

Arsenic in sediments from the southeastern Baltic Sea

Galina Garnaga^a, Eric Wyse^b, Sabine Azemard^b, Algirdas Stankevičius^a, Stephen de Mora^{b,*}

^a Centre of Marine Research, Taikos av. 26, LT-91149, Lithuania

^b International Atomic Energy Agency, Marine Environment Laboratory, 4 quai Antoine 1^{er}, MC 98000, Monaco

Received 8 April 2005; accepted 3 February 2006

Arsenic concentrations in sediments near chemical weapons dumpsites were only slightly elevated.

Abstract

Arsenic occurs as a persistent constituent in many of the chemical weapons dumped into the Baltic Sea; it can be used as an indicator of leakage and dispersal of released munitions to the marine environment. Total arsenic was analysed in sediment samples taken from the Lithuanian economic zone in the Baltic Sea, which included samples from the chemical munitions dumpsite in the Gotland Basin and national monitoring stations in the southeastern Baltic Sea. Arsenic concentrations in sediments ranged from 1.1 to 19.0 mg kg⁻¹, with an average of 3.4 mg kg⁻¹. Although there was evidence of slightly elevated arsenic content in sediments near the weapons dumpsite, arsenic concentrations were nevertheless quite low relative to other investigations in the Baltic and North Seas.

© 2006 Published by Elsevier Ltd.

Keywords: Baltic Sea; Sediment; Arsenic; Iron; Chemical munitions; Lithuania

1. Introduction

Large quantities of chemical munitions were dumped in European waters after World War II. More than 40 vessels loaded with such ordnance 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 (Duursma, 1999; Glasby, 1997; HELCOM CHEMU, 1994; Tørnes et al., 2002). 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) (HELCOM CHEMU, 1994). Arsenic is a major constituent of chemical munitions such as Clark I, Clark II, adamsite, lewisite and arsine oil. The quantity of these chemical compounds is approximately one-third of the chemical warfare agents dumped in the east of Bornholm and southeast of Gotland (HELCOM CHEMU, 1994).

Lewisite (C₂H₂AsCl₃) reacts with water to form chlorvinyl arsine oxide, which in alkaline solution can react further to produce arsenic acid and acetylene (HELCOM CHEMU, 1994). Arsine oil is a technical mixture of arsenic(III) chloride, phenylarsine dichloride, diphenylarsine chloride and triphenylarsine (Haas et al., 1998). Clark I [(C₆H₅)₂AsCl] and Clark II [(C₆H₅)₂AsCN] are expected to adsorb onto sediments and react only very slowly with water. Both degrade eventually to form tetra-phenyldiarsine oxide, which is itself toxic and is hydrolysed very slowly. 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

* Corresponding author. Tel.: +377 9797 7272; fax: +377 9797 7276.

E-mail address: stephen.demora@gmail.com (S. de Mora).

preserved for a long time on the sea bed. However, they might also bioaccumulate in organisms (Glasby, 1997; HELCOM CHEMU, 1994; Tørnes et al., 2002). Clark I, Clark II and adamsite are expected to spread very slowly from the chemical munitions source and only contaminate local sediments (Duursma, 1999; HELCOM CHEMU, 1994; Tørnes et al., 2002). Thus, elevated arsenic concentrations in the sediments can indicate a leakage of chemicals from the containers.

The chemical warfare agents dumped in the sea pose three main threats (Glasby, 1997). 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 (Glasby, 1997). 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, with only slight bottom currents except during exceptional periods of flushing to the basins (Voipio, 1981). In addition, the dumped material would need to be moved upwards from a depth below 100 m in order to be washed ashore (Glasby, 1997; HELCOM CHEMU, 1994). The second threat is to fisherman who can trawl lumps of viscous mustard gas from the sea floor with their nets. Over the period 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 (Glasby, 1997). The third is the threat to the marine environment. There is a possibility of bioaccumulation of arsenic compounds in marine organisms (HELCOM CHEMU, 1994; Tørnes et al., 2002). 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 (Tørnes et al., 2002).

In Lithuania, the lack of information has caused public concern about the issue of chemical munitions in the sea. This investigation represents a preliminary survey to assess the potential hazard of the chemical munitions dumpsite in the Lithuanian economic zone. Relying on the fact that arsenic can be an indicator of leakage of toxic substances, total arsenic was analysed in sediment samples taken from the dumpsite and other stations in the southeastern part of the Baltic Sea.

2. Methods

2.1. Sample collection

The sediment samples were collected during two expeditions of the scientific research vessel *Vėjas* organized by the Ministry of Environment (Centre of Marine Research) and the Ministry of National Defence of Lithuania. The first mission in June 2003 went to the chemical weapons dumpsite. Sampling stations at the dumpsite were chosen near chemical

weapon units, according to sonar data obtained from scanning the seafloor by a Lithuanian naval vessel. The second mission in August 2004 visited Lithuanian national monitoring stations. Five stations, which were sampled during the first mission, were revisited to check sampling variability. Sampling locations are illustrated in Fig. 1, distinguishing samples collected on the first mission by the prefix ChG. Fourteen sediment samples were collected during the first expedition in June 2003, of which 5 samples were from the chemical munitions dumpsite (ChG1–ChG5 stations), and 16 samples during the expedition in August 2004. Samples 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. After transportation to the laboratory, samples were stored in a deep-freezer at a temperature of ~−23 °C.

2.2. Chemical analyses

Frozen samples were carried from Lithuania to the International Atomic Energy Agency—Marine Environment Laboratory in Monaco, where they were freeze-dried. They were then transferred to individual clean Ziplock bags and shaken to obtain a homogeneous powder. All samples were digested using a CEM MARS5 high-pressure microwave digestion system. Approximately 250 mg of dried sediment was weighed and digested in acid-cleaned Teflon microwave vessels using 5 ml of nitric acid and 2 ml of concentrated hydrofluoric acid (Merck Suprapur in both cases). 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. To permit the use of a higher ashing temperature Pd(NO₃)₂ and Mg(NO₃)₂ matrix modifiers were used. The injection volumes were 1 µl of a 10 g L^{−1} Pd(NO₃)₂ solution and 3 µl of a 10 g L^{−1} Mg(NO₃)₂ solution. The sample volume varied from 2 to 20 µl, depending on sample concentration. Calibration was carried out by the standard addition method. Replicate blanks, replicate samples and reference material (IAEA 433) were analysed for quality control purposes. The relative standard deviation of four replicate digestions of the reference material, IAEA 433, was 3%. With respect to sediment samples, the relative standard deviation estimated from three or four replicate digestions of three different samples varied from 3% to 7%.

Download English Version:

<https://daneshyari.com/en/article/4427322>

Download Persian Version:

<https://daneshyari.com/article/4427322>

[Daneshyari.com](https://daneshyari.com)