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Weight-of-evidence environmental risk assessment of dumped chemical weapons after WWII along the Nord-Stream gas pipeline in the Bornholm Deep

Hans Sanderson^{a,*}, Patrik Fauser^a, Marianne Thomsen^a, Jørn Bo Larsen^b

^a Aarhus University, Department for Environmental Science, Denmark

^b Ramboll Oil and Gas, Denmark

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ABSTRACT

In connection with installation of two natural gas pipelines through the Baltic Sea between Russia and Germany, there has been concern regarding potential re-suspension of historically dumped chemical warfare agents (CWA) in a nearby dump site and the potential environmental risks associated. 192 sediment and 11 porewater samples were analyzed for CWA residues, both parent and metabolites in 2008 and 2010 along the pipeline corridor next to the dump site. Macrozoobenthos and background variables were also collected and compared to the observed CWA levels and predicted potential risks. Detection frequencies and levels of intact CWA found were low, whereas CWA metabolites were more frequently found. Re-suspension of CWA residue-containing sediment from installation of the pipeline contributes marginally to the overall background CWA residue exposure and risk along the pipeline route. The multivariate weight-of-evidence analysis showed that physical and background parameters of the sediment were of higher importance for the biota than observed CWA levels.

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1. Introduction

In their Feature in *Environmental Science and Technology* Brewer and Nakayama [1] pleaded for better or complete information concerning the whereabouts of thousands of tonnes of chemical weapons disposed of at sea globally in order to better assess the environmental risks they may pose. There are a number of reasons for the decades of lack of information and delay in addressing this problem in the United States, the European Union (EU) and elsewhere. Many dumping operations were carried out secretly and it is not always clear who can be held responsible. Moreover, there is often a lack of official records of the dumping operations, which often took place under chaotic circumstances decades ago [1].

Sanderson et al. [2] responded in a new Feature in *Environmental Science and Technology* with the most comprehensive study so far regarding the environmental risks of sea dumped CWA (MERCW [W1]). The study area was the Bornholm Deep, nearby the Danish island Bornholm in the Baltic Sea, where approximately 32,000 tonnes of German chemical weapons, containing about 11,000 tonnes of highly toxic agents [3] were dumped after World War II. Fig. 1 illustrates the primary dumpsite area marked by a circle with a radius of three nautical miles with water depths ranging from 70 to over 96 m. However, it is likely that the chemical munitions were spread over a larger area. The extended dumpsite is marked by a rectangular area roughly ranging between $55^{\circ}07'N-55^{\circ}26'N$ and $15^{\circ}25'E-15^{\circ}55'E$. The primary dump site covers approximately 100 km^2 , and the secondary dump site covers a total of approximately 800 km^2 (Fig. 1) [3].

In December 2010 the United Nations General Assembly adopted resolution A/RES/65/149: Cooperative measures to assess and increase awareness of environmental effects related to waste originating from chemical munitions dumped at sea [W2]. The resolution stipulates the global sharing of information on this topic.

Chemical warfare agents are illicit compounds that have been used in conflicts for centuries from poisonous smoke to nerve gas. The use of CWA in conflicts was banned following the third Geneva Convention in 1925 [4]. In 1993 most countries in the world ratified the Chemical Warfare Convention mandating the destruction of CWA by 2012. Previously dumping was the preferred destruction method, but this was prohibited with the London Convention on the prevention of marine pollution by dumping of wastes and other matter (MARPOL) in 1973. Nowadays the destruction methods involve more costly incineration and conversion to peaceful products [5].

CWAs represent environmental legacy contaminants as the bulk production and subsequent dumping of CWA typically occurred decades ago. Despite of being legacy contaminants it is not only the location and amounts of ocean dumped CWA that is unknown. Due to their illicit status, their inherent properties with regards to physico-chemical, fate, long-term human and environmental

^{*} Corresponding author. Tel.: +45 8715 8632; fax: +45 8715 8904. *E-mail address:* hasa@dmu.dk (H. Sanderson).

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Fig. 1. Bathymetry and location of the chemical munition dumpsite in the Bornholm Basin in the Danish territory zone (dashed line), the dotted line represents survey area. The grey line marks the area where fishermen have caught chemical munitions.

toxicity properties have not been characterised comprehensively [6]. CWA dissipation has been described under laboratory conditions [7] but little is known about the dissipation of CWA at deep sea [8]. Some environmental toxicity data exists, but the majority of these are purely anecdotal, derived during the 1950–1970s and not meeting current standard methods for dosimetry and statistical control [5].

In May 2011 the company Nord Stream AG completed the first of two 1224 km natural gas pipelines through the Baltic Sea connecting Russia and Germany. The 7.4 billion Euros Nord Stream AG project provides a fixed link between the European gas grid and some of the world's largest gas reserves in Russia for at least the next 50 years. The pipelines will supply 55 billion cubic meters of Russian gas per year to the EU. The pipelines by-pass the CWA dump site – but are within the waters where fishermen previously have caught munitions causing concerns regarding perturbation and re-suspension of CWA contaminated sediments [W3].

The aim of this study is to report the findings of CWA residues along the pipeline route, and to assess the risk that perturbed sediments containing CWA residues near the dump sites may represent towards the environment in the Bornholm Deep.

2. Materials and methods

2.1. Sampling and route description

Sampling of CWAs, benthos and background parameters along the Nord Stream AG pipeline route was carried out in May 2008 and again in July 2010. Sediment samples for chemical analyses were taken with a Haps core sampler (4.5 L) at 28 stations. At 11 of the 28 main positions, duplicate samples were taken for porewater from the upper 5 cm of the sediment core. At 10 positions, four locations were sampled perpendicular to the pipeline route. The locations of these stations were 500 m north, 250 m north, 250 m south and 500 m south of the main station (annotated as e.g. 250S) (Fig. 2). At all stations, sediment samples were taken from the upper 5 cm of the core, moreover 15 samples were collected at 5–50 cm and four at 50–100 cm depth. A total of 94 sediment samples and 11 porewater samples have been collected for chemical analyses (CWA 1–28).

Moreover, sediment samples were collected using a Van Veen grab sampler (0.1 m^2) for analysis of macro zoobenthos and sediment classification (grain size distribution, loss on ignition (LOI),

total organic carbon (TOC)), measurements of near-bottom water dissolved oxygen levels, salinity, temperature, depth and turbidity at 22 central sampling stations along the entire sampling stretch along the pipeline route. A PVC NISKIN 5.0 L was used to collect near bottom water. Macrozoobenthos wet and dry weight were measured and the total abundance and total species richness counted for each sample in the lab. The sediment characteristics for each of the sampling locations were reported and a video recording of the bottom at the sampling stations was performed.

Additional details and other aspects in the Espoo Environmental Impact Analysis, for the entire pipeline route are available [W2].

2.2. Analytes

The dump site in the Bornholm Deep is one of the better characterised in terms of dumped materials. The Russian authorities provided this information in 1994 to the Helsinki Commission the Baltic Marine Environment Protection Commission [3] (Table 1).

Hence, these compounds were the primary initial target analytes of the sampling and analytical efforts. Since mustard gas (yperite) is by far the largest constituent analytical, emphasis was also placed on its primary degradation products: thiodiglycol (TGD) and thiodiglycol sulfoxide (TGDS).

Table	1
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Confirmed dumped chemical warfare agents in Bornholm basin [6].

Compound	CAS number	Dumped CWA (tonnes)
Chloroacetophenone (CAP) ^a	532-27-4	515
Sulphur mustard gas (yperite) ^b	505-60-2	7027
Adamsite ^c	578-94-9	1428
Clark I ^d	712-48-1	711.5
Triphenylarsine ^d	603-32-7	101.5
Phenyldichloroarsine ^d	696-28-6	1017
Trichloroarsine ^d	7784-34-1	101.5
Other (Tabun) ^e	77-81-6	74

^a Riot control agent.

^b Blistering agent.

^c Organoarsenic blistering agent.

^d Arsine oil constituents – organoarsenic blistering agent.

^e Nerve gas.

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