



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

Hans Sanderson<sup>a,\*</sup>, Patrik Fauser<sup>a</sup>, Marianne Thomsen<sup>a</sup>, Jørn Bo Larsen<sup>b</sup>

<sup>a</sup> Aarhus University, Department for Environmental Science, Denmark

<sup>b</sup> Ramboll Oil and Gas, Denmark

## ARTICLE INFO

### Article history:

Received 10 November 2011  
Received in revised form 20 February 2012  
Accepted 21 February 2012  
Available online 1 March 2012

### Keywords:

CWA  
Marine  
Pipeline  
Sediment  
Weight-of-evidence

## 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 pipelines 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.

© 2012 Elsevier B.V. All rights reserved.

## 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

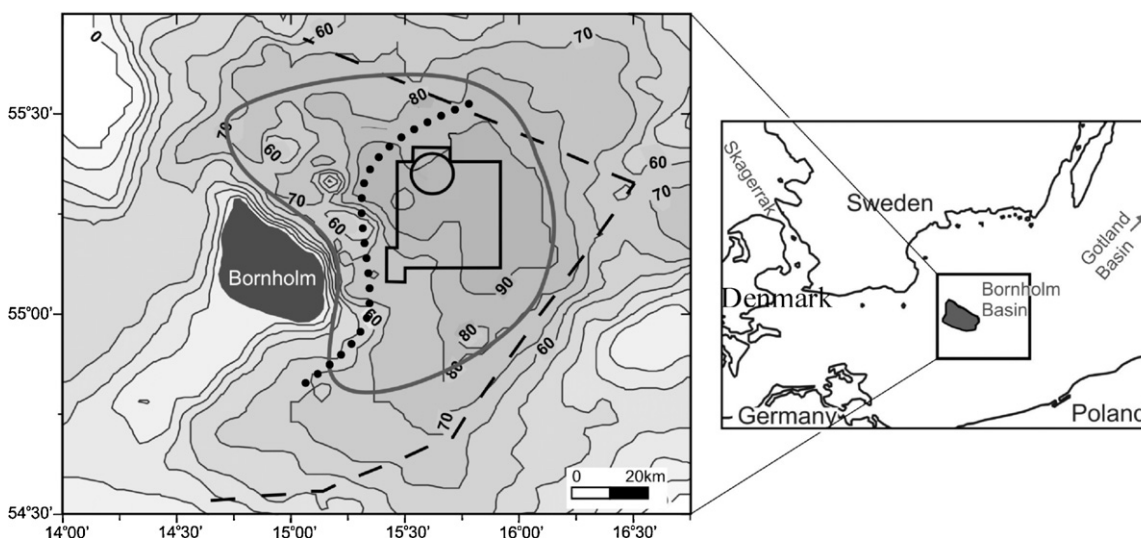
area. The extended dumpsite is marked by a rectangular area roughly ranging between 55°07'N–55°26'N and 15°25'E–15°55'E. The primary dump site covers approximately 100 km<sup>2</sup>, and the secondary dump site covers a total of approximately 800 km<sup>2</sup> (Fig. 1) [3].

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](mailto:hasa@dmu.dk) (H. Sanderson).



**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<sup>2</sup>) 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**  
Confirmed dumped chemical warfare agents in Bornholm basin [6].

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

<sup>a</sup> Riot control agent.

<sup>b</sup> Blistering agent.

<sup>c</sup> Organoarsenic blistering agent.

<sup>d</sup> Arsine oil constituents – organoarsenic blistering agent.

<sup>e</sup> Nerve gas.

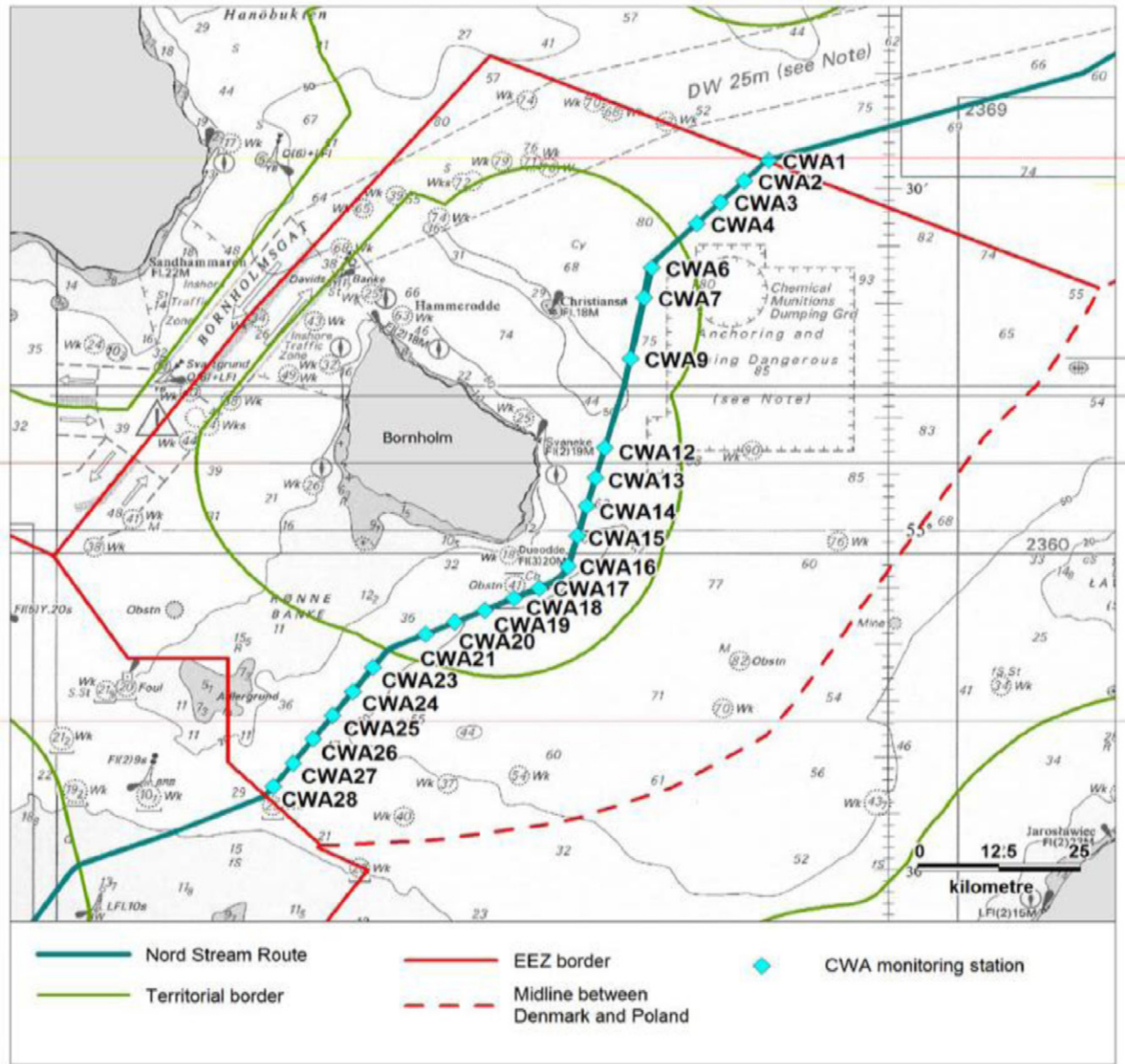


Fig. 2. Sampling stations (CWA 1–28) along the pipeline route.

### 2.3. Sample handling, background variables, biota and chemical analysis

All samples collected for chemical analysis were frozen onboard the ship and sent to the Finnish Institute for Verification of the Chemical Weapons Convention (VERIFIN) [W4] appointed by the United Nations for chemical analysis as the global reference laboratory for CWA identification [9]. Both GC–MS and LC–MS–MS methods were used depending upon the CWA. Agilent 6890N gas chromatograph (GC) equipped with an automatic liquid injector and an Agilent 5975B mass selective detector (MSD) was used. The capillary column used was a DB-5ms (Agilent, 30 m × 0.25 mm i.d., 0.25 μm film). The column temperature was programmed from 40 °C (isothermal time 1 min) to 280 °C at 10 °C/min and held at final temperature for 10 min. On-column injection was used with the injector temperature programmed to stay 3 °C above the oven temperature. The carrier gas was helium with a flow of 35 cm/s at 40 °C.

The transfer line between the GC and MSD temperature was kept at 280 °C. The LC–MS–MS analysis of target chemicals was performed using a ThermoScientific Accela liquid chromatograph and ThermoScientific TSQ Quantum Ultra mass spectrometer. The analysis was done using atmospheric pressure chemical ionisation (APCI) technique followed by multiple reaction monitoring (MRM). The ionisation method was positive APCI, except for L1 negative APCI was used. A six-point calibration (ca. 10–400 pg/μL) was applied using dimethyl methylphosphonate (DMMP) as internal standard (ISTD) [9].

Macro zoobenthos samples were collected and sieved through a 1 mm mesh sieve and conserved with 96% alcohol and shipped to the lab at the Danish Biology Lab [W5] in Nærum, Denmark, for identification and initial analysis. Sediment characteristic and background variables were identified instantaneously aboard the ship using a CTDO-recorder (model SD204), WTW salinity probe and a HQ40D multi electrode for dissolved oxygen [10].

#### 2.4. Sediment suspension and Predicted Environmental Concentrations (PECs)

The sediment concentrations,  $C_s$  (mg/kg dry matter (DM)), was used to calculate the fish bioavailable porewater CWA concentrations,  $C_{pw}$  (mg/L), for all the samples based on adapted equilibrium partitioning [11,12] Eq. (1).

$$C_{pw} = \frac{C_s \times X_s}{R_s} = \frac{C_s / (\theta + K_d \times X_s)}{X_s} \quad (1)$$

where  $R_s = (\theta + K_d \times X_s)$  is the retention factor,  $\theta$  is the pore volume fraction in the sediment 0.55 (clay/silt to sandy sediments) [13],  $K_d = f_{oc} \times K_{oc}$  is the partitioning coefficient between dry matter and water in L/kg DM,  $f_{oc} = 0.0775$  is the fraction of organic carbon in particulate matter [14],  $K_{oc}$  is the partitioning coefficient (sorption coefficient) between organic matter and water (L/kg OM) and  $X_s$  is the density of sediment 1.2 kg DM/L [13].

Quasi steady-state sediment and porewater concentration ( $C_{pw}(qs)$ ) are calculated from Eq. (1). No measured sorption coefficient values are available for the considered chemicals, therefore modelled  $K_{oc}$  values from EPI Suite 4.10 [W6] and the US National Library of Medicine Hazardous Substances Data Base (HSDB) [W7] are used (Table 5). As a worst case assumption  $C_{pw}(qs)$  is also assumed in the bottom water boundary layer just above the sediment.

#### 2.5. Pipeline construction – sediment suspension and PECs

The added CWA risk from sediment agitation from installing the pipelines based on assumptions related to the installation of one gas pipeline is calculated. The contribution from the release of sediment particles during the following pipeline activities are described as follows.

- (1) Trenching of a 11.35 km section (West Pipeline) and a 9.49 km section (East Pipeline) by plough east of Bornholm. Disturbance and dispersion (spill) of suspended sediment is estimated to be 2200 tonnes (West Pipeline) and 1840 tonnes (East Pipeline), respectively [15]. The assessment of sediment suspension is based on a trenched distance of 10 km and performed with the numerical particle analysis model MIKE 3PA [16]. The affected area with concentrations of suspended sediment higher than 10 mg/L in bulk water between 0 and 10 m above the seabed is estimated to be 5.9 km<sup>2</sup> and the duration of this elevated sediment concentration will be approximately 3 h. The affected area is proportional with the trench-length, and the sediment concentration in the bulk water between 0 and 10 m above the seabed, for the West and East Pipeline sections, is thus:

$$\begin{aligned} C_w(\text{sed, trenching}) &= \frac{2200 \text{ tonnes}}{5.9 \times 10^6 \text{ m}^2 \times 1.135 \times 10 \text{ m}} \\ &= 33 \text{ mg sediment/L.} \end{aligned}$$

The time between trenching of the two pipelines exceeds the average duration of elevated concentrations so there should be no additivity of the sediment concentration in overlapping areas.

- (2) Pipe-laying directly on the seabed. Only small amounts of sediment, around 300 kg/km, have been found to be suspended during pipe-laying directly on the seabed for worst-case scenarios where the pipeline is placed on soft clay. Sediment suspension during pipe-laying is negligible compared with

suspension during trenching and is therefore not accounted for in the modelling of spreading and sedimentation [15].

- (3) Handling of 12 anchors during pipe laying, each weighing 25 tonnes, causes sediment suspension from laying anchor, lifting anchor and sweeping anchor wires across the seabed. The sweeping process is most predominant with respect to sediment disturbance and the total amount of suspended sediment has been calculated to range from 10 to 38 tonnes sediment/km of the pipeline in areas with soft sediment [15]. The area inside the anchor corridor with increased turbidity caused by anchor handling has been calculated to be approximately 0.04 km<sup>2</sup> (2% of the total anchor corridor). This gives a sediment concentration in the release area and lower 10 m (release water volume) of  $C_w(\text{sed, sweeping}) = 25\text{--}95$  mg sediment/L. When assuming that sediment particles from the release area are dispersed to the total anchor corridor area, the average sediment concentration is approximately 0.5–2 mg/L [15].

The worst-case scenario for additional concentration in bottom-layer bulk water from pipeline installations assumes that once sediment particles are suspended to the bulk water all the sorbed CWAs are instantaneously released and mixed within a release area of approximately 2% (0.04 km<sup>2</sup>/km) of the anchor corridor. This gives a sediment concentration in the release area and lower 10 m (release water volume) of:  $C_w(\text{sed}) = 95$  mg sediment/L, from sweeping, and  $C_w(\text{sed}) = 128$  mg sediment/L, from sweeping and trenching. Sweeping occurs along the entire pipeline, whereas trenching occurs only at a few mid-section sites.

The worst-case CWA concentration in the release bulk water volume from pipeline activities,  $C_w(pl)$  in mg CWA/L, is thus:

$$C_w(pl) = C_w(\text{sed}) \times C_s \quad (2)$$

where  $C_s$  is the highest measured CWA concentration in sediment, in mg/kg DW. The worst-case concentration is calculated for single CWAs and sum of CWAs. The total worst-case predicted biota CWA exposure concentration in the bulk boundary layer is thus a sum of the quasi steady-state concentration and the added concentration from pipeline activities:

$$C_w(\text{worst-case}) = C_{pw}(qs) + C_w(pl) \quad (3)$$

#### 2.6. Environmental toxicity

Predicted toxicity values for individual CWAs to be used in assessing the risk will be used according to Sanderson et al. [14]. For arsenicals it is recommended from a conservative point of view to use the toxicity of inorganic As [12]. We derived the toxicity data on inorganic As from HSDB. The data were used to derive a measured species sensitivity distribution (SSD) for 12 fish species (adult and juvenile). The assessment factors associated with the SSD-derived PNECs (predicted no observed effect concentrations) typically range between 1 and 5 on a case-by-case basis and have not been included in this analysis. The resulting acute HC5 represents the concentration where 95% of the acute LC50 of the fish species in the community is not exceeded, HC5 value = 0.29 mg/L (Fig. 3).

#### 2.7. Statistics

Uni- and multivariate data analyses were performed in the sampling station areas where biological and chemical measurements were available. Correlation analysis and pattern recognition were performed by means of principal component analyses (PCA) based on average and log-transformed measurements (Table 7 and Annex 1). PCA is performed by projecting information carried by a number of original variables onto a smaller number of underlying ('latent')

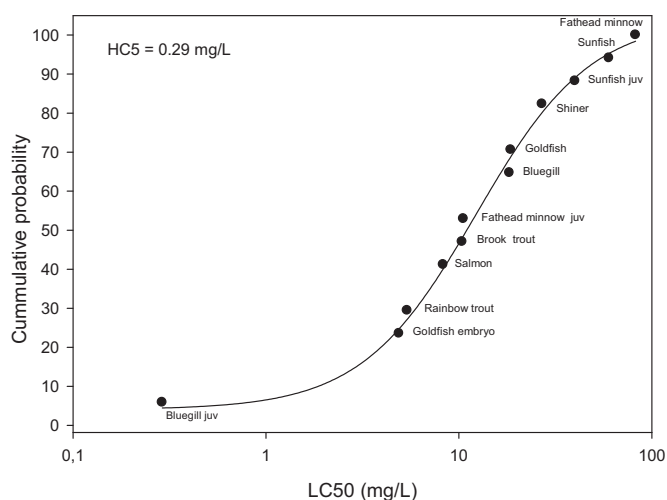


Fig. 3. Organoarsenic CWA fish community toxicity.

variables called principal components. The first principal component (PC) covers as much of the variation in the data as possible. The second PC is orthogonal to the first and covers as much of the remaining variation as possible and so on ( $PC_n$ ). The interrelationships between different variables may be visualised graphically by plotting the PCs; the PC plots may be used to detect and interpret sample patterns, groupings, similarities or differences among samples.

## 2.8. CWA degradation products

Sanderson et al. [4] have previously reported that the project MERCW collected 59 sediment samples and 61 near-bottom water samples (<0.2 m above the seafloor) from 63 sampling points in February 2008 that were analyzed by VERIFIN. No intact CWA was found in any of the samples, except for one stable component in arsenic oil, triphenylarsine in the sediment. 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. Several degradation products of yperite, Clark I, adamsite and arsenic oil components were detected in the 59 sediment samples [4]. With these findings in mind, we focused on adding all relevant degradation products to a second CWA sampling effort in 2010 along the pipeline route. All samples were collected, handled, and analyzed consistent with the previous analysis in 2008 by VERIFIN [9].

Sampling was carried out July 2010. To optimise detection frequencies sediment samples for CWA analyses were taken from the upper 5 cm of the core, porewater samples were not collected. A total of 98 sediment samples along 23 sampling stations and six transects of 15 stations perpendicular to the route were collected, which included the analytes from the 2008 effort plus the degradation products listed in Table 2.

Levels of Quantification (LoQ) ranged from 3.7 to 39  $\mu\text{g}/\text{kg}$ , with Clark I as the outlier at 156  $\mu\text{g}/\text{kg}$  due to instability due to rapid degradation in the lab.

## 3. Results

### 3.1. Measured CWA concentrations – 2008

Among the active CWAs only Adamsite and Clark I was detected in 3.5% and 19.5%, respectively, of all the collected samples. The highest concentrations of CWAs were found at sampling station

CWA16. The most frequently detected CWA was the arsenic oil constituent PDA at 26%. PDA also recorded the highest concentration at 0.6 mg/kg DM (Table 3). The majority of positive CWA residue samples were obtained from the upper sediment layers (5 cm) collected at all sampling sites, and only positive residues were found in a nine samples from the deeper samples up to 100 cm out of 19 samples.

There were few detections of CWA in porewater due to the relatively high hydrophobicity of the compounds (Table 4).

### 3.2. Measured CWA concentrations – 2010

During the second sampling effort in 2010 emphasis was on adding more degradation products to the existing list of analytes (Table 5).

Among the 98 samples collected in 2010 only two samples had CWA residues that exceeded the LoQ (Table 6) (detection frequency ~2%). No parent CWA compounds were detected. Both of the positive samples were obtained at sampling station CWA5.

Both of them are degradation products from organoarsenic CWAs. L2[ox] is a degradate originating from divinylarsinic acid, which again can originate from Lewisite II. PDCA[SPr] originates from phenylarsonic acid and phenylarsonous acid, which again may be degradates of the arsenic oil constituent phenyldichloroarsine [15].

### 3.3. CWA Predicted Environmental Concentrations (PEC)

The resulting worst case CWA exposure concentrations  $C_w$ (worst-case) are summarised in Table 7.

### 3.4. CWA risk towards the fish community

The combined highest CWA related exposure was found at site CWA19 (250N) and CWA16 (250S) at 0.029 mg/L and 0.014 mg/L, respectively. At CWA19 the risk is driven almost entirely by TCA with a risk quotient ( $RQ = PEC/HC5$ ) of 0.28. At CWA16 the risk is driven by PDA with a RQ of 0.09 (adamsite with  $RQ = 0.05$ , TCA with  $RQ = 0.03$ ). The CWA risk contribution from perturbed sediment is significantly lower compared with those in the conservative quasi steady-state background modelling risk estimate. Less than 5% of the sediment area will be directly perturbed by the construction. The predicted CWA risk, which is along the Nord Stream AG route from perturbed sediment, is greatest at CWA16 (250S and 500S) with  $RQ = 0.004$ . Hence, the maximum total RQ (quasi steady-state + perturbed sediment) is found at CWA19 (250N) and CWA16 (250S) with RQs of 0.29 and 0.18, respectively.

For the 2010 data the total calculated CWA residue exposure is 0.62 and 0.18  $\mu\text{g}/\text{L}$ , respectively at CWA5, for L2[ox] and PCDA[SPr] and thus the total CWA related exposure is 0.8  $\mu\text{g}/\text{L}$ . This results in a risk quotient of 0.02 and 0.006, respectively, for L2[ox] and PCDA[SPr], for the sum of quasi steady-state concentrations at the sediment boundary layer and the re-suspended sediment at the two sites, hence the total CWA related  $RQ = 0.026$ .

### 3.5. Weight-of-evidence risk analysis

It is clear from Fig. 4 that biota co-vary with DO; physical data/parameters are also not surprisingly intercorrelated. However, there is no strong intercorrelation between the sum of CWA and biota. The ecological quality, biota and DO, shows an inverse correlation to the physical parameter in PC1 and to a lesser extent CWA and turbidity. In PC2, i.e. vertical direction, an inverse relationship between turbidity and CWA concentration are observed.

**Table 2**  
Chemical names, CAS numbers and acronyms are stated for each compound.

Degradation products analytes	CAS #	Acronym	Relationship
Phenoarsazin-10(5H)-ol	18538-32-4	–	Hydrolysis product of DM
10-(Phenoarsazin-10(5H)-yloxy)-5,10-dihydropheno-arsazine	4095-45-8	–	Hydrolysis product of DM
5,10-Dihydropheno-arsazin-10-ol 10-oxide	4733-19-1	DM[ox]	Natural oxidation product of DM
Diphenylarsinous acid	6217-24-9	–	Derivative (H <sub>2</sub> O <sub>2</sub> ) of DM and its degradation products
Bis(diphenylarsinic)oxide	2215-16-9	–	Hydrolysis product of DA (and other diphenylarsine chemicals)
Diphenylarsinic acid	4656-80-8	DPA[ox]	Hydrolysis product of DA (and other diphenylarsine chemicals)
Vinylarsinous acid	85090-33-1	–	Natural oxidation product of DA
2-Chlorovinylarsinic oxide	3088-37-7	–	Derivative (H <sub>2</sub> O <sub>2</sub> ) of DA and its degradation products
2-Chlorovinylarsonic acid	64038-44-4	L1[ox]	Hydrolysis product of L1
Dipropyl 2-chlorovinyl-arsonodithioite	677354-97-1	L1[SPr]	Natural oxidation product of L1
Divinylarsinic acid	157184-20-8	–	Derivative (H <sub>2</sub> O <sub>2</sub> ) of L1
Bis(2-chlorovinyl)arsinic acid	157184-21-9	L2[ox]	(PrSH) of L1
Propyl bis(2-chlorovinyl)-arsinothioite	677355-04-3	L2[SPr]	Hydrolysis product of L2
Phenylarsonous acid	25400-22-0	–	Natural oxidation product of L2
Phenylarsonic acid	98-05-5	PDCA[ox]	Derivative (H <sub>2</sub> O <sub>2</sub> ) of L2
Dipropyl phenylarsonodithioite	1776-69-8	PDCA[SPr]	Derivative (PrSH) of L2
Tripropyl arsonotrithioite	5582-57-0	TCA[SPr]	Hydrolysis product of PDCA
			Natural oxidation product of PDCA
			Derivative (H <sub>2</sub> O <sub>2</sub> ) of PDCA
			Derivative (PrSH) of TCA

If we focus on the sediment characteristics in relation to the biology (PC2) and CWA concentration (PC1), it is clear that muddy sediments (M) do not overlap with sandy sediments (S). Sandy sediments co-vary with biota and muddy sediment co-vary with CWA residues (Fig. 5).

Muddy sediments (M) correlated with CWA detections (PC1 covariates) with low biological abundance and oxygen concentration in the water – resulting in positive score values in PC1. All types of sandy sediments have negative score values in PC1 characterised by high biological abundance,

**Table 3**  
Summary of measured CWAs in sediment from 35 sampling stations along the Nord Stream AG route.

Compound	Max. (mg/kg DM)	Mean ± SD (mg/kg DM)	Detection frequency (%)	Max. sampling station
Adamsite <sup>a</sup>	0.2	0.032 ± 0.074	3.5%	CWA16 (250S)
Clark I <sup>a</sup>	0.051	0.016 ± 0.012	19.5%	CWA16 (250S)
Lewisite I <sup>a</sup>	<LoD <sup>d</sup>	–	0	–
Lewisite II <sup>a</sup>	<LoD	–	0	–
Yperite <sup>a</sup>	<LoD	–	0	–
CAP <sup>a</sup>	<LoD	–	0	–
Tabun <sup>a</sup>	<LoD	–	0	–
TPA <sup>b</sup>	0.017	0.01 ± 0.005	2.5%	CWA16 (500N)
PDA <sup>b</sup>	0.606	0.036 ± 0.089	26%	CWA16 (250S)
TCA <sup>b</sup>	0.09	0.019 ± 0.023	12.5%	CWA19 (250N)
TGD <sup>c</sup>	<LoD	–	0	–
TGDS <sup>c</sup>	<LoD	–	0	–

<sup>a</sup> Active parent CWA compound.  
<sup>b</sup> Arsenic oil constituent.  
<sup>c</sup> Yperite degradation product.  
<sup>d</sup> LoD, limit of detection.

**Table 4**  
Summary of measured CWAs in porewater from 11 sampling stations along the Nord Stream AG route.

Compound	Max. (mg/L)	Mean ± SD (mg/L)	Detection frequency (%)	Max. sampling station
Adamsite <sup>a</sup>	<LoD <sup>d</sup>	–	0	–
Clark I <sup>a</sup>	0.002	0.002 ± 0	27%	CWA22
Lewisite I <sup>a</sup>	<LoD <sup>d</sup>	–	0	–
Lewisite II <sup>a</sup>	<LoD	–	0	–
Yperite <sup>a</sup>	<LoD	–	0	–
CAP <sup>a</sup>	<LoD	–	0	–
Tabun <sup>a</sup>	<LoD	–	0	–
TPA <sup>b</sup>	0.002	0.002 ± 0	18%	CWA22
PDA <sup>b</sup>	0.002	0.002 ± 0	18%	CWA22
TCA <sup>b</sup>	0.003	0.002 ± 0	27%	CWA22
TGD <sup>c</sup>	<LoD	–	0	–
TGDS <sup>c</sup>	<LoD	–	0	–

<sup>a</sup> Active parent CWA compound.  
<sup>b</sup> Arsenic oil constituent.  
<sup>c</sup> Yperite degradation product.  
<sup>d</sup> LoD, limit of detection.

**Table 5**  
CWAs and priority degradation, hydrolysis and oxidation products of CWAs that were analyzed in sediment and pore water samples. Koc and Rs (see Eq. (1)) are included for detected CWAs.

Target CWA analytes	Symbol	Koc	Rs
Sulphur mustard (yperite)	H	–	–
Adamsite	DM	5000	470
Clark I	DA	19,000	1770
Triphenylarsine	TPA	440,000	40,900
Chloroacetophenone (CAP)	CN	–	–
Tabun	GA	–	–
Lewisite I	L1	–	–
Lewisite II	L2	–	–
Phenyldichloroarsine	PDCA	817	77
Trichloroarsine	TCA	35	3.8
Thiodiglycol	TDG	–	–
Thiodiglycol sulfoxide	TDGS	–	–

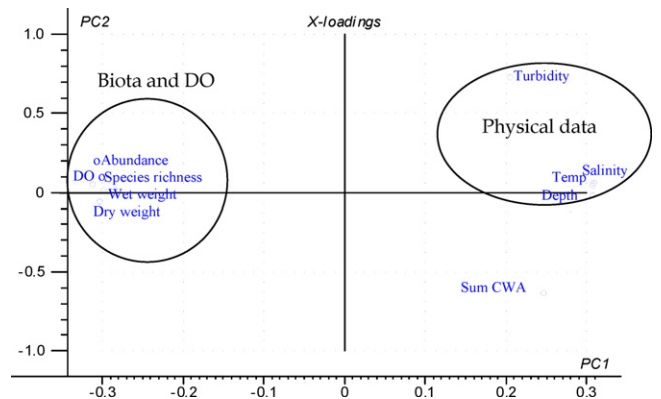
– not detected CWAs.

**Table 6**  
Summary of detected CWA residues in sediment (µg/kg (DM)).

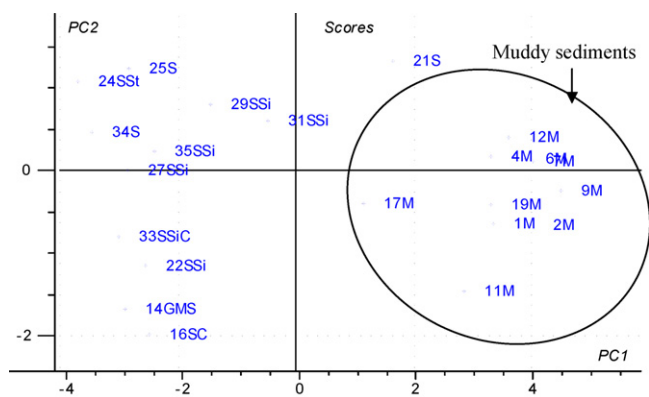
Compound	CAS#	Sample id	Concentration
Lewisite II (L2[ox])	157184-21-9	CWA5 (250S)	15 ± 5.4
Phenyldichloroarsine (PDCA[SPr])	1776-69-8	CWA5 (500N)	306 ± 24

**Table 7**  
Summary of calculated boundary layer exposure concentrations; Cw(worst-case) = Cpw(qs) + Cw(pl). Only CWAs that are detected in sediment samples.

Compound	Cpw(qs) (µg/L)	Cw(pl) (µg/L)	Cw(worst-case) (µg/L)
Adamsite	0.08 ± 0.19	0.004 ± 0.01	0.085 ± 0.20
Clark I	0.01 ± 0.008	0.002 ± 0.001	0.013 ± 0.009
TPA	0.0003 ± 0.0001	0.001 ± 0.0007	0.0014 ± 0.0009
PDA	0.61 ± 1.5	0.004 ± 0.01	0.62 ± 1.5
TCA	5.8 ± 7.4	0.002 ± 0.002	5.8 ± 7.4



**Fig. 4.** The second principal component, PC2, versus the first principal component, PC1. The circle to the left represents the highly inter-correlated variables: DO (dissolved oxygen) and the biological parameters abundance, wet weight, dry weight and species richness. The oval circle to the right represents the intercorrelated physical parameters: temperature, salinity, turbidity and depth.



**Fig. 5.** Each sampling station is labelled with an acronym; e.g., 16SC=station 16 with sand–clay sediment type. Other sediment types: SSi: sand/silt; GMS: gravel–mud–sand; SSi: sand–stones; SSiC: sand–silt–clay; SC: sand–clay; S: sand; M: mud. Almost all muddy sediment samples are positioned to the right in the score plot, while all sandy sediments are positioned to the left.

**Table 8**  
Regression statistics between biological abundance and abiotic factors.

Y(X)	Slope	<i>p</i>	Intercept	<i>R</i> <sup>2</sup>
Biological abundance (sum CWA)	−1.3	0.02	0.3	0.42
Biological abundance (DO)	3.3	0.00004	−0.7	0.71
Biological abundance (temp)	−10.8	0.00000004	10.3	0.89
Biological abundance (turbidity)	−0.6	0.04	2.5	0.26
Biological abundance (depth)	−7.3	0.00000002	15.2	0.86

species richness and high oxygen content of the water.

In the direction of PC2, i.e. vertical direction, samples with high positive score value are characterised by having low CWA concentration compared to samples with high negative score values. The variables turbidity and sum CWA are inversely correlated in PC2 accounting for 7% of the X-variance. Results for simple regressions of biological abundance as function of sum CWA are given in Table 8. All the biological parameters are highly intercorrelated and the abundance is thus representative of the biota responses.

Overall, it is clear that biological abundance is best described by temperature (lowest *p* value and highest *R*<sup>2</sup>). Biological abundance is furthermore most sensitive towards changes in temperature (highest numerical value of the slope). The potential for influencing biological abundance is as follow in decreasing order: temperature < depth < dissolved oxygen < sum CWA < turbidity. This implies that biological abundance is more sensitive towards physical parameters, which are intercorrelated, compared to CWA exposure.

#### 4. Discussion and conclusions

The detection frequencies and concentration levels of intact CWA found were low. CWA residues were more frequently found

but at concentrations, which does not constitute a significant risk to the fish community (Tables 4–6). Re-suspension of CWA residue containing sediment from installation of the pipelines contribute marginally (~1%) to the overall background CWA residue risk with total worst-case RQs of 0.18–0.29 in 2008 and 0.0026 in 2010. The relative sediment perturbation from the pipeline installation should moreover be considered in light of decades of trawling in the same area.

It is noticeable from a risk perspective that depth, salinity and temperature are co-variants and that they are strongly inversely correlated with the macro zoobenthos data ( $r = -0.86$  to  $-0.94$ ). On the other hand, DO is strongly positively correlated with the measured biota ( $r = 0.84$ – $0.86$ ). The total CWA risk is moderately to strongly negatively correlated with biota ( $r = -0.55$  to  $-0.73$ ) (see Pearson correlation matrix in Annex 1).

In other words, based on the statistical relationships the observed biota is primarily affected by the availability of DO, which is a function of water depth, which again govern water temperature; i.e. greater depth, less DO and less biota. Likewise, according to the multivariate analysis, there is a probability of observing reductions in biota where the total CWA risk is predicted to be elevated. Elevated DO levels suggest lower CWA concentration ( $r = 0.52$ ), e.g. due to more effective oxidation and degradation of the CWA and less dumped munition in the first place (Annex 1).

Results from sampling stations 16 and 19 predict a relative elevated risk towards the fish community. The biota data nearest station 16 were on par with the average biota data, and the habitat conditions are also relatively good with sandy/clay substrate; DO at 12.18 mg/L and low turbidity at 0.14 FTU, hence the predicted risk towards fish is not in agreement with the observed biota. The other sample station with elevated relative risk was station CWA19. CWA19 was characterised by low biota measurements, high turbidity, mud and acceptable DO (8.9 mg/L). The risk at CWA19 was driven by TCA at 0.09 mg/L.

Physical parameters of high importance for biota (sediment habitat quality – e.g. substrate and grain size) are associated with the muddy sediments characterised by a low ecological quality for the benthos and to co-vary with CWA residue exposure.

This paper provides the most comprehensive sampling of CWAs and assessment of environmental risks near a dumped chemical munition dump site to date in the open scientific literature. We hope that it will contribute to the aim of the UN resolution regarding sea dumped chemical munition, which stress the need to share exposure data and information as well as the site-specific assessment of CWA related risks [W1].

#### Acknowledgement

Nord Stream AG, Ramboll, Dansk Biologisk Laboratorium, VERIFIN, DHI, former MERCW partners.



**Annex 1. Pearson correlation matrix (high correlations (>.8) are in bold)**

	Conc. DM	Conc. DA	Conc. TPA	Conc. PDA	Conc. TCA	Conc. CWA	Sum	Depth (m)	Salinity (‰)	Temp	DO (mg/L)	Turbidity (FTU)	Species richness	Abundance	Biomass wet weight	Biomass dry weight	Risk DM	Risk DA	Risk TPA	Risk PDA	Risk TCA	Risk CWA	Risk Total	
DM conc.	<b>1.00</b>																							
DA conc.	-0.19	<b>1.00</b>																						
TPA conc.	-0.61	<b>0.94</b>	<b>1.00</b>																					
PDA conc.	-0.57	<b>0.96</b>	<b>1.00</b>	<b>1.00</b>																				
TCA conc.	-1.00	<b>0.87</b>	0.71	0.76	<b>1.00</b>																			
Sum CWA conc.	-0.93	<b>0.85</b>	<b>0.95</b>	<b>0.94</b>	0.74	<b>1.00</b>																		
Depth (m)	0.04	<b>0.85</b>	0.66	0.68	0.50	0.66	<b>1.00</b>																	
Salinity (‰)	-0.30	<b>0.87</b>	0.62	0.65	0.55	0.64	<b>0.98</b>	<b>1.00</b>																
Temp	-0.21	<b>0.83</b>	0.61	0.63	0.54	0.61	<b>0.96</b>	<b>0.99</b>	<b>1.00</b>															
DO (mg/L)	-0.50	-0.71	-0.66	-0.67	-0.31	-0.52	-0.92	-0.88	-0.91	<b>1.00</b>														
Turbidity (FTU)	-0.36	0.39	0.22	0.25	0.34	0.28	0.57	0.64	0.61	-0.48	<b>1.00</b>													
Species richness	<b>0.92</b>	-0.58	-0.55	-0.57	-0.78	-0.54	-0.86	-0.88	-0.88	<b>0.86</b>	-0.49	<b>1.00</b>												
Abundance	<b>1.00</b>	-0.82	-0.66	-0.68	-0.75	-0.65	-0.93	-0.94	-0.94	<b>0.84</b>	-0.51	<b>0.94</b>	<b>1.00</b>											
Biomass wet weight	<b>0.86</b>	-0.60	-0.58	-0.59	-0.76	-0.57	-0.88	-0.88	-0.91	<b>0.84</b>	-0.55	<b>0.92</b>	<b>0.95</b>	<b>1.00</b>										
Biomass dry weight	<b>0.83</b>	-0.56	-0.52	-0.54	-0.72	-0.54	-0.88	-0.89	-0.91	<b>0.85</b>	-0.54	<b>0.94</b>	<b>0.95</b>	<b>1.00</b>	<b>1.00</b>									
DM – risk	0.02	-0.80	-0.59	-0.67	-1.00	0.30	-0.99	-0.92	-0.96	<b>0.85</b>	-0.84	<b>0.92</b>	<b>1.00</b>	<b>0.86</b>	<b>0.83</b>	<b>1.00</b>								
DA – risk	-0.16	<b>1.00</b>	<b>0.95</b>	<b>0.97</b>	<b>0.85</b>	<b>0.86</b>	<b>0.84</b>	<b>0.86</b>	<b>0.81</b>	-0.70	0.37	-0.57	-0.81	-0.59	-0.55	-0.79	<b>1.00</b>							
TPA – risk	NA	0.77	<b>0.95</b>	<b>0.95</b>	<b>1.00</b>	<b>0.99</b>	0.20	-0.22	-0.22	-0.28	-0.19	0.51	<b>0.99</b>	0.04	-0.01	NA	<b>0.80</b>	<b>1.00</b>						
PDA – risk	-0.64	<b>0.93</b>	<b>1.00</b>	<b>1.00</b>	0.69	<b>0.95</b>	0.66	0.61	0.60	-0.65	0.21	-0.54	-0.65	-0.57	-0.51	-0.52	<b>0.95</b>	<b>0.95</b>	<b>1.00</b>					
TCA – risk	-1.00	<b>0.87</b>	0.71	0.76	<b>1.00</b>	0.63	0.47	0.52	0.53	-0.31	0.34	-0.76	-0.75	-0.75	-0.72	-1.00	<b>0.85</b>	<b>1.00</b>	0.69	<b>1.00</b>				
Total CWA – risk	-0.91	0.69	0.57	0.56	0.67	0.59	0.52	0.56	0.55	-0.31	0.38	-0.55	-0.73	-0.72	-0.71	0.21	0.70	<b>0.97</b>	0.57	0.59	<b>1.00</b>			

## References

- [1] P.G. Brewer, N. Nakayama, N. Feature, What lies beneath: a plea for complete information, *Environ. Sci. Technol.* 42 (2008) 1394–1399.
- [2] H. Sanderson, P. Fauser, M. Thomsen, P. Vanninen, M. Soderstrom, Y. Savin, I. Khalikov, A. Hirvonen, S. Niiranen, T. Missiaen, A. Gress, P. Borodin, N. Medvedeva, Y. Polyak, V. Paka, V. Zhurbas, P. Feller, Feature: environmental hazards of sea-dumped chemical weapons, *Environ. Sci. Technol.* 44 (2010) 4389–4394.
- [3] Report on chemical munitions dumped in the Baltic Sea, Report to the 15th meeting of Helsinki Commission, Danish Environmental Protection Agency, HELCOM. <http://www.ruociagi.com/spis.art/2005.4/raport.pdf>, 1994 (accessed 30.10.11).
- [4] L. Szinicz, History of chemical and biological warfare agents, *Toxicology* 214 (2005) 167–181.
- [5] H. Sanderson, Chemical warfare agents in the environment, in: J. Nriagu (Ed.), *Environ. Health*, vol. 1 (10), Elsevier, 2011, pp. 587–597, ISBN: 978-0-444-52273-3.
- [6] H. Sanderson, M. Thomsen, P. Fauser, P.B. Sørensen, PBT screening profile of chemical warfare agents (CWAs), *J. Hazard. Mater.* 148 (2007) 210–215.
- [7] N.B. Munro, S.S. Talmage, G.D. Griffin, L.C. Waters, A.P. Watson, J.F. King, V. Hauschild, The sources, fate, and toxicity of chemical warfare agent degradation products, *Environ. Health Persp.* 107 (1999) 933–974.
- [8] X. Zhang, K.C. Hester, O. Mancillas, E.T. Peltzer, P.M. Walz, P.G. Brewer, Geochemistry of chemical weapon breakdown products on the seafloor: 1,4-thioxane in seawater, *Environ. Sci. Technol.* 43 (2009) 610–615.
- [9] VERIFIN, Finnish Institute for Verification of the Chemical Weapons Convention, Final report on chemical analysis of sea-dumped chemical warfare agents in sediment samples, VER-MS-0221. By: Söderström, Taipalus, Hagström, Kostainen and Vanninen, 2010.
- [10] Danish Hydraulic Institute, Monitoring of benthic fauna and chemical warfare agents in Sweden and Denmark, Nord Stream PO 10-1149, Doc. No.: G-PE-EMS-REP-188-M10FR1IN-A, 2010.
- [11] D.M. DiToro, Technical basis for establishing sediment quality criteria for non-ionic organic chemicals using equilibrium partitioning, *Environ. Toxicol. Chem.* 10 (1991) 1541–1583.
- [12] H. Sanderson, M. Thomsen, P. Fauser, P.B. Sørensen, Screening level fish community risk assessment of chemical warfare agents in the Baltic Sea, *J. Hazard. Mater.* 154 (2008) 846–857.
- [13] S. Forster, B. Bobertz, B.B. Bohling, Permeability of sands in the coastal areas of the southern Baltic Sea: mapping a grain-size related sediment property, *Aquat. Geochem.* 9 (2003) (2003) 171–190.
- [14] E.M. Emelyanov, Chemical components and elements in the suspended matter and sediments of the Western Baltic, *Baltica* 9 (1996) 5–15.
- [15] Nord Stream Intervention Works in Denmark, Rambøll Oil & Gas, Memo G-PE-PER-REP-100-05170000-A, 2011.
- [16] Nord Stream AG, Rambøll, Memo 4.3a-1 – hydrodynamical model setup for the Baltic Sea, Nord Stream AG, Zug, Switzerland, 2007.

## Web links (accessed 20/2-12)

- [W1] United Nations resolution regarding chemical munitions: <http://www.un.org/Depts/dhl/resguide/r65.shtml>.
- [W2] MERCW: [www.mercw.org](http://www.mercw.org).
- [W3] Nord Stream Espoo report and Nord Stream Environment: <http://www.nord-stream.com/press-info/press-releases/nord-stream-s-espoo-report-sound-basis-for-assessment-of-potential-transboundary-impacts-293/> and <http://www.nord-stream.com/en/environment.html>.
- [W4] VERIFIN: <http://www.helsinki.fi/verifin/VERIFIN/english/>.
- [W5] DBL: <http://www.danskiolab.dk/index.htm>.
- [W6] EPI Suite: <http://www.epa.gov/opptintr/exposure/pubs/episuite1.htm>.
- [W7] HSDB: <http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB>.