ABRIDGED NARRATIVE FINAL REPORT[1]

John D. and Catherine T. MacArthur Foundation

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CHEMICAL WEAPONS DUMPED IN THE BALTIC SEA: FACTS, TENDENCY AND PREDICTION OF LEVEL AND SCALES OF POSSIBLE ECOLOGICAL DISASTER

1. Introduction: History and Geography of Warfare Chemicals Dumping

The consequences of dumping old chemical weapon (CW) and munitions at World Ocean are of growing concern. From World War I until the 1970s, dumping of chemical weapons at sea was the accepted practice for disposal. Little documentation of this practice can be found before the mid-1940s. In 1943, mustard (H) was released into the waters of Bari harbor in Italy. Since the end of World War II, ocean dumping has occurred in many areas, including the Baltic Sea, around Japan, in the Adriatic Sea near Bari, and in the coastal waters of the United States. During the period 1945-1948, The US scuttled at sea approximately 32,000 tons of captured German chemical weapons. The British dumped approximately 175,000 tons of chemical weapons at sea, with 100,000 tons coming from Scotland and the balance from the captured German stockpile. During 1955-56, the British dumped a further 17,000 tons of captured German munitions. During 1956-1957, the British disposed of the remainder of their stockpile of chemical weapons, 8,000 tons of World War II vintage mustard and phosgene munitions.1 News reports indicate that the ocean dumping in the 1950s occurred in the Irish Sea; some of the British dumps in the late 1940s may have occurred in the North Sea. The Adriatic, Baltic, and Japanese ocean dumps have provided evidence of the persistence of mustard under water.

Accidents due to ocean dumping of chemical weapons have been reported in the Baltic Sea as well as the Adriatic and in the Pacific Ocean and Japanese coastal waters. Most reports came from fishermen who had inadvertently snared plastic lumps of mustard gas in

[1] More Details in the paper by K.A. Korotenko "Warfare Chemicals Dumped in the Baltic Sea: Modeling Transport Processes of pollution Resulting from Possible Leakages". *Oceanology(Engl Transl by AGU)*, **43**(1)

their nets. When exposed to seawater, mustard forms a thick outer "crust" over a core of mustard, which allows the mustard to be brought to the surface where it can injure unsuspecting fishermen. These accidents began occurring shortly after the material was dumped and have continued throughout the intervening years/

Warfare chemicals dumped in the Baltic and North Seas soon after World War II cause great concern in Europe. Data about the amounts, which were dumped, are uncertain in part because of the passage of time and the lack of accurate records, and also because some of the countries involved in dumping operations are unwilling to disclose the information that they possess. Places where warfare chemicals were dumped and their approximate amounts are presented in Fig.2 and Table1. Three major dumping sites have been identified in the Baltic region: East of Bornholm, south-east of Gotland and south of the Little Belt. Munitions were dumped in these areas in 1945-1947 under the supervision of the Soviet and British occupation forces in Germany. Information on the amount of CW munitions actually dumped varies from one source to another. The Helsinki Commission (HELCOM) estimates that approximately 40,000 tones were dumped, equivalent to 13,000 tones of originally active chemical warfare agents. CW munitions from the Baltic Sea have been found to contain various types of mustard gas, irritants based on arsenicals, tear gas, the lung irritant phosgene and the nerve agent Tabun (southern Little Belt) and/or decomposition products. The munitions are covered by up to several metres of sediment at depths of 20-40 m (Bornholm), 70-120 m (Gotland) and 30m (Little Belt). According to other information, a further 90 tones of munitions were dumped in the Baltic Sea between 1943 and 1965.

Location	**Munitions Quantity, tons**	**Chemical Agent Type**
Bornholm basins	60,000	Clark I, Clark II, Adamsite, chloroacetophenone
Gotland basin	2,300	Clark-I, Clark-II, Adamsite, Tabun chloroacetophenone
Southeast Gotland Isl.	6,358	Arsenic-containg agents, Adamsite, mustard, Tabun chloroacetophenone
Little Belt	5,750	phosgene, Tabun
Skagerrak	270,000	phosgene, Tabun, Adamsite, mustard chloroacetophenone

Table1. Locations and quantity of warfare chemicals dumped in the Baltic Sea.

In the Skagerrak, approximaely 270,000 tones of CW munitions were sunk on German cargo ships at a depth of 800 m between 1945 and 1948. The munitions are reported to have contained mustard gas, chloroace-tophenone, phosgene and Tabun. Some of the chemical munitions were probably dumped overboard during transport from the harbor of Wolgast in Germany.

Clearly, the dumped CW has attracted considerable interest of public since sunken CW present real threat for those populations, which reside in the Baltic Sea region (over 50

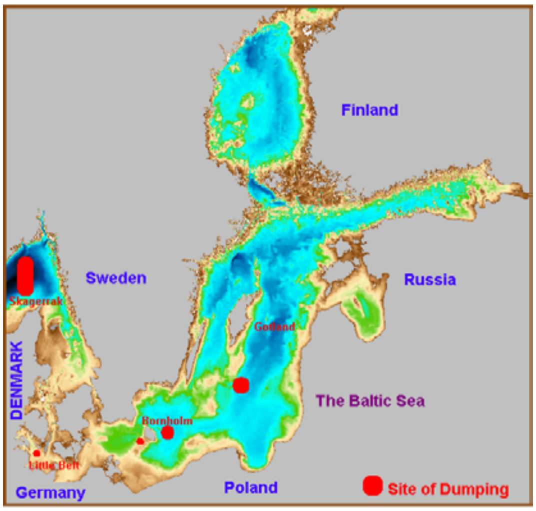

Fig1. Map of dumping of chemical weapon in the Baltic Sea

millions). In series of articles that appeared periodically in newspapers and magazines, dumped CW are considered a delayed-action ecological mine of a sort, which will blow up in several months. In fact, if thousands chemical bombs and shells were simultaneously destroyed owing to corrosion, and hundreds of thousands tones of war containers got into the Sea and then in atmosphere, nobody would remain alive over a vast area. However, there also are more moderate predictions. In this connection, the main goal of the performed project was to understand and estimate independently the scales of possible catastrophic events that might happen in cases of the predictable leakages of toxic agents in the Baltic Sea.

2. Main Aspects of the Work on the Project and Collected Materials.

During the grant period, since May 1, 2000, available materials on regions of chemical weapons dumping, characteristics of toxic agents, structure of water mass and their characteristics in the regions of CW damping have been collected. During this period I have also got in touch with international groups of scientists working on his problem to coordinate my work on the project. I used Internet and have had personal communications with specialists and the following organizations:

- FOA NBS Defence Research Establishment (Sweden);
- Helsinki Commission, *Ad Hoc* Working group on Dumped Chemical
- Munition-HELCOM CHEMU(Finland);
- Chemical Weapon Program, The Green Cross(Switserland);
- NATO Scientific and Environmental Affairs Division (Belgium);
- Chemical and Biological Program (Sweden);
- PAR Government System (USA);
- MEDEA (USA).

Much attention has been paid for physico-chemical properties of warfare chemical agents and their behavior in seawater. One should take into account that the sea medium- precisely medium and not merely water- imposes an extremely aggressiveness toward forcing objects. The basic factors of the sea medium's action are the following: strong chemical and electrochemical corrosion, chemical and microbiological oxidation and destruction, hydrolysis, and the action of hydrobionts. Contaminants themselves are also rather reactive and their contact with aggressive seawaters could lead to more or less toxic compounds. This raises the main question of the rate of the toxic agent transformations. If poisons are destroyed slowly, they are capably of wiping out a multitude of hydrobionts and then (via nutritive connections) inhabitants of dry land as well. It is obvious that action of CW results in the most terrible consequences in shelf and shallow waters, where the majority of sea inhabitants are localized. It is also apparent that the consequences will mainly depend on the initial local concentration of contaminants in the seawaters and on the currents and turbulence, which transport and dilute poisons. Unfortunately, the Baltic Sea is one of the inland sea, its depth being predominantly only 40-100 m. As was known from available literature sources all approaches to estimation of transport and dispersion of chemical pollution from dumped weapons is mainly based on simplified view on hydrodynamic processes in the Sea. For example, it is obvious supposed that water circulation in dumped areas rather slow. But this is partly true and only for deep layers of Bornholm basin. Such as areas like Little Belt and Skagerrak have relatively strong and complicated system of currents what breaks down existing imagination and estimations. Moreover, even in deep Bornholm basin, an intensive water mass exchange occurs periodically due to water inflowing from the North Sea.

As to various scientific reports on this problem, the main conclusion of the most of them is that ocean dumping is unlikely to cause a major ecosystem catastrophe, primarily because chemical warfare agents react with water to give considerably less toxic materials. This is also partly true since mostly products of hydrolysis often become more toxic than original agents.

According to the calculations done by military experts in /Journal of Royal. Chem. Soc. 1994, Vol.2/, the maximum rates of leakage of CW dumped near Bornholm Island 60 years after burying in 1947 (the first leakage maximum) is expected to be about 40 tones/year, that is nearly 100 kg/day) and 256 tones/year (700 kg/day) after 125 years (the second leakage maximum). Therefore the independent work on the project can shed light on this problem and give correct prediction and estimations.

Chemical Weapon characteristics

Existence of various kinds of chemical contaminants dumped in the Baltic Sea requires multi-tasking and multi-disciplinary approach to solution of the considered problem. Physico-chemical properties of different chemical reagents differ considerably. Therefore, mechanisms of transport these substances; their fate and behavior in sea medium should be treated separately for each reagent. Briefly, information collected for known warfare chemical agents dumped in the Baltic Sea itemized below:

- *Sarin*: Simplified estimations give that a bomb containing 100 kg toxic agents (TA) will lead to intolerable concentration of the chemical agent of a volume 10^{10} m^3. That means a water layer 100m of thickness (typical water depth of Baltic), 1km wide and 100 km long will be polluted. This simple estimation based on that only currents transport the pollution, i.e., without taking into account other hydrophysical processes. Hydrolysis, however, will reduce concentration and according to available estimations after 15 days, the concentration within the layer is expected to reduce by 2 orders. However, these are the laboratory estimations but in nature the process of hydrolysis goes much slowly so that the concentration will remain close to initial level. It should be remembered that under hydrolysis Sarin produces several compounds and only one can be considered as non-toxic;
- *Musturd:* The main concern with ocean dumping is that mustard is quite insoluble in water. According to scientific reports, mustard lying on the sea bottom intoxicates a smaller water volume but maintains high toxity for 400 years. Mustard does not give a plume of contaminated water; it tends to form plastic lumps on the bottom of the ocean, which can be brought to the surface by trawling. Thus, the small but steady number of fishermen who are injured every year through contact with the mustard.
- *Adamsite, Lewsite:* Both of these agents belong to group of arsenic-containing poisons. They form stable poisoning areas with solid hydrolysis products in locations of toxic agents burials. Adamsite has a low solubility in water and is very stable to hydrolysis. In water, Adamsite becomes a long-term continuous source of poison, which requires a different modeling approach in comparison with Sarin described above. Lewsite characteristics could be reminiscent Yprit; low soluble in water and considerably higher then water. Yet, it is much reactive than Yprit and its easily hydrolysed. The specific features of Lewsite is its hydrolysis resulting in an oxide of the same toxity.

Another part of my activity, according to the project, was devoted the collection available data on hydrodynamic and meteorological conditions in/over the Baltic Sea in a whole and in different regions close to dumping areas. Among these data major attention was paid to:
- average climatic current velocity, temperature and salinity fields in the Baltic Sea;
- characteristics of their seasonal variability;
- factors affecting this variability;
- intensity of turbulence and turbulent exchange processes in the investigated regions.

All these parameters were necessary for development a couple chemical-hydrodynamic model that allowed adequate prediction of the concentration level of chemical agents and to assess scales of pollution for different scenarios and regions of the Baltic Sea.

3. Main Achievements and Results.

3.1. Specific Hydrodynamic/Transport Model Developed in the Framework of the Project.

A new generation of the coupled model hydrodynamic/transport model has been developed with a special reference to transport and dispersal of warfare chemical dumped at the sea. The model consists of *Flow* and *Transport* modules. The *Flow* module was developed on a base of the Princeton Ocean Model (POM). However unlike POM, turbulence module was developed on a base of k-ε-τ model that predicts more accurately turbulence in the bottom layer, what is extremely important for a given problem.

The *Transport* module preliminary developed by author for oil spills was reconstructed and adjusted to chemical pollution transport. The module takes predetermined the velocity and turbulence characteristics supplied by POM and uses Lagrangian tracking, the random walk technique, to predict the motion of individual particles, the sum of which constitutes a considered chemical agent. The basic modeled processes affecting the chemicals are hydrolysis, solubility. Parameters of chemical reactions were obtained from literature sources and personal communications mentioned above and were used in modeling.

From the physical point of view, the model runs were used the source of chemical pollution being considered as either continuous *point* or *distributed* sources. It associated with principally different two methods have been used in dumping CW:

1) Concentrated dumping of containers, shells, and bombs together with ships – modeled by means of a *Point Source;*

Dispersed dumping of individual containers, shells and aircraft bombs from moving vessels. In addition, some munitions were dumped in wooden cases, which might have

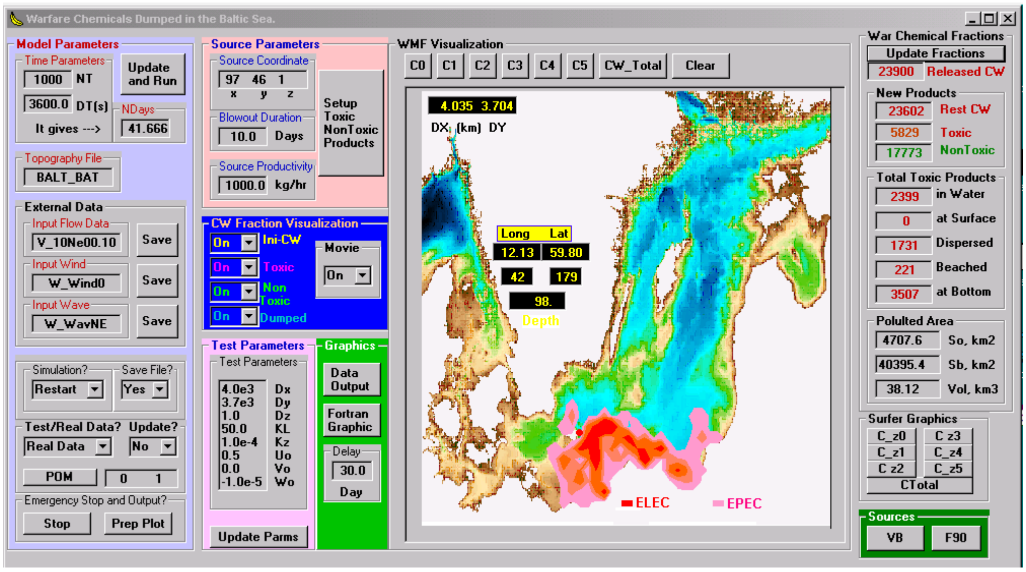

Fig. 2. Interactive Dialog of the coupled model; Red color denotes area an Estimated Lethal Effects Concentration (ELEC) , Pink color denotes an Estimated Probable Effects Concentration (EPEC).

2) remained floating for some time and might have drifted outside the intended dumping areas-modeled by means of a *Distributed Source*.

Operationally the hybrid model is controlled primarily by interactive Dialog with a map of the Baltic Sea as it shown in Fig.2. The model is started with “Update and Run” button, which reads in bathymetry, predetermined current velocities, and model and source parameters. A source position is determined by the mouse pointer location; in doing so the Lat/Long coordinates and instantaneous depth will be displayed. The user may chose whether the leakage is bulk or continuous, and specifies the period of spill in the later case. Once the model is running, the user may also specify the wind and wave conditions as well as chose which chemical fraction (toxic, non-toxic, beached, etc.) to be displayed during the calculations. Once the “Update and Run” button is clicked, it runs a separate graphic window displays real-time the motion of individual particles, the sum of which constitutes a considered chemical agent. The concentration recalculated from particle density and oil fraction distributions during the spilling process are displayed at the map and in correspondent frames at the upper right corner of the main Dialog. A special Properties Dialog, which appears by clicking “Setup Toxic/NonToxic Products” button allows the user to input warfare chemical type and properties described above.

3.2. Adaptation to Parameters of Chemical Agents.

The developed model was adapted to be used for chemical agents with various characteristics and behavior in seawaters. All available toxicity data regarding the chemical warfare agents of primary concern and the expected degradation products in the Baltic environment were gathered and summarized. This information was used to compare the toxicities of the different agents and their degradation products and to decide which chemicals may represent a toxic threat to the environment. For each of those chemicals that are potentially toxic, according to units input by MEDEA Group, an *estimated no effects concentrations* [ENRC] was derived, usually as one-tenth of the lowest LC_{50} value for marine organisms. In addition, to define areas affected by these chemicals, *estimated probable effects concentrations* [EPEC], and *an estimated lethal effects concentrations* [ELEC] were designated as ten one hundred times the ENEC concentrations, respectively.

For calculations Tabun (GA) and Sarin (GB), which have approximately equal toxicity were both assigned an ENEC of 1 µg/l. Mustard (H) is orders of magnitude less toxic with an ENEC of 200 µg/l. Lewisite has intermediate toxicity with an ENEC of 20 µg/l.

Cyanide is a breakdown product of Tabun and was assigned an ENEC of 7 µg/l. Dimethylamine is also a breakdown product of Tabun with an ENEC of 115 µg/l. Chlorobenzene is a component of the Tabun formulation, present up to twenty percent. Chlorobenzene was assigned an ENEC of 1,000 µg/l.

Most of the breakdown products of Sarin have toxicilies six orders of magnitude less than Sarin. Fluoride is the only exception to this and it was assigned an ENEC of 200 µg/l. Mustard breakdown products are thiodyglycol, with an ENEC of 1,470,000 µg/l and 1,4-thioxane with an ENEC of 26,000 µg/l.

Lewisite hydrolyzes to 2-chlorovinylarsonous acid, which was assigned an ENEC of 20 µg/l, the same as the parent compound Lewisite. Inorganic arsenic is the ultimate degradation product of Lewisite, with an ENEC of 90 µg/l.

According to laboratory experiments, the hydrolysis of the agents Tabun, Sarin and dissolved mustard can be modeled as simple reactions producing non-toxic products that are of no further concern here. On the other hand, the model for Lewisite, showed it hydrolyzing into a variety of toxic arsenical compounds with subsequent reactions simply redistributing arsenic into stable, inorganic, toxic compounds. For purposes of this project, the chemical conceptual model used as a part of the general coupled model is assumed to be one of the following three types:

$$(A) \qquad CWA \xrightarrow[k]{} SNP$$

$$(B) \qquad CWA \xrightarrow[k]{} (1-\varepsilon)SNTP + \varepsilon\ STP$$

$$(C) \qquad CWA \xrightarrow[k_1]{} (1-e_1)SNTP + e_1USTP$$

$$USTP \xrightarrow[k_2]{} (1-e_2)SNTP + e_2USTP$$

where ε is the mass fraction determined by the stoichiometry of the reaction and k is the hydrolysis rate constant. The abbreviations stand for Chemical Warfare Agent (CWA). Stable Toxic Products (STP). Unstable Toxic Products (USJP) and Stable Non-Toxic Products (SNTP). Reaction (A) applies to Sarin and Mustard. Reaction (B) applies to Tabun with STP being hydrocynanic acid (HCN). Reaction (C) applies to Lewisite where the products are organic and inorganic arsenicals. Fig.3 illustrates the behavior of the reaction (B) for hydrolysis rate, $k = 0.0000192$/s and $\varepsilon = 0.25$.

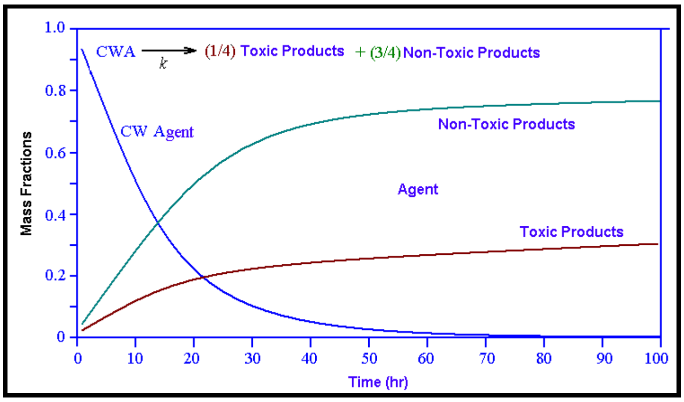

Fig.3. Fate of Mass Fraction During Hydrolysis

3.2. Bottom Topography used in the Model.

A high-resoluted bathymetry is a keystone in adequate modeling chemicals emitted by bottom source. Therefore the model was based on bathymetry presented by the last issue of the World Topography, ETOPO2. The grid step is chosen at 4′ and 2′ along x and y axes (that is, about 4.0 km and 3.7 km, respectively). In total, the grid dimension was chosen to be of 231×191×30 along the x, y, and z axes, respectively. Model grid covers the Baltic from 9.3^o to 24.6^{o}E and from 53.0^o to 60.2^{o}N. Colored bathymetry used in the model is shown in Fig. 1. Shallow areas of the Baltic are marked light brown to green, and deep parts (depth is more than 100m) of the Sea changes from light blue to dark blue.

3.3. Water exchange between the North Baltic Seas.

In the project, much attention was paid for major inflow of saline water from the North Sea to the Baltic Sea and its possible effect on the deep water exchange and chemical pollution transport. The Baltic Sea is a fjord-like landlocked sea and is among the largest brackish sea areas of the world. Its water exchange with the North Sea is greatly restricted by the narrow and shallow transition area with three channels: the Little Belt, the Great Belt and the Sound. The exchange is generally accepted to be around 10% through the Little Belt, 65% through the Great Belt and 25% through the Sound. Inflows of saline water maintain both the brackish character of the Baltic, the haline stratification and the ventilation of the deep water. This effective mechanism renewing the central Baltic deep water and significantly changing the marine environment of the Baltic is the advective transport of large amounts of highly saline and oxygenated water from the Kattegat into the Baltic known as major Baltic inflows. Such events are very intermittent and relatively rare (period between them can vary from 5 to 15 years) but the inflows may cause to long-term transport of chemical pollution from munitions dumped at the Sea. Particularly it concerns to burials in the Little Belt and Skagerrak.

3.4. Climatic Winds over the Baltic Seas and Pollution Transport.

Despite the processes of water exchange between the North and Baltic Sea in important factor for the transport of chemical pollution it is a considerable slow process in comparison with those caused by winds. The renewal of bottom water in the central Baltic Sea is a combined effect of wind and density-driven flow of bottom water. Whereas the thermohaline flow is slow (but persistent), sudden winds produce strong currents in the bottom layers also and thus can be much more efficient in transporting water of high salinity. It was obtained that westerly winds are only in part responsible for the renewal of deep waters in the Baltic Sea. Numerical experiments with idealized wind fields show that this is not the case between Bornholm and Gotland basins. Westerly winds are required in order to transport saline and oxygen-rich waters and pollution from the Skagerrak into the western Baltic Sea. The Bomholm Basin is not separated from the Arkona Basin by a shallow sill. Thus, bottom water can easily leak into Bornholm Basin. However, this water will be strongly diluted before it fills up the basin to the sill depth of Stolpe Channel. Consequently, in most cases it will not be dense enough to replace the bottom water in Gotland Basin and transport the chemical pollution. Proper wind conditions are much more efficient for this replacement. Numerical calculations show that the dominant wind-produced circulation is described by coastal jets in the wind direction and countercurrents in the central region, deflected by bottom topography. It intensifies an elevation of polluted water from the sea floor to subsurface layers that may lead to large-scale contamination of the Baltic Sea.

The water exchange between Bornholm and Gotland basins important for transport of pollution from major damping sites occurs through Stolpe Channel, which is close to the center of the Baltic Sea at this longitude. Accordingly, bottom currents opposite to the wind direction prevail. It turns out that northerly and easterly winds are most efficient to transport water from Bornholm Basin into Gotland Basin and further to the north.

According to statistics, predominance of westerly to south-westerly winds during the autumn and winter, and weak winds in summer season. The model was run with four most recurrent climatic wind fields.

3.3. Main Results.

Collected data and numerical simulations of chemical pollution resulting from hypothetical blowouts toxic agents allow assessing character and scales of possible catastrophic events in different region of the Baltic Sea. Forecasting numerical experiments were performed separately for each site of chemical munitions dumping. The experiments were conducted for the most possible climatic conditions in order to predict pollution areas more realistically. Obtained results have given the following important information:

- The Baltic Sea is a very shallow water body and wind-driven circulation and countercurrents play a dominant role in ventilation deep water and transport of natural tracers and pollution. In this connection even relatively deep Bornholm and Gotland Basins cannot be considered as protected area for dumped chemical weapons. Near-bottom currents generated by winds are deflected by irregularities of bottom topography in doing so vertical component of currant velocity may have relative high value. It leads to vertical transport of bottom pollution up to the surface layer where strong winds spread the pollution over a large area. The system of jet-like currents generated by winds along shores causes to large-scale contamination of shallow coastal waters and coasts. Lethal levels of contamination from the Bornholm dumping site can approach Germany and Poland in a month after a leakage (fig.2). It is clear that wind changes will lead in turn to changes in direction of pollution transport.

4. Conclusions.

Numerical simulation performed on base high-resolution model provides more detailed data on character and scale of possible pollution zone formed under various meteorological conditions. The model can be used as real-time forecasting system allowing prediction of concentrations and scales of possible pollution zone in resulting from real leakages might happen in locations of dumping. Numerical simulations were conducted with a use of so-called moderate scenario, according to which the rate of release of chemicals does not extent 24 kg/day. In case of the abovementioned catastrophic releases the pollution occupied entire the Baltic Sea within a relatively short period. The model experiments confirm these "extreme" scenarios.

It should be emphasized that widely used estimations of spatial and temporal scales and concentration obtained with a use of simplified approaches based on "average" marine conditions give very rough estimations frequently having nothing similar with nature.

To summarize results achieved in the project the following itemization is given below:

1. Prediction of probability of leakage of the toxic agents for each dumping regions.
2. Adaptation of the model to major conditions and parameters of chemical agents and water characteristics, bottom topography, climatic data and features of each region of CW damping.
3. Calculation of circulation in Baltic on base of the general hydrodynamic model.
4. Estimation and description regional water characteristics and fluxes for areas of dumping.
5. Estimation North Sea water inflow in the Baltic Sea and its possible effect on the deep water exchange and chemical pollution transport processes.
6. Estimation and prediction strong storm situations in Baltic and their effect on the deep water exchange and chemical pollution transport processes.
7. Adaptation of the transport model for physico-chemical characteristics of modeled toxic agents such as solubility, hydrolysis rate, polycondensation, microbiological destruction, etc..
8. Calculation of toxic pollution concentration fields for each studied region and in Baltic in a whole.

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