Arsenic and Other Environmental Parameters at the Chemical Munitions Dumpsite in the Lithuanian Economic Zone of the Baltic Sea

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Large quantities of chemical munitions were dumped in European waters after the World War II. Part of the chemical munitions dumpsite in the Gotland Basin lies within the Lithuanian economic zone. The lack of information causes public concern about the issue of chemical munitions. Using data obtained from the expedition to the chemical munitions dumpsite, a preliminary survey to assess the potential hazard of a chemical munitions dumpsite in the Lithuanian economic zone was made. Hydrological, hydrochemical, ecotoxicological, biological, and sedimentological parameters were investigated. None of the measured parameters showed sharp anomalies, although some parameters, like arsenic, arsenic tolerating bacteria, and zooplankton didn’t give a well-defined answer. An analysis of arsenic data showed that there were elevated arsenic values at some stations at the dumpsite. However, arsenic concentrations are low relative to other investigations of sediments in the Baltic and the North Seas. Although not apparently a problem, further studies would be necessary to make unequivocal conclusions about the leakage of chemical munitions at this dumpsite.

Keywords: the Baltic Sea, chemical munitions, arsenic, Lithuania.

1. Introduction

Large quantities of chemical munitions were dumped in European waters after the World War II. More than 40 vessels loaded with chemical munitions were sunk in Skagerrak and Little Belt, while in the Baltic Sea the warfare agents were mainly discarded overboard in the form of munitions or containers primarily into two basins, with ~11 000 t in the Bornholm Basin at depths of 70-105 m and ~1000 t in the Gotland Basin at depths of 70-120 m [1, 2, 3, 4]. Part of the chemical munitions dumpsite in the Gotland Basin lies within the Lithuanian economic zone.

Chemical warfare agents can be classified according to their effects: tear gases or lachrymators (chloroacetophenon), nose and throat irritants (Clark I, Clark II, adamsite), lung irritants (phosgene, diphosgene), blister gases or vesicants (sulphur mustard, nitrogen mustard, lewisite) and nerve gases (tabun) [3].

During previous investigations of chemical munitions dumpsites, experts tried to measure their direct evidence (e.g., mustard, Clark, sarin) [3, 4, 5]. Although, a different approach is to focus on changes in environmental conditions, which could be caused by chemical warfare agents and their degradation products and which could be detected by techniques generally accepted in oceanology [5, 6].

Arsenic is a constituent of chemical munitions, such as: Clark I, Clark II, adamsite, lewisite, and arsine oil. The quantity of these chemical compounds is approximately 1/3 of the chemical warfare agents dumped in the east of Bornholm and southeast of Gotland [3].

Lewisite (C₅H₂AsCl₃) reacts with water to form chlorvinyl arsine oxide, which in alkaline solution can react further to produce arsenic acid and acetylene [3]. Arsine oil is a technical mixture of arsenic (III) chloride, phenylarsine dichloride, diphenylarsine chloride, and triphenylarsine [7]. Clark I
((C₆H₄)₂AsCl) and Clark II ((C₆H₅)₂AsCN) are expected to adsorb onto sediments and react very slowly with water. Both degrade eventually to form tetra-phenyl-diarsonic acid, which is toxic itself and is hydrolysed in a very slow form. Similarly, adamsite (NH(C₆H₄)₂AsCl) is practically insoluble in water, adsorbs onto sediments, and hydrolyses very slowly forming phenarsazinic oxide. Thus, the chemical munitions Clark I, Clark II, and adamsite, together with toxic reaction products, can be preserved for a long time on the sea bed. However, they might also bioaccumulate in organisms [2, 3, 4]. Clark I, Clark II, and adamsite are expected to spread very slowly from the chemical munitions source and only contaminate local sediments [1, 3, 4]. Thus, elevated arsenic concentrations in the sediments can indicate a leakage of chemicals from the containers.

Hydrochemical parameters, such as dissolved oxygen and pH can influence the corrosion process of metallic casings of chemical weapons. Degradation products of chemical weapons are able to change bottom water pH [5]. Hydrogen sulphide, total phosphorus and phosphates reflect the changes in the environmental state of the Baltic Sea. An increase of organic phosphorus in the near-bottom layer can indicate a presence of additional source of phosphorus, e.g. phosphorus containing gases [5, 6].

Microorganisms are sensitive indicators of environmental state. Because of the special biochemical composition of the cell, they react fast to abiotic changes in the environment. Quantity of appropriate microorganisms is like a test, which shows what pollutant is present in water [8]. Microorganisms, like arsenic tolerating bacteria or mustard tolerating bacteria, can be used as a pollutants identification method [5, 6].

Phytoplankton and zooplankton are important components of the sea ecosystem. They quickly respond to environmental changes and reflect a complex of conditions of the water body. The impact of chemical pollutants can be seen indirectly from the changes in population structure, behaviour, physiological processes or appearance of separate individuals [6].

It is very important to include hydrologic conditions in the chemical munitions dumpsite investigations. It is necessary to measure water currents, lateral and vertical water exchange especially in the near-bottom layer in order to understand the spread of dissolved and particulate substances in water. Low water temperatures and salinity determine slow corrosion process. An increase of water temperature fastens chemical reaction speed up to several times [5, 6].

The knowledge of granulometric composition helps in evaluation of pollutants concentration in sediments. The <2 µm fraction of the sediment is one of the major sinks for contaminants introduced into natural waters [9, 10].

The chemical warfare agents dumped in the sea pose three main threats [2]. The first one is the threat to the general public from agents washed ashore. This could only take place as a result of material in wooden crates being thrown overboard from moving vessels during the original dumping operation. Such occurrences were reported on Polish beaches, mainly between 1952 and 1955 [2]. The possibility that chemical munitions can now be washed ashore from the dumping areas is extremely unlikely. The Bornholm and Gotland basins are characterized by stable stratification with anoxic conditions developing below the halocline and with only slight bottom currents except during exceptional periods of flushing to the basins [11]. In addition, the dumped material would need to be moved upwards from a depth of up to 100 m in order to be washed ashore [2, 3]. The second threat is to fisherman who can trawl lumps of viscous mustard gas from the sea floor with their nets. Over the period of 1995-2002 about 3-11 incidents were reported each year where chemical munitions were netted by fishermen, showing that these chemicals are still a risk for the crews of fishing vessels operating in this part of the Baltic [2, 12]. The third is the threat to the marine environment. There is a possibility of bioaccumulation of arsenic compounds in marine organisms [3, 4].

The lack of information causes public concern about the issue of chemical munitions in the sea. Using data obtained from the expedition to the chemical munitions dumpsite, a preliminary survey to access the potential hazard of a chemical munitions dumpsite in the Lithuanian economic zone was made.

2. Methods

2.1. Sample collection

Ministry of Environment (Center of Marine Research) and the Ministry of National Defence of Lithuania performed environmental impact assessment of chemical munitions dumpsite in the Lithuanian economic zone. Lithuanian naval vessel “Kuršis” made the sonar scanning of the bottom for the chemical munitions units in October of 2002. Sampling stations at the dumpsite for the scientific research expedition were chosen near chemical weapon units according to the obtained sonar data. Some other stations were sampled outside the dumpsite to get samples for comparison from the non-dumpsite area. Fourteen stations were sampled during the expedition in June of 2003 (stations marked with prefix Ch), 5 of them were from the chemical munitions dumpsite (ChG1-ChG5 stations). Lithuanian national monitoring stations were visited and sediment samples for arsenic analysis were taken in August of 2004. Sampling locations are illustrated in Fig.1, coordinates, sampling date, depth, and distance from the shore of the sampling stations are presented in Table 1.

During the expedition to the chemical munitions dumpsite, hydrological, hydrochemical, ecotoxicological, hydrobiological, and sedimentological parameters were measured.
Water samples for hydrochemical parameters were taken by rosette of bathometers (1 l); water temperature, salinity, and depth were measured by CTD device. Bacterioplankton samples were taken by
modified ZoBelo water sampler. Phytoplankton samples were taken by 5 l water sampler. Zooplankton sampling was performed by standard plankton net type WP-2 from the vertical water mass. The method used for phyto- and zooplankton sampling is recommended by HELCOM [13]. Sediment samples from the surface were collected using a large Van Veen grab sampler (75 kg, with a sampling area of 0.1 m²). Sediment from the top ~1 cm was sub-sampled and frozen immediately onboard for arsenic analysis. After transportation to the laboratory, samples were stored in a deep-freezer at a temperature of ~23°C. Gemini gravitational tube was used in order to take samples from deeper sediment layers for sedimentological analysis.

2.2. Analyses

Hydrochemical parameters were measured onboard. Dissolved oxygen concentration was determined by Winkler method, water pH by electrometric method; hydrogen sulphide, phosphates and total phosphorus – by spectrophotometric method. Biological samples [bacterioplankton (total bacteria number, saprophytes, arsenic tolerating bacteria), phytoplankton, zooplankton] were fixed onboard and analysed later in laboratories of Center of Marine Research. Inoculation method on liquid medium for arsenic tolerating bacteria was used [14]. Phytoplankton from the integrated sample was analysed by quantitative Ütermohl method. Zooplankton analysis was done by a microscopic method [13]. Sediment samples for sedimentological parameters were analysed in the Institute of Geology and Geography. Granulometric composition of the sediments was analysed by sieving and pipette methods [6]. Arsenic concentration in sediment samples was analysed in International Atomic Energy Agency – Marine Environment Laboratory in Monaco. All samples were freeze-dried and digested using a CEM MARSS high-pressure microwave digestion system using 5 ml of nitric acid and 2 ml of concentrated hydrofluoric acid. Samples were prepared in batches of 11 or 12, which included at least one reagent blank, a representative marine sediment reference material (IAEA 433) and a duplicate sample or reference material. For digestion, the temperature was ramped to 200°C over a 30 min span and then held at that temperature for an additional 12 min. After cooling for at least 1 h, the sample digestates were transferred to graduated 50-ml plastic test tubes containing 0.8 g boric acid for the dissolution of fluoride precipitates. Following dilution to 50 ml with Milli-Q water, tubes were capped and placed in an ultrasonic bath for ~1 h to ensure the complete dissolution of residual solid material. Arsenic was determined by electrothermal atomic absorption spectrometry using a Varian SpectrAA Zeeman 220 instrument equipped with Zeeman background correction and using pyrolytically coated tubes with platform. Pd(NO₃)₂ and Mg(NO₃)₂ were used as matrix modifiers to permit the use of a higher ashing temperature. Calibration was carried out by the standard addition method.

Iron was determined by flame atomic absorption spectrometry on a Varian instrument SpectrAA 220FS. Good results were found for arsenic and iron in sediment reference material IAEA 433 with most analytical data falling within the standard deviation of the reference sediments.

2.3. Statistical methods

The interpretation of metal distributions in sediments has often relied upon some methods of normalisation in order to account for variations based on grain size rather than source strength. In this vein, iron has commonly been used for the normalization of heavy metal distributions in the marine sediments [10]. In the Baltic Sea, iron plays an important role in diagenetic geochemical reactions in sediments. For this reason, it has been suggested previously that iron may not be appropriate for normalizing heavy metal concentrations [15]. However, some metals, arsenic among them, have positive correlations with iron in the Baltic [16] and in the North Sea [10]. Therefore, iron has proved to be a useful reference element specifically in the case of arsenic.

An approach to present normalised data is based on calculating the residuals about the regression line. The residual is the difference between measured concentration and that calculated from the regression equation. Large positive residuals may be regarded as representing samples with higher than expected contaminant concentrations [10].

3. Results and discussion

The main attention of the expedition was paid to five stations of the dumpsite area. With respect to the chemical munitions dumpsite (stations ChG1-ChG5), during the expedition, the bottom water temperature was about 4-6°C, the salinity of the bottom waters varied from 9.8‰ at the station ChG5 to 12.3‰ at the deepest station ChG1. The water depth varied from 84 to 126 m.

Bottom water velocities in the southeastern Baltic can change from 0 to 40 cm s⁻¹ [17], in summer time, in Lithuanian coastal zone the bottom water velocity was only about 4 cm s⁻¹ (at 59 m depth) [18]. During the expedition bottom currents were not measured, although measured sedimentation rates helps in understanding of the situation: there are minimal bottom water velocities at sediment accumulation zones and maximal at moraine and sandy bottoms. It was found that there is a sediment accumulation zone in the north and north-western part of the dumpsite (ChG1, ChG2) with the sedimentation rate of 0.02-0.03 cm per year. Other dumpsite stations
(ChG3, ChG4, ChG5) have a zero- or low accumulation [6]. The dominating north direction bottom water currents, weak bottom currents velocities and bottom relief would prevent chemical munitions from reaching the Lithuanian coast.

The dissolved oxygen concentration in the bottom waters of the chemical munitions dumpsite varied from 1.7 to 4.5 mg/l. There was an oxygen deficit at five stations of the dumpsite. Although, an oxygen deficit below the halocline is often situation for the Baltic and it depends on dynamics of water masses. Oxygen concentration increases after the influxes of saline waters from the North Sea [19]. The hydrogen sulphide was not found at these stations. The pH of bottom layer was more close to neutral values (from 7.3 to 7.6), comparing to the pH of the surface water (~ 8.3). It can be explained by the accumulation of carbon dioxide due to degradation of organic mater and stable water stratification [20]. Paka and Spiridonov [5] during their research did not find any anomalies of pH values at the dumpsite in Gotland, too. The distribution of phosphates and total phosphorus depends on the water mass structure. The concentration of these compounds in the surface layer is low, because of the photosynthesis process; organic material sinks to the bottom and creates higher concentrations there. At the bottom layer of the dumpsite due to greater depth (deeper then 80 m) and stratification, concentration of phosphates was higher up to 0.13 mg/l (ChG5), than at the other stations (0.02 mg/l). Similar results were obtained for the total phosphorus; the concentration of the bottom water layer of the deeper then 80 m stations was higher (up to 0.15 mg/l, comparing to 0.04 mg/l). Mineral phosphorus dominated over organic in the deeper water layers. All hydrochemical parameters did not show any changes of the environment; the concentrations of all parameters were typical for this area of the Baltic Sea [6].

Biological parameters were investigated only at five stations: at three stations of the dumpsite (ChG1, ChG3, ChG5) and at two stations outside the dumpsite (ChG7, ChG9). Arsenic concentration in the water of the Baltic Sea is too low for arsenic tolerating bacteria (~0.1-2.1 µg/l) [6, 8, 19], but every concentration anomaly can cause an appearance of such bacteria. Arsenic tolerating bacteria were found only at two stations of the dumpsite (ChG1 and ChG3), but the concentration of 6 cells ml⁻¹ was near the method sensitivity limit. The total bacteria quantity and saprophyte bacteria numbers were typical to the Baltic Sea environment [6].

The species composition, abundance, and biomass of phytoplankton were typical to the open Baltic Sea at the beginning of the summer. Phytoplankton cells, their shape, and color looked healthy.

Zooplankton analysis showed that crustaceans were ~37 % of all zooplankton and this number is the indicator of clean environment. However, 44-55 % of all crustaceans were *Evadne nordmanni*. Such a high density of this organism is not typical for that area of the Baltic. There were some anomalies in the physiology of organisms (small number of winter eggs, death of embryos at early stages, death of males). All that can indicate that there was a deterioration of nourishment conditions for *E.nordmanni* at the end of June 2003 [6, 21]. Although, to make some conclusions about chemical munitions impact on zooplankton, one study is not enough. It is not enough research done to know the impact of chemical warfare agents on the living organisms. The chemical munitions dumpsite in the Skagerrak was investigated and fauna around the shipwrecks looked to be generally healthy and representative of a normal deep-sea environment [4]. Although, more research and laboratory experiments are needed.

Arsenic concentration data are plotted in Fig.2. The concentration of arsenic in the sediments ranged from 1.1 to 19.0 mg/kg.
Sediments in the vicinity of the chemical munitions dumpsite had a slightly higher arsenic content compared to those from the other locations. However, as discussed below, these data, even from the dumpsite region, are low relative to other investigations of sediments in the Baltic and the North Seas.

For comparison, other studies have reported background values of total arsenic in sediments of the Baltic Sea ranging from 4 mg/kg in the Gulf of Finland [22] to 320 mg/kg in the Bothnian Bay [15]. The concentration of arsenic was about 15 mg/kg in the Baltic Proper sediments [16] and in the surface sediments of Bornholm Basin [23]. However, these later authors found lower values of about 9 mg/kg in the Gotland and North Central Basins of the Baltic Sea. In the western North Sea, minimum concentrations of arsenic in the sediments reported by Whalley et al. [10] were less than 0.15 mg/kg and reached 135 mg/kg in the coastal area.

With respect to chemical munitions dumpsites, some much higher concentrations in sediments have been reported whereby total arsenic varies from 9 to 480 mg/kg. The highest concentration was found in the samples from the dumpsite in Skagerrak; high concentrations of Clark I, triphenylarsine, and bis(diphenylarsino)oxide were found in the same samples [4]. 10 mg/kg of Clark I was found in the samples from the Bornholm dumpsite in 1992; this site is characterized by high dispersion and sharp anomalies for total arsenic, which range from 18 to 210 mg/kg [3, 5]. High arsenic levels of up to 200 mg/kg were found in the samples from the Skagerrak several centimetres below the bottom/water interface [5]. Deeper sediment horizons (10-11 cm) at the Gotland (Liepaja) dumpsite had elevated arsenic contents with concentrations up to 100 mg/kg [24]. Such pollution was not evident in the upper layers of sediments and in bottom water at this site. In contrast, Paka and Spiridonov [5] concluded that arsenic distribution in the surface sediments of the Gotland dumpsite is characterized by low dispersion and the absence of high levels, reporting arsenic concentrations from 18 to 28 mg/kg. The maximum arsenic value obtained in the Lithuanian sector as reported here, namely 19 mg/kg, falls within this interval.

Metal concentrations in sediments vary as a function of grain size. The <2 µm fraction of the sediment is one of the major sinks for contaminants introduced into natural waters, largely due to the presence of clay minerals, together with associated coatings of organic material and iron and manganese (oxy-)hydroxide precipitates. Such substances scavenge dissolved trace metals from the water column and act to transport metals to the sediments [9, 10]. Sedimentological analysis showed that fine-grained sediments had higher metal concentrations. Sediment types at the chemical munitions dumpsite vary from fine-grained sand (stations ChG5, ChG4, ChG3) to silt mud (ChG2) and extra-silt mud (ChG1) [6].

A good correlation (coefficient of 0.9) between iron and arsenic was observed in these sediments (Fig.3), given that iron can be used to normalize the arsenic data from the Lithuanian coastal zone. The concentration of iron ranged from 2.2 to 47.8 g/kg, with an average of 10.7 g/kg.

\[
As = -0.884118 + 0.399141 \times Fe \\
r = 0.913
\]

Fig.3. Correlation between Fe and As in the Baltic Sea sediment (95 % confidence limits are shown, r - correlation coefficient)

Fig.4. Residual arsenic normalized to iron
Arsenic residuals plotted against the station (Fig. 4) showed slightly higher concentrations in some samples from the chemical munitions dumpsite, notably at stations ChG2-4. There are large negative residuals in the samples from the dumpsite of dredged port sediments (stations 20 and 20A). These sediments are not contaminated with arsenic and indicate that the port is not a source of arsenic to the marine environment.

4. Conclusions

All the studied parameters did not show any drastic changes of the Baltic Sea environment at the chemical munitions dumpsite. Such parameters, as dissolved oxygen, pH, phosphates, total phosphorus, phytoplankton, total, and saprophyte bacteria numbers were typical to the Baltic Sea environment during the summer season. Although, such parameters, as arsenic, arsenic tolerating bacteria, and zooplankton didn’t give a well-defined answer.

An analysis of sediment samples taken from the Lithuanian economic zone of the Baltic Sea showed that there were higher arsenic concentrations near the chemical munitions dumpsite (average 9.7 mg/kg) compared to other coastal locations (2.1 mg/kg). Normalization of results to iron showed slightly elevated residual arsenic concentrations near the dumpsite. However arsenic concentrations data, even from the dumpsite region, were low relative to the other investigations in the Baltic and North Seas.

This preliminary study focussed on some parameters, measured during the expedition to the chemical munitions dumpsite. For a definitive assessment about the possible leakage of poisonous contaminants, more research is needed, such as the determination of various individual toxic substances, including arsenic-containing munitions, measuring long-time series of different parameters, using different equipment to obtain a visual expression of the dumped munitions. Thus, chemical munitions remain an important subject for future environmental investigations.

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Arsenas ir kai kurie aplinkos parametrai Baltijos jūros Lietuvos ekonominės zonos nuskandinto cheminio ginklo rajone

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