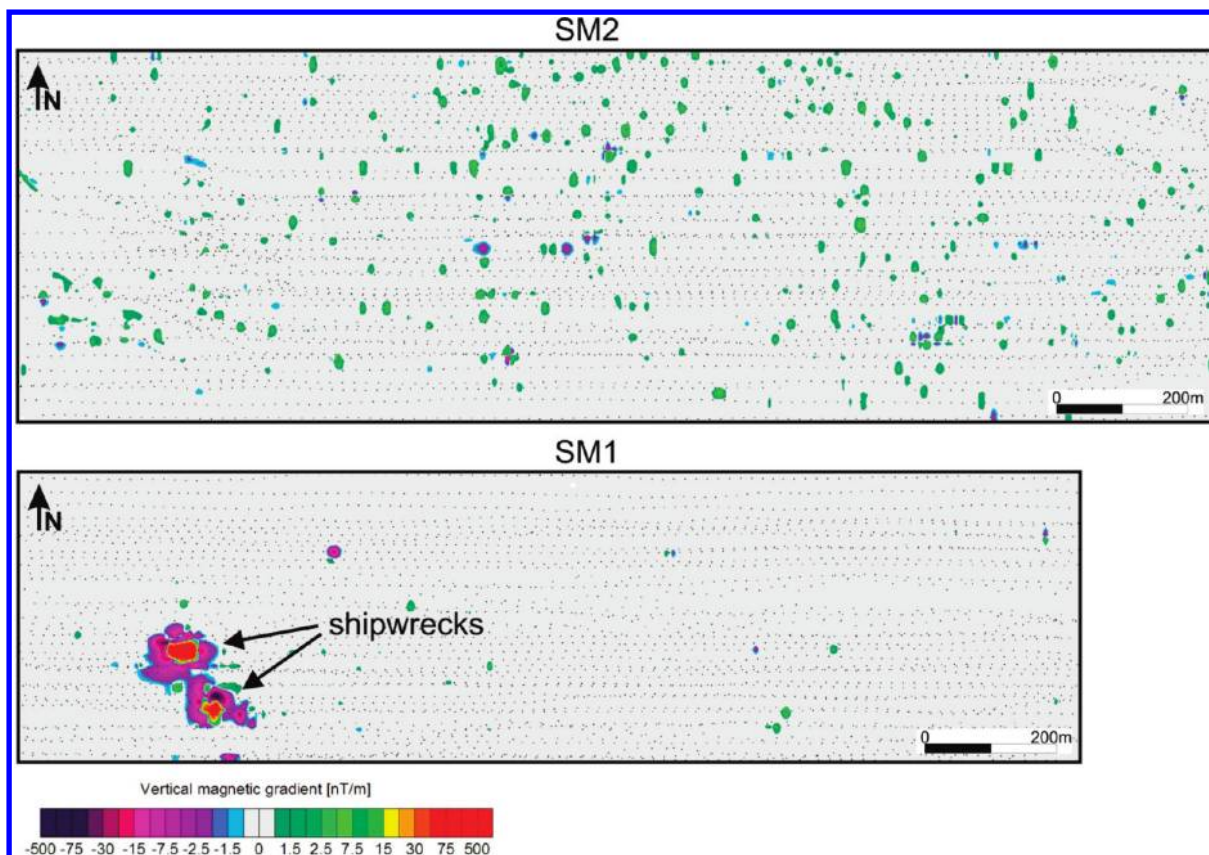


FIGURE 2. Vertical magnetic gradient maps of the two seismic-magnetic grids SM1 and SM2. Green and red indicate positive magnetic anomalies, purple and blue indicate negative anomalies (unit = nT/m). Whereas the northern grid SM2 is marked by the presence of numerous anomalies (over 440), the southern grid SM1 shows only relatively few anomalies (just over 40). The two large anomalies observed in grid SM1 are related to shipwrecks.

of war material in the Bornholm Basin is most likely very heterogeneous, with locally high object concentrations. The total amount of war material dumped in the Bornholm Basin amounts to over 560,000 objects, mainly involving artillery shells and aircraft bombs. If we assume that 50% of the dumped war material is located within the primary dumpsite area (a conservative estimate), we obtain a mean object density of roughly 3000 objects/km². This is almost four times higher than the highest object density measured in the seismic-magnetic grids. This suggests that a large number of objects, most likely shells and mines, were probably not detected while these objects make up a substantial part of the dumped material. The latter is probably a result of their small size (average length 30–40 cm) and mass (magnetizable mass ~10 kg) as compared to the track-line spacing (10 m). Furthermore, an advanced state of corrosion likely reduces the detectability of the objects (24).

3. Sampling and Chemical Analysis of Water and Sediment. The sampling for chemical analysis of CWAs was conducted to cover as much as possible of the primary dumpsite near the wrecks, and in the secondary dumpsite (Figure 3). In addition to sampling points within the dumpsites, five transects reaching 30 km from the primary dumpsite were defined.

The transects (TR 1–7) all started from the southern part of the primary dumpsite and sampling was made with approximate intervals of 50 m, 100 m, 500 m, 1 km, 5 km, 10 km, 20 km, and 30 km. The samples were taken with a Niemistö bottom corer. This was performed over 6 days at 63 sampling points during February 2008. Fifty-nine sediment samples and 61 near-bottom water samples (<0.2 m above the seafloor) from 63 sampling points were collected. The samples were frozen and shipped to VERIFIN in Helsinki,

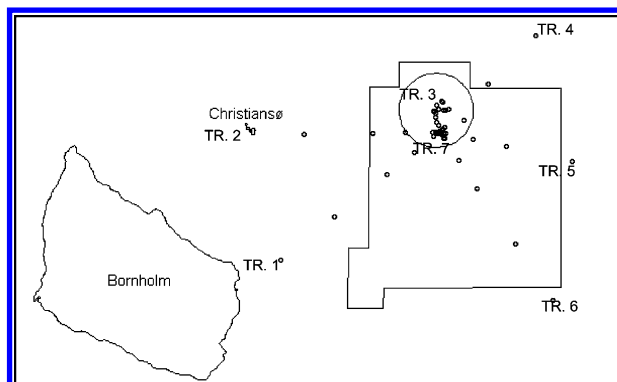


FIGURE 3. Sampling points.

Finland, for chemical analysis of traces of CWA and their major degradation products.

Sediment and near-bottom water samples at the Bornholm dumpsite were analyzed for the presence of CWAs and their primary degradation and oxidation products, using the recommended operating procedures for aqueous and soil samples (25). The selected target CWA included sulfur mustard (yperite), Clark I, adamsite, α -chloroacetophenone, and As oil constituents. The analysis of the samples was carried out using gas chromatography–mass spectrometry (GC–MS) and liquid chromatography–tandem mass spectrometry (LC–MS/MS).

No intact CWA was found, except one stable component in As oil, triphenylarsine, in the sediment. Several degradation products of yperite, Clark I, adamsite, and As oil components were detected in the 56 sediment samples. In many samples,

some degradation products were not present above the lowest concentration limit, but most samples contained at least one degradation product that was quantifiable. The highest detected amounts of the measured CWA-related chemicals in the sediment were between 0.7 and 81 250 µg/kg depending upon the proximity to the hotspots as identified in the geophysical survey (Figure 2). An oxidation product of adamsite detected in the sediment was 20 km away from the hotspot in the primary dump site along the transect 2 (TR 2) at 1.2 µg/kg (dw) toward the island Christiansø. Only four porewater portions of the sediment samples contained oxidation products of organoarsenic CWA. No CWA-related chemicals were found in the near-bottom water samples. Elevated concentrations of As (>45 mg/kg) were found in 9 samples of bottom sediments in the primary dumpsite area (more frequently in the upper 0–5 cm layer). The highest As concentration (210 mg/kg) registered in the pelitic mud was found near the hotspots in the primary dump site (see SI for more information).

4. Microbial Community. Due to the frequent hypoxic conditions near the bottom of the dumpsite (18) and the often soft sediment (24) it is less likely that there is a significant macrozoobenthic community near the hotspots; hence, the initial ecological assessment end point chosen was the microbial community. Moreover, to assess the risk relating to dumped CWAs, it is necessary to evaluate the ability of the ecosystem itself for self-purification of contaminated water and sediments mediated by microbes. The analysis of the microbial community was also used as an indicator of CWA presence, as some species of microbes are tolerant to mustard gas hydrolysis products (MGHP) (primarily thiodiglycol) and use these as their sole source of carbon and energy (26).

Yperite can rapidly penetrate cells, and is able to alkylate DNA, RNA, and proteins affecting a variety of cell functions, including altering proteins that have been coded by alkylated RNA and structurally altering cell membranes (27). Some microbes are however as mentioned resistant to these toxic mechanisms, these organisms oxidize, and cleave C–S bonds in the MGHP. The hydrolysis products of mustard gas have a wide spectrum of toxic action on other microbiota (26). The samples taken at the Bornholm dumpsite yielded up to 7.1×10^6 cells/mL for the total amount of microbiota, up to 6.5 mg/L for bacterial biomass, and up to 4.9×10^4 cells/mL for the amount of heterotrophic microorganisms. At several stations we observed significant amounts of bacterial cultures tolerant to mustard gas products (both chlorinated and nonchlorinated) in the near-bottom water. The tolerant microorganisms were found at about 40% of stations in the dump site area. Outside of the dumpsite the concentration of MGHP tolerant microorganisms in near-bottom water was only between 0% and 3% (26).

The near-bottom water heterotrophic microorganism community in the dumpsite comprised up to 58% microorganisms tolerant to mustard gas hydrolysis products represented by microorganisms of *Pseudomonas*, *Bacillus*, *Sphingomonas*, *Flavobacterium*, *Micrococcus*, *Alcaligenes*, *Achromobacter*, and other genera, with *Pseudomonas* and *Bacillus* dominating. The primary dumpsite demonstrated further marked reduced diversity of microbiota typically represented by *Pseudomonas*, *Bacillus*, *Arthrobacter*, and *Achromobacter*. The species diversity of the microbial population at the dumpsite was reduced compared to reference sites, most probably because of an increase in the number of yperite-tolerant microorganisms, thus indicating the presence and effect of dumped CWA in the dumpsite and near the wrecks. Parallel laboratory studies, moreover, confirmed that MHGP-tolerant microbes can mineralize MGHP even at low temperatures (7 °C) and thus contribute to self-purification of the dumpsite (26). These results suggest

that the time scale of the threat from dumped chemical munitions under similar low oxygen conditions is limited to <100 years; probably closer to 50 y, by which time the released CWAs will have been significantly hydrolyzed and mineralized (see SI for more information).

5. Historical Review and Interviews. HELCOM has provided a sound baseline of information on the amounts of CWA dumped in the Baltic Sea. These data were supplemented by a review of the newspaper articles related to CWA from the largest daily newspaper (Social-Demokraten Bornholm) on the island of Bornholm for the period 1947 to 1992. The main result of the review was the consistency between the HELCOM reports and the news clippings for the period. Moreover, dumped munitions were revealed to have drifted to the shores of Bornholm, i.e., not all the dumped munitions remain in the designated dumpsite. The outcome of the interviews with local experts and stakeholders were principally as follows. Most fishermen from Bornholm have had encounters with dumped munitions; some 200 fishermen have over the years sustained injuries requiring medical assistance as a result. The munitions caught nowadays are completely corroded and the CWA appears as solid brittle lumps. The interviewees cannot ascribe impacts on the fish stocks to the presence of dumped CWA.

Conclusions

It was concluded, based on the conservative desk-based risk assessment, that risks toward the fish community could not be ruled out and that a site-specific assessment was warranted. The geophysical survey detected buried objects and wrecks in the primary dumpsite and identified these to be potential hotspots for CWA. Several CWA degradation products were found in the sediment samples near the wrecks and near the buried magnetic objects (56 out of 59 samples). Four porewater samples out of 59 samples contained organoarsenic CWA degradation products. None of the near-bottom water samples contained CWAs or their degradation products. Analysis of the microbial communities indicated presence of CWA degradation products, that the communities were affected, and that the microbes can degrade MGHP. The historical and local expert analysis suggests that the majority of dumped munitions caught for the past 20 y have been corroded and empty.

There are still significant uncertainties regarding CWA risks in the Baltic Sea, specifically due to the size of the disposal site, the ratio between intact buried munitions and empty shells, and the statistical power limitations in relation to the sampling. Thus more samples are needed. More generally there are uncertainties regarding the location, types, and amounts of CWA dumped globally (1). These findings indicate that there is a clear need for the following:

- further development of the chemical analytical methods;
- up-to-date ecotoxicological and physicochemical data;
- better site-specific knowledge about the materials fate and transport properties in deep sea environments (26);
- improved environmental ecotoxicological indicators specific for CWA (29).

The marine environment is protected against dumping of CWA via international maritime conventions: the London Convention (marine dumping of waste), the Basel Convention (controlling movement/trade of [hazardous] waste across international boundaries, and CWA's regulation by the Chemical Weapons Convention mandating the safe destruction of all CWA by 2012. There are, however, as mentioned above remaining policy issues regarding assessment of the human and environmental risks posed by dumped CWA, not only scientifically but also who may be held accountable

and what should be done about the munitions; ultimately, this is a site-specific question.

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Supporting Information Available

Additional text, figures, and a table. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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