ENVIRONMENTAL ASSESSMENTS OF SEA DUMPED CHEMICAL WARFARE AGENTS

CWA report

Scientific Report from DCE – Danish Centre for Environment and Energy No. 174 2015

AARHUS
UNIVERSITY
DCE – DANISH CENTRE FOR ENVIRONMENT AND ENERGY

[Blank page]

ENVIRONMENTAL ASSESSMENTS OF SEA DUMPED CHEMICAL WARFARE AGENTS

CWA report

Scientific Report from DCE – Danish Centre for Environment and Energy No. 174 2015

Hans Sanderson
Patrik Fauser

Aarhus University, Department of Environmental Science

AARHUS
UNIVERSITY
DCE – DANISH CENTRE FOR ENVIRONMENT AND ENERGY

Data sheet

Series title and no.: Scientific Report from DCE – Danish Centre for Environment and Energy No. 174

Title: Environmental assessments of sea dumped chemical warfare agents
Subtitle: CWA report

Authors: Hans Sanderson, Patrik Fauser
Institution: Aarhus University - Department of Environmental Science

Publisher: Aarhus University, DCE – Danish Centre for Environment and Energy ©
URL: http://dce.au.dk/en

Year of publication: December 2015
Editing completed: December 2015

Referees: Pia Lassen, Department of Environmental Science
Quality assurance, DCE: Susanne Boutrup

Financial support: The research was funded by Nord Stream AG and the European Commission FP6 MERCW project (contract 013408).

Please cite as: Hans Sanderson, Patrik Fauser. 2015. Environmental assessments of sea dumped chemical warfare agents. Aarhus University, DCE – Danish Centre for Environment and Energy, 116 pp. Scientific Report from DCE – Danish Centre for Environment and Energy No. 174 http://dce2.au.dk/pub/SR174.pdf

Abstract: This is a report on the information gathered during work related to sea dumped chemical warfare agents. It mainly reviews the work conducted in relation to the installation of the two Nord Stream gas pipeline from 2008-2012. The focus was on the weight-of-evidence risk assessment of disturbed CWA residues in connection with the installation of the pipelines. Novel exposure and toxicity assessments are presented and the risk is assessed. The overall conclusion is that there is a negligible acute added CWA risk towards the fish community from the installation of the pipelines.

Keywords: Sea-dumped chemical warfare agents, Baltic Sea, Environmental risks Nord Stream gas pipeline

Layout: Ann-Katrine Holme Christoffersen
Front page photo: Colourbox

ISBN: 978-87-7156-181-4
ISSN (electronic): 2245-0203

Number of pages: 116

Internet version: The report is available in electronic format (pdf) at http://dce2.au.dk/pub/SR174.pdf

Contents

Preface **5**

Summary **6**

Sammenfatning **8**

1 Risk screening of chemical warfare agents towards humans and the fish community resulting from sediment perturbation from construction of the planned Nord Stream offshore pipelines through risk area 3 (S-route) in the Baltic Sea **9**

1.1 Summary 9
1.2 Introduction 9
1.3 Methods 11
1.4 Results 13
1.5 Discussion and conclusions 15
1.6 References 16

2 Historical and qualitative analysis of the state and impact of dumped chemical warfare agents in the Bornholm basin from 1947-2008 **18**

2.1 Summary 18
2.2 Introduction 19
2.3 Methods 22
2.4 Results 23
2.5 Discussion and conclusions 28
2.6 References 29
2.7 Annex 1: Newspaper samples 30

3 RAMBOLL OIL & GAS - Nord Stream A/G. Offshore pipelines through the Baltic Sea Summary of NERI generated chemical warfare agent (CWA) analytical data in a risk context towards the fish community from construction of the planned Nord Stream offshore pipelines through risk area 3 (S-route) in the Baltic Sea **38**

3.1 Summary 38
3.2 Introduction 38
3.3 Methods 39
3.4 Results 41
3.5 Conclusions 49
3.6 References 49

4 RAMBOLL OIL & GAS - Nord Stream A/G. Offshore pipelines through the Baltic Sea - Analysis of additional risk to the fish community from chemical warfare agents (CWA) associated with construction of the planned Nord Stream route south of Bornholm **51**

4.1 Introduction 51
4.2 Methods 52
4.3 Results 56
4.4 Discussion 63

4.5 Conclusions 64
4.6 References 65
4.7 Annex 1. Summary of measured concentrations 66
4.8 Annex 2. Pearson correlation matrix 68
4.9 Annex 3. PC1 and PC2 of PCA including individual CWAs 69

5 RAMBOLL OIL & GAS - Nord Stream A/G. Offshore pipelines through the Baltic Sea - Analysis of fish community risk due to exposure to chemical warfare agents (CWAs) perturbed sediment during the placement of the gas pipeline east of Bornholm 71

5.1 Summary 71
5.2 Introduction 71
5.3 Methods 72
5.4 Results 76
5.5 Discussion and conclusions 79
5.6 References 79

6 Nord Stream A/G. Offshore pipelines through the Baltic Sea - Analysis of fish community risk due to exposure to Chemical Warfare Agents (CWAs) from perturbed sediment along and between the two gas pipelines east of Bornholm 81

6.1 Preface 81
6.2 Summary 81
6.3 Introduction 82
6.4 Methods 82
6.5 Results 87
6.6 Discussion and conclusions 90
6.7 Annex 1 - Summery of sediment CWA residue concentrations: 2008-2012(µg/kg dw) 92

7 Qualitative evaluation of the sources to selected organoarsenicals along the Nord-Stream pipeline route in the Bornholm Deep 95

7.1 Background 95
7.2 Approach 96
7.3 Findings 97

Preface

1915 was the year where chemical warfare weapons were used in large scale in the field of Flanders near the village Ypres in Belgium against Canadian troops. It was decided that these weapons of mass destruction should be eliminated from the face of the Earth. Weapons were however stockpiled by the German forces with the intent of potential use against the Soviet army in Leningrad, luckily they were never used. After the Second World War end Germany was de-militarized and in this process their stock-piled chemical warfare agents were dumped at sea in 1947. Similarly elsewhere in the world chemical warfare weapons were also disposed of at sea before this was made illegal. The dumping of these weapons has caused concern for the environment when the munition shells corrode and their content is released to the sea. The seafloor nowadays is extensively used for various purposes such as fixed installations e.g. power cables and gas pipeline. This report addresses the environmental risks installation of the Nord Stream AG twin gas pipeline 2008-2012.

Summary

Following the end of the Second World War Germanys approximately 65,000 tonnes stockpiled Chemical Warfare Agent (CWA) munitions were ordered by the allied forces to be destroyed during the second half of 1947 as a result of the Potsdam Conferences. The Russian forces undertook the major part of this task during the summer of 1947 with German barges and crews. The Bornholm basin in the Baltic Sea received more than half of Germanys CWA arsenal with dumping of approximately 11,000 tonnes active CWA chemical substances. There are significant uncertainties and confounding factors to consider when assessing the risk of CWA towards human and environmental health.

Here we assess the potential added indirect human and fish community risks associated with construction of the planned Nord Stream gas pipelines along the S-route in the risk area 3 in the Bornholm basin was modelled using conservative screening level risk methods and assumptions in a desk-top assessment. Risk may arise from perturbation of sediment containing traces of chemical warfare agents (CWA) dumped after the Second World War. Two different risk scenarios (A & B) were developed. In scenario A we assumed a homogeneous distribution of the entire available CWA across the entire area around Bornholm.

Subsequently we found based on measured data that the arsenicals measured along the route do not correlate with total CWA concentrations ($r^2 = 0.01$). Therefore the predominant part of the arsenic in the sediment has other anthropogenic and potential natural sources than CWA. The fish community risk relative to the toxic forms of As is generally low along the S-route. The total As levels found along the S-route are close to the background levels for the Bornholm Deep. Mean arsenic concentrations in sediments range from 5 to 3000 mg/kg, with the higher levels occurring in contaminated areas (IPCS, 2001). The observed average sediment concentration, averaging at 11 mg/kg DM, found by Fauser et al. (2013) is comparable to the average total As in the Bornholm Deep of approximately 20 mg/kg reported by Garnaga et al. (2006). Arsenic concentrations in sediment in the Baltic Sea are quite variable and primarily dependent on the geology and grain size (Emelyanov, 1996).

Further, the statistical analysis suggests that biological abundance is better described by physical parameters than As and CWA contamination levels. There are no strong correlations between the CWA and the biological observations. The ratio between CWA munitions above and below the sediment is unknown; hence special caution should be exercised in connection with laying anchors, since these sink furthest into the sediment and may disturb buried munitions shells when installing the pipelines.

In summary from 2008-2012, re-suspension of CWA-contaminated sediment will cause a maximum added risk corresponding to a risk quotient of 0.0001 at the highest risk location (CWA 22.81) (in comparison to the max. RQs found in 2010 of 0.00107, and 0.003 in 2011), towards the fish community. Compared to the total risk quotient from the prevailing quasi steady-state CWA residues concentrations in the pore water of up to

0.0037 (0.025 in 2010; and 0.17 in 2011), this indicates no significant additional risk from pipe laying activities.

We moreover, collected qualitative data from interviews with local experts and reviewed the historical archives covering the dumping, these suggested low current risk.

Sammenfatning

Denne rapport sammenfatter risikoanalyser af kemiske våben, der blev dumpet ud for Bornholm efter Anden Verdenskrig. I 1947 blev i alt ca. 65.000 tons kemiske våben, indeholdende 11.000 tons kemiske kampstoffer, dumpet udfor Bornholm i Bornholmerdybet på 70-100m vand, da Tyskland blev demilitariseret. Dumpningerne blev fortrinsvis foretaget af de russiske styrker på tyske skibe og med tysk besætning.

Arbejdet omhandler især den øgede miljørisiko som følge af en ophvirvling af rester af de kemiske våbens indholdsstoffer i forbindelse med installationen af to gasrørledninger mellem Rusland og Tyskland som Nord Stream AG står for. En række modeller er udviklet og data er indsamlet for at belyse dette og er gengivet i denne samlede rapport. Udover disse kapitler er der en række artikler som er tilgængelige i den videnskabelige litteratur, især i tidsskriftet *Journal of Hazardous Materials*.

Det er fundet at koncentrationen af arsenikforbindelser, der er målt langs rørlægningsruten, som ikke korrelerer med den totale målte mængde kemisk kampstof (CWA) ($r^2 = 0.01$). Den overvejende del af arsenik i sedimentet har derfor andre antropogene og potentielle naturlige kilder, da koncentrationerne er i samme størrelsesorden som baggrundsværdierne i Bornholmerdybet. Desuden er risiko af de giftige former af arsenik overfor fisk generelt lav. De statistiske analyser viser, at den biologiske forekomst beskrives bedre ved fysiske parametre end ved arsenik- og CWA-koncentrationer.

Fordelingen af våben med krigsgasser over og under sedimentoverfladen kendes ikke, derfor skal der udvises speciel opmærksomhed ved lægning af ankre, da disse kan synke dybere ned i sedimentet og forstyrre begravede intakte våben.

Sammenfattende kan det konstateres, at rørlægningen ikke udgør et signifikant bidrag til en i forvejen minimal akut miljørisiko for fiskebestanden omkring Bornholm som følge af rørlægningsaktiviteter.

1 Risk screening of chemical warfare agents towards humans and the fish community resulting from sediment perturbation from construction of the planned Nord Stream offshore pipelines through risk area 3 (S-route) in the Baltic Sea

Hans Sanderson & Patrik Fauser

1.1 Summary

The potential added indirect human and fish community risks associated with construction of the planned Nord Stream gas pipelines along the S-route in the risk area 3 in the Bornholm basin was modelled using conservative screening level risk methods and assumptions. Risk may arise from perturbation of sediment containing traces of chemical warfare agents (CWA) dumped after the Second World War. Two different risk scenarios (A & B) were developed. In scenario A we assumed a homogeneous distribution of the entire available CWA across the entire area of risk area 3. Scenario B we assumed that the majority of the CWA was actually dumped in the designated dumping areas 1 and 2, resulting in 17 % of the total available amount spread homogeneously across the risk area 3. Both are conservative worst-case assumptions, where it is assumed that the entire available CWA amount is released instantaneously upon construction of the pipeline. Scenario B is the more realistic of the two scenarios. The results indicate low risk towards humans and the fish community. The margins of safety for the fish community ranges from 333 to 2000 for Scenario A and B, respectively, and that the margin of exposure for human health ranges from 50 to 300 per constructed pipeline. The final assessment of the risks should be based on measured data to elucidate the inherent uncertainties in the above assumptions.

1.2 Introduction

Following the end of the Second World War Germanys approximately 65,000 tonnes stockpiled Chemical Warfare Agent (CWA) munitions were ordered by the allied forces to be destroyed during the second half of 1947 as a result of the Potsdam Conferences. The Russian forces undertook the major part of this task during the summer of 1947 with German barges and crews. Initially the intended dump site was outside the Faroe Islands but these plans were changed to meet the deadlines and financial restrictions. The Bornholm basin in the Baltic Sea consequently received more than half of Germanys CWA arsenal with dumping of approximately 11,000 tonnes active CWA chemical substances (HELCOM, 1994). With the Potsdam agreement after the war there followed an international moratorium upon the revealing of the nature and location of the dumping locations (Brewer and Nakayama, 2008). In 1997 the U.S.A. and Great Britain prolonged their moratorium for another 20 years, whereas the Russians, as a part of their Glasnost policy and end of the cold war, disclosed their CWA dumping activities in the Baltic Sea in the early 1990s to HELCOM. It is known but associated with both secrecy, uncertainty and lack of knowledge that Great Britain also dumped CWA in the Baltic Sea mainly west of Bornholm, and that East-Germany in 1962 with operation Hanno dumped CWA east of Bornholm. These amounts are expected to be significantly less than the amounts dumped by the Russians by international orders east of Bornholm. Table 1 is a list of the confirmed and known dumped active CWA from Russian reports.

Table 1 Confirmed dumped chemical warfare agents in Bornholm basin (HELCOM, 1994)

Compound	CAS number	Dumped CWA (tonnes)
Chloroacetophenone (CAP)[1]	532-27-4	515
Sulphur mustard gas (Yperite)[2]	505-60-2	7027
Adamsite[3]	578-94-9	1428
Clark I[3*]	712-48-1	711.5
Triphenylarsine[3*]	603-32-7	101.5
Phenyldichloroarsine[3*]	696-28-6	1017
Trichloroarsine[3*]	7784-34-1	101.5
Other (Zyklon B)[4]	74-90-8	74
Monochlorobenzene[5]	108-90-7	1405

1) Riot control agent; 2) Blistering agent; 3) Organoarsenic blistering agent; 3*) Arsine oil constituents - organoarsenic blistering agent; 4) Blood agent; 5) Additive.

The exact locations of the dump sites are ambiguous. The primary, and designated, dumping was conducted in a circular area with a radius of 3 nautical miles, with the centre coordinates at 55°E21"N and 15°E37'02"E covering an area of 99 km^2. However, not all CWA was dumped at the designated site, hence a secondary, and more realistic dump site is located roughly at 55°10"N to 55°23"N and 15°24"E to 15°55"E, covering 892 km^2. Lastly, there is a third dump site area covering 9104 km^2 (Figure 1).

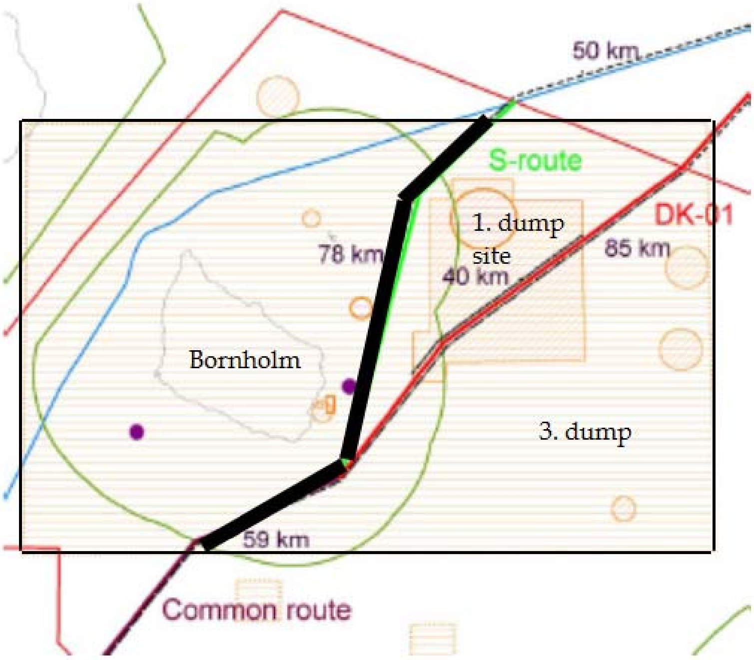


Figure 1 Primary dump site (circle) within in the secondary dump site box, and the larger tertiary dump site, the entire lined box. The thick black line is the S-route under investigation.

The waters in the Bornholm basin can be divided into an upper and a lower layer. The upper layer (depth of 50 to 70 m) consists primarily of brackish water flowing in from the northern and eastern parts of the Baltic Sea flow slowly out of the Baltic Sea towards the North Sea. The lower layer (< 20 m above sediment) originates in the North Sea and is on its way into the Bornholm basin. There is a weak south-easterly bottom water current of 5 cm/s causing an advective transport of agent, a vertical dispersion coefficient of 0.2 cm^2/s (Stigebrandt, 1982), which induces a turbulent mixing of the near bottom bulk water, sedimentation, diffusion to sediment, degradation (hydrolysis) and accumulation in sediment, which will all be taken into account in the exposure calculations.

1.3 Methods

1.3.1 Chemical Warfare Agents

The munitions have been resting on the seabed and in the sediment of the Baltic Sea for more than sixty years and the extent of corrosion of the shells, and thus release, of the toxic chemicals into the marine environment is poorly understood, some shells will have leaked their content whereas others might still be intact. The ratio between corroded and empty munitions versus intact munitions is not known, it is however clear that oxygen is needed for corrosion of the munitions iron walls, and that munitions situated in anoxic sediments will be better conserved than munitions exposed to oxygen in either the sediment or water. Hence, the ratio corroded and potential empty munition versus intact potential full munitions to a large extend is the ratio of the munitions above and below sediment.

The human and environmental toxicity along with most physico-chemical properties of CWAs have not been thoroughly investigated with modern methods and reported in the public literature, hence modelling of these properties are warranted to derive comparable datasets (Sanderson et al. 2007, 2008ab), see Sanderson et al. (2007) for individual CWA parent and primary metabolite physico-chemical properties (Table 2).

Table 2 Substance-specific physicochemical parameters (dissipation half life (DT50); water solubility (Water sol.); hydrophobicity (Log Kow); and sorption coefficient (Koc)) (Sanderson et al. 2008a).

Compound	DT50 (days)	Water sol. (mg L^{-1})	Log Kow	Koc
Chloroacetophenone (CAP)	114	1635	1.93	89
Yperite	56	605 and 0.8[1)]	2.41	275
Adamsite	1247	0.4	4.05	5000
Clark I	18	3	4.53	19,000
Triphenylarsine	17	0.089	5.97	440,000
Phenyldichloroarsine	19	639	3.06	817
Trichloroarsine	20	2291	1.61	35
Zyklon B	3	95,000	-0.69	2.7
Monochlorobenzene	4	400	2.64	268

[1)] For viscous Yperite that constitutes 20 % (1405 tonnes) of the total Yperite mass.

The potential for biomagnification in the marine foodweb and thus also indirect exposure towards humans consuming potentially contaminated fish plus the toxicity of the CWAs towards the fish community and humans (Opresko et al. 2001) are outlined in Table 3. The HC5 is the statistically calculated concentration where 95 % of the species will not be impacted. The oral RfD is the measured and predicted safe human exposure concentration.

Table 3 CWA bioconcentration faction (BCF) and biomagnification factor (BMF), fish community and human health toxicities (Sanderson et al. 2008b)

Compound	BCF/BMF	Fish community HC5 (mg/L)	Oral RfD (mg/kg BW/d)
CAP	0.8/1	0.5	0.005
Yperite	14.3(.3)*/1	0.1	0.000007
Adamsite	262/1	0.01	0.0003
Clark I	600/1	0.01	0.0003
Triphenylarsine	7901/10	0.0005	0.0003
Phenyldichloroarsine	45.6/1	0.1	0.0003
Trichloroarsine	3.5/1	0.1	0.0003
Other (Zyklon B)	3.2/1	0.001	0.002
Monochlorobenzene	30.7/1	0.1	0.002

* The BCF of 0.3 in brackets is a measured value in 1985, but the reliability the study has been questioned, hence to be conservative and consistent we use the value of 14.3 in the analysis.

1.3.2 Risk assessment

There are recognized uncertainties concerning the exact location of the dumping and to a lesser degree the amounts dumped we make conservative assumptions concerning the presence of chemical warfare munitions and CWA. This in order to perform a screening level indirect human health and fish community risk assessment, for the risks associated with the construction of the planned Nord Stream pipelines. The methodologies adhere to the European Union’s Technical Guidance Document (EU TGD, 2003) for marine and indirect human risk assessment from consuming potentially contaminated seafood and are detailed in Sanderson et al. (2008ab). The human risk quotient is based on the water concentration and the conservative default values of 70 kg body weight (BW) and a daily fish intake of 0.115 kg / person, and the safe oral reference doses for all the CWAs. We can calculate the indirect human health risk quotient based on the EU TGD (2003) from equation (1):

$$\frac{\text{RfD(ng/kgBW/d)}}{\text{Water concentration (ng/L)*BCF*BMF * 70 (kg BW)*0.115 (kg fish/d)}}$$

We applied the following conservative exposure assumptions related to construction of one gas pipeline, hence if e.g. two gas pipelines are constructed the overall risk at a screening level will be doubled. We developed two different conservative risk scenarios, A) which is very conservative and less probable, and B) which is still very conservative but more probable than A). Assumptions:

- Total risk area 3 = 9104 km^2
- Total pipeline length = 104 km
- Pipeline diameter = 0.00126 km
- Pipeline anchor corridor = 2.040 km of which 2 % of the sediment surface is perturbed (Rambøll, 2008)

- Total area of perturbed sediment per gas pipeline constructed along S-route = 4.3742 km^2
- All CWA is in its parent form and released instantaneously upon construction of the pipeline in the area described above
- The relative risk of each CWA and the total risk assuming additivity is calculated
- **Risk scenario A:** Conservative assumption that all CWA dumped (Table 1) is homogeneously distributed across the entire risk area 3

  Risk scenario B: A more realistic but still very conservative assumption is that the majority (50 %) of CWA was actually dumped in the designated primary dump site. Of the remaining amount 2/3 were assumed dumped in the secondary dump site (33 %) and one third (17 %) in the tertiary dump site.

1.4 Results

1.4.1 CWA exposure concentrations

CWA concentrations were found from finite difference solutions of the diffusion-advection model Sanderson et al. (2008a). The results of the calculated CWA exposure concentrations following an instantaneous release of the entire CWA potential for Scenario A & B was calculated for the near bottom water (at 20 cm above seafloor) and 20 m above the sediment within the lower water layer (Sanderson et al. 2008a).

Table 4 Water exposure concentrations for Scenario A & B at 20 cm above sediment and at 20 m above sediment in ng/L.

Compound	A at 20 cm (ng/L)	B at 20 cm (ng/L)	A at 20 m (ng/L)	B at 20 m (ng/L)
CAP	3.13E+00	5.01E-01	8.35E-04	1.34E-04
Yperite	4.24E+01	6.78E+00	1.06E-02	1.69E-03
Adamsite	8.64E+00	1.38E+00	2.16E-03	3.46E-04
Clark I	4.31E+00	6.9E-01	1.08E-03	1.72E-04
Triphenylarsine	5.47E-01	8.75E-02	1.09E-04	1.75E-05
Phenyldichloroarsine	6.01E+00	9.62E-01	1.0E-03	1.6E-04
Trichloroarsine	5.97E-01	9.55E-02	9.95E-05	1.59E-05
Other (zyklon B)	3.8E-01	6.08E-02	2.85E-05	4.56E-06
Monochlorobenzene	7.5E+00	1.2E+00	7.5E-04	1.2.-04
Total	*73.5*	*11.8*	*0.016*	*0.0026*

The water concentrations in Table 4 result in the following total fish concentrations assuming that the fish is 5 % of its life time at 20 cm above the seafloor and 95 % of its life time at 20m depth above the seafloor in accordance with Sanderson et al. (2008a).

Table 5 CWA concentration in fish in ng/kg.

Compound	A (ng/kg)	B (ng/kg)
CAP	1,26E-01	2,01E-02
Yperite	3,04E+01	4,87E+00
Adamsite	1,14E+02	1,82E+01
Clark I	1,30E+02	2,08E+01
Triphenylarsine	2,17E+03	3,47E+02
Phenyldichloroarsine	1,38E+01	2,20E+00
Trichloroarsine	1,05E-01	1,68E-02
Other (zyklon B)	6,09E-02	9,74E-03
Monochlorobenzene	1,15E+01	1,85E+00
Total	*2469,31*	*395,09*

1.4.2 Risk assessment

With the safe fish community HC5 values (hazardous concentration where 95 % of the fish community will not be affected) in Table 3 and the CWA water exposure concentration in Table 4 we can derive the risk quotient (Predicted Environmental Concentration (PEC) / Predicted No observed Effect Concentration (PNEC)) for the fish community (Table 6).

Table 6 Fish community risk quotient for Scenario A and B.

Compound	A	B
CAP	6.26E-06	1.0E-06
Yperite	4.24E-04	6.78E-05
Adamsite	8.64E-04	1.38E-04
Clark I	4.31E-04	6.9E-05
Triphenylarsine	1.09E-03	1.75E-04
Phenyldichloroarsine	6.01E-05	9.62E-06
Trichloroarsine	5.97E-06	9.55E-07
Other (Zyklon B)	3.8E-04	6.08E-05
Monochlorobenzene	7.5E-05	1.2E-05
Total	*0.003*	*0.0005*

The relative fish community risk contributions of the different CWAs are represented in Figure 2.

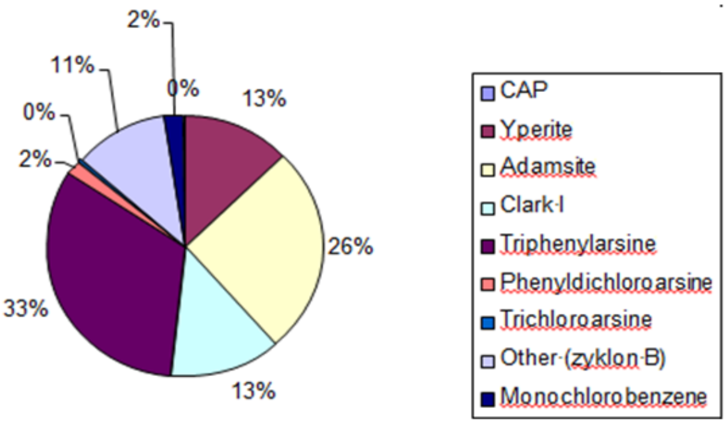


Figure 2 Risk towards fish, one pipeline. Total risk = 0.003 (A). Total risk = 0.0005 (B).

We can moreover with the indirect CWA concentrations via fish and Eq (1) calculate the conservative screening level human health risk quotient, which can then be converted into a margin of exposure (MOE) as the reciprocal (1 / human PEC / PNEC) value (Table 7).

Table 7 Indirect human health MOE.

Compound	A	B
CAP	2,42E+07	1,51E+08
Yperite	1,40E+02	8,75E+02
Adamsite	1,61E+03	1,00E+04
Clark I	1,41E+03	8,78E+03
Triphenylarsine	8,42E+01	5,26E+02
Phenyldichloroarsine	1,33E+04	8,30E+04
Trichloroarsine	1,74E+06	1,09E+07
Other (zyklon B)	2,00E+07	1,25E+08
Monochlorobenzene	1,05E+05	6,59E+05
Total	*49*	*306*

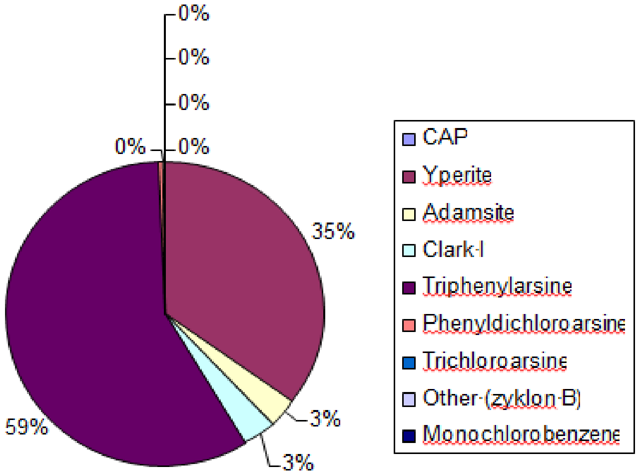


Figure 3 Human risk, one pipeline. Total risk = 0.02 (A). Total risk = 0.003 (B).

The relative indirect human health risk contributions of the different CWAs are represented in Figure 3 for Scenario A and B.

1.5 Discussion and conclusions

It can be concluded that based on this screening level risk assessment of the fish community and the indirect human health risks are low. The margins of safety for the fish community ranges from 333 to 2000 for Scenario A and B, respectively, and that the margin of exposure for human health ranges from 50 to 300. Scenario B is more probably than Scenario A, the dumping was not uniform across the entire risk area 3, the majority was dumped in the designated primary dump site or in the adjacent secondary dump site.

There are a number of worst-case assumptions integrated in to this analysis as mentioned above. In relation to the CWA exposure component, the solution to the diffusion-advection model assumes a semi-infinite space, which is appropriate for modelling transport of substance released over a large area. The pipeline corridor makes up a patchwork of smaller disturbed sediment areas, which causes a dilution with bulk water over adjacent non-disturbed, and thus not CWA emitting, sediments. Overall this makes the model results conservative, which is in line with the worst-case approach applied for screening level assessments. Measurements in the Bornholm basin have shown a near-bottom boundary layer

2-3 m thick with an eddy diffusivity a factor of 2000 larger than the one used in the model. Zhurbas (2008) has shown that the inclusion of such a high diffusivity bottom boundary layer results in a 45 % decrease of the maximum PEC estimates for the short-living CWAs, i.e. Zyklon B and Monochlorobenzene, and a 7 % decrease of the long-living Adamsite. An exclusion of a high diffusivity bottom layer thus yields a conservative estimate.

It is moreover unlikely that all the potential CWA will be instantaneously released in its parent form upon pipeline construction, furthermore a significant fraction of the CWA may be buried more than 10 cm below the sediment surface and are thus not perturbed by the construction. The munitions in contact with water will most likely be corroded and will thus potentially already have leaked their content - or the content may is still be within the shell but in a less hazardous hydrolysed form. These qualitative factors will further decrease the potential for risk.

As this is a model based screening level assessment the conclusions hereof should be investigated based upon measured exposure concentrations collected along the designated pipeline route in order to accurately asses the added potential CWA related risks towards human health and the environment.

1.6 References

Brewer, P.G. & Nakayama, N., 2008: What lies beneath: A plea for complete information. *Environ Sci Technol.* 42: 1394-1399.

EU TGD, 2003: Technical Guidance Document in support of Commission Directive 93/67/EEC on Risk Assessment for new notified substances, Commission Regulation (EC) No 1488/94 on Risk Assessment for existing substances and Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market.

HELCOM, 1994: Report on chemical munitions dumped in the Baltic Sea. Report to the 15th meeting of Helsinki Commission. Danish Environmental Protection Agency. Available at:
http://www.rurociagi.com/spis_art/2005_4/raport.pdf

Opresko, D.M., Young, R.A., Watson, A.P., Faust, R.A., Talmage, S.S. Ross, R.A., Davidson, K.A., King, J. & Hauschild, V., 2001: Chemical warfare agents: Current status of oral reference doses. *Rev Env Contam Toxicol*. 172: 65-85.

Rambøll, 2008: Offshore pipeline through the Baltic Sea. Nordstream AG. Memo 4.3A-9. Release of sediments from anchor operation. Ref#: G-PE-PER-EIA-100-43A90000.

Sanderson, H., Thomsen, M., Fauser, P. & Sørensen, P.B., 2007: PBT screening profile of chemical warfare agents (CWAs). *Jour Haz Mat*. 148: 210-215.

Sanderson, H., Thomsen, M., Fauser, P. & Sørensen, P.B., 2008a: Screening level fish community risk assessment of chemical warfare agents in the Baltic Sea. *Jour Haz Mat*. 154: 846-857.

Sanderson, H., Thomsen, M., Fauser, P. & Sørensen, P.B., 2008b: Human health risk screening due to consumption of fish contaminated with chemical warfare agents in the Baltic Sea. Jour Haz Mat. Available at: http://dx.doi.org/10.1016/j.jhazmat.2008.05.059

Stigebrandt, A., 1987: A model for the vertical circulation of the Baltic deep water. *J Phys Oceano.* 17, 1772-1785.

Zhurbas, V., 2008: Calculations of Maximum CWA Predicted Environmental Concentrations in the Bornholm Basin (Scenario Studies). Internal Deliverable 4.5 in EU project: Modelling of Ecological Risks Related to Sea-Dumped Chemical Weapons (MERCW).

2 Historical and qualitative analysis of the state and impact of dumped chemical warfare agents in the Bornholm basin from 1947-2008

Hans Sanderson & Patrik Fauser

2.1 Summary

There are significant uncertainties and confounding factors to consider when assessing the risk of CWA towards human and environmental health. Hence collection of qualitative data from interviews and historical archives, with respect to the following issues, are needed;

- The spatial scale - potential CWA contamination of up to >9000 km^2 at depths as deep as >100m in the Bornholm basin
- The time scale - inaccurate information concerning the dumping activities occurring for the past 60 years
- Corrosion state of the munitions - not only those retrieved but also those embedded in sediment
- The high chronic toxicity of the compounds especially mustard gas

The main results of the interviews with local experts and the analysis of the newspaper articles can be summarized to:

- Dumping was secret and it started during the summer of 1947 and ended Dec 27 1947, some 12,000 tonnes active CWA was dumped in the Bornholm basin. The historical records are not complete.
- Different types of CWAs were dumped, primarily mustard gas and other blistering agents but also a small amount of nerve agents
- The dumping caused effects on the fish stock in 1947
- There are plenty of fish at dump site depending upon the oxygen levels and the fish go all the way to bottom. Fishing is restricted at primary dump site and not recommended at secondary dump site
- No extraordinary frequency of lesions on fish from the dump site are reported
- Munitions above the sediment (with access to oxygen) are completely corroded and mustard gas lumps are solid, Adamsite is still sticky
- Munitions in the sediment are likely intact due to anoxic conditions preventing corrosion. The relative amounts of buried (intact) CWAs and CWAs at the sediment surface (corroded) are not known
- The munitions are not ‘live’ as the detonator is not inserted
- No reports of caught nerve agents
- Munitions are disperse due to inaccurate dumping and trawling and drifting of munition boxes
- No reports of munitions or CWA lumps washing ashore
- There are wrecks at the dump site but uncertainty about sinking of munitions ships
- Some 200 fishermen have been injured since 1947 from direct contact with the gas, there are no records of potential chronic illness sustained
- There are generally limited environmental concerns but interest in the topic from the local stake holders

2.2 Introduction

Chemical Warfare Agents (CWA) must be viewed within their complicated societal and environmental context. CWA is often surrounded by secrecy, suffers from lack of recent data and is associated with security issues of a personal and national character. CWAs have been used for centuries but are still quite poorly described in terms of their environmental hazard characteristics. Moreover, analytical methods for detection of CWA in the environment and controlled exposure in the laboratory need to be developed. CWA cover a broad spectrum of roughly 70 chemicals. CWA was first used in significant amounts during World War I on the battlefields near the city of Ypres in Belgium in 1915. They proved to be powerful weapons in World War I trench warfare and, during the course of the war, ended up killing and injuring more than 1.4 million people. In 1925 the use of CWA was declared illegal with the Third Geneva Convention and, therefore, was not used in combat either by Germany or the Allied Forces during World War II. However, both sides did stockpile somewhere between half and one million tons of chemical munitions and CWA in total. Following the end of the Second World War Germanys approximately 65,000 tonnes stockpiled Chemical Warfare Agent (CWA) munitions were ordered by the allied forces to be destroyed during the second half of 1947 as a result of the Potsdam Conferences. The Russian forces undertook the major part of this task during the summer of 1947 with German barges and crews. Initially the intended dump site was outside the Faroe Islands but these plans were changed to meet the deadlines and financial restrictions. The Bornholm basin in the Baltic Sea was chosen as the deepest location (100m) near the German harbour from where the munitions were shipped out, and consequently received more than half of Germanys CWA arsenal with dumping of approximately 11,000 tonnes active CWA chemical substances (HELCOM, 1994). With the Potsdam agreement there followed an international moratorium upon the revealing of the nature and location of the dumping locations (Brewer and Nakayama, 2008). In 1997 the U.S.A. and Great Britain prolonged their moratorium for another 20 years, whereas the Russians as a part of their Glasnost policy and end of the cold war disclosed their CWA dumping activities in the Baltic Sea in the early 1990s to HELCOM. It is known but associated with both secrecy, uncertainty and lack of knowledge that Great Britain also dumped CWA in the Baltic Sea mainly west of Bornholm, and that East-Germany in 1962 with operation Hanno dumped CWA east of Bornholm. These amounts are expected to be significantly less than the amounts dumped by the Russians by international orders east of Bornholm. During the Cold War further development, stockpiling and replacement of CWA continued until 1993, at which point the multilateral Chemicals Weapons Convention (CWC) was adopted, augmenting the Geneva Convention. The CWC, to which 183 countries currently are signatories, entered into force in 1997 and is managed by the Organization for the Prohibition of Chemical Weapons (OPCW) in The Hague, Netherlands. According to the CWC all CWA must be completely eradicated by the year 2012, mostly by conversion to chemicals for peaceful purposes or by incineration.

The exact locations of the dump sites and thus associated risk areas are ambiguous (Brewer & Nakayama, 2008) Figure 1 show the most probable dump sites and risk areas near Denmark.

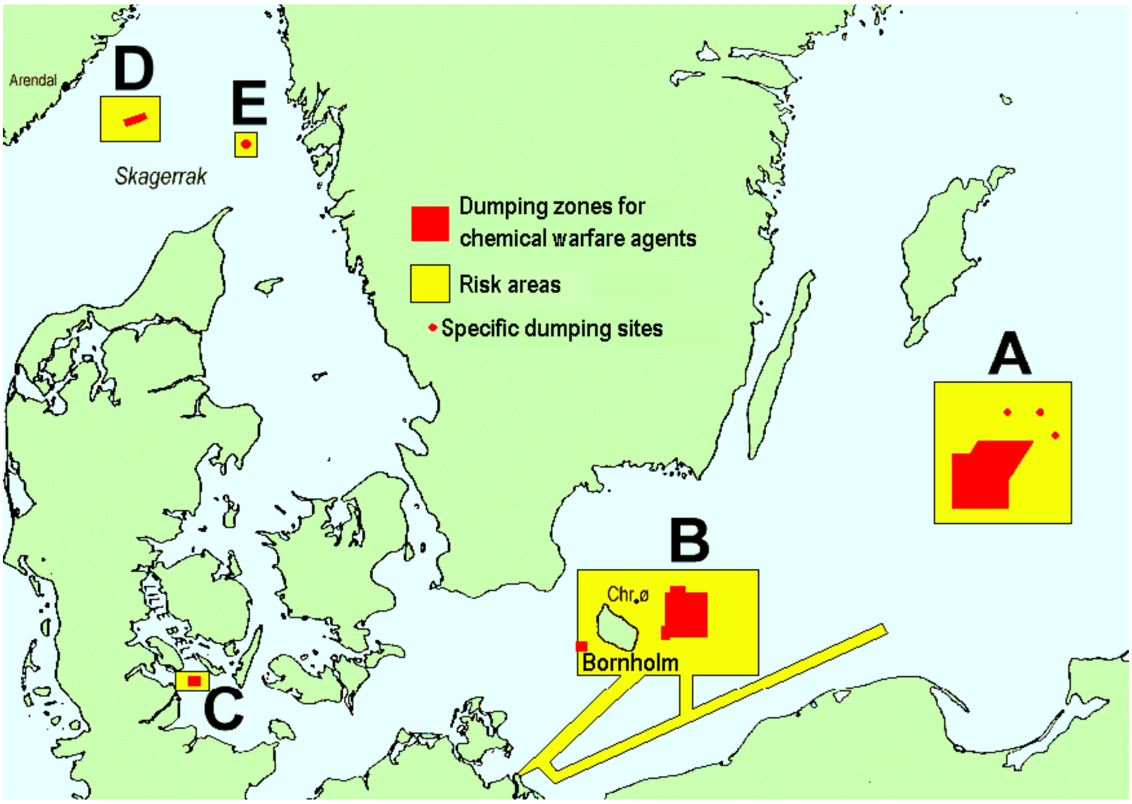


Figure 1 CWA dumping areas near Denmark. A is the Gotland dump site; B is the Bornholm dump site; C is the Lille-belt dump site; D & E are the Skagerrak dump sites (HELCOM, 2002).

The primary, and designated dumping site in the Bornholm basin (area B), is a circular area with a radius of three nautical miles, with the centre coordinates at 55°E21"N and 15°E37'02"E covering an area of 99 km^2. However, not all CWA was dumped at the designated site, hence a secondary, and more realistic dump site is located roughly at 55°10"N to 55°23"N and 15°24"E to 15°55"E, covering 892 km^2, the red area. The dumping zone west of Bornholm is less well described and was conducted by the United Kingdom after the war. The yellow box indicates the risk area in the Bornholm basin covering more than 9000 km^2 and has been expanded with the likely sail routes of the ships conducting the dumping and assuming en route dumping (Figure 1). Figure 2 is an approximate representation of the entire Bornholm risk area, with the designated primary dump site in the circle, the more likely secondary dump site (the box) and the entire tertiary risk area. Dump site is where the munitions were dumped (primary), and where they probably were dumped (secondary), and the risk area is the area where there might be munitions (tertiary).

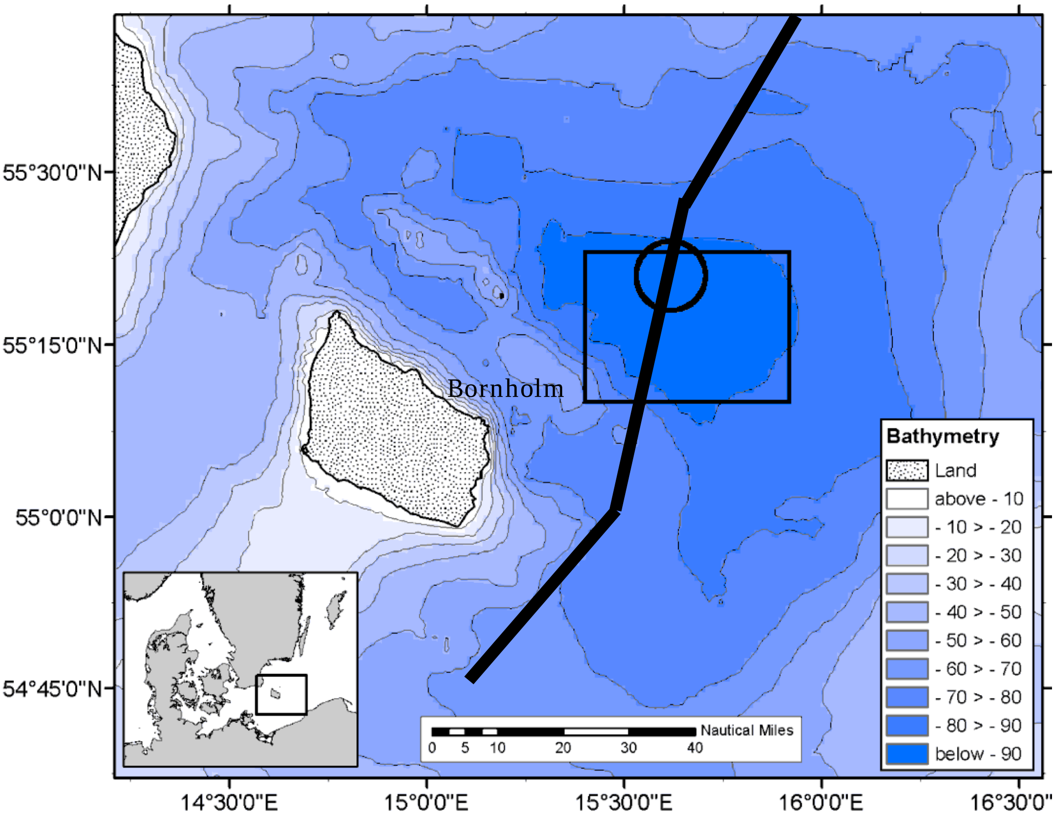


Figure 2 Approximate primary dump site (circle) within in the larger and more probable secondary dump site box, the larger tertiary risk area (the entire mapped area here), and the S-route and the Bornholm basin bathymetry.

The munitions have been resting on the seabed and in the sediment of the Baltic Sea for more than sixty years and the extent of corrosion of the shells, and thus release, of the toxic chemicals into the marine environment is poorly understood, some shells will have leaked their content whereas others might still be intact. The ratio between corroded and empty munitions versus intact munitions is not known, it is however clear that oxygen is needed for corrosion of the munitions iron walls, and that munitions situated in anoxic sediments will be better conserved than munitions exposed to oxygen in either the sediment or water. Hence, the ratio corroded and potential empty munition versus intact potential full munitions to a large extend is the ratio of the munitions above and below sediment. Due to the national security issues and hence secrecy concerning both the location and environmental properties of CWA there have been performed very few qualified site specific environmental risk assessments of CWA in and around dump sites at all. Screening level risk assessments towards the humans consuming fish caught in the dumping areas in the Bornholm basin cannot rule out potential risks towards the consumer as the total margin of exposure (MoE) for the total CWA mixture = 0.5 to 2.6, for the primary and secondary dump site, respectively, warranting further investigation to accurately evaluate the potential risk (Sanderson et al. 2008b). Similarly, the more realistic worst-case risk scenario towards the fish community has been screened which yielded a total CWA mixture margin of safety (MoS) of less than 2 also warranting further investigation for the primary and secondary CWA dump area (Sanderson et al. 2008a). The added CWA risk towards both human health and the health of the fish community as a consequence of the proposed gas pipeline along the S-route in the tertiary risk area has been screened, and it was concluded that the human health MoE ranged from

50 to 300 and the MoS towards the fish community ranged from 333 to 2000 per constructed pipeline in the tertiary risk area. Due to the high toxicity of the CWA and the scientific exposure uncertainties it was concluded that despite the high safety margins towards humans and the fish community empirical evidence is needed to assess the potential added risk from construction of a gas pipeline through the tertiary risk area (Sanderson and Fauser, 2008c). As evident from the historical context of secrecy for CWA, and lack of updated property information and the sheer size of risk area 3, of more than 9000 km^2, and the evident potential risks and severity of the CWA toxicological properties warrant further investigation. These should be both quantitative but also quality in nature, as the overall assessment of risks will be based both on the measured and modelled data but also on the qualitative local expert experience generated over decades among fishermen, the navy and other local stake holders on the island of Bornholm.

Hence, the aim of this report is to supplement the ongoing empirical scientific investigations with qualitative investigations of the publicly available records concerning the dumping of CWA munitions in the Bornholm basin as well as reporting the experience of local experts in relation to the state and impact dumped chemical munitions may have.

2.3 Methods

2.3.1 Qualitative analysis – interviews

The rationale for conducting qualitative interviews with local experts is to support lines-of-evidence to the scientific data and the historical analysis. Qualitative interviews were performed during the last week of April 2008 with the following stake-holder groups on Bornholm:

- Bornholm Fishermen’s association (Bornholms Fiskeriforening)
- Local municipal authority (Bornholms Regionskommune)
- Local Natural Conservation Society (Danmarks Naturfredningsforening, Bornholm (DN Bornholm))
- The Naval District of Bornholm (Marine Distrikt Bornholm)
- Local professional deep-sea divers
- Local media (Bornholmstidende)
- Bornholm’s Museum

The respondent’s identity are kept anonymous but known to NERI. The main results of the interviews will be summarized in this report.

2.3.2 Qualitative analysis – news articles

Accurate and full disclosure of the dumping of CWA after WWII has been impaired first by the 50 years international secrecy moratorium (Brewer & Nakayama, 2008) allowing the information to withhold and subsequently by the cold war following WWII. Information on the major dumping of CWA in the Bornholm basin, performed by the Russian authorities, was held secret from 1947 until 1993. During these almost 50 years important pieces of information may have been lost, moreover, the scientific accuracy and completeness of the disclosed information provided by the Russian authorities to HELCOM in 1993 can be questioned. We therefore obtained copies of newspaper articles, especially from Bornholm newspapers, from the beginning of the dumping in August 1947 until the end of 1992 in association with Bornholm’s Museum who graciously provided NERI with the documentation, see annex 1 for samples of the newspaper articles. More than 900 news articles were uncovered for the period. These represent the significant portion of the Danish public record concerning the dumping of CWA munitions near Bornholm. The articles were analysed with special emphasis on when, where, how much, how and by whom the munitions were dumped. They were moreover analysed for potential impacts reported both towards human and environmental health. Combined they make up a series of qualitative lines-of-evidence supporting the scarce quantitative scientific and empirical evidence.

2.4 Results

2.4.1 Interviews

The main message results of the interviews are summarized below for the various respondents.

Bornholms Regionkommune (Municipality):
- They do not collect samples or monitor impacts of CWA on the marine environment
- They do not receive inquiries by concerned members of the public as there is in general very limited public and media concern
- Lumps of gas and munitions are less frequently reported now relative to for 20-30 years ago due to less fishing activities
- There are no reports of exposure (wash ashore) or contact / effects on people bathing
- They do not believe that the currents and waves are strong enough to transport munition to the shore
- They do not consider there to be a significant environmental and human health threat and that the munitions are best left alone

Bornholms Fiskeriforening (Fishing association)
- There are high abundances of fish at the dump site when there is influx of oxygen (e.g. plenty of oxygen in 2003 and 2007) all the way to the seafloor (cod, sole, sprat, herring and other fish are found). They follow preys in diurnal cycles in the water column and seek refuge near the wrecks. They see no lesions on any fish. Fish only have contact with CWA in the net and the catch is then discarded
- They only catch lumps of hard gas nowadays (ranging from tennis-ball size to large lumps of up to 50kg. Twenty to thirty years ago the lumps were greasier and like honey
- All the gas munitions shells they catch now are very corroded and they are caught over large areas
- They have not caught any other weapons than German gas bombs
- They catch fewer lumps nowadays and they do not consider there to be threat and that the munitions are best left alone

Professional deep sea diver
- There are plenty of fish at the dump site. There are also fishes with lesions up to 5cm in diameter at higher frequency in the dump site than in the surrounding areas
- Munitions are more disperse now due to trawling and re-dumping
- Munitions in the sediment (anoxic) are largely intact with paint and all. The mud can be very deep and soft and munitions shells can thus be buried

- There are heaps of munitions and plenty of wrecks but not wrecks with munitions to his knowledge
- Debris and munition is spread over large areas

Bornholms Marine District

- They have had 720 cases of caught munitions since 1960 – mostly mustard gas, Adamsite and CAP – never nerve agents
- Most munitions have been KC250 with 2.5 cm iron casing, they are not armed but have a small amount (3 kg)of explosives to disperse the gas typically 100kg mustard gas in liquid form (Figure 3)

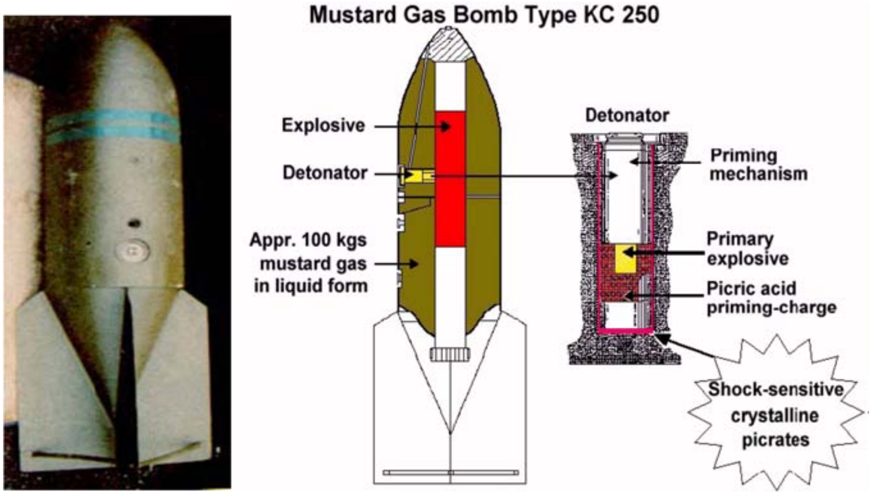


Figure 3 Mustard Gas Bomb type KC 250 (Bornholms Marine District).

- CAP was dumped later than the 1947 dumping, CAP and Adamsite was primarily dumped in wood casing
- Since 1992 all the caught munitions have been either empty or completely corroded and now they only get free lumps of gas
- No sinking of ships occurred during the dumping in 1947 with munitions at the Bornholm site
- Over recent years the mustard lumps are solid all the way through – previously (>10 yrs ago) there could be liquid in side but not any longer (Figure 4). Adamsite are still sticky lumps

Figure 4 Navy personnel in protective ABC suit with a lump of mustard gas (Bornholms Marine District).

- Lumps vary in size and the annual total amount caught is less than 1000 kg (typically around 100 kg roughly)
- The dumped munitions are wide spread. Caught gas with explosives are re-dumped for safety concerns, those without explosives are brought in and incinerated
- Fishing is illegal in the primary dump site and not recommended in the secondary dump site – there are plenty of healthy fish at dump site
- There are also surprises such as 1000 kg container with adamsite on the harbour of Nexø dumped after 1960 of eastern European origin

Bornholmstidende (journal), Bornholms Museum, Danmarks Naturfrednings forening (Environmental NGO), Bornholm

Common for these respondents was that they have no or very little specific information concerning the state, impact and risks of the dumped chemical munitions but are interested in receiving information on the topic. Their organizations and memberships and stake-holders do not report significant human and environmental concerns but interest in the research being conducted in relation to the risk assessment.

2.4.2 Historical analysis (news articles)

The dumping started summer approx. July 1 1947 and ended December 30 1947. The first public report in the news was on August 14 1947 where the miner ‘Elbing VIII’ of Lybäk started dumping at 55”20N and 15”37Ø 3 nautical miles radius. With up to 2000 gas munitions per trip and many of them leaking, the ship reeks of gas. Dumping was conducted by the Russian navy in secrecy in international waters. August 15 1947 dead fish wash ashore due to leaking bombs, and August 18 1947 bombs are caught during fishing in the Bornholm basin, four fishermen get sick. On August 19 more than 25 bomb chests with munitions washed ashore. A few days later > 50 chests wash ashore all along the island coastline (Figure 5). The munitions so to speak ’sailed’ ashore in their wooden chests after been thrown overboard.

Figure 5: Washed/sailed ashore KC250 aerial mustard gas munitions shell in its original wood chest (Bornholm’s Museum).

After becoming aware of the dumping the Danish ship MR 242 starts to oversee the dumping in the Danish territory from time to time. There are expressions of fear among the Bornholm tourist association on August 23

1947 due to dumping of 200.000 tonnes munitions. Sept 4 1947, four ships are now dumping; three German and one Russian (Christian, Odamunde, Brake, Elbing), roughly 2-300 tonnes are thrown overboard per day. Commander Capt. Terzkoff gives orders to shooting of drifting chests after reports of these washing ashore in Bornholm, Sweden and Poland. The munitions were luckily not ‘live’, the chock sensitive detonator device for the explosives was not inserted into the munitions, hence the munitions did not explode when washing ashore along the rocky coast of Bornholm. Empty TNT holsters wash ashore Dec. 8 1947. Adamsite and arsenic oils are observed in wooden chests and barrels only. There are rumours that some of the munitions were emptied of gas before dumped (March 1 1948). Sweet smelling greenish crystals in a tin can wash ashore in Sweden labeled ‘Gift’ (poison), there are concerns that this might be Zyklon B. June 6 1948 further reports that nerve agents is dumped and drift ashore in Sweden. Poisoned cod eggs from Bornholm sends four consumers in Copenhagen to the hospital. Over the next days more than ten people get sick and there is a ban on selling this product for two weeks, April 11 to January 25 1948, due to contamination with mustard gas after contact aboard the ship. April 4 1951 three people get sick again from eating cod eggs. On April 16 1952 bombs still leaking and hissing in water when lifted out of the water. No fishing restriction in the dump site in late 1960s – need further assessments. In 1962 the East Germany navy is engaged in Operation Hanno. An old wooden barge is filled with CWA and scuffled near the primary dump site in the Bornholm basin. Figure 6 is a series of pictures of the Operation Hanno.

Figure 6: Operation Hanno 1962. Sinking of vessel filled with CWA munitions (Bornholm’s Museum).

In the later part of the 1960s there are reports of dead fish outside the Swedish coast due to released CWA from corroded shells. In 1971 there is an emerging understanding that arsenic oils and mustard gas mixtures in liquid form are prevalent in the munitions and that the content is liquid and sticky. The navy reports on Aug. 5 1972, that all munitions are corroded, broken or empty and are present as lumps on the seafloor. January 25 1975 there are reports of cancer lesions on cod that are related to gas. In 1977 it is reported that more than 500.000 CWA shells were dumped. March 27 1984; fishing restrictions in the primary dump site are put in place. The German archives are opened and the Jäckel-report comes out on June 15 1985 suggesting that 36-50.000 tonnes German CWA munitions were dumped during the 1947 operation. In the mid-1980s the Danish authorities began operation Pegasus on collection and destruction of dumped munitions outside Bornholm, this effort was however abandoned as the costs and related security risks and public opinion turned against the operation. Citizens in a 2 km wide corridor along the transportation route to the storage bunker in the center of Bornholm were handed gasmasks and there was public concern about truckloads of chemical munitions being transported through Bornholm cities. Moreover, there were no options to incinerate munition containing explosives, so the Navy had to manually remove the explosives so the chemicals could be disposed of separately at the incineration facility Kommune Kemi. One intact bomb was caught January 20 1988 by Danish fishermen, which was reported as a rarity. In 1992 the European Parliament decided by more than a 93 % majority vote that the environmental and human health risks of dumped CWA in the Baltic Sea should be investigated and described in support of deciding further actions relative to potential remediation needs. The HELCOM organized an *ad hoc* chemical munitions working group (CHEMU) that collected information provided by the Russian authorities in 1993 with regard to the dumping of CWA during 1947. The HELCOM CHEMU (1994) concluded that the CWA would either be insoluble or degrade and dilute rapidly so that remediation was not needed. These conclusions were drawn without thorough scientific investigations. During the second half of the 1990s and early 2000s increased scientific investigations was performed at other dump sites (Skagerrak and elsewhere) but not at the Bornholm dump site. In 2005 the EU Commission funded through the 6th Framework Programme the project MERCW (Modelling the Environmental Risks of Chemical Weapons in the Baltic Sea), which will be concluded November 1 2008. Preliminary model based screening assessment of MERCW suggest that CWAs at the primary and secondary dump sites could potentially cause risks (Sanderson et al. 2008ab), and that measured data are needed to fully evaluate the risks. The preliminary measured CWA concentrations are highest at the primary dump site in the secondary dump site only metabolites of CWA have been detected in the top 5 cm of the sediments. In total some 200 Danish fishermen have recorded injuries sustained via direct contact with the munitions, unofficial numbers suggest that most fishermen around Bornholm at some point have been in contact with the gas with no or minor injuries. Figure 7 depicts the recent number of shells caught and the tonnage per year for the entire Baltic Sea in the period 1995 to 2006 on a log scale.

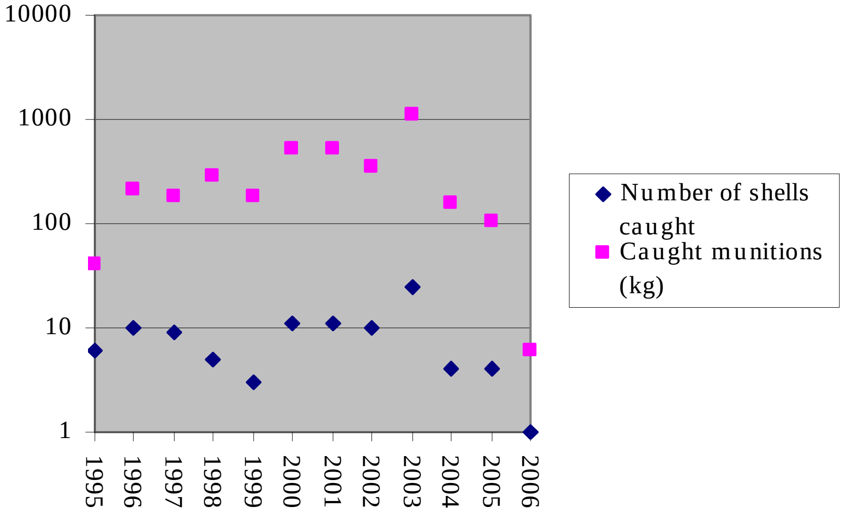


Figure 7: Number and total kg caught CWA munition (1995-2006) (HELCOM, http://www.helcom.fi/environment2/hazsubs/en_GB/chemu/)

2.5 Discussion and conclusions

There are significant uncertainties and confounding factors plus the high chronic toxicity of the compounds to consider when assessing the risk of CWA towards human and environmental health: The spatial scale - potential CWA contamination of up to >9000 km² at depths as deep as >100m in the Bornholm basin:

- The time scale - inaccurate information concerning the dumping occurring for the past 60 years
- Uncertainty concerning the corrosion state of all the munitions not only those retrieved
- The high chronic toxicity of the compounds especially mustard

Hence the collection of qualitative data from interviews and analysis of the history records hereunder the newspaper writings with respect to the CWA dumping. The main results of the interviews with local experts and the analysis of the newspaper articles can be summarized to that the dumping was secret and it started during the summer of 1947 and ended Dec 27 1947, and that some 12,000 tonnes active CWA was dumped in the Bornholm basin, and that the historical records are not complete. Different types of CWA were dumped primarily as mustard gas and other blistering agents but also a small amount of nerve agents.

The dumping caused fish kills in 1947. It is important to note that there are plenty of fish at the dump site and that the stocks fluctuate with the oxygen levels and the fish go all the way to bottom. Fishing with bottom-trawls are not permitted in the primary dump site and not recommended at secondary dump site. No extraordinary frequencies of lesions on fish from the dump site are reported. The munitions that lie on top of the sediment (with access to oxygen) are completely corroded and mustard gas lumps are solid, while Adamsite is still sticky. Munitions buried in the sediment are likely intact due to anoxic conditions preventing corrosion. The relative amounts of buried (intact) CWAs versus the CWAs at the sediment surface (corroded) are not known. The munitions are not ‘live’ as the detonator is not inserted. There are no reports of fishermen catching nerve agents. Occurrence of munitions is wide spread due to inaccurate dumping and trawling that have occurred for the past 60 years. There are no reports of munitions or CWA lumps washing ashore of Bornholm for the past decades. Munitions did wash ashore in the late 1940s, or rather they ‘sailed’ ashore in their wood chests (see Figure 4) There are ship wrecks at the dump site but uncertainty about sinking of munitions ships. There are reports of East Germany scuffling a wooden barge in 1962 filled with CWA munitions (Operation Hanno).

Some 200 fishermen have been injured since 1947 from direct contact with the gas, but there are no records of potential chronic illness sustained such as liver cancer or neurotoxic effects. There have not been reports of serious acute occupational accidents for the at least the past decade in Danish media. There are generally limited human and environmental health concerns as a result of the dumped CWA, but interest in the topic from the local stake holders. Sound risk assessment of very hazardous and intentional harmful compounds such as the CWA with significant uncertainties requires further scientific investigations and site specific information to reach unequivocal risk conclusions.

2.6 References

Brewer, P.G. & Nakayama, N., 2008: What lies beneath: A plea for complete information. *Environ Sci Technol*. 42: 1394-1399.

HELCOM, 1994: Report on chemical munitions dumped in the Baltic Sea. Report to the 15th meeting of Helsinki Commission. Danish Environmental Protection Agency. Available at:
http://www.rurociagi.com/spis_art/2005_4/raport.pdf

HELCOM, 2002: Response Manual, Vol. 2 Chapter 6. Dec 1 2002 - Amendment No. 27/02/03.

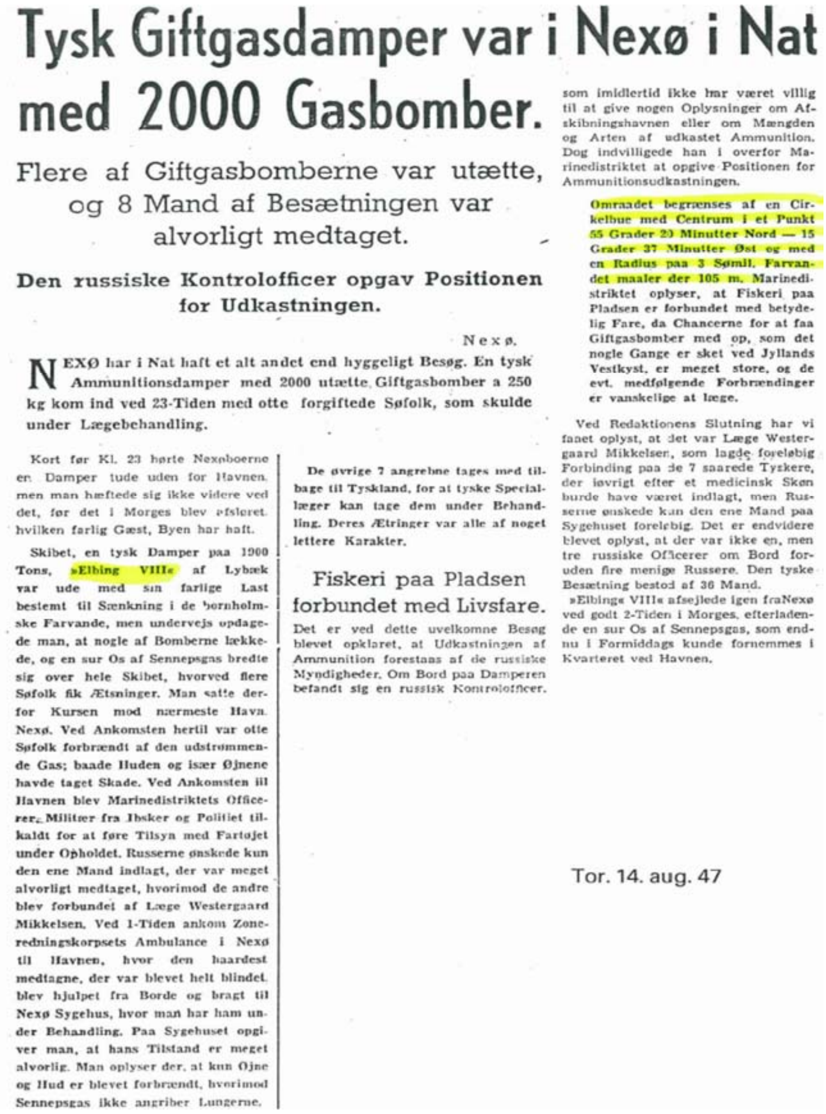
Sanderson, H., Thomsen, M., Fauser, P. & Sørensen, P.B., 2007: PBT screening profile of chemical warfare agents (CWAs). *Jour Haz Mat*. 148: 210-215.

Sanderson, H., Thomsen, M., Fauser, P. & Sørensen, P.B., 2008a: Screening level fish community risk assessment of chemical warfare agents in the Baltic Sea. *Jour Haz Mat*. 154: 846-857.

Sanderson, H., Thomsen, M., Fauser, P. & Sørensen, P.B., 2008b: Human health risk screening due to consumption of fish contaminated with chemical warfare agents in the Baltic Sea. *Jour Haz Mat*. Available at:
http://dx.doi.org/10.1016/j.jhazmat.2008.05.059

Sanderson, H. & Fauser, P. 2008c: Risk screening of chemical warfare agents towards humans and the fish community resulting from sediment perturbation from construction of the planned Nord Stream offshore pipelines through risk area 3 (S-route) in the Baltic Sea. DMU File 75-00061.

2.7 Annex 1: Newspaper samples



Tysk Giftgasdamper var i Nexø i Nat med 2000 Gasbomber.

Flere af Giftgasbomberne var utætte, og 8 Mand af Besætningen var alvorligt medtaget.

Den russiske Kontrolofficer opgav Positionen for Udkastningen.

Nexø.

NEXØ har i Nat haft et alt andet end hyggeligt Besøg. En tysk Ammunitionsdamper med 2000 utætte Giftgasbomber a 250 kg kom ind ved 23-Tiden med otte forgiftede Søfolk, som skulde under Lægebehandling.

Kort før Kl. 23 hørte Nexøboerne en Damper tude uden for Havnen, men man hæftede sig ikke videre ved det, før det i Morges blev afsløret, hvilken farlig Gæst, Byen har haft.

Skibet, en tysk Damper paa 1900 Tons, »Elbing VIII« af Lybæk var ude med sin farlige Last bestemt til Sænkning i de bornholmske Farvande, men undervejs opdagede man, at nogle af Bomberne lækkede, og en sur Os af Sennepsgas bredte sig over hele Skibet, hvorved flere Søfolk fik Ætsninger. Man satte derfor Kursen mod nærmeste Havn, Nexø. Ved Ankomsten hertil var otte Søfolk forbrændt af den udstrømmende Gas; baade Huden og især Øjnene havde taget Skade. Ved Ankomsten til Havnen blev Marinedistriktets Officerer, Militær fra Ibsker og Politiet tilkaldt for at føre Tilsyn med Fartøjet under Opholdet. Russerne ønskede kun den ene Mand indlagt, der var meget alvorligt medtaget, hvorimod de andre blev forbundet af Læge Westergaard Mikkelsen. Ved 1-Tiden ankom Zoneredningskorpsets Ambulance i Nexø til Havnen, hvor den haardest medtagne, der var blevet helt blindet, blev hjulpet fra Borde og bragt til Nexø Sygehus, hvor man har ham under Behandling. Paa Sygehuset opgiver man, at hans Tilstand er meget alvorlig. Man oplyser der, at kun Øjne og Hud er blevet forbrændt, hvorimod Sennepsgas ikke angriber Lungerne.

De øvrige 7 angrebne tages med tilbage til Tyskland, for at tyske Speciallæger kan tage dem under Behandling. Deres Ætringer var alle af noget lettere Karakter.

Fiskeri paa Pladsen forbundet med Livsfare.

Det er ved dette uvelkomne Besøg blevet opklaret, at Udkastningen af Ammunition forestaas af de russiske Myndigheder. Om Bord paa Damperen befandt sig en russisk Kontrolofficer, som imidlertid ikke har været villig til at give nogen Oplysninger om Afskibningshavnen eller om Mængden og Arten af udkastet Ammunition. Dog indvilligede han i overfor Marinedistriktet at opgive Positionen for Ammunitionsudkastningen.

Omraadet begrænses af en Cirkelbue med Centrum i et Punkt 55 Grader 20 Minutter Nord — 15 Grader 37 Minutter Øst og med en Radius paa 3 Sømil. Farvandet maaler der 105 m. Marinedistriktet oplyser, at Fiskeri paa Pladsen er forbundet med betydelig Fare, da Chancerne for at faa Giftgasbomber med op, som det nogle Gange er sket ved Jyllands Vestkyst, er meget store, og de evt. medfølgende Forbrændinger er vanskelige at læge.

Ved Redaktionens Slutning har vi faaet oplyst, at det var Læge Westergaard Mikkelsen, som lagde foreløbig Forbinding paa de 7 saarede Tyskere, der iøvrigt efter et medicinsk Skøn burde have været indlagt, men Russerne ønskede kun den ene Mand paa Sygehuset foreløbig. Det er endvidere blevet oplyst, at der var ikke en, men tre russiske Officerer om Bord foruden fire menige Russere. Den tyske Besætning bestod af 36 Mand.

»Elbing« VIII« afsejlede igen fra Nexø ved godt 2-Tiden i Morges, efterladende en sur Os af Sennepsgas, som endnu i Formiddags kunde fornemmes i Kvarteret ved Havnen.

Tor. 14. aug. 47

Over 25 „Gaskister“ dreve op paa Bornholms Øststrand

Er Sennepsgasbomberne gaaet til Bunds, da „Gaskisterne stødte paa de yderste Skær?

Drivende Bombe rapporteret Sydøst om Nexø.

Rønne.

Med den nord-nordøstlige Vind er der drevet adskillige uhyggelige Genstande i Land paa Bornholms Østkyst i Løbet af Natten og Formiddagstimerne. Befolkningen har allerede døbt de ofte 2 m lange Kasser, som er drevet op paa Kysten, til »Gaskister«. — Det menes, at en Del af Gasbomberne, som Kasserne har indeholdt, befinder sig paa Forstranden i Vandet.

Det er især paa Kyststrækningen mellem Listed og Gudhjem, at Befolkningen i Morgentimerne har gjort de uhyggelige Fund. Medens dette skrives, meldes der stadig om nye »Gaskister«, som driver i Land og nu findes i et Antal af godt 25 paa denne Strandstrækning.

Længere Syd paa omkring ved Nexø, er der rapporteret et Par Kasser til Søs, og i en af disse mener man, at der endnu befinder sig en Sennepsgasbombe. Ind i selve Havnen i Nexø er der drevet 3 Kasser, der dog alle var tomme, men som iøvrigt bar Mærker af at have indeholdt en Bombe hver.

Bomber i Forstranden?

Hr. *Johannes Hansen*, Fiskemelsfabriken, Gudhjem, der har været med til at tage imod de første »Gaskister«, fortæller, at Kasserne bærer tydeligt Præg af at have indeholdt Bomber. Spørgsmaalet er bare, hvor disse er faldet ud. Der er meget, som tyder paa, at Bomberne har ligget ret længe i Kisterne, men at de er faldet ud ved at stødes mod Klipperne.

— I saa Fald, forsætter Hr. Johs. Hansen, er der opstaaet en meget farlig Situation, idet Kysten paa Østlandet overalt vil være usikker for Sennepsgasbomber. Det vil selvfølgelig blandt andet være til stor Fare for Badningen.

Kasserne er fra 1,80 til 2 Meter lange. De er en lille halv Meter høje og maaske lidt mere i Bredden. Der er Haandtag paa begge Sider, og de ligner grangiveligt Ligkister. Overalt, hvor de er drevet i Land, har Befolkningen samlet sig omkring dem, men tilkaldt Militær sørger for, at ingen kommer til at røre dem.

De uhyggelige ligkisteagtige Kasser.

En Del af Kisterne er inddrevet med Laag paa, og noget tyder paa, at disse indeholder Sennepsgasbomber. Før Bornholms Marinedistrikt kommer til Stede i Løbet af Eftermiddagen, forbydes det imidlertid at tage Laaget til Side. Alle Hunde og Børn holdes borte fra de Steder, hvor »Gaskisterne« staar paa Stranden.

Iøvrigt meldes der rapporteret en drivende Bombe Sydøst om Nexø Havn. Ogsaa den vil Marinedistriktet tage sig af i Løbet af Eftermiddagen. Det ventes, at der i Løbet af Dagen i Dag vil drive flere Bomber i Land paa Bornholms Østkyst.

Med de Strømforhold, der hersker i Farvandene omkring Bornholm, er der meget, der tyder paa, at man snart kan vente, at ogsaa Bornholms Vestkyst vil blive hjemsøgt af de uhyggelige »Gaskister«. Endnu er der dog ikke rapporteret nogle Tilfælde af inddrevne Kister paa Vestkysten.

En »Gaskiste« ved Svaneke.

Ogsaa paa Kysten ved Svan
er der i Formiddagstimerne dre
en ligkisteagtig Kasse i Land, s
menes at have indeholdt Senne
gasbombe. Der er blevet sat M
nevagt ved Gaskisten, saaledes
ingen kommer i Berøring med d
indtil Bornholms Marinedistr
naar frem til Pladsen.

Tir. 19. aug. 47

Forgiftede Fisk drevet i Land paa Østkysten?

Den russiske Marines Giftgasudkastninger til stor Skade for Fiskebestanden i Farvandene øst for Bornholm.

Er Kasserne med Giftgassen utæt, udsættes Fiskene for Kvælning.

Rønne.

DER har gaaet haardnakkede Rygter i Formiddagstimerne, som gaar ud paa, at der flere Steder paa Østkysten skulde være drevet døde Sild i Land som Følge af Giftgasudkastningerne ved Christiansø. Det har dog ikke været muligt at faa nogen Bekræftelser paa disse Rygter fra lokal Side, men »Bornholms Social-Demokrat« har henvendt sig til Dr. phil. Poul Jespersen i København og spurgt om, hvorvidt Udkastningerne kan være til Skade for Fiskebestanden.

— Det er der ingen Tvivl om, at de kan, siger Dr. Jespersen. Jeg tror dog ikke, man skal frygte for, at Udkastningerne fuldstændig lammer det bornholmske Fiskeri, men hvis Kasserne og Beholdningerne, hvori Giften udkastes, ikke er helt tætte eller springer op i Storm, vil Giften meget let kunne kvæle en Del af Fiskebestanden, som findes indenfor det paagældende Omraade.

Forgiftede Sild paa danske Frokostbord.

Det farlige ved saadanne Udkastninger er jo de Tilfælde, hvor Kasserne, der ikke altid kan være helt tætte, ikke gaar til Bunds, saaledes at de driver omkring i Søen, medens Giftgassen siver ud. I saadanne Tilfælde kan Kasserne anrette meget stor Skade, ikke bare paa Fiskebestanden, men de kan ogsaa være uhyre farlige for Skibstrafikken og vel nærmest virke som en Slags Gasmine.

— De Kasser, der gaar til Bunds, maa vel ogsaa kunne ramme Bundfiskene?

— Ja, det kan meget vel gaa ud over Bundfiskene, for Eksempel Rødspætter og en Del af Fiskeynglen.

— En Del af Fiskene bliver maaske ikke slaaet helt ihjel. Kan de saa ikke være farlige at spise for Mennesker?

— Det er nu saa specielt igen, det De der opstiller, og jeg ved ikke rigtigt, hvad jeg skal svare paa Spørgsmaalet. Men det er jo muligt, at en Del af Fiskene kun besvimer, medens Gassen bliver siddende i dem. I saa Fald bliver der altsaa Tale om en Slags gasforgiftede Fisk. Man maa jo ikke glemme, at der er Tale om en meget kraftig Sammensætning af Giftstoffer.

Ogsaa fra andre Sider, især fra Erhvervsorganisationerne og Fiskeriside, er man ængstelig for, at Giftudkastningerne skal indvirke paa Fiskebestanden, der som bekendt har været særdeles god i den forløbne Sæson paa den opgivne Position. *Falk.*

Fre. 15. aug. 47

MR 242 vil følge efter Giftskibet „Elbing VIII" til Dumping Feltet.

Fra Luften vil en Marineflyver forsøge at fotografere Russernes fortsatte Udkastninger af Giftstofferne.

250 kg Senneps-Bombe efterlod et næsten evakueret Listed.

I Overmorgen vender som bekendt Giftgasskibet »Elbing VIII« tilbage og ankrer op 1 Sømil fra Nexø for at tage den saarede tyske Sømand ombord. Den danske Marine har i den Anledning truffet Foranstaltninger til at følge efter »Elbing VIII« for at undersøge, under hvilke Forhold Ammunitions - Udkastningen foregaar. Det er MR 242, der er udset til at udføre dette Hverv med Kaptajnløjtnant Heisterberg Andersen som Chef. Desuden vil man sende en Flyvemaskine til Dumping Feltet i Haab om at kunne fotografere Udkastningerne.

Søløjtnant Espersen med 3 Marinere omkring en Sennepsgasbombe paa 250 kg.

Tor. 21. aug. 47

Ons. 27. apr. 49

Omfattende undersøgelse af farvandet ved Christiansø.

Havforskningsskibet „Biologen" skal i de nærmeste dage undersøge farvandet omkring dumpingfeltet. — Fiskerne instrueres i brugen af kloramin.

Rønne

Fra fiskeriministeriets side gøres i disse dage store bestræbelser for at undgå forgiftningstilfælde fra fiskeriet omkring Bornholm. Samtidig med ophævelse af forbudet mod salg af torskerogn i København og Frederiksberg udsendes meddelelse om, at fiskerne skulle iagttage visse forsigtighedsforanstaltninger i de tilfælde, hvor trawlet bragte giftgasbeholdere med op. I dag oplyses det, at havundersøgelsesskibet »Biologen« kommer til de farlige farvande for at foretage undersøgelser til gavn for fiskeriet.

Ingeniør Nielsen fra fiskeriministeriets forsøgslaboratorium er samtidig blevet stationeret i Rønne for at foretage analyser af alle fisk, der har været i trawl med giftgas, og et nøje samarbejde med den stedlige fiskerikontrol er i dag blevet indledet.

Gentagelser skulle være udelukket.

— Fiskerne er nu fra ministeriet blevet instrueret om, hvorledes de skal forholde sig, hvis de får gasbeholdere med op i trawlet, og gentagelser af forgiftningstilfældene skulle kunne undgås, udtaler ingeniør Nielsen i dag. Det er konstateret, at i de tilfælde, hvor der virkelig har været tale om forgiftning, har fiskerne haft gasbeholdere stående på dækket ved siden af kasser med fiskerogn, og det er selvfølgelig farlig. Det er ikke fisken i vandet, der bliver inficeret med gassen, idet giftgas hurtigt destrueres ved forbindelse med vand. I andre tilfælde, hvor folk er blevet syge, er det måske lige så meget læsning af avisernes beretning om giftgassen, der har gjort dem syge.

Der er imidlertid grund til at indskærpe, at fiskerne skal være forsigtige. De har nu fået udleveret alle nødvendige materialer til en grundig rengøring af redskaber og kutter, hvis de har været uheldige. Vort vigtigste våben mod de to giftgasarter, der er konstateret, er kloramin, og alle kuttere har dette stof ombord.

Gassen destrueres langsomt.

— Hvor store mængder giftgas er der sænket?

— Helt nøjagtigt kan jeg ikke opgive det, men der tales om ca. 20.000 tons i kister, kasser, tønder og andre beholdere. De er sænket ned i træemballage, og selve gassen er indesluttet i en metalbeholder. Som årene går rådner træet, og metallet ætses lidt efter lidt, hvorefter gassen trænger ud i vandet og destrueres.

— Der vil altså ikke blive tale om et evigt farligt farvand?

— Nej, men der vil sikkert gå endnu nogle år, før det hele er forsvundet. »Biologen« med dr. Aage Jensen som leder skal nu foretage praktiske undersøgelser og se, om der virkelig er tale om, at der flyder giftgaskasser rundt i farvandet.

I øvrigt er fiskerne opfordret til af marineministeriet straks at meddele, hvis de får beholdere i trawlet, men ikke alle fiskere har rettet sig efter henstillingen. Enkelte har brugt den taktik at samle giftgassen op, stille den på dækket og derefter sænke den igen på et sted, hvor de ved, at deres kolleger meget sjældent kommer. Dette er selvfølgeligt prisværdigt, men det ville være bedre, hvis de endelig ikke vil give meddelelse til marinedistriktet, om de slæbte beholderen efter skibet.

Der er grund til at indskærpe forsigtigheden overfor fiskerne, men forhåbentlig vil de nu iværksatte forholdsregler virke beroligende på det opskræmte publikum. Risikoen for at få forgiftede fisk er faktisk forsvundet med de nye regler.

— rald.

Lør. 16. apr. 49

De bornholmske fiskere venter en anden afgørelse.

Forbudet mod salg af torskerogn får alvorlige følger for fiskernes økonomi. — Krogfiskerne også ramt af den drastiske bekendtgørelse.

RØNNE

Forbudet mod salgt af torskerogn fra bornholmske farvande betyder et alvorligt indgreb i fiskernes muligheder for at drive rentabelt torskefiskeri. Især føler krogfiskerne sig ilde behandlet, idet der endnu aldrig er ført sennepsgasforgiftede fisk eller fiskevarer i land fra de kuttere, som udelukkende har anvendt kroge til fiskeriet.

Man har erkendt, at trawlfiskerne af og til kan få rester af krigsgas i trawlet, men det sker kun i nærheden af dumpingfeltet, og man finder det uretfærdigt, at samtlige bornholmske fiskere rammes af bestemmelsen. I fiskerikredse anslår man tallet af krogfiskende kuttere til at ligge omkring en fjerdedel af den samlede flåde, som i øjeblikket fanger torsk i de bornholmske farvande, og man henviser til, at det aldrig er sket, at sennepsgas eller andre krigsefterladenskaber har bidt på krogene. Man har kun i to tilfælde konstateret gasforgiftning i torskerogn og fiskefars, og man lægger ikke skjul på, at man venter nye bestemmelser fra ministeriet.

Spørgsmålet har endnu ikke været særlig aktuelt for fiskerne, idet der i de sidste dage ikke er fanget mange torsk, men hvis der ikke kommer nye bestemmelser, bliver fiskerne tvunget til at kaste en stor del af deres fortjeneste over bord sammen med den torskerogn, som ikke må sælges i København. Torskene kan godt bringes i land og afsættes til Tyskland som hidtil, idet denne eksport ikke er omfattet af forbudet mod salg af rogn og anden fiskeindmad.

Skagenfiskerne er i vid udstrækning begyndt at lægge deres fiskeri om, og en del af dem har bebudet, at de ville gå til bornholmske farvande for at deltage i torskefiskeriet her, men efter den vending, dette fiskeri har taget, er det tvivlsomt, om ret mange af Skagensfiskerne ønsker at deltage. De bornholmske kunder har ikke ladet sig afskrække af den megen blæst, der i København har været om spørgsmålet, og salget af fisk til hjemmeforbrug er ikke dalet. Fiskerne kan imidlertid ikke leve udelukkende af dette salg, og derfor kan det sikkert ventes, at ministeriet i næste uge vil tage hele spørgsmålet op til ny overvejelse og søge at skabe mulighed for at sikre de bornholmske fiskeres afsætningsmuligheder.

Tor. 11. okt. 84

Søværnets depot til sennepsgas - en bunker i Vestermarie plantage. Militære eksperter har anslået, at der højst bør opbevares 300 kg. sennepsgasbomber eller bomberester i depotet. Der er 1.700 kg.

Søværnets frygt ikke ubegrundet:

Livsfarlig gassky over Bornholm hvis krigsgas eksploderer

»Det kan koste en frygtelig masse menneskeliv«, siger chefen for Bornholms Marinedistrikt

Af Palle Smed

Det er ikke bare pjank og pjat, når søværnet advarer mod den uforsvarligt store mængde krigsgas, som ligger oplagret i et depot i Vestermarie plantage. Det er ramme alvor, understreger chefen for Bornholms Marinedistrikt, kommandørkaptajn O. Bretting. Sennepsgasbomberne kan muligvis eksplodere - ved selvantændelse. Ingen ved det. I så fald vil en livsfarlig gassky spredes over Bornholm til fare for den bornholmske befolkning.

Kommandørkaptajn O. Bretting lægger ikke længere skjul på sin frygt ved at have en langt større mængde krigsgas opbevaret end selv søværnets egne regler anbefaler. Nu må der gøres noget alvorligt ved det.

»Der er to alternativer«, siger O. Bretting. »Enten kan man opbevare skidtet på land, eller også kan man lægge det tilbage i havet. Ved at opbevare det på land risikerer man en miljøkatastrofe. En katastrofe, som kan koste en frygtelig masse menneskeliv eller skader på mennesker. Ved at dumpe gasbomberne i Østersøen, kan der opstå problemer med de øvrige Østersø-lande. Og så er man nødt til at gå på kompromis med sine principper.«

At de gamle tyske bomber er ikke i tvivl om. Hvor farlige bomberne er, ved man ikke nøjagtigt. Men der er god grund til at tro, at bomberne i dag er så skrøbelige, at de rent faktisk kan eksplodere af sig selv eller ved et ganske lille stød.

Sprængstof ufarligt

»Almindeligt sprængstof er under normale omstændigheder ganske uskadeligt. Man kan hamre, save eller spille fodbold med det. Man er nødt til at have en lille tændpatron - en forsprængning - for at få sprængstoffet til at eksplodere«, fortsætter kommandørkaptajn O. Bretting.

Uden detonator

»Men på mange af de sennepsgasbomber, som er fisket op de senere år, har metaldelene været tæret væk, så man ikke kan se, om der er overhovedet er nogen detonator i bomberne. Mange af bomberne er taget direkte fra det gamle Nazi-tysklands ammunitionslagre. Her har det garanteret ligget uden tændladning.«

Påvirkningerne

Men det er langt fra detonatoren, som er farligst i gammelt sprængstof. Alderen - tidens tand kan få det til at eksplodere. Med tiden ændrer sprængstoffets kemiske

Først har sprængstoffet ligget i de tyske ammunitionslagre. Derved er det blevet ilhet med luft. Og netop ilten sætter de kemiske reaktioner igang.

Dernæst er det blevet indkapslet i containere med gas af forskellig art.

Det er blevet smidt på havbunden, hvor det nu har ligget i 30 år under en konstant lav temperatur. Men skallen er tæret væk og sprængstoffet kommer både i direkte kontakt med gas og havvand.

Resterne er revet fri af bunden af et trawl. Under trykpåvirkning er det trukket op til overfladen, udsat for nye temperaturer og kommet i forbindelse med ilt.

Transporten over landjorden har yderligere rystet bomberne. Og i depotet sker der hele tiden temperatursvingning og luftfornyelse.

Bekymrer eksperter

»Det er disse kendsgerninger, som bekymrer militære kredse og foranlediger eksperterne til at tro, at der kan være sket en kemisk ændring i sprængstoffets sammensætning. Der kan være opstået nogle stødfølsomme blyforbindelser, som vil kunne gå af blot ved et lille stød. Men rent kemisk kan sprængstoffet også gå af af sig selv. Det

at opbevare det på land. Med et populært udtryk, som alle mennesker forstå, kan man kalde det selvantændelse«, siger kommandørkaptajn O. Bretting.

Depotet

Forsvarets ammunitionsdepoter er normalt bygget efter meget nøjagtige beregninger. Betonvæggenes tykkelse og depoternes konstruktion er kun beregnet til en vis mængde sprængstof.

Men den gamle bunker i Vestermarie Plantage er ikke bygget til formålet. Og da problemet med den store mængde krigsgas meldte sig, undersøgte eksperter forholdene: Kun 300 kg. gasbomber og bomberester bør opbevares i depotet svarende til tre, hele, ubeskadigede sennepsgasbomber.

Gassky

»En eksplosion vil ikke alene skabe en trykbølge, vil vil forstøve og fordampe gasklumperne og derved slippe ud i den fri luft. Ingen ved med sikkerhed hvor farligt, det er«, siger kommandørkaptajn O. Bretting videre.

»Måske vil der dannes en hel gassky. Og så virker bomberne jo fuldstændig efter samme hensigt, som de

Bornholms Marinedistrikt har meddelt Åkirkeby Kommune, at der ikke er mere sennepsgas tilbage i Vestermarie-depotet.
ARKIVFOTO

VESTERMARIE-DEPOTET ER NU TØMT

Der er ikke skygge af sennepsgas tilbage i Vestermarie-depotet. Det har Bornholms Marinedistrikt meddelt Åkirkeby Kommune og samtidig oplyst, at de sidste rester blev sendt til Kommunekemi i Nyborg.

»Det har vi blot taget til efterretning«, siger Frits Christensen som formand for Udvalg for Teknik og Miljø.

Hvor opfiskede sennepsgasfragmenter nu skal opbevares, er han ikke vidende om: »Det er også uinteressant for Åkirkeby Kommune nu, hvor der ikke mere er gasrester i Vestermarie Plantage og heller ingen mulighed for opbevaring i Lindesbjerg-depotet«. *Jans*

Tir.10.nov.92

3 RAMBOLL OIL & GAS - Nord Stream A/G. Offshore pipelines through the Baltic Sea Summary of NERI generated chemical warfare agent (CWA) analytical data in a risk context towards the fish community from construction of the planned Nord Stream offshore pipelines through risk area 3 (S-route) in the Baltic Sea

Hans Sanderson & Patrik Fauser

3.1 Summary

The potential risk towards fish communities from dumped Chemical Warfare Agents (CWAs) following the Second World War is assessed in association with the construction of the gas pipeline S-route transecting the CWA dumpsite in the Bornholm Deep in risk area 3. The assessment is made based on measurements of five arsenic containing CWAs and for the toxic inorganic form of arsenic, namely $As_{III\&V.}$ Literature and calculated sorption coefficients are used to transform measured sediment concentrations into the bioavailable pore water fraction. The relatively most hydrophilic CWA Trichloroarsine has the highest pore water concentration and risk towards the fish communities.

The overall total risk of CWA along the S-route towards the fish community is low, with sample stations 16 & 19 as the potentially highest risk areas.

There is a low risk for the sum of $As_{III\&V}$ in the pore water and considering that the potential contribution of all CWAs to the total arsenic concentration is insignificant compared to the measured total arsenic concentrations, the predominant part of the arsenic in the sediment has other anthropogenic and natural sources than CWA.

Further analysis of CWA degradation products and Yperite should be analyzed in a risk context together with presented data by Bossi et al. (2008) and the collected *in situ* fauna investigations, to derive the final conclusion regarding risk.

3.2 Introduction

Following the end of the Second World War Germanys approximately 65,000 tonnes stockpiled Chemical Warfare Agent (CWA) munitions were ordered by the allied forces to be destroyed during the second half of 1947 as a result of the Potsdam Conferences. Significant amounts were dumped in the Bornholm Deep. There are concerns that environmental risks may arise from perturbation of sediment containing traces of dumped chemical warfare agents (CWA) in connection with building gas pipelines in the Bornholm Deep. First tier model based screening risk assessment performed by Sanderson & Fauser (2008a) suggest a low indirect risk towards humans and the fish community associated with the construction of the proposed gas pipelines. Semi-qualitative interviews with local experts and review of contemporary local newspaper articles and interviews with responsible officers and seamen, further suggest low potential for risk. No extraordinary frequencies of lesions on fish from contact with CWA blistering agents from the dump site are reported. Munitions above the sediment (with access to oxygen) are completely corroded. Munitions in the sediment are likely intact due to anoxic conditions preventing corrosion. The relative amounts of buried (intact) CWA munitions and CWA munitions at the sediment surface (corroded) are not known for the dump site. Rambøll has surveyed the entire surface and subsurface sediment along the S-route for munition related anomalities and found no chemical related munitions. The CWA munitions are not 'live' as the detonators are not inserted. Munitions are dispersed due to inaccurate dumping, trawling and drifting of munition boxes (Sanderson & Fauser, 2008b). The first tier risk screening and the qualitative and historical analyses needed further investigation supported by chemical analysis of actual measured sediment and pore water concentrations of CWAs along the proposed S-route. Hence, a cruise was designed along the S-route where a total of 95 sediment samples and 11 pore water samples were collected for chemical analyses at NERI (Bossi et al. 2008). The aim of this report is summarize these results in a risk context.

3.3 Methods

The results for the analysis of total arsenic, organoarsenic compounds and some of their degradation products in sediment samples and sediment pore water samples from the Baltic Sea were performed by the Danish National Environmental Research Institute, Aarhus University. The methods are described by Bossi et al. (2008). The following compounds have been included in the analytical program:

Arsenic compounds: Total arsenic (As_{total}), sum of arsenite As(III), arsenate As(V), monomethylarsonic acid (MA), dimethylarsonic acid (DMA), trimethylarsine oxide (TMAO), tetramethylarsonium ion (TETRA), arsenobetaine (AB). The concentration of As (III) and As (V) is given as the sum as the oxidation and the reduction of As (III) and (V) respectively during sampling, storage, preparation and analysis cannot be controlled. The individual concentrations are therefore not reliable. As_V is however thermodynamically more stable hence one would expect the majority of the inorganic As to be arsenate. From a toxicological perspective the sum of $As_{III\&V}$ presenting primarily the more toxic inorganic fraction of the total As is of most interest.

Organoarsenic warfare agents and their main degradation products: Adamsite, Clark I, triphenylarsine (TPA), phenyldichloroarsine (PDA), trichloroarsine (TCA).

Sampling was carried out late May 2008. The samples were received by NERI as frozen and kept at -18° C until analysis. Sediment samples for chemical analyses were taken with a Haps core sampler at the 35 stations along the planned pipeline route going south of the island of Bornholm. At 11 main positions additional samples were taken for pore water from the upper 5 cm of the core and 2 samples per station. In addition 2 samples were taken from the middle and 2 samples from the bottom of the core. At 10 positions 4 stations were sampled perpendicular to the pipeline route. The distance of these stations were 500m north, 250m north, 250m south and 500m south of the main station. The total number of sampling positions was 75 (Figure 1). At all stations 2 samples were taken from the upper 5 cm of the core. A total of 95 sediment samples and 11 pore water samples have been collected for chemical analyses. Each sample was equally divided and marked with A and B. The samples were frozen immediately after sampling. Samples labelled A were analyzed by NERI, while B samples have been shipped to VERIFIN, Finland for additional analysis of other types of CWAs and their degradates (Bossi et al. 2008), these results were not included in this report.

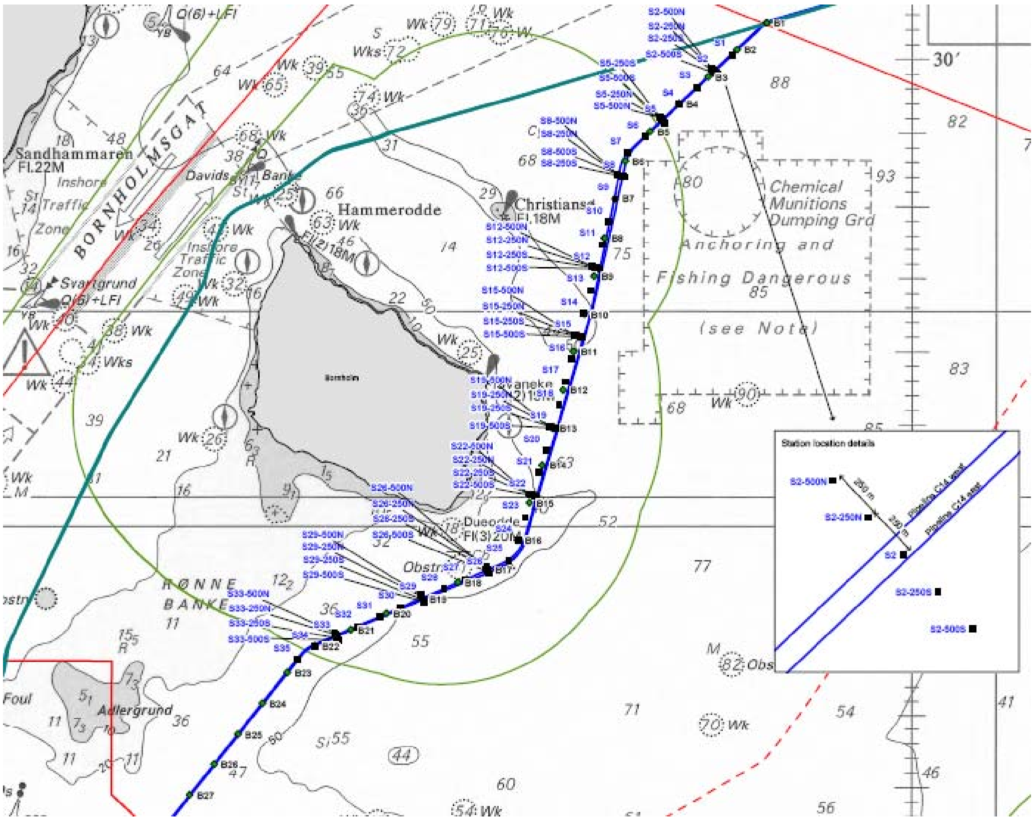


Figure 1 Sampling stations along the S-route near Bornholm.

3.3.1 Data analysis

The munitions have been resting on the seabed and in the sediment of the Baltic Sea for more than sixty years and the extent of corrosion of the shells, and thus release, of the toxic chemicals into the marine environment is poorly understood; some shells will have leaked their content whereas others might still be intact. During the past 20 years all the recovered munition shells at the sediment surface have all been broken and heavily corroded with no or completely oxidised yperite lumps (Sanderson & Fauser, 2008b). The ratio between corroded and empty munitions versus intact munitions is not known. The environmental toxicity along with most physico-chemical properties of CWAs have not been thoroughly investigated with modern methods and reported in the public literature, hence modelling of these properties are warranted to derive comparable datasets (Sanderson et al., 2008c). For chemicals to be incorporated into organisms such as fish and exert toxicity they generally need to be in solution, hence the sediment concentrations, Cs (mg/kg DM), will be used to calculate pore water concentrations, Cpw (mg/L), for all the samples based on adapted equilibrium partitioning (DiToro, 1991 and Sanderson et al., 2008c), cf. Eq. 1.

$$Cs = Cpw * Rs / Xs = Cw * (\theta + Kd * Xs) / Xs \qquad \text{(Eq. 1)}$$

Where; Rs = (θ + Kd * Xs) is the retention factor, θ is the pore volume fraction in the sediment 0.55 (Forster et al., 2003), Kd = foc * Koc is the partitioning coefficient between dry matter and water in L/kg DM, foc = 0.0775 is the fraction of organic carbon in particulate matter (Emelyanov, 1996), Koc is the partitioning coefficient (sorption coefficient) between organic matter and water (L/kg OM) and Xs is the density of sediment 1.2 kg DM/L (Forster et al., 2003).

Table 1 Sorption coefficient between organic matter (OM) and water and calculated retention factor (Rs) from Eq. 1. (Sanderson et al. 2008c)

Compound	Koc (L/kg OM)	Rs
Adamsite	5000	470
Clark I	19,000	1770
Triphenylarsine (TPA)	440,000	40,920
Phenyldichloroarsine (PDA)	817	77
Trichloroarsine (TCA)	35	3.8

The measured and calculated pore water concentrations will be used as the worst case predicted biota CWA exposure concentration (PEC). Kd values for $As_{III\&V}$ are not available from the literature and US EPA (2004) emphasises that partition coefficient values measured at site-specific conditions are absolutely essential. In this work Kd values are derived based on the 11 site-specific measurements of $As_{III\&V}$ sum concentration in the pore water and sediment, according to Eq. 2.

$$Kd = Cs/Cpw - \theta/Xs = 300\ (\pm 226SD)\ L/kg\ DM \qquad \text{(Eq. 2)}$$

Assuming constant sediment properties throughout the sampling area Koc = 3880 (± 2910SD) L/kg OM and the mean value for the retention factor is Rs($As_{III\&V}$) = 361. The PECs will be compared with toxicologically acceptable exposure concentrations towards the fish communities as reported in Sanderson et al. (2008c) with fish community extrapolated HC5 value. The HC5 represent the concentration where 95 % of the fish species LC50 in the community is not exceeded. The toxicity of $As_{III\&V}$ was derived from the US National Library of Medicine Hazardous Substances Data Base
(HSDB: http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB) for arsenic compounds the data was used to derive a species sensitivity distribution (SSD) for 17 aquatic organisms. The resulting HC5 value (protective of 95 % of the community) equals 0.29 mg/L (Figure 12). Due to the lack of *in situ* sediment dwelling organisms and recognized general low oxygen levels in the sediment, pore water, and near bottom water there is currently little documentation for specific sediment toxicity hence the measured and calculated pore water concentrations will be used as the PEC of toxicological relevance.

3.4 Results

3.4.1 Measured CWA in sediment

Figure 2 illustrate the measured CWA in sediment dry weight. The dry weight (DW) analysis is more robust than the wet weight and the DW CWA concentrations were thus used to derive the calculated pore water concentrations. The mean concentrations of the CWAs and their standard deviation are reported together with detection frequencies. Figure 4 shows the relative distribution of the CWA in the sediment column, because of the variable sample size (0-5cm n = 75; 5-50cm n = 15; 50-100cm n = 4) the statistical difference are not evident. There were no detects of CWA at 50-100 cm depths and higher frequency and levels in the top 5 cm of sediment.. Detection frequencies are 0 %, 13 %, 5 %, 43 % and 40 % for Adamsite, TCA, TPA, PDA and Clark I, respectively. The spike in PDA at station 16 is 250m south of the S-route.

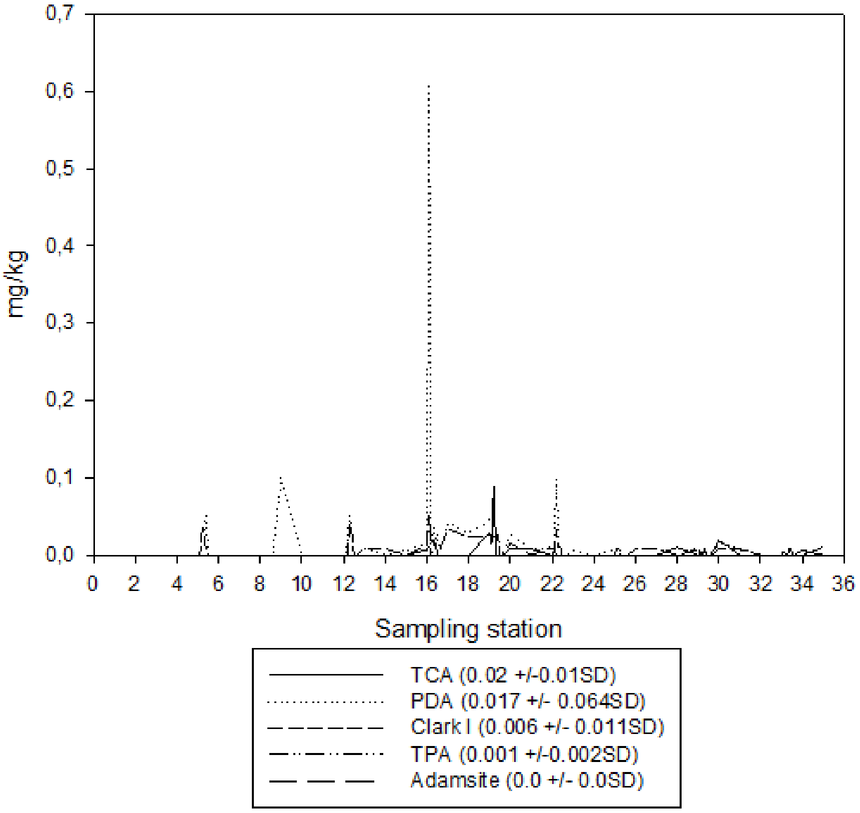


Figure 2 CWA in sediment (DW).

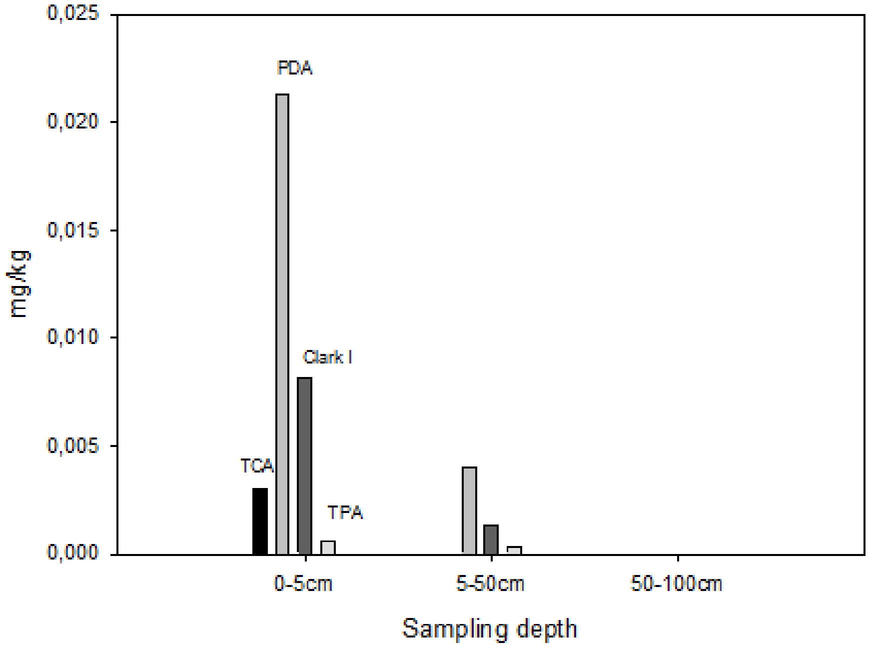


Figure 3 CWA distribution in sediment (DW).

3.4.2 Measured and modelled CWA in pore water

There were, not surprisingly, relatively few detections of CWA in the pore water due to the relatively high hydrophobicity of the compounds. Pore water concentrations are however, the primary direct exposure route to fish and other none sediment dwelling organisms, and the pore water concentrations are therefore of primary risk concern. Hence, the scarce measured pore water concentrations were bolstered with calculated CWA pore water concentrations based on equilibrium partitioning (EqP) modelling as described in the methods. Table 2 contains the measured pore water concentrations typically ranging between the level of detection (LOD) (Bossi et al. 2008) and 0.003 mg/L.

Table 2 Measured CWA in pore water (mg/L).

Sampling station	TCA	PDA	Clark I	TPA	Adamsite
2	<LOD	<LOD	<LOD	<LOD	<LOD
5	<LOD	<LOD	<LOD	<LOD	<LOD
8	<LOD	<LOD	<LOD	<LOD	<LOD
12	<LOD	<LOD	<LOD	<LOD	<LOD
15	<LOD	<LOD	<LOD	<LOD	<LOD
16	<LOD	<LOD	<LOD	<LOD	<LOD
19	<LOD	<LOD	<LOD	<LOD	<LOD
22	0.003	0.002	0.002	0.002	<LOD
25	0.002	0.002	0.002	0.002	<LOD
29	0.002	<LOD	0.002	<LOD	<LOD
33	<LOD	<LOD	<LOD	<LOD	<LOD
Detection frequency	27 %	18 %	27 %	18 %	0 %

The modelled pore water concentrations are shown in Figure 4. TCA having a lower Rs value than the rest of the CWAs dominates the calculated fraction predicted in the pore water, followed by Adamsite and PDA, both with relatively low Rs values and relatively higher measured sediment concentrations.

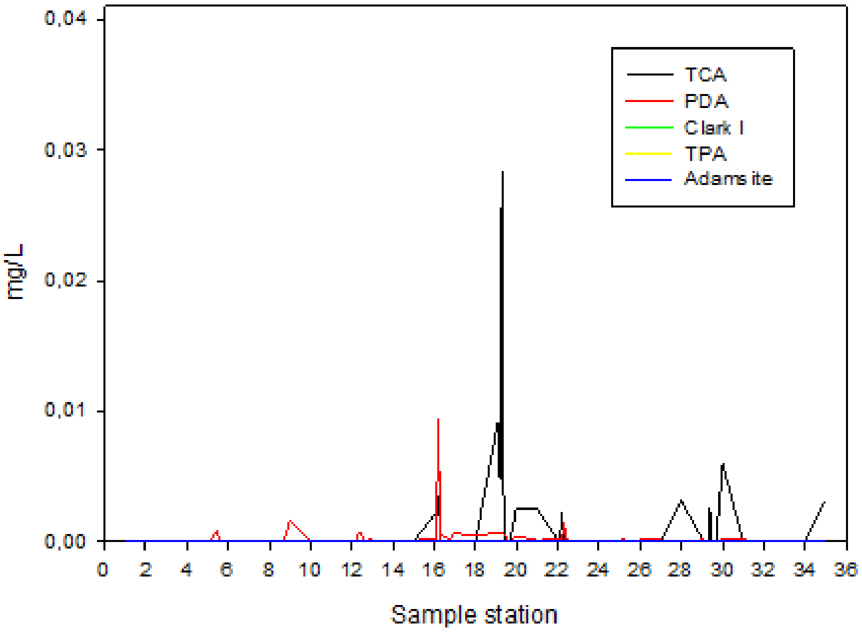


Figure 4 Modelled CWA pore water concentrations.

3.4.3 Measured arsenicals in sediment

Figure 6 includes the measured arsenicals in sediments along the S-route, the mean values and SD are reported in the box below the graph. It is notable that only DMA was detected above the LOD among the organic arsenicals. The most relevant value is the sum of As$_{III\&V}$ as this represents the more toxic inorganic fraction of the measured arsenicals. Detection frequencies are 100 % for total As and the sum of As$_{III\&V}$, and 72 % for DMA.

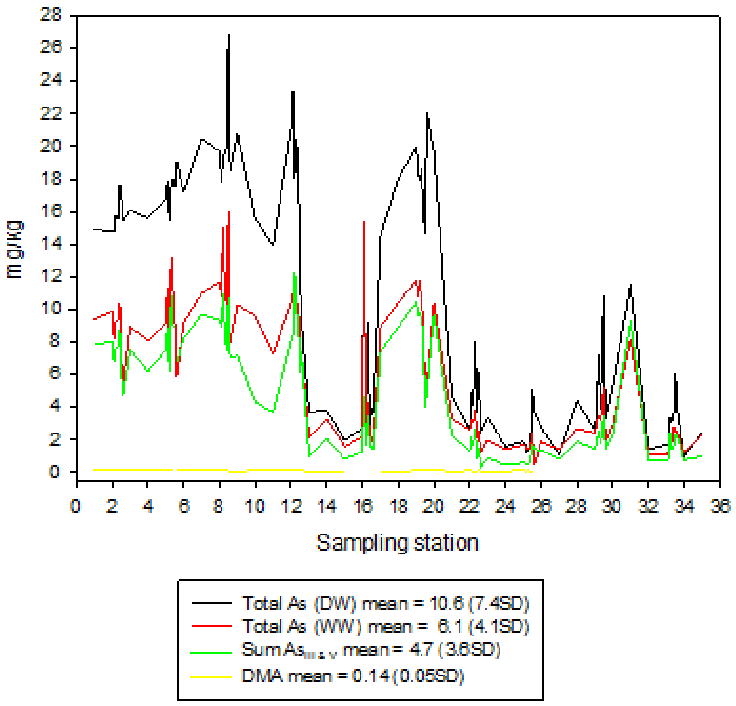


Figure 5 Arsenicals in sediment.

Figure 6 represents the vertical distribution of arsenicals in the sediment, again the direct comparison is impaired due to asymmetrical sample size, however, there does not appear to significant differences to report.

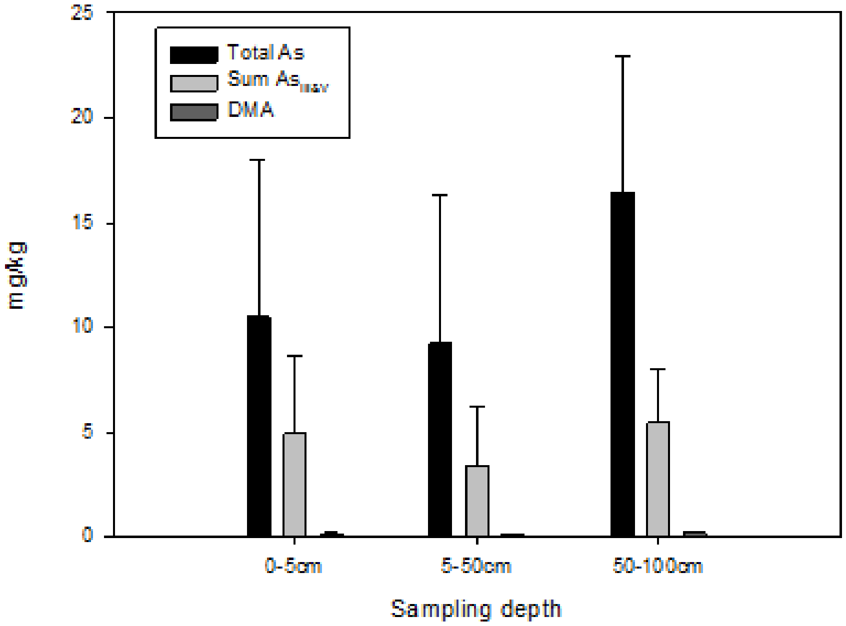


Figure 6 Distribution of Arsenicals in sediment (DW).

There is no correlation between total As and the total organoarsenic CWA levels in the sediment as evident from Figure 7. The potential cumulative contribution of CWA to total As in the sediment is not significant compared to the measured As concentrations, which implies that the variation in total As in the sediment has other natural and anthropogenic causes than CWA.

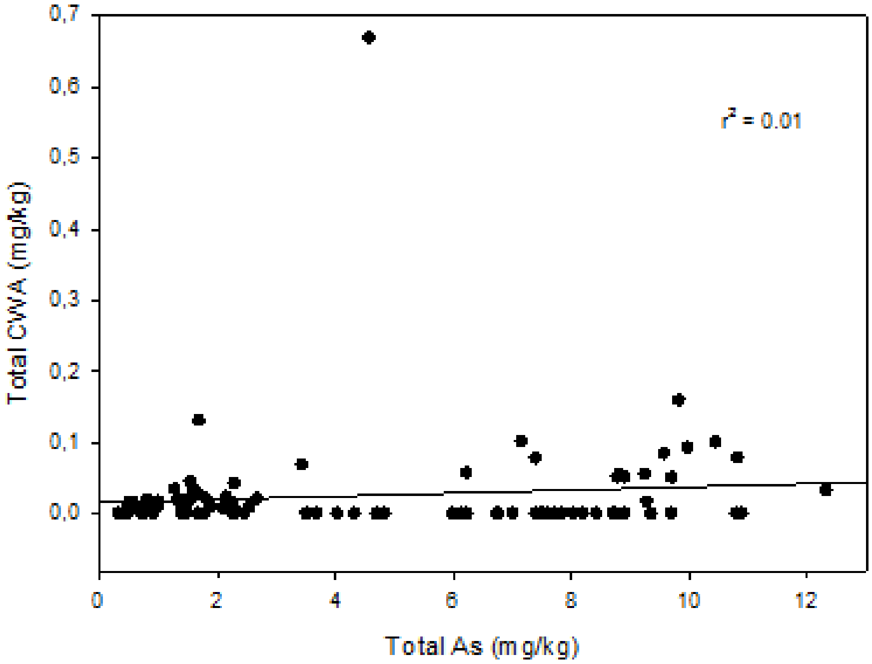


Figure 7 Total As vs. total CWA in sediment (DW).

3.4.4 Measured and modelled inorganic arsenicals in pore water

The content of inorganic $As_{III\&V}$ varies by a factor of 7 between the lowest and highest measured values, which is also obvious from the SD of the mean value. The detection frequency is 100 %.

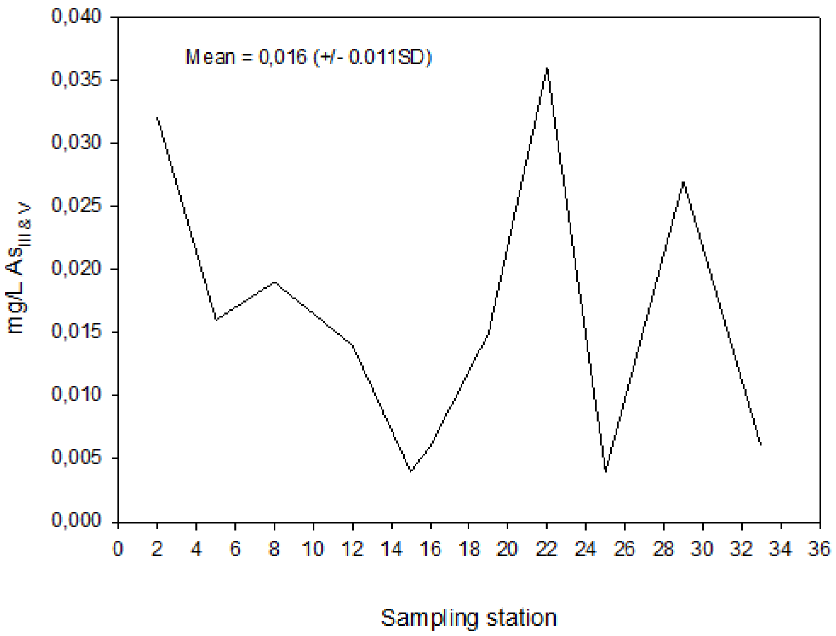


Figure 8 Sum of AS$_{III\,\&\,V}$ in pore water.

The derived Kd values for As$_{III\&V}$ are used to calculate the concentration of As$_{III\&V}$ in pore water and is shown in Figure 9. The measured data points are inserted in red. There is an overall good agreement between the measured and modelled As$_{III\&V}$ values. The modelled concentrations are conservative relative to the measured data.

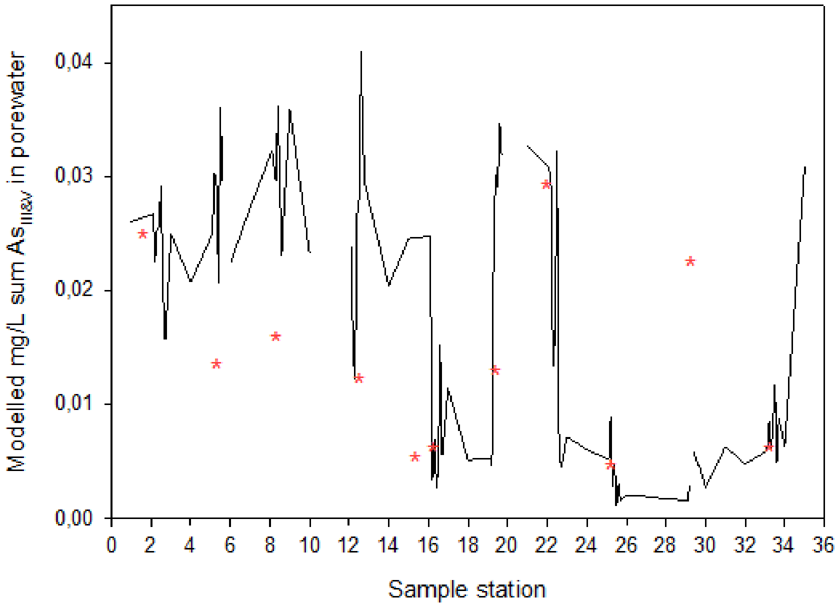


Figure 9 Modelled sum of AS$_{III\,\&\,V}$ in pore water.

3.4.5 Pore water risk estimates of CWA and As$_{III\&V}$

Pore water risk estimates of CWA

Figure 10A-F shows the risk quotient of CWAs towards the fish community as a PEC/HC5(PNEC) ratio. The HC5 is derived from Sanderson et al. (2008c) and is used as a surrogate for the predicted no observed effect concentration (PNEC). The assessment factor for associated with SSD derived PNECs typically range between 1 and 5 (Sanderson et al. 2008c). The assessment factor associated with HC5 values derived by species sensitivity distributions (SSD) ranges between 1 and 5, and has not been included in this analysis as the determination hereof is subjective matter of negotiation between the decision-maker and stake-holder.

Figure 10E represents the cumulative CWA risk based on additivity of the CWAs toxic units (TU), without an assessment factor. It is quite evident that the risk is generally low.

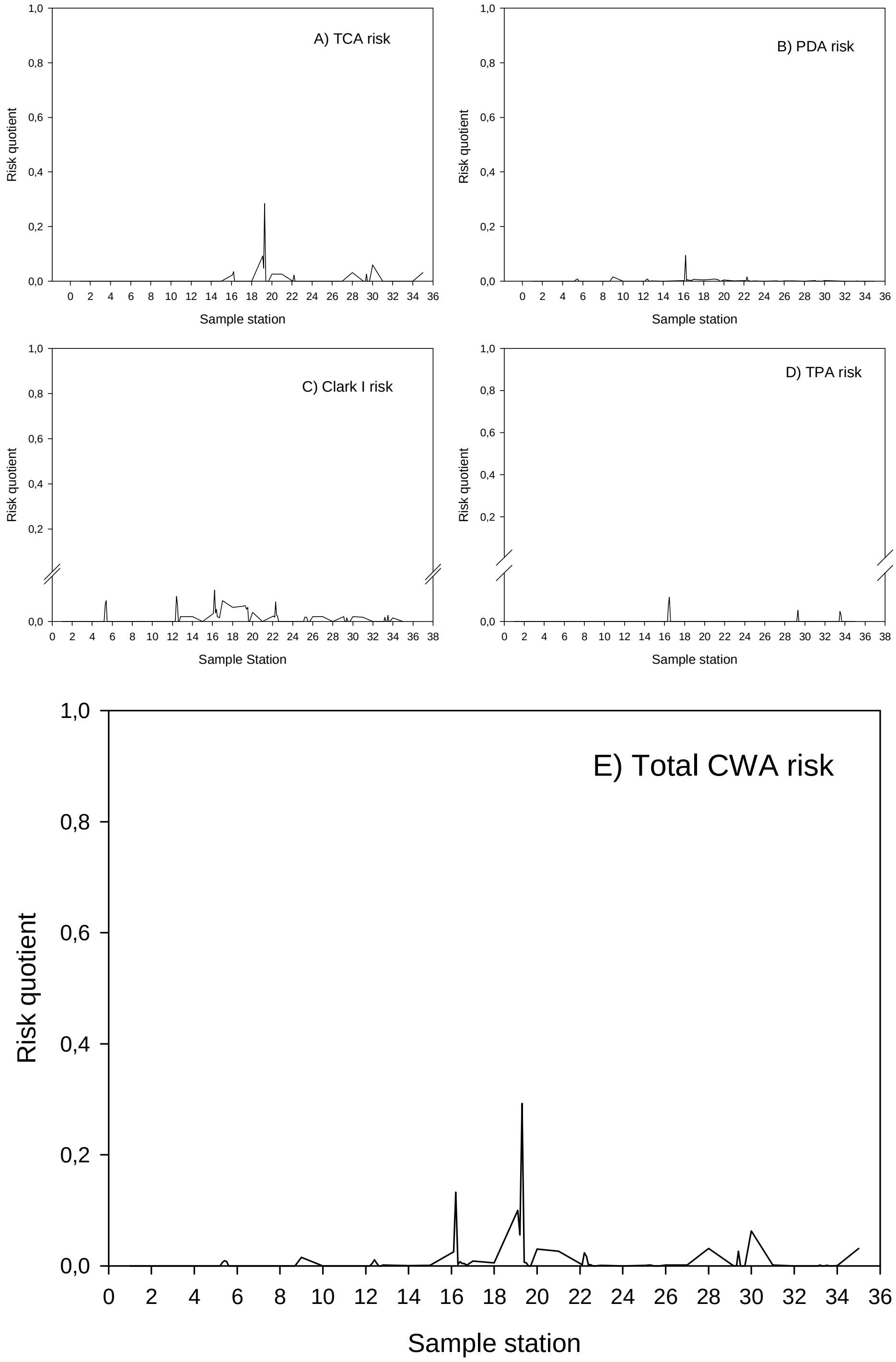


Figure 10A-E CWA risk estimates towards the fish community.

Pore water risk estimates of $As_{III\&V}$

The overall mean of the measured sum of $As_{III\&V}$ in pore water is 0.016 mg/L (±0.011SD) and the ditto for the modelled $As_{III\&V}$ is 0.016 mg/L (±0.012SD). The acute HC5 for arsenic compounds is 0.29 mg/L, (Figure

11) based on acute toxicity data for 17 tested species derived from the HSDB database.

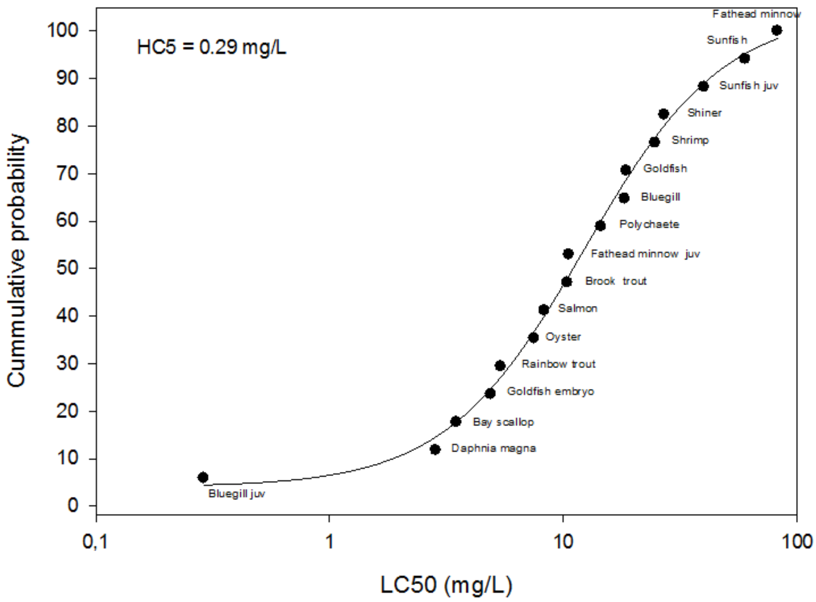


Figure 11 AS$_{III \& V}$ SDD.

Figure 12 below suggest a low risk towards the fish community based upon the HC5 value. Arsenical are natural and ubiquitous elements, the typical levels of total As in ocean water and in Danish inland lakes is 0.001 mg/L The safe drinking water limit in Denmark for As is 0.005 mg/L, or roughly a factor 3 lower than the mean predicted and measured As, in the U.S. the limit is 0.01 mg/L. The observed sediment concentrations are moreover, not compared to the average total As in the Bornholm deep of 25 mg/kg (Garnaga et al. 2006) relative to the average of 7-10 mg/kg found in this study (Figure 6). This suggests that the As found in the pore water and sediment along the S-route does not pose an extraordinary immediate risk towards the fish community and that the contribution of total As from dumped organoarsenic CWAs are not significant.

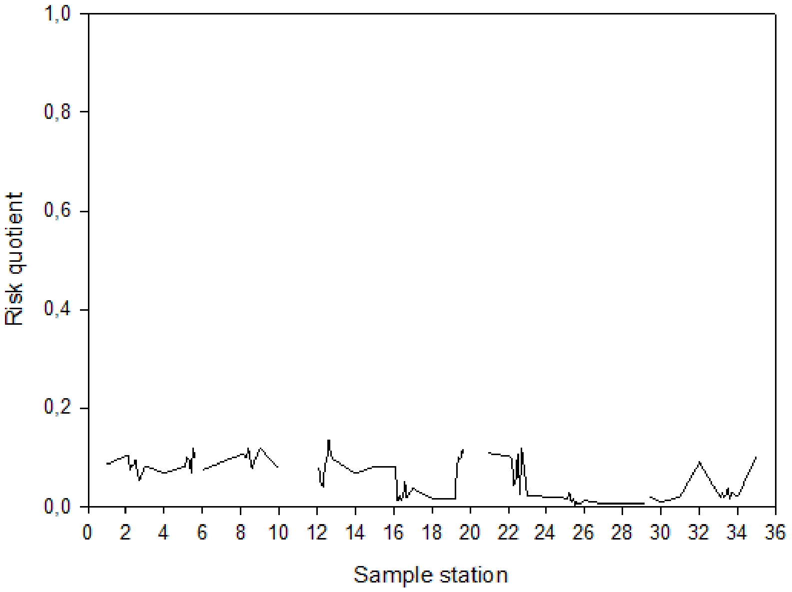


Figure 12 Sum AS$_{III \& V}$ risk quotient.

3.5 Conclusions

The present data material indicates generally a low risk of CWA towards the fish community along the S-route.

The arsenicals measured along the S-route do not correlate with total CWA concentrations ($r^2 = 0.01$). Therefore the predominant part of the arsenic (arsenicals?) in the sediment has other anthropogenic and natural sources than CWA.

The fish community risk relative to the toxic forms of As is generally low along the S-route.

The total As levels found along the S-route are close to the background levels for the Bornholm Deep.

Further analysis of CWA degradation products and Yperite should be analyzed in a risk context together with presented data by Bossi et al. 2008 and the collected in situ fauna investigations.

3.6 References

Bossi, R., Krongaard, T. & Christoffersen, C., 2008: Analysis of arsenic compounds in sediment samples and sediment pore water samples from the Baltic Sea. NERI Technical report.

DiToro, D.M., 1991: Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. *Env. Tox & Chem*. 10: 1541-1583.

Emelyanov, E.M., 1996: Chemical Components and Elements in the Suspended Matter and Sediments of the Western Baltic. *Baltica* 9: 5-15.

Forster, S., Bobertz, B. & Bohling, B., 2003: Permeability of Sands in the Coastal Areas of the Southern Baltic Sea: Mapping a Grain-size Related Sediment Property. *Aquatic Geochemistry*. 9: 171-190.

Garnaga, G., Wyse, E., Azemard, S., Stanekvicius, A. & de Mora, S., 2006: Arsenic in sediments from the southeaster Baltic Sea. *Env Poll*. 144: 855-861.

HELCOM, 1994: Report on chemical munitions dumped in the Baltic Sea. Report to the 15th meeting of Helsinki Commission. Danish Environmental Protection Agency. Available at:
http://www.rurociagi.com/spis_art/2005_4/raport.pdf

Rambøll, 2008: Offshore pipeline through the Baltic Sea. Nordstream AG. Memo 4.3A-9. Release of sediments from anchor operation. Ref#: G-PE-PER-EIA-100-43A90000.

Sanderson, H. & Fauser, P., 2008a: Risk screening of chemical warfare agents towards humans and the fish community resulting from sediment perturbation from construction of the planned Nord Stream offshore pipelines through risk area 3 (S-route) in the Baltic Sea. NERI memo# DMU-75-00061.

Sanderson, H. & Fauser, P., 2008b: Historical and qualitative analysis of the state and impact of dumped chemical warfare agents in the Bornholm basin from 1947-2008. NERI memo# DMU-75-00061b.

Sanderson, H., Thomsen, M., Fauser, P. & Sørensen, P.B., 2008c: Screening level fish community risk assessment of chemical warfare agents in the Baltic Sea. *Jour Haz Mat*. 154: 846-857.

US EPA, 2004: Understanding the variation in partitioning coefficient, Kd, values. Vol III, EPA 402-R-04-002C. Available at: http://www.epa.gov/rpdweb00/docs/kdreport/vol3/402-r-04-002c.pdf

4 RAMBOLL OIL & GAS - Nord Stream A/G. Offshore pipelines through the Baltic Sea - Analysis of additional risk to the fish community from chemical warfare agents (CWA) associated with construction of the planned Nord Stream route south of Bornholm

Hans Sanderson, Patrik Fauser & Marianne Thomsen

4.1 Introduction

Following the end of World War II and as a result of the Potsdam Conferences, the Allied Forces ordered the destruction of Germany's approximately 65,000 tonnes of stockpiled chemical warfare agent (CWA) munitions during the second half of 1947. Significant amounts of these munitions were dumped in the Bornholm Deep. Concerns have been raised with regard to the environmental risks associated with perturbation of sediment containing traces of dumped CWA during the building of the planned Nord Stream gas pipelines in the Bornholm Deep. Risk assessment performed by Sanderson & Fauser (2008a) comprising first-tier model-based screening suggests a low, indirect risk towards humans and the fish community in relation to the construction of the proposed gas pipelines. Semi-qualitative interviews with local experts as well as review of contemporary local newspaper articles and interviews with responsible officers and seamen further suggest low risk potential (Sanderson & Fauser, 2008b).

The Nord Stream Route transects the CWA dumpsite in the Bornholm Deep in what is known as Risk Area 3. During a sampling campaign along the Nord Stream route during the spring of 2008, a total of 95 sediment samples and 11 pore water samples were collected for chemical analyses at NERI (Bossi et al. 2008) and VERIFIN (2008). Literature-based and calculated sorption coefficients were used to transform measured sediment concentrations into bioavailable pore water concentration for fish. The potential direct environmental risks towards fish communities from CWA dumped following World War II associated with the construction of the proposed Nord Stream gas pipeline are assessed.

The assessment is based on all the measured compounds (see Annex 1), hereunder measurements of five arsenic-containing CWAs (Adamsite, Clark I, triphenylarsine (TPA), phenyldichloroarsine (PDA), trichloroarsine (TCA)) and a speciation of the arsenic present as ultimate degradation products of these CWAs (total arsenic (As_{total}), sum of arsenite As(III), arsenate As(V), monomethylarsonic acid (MMA), dimethylarsonic acid (DMA), trimethylarsine oxide (TMAO), tetramethylarsonium ion (TETRA) and arsenobetaine (AB)). The concentrations of As (III) and As (V) are given together as one, as the oxidation and the reduction of As (III) and As (V), respectively, during sampling, storage, preparation and analysis cannot be controlled. The individual concentrations are therefore not reliable. $As_{V,}$ however, is thermodynamically more stabile; therefore, one would expect the majority of the inorganic As to be arsenate. From a toxicological perspective, $As_{III\&V}$, presenting primarily the more toxic inorganic fraction of the total As, is of most interest (Bossi et al. 2008). In addition, all other potentially dumped CWA, according to HELCOM (1994), were analysed by the institute VERIFIN; hereunder, sulphur mustard gas (yperite), chloroacetophenone, Lewisite I & II, Tabun. VERIFIN also analysed for Adamsite (DM), Clark I (DA), triphenylarsine (TPA) and phenyldichloroarsine (PDA), as reported by Bossi et al. (2008). Finally, VERIFIN analysed for the two most common metabolites of sulphur mustard gas Thiodiglycol (TGD) and Thiodiglycol sulfoxide (TGDS) (VERIFIN, 2008). All of the above compounds were assessed relative to their direct risk potential towards the fish community.

Table 1 Confirmed dumped chemical warfare agents in the Bornholm basin dumpsite east of the Nord Stream route in tonnes (HELCOM, 1994).

Compound	CAS number	Dumped CWA (T)
Chloroacetophenone (CAP)[1]	532-27-4	515
Sulphur mustard gas (Yperite)[2]	505-60-2	7027
Adamsite[3]	578-94-9	1428
Clark I[3*]	712-48-1	711.5
Triphenylarsine (TPA)[3*]	603-32-7	101.5
Phenyldichloroarsine (PDA)[3*]	696-28-6	1017
Trichloroarsine (TCA)[3*]	7784-34-1	101.5
Other (nerve agent)[4]	74-90-8	74
Monochlorobenzene[5]	108-90-7	1405

1) Riot control agent; 2) Blistering agent; 3) Organoarsenic blistering agent; 3*) Arsine oil constituents - organoarsenic blistering agent; 4) e.g., Tabun; 5) Additive.

Fish community sensitivity is based on species sensitivity distribution (SSD) analysis for each CWA and arsenical. The sensitivity is then compared with the measured environmental concentration (primarily the calculated pore water concentration) at each sampling station to assess the risk of effects.

The measured exposure concentrations and thus predicted risk towards the fish community will also be evaluated using multivariate statistical analysis to identify any correlations and patterns in the *in situ* observation on benthos and background variables (Mortensen, 2008).

4.2 Methods

4.2.1 Data generation

Sampling of CWAs, arsenicals, benthos and background parameters was carried out May 2008. Sediment samples for chemical analyses were taken with a Haps core sampler at the 35 stations along the planned pipeline route south of the island of Bornholm. At 11 of the 35 main positions, additional duplicate samples were taken for pore water from the upper 5 cm of the core per station. In addition, two samples were taken from the middle of the core and two samples from the bottom at each station. At 10 positions, four stations 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. The total number of sampling positions was thus 75 (Figure 1). At all stations, two samples were taken from the upper 5 cm of the core. A total of 95 sediment samples and 11 pore water samples have been collected for chemical analyses (Bossi et al. 2008).

Moreover, sediment samples were collected for analysis of macrozoobenthos, to measure near-bottom water dissolved oxygen levels, salinity, temperature, depth and turbidity at 28 stations. A Van Veen grab sampler (0.1 m^2) was used to collect the samples (Mortensen, 2008). The sediment characteristics for each of the sampling locations were also reported, and video recording of the bottom at the sampling stations was performed. Of the 28 stations (Mortensen, 2008), 22 biological sampling stations (B2-B23) were identified as closest to the chemical sampling stations. As such, the biological measurements are assumed to be representative of the closest sampling areas of chemical measurements as described above. Uni- and multivariate data analysis was performed on a subset of sampling station areas for which biological and chemical measurements were available. Correlation analysis as described in Section 3.8 is based on average and log-transformed measurements within each sampling station area within a radius of 500 m from the main sampling stations (Mortensen, 2008).

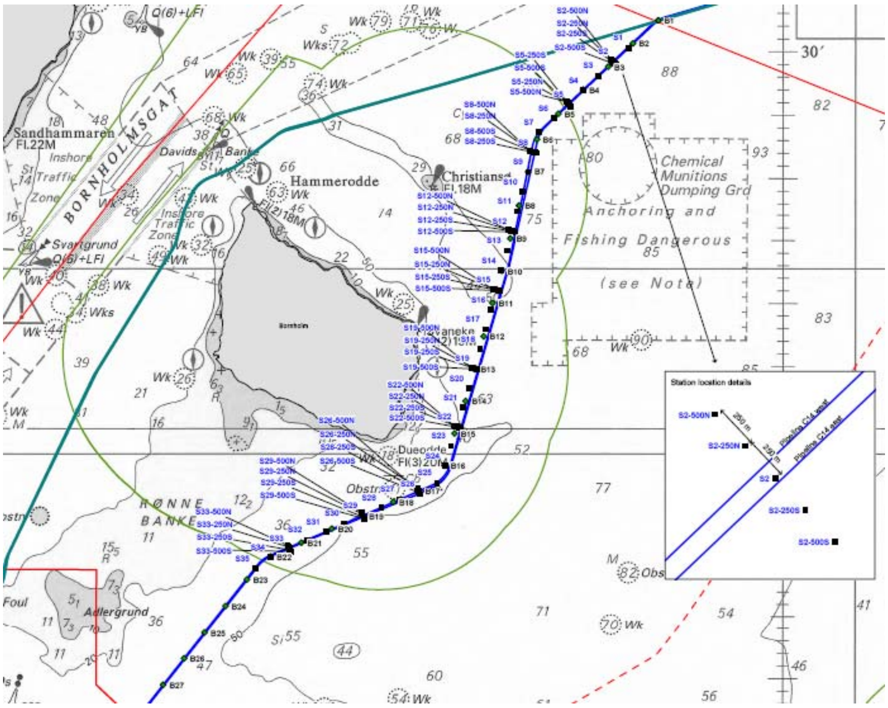


Figure 1 Chemical sampling stations along the Nord Stream route near Bornholm.

For a detailed description of the chemical analytical methods for the CWA analysis as well as biota and physico-chemical characterisations, the reader is referred to the reports by VERIFIN (2008), Bossi et al. (2008) and Mortensen (2008).

4.2.2 Measured and predicted environmental concentrations (PEC) of CWAs

The environmental toxicity associated with most physico-chemical properties of CWAs has not been thoroughly investigated with modern methods and reported in the public literature; hence modelling of these properties is warranted to derive comparable datasets (Sanderson et al., 2008c). For chemicals to be incorporated into organisms, such as fish, and exert toxicity they generally need to be in solution. Therefore, sediment concentrations (mg/kg dry matter (DM)) will be used to calculate pore water concentrations (mg/L) for all the samples based on adapted equilibrium partitioning (Sanderson & Fauser, 2008). The measured and calculated pore water concentrations will be used as the worst-case predicted fish community CWA exposure concentration (PEC) for the steady-state risk analysis, where it is assumed that the fish water exposure concentration equals the pore water concentration.

Partitioning values (Kd values) for $As_{III\&V}$ are not available from the literature and US EPA (2004) emphasises that partition coefficient values measured at site-specific conditions are absolutely essential. In this work, Kd values are derived based on the 11 site-specific measurements of $As_{III\&V}$ sum concentration in the pore water and sediment, according to Eq. 1:

$$Kd = Cs/Cpw - \theta/Xs = 300\ (\pm\ 226SD)\ L/kg\ DM \qquad \text{(Eq. 1)}$$

where Kd is the partitioning coefficient of $As_{III\&V}$ between sediment and pore water, Cs is the sediment concentration, Cpw is the pore water concentration, θ is the pore volume fraction in the sediment (0.55), Xs is the sediment density (1.2 kg/L), assuming constant sediment properties throughout the sampling area Koc = 3880 (± 2910SD) L/kg organic matter (OM) and the mean value for the retention factor is $Rs(As_{III\&V}) = 361$ (Sanderson & Fauser, 2008). First, the steady-state potential fish community risk based on the measured and derived exposure concentrations is estimated.

Thereafter, the added risk from sediment agitation from installing the pipelines based on assumptions related to the construction of one gas pipeline is calculated. So, in addition to the quasi steady-state concentration of CWAs in the bottom boundary layer originating from the dumped CWAs, there is a contribution from the release of sediment particles during the following pipeline activities:

1) Trenching of a 10 km section (West Pipeline) and 15 km section (East Pipeline) by plough east of Bornholm. Disturbance and spreading of sediment material is estimated to be 6.9 m^3/m pipeline, corresponding to 2,160 tonnes (West Pipeline) and 3,240 tonnes (East Pipeline) suspended sediment, respectively (Rambøll, 2008b). The estimated area with concentrations higher than 10 mg/L in bulk water between 0-10 m above the seabed is 5.9 km^2 (West Pipeline) and 8.9 km^2 (East Pipeline), respectively (Rambøll, 2008b). A worst-case sediment concentration, Cw(sed,trenching) in the bulk water between 0-10 m above the seabed is found to be:

$$Cw(sed,trenching) = 3{,}240\ tonnes/(8{,}9 * 10^6 m^2 * 10m) = 36\ mg\ sediment/L \qquad \text{(Eq. 2)}$$

The average duration of elevated concentrations is three hours. Trenching of the two pipelines is performed one year apart, 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 (Rambøll, 2008b).

3) Handling of 12 anchors, 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 release to the bulk water is 10 - 38 tonnes sediment/km of the pipeline in areas with soft sediment (Rambøll, 2008a). The release area is approximately 2 % (0.04 km^2/km) of the anchor corridor. This gives a sediment concentration in the release area and lower 10 m (release water volume) of Cw(sed,sweeping) = 25 - 95 mg sediment/L. When assuming that sediment particles from the release area are spread to the total anchor corridor area, the average sediment concentration is approximately 0.5 - 2 mg/L (Rambøll, 2008a).

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^2/km) of the anchor corridor. This gives a sediment concentration in the release area and lower 10 m (release water volume) of: Cw(sed) = 95 mg sediment/L, from sweeping, and Cw(sed) = 131 mg sediment/L, from sweeping and trenching. Sweeping occurs along the entire pipeline, whereas trenching occurs only at sampling stations S14, S15 and S16.

The worst-case CWA concentration in the release water volume, Cw(CWA) in mg CWA/L, is thus:

$$Cw(CWA) = Cw(sed) \times Cs(CWA) \qquad \text{(Eq. 3)}$$

Where Cs(CWA) is the highest measured CWA concentration in sediment, in mg/kg DW. The worst-case concentration is calculated for single CWAs, As(III & V) and sum of CWAs. As mentioned, these calculations are conducted for each pipeline.

4.2.3 Predicted CWA HC5 fish community concentrations

The PECs will be compared with toxicologically acceptable exposure concentrations towards the fish communities as reported in Sanderson et al. (2008c), using the fish community extrapolated HC5 value. HC5 (hazard concentration 5 %) represents the concentration where 95 % of the acute LC50 of the fish species in the community is not exceeded; or, in other words, a potential risk for the community of 5 % is accepted. The toxicity of $As_{III\&V}$ was derived from the US National Library of Medicine Hazardous Substances Data Base (HSDB: http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB). For arsenic compounds, the data was used to derive a species sensitivity distribution for 12 fish species (adult and juvenile). The resulting acute HC5 value (protective of 95 % of the community) equals 0.29 mg/L (Sanderson & Fauser, 2008). The relative risk of each CWA and the total risk-assuming additivity of the CWAs are calculated for the fish community. The assessment factors associated with HC5 values derived by SSD range typically between 1 and 5, and have not been included in this analysis, as determination of the size of the factor is a subjective matter of negotiation between the decision-makers and stakeholders, derived on a case-by-case basis.

4.2.4 Statistical analysis

We applied multivariate statistical analysis, principle component analysis (PCA), to determine the overall covariance of all the measured and calculated parameters. Briefly described, PCA is performed by projecting information carried by a number of original variables onto a smaller number of underlying ('latent') 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. The interrelationships between different variables may be visualised graphically by plotting the PCs. PC plots may be used to detect and interpret sample patterns, groupings, similarities or differences in samples (see Figure 8 and Figure 9).

4.2.5 Summary conclusions

There are three lines of evidence in this direct CWA-related fish community risk analysis: 1) the quasi steady-state before pipeline construction; 2) the added risk from construction of the pipelines related to the suspension of sediment containing CWAs; 3) the statistical analysis of all the measured variables with an emphasis on CWA risk and macrozoobenthos. These three lines of evidence will be evaluated in the overall conclusion, with an emphasis on the last two aspects, added risk (2) and correlations (3).

4.3 Results

4.3.1 Arsenicals in the sediment

The average total As concentration found was 10.6 ±7.4SD mg/kg DM, and the highest concentration was observed at station S8 at 26.9 mg/kg DM. The highest concentration of the most ecotoxicologically relevant fraction of the measured arsenicals is the inorganic $As_{III\&V}$ at 12.3 mg/kg DM at station S12. It is notable that only DMA was detected above the limit of detection (LoD) among the organic arsenicals. (Annex 1, Table 1a) (Sanderson & Fauser, 2008).

4.3.2 Measured and modelled inorganic arsenicals ($As_{III\&V}$) in pore water

The content of inorganic $As_{III\&V}$ varies by a factor of 7 between the lowest and highest measured values, which is also obvious from the standard deviations (SD) of the mean value. The derived Kd values for $As_{III\&V}$ are used to calculate the concentration of $As_{III\&V}$ in pore water and are shown in Figure 2. The measured data points are inserted as red stars. Overall, there is good agreement between the measured and modelled $As_{III\&V}$ values. The modelled concentrations are comparable to the measured data.

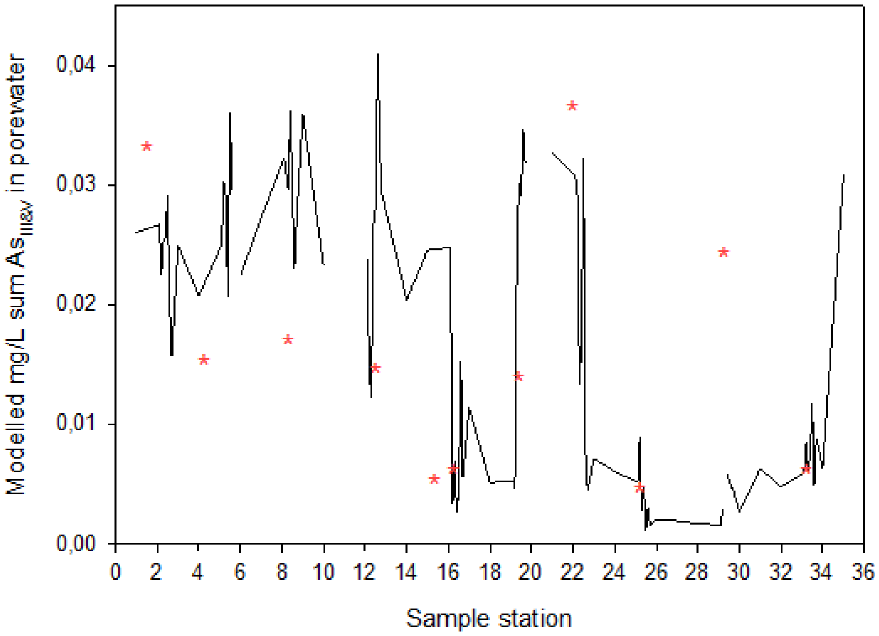


Figure 2 Measures and modelled sum of $As_{III\&V}$ in pore water.

4.3.3 Quasi steady-state fish community risk estimates of $As_{III\&V}$

The overall mean of the measured sum of $As_{III\&V}$ in pore water is 0.022 mg/L ±0.02SD, and the mean modelled pore water concentration of $As_{III\&V}$ is 0.016 mg/L (±0.012SD). Reflecting the measured and calculated risk quotients (RQ) (PEC/HC5), Figure 3 below suggests a low steady-state risk towards the fish community. A risk quotient greater than 1 indicates a potential risk towards the fish community.

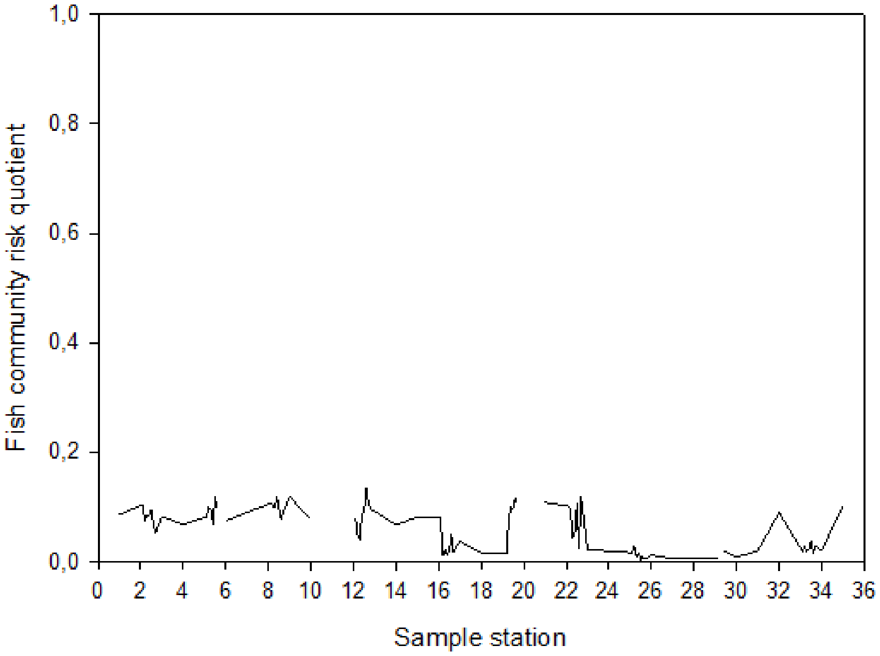


Figure 3 Sum $As_{III\&V}$ steady-state fish community risk quotient.

Arsenicals are natural and ubiquitous elements; the typical levels of total As in ocean water and in Danish inland lakes is 0.001 mg/L. The safe drinking water limit in Denmark for As is 0.005 mg/L, or roughly a factor 3 lower than the mean predicted and measured As. In the US, the limit is 0.01 mg/L. The observed sediment concentrations (averaging 7-10 mg/kg) found in this study are comparable to the average total As in the Bornholm Deep of approximately 20 mg/kg reported by Garnaga et al. (2006). The sediment concentration of As in the Baltic Sea is quite variable and dependent on the geology and grain size, among other factors (Emelyanov, 1996). In this light, the observed As concentrations in the present study are relatively close to the values reported by Garnaga et al. (2006). This suggests that the As expected to be found in pore water and sediment along the Nord Stream route does not pose an extraordinary immediate steady-state risk towards the fish community.

4.3.4 Measured CWA in sediment

Table 1a in the annex summarises the measured CWA concentrations in the sediment. The highest concentrations of CWAs are typically found at sampling station S16. Among the active CWAs, only Adamsite and Clark I were detected, with frequencies of 3.5 % and 19.5 %, respectively. The most frequent arsenic oil constituent detected was PDA at 26 %. PDA also recorded the highest concentration at 0.6 mg/kg DM (Annex 1, Table 1A).

4.3.5 Measured and modelled CWA in pore water

Not surprisingly, there were relatively few detections of CWA in pore water due to the relatively high hydrophobicity of the compounds. Pore water concentrations, however, are the primary direct exposure route to fish and other non-sediment dwelling organisms. Hence, the scarce measured pore water concentrations were bolstered with calculated CWA pore water concentrations based on equilibrium partitioning (EqP) modelling (Sanderson & Fauser, 2008). Figure 4 shows the calculated pore water concentrations and the measured pore water concentrations (coloured stars) on a log axis.

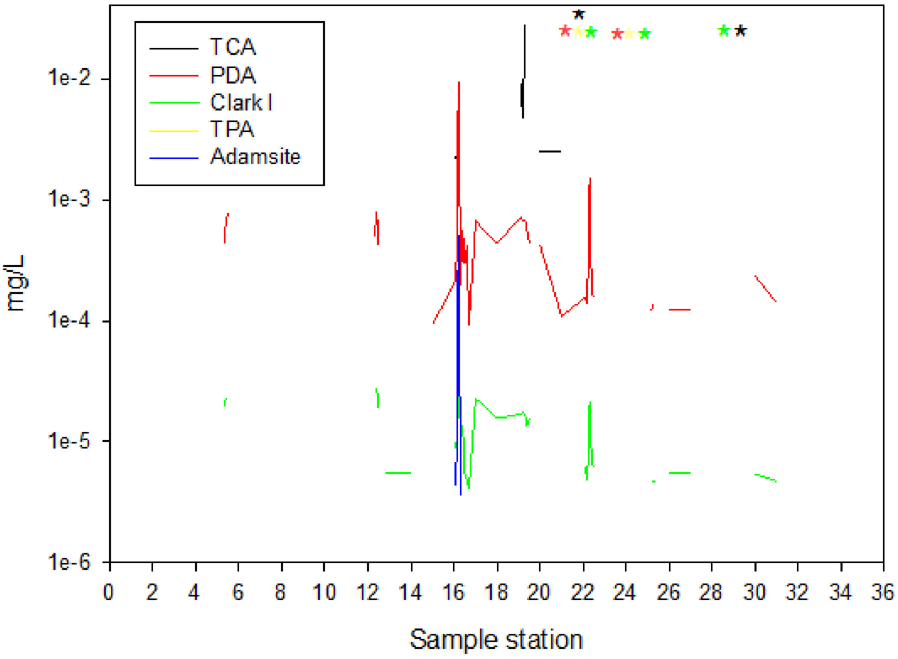


Figure 4 Modelled CWA pore water concentrations.

These values were used as the PEC for the fish community risk assessment.

4.3.6 Quasi steady-state fish community CWA risk estimates

The total direct quasi steady-state risk towards the fish community is illustrated in Figure 5 below. The potential risks are greatest at sampling stations S16 and S19. At S16, the risk is driven by PDA with a risk quotient (RQ) of 0.1 and Adamsite with a risk quotient of 0.05. The remaining CWA as a whole is associated with a minor risk contribution. The predicted risk at station 19 is driven almost entirely by TCA. The risks at all the other sampling stations are miniscule. Again, a risk quotient greater than 1 indicates a potential risk towards the fish community.

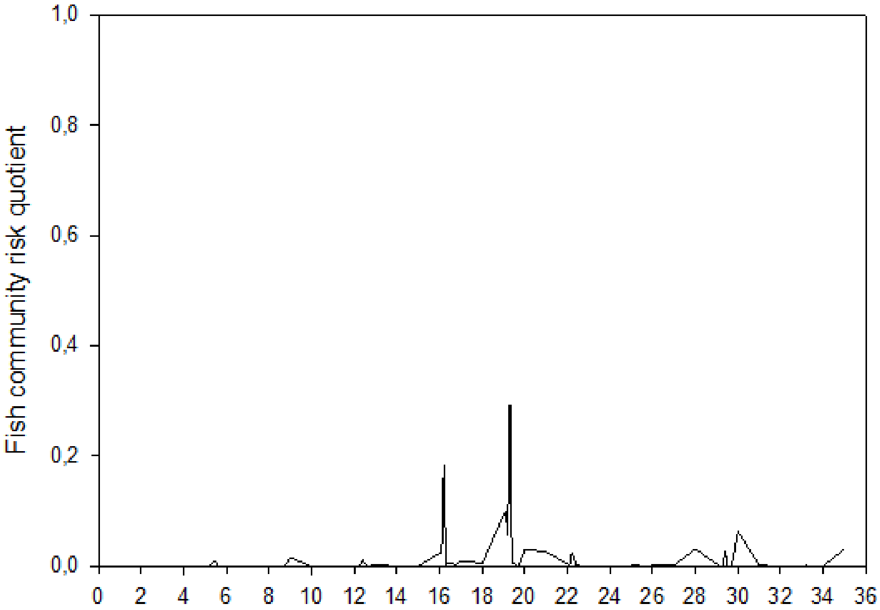


Figure 5 Total CWA fish community steady-state risk.

Figure 6 below plots all reported chemical munitions caught by Danish fishermen up until 1985 as red dots (Rambøll, 2008a). The larger yellow dots are potential CWA re-dumping sites. The yellow box and the large red circle are the designated post-World War II chemical munitions dumpsites. The blue line indicates the Nord Stream route.

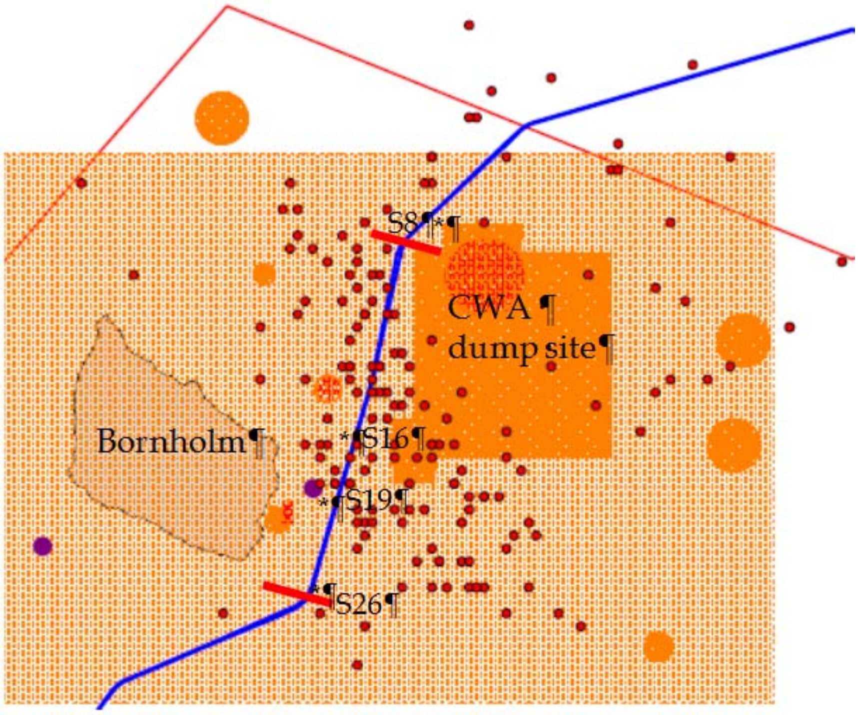


Figure 6 CWA caught by Danish fishermen.

Based upon Figure 6, one would expect to observe the most frequent and highest CWA concentrations between the two red bars between sampling stations S8 and S26. The potentially more risky steady-state sampling stations S16 and S19 are indicated on the map.

4.3.7 Additional risk from pipeline construction

The total added risk both from CWAs and arsenicals from construction of each pipeline is illustrated in Figure 7, below. The major risk contributor is the arsenicals (sum $As_{III\ \&V}$). The perturbed sediment amounts are significantly lower compared with those in the conservative quasi steady-state modelling, hence the overall risk from perturbation of CWA containing sediment is also lower. Less than 5 % of the sediment area will be directly perturbed by the construction. The predicted risk is low all along the Nord Stream route, ranging between 0.0005 and 0.0062.

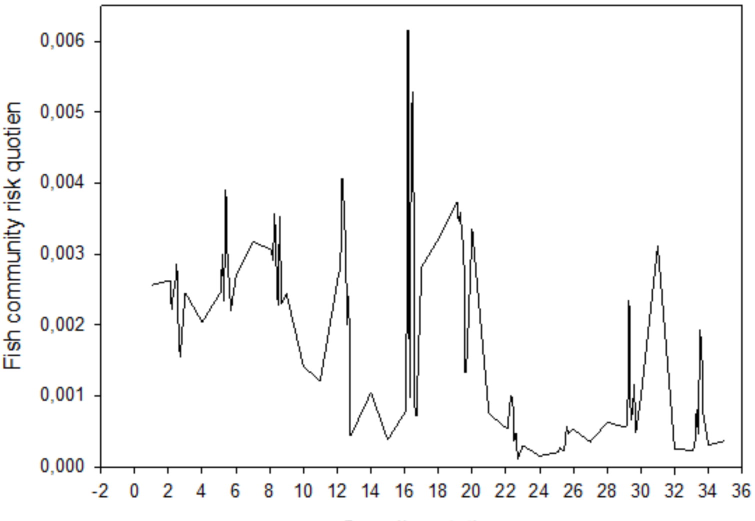


Figure 7 Total CWA related fish community risk.

4.3.8 Multivariate data analysis

Pattern recognition was performed by means of principal component analyses (PCA); the results are shown in Figure 8 and Figure 9. The purpose of the PCA is to interpret the correlation patterns from a data subset for which biological and physico-chemical measures are available. As the biological and physico-chemical data collected / available has been at a less detailed scale compared with that for the chemical measures, the dataset included in Figure 8 is reduced to include sampling stations for which a high degree of completeness regarding chemical, biological and physical characteristics was available. An average of the amounts of chemical measured within a radius of 0-500 m of each station was derived, and the biological and physico-chemical parameters of closest distance were included in the data analysis below in Figure 8. The below results are based on average and log-transformed chemical, physical and biological measured parameters for a subset of 22 main sampling stations as described in Section 2.1.

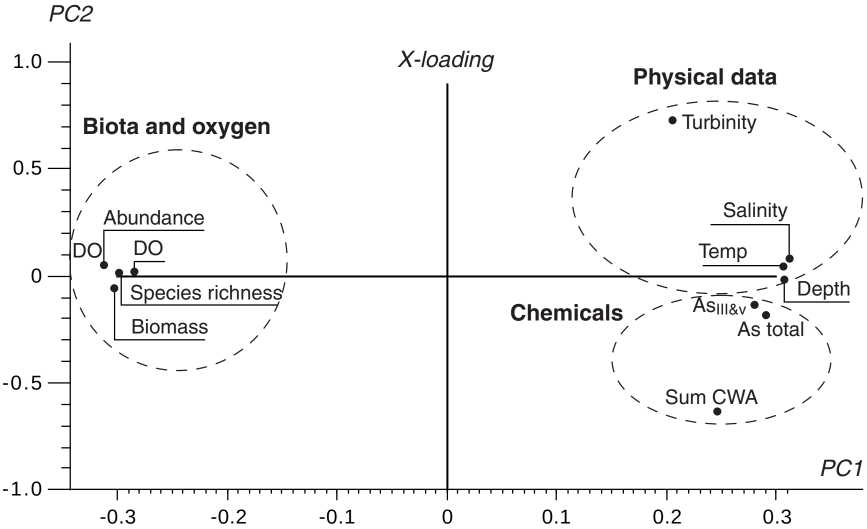


Figure 8 Plot of the second principal component, PC2, versus the first principal component, PC1. The circle to the left represents the highly inter-correlated variables: DO (dissolved oxygen) and the biological parameters Abundance, Wet Weight, Dry Weight and Species Richness. The oval to the right represents the physical parameters: Temperature, Salinity, Turbidity and Depth. In the fourth quadrant, the original variable Sum CWA are positioned, together with the $As_{III\&V}$. PC1 explains 79 % of the variance in sample stations characteristics. Opposite positioned variable; i.e., Physical data, $As_{III\&V}$ and CWA exposure variables, with high positive X-loadings, and Biota and DO variables, with high negative X-loadings, are inverse correlated. PC2 explains 7 % X-variance only. In PC2, the variable sum CWA and Turbidity have highest X-loadings, i.e., explanatory capacity, and are inverse correlated.

The variation in sample characteristics follows the X-loadings. As such, the X-loading may be used to interpret sample characteristics. Samples with high negative score values in PC1 are characterised by having high values on variables with high negative X-loadings in PC1.

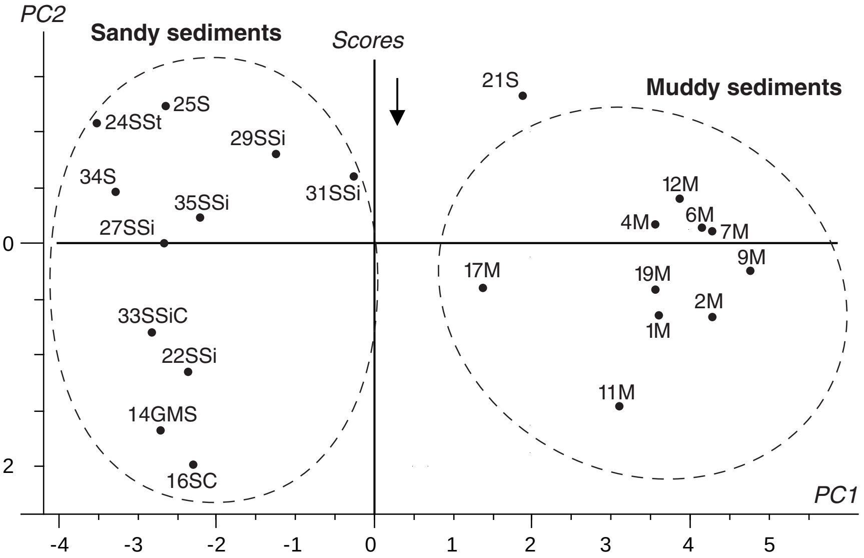


Figure 9 Score plot showing the similarities and dissimilarities within and between samples along the Nord Stream route. Each sampling station is labelled with an acronym; e.g., 16SC should be read as station 16 with sand-clay sediment type. Other sediment types are labelled as follows: SSi for sand/silt, GMS for gravel-mud-sand, SSt for sand-stones, SSiC for sand-silt-clay, SC for sand-clay, S for sand and M for mud. As marked by the circle, all muddy sediment samples are positioned to the right in the score plot, while all sandy sediments are positioned to the left.

In general, the high sampling numbers have high negative score values, while low sampling numbers have high positive score. There is a tendency for the high-numbered sampling stations (sampling stations with negative PC1 score values) to have high biological life status and abundance, while 1, 2, 4, 6, 7, 9, 11, 12, 19, and to a lesser extent 17 and 21, have low biological health status and oxygen content in the water and the highest CWA exposure and risk.

As may be observed by the ending letters of the sampling stations in the score plot, all muddy sediments, ‘M’, are high-contamination sediments, with low biological abundance and oxygen concentration in the water; having positive score values in PC1. All types of sandy sediments have negative score values in PC1 characterised by high biological abundance, 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 with samples with high negative score values. The variables Turbidity and sum CWA are inversely correlated in PC2, accounting for 7 % X-variance.

The two variables, Turbidity and sum CWA, have lower positive X-loadings in PC1 compared with the remaining variables. This may indicate that PC1 mainly explains the inverse relationship: high biological life status and abundance accompanied by lowest depths, salinity, temperature, $As_{III\&V}$ and sum CWA *vice versa.*

Results for simple regressions of biological abundance and $As_{III\&V}$ as function of sum CWA are given Table 2.

Table 2 Results of the linear regression analysis. The variables were log transformed to reduce skewness. The p-values express the probability for a slope of an opposite sign than estimated.

Y(X)	Slope	p	Intercept	R^2
1. $As_{III\&V}$(sum CWA)	0.9	0.0006	2.2	0.64
2. Biological abundance(sum CWA)	-1.3	0.02	0.3	0.42
3. Biological abundance($As_{III\&V}$)	-1.8	0.000005	3.6	0.73
4. Biological abundance(DO)	3.3	0.00004	-0.7	0.71
5. Biological abundance(Temp)	-10.8	0.00000004	10.3	0.89
6. Biological abundance(Turbidity)	-0.6	0.04	2.5	0.26
7. Biological abundance(Depth)	-7.3	0.00000002	15.2	0.86

Table 2 shows that total arsenic compounds are better predictors of macrozoobenthos abundance than sum CWA; both in terms of the probability for an opposite sign of the slope (lower p value for 3 compared with 2) and the squared correlation coefficients. Overall, is it seen that biological abundance is best described by temperature (lowest p value and highest R^2). 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, total $As_{III\&V}$, sum CWA and Turbidity. This implies that biological abundance is more sensitive towards physical parameters compared with chemical exposure. All the biological parameters are highly inter-correlated, and the abundance is thus representative of the biota responses.

4.4 Discussion

This section briefly describes the limitations and overall recommendations with regard to the risk analysis.

The assessment report addresses the direct and acute risks to the fish community from CWA and arsenicals exposure due to construction of one pipeline along the Nord Stream route. Therefore, the impact of two pipelines is, *ceteris paribus*, twice as large. However, the pipelines will be constructed one year apart, so there should be no additivity of the sediment concentration in overlapping areas. This assessment does not address indirect risks (e.g., failed food sources), chronic risks (reproduction and health), nor does it address potential risks towards other organisms (e.g., benthos). The measured exposure concentrations (primarily total sediment concentration) are converted into the bioavailable fraction in the pore water, and the fish are assumed to be exposed entirely to the pore water concentration, to err on the side of caution. These are the conditions for both the quasi steady-state and the added risk analysis. The report first assesses the quasi steady-state condition before any sediment perturbation occurs. This analysis addresses only the relative background risk conditions at the time of the sampling.

The more relevant risk analysis is the added risk scenario when the pipeline is actually being constructed and sediments are disturbed. The analysis is based upon the assessment and modelling by Rambøll (2008a and 2008b) with regard to suspended amounts and concentration of sediment in bulk water. Under these conditions, re-suspension of CWA-contaminated sediment will cause only minor risks towards the fish community. It is recommended, however, that special care is taken, and if possible, *a priori* analysis of potentially deeply buried CWA munitions shells in the soft sediments where the anchors are placed, since this activity likely will penetrate furthest into the sediment layers and may disturb any buried, intact munitions shells.

It is noticeable that depth, salinity, temperature are co-variants and that they are strongly inversely correlated with the macrozoobenthos data (r = -0.86 to -0.94). On the other hand, DO is strongly positively correlated with the measured biota (r = 0.84 to 0.86). The total CWA risk is moderately to strongly negatively correlated with biota (r = -0.55 to -0.73). The sum of $As_{III \& V}$ is strongly negatively correlated with biota (r = -0.75 to -0.88). The total concentration of CWA is strongly positively correlated with the total As and sum of $As_{III \& V}$ (r = 0.8) (Annex 2).

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; i.e., greater depth, less DO and less biota. One can expect to find slightly elevated As concentrations where the total CWA concentrations are also elevated. 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) due to more effective oxidation and degradation of the CWA (Annex 2).

If we focus on the steady state risks predicted in Figure 5, sampling station 16 and station 19 predict an elevated risk towards the fish community. The biota data nearest this station is on par with the average, 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 full agreement with the observed biota, which may be due to local variation in measured concentrations. It should be noted in this connection that a significant risk contributor at S16 was Adamsite; however, the concentration used to predict risk was 100 times higher than at other S16 sampling stations, and the sum of oxidation and hydrolysis products was used/applied and not solely parent Adamsite. Hence the 0.2 mg/L Adamsite sample value is potentially an outlier. The other sample station with elevated relative risk is station S19. This station is characterised by low biota measurements, high turbidity, mud and acceptable DO (8.9 mg/L). The risk at S19 is driven by TCA at 0.09 mg/L, which was used in the conservative analysis, while the average of TCA for the five samples taken from station 19 is 0.027 (±0.037SD) – suggesting that the risk could be a factor of three lower. Physical parameters of high importance for biota have been shown to be in a critical state in association with muddy sediments characterised by high contamination level.

4.5 Conclusions

The steady state risk to the fish community associated with the toxic forms of As result in RQs < 0.2 along the Nord Stream route.

The total As levels found along the Nord Stream route are close to the background levels for the Bornholm Deep.

The conservative, quasi steady-state risk to the fish community with peaks from CWA exposure at station 16 and station 19 RQ = 0.2 - 0.3.

The more relevant fish community risk estimate for the construction of each pipeline is lower than the quasi steady-state risk, since the amount of sorbed CWA on perturbed sediment is low due to the small scale of the affected area (RQ < 0.0063).

The statistical analysis suggests that biological abundance is better described by physical parameters than As and CWA contamination levels.

There are no strong correlations between the CWA and the biological observations.

The ratio between CWA munitions above and below the sediment is unknown; hence special caution should be exercised in connection with laying anchors, since these sink furthest into the sediment and may disturb buried munitions shells.

4.6 References

Bossi, R., Krongaard, T. & Christoffersen, C., 2008: Analysis of arsenic compounds in sediment samples and sediment pore water samples from the Baltic Sea. NERI Technical report.

Mortensen, S.M., 2008: Offshore Pipeline through the Baltic Sea Additional Environmental Field Investigations – S – Route South of Bornholm. Project No 11801334.

Emelyanov, E.M., 1996: Chemical Components and Elements in the Suspended Matter and Sediments of the Western Baltic. *Baltica* 9: 5-15.

Garnaga, G., Wyse, E., Azemard, S., Stanekvicius, A. & de Mora, S., 2006: Arsenic in sediments from the southeaster Baltic Sea. *Env Poll*. 144: 855-861.

HELCOM, 1994: Report on chemical munitions dumped in the Baltic Sea. Report to the 15th meeting of Helsinki Commission. Danish Environmental Protection Agency. Available at:
http://www.rurociagi.com/spis_art/2005_4/raport.pdf

Rambøll, 2008a: Offshore pipeline through the Baltic Sea. Nordstream AG. Memo 4.3A-9. Release of sediments from anchor operation. Ref#: G-PE-PER-EIA-100-43A90000.

Rambøll, 2008b: Chapter 1.1 Impacts from sediment spreading and sedimentation (OM).

Sanderson, H. & Fauser, P., 2008a: Risk screening of chemical warfare agents towards humans and the fish community resulting from sediment perturbation from construction of the planned Nord Stream offshore pipelines through risk area 3 (Nord Stream Route) in the Baltic Sea. NERI memo# DMU-75-00061.

Sanderson, H. & Fauser, P., 2008b: Historical and qualitative analysis of the state and impact of dumped chemical warfare agents in the Bornholm basin from 1947-2008. NERI memo# DMU-75-00061b.

Sanderson, H., Thomsen, M., Fauser, P. & Sørensen, P.B., 2008c: Screening level fish community risk assessment of chemical warfare agents in the Baltic Sea. *Jour Haz Mat*. 154: 846-857.

US EPA, 2004: Understanding the variation in partitioning coefficient, Kd, values. Vol III, EPA 402-R-04-002C. Available at: http://www.epa.gov/rpdweb00/docs/kdreport/vol3/402-r-04-002c.pdf

VERFIN, 2008: VERIFN data spread sheet provided by Rambøll.

4.7 Annex 1. Summary of measured concentrations

Table 1a Summary of measured CWAs and arsenicals in sediment from 35 sampling stations along the Nord Stream route (VERIFIN and NERI data combined).

Compound	Max. (mg/kg DM)	Mean ±SD (mg/kg DM)	Detection frequency (%)	Max. sampling station
Adamsite[1]	0.2	0.032 ±0.074	3.5	S16 (250S)
Clark I[1]	0.051	0.016 ±0.012	19.5	S16 (250S)
Lewisite I[1]	< LoD[5]	-	0	-
Lewisite II[1]	< LoD	-	0	-
Yperite[1]	< LoD	-	0	-
CAP[1]	< LoD	-	0	-
Tabun[1]	< LoD	-	0	-
TPA[2]	0.017	0.01 ±0.005	2.5	S16 (500N)
PDA[2]	0.606	0.036 ±0.089	26	S16 (250S)
TCA[2]	0.09	0.019 ±0.023	12,5	S19 (250N)
TGD[3]	< LoD	-	0	-
TGDS[3]	< LoD	-	0	-
Total As[4]	26.9	10.6 ±7.4	100	S8
Sum $As_{III\&V}$[4]	12.3	4.7 ±3.6	100	S12 (250N)
MMA[4]	< LoD	-	0	-
DMA[4]	0.23	0.147 ±0.05	72	S3
TMAO[4]	< LoD	-	0	-
TETRA[4]	< LoD	-	0	-
AB[4]	< LoD	-	0	-

1) Active parent CWA compound; 2) Arsenic oil constituent; 3) Yperite degradation product; 4) Arsenical (potential ultimate degradation product of organoarsenic CWAs); LoD =limit of detection.

Table 1b Summary of measured CWAs and arsenicals in pore water from 11 sampling stations along the Nord Stream route (VERIFIN and NERI data combined).

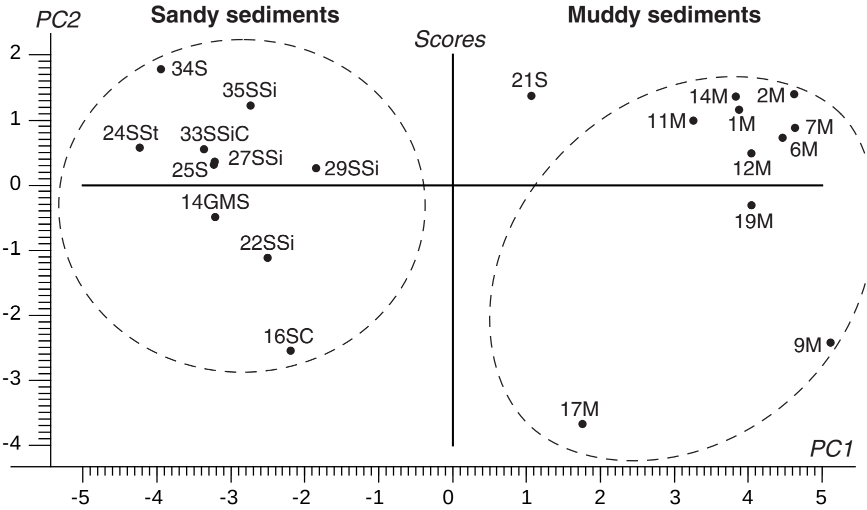
Compound	Max. (ml/L)	Mean ±SD (ml/L)	Detection frequency (%)	Max. sampling station
Adamsite[1]	< LoD[5]	-	0	-
Clark I[1]	0.002	0.002 ±0	27	S22
Lewisite I[1]	< LoD[5]	-	0	-
Lewisite II[1]	< LoD	-	0	-
Yperite[1]	< LoD	-	0	-
CAP[1]	< LoD	-	0	-
Tabun[1]	< LoD	-	0	-
TPA[2]	0.002	0.002 ±0	18	S22
PDA[2]	0.002	0.002 ±0	18	S22
TCA[2]	0.003	0.002 ±0	27	S22
TGD[3]	< LoD	-	0	-
TGDS[3]	< LoD	-	0	-
Total As[4]	< LoD	-	0	-
Sum $\text{As}_{\text{III\&V}}$[4]	0.036	0.022 ±0.02	100	S22
MMA[4]	< LoD	-	0	-
DMA[4]	< LoD	-	0	-
TMAO[4]	< LoD	-	0	-
TETRA[4]	< LoD	-	0	-
AB[4]	< LoD	-	0	-

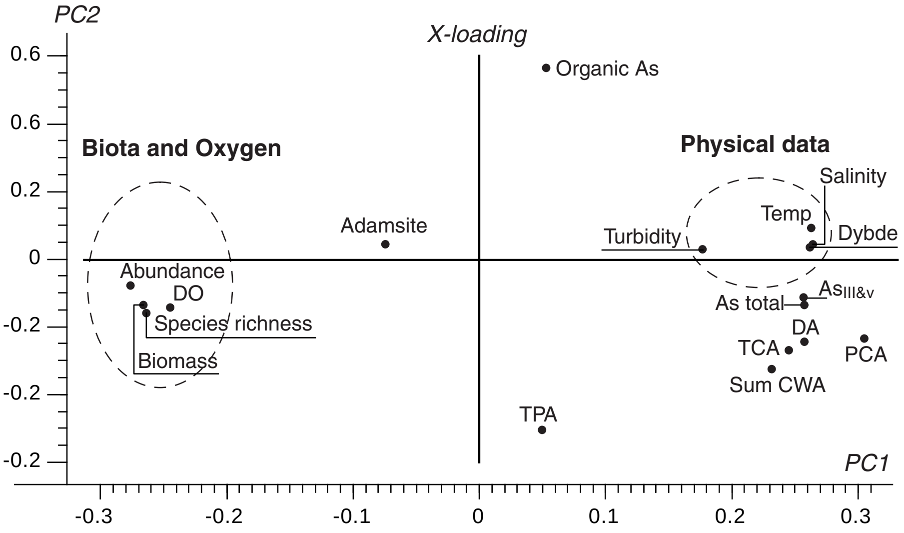
1) Active parent CWA compound; 2) Arsenic oil constituent; 3) Yperite degradation product; 4) Arsenical (potential ultimate degradation product of organoarsenic CWAs); LoD = limit of detection.

4.8 Annex 2. Pearson correlation matrix

	Conc Adamsite - DM	Conc Clark I – DA	Conc Triphenylarsine - TPA	Conc Phenyldichloroarsine - PDA	Conc Trichloroarsine - TCA	Conc Sum CWA	Conc As total	Conc As3&5	Conc AsDMA	Depth (m)	Salinity (‰)	Temp	DO (mg/L)	Turbidity (FTU)	Spe richness	Abundance	Biomass wet weight	Biomass d ry weight	Risk DM	Risk DA	Risk TPA	Risk PDA	Risk TCA	Risk Total CWA
Adamsite – DM conc	1.00																							
Clark I – DA conc	-0.19	1.00																						
Triphenylarsine – TPA conc	-0.61	0.94	1.00																					
Phenyldichloroarsine – PDA conc	-0.57	0.96	1.00	1.00																				
Trichloroarsine – TCA conc	-1.00	0.87	0.71	0.76	1.00																			
Sum CWA conc	-0.93	0.85	0.95	0.94	0.74	1.00																		
As total conc	-0.46	0.76	0.77	0.78	1.00	0.80	1.00																	
As sum 3&5 conc	-0.37	0.70	0.65	0.67	0.97	0.71	0.96	1.00																
As DMA conc	0.23	-0.20	-0.46	-0.46	0.95	-0.45	0.16	0.16	1.00															
Depth (m)	0.04	0.85	0.66	0.68	0.50	0.66	0.85	0.82	0.23	1.00														
Salinity (‰)	-0.30	0.87	0.62	0.65	0.55	0.64	0.84	0.81	0.20	0.98	1.00													
Temp	-0.21	0.83	0.61	0.63	0.54	0.61	0.83	0.81	0.30	0.96	0.99	1.00												
DO (mg/L)	-0.50	-0.71	-0.66	-0.67	-0.31	-0.52	-0.77	-0.73	-0.42	-0.92	-0.88	-0.91	1.00											
Turbidity (FTU)	-0.36	0.39	0.22	0.25	0.34	0.28	0.56	0.57	-0.11	0.57	0.64	0.61	-0.48	1.00										
Species richness	0.92	-0.58	-0.55	-0.57	-0.78	-0.54	-0.78	-0.75	-0.16	-0.86	-0.88	-0.88	0.86	-0.49	1.00									
Abundance	1.00	-0.82	-0.66	-0.68	-0.75	-0.65	-0.85	-0.86	-0.01	-0.93	-0.94	-0.94	0.84	-0.51	0.94	1.00								
Biomass Wet Weight	0.86	-0.60	-0.58	-0.59	-0.76	-0.57	-0.77	-0.77	-0.08	-0.88	-0.88	-0.91	0.84	-0.55	0.92	0.95	1.00							
Biomass Dry Weight	0.83	-0.56	-0.52	-0.54	-0.72	-0.54	-0.76	-0.75	-0.14	-0.88	-0.89	-0.91	0.85	-0.54	0.94	0.95	1.00	1.00						
DM – risk	0.02	-0.80	-0.59	-0.67	-1.00	0.30	-0.87	-0.88	-0.85	-0.99	-0.92	-0.96	0.85	-0.84	0.92	1.00	0.86	0.83	1.00					
DA – risk	-0.16	1.00	0.95	0.97	0.85	0.86	0.76	0.69	-0.20	0.84	0.86	0.81	-0.70	0.37	-0.57	-0.81	-0.59	-0.55	-0.79	1.00				
TPA – risk	NA	0.77	0.95	0.95	1.00	0.99	0.67	0.70	NA	0.20	-0.22	-0.22	-0.28	-0.19	0.51	0.99	0.04	-0.01	NA	0.80	1.00			
PDA – risk	-0.64	0.93	1.00	1.00	0.69	0.95	0.76	0.65	-0.46	0.66	0.61	0.60	-0.65	0.21	-0.54	-0.65	-0.57	-0.51	-0.52	0.95	0.95	1.00		
TCA – risk	-1.00	0.87	0.71	0.76	1.00	0.63	0.85	0.87	0.95	0.47	0.52	0.53	-0.31	0.34	-0.76	-0.75	-0.75	-0.72	-1.00	0.85	1.00	0.69	1.00	
Total CWA – risk	-0.91	0.69	0.57	0.56	0.67	0.59	0.51	0.39	-0.26	0.52	0.56	0.55	-0.31	0.38	-0.55	-0.73	-0.72	-0.71	0.21	0.70	0.97	0.57	0.59	1.00

4.9 Annex 3. PC1 and PC2 of PCA including individual CWAs





The figures above visualises patterns analogue to Figure 8 and Figure 9, Section 3.2 in the main report; with one exception that the single CWA concentration have been included in the PCA. The upper figure shows patterns in samples characteristics as explained by variable loadings in PC1 and PC2, as shown in the below figure. The pictures give the overall message that samples are explained by the loadings in PC1 corresponding to 68 % X-variance. The contamination levels of samples in general decrease from the left towards the right, and the pattern is inversely correlated to the biodiversity pattern. The plots show that the explained pattern of increasing biodiversity and decreasing contamination from the left towards the right in the score plots is accompanied by increasing oxygen and decreasing temperature and salinity. It is apparent that the muddy samples dominate in the first and fourth quadrant and seem to be characterised by high contamination, low oxygen, high salinity, temperature and turbidity. It is believed that high turbidity and low oxygen, which are characteristic for all muddy sediments, influence the conditions for biota. Sample 16 differs from the remaining CWA contaminated samples by having high concentration of Adamsite but low contamination level of the remaining CWAs. Therefore, sample station 16 differs from the muddy samples. Samples 17 and 21 have relatively high contamination levels but also high concentrations of dissolved oxygen, which is the reason for their position in the score plot having lower positive scores compared with the remaining sample stations with positive scores values in PC1. Sampling station 19 has a high concentration of TCA, which is correlated to DA and PCA compared with the sampling stations positioned in the first quadrant.

5 RAMBOLL OIL & GAS - Nord Stream A/G. Offshore pipelines through the Baltic Sea - Analysis of fish community risk due to exposure to chemical warfare agents (CWAs) perturbed sediment during the placement of the gas pipeline east of Bornholm

Hans Sanderson & Patrik Fauser

5.1 Summary

The potential risk towards fish communities from dumped Chemical Warfare Agents (CWAs) following the Second World War is assessed in association with the construction of the gas pipeline S-route transecting close to the CWA dumpsite in the Bornholm Deep in risk area 3. The assessment is made based on measurements of CWAs and their primary degradation products measured in the sediment. Calculated sorption coefficients are used to transform measured sediment concentrations into the bioavailable pore water fraction and the re-suspended fraction as a function of trenching section for placing of the pipelines. A degradation product of phenyldichloroarsine (PDCA [SPr]) and a degradation product of lewisite (L2[ox]) were detected in two out of 98 samples. The detection frequencies and overall exposure levels analyzed by VERIFIN are comparable between the 2008 assessments and this analysis. The total CWA related exposure is 0.8 µg/L, and the total fish community risk quotient (RQ) is 0.026, indicating a negligible risk. The added exposure contributed by the trenching alone is 0.039 and 0.0019 µg/L for PDCA[SPr] and L2[ox], respectively. These exposures represent an added CWA related RQ towards the fish community from installation of the pipelines of 0.00107 - an insignificant risk. It was not possible to directly compare the CWA related risks to the analysis of the benthos analysis since benthos was not sampled in the two locations where CWA residues were detected. However, the habitat and the dissolved oxygen (DO) conditions at these two locations suggest that benthos would be limited due to these factors rather than the CWA residue exposure, as also shown by Sanderson et al. (2008).

5.2 Introduction

Following the end of the Second World War Germanys approximately 65,000 tonnes stockpiled Chemical Warfare Agent (CWA) munitions were ordered by the allied forces to be destroyed during the second half of 1947 as a result of the Potsdam Conferences. Significant amounts were dumped in the Bornholm Deep. There are concerns that environmental risks may arise from perturbation of sediment containing traces of dumped chemical warfare agents (CWA) in connection with building gas pipelines in the Bornholm Deep. An initial risk assessment performed by Sanderson et al. (2008) based on 95 sediment and 11 pore water samples collected in May 2008 along the pipeline s-route. CWA concentrations, benthos assessment and habitat and sediment quality and characteristics, and phys/chem. were measured and correlated. The study showed that the suspended CWA residues did not constitute a significant risk to the fish community, moreover, that the benthos community was limited by habitat and dissolved oxygen levels and not CWAs (Sanderson et al. 2008b). The present study builds upon the 2008 study using similar methods and approximately the same number of sediment samples (98) collected during the summer of 2010.

5.3 Methods

Sampling was carried out late July 2010. Samples for CWA analysis were taken from the upper 5 cm of the core, as it was shown in the previous study by Sanderson et al. (2008) that CWA are primarily found in the upper 5 cm of the sediment. It was moreover shown in the study that the CWAs primarily were found in the sediment and not in the pore water, hence this sampling campaign concentrated on sediment concentrations. A total of 98 sediment samples along 23 sampling stations and 6 transects of 15 stations *perpendicular* to the lines (Figure 1) were collected.

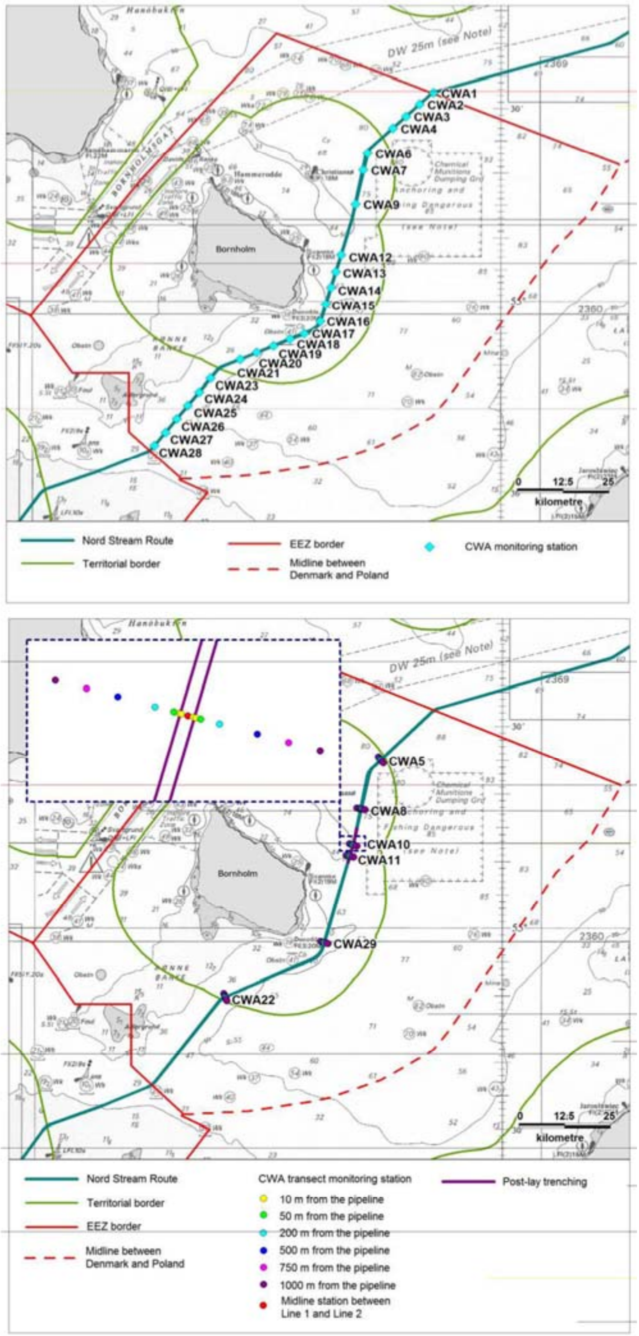


Figure 1 Sampling stations along the S-route and on six transects near Bornholm.

The samples were frozen immediately after sampling. The samples were received by the analytical lab, VERIFIN, as frozen and kept at -18° C until analysis a few weeks later. Sediment samples for chemical analyses were taken with a Haps core sampler at the sampling stations along the planned pipeline route going south of the island of Bornholm (DHI, 2010). The list of 10 target CWAs for analysis are shown in Table 1. A total of 21 degradation products were analysed (DHI, 2010).

Table 1 Target CWA related analytes (VERIFIN, 2010).

CAS #	Compound
505-60-2	Sulphur mustard gas and its main degradation products
578-94-9	Adamsite and its main degradation product
712-48-1	Clark I and its main degradation products
603-32-7	Triphenylarsine
532-27-4	Chloroacetophenone
696-28-6	Phenyldichloroarsine and its main degradation products
7784-34-1	Trichloroarsine and its main degredation products
77-81-6	Tabun
541-25-3	Lewisite I and its main degradation products
40334-69-8	Lewisite II and its main degradation products

The compounds were analysed by GC-MS and LC-MS/MS, with the aim of a minimum Limit of Quantification (LoQ) of 100 µg/kg (ppb) dry weight (DW) sediment. The actual measured LoQ ranged from 3.7 to 39 µg/kg (DW), with an average of 14.5 µg/kg (DW) for the analysed compounds. Clark I was an outlier at 156 µg/kg (DW) due to its rapid degradation and instability in the lab (VERIFIN, 2010).

In addition background variables; salinity, dissolved oxygen (DO), and sediment characterization and photo documentation was performed on-site (DHI, 2010). Moreover, the benthos community was assessed in the lab based on the samples collected at transects B 10, 11, and 29 corresponding to transects CWA 10, 11 and 29, respectively. However, quantitative sediment sampling had to be given up at transect B 29 (CWA 29) due to hard surface, however the mid station was taken from this transect (CWA 29.68) (DHI, 2010).

5.3.1 Predicted Environmental Concentrations (PEC) towards fish

The munitions have been resting on the seabed and in the sediment of the Baltic Sea for more than sixty years and the extent of corrosion of the shells, and thus release of the toxic chemicals into the marine environment and the exposure to organisms need site specific investigation.

The environmental toxicity along with most physico-chemical properties of CWAs have not been thoroughly investigated with modern methods and reported in the public literature, hence modelling of these properties are warranted to derive comparable datasets (Sanderson et al., 2008). For chemicals to be incorporated into organisms such as fish and exert toxicity they generally need to be in solution, hence the sediment concentrations, Cs (mg/kg DM), will be used to calculate pore water CWA concentrations which are bioavailable to the fishes, Cpw (mg/L), for all the samples based on adapted equilibrium partitioning (DiToro, 1991 and Sanderson et al., 2008), cf. Eq. 1.

$$Cs = Cpw * Rs / Xs = Cpw * (\theta + Kd * Xs) / Xs \qquad \text{(Eq. 1)}$$

Where; Rs = (θ + Kd * Xs) is the retention factor, θ is the pore volume fraction in the sediment 0.55 (Forster et al., 2003), Kd = foc * Koc is the partitioning coefficient between dry matter and water in L/kg DM, foc = 0.0775 is the fraction of organic carbon in particulate matter (Emelyanov, 1996), Koc is the partitioning coefficient (sorption coefficient) between organic matter and water (L/kg OM) and Xs is the density of sediment 1.2 kg DM/L (Forster et al., 2003).

Thereafter, the added CWA risk from sediment agitation from installing the pipelines based on assumptions related to the construction of one gas pipeline is calculated. So, in addition to the quasi steady-state concentration of CWAs in the bottom boundary layer originating from the dumped CWAs, there is a contribution from the release of sediment particles during the following pipeline activities:

1) Trenching of a 11.35 km section (West Pipeline) and 9.49 km section (East Pipeline) by plough east of Bornholm. Disturbance and spreading (spill) of sediment material is estimated to be 2,200 tonnes (West Pipeline) and 1,840 tonnes (East Pipeline), respectively (Rambøll, 2011). The estimated area with concentrations higher than 10 mg/L in bulk water between 0-10 m above the seabed has not been estimated for the second study, however, based on the calculations for the first study there is assumed a proportionality with the trench-length. A worst-case sediment concentration in the bulk water between 0-10 m above the seabed is thus:

$$Cw(sed,trenching) = 2{,}200 \text{ tonnes}/(5{,}9*10^{6} m^{2}*1.135*10 m) = 33 \text{ mg sediment}/L \qquad \text{(Eq. 2)}$$

The average duration of elevated concentrations is three hours. 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 (Rambøll, 2008b).

3) Handling of 12 anchors, 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 release to the bulk water is 10 - 38 tonnes sediment/km of the pipeline in areas with soft sediment (Rambøll, 2008c). The release area is approximately 2 % (0.04 km^2/km) of the anchor corridor. This gives a sediment concentration in the release area and lower 10 m (release water volume) of Cw(sed,sweeping) = 25 - 95 mg sediment/L. When assuming that sediment particles from the release area are spread to the total anchor corridor area, the average sediment concentration is approximately 0.5 - 2 mg/L (Rambøll, 2008c).

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^2/km) of the anchor corridor. This gives a sediment concentration in the release area and lower 10 m (release water volume) of: Cw(sed) = 95 mg sediment/L, from sweeping, and Cw(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, Cw(CWA) in mg CWA/L, is thus:

$$Cw(CWA) = Cw(sed) \times Cs(CWA) \qquad \text{(Eq. 3)}$$

Where, Cs(CWA) 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 calculated pore water concentrations will be used as the worst case predicted biota CWA exposure concentration (PEC).

5.3.2 Predicted No observed Effect Concentration (PNEC) towards fish

The PECs will be compared with toxicologically acceptable exposure concentrations towards the fish communities as reported in Sanderson et al. (2008) with fish community extrapolated HC5 value. The HC5 (Hazard Concentration 5 %) represent the concentration where 95 % of the fish species' acute LC50 in the community is not exceeded, or in other words accepting a potential risk for 5 % of the community. The fish community toxicity value of detected organoarsenic CWA residues was derived from the US National Library of Medicine Hazardous Substances Data Base (HSDB: http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB) for arsenic compounds, as it is recommended as a precautionary, and data quality measure, to use the well documented high toxicity of inorganic arsenic as a surrogate for compounds containing organic arsenic but with uncertain ecotoxicity. The measured acute toxicity data used to derive a species sensitivity distribution (SSD) for 12 fish species (adult and juvenile) was derived from the HSDB database. The resulting acute HC5 value (protective of 95 % of the community) equals 29 µg/L (Figure 2). To derive a PNEC the HC5 value is assigned an assessment factor. The assessment factor associated with HC5 values derived by species sensitivity distributions (SSD) ranges between 1 and 5, and has not been included in this analysis as the determination hereof is subjective matter of negotiation between the decision-maker and stakeholder.

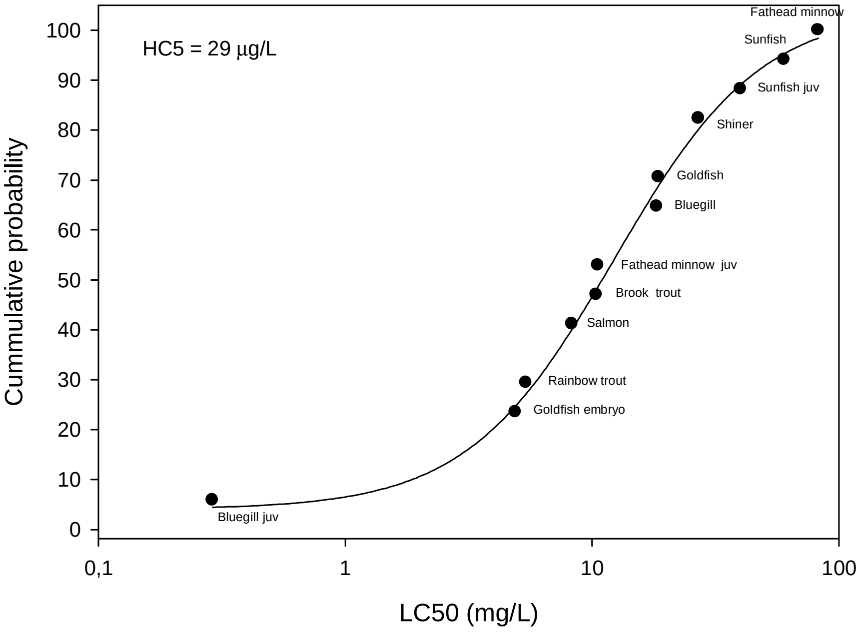


Figure 2 Organoarsenic CWA species sensitivity distribution and HC5.

5.4 Results

5.4.1 Measured CWA in sediment

Among the 99 samples collected and analysed for all the targets in Table 1, only two samples had CWA residues that exceeded the LoQ (Table 2), in other words a detection frequency of just below 2 % for the total number of CWA related compounds measured in all samples. No parent CWA compounds were detected. Both of the positive samples were obtained at sampling station 5 (CWA5.1 and CWA 5.14), which is the sampling station most close to the circular primary CWA dump site (Figure 1).

Table 2 Summary of detected CWA residues in sediment (µg/kg (DW)).

Compound	CAS#	Sample id	Concentration
Lewisite II (L2[ox])	157184-21-9	CWA5.1	15 ±5.4
Phenyldichloroarsine (PDCA[SPr])	1776-69-8	CWA5.14	306 ±24

Both of these are degradation products, bis(2-chlorovinyl)arsenic acid (L2[ox]) and dipropylphenylarsonodithioite (PDCA[SPr]), which may stem from organoarsenic CWAs. L2[ox] is a degradate originating from at least divinylarsinic acid, which again can originate from Lewisite II. PDCA[SPr] originates from at least phenylarsonic acid and phenylarsonous acid, which again may be degradates of the arsenic oil constituent phenyldichloroarsine (VERIFIN, 2010).

5.4.2 CWA related PEC towards the fish community

Pore water concentrations are the primary direct exposure route to fish and other none sediment dwelling organisms. In order to extrapolate from measured sediment concentrations to bio-available pore water concentrations Eq. 1 is employed, which requires estimation of the sorption coefficient between organic matter and water (Table 3).

Table 3 Sorption coefficient between organic matter (OM) and water and calculated retention factor (Rs) from Eq. 1. (Sanderson et al. 2008).

Compound	Koc (L/kg OM)	Rs (Eq. 1)
Lewisite II residue (L2[ox])	307.3*	29
Phenyldichloroarsine residue (PDCA[SPr])	28,010*	2600

*) Based on Molecular Connectivity Index (MCI) in KOCWIN v2.00.

The measured sediment concentrations represent quasi steady-state concentrations and as a worst-case scenario it is assumed that the concentration in the immediate bulk water boundary layer is equal to the pore water concentration, whereas the added bulk water concentration is the re-suspended CWA from the installation of the pipeline. Adding these two concentrations produces the total water concentration. The fishes are thus exposed to the sum of quasi steady-state concentrations and added concentrations from pipe laying (Table 4).

Table 4 Calculated worst-case CWA residue concentrations (µg/L).

Compound	Pore water concentration	Added bulk water concentration	Total water concentration
Lewisite II residue (L2[ox])	0.62 ± 0.22	0.0019 ± 0.0007	0.62 ± 0.22
Phenyldichloroarsine residue (PDCA[SPr])	0.14 ± 0.011	0.039 ± 0.0031	0.18 ± 0.011

5.4.3 CWA related fish community risk assessment

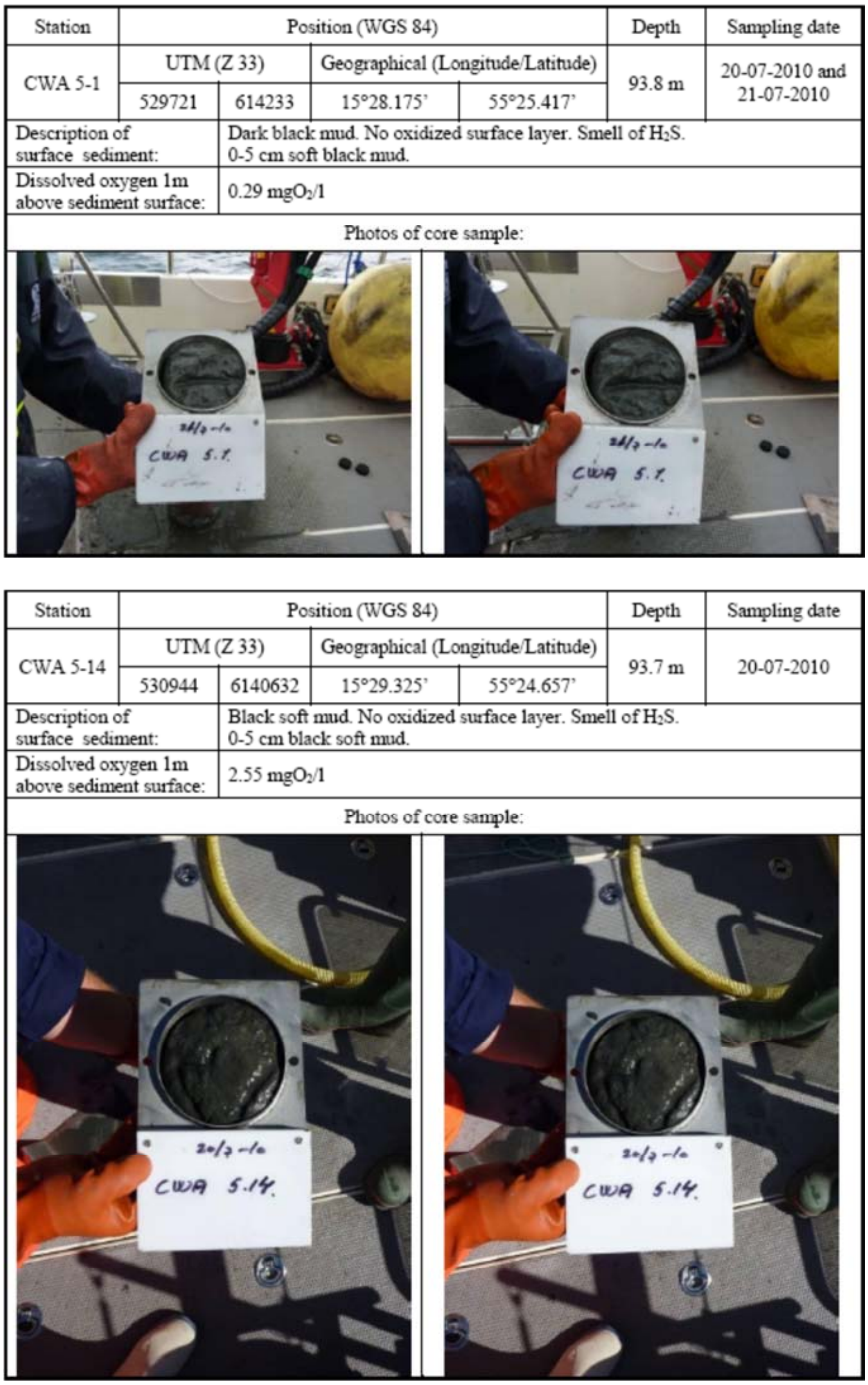
The HC5 value without an assessment factor for both these organoarsenic CWA degradates is 29 µg/L (Figure 2). The total calculated exposure is 0.62 and 0.18 µg/L, respectively for L2[ox] and PCDA[SPr], and thus the total CWA related exposure is 0.8 µg/L. This results in a risk quotient without assessment factor (RQ = PEC/HC5) 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 (Table 5).

Table 5 Risk quotients (RQ) towards fish.

Compound	RQ Pore water	RQ Added bulk water	Total RQ
Lewisite II residue (L2[ox])	0.02	0.00007	0.02
Phenyldichloroarsine residue (PDCA[SPr])	0.005	0.001	0.006
Total CWA residue	0.025	0.00107	0.026

5.4.4 Habitat and sediment quality

We know from the correlation assessment in the previous report that the water depth, DO, Temp, and sediment characteristics to a greater degree than CWA residue exposure govern the observed abundance and diversity of benthos along the pipeline route (Sanderson et al. 2008). Figure 3 illustrates the observations made at the two CWA residue positive samples, CWA5.1 and CWA 5.14, respectively.



Station	Position (WGS 84)				Depth	Sampling date
	UTM (Z 33)		Geographical (Longitude/Latitude)			
CWA 5-1	529721	614233	15°28.175’	55°25.417’	93.8 m	20-07-2010 and 21-07-2010
Description of surface sediment:	Dark black mud. No oxidized surface layer. Smell of H_2S. 0-5 cm soft black mud.					
Dissolved oxygen 1m above sediment surface:	0.29 mgO_2/1					
Photos of core sample:						

Station	Position (WGS 84)				Depth	Sampling date
	UTM (Z 33)		Geographical (Longitude/Latitude)			
CWA 5-14	530944	6140632	15°29.325’	55°24.657’	93.7 m	20-07-2010
Description of surface sediment:	Black soft mud. No oxidized surface layer. Smell of H_2S. 0-5 cm black soft mud.					
Dissolved oxygen 1m above sediment surface:	2.55 mgO_2/1					
Photos of core sample:						

Figure 3 Description of samples CWA 5.1 and CWA 5.14 (DHI, 2010).

The samples were collected less than 1000m apart (Figure 1), and display similar poor sediment characteristics (very soft) from a diverse benthic invertebrate community perspective. The DO is very low (0.29 mg O_2/L) 1 m above sediment at CWA5.1, which would be at the very lower level to support benthic communities, whereas CWA5.14 with 2.55 mg O_2/L should be able to support a benthic community. It is, based upon previous analysis (Sanderson et al. 2008), unlikely that effects on the benthic community from exposure to L2[ox] and PCDA[SPr] would be discernible, as the physical and chemical properties and habitat characteristics would govern the probable low abundance and diversity of benthos at these two sites rather than occurrence of L2[ox] and PCDA[SPr].

5.5 Discussion and conclusions

The 2010 sampling effort detected two CWA related compounds (L2[ox] and PDCA[SPr]) they are secondary degradation products of Lewisite and Phenyldichloroarsine, respectively. They can originate from degradation products from Lewisite and Phenyldichloroarsine, but they can also originate from transformation of other organoarsenicals. PDCA[SPr] can e.g. originate from phenylarsonous acid and phenylarsonic acid. Phenylarsonic acid (CAS# 98-05-5), has multiple uses e.g. as a buffering agent and precursor to other organoarsenic compounds, some of which are used in animal nutrition, e.g. 4-hydroxy-3-nitrobenzenearsonic acid. L2[ox] can also originate from divinylarsinic acid (CAS# 157184-20-8) the industrial usage of this compound is rarer than the usage of phenylarsonic acid. However, due to the fact that L2[ox] and PCDA[SPr] was only found in the samples taken most close to the primary CWA dump site we assume that they originate from the organoarsenic CWAs Lewisite and Phenyldichloroarsine.

The present exposure and risk analysis is based upon the assessment and modelling by Rambøll (2008a, 2008b, 2008c and 2011) with regard to suspended amounts and concentration of sediment in bulk water. Under these conditions, re-suspension of CWA-contaminated sediment will cause an added risk corresponding to a risk quotient of 0.00107, towards the fish community. Compared to the risk quotient from the prevailing quasi steady-state CWA residues concentrations in the pore water of 0.025, this indicates no significant additional risk from pipe laying activities. It is not possible to compare the CWA related risks to the analysis of the benthos since benthos were not sampled and analysed in the two locations where CWA residues were detected. However, the habitat and DO conditions at these locations suggest that benthos would be limited due to these factors rather than the CWA residue exposure, as also shown by Sanderson et al. (2008).

Sampling and assessments along the same route in 2008 (Sanderson et al. 2008) by VERIFIN showed traces of total PCDA in 4.2 % of all the collected sediment samples. In the current assessment only one sample exceeded the LoQ of 19 µg/kg (DW) with a resulting the detection frequency of 1 %. This suggests that the detection frequencies of PCDA related compounds are lower in the 2010 sampling regime than in the 2008 sampling regime. In the 2008 sampling Lewisite II or its degradation products (e.g. L2[ox]) were not detected above LoQ in any of the samples (Sanderson et al. 2008), whereas L2[ox] was found in one sample in the 2010 sampling effort. Comparing the two sampling rounds would suggest that the detection frequencies are comparable between the two years, and that the potential CWA related risks towards the fish and benthic communities are also comparable or maybe slightly lower in 2010 than in 2008 due to the overall slightly lower exposure potential based on the VERIFIN analysis.

5.6 References

DiToro DM. 1991. Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. *Env. Tox & Chem.* 10: 1541-1583.

DHI, 2010. 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.

Emelyanov, E.M. 1996. Chemical Components and Elements in the Suspended Matter and Sediments of the Western Baltic. *Baltica* 9: 5-15.

Forster, S., Bobertz, B., Bohling, B. 2003. Permeability of Sands in the Coastal Areas of the Southern Baltic Sea: Mapping a Grain-size Related Sediment Property. *Aquatic Geochemistry*. 9: 171-190.

Rambøll, 2008a. Chapters from word document: Impacts from sediment - spreading and sedimentation - Spreading of sediment during trenching.

Rambøll. 2008b. Offshore pipeline through the Baltic Sea. Nord Stream A/G. Memo 4.3A-9. Spreading of sediments during pipeline layout. Ref#: 7774001 G-PE-PER-100-EIA-43A40000-04.

Rambøll. 2008c. Offshore pipeline through the Baltic Sea. Nord Stream A/G. Memo 4.3A-9. Release of sediments from anchor operation. Ref#: G-PE-PER-EIA-100-43A90000.

Rambøll. 2011. Nord Stream Intervention Works in Denmark. Rambøll Oil & Gas. Memo G-PE-PER-REP-100-05170000-A

Sanderson H, Fauser P, Thomsen M. 2008. RAMBOLL OIL & GAS. Nord Stream A/G. Offshore pipelines through the Baltic Sea. Analysis of additional risk to the fish community from chemical warfare agent (CWA) associated with construction of the planned Nord Stream Route South of Bornholm. NERI file# DMU-75-00061.

US EPA. 2004. Understanding the variation in partitioning coefficient, Kd, values. Vol III, EPA 402-R-04-002C. Available at: http://www.epa.gov/rpdweb00/docs/kdreport/vol3/402-r-04-002c.pdf

VERIFIN, 2010. 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, Kostiainen and Vanninen.

6 Nord Stream A/G. Offshore pipelines through the Baltic Sea - Analysis of fish community risk due to exposure to Chemical Warfare Agents (CWAs) from perturbed sediment along and between the two gas pipelines east of Bornholm

Hans Sanderson, Patrik Fauser

6.1 Preface

This report is part of an ongoing assessment of the environmental risks suspension of chemical warfare agents from the sediment may represent in the Bornholm Deep in the Baltic Sea. This report assesses the risks in 2012 and compares to the baseline study in 2010 and the risk assessment from 2011 from the same area. The work was funded by Ramboll Oil and Gas (contact person: Jørn Bo Larsen).

6.2 Summary

The aim of this report is to assess the predicted risk towards fish communities from dumped Chemical Warfare Agents (CWAs) following the Second World War in association with the gas pipeline S-route (South route) running close to the CWA dumpsite in the Bornholm Deep in the Baltic Sea. And to compare the findings in this study (2012) with the findings of the baseline study in 2010 and the findings in 2011 from the same locations and with the same methods. Moreover, the correlation between CWA exposures and benthic infauna is also analysed. The assessment is made based on measurements of CWAs and their primary degradation products in sediment. Sorption coefficients estimated from Molecular Connectivity Index are used to transform measured sediment concentrations into the fish bioavailable pore water fractions for the risk estimation. Ninety-eight samples were collected along the 28 sampling locations (CWA 1-28), plus six transects perpendicular to the pipelines. The sampling and results of the sediment conditions, background variables, benthic infauna, and CWA exposures in 2012 are directly comparable to the measurements in the 2010 baseline study and the 2011 study. No parent CWAs were detected in the sediments, however, nine out of the 98 samples had one or more residues of CWA (degradation products of Adamsite, Clark I, phenyldichloroarsine, trichloroarsine), total detection frequency = 10.2 %. In the 2010 sampling only two out of 98 samples contained residues (phenyldichloroarsine and Lewisite II), in 2011 10 samples had traces of CWA residuals (degradation products of Adamsite, Clark I, phenyldichloroarsine, trichloroarsine and Lewisite II). The maximum total calculated fish community exposure concentration was 0.108 (± 0.029) µg/L at sampling station CWA 22.81 (residues of TCA (SPr)). The total risk quotient (RQ) for individual CWA residues ranges between 0 to 0.0037 for TCA(SPr) with station CWA 22.81 as the highest suggesting a negligible CWA risk. The added risk from sediment disturbance in relation to installation of the pipelines represents less than 1 % of the total risk in the area (RQ = 0.0001), the comparative risk in 2010 and 2011 was calculated to be 0.0017 and 0.003 (RQ), respectfully. The risks are insignificant and hence the difference between them is also insignificant. The analysis of infauna

corroborate the finding of low risk as the abundance, biomass, and diversity of the biota were quite similar compared to the other locations, moreover, biota is governed by other factors (e.g. total organic carbon, dissolved oxygen (DO), depth, sediment characteristics) than predicted the CWA risk at sites CWA 22.81.

When comparing the 2010 and 2011 measurements with the 2012 measurements it is clear that; no parent CWA were detected; the exposure concentrations are predicted not to represent a risk towards the fish community; the detection frequencies are comparable (2 and 10 %) noting the patchiness of detections and hence sample variability; that the pipeline installation only contribute less than 1 % of the steady-state background risk (0.0001 (2012); 0.003 (2011); and 0.0017 (2010)), and that this risk is insignificant towards the fish community and that the CWA residue risks are not reflected in the biota measurements.

6.3 Introduction

Following the end of the Second World War Germanys approximately 65,000 tonnes stockpiled Chemical Warfare Agent (CWA) munitions were dumped in the Bornholm Deep. There are concerns that environmental risks may arise from perturbation of sediment containing traces of dumped chemical warfare agents (CWA) in connection with the construction and establishment of the gas pipelines on / in the seabed in the Bornholm Deep in the Baltic Sea within the Danish territorial area. An initial risk assessment was performed by Sanderson et al. (2008) based on 95 sediment and 11 pore water samples collected in May 2008 along the pipeline S-route. CWA concentrations, benthos assessment and habitat and sediment quality and characteristics, and background physical / chemical parameters were measured and correlated. The study showed that the suspended CWA residues did not constitute a significant risk to the fish community, moreover, that the benthos community was limited by habitat and dissolved oxygen levels and not by CWAs (Sanderson et al. 2008). The 2010 study expanded the number of analytes to include more degradation products. In 2010 the study confirmed the findings for 2008; as only two positive CWA samples were found it is unlikely that effects on the benthic community from exposure to L2[ox] and PCDA[SPr] would be discernible, as the physical and chemical properties and habitat characteristics would govern the probable low abundance and diversity of benthos at these two sites rather than occurrence of L2[ox] and PCDA[SPr]. The present study in 2012 builds upon the 2008 and particularly the 2010 baseline study using similar methods and the same number of sediment samples (98) to ensure comparability.

6.4 Methods

All methods and analysis replicated the baseline study of 2010 to ensure comparability. Sampling was carried out June 2012. Samples for CWA analysis were taken from the upper 5 cm of the sediment core, as it was shown in the previous study by Sanderson et al. (2008) that CWA are primarily found in the upper 5 cm of the sediment. It was moreover shown in the 2008 study that the CWAs primarily were found in the sediment and not in the pore water, hence this sampling campaign focussed on sediment concentrations. A total of 98 sediment samples along 23 sampling stations and six transects of 15 stations perpendicular to the lines (Figure 1a & Figure 1b) were collected.

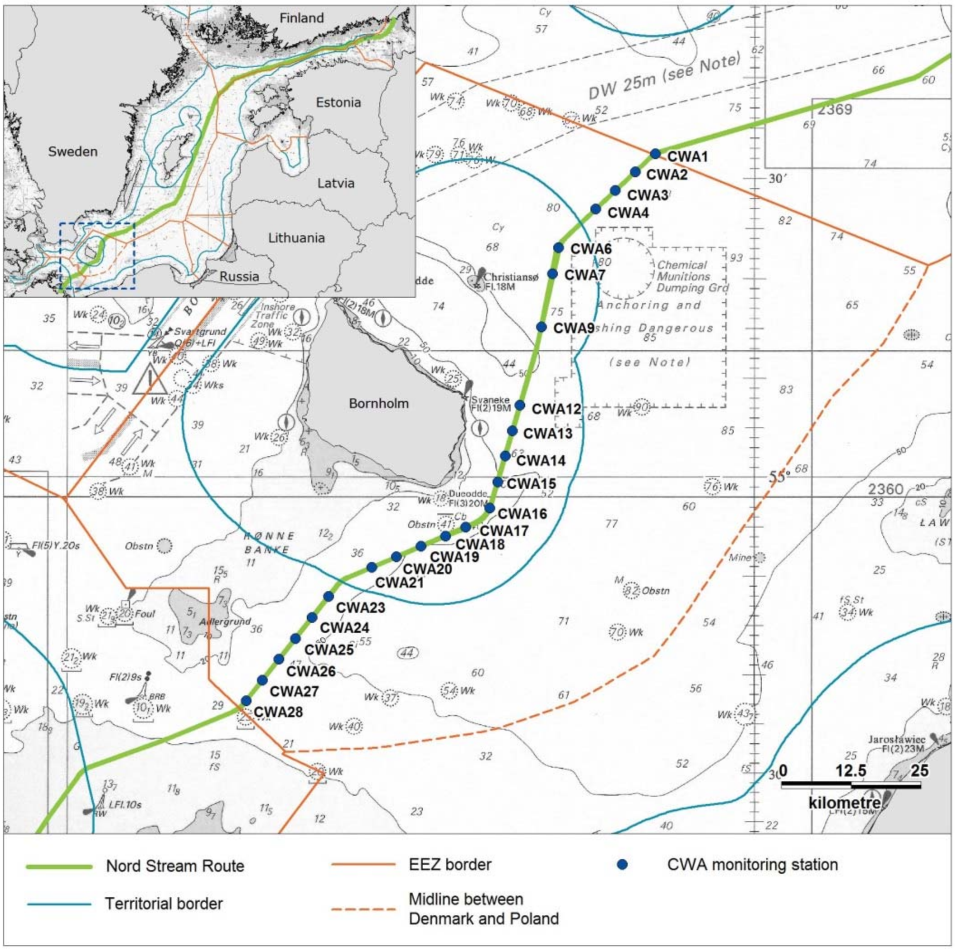


Figure 1a Sampling stations along the S-route and transects near Bornholm (DHI, 2012).

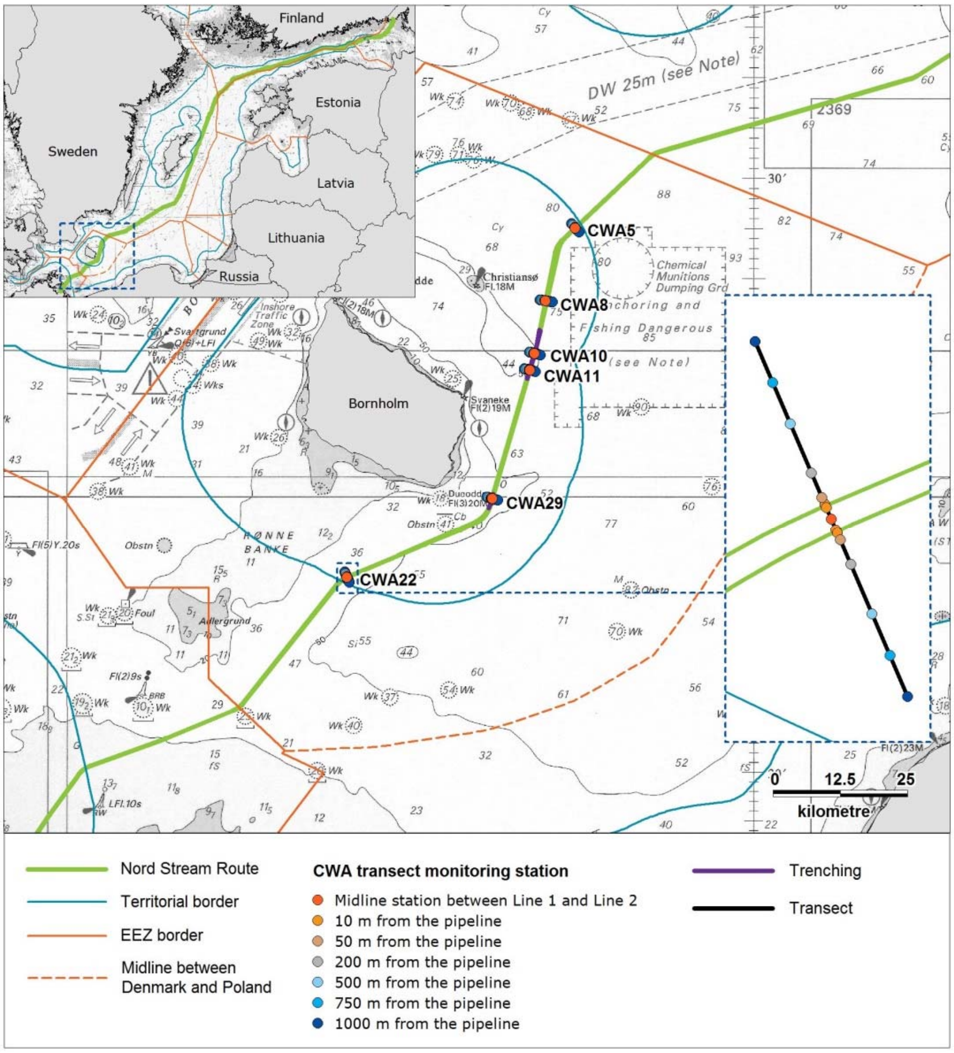


Figure 1b Sampling stations along the S-route and transects near Bornholm (transect CWA 29 had to be omitted), biota was sampled for transect CWA 10 and 11 (DHI, 2012).

The samples were frozen immediately after sampling. The samples were received by the analytical lab, VERIFIN, as frozen and stored at -18° C until analysis a few weeks later. Sediment samples for chemical analyses were taken with a Haps core sampler at the sampling stations along the planned pipeline route going east and south of the island of Bornholm (DHI, 2012). The list of 10 target CWAs for analysis are shown in Table 1. A total of 21 degradation products were analysed (VERIFIN, 2012).

Table 1 Target CWA related analytes (VERIFIN, 2012).

CAS #	Compound
505-60-2	Sulphur mustard gas and its main degradation products
578-94-9	Adamsite and its main degradation product
712-48-1	Clark I and its main degradation products
603-32-7	Triphenylarsine
532-27-4	Chloroacetophenone
696-28-6	Phenyldichloroarsine and its main degradation products
7784-34-1	Trichloroarsine and its main degradation products
77-81-6	Tabun
541-25-3	Lewisite I and its main degradation products
40334-69-8	Lewisite II and its main degradation products

The compounds were analysed by GC-MS and LC-MS/MS, with the aim of a minimum Limit of Quantification (LoQ) of 100 µg/kg (ppb) dry weight (DW) sediment. The actual measured LoQ ranged from 3.3 (for Adamsite oxidation product) to 32 µg/kg (PDCA residues). Adamsite was only measurable as its oxidation product. The LoQs for the LC-MS/MS analytes were similar to the LoQs from 2011 and 2010, whereas the LoQs for the GC-MS analytes were 2 to 10 times lower than in the 2010 study (VERIFIN, 2012).

In addition background variables; salinity, dissolved oxygen (DO), and sediment characterization and photo documentation was performed on-site (DHI, 2012). Moreover, the benthos community was assessed in the lab based on the samples collected at transects B 10, 11 corresponding to transects CWA 10, 11, biota transect CWA 29 had to be omitted due to hard sediment (DHI, 2012).

6.4.1 Predicted Environmental Concentrations (PEC) towards fish

The munitions have been resting on the seabed and in the sediment of the Baltic Sea for more than sixty years and the extent of corrosion of the shells, and thus release of the toxic chemicals into the marine environment and the following exposure to organisms need site specific investigation.

The environmental toxicity along with most physico-chemical properties of CWAs have not been thoroughly investigated with modern methods and reported in the public literature, hence modelling of these properties is warranted to derive comparable datasets (Sanderson et al., 2008). In order for chemicals to be incorporated into organisms such as fish and thereby exert toxicity they generally need to be in solution. Hence, the sediment concentrations, C_s (mg/kg DM), will be used to calculate pore water CWA concentrations, C_{pw} (mg/L), which are bioavailable to the fishes, for all the samples based on adapted equilibrium partitioning (DiToro, 1991 and Sanderson et al., 2008), cf. Eq. 1.

$$C_s = C_{pw} \cdot R_s / X_s = C_{pw} \cdot (\theta + Kd \cdot X_s) \; / X_s \qquad \text{(Eq. 1)}$$

Where; $R_s = (\theta + Kd * X_s)$ is the retention factor, $\theta = 0.55$ is the pore volume fraction in the sediment (Forster et al., 2003), $Kd = f_{oc} \cdot K_{oc}$ 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 (Emelyanov, 1996), K_{oc} is the partitioning coefficient (sorption coefficient) between organic matter and water (L/kg OM) and $X_s = 1.2$ kg DM/L is the density of sediment (Forster et al., 2003).

Thereafter, the added CWA risk from sediment agitation from installing the pipelines based on assumptions related to the construction of one gas pipeline is calculated. The conditions for estimating the re-suspension of sediment particles in the lower bulk water are similar to the previous assessment for 2010; this ensures maximum comparability and worst-case conditions (DHI, 2011).

Accordingly, in addition to the quasi steady-state concentration of CWAs in the bottom boundary layer originating from the dumped CWAs, there is a contribution from the release of sediment particles during the following pipeline activities:

- 1) Trenching which occurs at two sections, and comprises sampling stations 10, 11 and 16. At these stations the increase in sediment concentration in the bulk water between 0 and 10 m above the seabed is $C_{w(sed,trenching)}$ = 33 mg sediment/L, as shown in Sanderson and Fauser (2011).
- 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 (Rambøll, 2008b).
- 3) Handling of 12 anchors, each weighing 25 tonnes, which 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 release to the bulk water is 10 - 38 tonnes sediment/km of the pipeline in areas with soft sediment (Rambøll, 2008c). The release area is approximately 2 % (0.04 km^2/km) of the anchor corridor. This gives a sediment concentration in the release area and lower 10 m (release water volume) of $C_{w(sed,sweeping)}$ = 25 - 95 mg sediment/L. When assuming that sediment particles from the release area are spread to the total anchor corridor area, the average sediment concentration is approximately 0.5 - 2 mg/L (Rambøll, 2008c).

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^2/km) of the anchor corridor. This gives a sediment concentration in the release area and lower 10 m above the sediment (release water volume) of: $C_{w(sed)}$ = 95 mg sediment/L, from sweeping, and $C_{w(sed)}$ = 128 mg sediment/L, from sweeping and trenching. Sweeping occurs along the entire pipeline, whereas trenching occurs only at sections 10, 11 and 16.

The worst-case CWA concentration in the release bulk water volume, $C_{w(CWA)}$ in mg CWA/L, is thus:

$$C_{w(CWA)} = C_{w(sed)} \cdot C_{s(CWA)} \qquad \text{(Eq. 2)}$$

Where, $C_{s(CWA)}$ 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 calculated pore water concentrations will be used as the worst case predicted CWA exposure concentration (PEC) of biota (Sanderson et al. 2012).

6.4.2 Predicted No observed Effect Concentration (PNEC) towards fish

The PECs is compared with toxicologically acceptable exposure concentrations towards the fish communities as reported in Sanderson et al. (2008) with fish community extrapolated HC5 value (Hazard Concentration 5 %). The HC5 represent the concentration where 95 % of the fish species' acute LC50 in the community is not exceeded, or in other words accepting a potential risk for 5 % of the community. The measured fish toxicity values of detected organoarsenic CWA residues were derived from the U.S. National Library of Medicine Hazardous Substances Data Base (HSDB:

http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB). For arsenic compounds, it is recommended, as a precautionary and data quality measure, to use the well documented high toxicity of inorganic arsenic as a surrogate for compounds containing organic arsenic lacking ecotoxicity data. The measured acute toxicity data used to derive a species sensitivity distribution (SSD) for 12 fish species (adult and juvenile). The resulting acute HC5 value (protective of 95 % of the community) equals 29 µg/L (Figure 2). To derive a predicted no effect concentration (PNEC) the HC5 value is assigned an assessment factor. The assessment factor associated with HC5 values derived by species sensitivity distributions (SSD) ranges between 1 and 5, and has not been included in this analysis (Sanderson and Fauser, 2011; Sanderson et al. 2012).

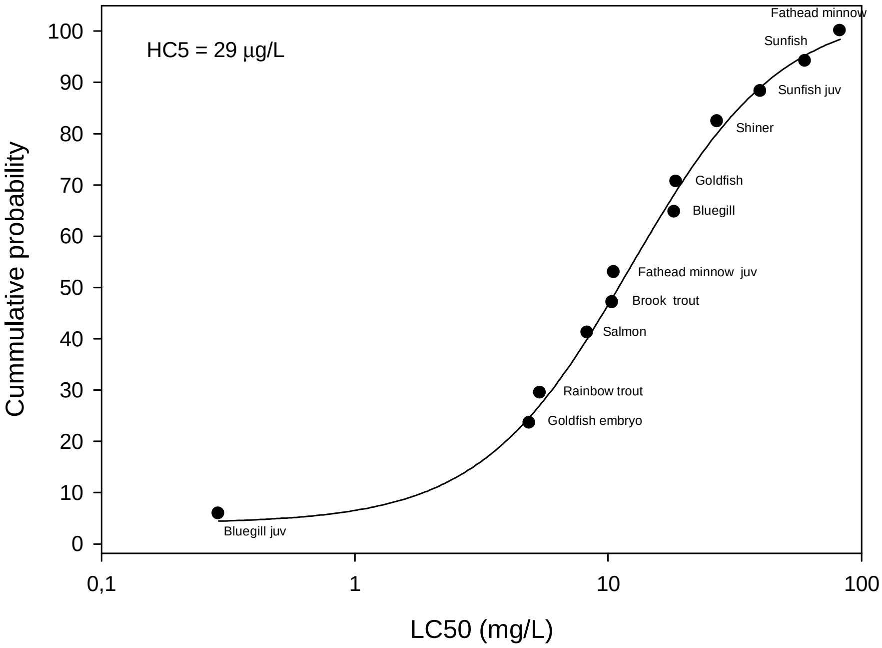


Figure 2 Organoarsenic CWA species sensitivity distribution and HC5 (from Sanderson and Fauser, 2011).

6.5 Results

6.5.1 Measured chemical warfare agents in sediment

Among the 98 samples collected and analysed for all the compounds listed in Table 1, nine samples had CWA residues that exceeded the LoQ (one sample had two CWA residues) (Table 2), in other words a detection frequency of approx. 10 % for the total number of CWA related compounds measured in all samples. No parent CWA compounds were detected (Table 1).

Table 2 Detected CWA residues in sediment (µg/kg (DW)) in June 2012. Name of residue is given in parenthesis after parent CWA

Compound	Concentration (µg/kg DM)	Sampling station
Adamsite (DM[ox])	7.7 ±0.92	CWA 11.51
Adamsite (DM[ox])	10 ±1.2	CWA 12
Clark I (DA[ox])	5.5 ±0.66	CWA 10.37
Clark I (DA[ox])	8.8 ±1.1	CWA 13
Phenyldichloroarsine (PDCA[SPr])	88 ±27	CWA 10.33
Phenyldichloroarsine (PDCA[SPr])	40 ±12	CWA 22.80
Trichloroarsine (TCA[SPr])	28 ±8.0	CWA 17
Trichloroarsine (TCA[SPr])	28 ±8.1	CWA 22.80
Trichloroarsine (TCA[SPr])	39 ±11	CWA 22.81
Trichloroarsine (TCA[SPr])	32 ±9.3	CWA 24

All detected compounds in Table 2 are degradation products, which can originate from parent CWAs. They can be primary degradation products via natural oxidation of parent CWA and/or secondary degradation products via initial hydrolysis followed by oxidation (VERIFIN, 2012). See Annex 1 for a complete list of detected CWA residues in sediment (2008-2012). Interestingly, CWA residues were only found in the vicinity of pipeline 1.

6.5.2 Chemical warfare agents related predicted environmental concentration towards the fish community

Porewater concentrations are the primary direct exposure route to fish and other none sediment dwelling organisms. In order to extrapolate from measured sediment concentrations to bio-available pore water concentrations Eq. 1 is employed, which requires estimation of the sorption coefficient between organic matter and water (Table 3).

Table 3 Sorption coefficient between organic matter (OM) and water (K_{oc} based on Molecular Connectivity Index (MCI) in KOCWIN v2.00) and calculated retention factor (Rs) from Eq. 1. (Sanderson et al. 2008).

Compound	K_{oc} (L/kg OM)	Rs (Eq. 1)
Adamsite (DM[ox])	4401	410
Clark I (DA[ox])	22830	2124
Phenyldichloroarsine (PDCA[SPr])	28010	2605
Trichloroarsine (TCA[SPr])	4815	448

The measured sediment concentrations represent quasi steady-state concentrations and as a worst-case scenario it is assumed that the concentration in the immediate bulk water boundary layer is equal to the pore water concentration, whereas the added bulk water concentration is the re-suspended CWA from the installation of the pipeline. The sum of these two concentrations equals the total water concentration. The fish are thus exposed to the sum of quasi steady-state concentrations and added concentrations from pipe-laying (Table 4).

Sorption and partitioning of compounds is context dependent and hence complex, and different assumptions and models impact the outcome (US EPA, 2004). Herein we used the US EPA model KOCWIN v2.00 and the MCI result to be consistent between the 2010, 2011 and 2012 sampling to ensure comparability.

Table 4 Calculated worst-case CWA residue concentrations (µg/L) (± standard deviation). Sampling stations for max. total CWA water concentrations are as in Table 2.

Compound	Pore water concentration	Added bulk water concentration	Total water concentration
Adamsite (DM[ox])	0.023 ±0.0027	0.0010 ±0.00012	0.024 ±0.0027
Adamsite (DM[ox])	0.029 ±0.0035	0.00095 ±0.00011	0.030 ±0.0035
Clark I (DA[ox])	0.0031 ±0.00037	0.00072 ±0.00009	0.0038 ±0.00038
Clark I (DA[ox])	0.0050 ±0.00062	0.00084 ±0.0001	0.0058 ±0.00063
Phenyldichloroarsine (PDCA[SPr])	0.041 ±0.012	0.012 ±0.0035	0.052 ±0.013
Phenyldichloroarsine (PDCA[SPr])	0.018 ±0.0055	0.0038 ±0.0011	0.022 ±0.0056
Trichloroarsine (TCA[SPr])	0.075 ±0.021	0.0027 ±0.00076	0.078 ±0.021
Trichloroarsine (TCA[SPr])	0.075 ±0.022	0.0027 ±0.00077	0.078 ±0.022
Trichloroarsine (TCA[SPr])	0.104 ±0.029	0.0037 ±0.0011	0.108 ± 0.029
Trichloroarsine (TCA[SPr])	0.086 ±0.025	0.0030 ±0.00088	0.089 ±0.025

The maximum total calculated water concentrations (exposures) are derived from the measured sediment concentrations (Table 2) and Eq. 1, as explained above, and are found to be 0.108 (±0.029 SD) for TCA[SPr] at sampling location CWA 22.81.

6.5.3 Chemical warfare agent related fish community risk assessment

The HC5 value without an assessment factor for all organoarsenic CWA degradates is 29 µg/L (Figure 2). This results in maximum summed risk quotients without assessment factor (RQ = PEC/HC5) of 0.108/29(±0.029 SD) = 0.0037 at sampling station CWA 22.81. This RQ represent the sum of the quasi steady-state CWA residue concentration at the sediment boundary layer and the re-suspended sediment exposures at the site. Table 5 provides the RQs for all sites.

Table 5 Risk quotients (RQ) towards fish calculated from Table 2 and the fish community HC5 of 29 µg/L. Total RQ = steady-state RQ + added RQ

Compound	Total RQ	Added RQ	Sampling station
Adamsite (DM[ox])	0.00081	0.00003	CWA 11.51
Adamsite (DM[ox])	0.0010	0.00003	CWA 12
Clark I (DA[ox])	0.00013	0.00002	CWA 10.37
Clark I (DA[ox])	0.00020	0.00003	CWA 13
Phenyldichloroarsine (PDCA[SPr])	0.0018	0.0004	CWA 10.33
Phenyldichloroarsine (PDCA[SPr])	0.00077	0.0001	CWA 22.80
Trichloroarsine (TCA[SPr])	0.0027	0.00009	CWA 17
Trichloroarsine (TCA[SPr])	0.0027	0.00009	CWA 22.80
Trichloroarsine (TCA[SPr])	0.0037	0.0001	CWA 22.81
Trichloroarsine (TCA[SPr])	0.0031	0.0001	CWA 24

The calculated added CWA risk from suspended sediment with CWA residues during the installing the pipelines were also calculated to be highest at location CWA 22.81with a RQ = 0.0001.

6.5.4 Habitat and sediment quality

We know from the correlation assessment in the previous report that the water depth, dissolved oxygen (DO), temperature, and sediment characteristics and total organic content to a greater degree than CWA residue exposure govern the observed abundance and diversity of the benthic infauna/biota along the pipeline route (Sanderson et al. 2008).

The background and sediment conditions were analysed for CWA 10 and 11 sampling locations. The biota data are especially interesting relative for the location CWA 10.33 as the RQ of 0.0018 is a factor ten higher than the other sites with biota measurements (CWA 10.37 (RQ = 0.00013) and CWA 11.51 (RQ = 0.00081)) – is this predicted risk reflected in the measured biota?

Station CWA 10.33: This location has a depth of 57 m, with above average (for CWA 10 locations) background conditions (temperature and oxygen). The location has a higher than average total organic carbon content of 1.9 % dry weight. The distribution of important species shows that the site has the highest abundance of the polycheate *Scoloplos armiger* among all the collected samples and the highest abundance of another polycheate *Pygospio elegans*. Regarding the bivales the site had the highest abundance and biomass of *Macoma balthica*.

The species abundance similarity to the other sites was 77.1 % for CWA 10.33 with *Scoloplos armiger* as the main contributing species. Site CWA 10.33 had a similarity and average biomass with the sites that were analyzed at 73.8 %, again with the sea worm (polycheate) *Scoloplos armiger* as the species contributing most to the similarity, as was the case for the majority of CWA 10 sites. The overall biomass was however lowest at CWA 10.31; 32 and 33 locations in the CWA 10 transect mainly due the fact that the otherwise abundant bivalve *Astarte borealis* was not detected in large numbers at the sites, which drove the biomass in the other samples. The relatively low organic carbon content could also explain the lower biomass and abundance and species richness per square meter at the sites (CWA 10.32 had the lowest counts - and no CWA detects) (DHI, 2012).

In conclusion, there is no clear evidence that the CWA predicted risk is reflected in the biota measurements at CWA 10.33. Biota was not measured at location CWA 22.81, which had the highest predicted risk, but the sediment was described at brown coarse sand, with an oxidized surface layer, no smell of H_2S and a dissolved oxygen level 1 m above the sediment surface of 1.57 mgO_2/L suggest good living conditions for benthos.

Background variables such as habitat/sediment quality, dissolved oxygen, and total organic content are more determining for the biota data than CWA exposures in this study, which has also been shown in other studies (Sanderson et al. 2012). Natural variations and sampling variability, ecological niches and competition, plus other un-quantified biotic and abiotic factors which affect the abundance, diversity and biomass of biota may further explain any biota differences between the stations.

6.6 Discussion and conclusions

The present exposure and risk analysis are based upon the assessment and modelling by Rambøll (2008a, 2008b, 2008c and 2011a) with regard to suspended amounts and concentration of sediment in bulk water. Under these conditions, re-suspension of CWA-contaminated sediment will cause a maximum added risk corresponding to a risk quotient of 0.0001 at the highest risk location (CWA 22.81) (in comparison to the max. RQs found in 2010 of 0.00107, and 0.003 in 2011), towards the fish community. Compared to the total risk quotient from the prevailing quasi steady-state CWA residues concentrations in the pore water of up to 0.0037 (0.025 in 2010; and 0.17 in 2011), this indicates no significant additional risk from pipe laying activities.

The 2010 sampling effort detected two CWA related compounds (L2[ox] and PDCA[SPr]) with a total CWA related exposure of 0.8 µg/L, resulting in a negligible total CWA risk estimate towards the fish community of 0.026 at sampling station CWA 5.1 and CWA 5.14. It was not possible to compare the predicted risk to biota since there were no biota data for the two locations in 2010. In 2011 only one compound was found at the CWA 5 transect, i.e. Adamsite (DM[ox]) (0.03 µg/L with a resulting RQ of 0.001) at CWA 5.11 (see Annex 1).

In 2011 the calculated maximum summed risk quotients was 0.17 and 0.15 at CWA 10.45 and CWA 11.60, respectively. Both sampling stations are nearest the dumpsite in their respective east-west transects. The CWA 10.45 RQ was dominated by Lewisite II (L2[ox]) and Phenyldichloroarsine (PDCA[ox]) with RQs of 0.078 and 0.056, respectively. The CWA 11.60 RQ was dominated by Phenyldichloroarsine (PDCA[ox]) with RQ=0.146. The highest added risk from the installation of the pipelines due to sediment disturbance (laying; trenching; sweeping) was calculated to be 0.003 at CWA 10.45. This added risk is less than 1 % of the background steady state CWA related risk in the area.

The results of the 2012 sampling and risk calculations resulted in similar results as in the previous years, with no parent CWAs detected, concentration ranges between LoQ and 100 µg/kg dw in the sediment, and low fish community risk quotients RQ = 0.0037 under quasi-steady state, and RQ = 0.0001 from the sediment re-suspension, suggesting a negligible fish community risk. There were no biota measurements from the highest exposure site. However, the biota and background parameters from the CWA 10.33 site with the highest predicted risk (by a factor of ten among the sites with biota measurements) did show reduced biota counts. These reductions were driven by the lack of the bivalve *Astarte borealis* and, likely due to the relatively reduced organic carbon content in the sediment resulting in reduced grazing potential for benthos and thus lower biomass and abundance, as the diversity was on par with the average for all sites.

The implications of altered level of quantification (LoQs) on comparability of measured sediment concentrations between 2010 and 2011 & 2012 was examined by identifying findings in 2012 that would not have been identified in 2010 or 2011 given the higher LoQs. One finding of DA [ox] = 5.5 and 8.8 µg/kg dw at CWA 10.37 and CWA 13, respectively, would not have been found in the 2010 sampling round. Moreover, the measurement of TCA [SPr] of 22.1 µg/kg dw in CWA 27 in 2011 would not have been detected in 2012. The 2010; 2011 and 2012 data sets are therefore overall directly comparable with respect to detection frequencies and concentration levels.

No conclusions can be made regarding increasing concentration gradients along transects towards the dumpsite, in 2012 the highest exposures were detected at one of the sampling locations (CWA 22.81) furthest away from the primary dump site. In 2010 and 2011 most of the detections were done closer to the dump site than in 2012. Moreover, interestingly, the detections in 2012 were all in the vicinity of pipeline 1.

The conclusions relative to exposure for 2010, 2011 and 2012 is that no parent CWA was found; that the exposure concentrations are predicted not to represent a risk towards the fish community; compared to the 2008 data that biota is not governed by CWA exposures but rather other background parameters (such as DO; total organic content, depth, sediment characteristics) (Sanderson et al. 2012); the detection frequencies are comparable (2 and 10 %) noting the patchiness of detections and hence sample variability; improvement of limits of detection between the years does not explain the difference in detection frequency.

Comparing the sampling rounds (2008; 2010; 2011; 2012) would suggest that the detection frequencies and levels of CWA residues are comparable between the years, and that the potential CWA related risks towards the fish and benthic communities are also comparable and low.

6.7 Annex 1 - Summery of sediment CWA residue concentrations: 2008-2012(µg/kg dw)

Results of CWA analyses in sediment samples, which showed a content of CWA dissipation products. The year 2008 is based on centrifuged samples. Where two results are given as 53.1 / 66.8, the first figure is from the GC-MS-analysis, the second from the LC-MS / MS-analysis (Rambøll, 2012; VERIFIN 2012). See table next page.

Sediment sample year and station	Adamsite (DM[ox])	Clark I (DA[ox])	Lewisite II (L2[SPr&ox])	Phenyl-dichloroarsine (PDCA[SPr&ox])	Trichloro-arsine (TCA[SPr])
2008:					
S 8				2.6	
S 12	10				
S 13	2.4				
S 16	1.7			2.3	
S 16-250N	1.4			1.8	
S 16-250S	200	2.5		9.6	
S 17	3.2				
S 19-250S	1.9				
2010:					
CWA 5.1			-* / 15		
CWA 5.14				306 / - *	
2011:					
CWA 5.11	9.47				
CWA 10.32		8.19		53.1 / 66.8	
CWA 10.45	177		70.3 / 54.9	170 / 126	
CWA 11.46	9.76				
CWA 11.53	15.9				
CWA 11.60		140		116 / 327	
CWA 12				34.1 / -*	
CWA 13				29.9 / -*	
CWA 16			43.5 / - *		
CWA 27					22.1
2012:					
CWA 10.33				88	
CWA 10.37		5.5			
CWA 11.51	7.7				
CWA 12	10				
CWA 13		8.8			
CWA 17					28
CWA 22.80				40 / -*	28
CWA 22.81					39
CWA 24				32	

-* : Not found above the limit of quantification.

References

DiToro, D.M. 1991: Technical basis for establishing sediment quality criteria for non-ionic organic chemicals using equilibrium partitioning. *Environmental Toxicology and Chemistry*, Vol 10: pp. 1541-1583.

DHI, 2011: Monitoring of Benthic Fauna and Chemical Warfare Agents in Sweden and Denmark, Nord Stream Project No 10-1149, Doc. No.: G-PE-EMS-MON-188-M11DENIN-A, Monitoring of Benthic Fauna in Danish Waters in 2011, Final Report for 2011).

Monitoring of Benthic Fauna and Chemical Warfare Agents in Sweden and Denmark, Nord Stream Project No 10-1149, Doc. No.: G-PE-EMS-MON-188-M11DENIN-A, Monitoring of report for Benthic Fauna in Danish Waters in 2012.

Emelyanov, E.M. 1996: Chemical Components and Elements in the Suspended Matter and Sediments of the Western Baltic. *Baltica*, Vol 9: pp. 5-15.

Forster, S., Bobertz, B. & Bohling, B. 2003: Permeability of Sands in the Coastal Areas of the Southern Baltic Sea: Mapping a Grain-size Related Sediment Property. *Aquatic Geochemistry*, Vol 9: pp. 171-190.

Rambøll, 2008a: Assessment of environmental impact (6.1.1) - Impacts from sediment spreading and sedimentation. Available at: http://www.nord-stream.com/da/presse-og-information/bibliotek/

Rambøll. 2008b: Offshore pipeline through the Baltic Sea. Nord Stream A/G. Memo 4.3A-9. Spreading of sediments during pipeline layout. Ref#: 7774001 G-PE-PER-100-EIA-43A40000-04.

Rambøll. 2008c: Offshore pipeline through the Baltic Sea. Nord Stream A/G. Memo 4.3A-9. Release of sediments from anchor operation. Ref#: G-PE-PER-EIA-100-43A90000.

Rambøll. 2011a: Nord Stream Intervention Works in Denmark. Rambøll Oil & Gas. G-PE-PER-REP-100-05150000-A.

Rambøll, 2012: CWA analysis report, Denmark 2011. Rambøll Oil & Gas. Memo G-PE-PER-MON-100-CLRE012

Sanderson, H., Fauser, P. & Thomsen, M. 2008: RAMBOLL OIL & GAS. Nord Stream A/G. Offshore pipelines through the Baltic Sea. Analysis of additional risk to the fish community from chemical warfare agent (CWA) associated with construction of the planned Nord Stream Route South of Bornholm. NERI file# DMU-75-00061.

Sanderson, H. & Fauser, P. 2011; Analysis of fish community risk due to exposure to chemical warfare agents (CWAs) perturbed sediment during the placement of the gas pipeline east of Bornholm. File No. DMU-33787.

Sanderson, H., Fauser P., Thomsen, M., Larsen J.B. 2012: Weight-of-evidence environmental risk assessment of dumped chemical weapons after WWII along the Nord-Stream gas pipeline in the Bornholm Deep. *Jour Hazardous Materials*, Vol 215-216: pp. 217-226.

US EPA. 2004: Understanding the variation in partitioning coefficient, Kd, values. Vol III, EPA 402-R-04-002C. Available at: http://www.epa.gov/rpdweb00/docs/kdreport/vol3/402-r-04-002c.pdf

VERIFIN, 2011: VERIFIN, Finnish Institute for Verification of the Chemical Weapons Convention. Report on chemical analysis of sea-dumped chemical warfare agents in sediment samples. VER-MS-0245. By: Söderström, Taipalus, Hakala, Kostiainen, Isomaa, and Vanninen.

VERIFIN, 2012: VERIFIN, Finnish Institute for Verification of the Chemical Weapons Convention. Report on chemical analysis of sea-dumped chemical warfare agents in sediment samples, 2012 report. VER-MS-J151. By: Martin Söderström, Annette Pettersson, Olli Kostiainen, Ullastiina Hakala, Jere Häyrynen, Keijo Isomaa, Maaret Karjalainen, Matti Kuula, Terhi Taure and Paula Vanninen

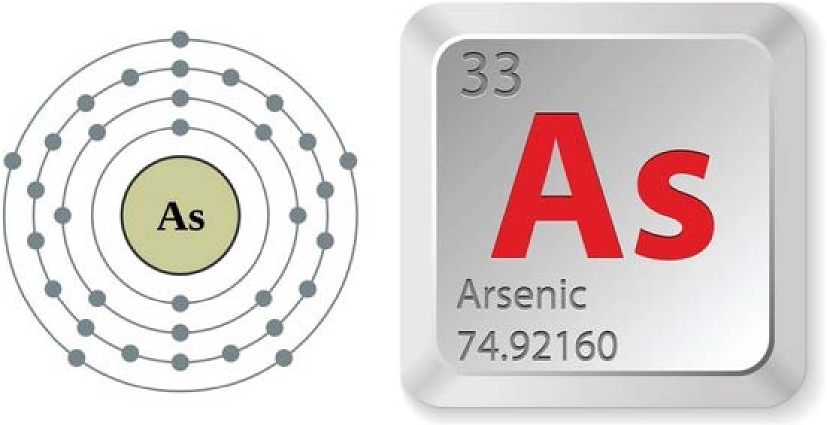
7 Qualitative evaluation of the sources to selected organoarsenicals along the Nord-Stream pipeline route in the Bornholm Deep

Hans Sanderson (DCE-AU); Stephen Mudge (Exponent); Patrik Fauser (DCE-AU); Anders Johansen (DCE-AU)

7.1 Background

Chemical weapons in the form of shells and bombs were disposed of after World War II into a designated area of the Bornholm Deep (Sanderson et al. 2010). Subsequently, Nord-Stream AG laid gas pipelines to Europe around the edge of the site. Samples from the adjacent area and along the pipeline route near the dump site (Sanderson et al. 2012) had positive results for a limited number of parent and dissipation products of the chemical weapons agents (CWAs); greater than 98 % of the positive samples have traces of dissipation products in the form of organoarsenicals (OAs). These OAs may originate from CWAs but could they also have other sources, and could this be qualified and later on quantified? This has never been investigated.

The answer to this question is of critical importance to enable the accurate assessment and management of the environmental risks of the historically dumped chemical munitions. In terms of accurate risk perception, sustainable exploitation of the sea-floor, and consideration of potential risk remediation actions in the Bornholm Deep, accurate answers to the above questions are vital.



Arsenic and OAs has for a long time been a top priority chemical on the US Agency for Toxic Substances & Disease Registry (ATSDR) and US EPA Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) lists, which prioritized the chemicals with the most significant potential threat to human health due to the known toxicity and exposure to humans and the environment (http://www.atsdr.cdc.gov/SPL/index.html). Arsenic is the 20th most abundant element in the earth's crust (Tarvainen et al. 2013) and may also enter the environment from anthropogenic sources and activities. There has been an effort to differentiate between natural and anthropogenic impacts, particularly in areas where expansion and development is occurring and with limited drinking water supplies (e.g. Li et al., 2011; Uddin et al., 2011). There is also a growing appreciation of the regional nature of residual arsenic contamination from agricultural and other anthropogenic sources such as copper and sodium-based arsenicals from herbicides and pesticides – but these are of course very site specific.

Due to the apparent lack of research in this area, the remaining research challenges and the need to apply site specific assessments, the aim of this study is to:

- Qualitatively assess the potential sources to OAs in the Bornholm Deep, both from natural and anthropogenic sources
- Assess the technical possibilities of quantifying the different sources - i.e. quantify the contribution from all other sources combine vs. the contribution from CWAs
- Recommend the next steps of research in this area based on a feasibility assessment of the work needed on the positive samples already collected by Nord-Stream AG and stored by VERIFIN considering the qualitative power of the assessment and the effort needed to differentiate the OA sources (CWA vs. all other)

The product of the work will be a brief mainly qualitative report outlining the potential resource needs for forensic elucidation of the detected organoarsenicals along the Nord-Stream AG pipeline route near Bornholm based on the existing positive sediment samples stored at VERIFIN. The project serves only scientific purposes and is not an assessment or evaluation of environmental effects of the Nord-Stream AG pipeline. The joint draft final report was submitted to Nord-Stream mid-July 2013, to be finalized in early Sept. 2013 after Nord-Stream AG review.

7.2 Approach

A screening level desk-top assessment will be performed to assess the environmental exposure pathway as a result of the many natural and anthropogenic sources; these may have emissions to air, water and soil as arsenic is a ubiquitous element in the environment. A conceptual site model (CSM) will be developed to show the potential for natural or anthropogenic arsenic sources (other than CWAs) to contribute organoarsenicals to the Baltic Sea. We will:

- Review organoarsenicals in marine sediments near Bornholm, mapping what is known about potential sources of arsenicals (and specifically organic forms of As) in the environment
- Research and map known natural releases and deposits in the Baltic, currents in the area (if transport from external sources is a possible route), stability of different chemical species, local sediment conditions (toxic, pH etc.), and the local geology
- Conduct a literature study looking in to industrial activities in the greater Baltic area and identify potential anthropogenic arsenic emitters. All reported significant arsenic (with a focus on the measured OAs) emissions from these industries to water and air will be retrieved. In this work we will also do a literature screening of previous studies on arsenic emission to sea water and air in the area and on measured elevated concentrations in water and sediment
- Assess possible other sources to arsenic emissions on land, e.g. landfills and historic mining sites, and sea, e.g. dumping of (CWA) waste.

-
- Lastly, we will address the biotransformation of organoarsenicals by marine microorganisms

For the feasibility assessment of the efforts needed to quantify the contributions from CWA vs. all other sources we have:

- Supplemented the assessment of what is needed, from an analytical perspective, to separate the CWA organoarsenicals from other sources of OAs.
- Hosted a workshop in Roskilde at DCE-Aarhus University to review and finalize the draft report on July 4th 2013

7.3 Findings

7.3.1 Arsenicals

Arsenic is present in more than 200 mineral species and the primary natural sources of releases to the environment are hot springs (geothermal), igneous rock (basalt), sedimentary rock (organic / inorganic clays, shale), metamorphic rock (slate), seawater, mineral deposits, and volcanoclastic materials / releases. About one-third of the atmospheric flux of arsenic is estimated to be of natural origin (Fauser et al. 2013). The primary anthropogenic sources of arsenic releases to the environment include wood preserving, pesticide / herbicide use, historic mining sites, refining operations, combustion by-products from burning fossil fuels, animal feeds / waste by-products, medicinal uses, fertilizer use, landfill leachate, glass production, and tanneries. It has been estimated that 70 % of the world arsenic production is used in timber treatment as copper chrome arsenate (technically chromated copper(II) arsenate or CCA – the chromium “fixes” the copper arsenate to the wood), 22 % in agricultural chemicals, and the remainder in glass, pharmaceuticals and non-ferrous alloys and small amounts in chemical warfare weapons. Case studies show that arsenic wastes that have been treated to U.S. regulatory standards are found to leach out of landfilled waste. Work has therefore been done to investigate the possibilities for effective treatment and stabilization of arsenic wastes to minimize risk to health and the environment. Arsenic wastes are generated from several industries such as mining and smelting operations (US EPA, 2012). Hence, the sources, forms and levels of arsenicals can vary greatly necessitating a site specific assessment as also evident from the USEPA (CERCLA) lists priority ranking of As.

The natural and anthropogenic sources combine in the environment and lead to the distribution in the soils of Europe seen in Figure 1. In general, the concentrations are low in the Scandinavian countries and higher in the metal extractive regions such as Cornwall in the UK.

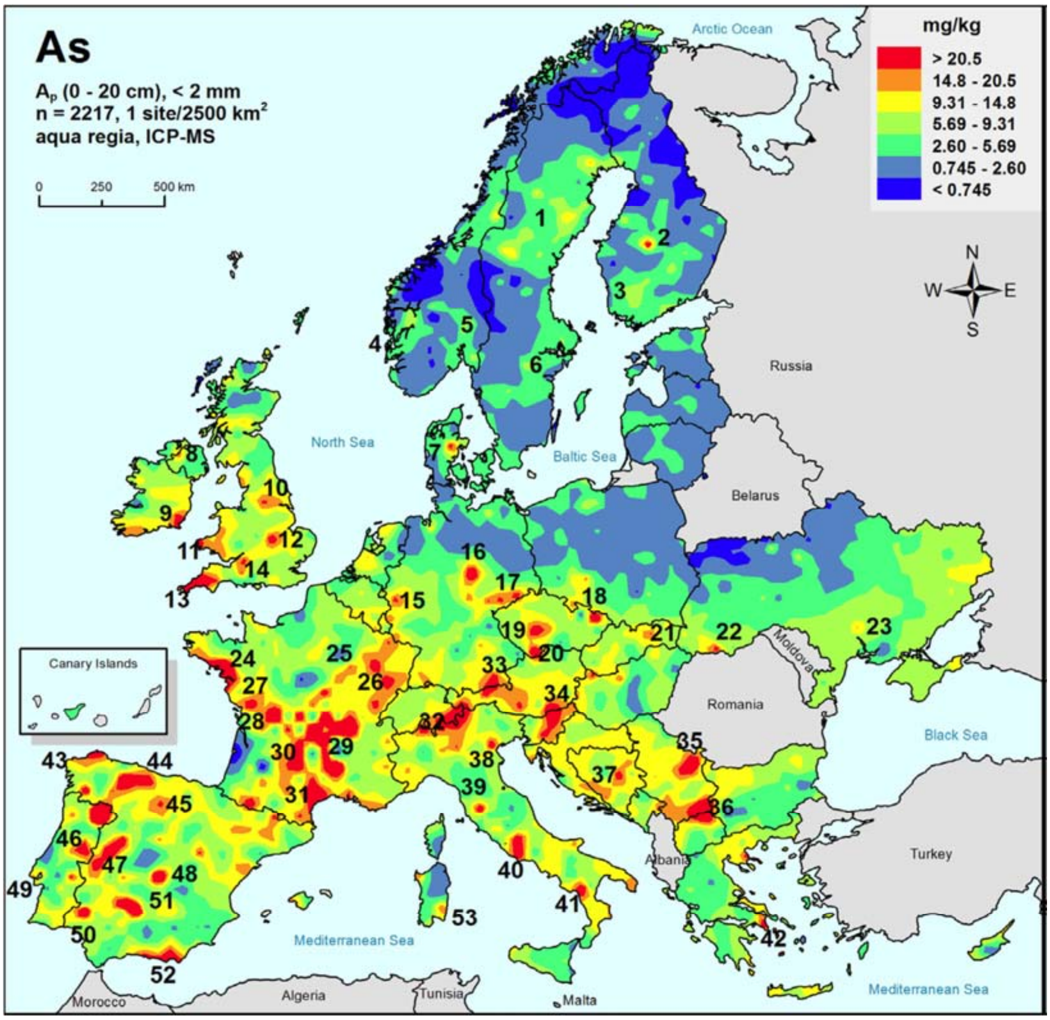


Figure 1 Surface As concentrations in soils in Europe (Tarvainen et al. 2013).

There are three biologically important arsenic valence states: elemental arsenic As(0), As(III) and As(V). The chemical nature of arsenic compounds, in particular their tendency to change valence states or chemical form under a wide range of pH and redox conditions, makes it difficult to assess their fate and mobility in the environment. Under reducing conditions, As (III) is the dominant species. As (V) is generally the stable species in oxygenated environments. Inorganic compounds exhibit a wide range of solubilities depending on pH and the ionic environment (Schnoor, 1996). As(V) absorbs to particles more effectively at low pH values and will have a low mobility in acid soils or sediments with a high clay or oxide content (Tijhuis et al. 2007) (Table 1).

Table 1 Parent CWA and other potential sources of arsenic to the Baltic Sea around Bornholm.

Trivial Name	Systematic name	Usage and emission sources	CAS number	Water Solubility (g/l)
Clark I (DA or DPA)	Diphenylchlorarsine	Mask breaker, vomiting agent, CWA	712-48-1	2
Clark II	Diphenylcyanorarsine	Vomiting agent, CWA	23525-22-6	2
Adamsite (DM)	Diphenylaminechlorarsine	Vomiting agent; In the formulation of wood treating solutions against marine borers and similar pests, CWA	578-94-9	0.002
Lewisite I (L1)	2-chloroethenylarsonous dichloride	Vesicants, CWA	541-25-3	0.5
Lewisite II (L2)	2-chloroethenylarsinous chloride	Vesicants, CWA	40334-69-8	0.5
TPA	triphenyl arsine	Blister agents, CWA	603-32-7	0.0001
TCA	trichloroarsine	Lacrymator poison gas; solvent for diphenylcyanoarsine. Ceramics industry. Arsenic pharmaceuticals. Insecticides, CWA	7784-34-1	
PDCA (PD)	phenyldichloroarsine	Vesicants , medication, security agent	696-28-6	0.6
PDCA(ox)	phenylarsonic acid	Reagent for tin. Precipitant in niobium analysis	98-05-5	
MSMA	Monosodium methyl arsenate	Herbicide (golf courses)	2163-80-6	1000
DSMA	Disodium methyl arsenate	Herbicide	144-21-8	1000
CCA	Chromated copper arsenate	Wood preservation	7778-41-8	Insol.
Cacodylic acid (DMA)	Dimethylarsinic acid	Herbicide	75-60-5	667
Lead arsenate	Lead hydrogen arsenate ($PbHAsO_4$)	Insecticide	7784-40-9	848
Paris Green	Copper acetoarsenite	Insecticide / Pigment	12002-03-8	Insol.
Calcium arsenate	Calcium arsenate	Herbicide / insecticide	7778-44-1	NA
As(0), As(III), As (V) and inorganic and organic arsenic compounds		Component of alloys and electrical devices. In metallurgy for hardening copper, lead, nonferrous alloys. Automotive body solder. In semiconductor materials. In the manufacture of low-melting glass. Wood preservative. Herbicide, pesticide (former use). To make gallium arsenide for dipoles and other electronic devices. Doping agent in germanium and silicon solid state products. Special solders. Medicine (also veterinarian). As radioactive tracer in toxicology. Used as a catalyst in the manufacture of ethylene oxide. In the manufacture of chemicals. In the manufacture of photoreceptor arsenic-selenium alloys for xerographic plain paper copiers. In III-V compounds, such as InAs, GaAs, AlAs, etc. Used in semiconductor devices. Emissions occur from tobacco smoke, metal smelting, coal burning, and other industrial activities	7440-38-2 Elemental arsenic (v0)	variable

Table 2 below summarizes the OAs detected since 2008 along the pipeline route, their CAS numbers; which sampling year they were detected, and their overall detection frequency (DF%), as well as which parent CWAs they are assumed to originate from.

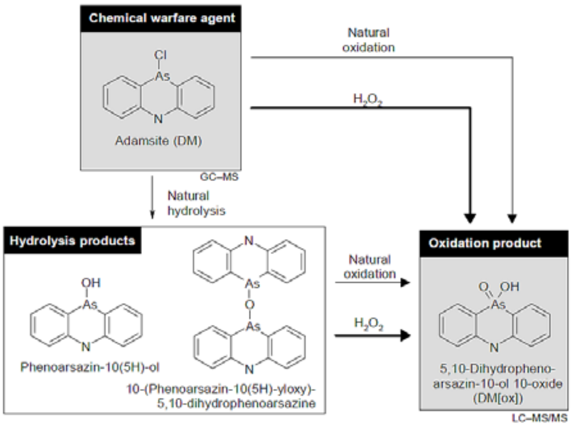
Table 2 Dissipation products found between 2008 (year 1), 2010 (year 2), 2011 (year 3) and 2012 (year 4).

Name	CAS#	Year	DF (%)
DM(ox): 5,10-dihydropheno-arsasin-10-ol 10-oxide[1]	4733-19-1	1,3,4	3.5
DPA(ox): diphenylarsinic acid[2]	4656-80-8	1,3,4	19.5
L2(ox): bis(2-chlorovinyl)arsinic acid[3]	157184-21-9	2,3	2
L2(SPr): propyl bis(2-chlorovinyl)-arsinothioite[3]	677355-04-3	3	2
PDCA(ox): phenylarsonic acid[4]	98-05-5	1,3	2
PDCA(SPr): dipropyl phenylarsonodithioite[4]	1776-69-8	2,3,4	26
TCA(SPr): tripropyl arsonothioite[5]	5582-57-0	3,4	13.5

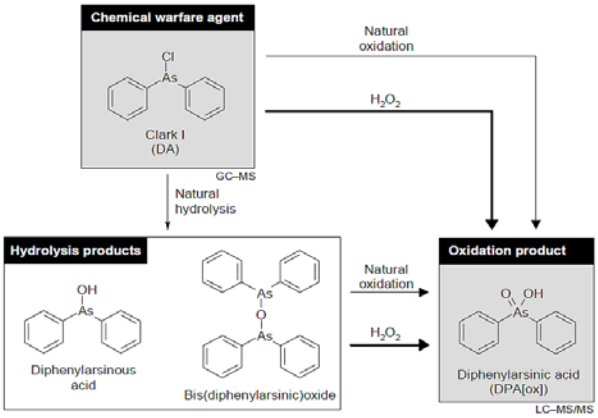
Parent CWAs: Adamsite[1]; Clark I[2]; Lewisite II[3]; PDCA[4]; TCA[5].

Table 3 below outlines the dissipation pathways the compounds in Table 2 may have from CWA origins via hydrolysis and oxidation. In essence the aim of this report is to investigate if there are other plausible and quantifiable pathways to develop the same compounds – from natural or anthropogenic stating materials other than the CWAs.

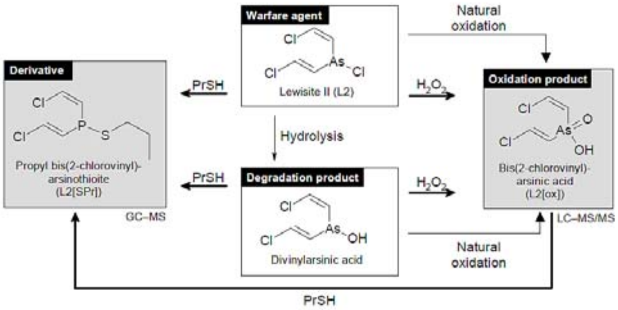
Table 3 Tabulation of dissipation pathways of organic arsenicals (OAs) from CWAs (VERIFIN; 2010-2012).



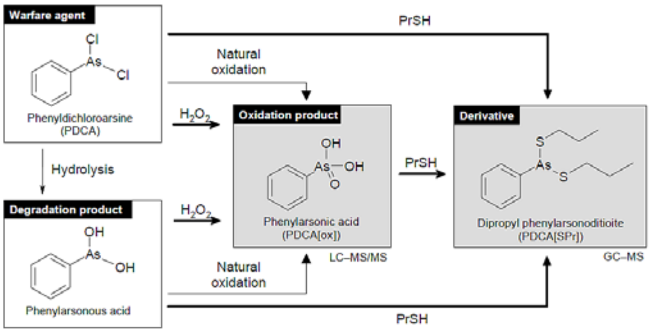
Adamsite (DM-ox)



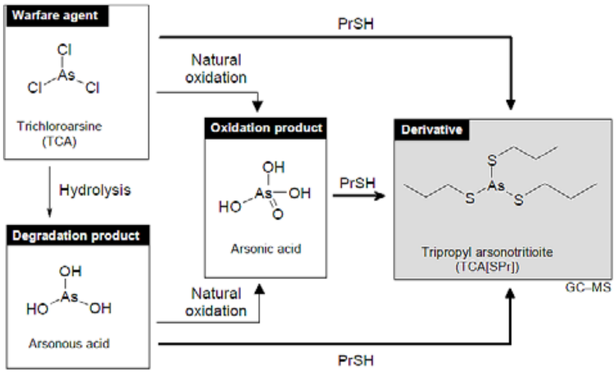
Clark I (DPA-ox)



Lewisite II (L2-ox + SPr)



PDCA (PDCA-ox + SPr)



TCA (TCA-SPr)

7.3.2 Conceptual site model

The potential sources of arsenic containing compounds to the Bornholm Deep close to the dump site (location of the disposal site and Nord-Stream pipelines can be seen in Figure 2) have been investigated.

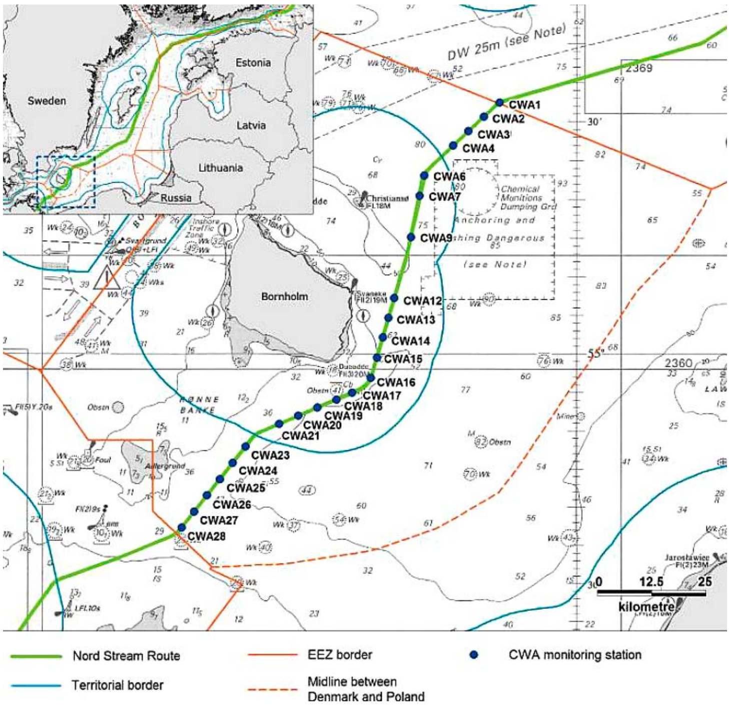


Figure 2 Pipeline route and area for the conceptual site model.

The conceptual site model is a graphical representation of the potential sources of OAs to the study area in the Bornholm Deep (Figure 3). The model is qualitative and will be qualified in the results section.

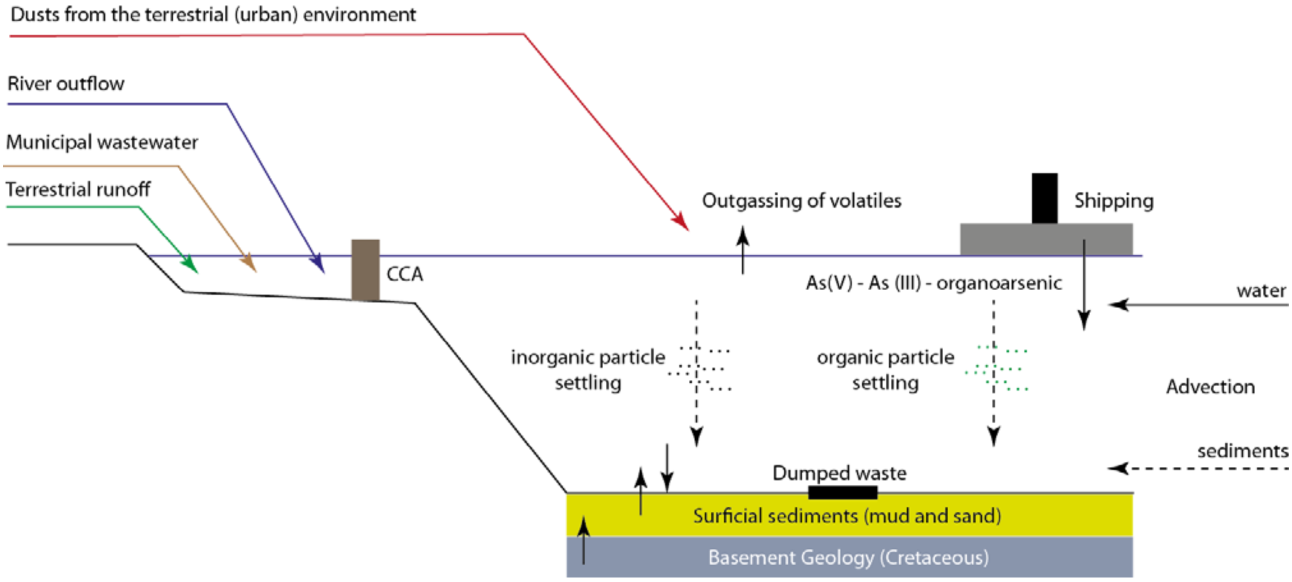


Figure 3. Conceptual Site Model showing the potential pathways by which arsenic may reach the Bornholm Deep disposal site.

This figure 3 highlights the potential routes by which arsenic may enter the Bornholm Deep. The pathways include:

- Terrestrial runoff from agricultural systems where arsenicals may have been used as a herbicide or pesticide. Leachates arising from landfills may enter surface or ground waters and enter the marine environment. Effluents from pig and poultry farming (Waeles et al. 2013). Mining and metal processing (e.g. Svartliden gold mine, Sweden).
- Municipal wastewaters containing a range of arsenicals. Some sewage sludge is applied to land and may lead to bacterially-mediated transfor-

mations and runoff in the dissolved phase or with the particulate load. Incineration of waste may lead to arsenicals in atmospheric phase. Pulp and paper discharges. Glass production.

- Inflow from rivers with surface runoff containing atmospheric dry and wet depositions from various anthropogenic emissions and non-marine wastewater treatment plant effluents etc. This pathway is a mixture of diffuse exposure pathways/sources on land which at some point reach the Baltic Sea.
- Ship emissions from the combustion of fuel and marine disposal of wastes.
- Emissions from dumped waste lying on the sea floor apart from munitions.
- Natural and anthropogenic arsenicals which may be volatilised from soil. As contained in coal (1 – 4 mg/kg) and peat (28 mg/kg) from Denmark. Entry through ash and volatilisation from thermal energy production and incineration. The burning of fossil fuels and biomass for transport and home heating may also contribute to the atmosphere.
- CCA – chromated copper(II) arsenate used as a wood preservative. Often used in marine environments and some terrestrial. When burned, arsenicals may enter the atmosphere. Can also enter atmosphere when treated wood is worked.
- Due to surface area and organic matter effects, arsenical concentrations are likely to be higher in fine-grained organic sediments such as muds and clays. Interaction between As(V) and As(III) depending on redox and oxygen content. Bacteria-mediated transformations in anaerobic sediments.
- Some exchange between the basement geology of the zone and surficial sediments.
- Advection of surface water from NE bringing dissolved and suspended particles of arsenicals from the rest of the Baltic Sea. Anthropogenic inputs from industries bordering the Baltic Sea to the NE of Bornholm. Copper (e.g. Falun, Sweden) and gold production (e.g. Svartliden). Gulf of Bothnia particularly affected by arsenicals from metal processing in the last 50 years.
- The advection of particles along the sea floor from the NE.
- Phytoplankton is known to form a range of small organoarsenicals, especially arseno-sugars. Carnivorous zooplankton and fish form arsenobetaine. There will be some settling of these materials with settling particles.

7.3.3 Data Sources

The basis for the data collection was a screening of the core scientific literature databases (Web-of-Science; Sci-Finder; SCOPUS; Google Scholar) and the production and emissions databases such as USEPA Hazardous Substances Database (HSDB) and the European E-PRTR (2011) database and the EMEP/EEA emission inventory guidebook 2009 for international navigation, national navigation, national fishing (EMEP/EEA, 2011) to derive production and emission information.

7.3.4 Arsenic chemistry and background

Arsenic is released into the atmosphere primarily as As_2O_3 and exists mainly adsorbed on particulate matter. These particles are dispersed by the wind and water and are returned to the ground and bottom sediment by deposition.

Arsenicals released from microbial sources in soils or sediments undergo oxidation in the air, reconverting the arsenic to non-volatile forms, which settle back to the ground. Dissolved forms of arsenic in the water column include As(III), As(V), monomethylaronic acidc (MA) and dimethylarsinic acid (DMA). In well-oxygenated water and sediments, nearly all arsenic is present in the thermodynamically more stable As(V) state. Some arsenite and arsenate species can interchange oxidation state depending on redox potential (Eh), pH and biological processes.

Some arsenic species have an affinity for clay mineral surfaces and organic matter and this can affect their environmental behaviour. There is potential for arsenic release when there is fluctuation in Eh, pH, soluble arsenic concentration and sediment organic content. Weathered rock and soil may be transported by wind or water erosion. Many arsenic compounds tend to adsorb to soils, and leaching usually results in transportation over only short distances in soil. Three major modes of arsenic biotransformation have been found to occur in the environment: redox transformation between arsenite and arsenate, the reduction and methylation of arsenic, and the biosynthesis of organoarsenic compounds. There is biogeochemical cycling of compounds formed from these processes.

Due to the many natural and anthropogenic sources and their emissions to air, water and soil arsenic is a ubiquitous pollutant in the environment. There is an increasing focus on arsenic both with respect to the use and release to the environment, but also on the mobility and fate once present in the environment, which will determine the availability and accumulation of arsenic in organisms. If arsenic is present predominantly in the particulate phase it will only have limited potential accumulation in e.g. sea food and furthermore the occurrence in drinking water will be limited. It is important to understand the key processes controlling the contaminant fate. For example where high contaminant concentrations prevail or steep pH or redox gradients exist, which can be the case near point sources, emissions, advection, precipitation are more likely to be of importance, whereas sorption can be the key process in areas where chemical steady-state exist (US EPA, 2004), such as the sediment phase in the Bornholm Basin where there are no immediate point sources. The present concentrations are thus representative of marine sediments influenced mainly by natural sources, i.e. geology, as opposed to sites with considerable anthropogenic sources.

7.3.5 Industrial uses of organoarsenicals in the Baltic region

The following CWA parent compounds have uses other than as CWAs:

- Adamsite: in formulation of wood treating solutions against marine borers and similar pests,
- PDCA: medication,
- TCA: ceramics industry, arsenic pharmaceuticals; insecticides,
- PDCA(ox): reagent for tin, as precipitant in niobium analysis.

Comparing the list of compounds (Table 2) detected in the sediments and the preliminary list of compounds with other anthropogenic uses (based on the USEPA Hazardous Substances Data Base (HSDB)) only PDCA(ox) is used directly and the others are derivatives. This means that six identified compounds (derivatives of Adamsite, PDCA, TCA, Clark I and L2) do not have other anthropogenic origins except CWA. The exact quantities used are not known but the usage is likely to be less than 1000kg per year and TCA may be the most important.

7.3.6 Total arsenic discharges

The EU collates emissions from a range of industries of potentially hazardous chemicals. Arsenic is included within this database, the most recent information recorded is for 2011 (see Tables 4 and 5).

Table 4 The notified released of arsenic to AIR from the E-PRTR for 2011 (quantities in kg/yr).

Country	Thermal Power	Oil & Gas	Ferrous industry	Pig Iron	Non-Ferrous	Mining	Phosphate production	Landfill	Glass	Incineration
Sweden			68.1		322					
Finland	1040		31.2	75.5	146					
Estonia	10600									
Latvia										
Lithuania										
Poland	1030				985	89.5	32.8	203		
Germany	1420	64.4		176	711				105	
Denmark	23.1									108

The major source to the air is through the combustion of coal and oil used to generate electrical power. Other mining and metal processing industries make up the majority of the remainder.

Table 5 The notified releases of arsenic to WATER from the E-PRTR for 2011 (quantities in kg/yr).

Country	Thermal Power	Oil & Gas	Ferrous industry	Pig Iron	Non-Ferrous	Mining	Chemical Industry	Waste water treatment plant	Paper	Food
Sweden		11.2	5.64	14.3	456	5.3	29	215	428	
Finland	7.97			25.1	301	7	15	937	551	
Estonia	32.6							223		
Latvia								8.2		
Lithuania										
Poland	130	95			33.2	2210	144	1970		30.9
Germany	587	157			34.3	103	515	730	58.7	
Denmark							165	19		

The liquid discharges for the circum-Baltic Sea countries are shown in Table 5 and in Figure 4. Although these discharges may have receptors other than the Baltic Sea, it is seen that many emission sites are along the Baltic shore line. For conservative assumptions, all are assumed to reach the Baltic Sea through rivers. Here, the discharges associated with wastewater treatment make the largest component with metal mining and processing making the second major contribution.

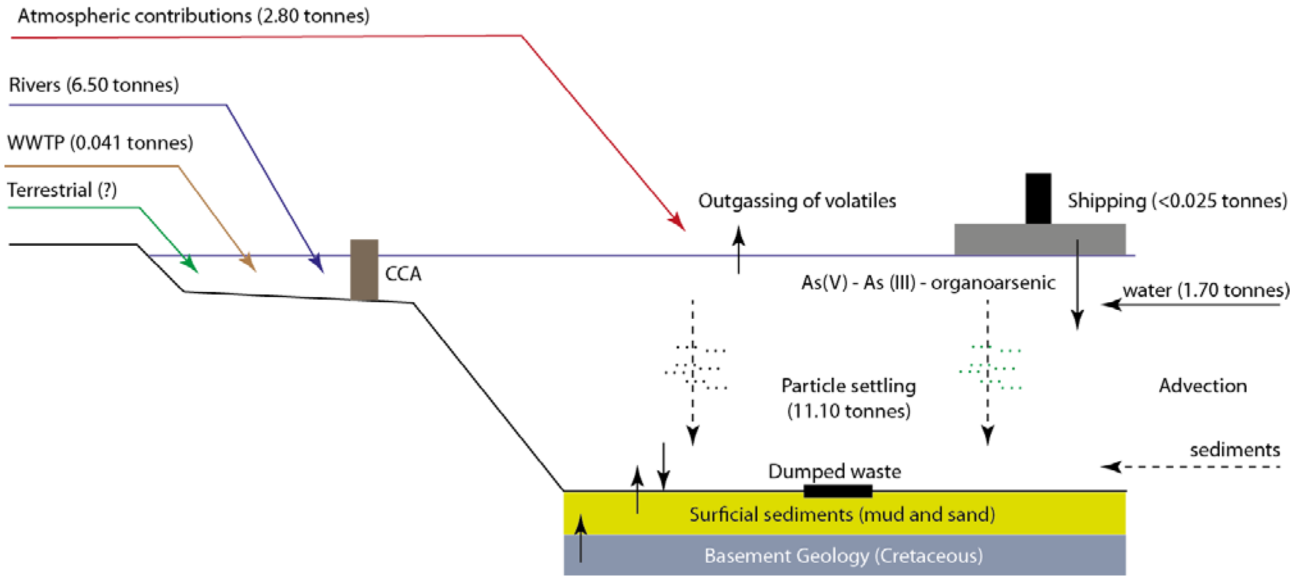


Figure 4 Annual contributions to the Bornholm expanded CWA dumpsite based on a 1 % area of the Baltic Sea which has been enhanced to account for the depositional nature of the location.

Atmospheric contributions have been estimated from the data of Andreae et al. (1984) for the whole of the Baltic Sea. This was estimated to be 280 tonnes/year and a conservative 1 % values has been ascribed to this location.

The riverine contribution was estimated to be 6.5 tonnes per year to this location (Andreae et al., 1984). The bulk of this will be inorganic natural compounds derived from the weathering of rocks. There will be supplemental inputs from anthropogenic compounds used in the terrestrial environment which have leached into the river systems. This will include pesticides and herbicides.

The sum of the wastewater treatment plant discharges across the Baltic Sea countries is relatively small at 41 kg per year (Table 5). This also assumes that all discharges are made to the Baltic Sea and that 1 % of these can be found in the Bornholm dumpsite. The majority of the arsenic will be as inorganic species with smaller amounts of simple organic molecules derived from microbial synthesis of methylated forms in reducing environments.

Ship emissions are estimated in the national reporting to UNFCCC, Kyoto and EU, but spatial assignment of ship emissions cannot be derived from these inventories. The EMEP/EEA (2011) emission inventory guidebook has the following emission factors for international navigation, national navigation, national fishing and military shipping:

- Emission factor for ships using bunker fuel oil: 0.68 g As/tonnes fuel
- Emission factor for ships using marine diesel oil/marine gas oil: 0.04 g As/tonnes fuel

If we assume 100 ships traversing the designated secondary CWA dumpsite daily, each using 1 tonne of bunker fuel per ship, this only contributes 25 kg per year to the location. Although the Baltic Sea has intense ship traffic the arsenic emissions are small in comparison to other potential sources.

Advected seawater inflow from the North Sea and Atlantic is around 170 tonnes per year (Andreae et al., 1984); this will not be homogeneously spread across the Baltic Sea with higher contributions near the point of exchange. If we again assume 1 % is contributing to the location of interest, this leads to an addition of 1.7 tonnes of arsenic per year.

With an estimated sediment deposition rate in the Baltic of 74 x 10^{12} g/year and an arsenic content of 15 ppm the annual net arsenic sedimentation to the seafloor is 11.1 tonnes per year (Andreae et al., 1984), again assuming 1 % contribution in the dumpsite.

7.3.7 Bacterial processes

In general, arsenic is toxic to organisms, although some microorganisms have developed mechanisms to tolerate high concentrations in arsenic-rich environments. Microbial strategies for detoxifying arsenic often leads to biomethylated volatile compounds (like trimethylarsine produced by bacteria and fungi) from where a range of organoarsenic compounds may be produced (Slyemi and Bonnefoy 2012). These may be utilized by some bacteria for energetic purposes to produce inorganic arsenic again. In the scientific literature, it is possible to find several examples of bacteria able to degrade organoarsenic warfare agents. They are often isolated from soil or groundwater habitats contaminated with these agents. As an example, it has been demonstrated that diphenylarsinic acid (degradation product of Clark I) were degraded further by microbial activity in different soils and at both aerobic and anaerobic conditions, but without final transformation into inorganic arsenic. Hempel et al. (2009) demonstrated that phenylarsenic acid was degraded by microorganisms derived from contaminated groundwater/sediments. However, it has not from the literature been possible find evidence that microbes or microbial processes are able to form organoarsenic compounds which resembles chemical warfare agents (Clark I, Lewisite I) or their first natural degradation products. This, however, may reflect that scientific interests have focused on bioremediation of contaminated environments– not the possibility that microorganisms might produce such compounds.

It is less likely that the above mentioned processes could be reversible due to the complexity of the compounds and the resulting significant numbers of enzymatic systems - and hence significant energetic investment required by the organisms needed for them to synthesize the compounds from a basis of methylarsene. There may, however, be specific microorganisms able to synthesize aromatic organoarsenicals, e.g. as a way to combat other competing microorganisms. However, this is largely unknown at this stage.

The CWA trichloroarsine (TCA) is, however, a simpler compound degraded to arsenic or arsenous acids by oxidation or hydrolysis, respectively. Arsenic acid (also in the form of arsenate) is commonly found in the environment probably as a degradation product from naturally occurring organoarsenic compounds like demethylarsinic acid or arsinobetaine. An Arsenous acid (or arsenite) is probably formed from arsenic acid (and *vice versa*) in microbial processes commonly occurring in the environment (Turpinen et al., 2002).

7.3.8 Geological setting

The basement (bedrock) geology of the Baltic Sea around Bornholm can be seen in Figure 5. The Bornholm Deep to the east of the island of Bornholm is typified by Cretaceous limestones and chalks of biogenic origin, Pre-Cambrian crystalline and metamorphic rocks and some undifferentiated

Paleozoic sedimentary rocks. Inorganic arsenic may be present in these geological units as several minerals contain arsenic including arsenopyrite. It is likely, however, that as a source these forms will be entirely inorganic rather than organic.

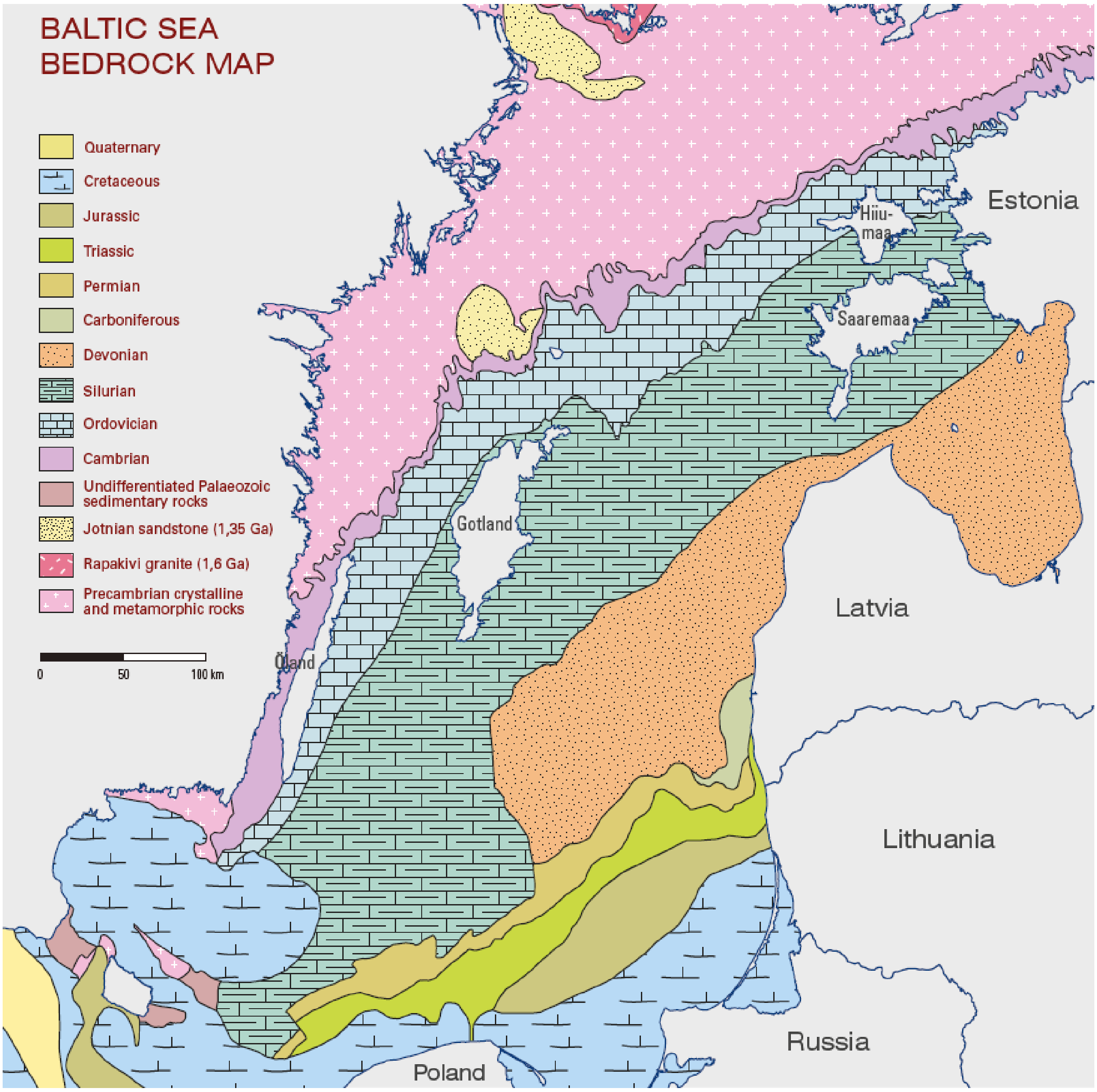


Figure 5 Bedrock Geology - The Baltic Sea – geology and geotourism highlights, NGO GEOGuide Baltoscandia, source: www.centralbalticgeotourism.eu/.../baltic_sea_100dpi

The surface drift or overlying surface sediments of the basement rocks is typically sand or fine-grained mud (Figure 6) in the deep parts. In this figure, the sediments to the east of Bornholm are principally muds or clays. This is the normal state for basins that tend to infill with soft sediments. The site specific sediment types along the pipeline route are outlined in the reports by DHI (2010). The sediment at the deeper part is typically muddy and soft, whereas at the less deep areas the sediment is coarse sandy / gravel and stones.

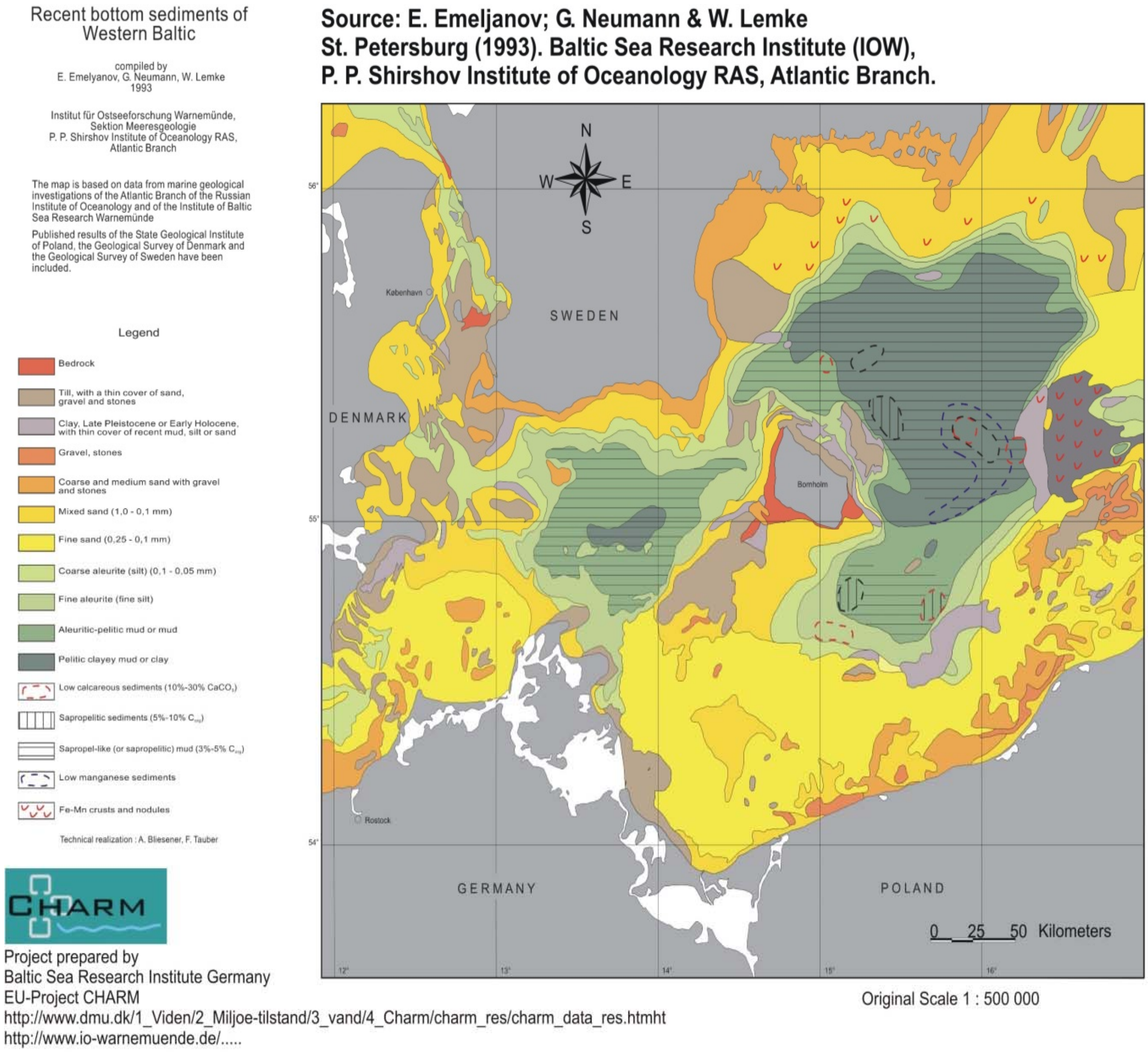


Figure 6 Surface sediment types (grain size) around Bornholm from Emeljanov et al.1993.

The typical level of total arsenic in open sea water is 0.001 – 0.002 mg/L (IPCS, 2001) and for the Baltic Sea, levels around 0.001 have been found with some seasonal variation (Stoeppler, 1986). Arsenic is widely distributed in surface freshwaters, and concentrations in rivers and lakes are generally below 0.01 mg/L, although individual samples may range up to 5 mg/L near anthropogenic sources. Arsenic levels in groundwater average about 0.001–0.002 mg/L except in areas with volcanic rock and sulphide mineral deposits where arsenic levels can range up to 3 mg/L. In Danish inland lakes the arsenic concentration is typically 0.001 mg/L and in 2003 the average arsenic concentration in groundwater was 0.003 mg/L where 16 % of the measurements were above 0.005 mg/L (Kristiansen et al., 2005). The average sediment pore water concentration found by Fauser et al. (2013) in the Bornholm Deep is 0.016 mg/L, which is considerably higher than open sea water concentrations but may be representative of sediment-bulk water boundary layer concentrations. Mean arsenic concentrations in sediments range from 5 to 3000 mg/kg, with the higher levels occurring in contaminated areas (IPCS, 2001). The observed average sediment concentration, averaging at 11 mg/kg DM, found by Fauser et al. (2013) is comparable to the average total As in the Bornholm Deep of approximately 20 mg/kg reported by Garnaga et al.

(2006). Arsenic concentrations in sediment in the Baltic Sea are quite variable and primarily dependent on the geology and grain size (Emelyanov, 1996).

7.3.9 Currents in the Baltic Sea

The predominant current circulation in the Baltic Sea is anti-clockwise with the currents travelling towards the south west down the coast of Sweden. This means that discharges to the NE of the Bornholm Deep may be carried towards the deposition site (Figure 7).

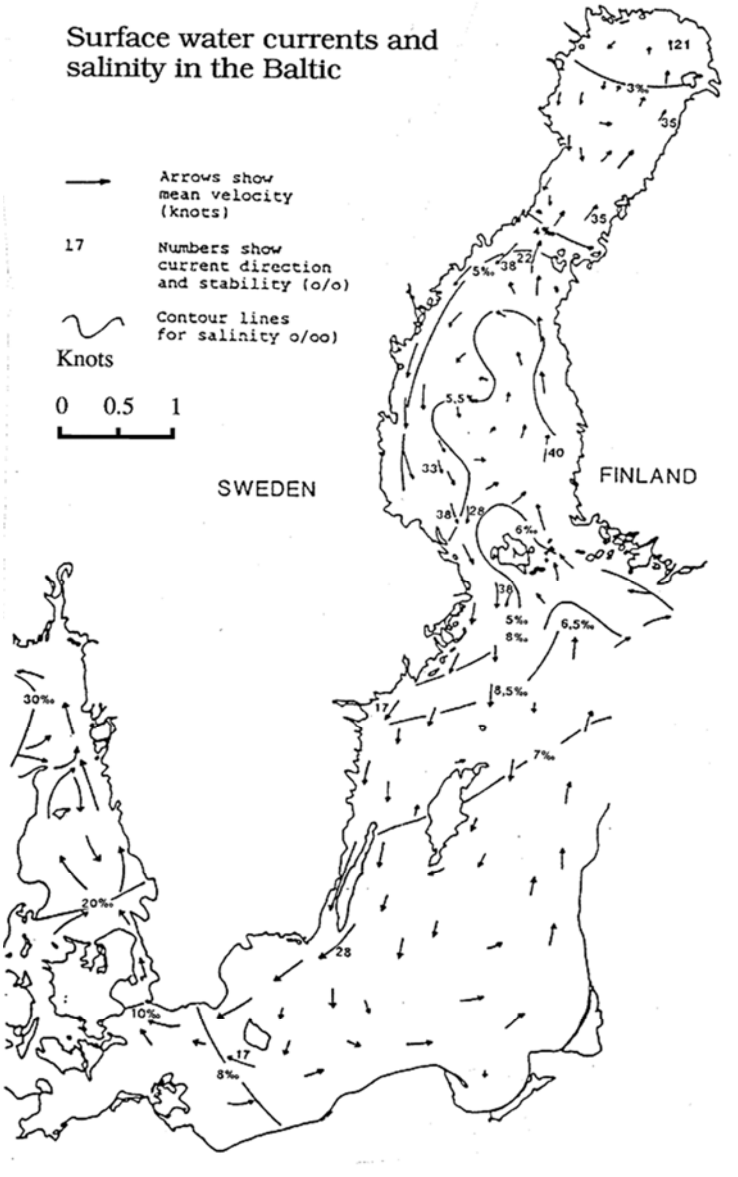


Figure 7 The currents in the Baltic Sea.

The currents mean that sources of arsenic in the Gulf of Bothnia may contribute to the Bornholm Deep inventory (Figure 7) from Hallberg 1979.

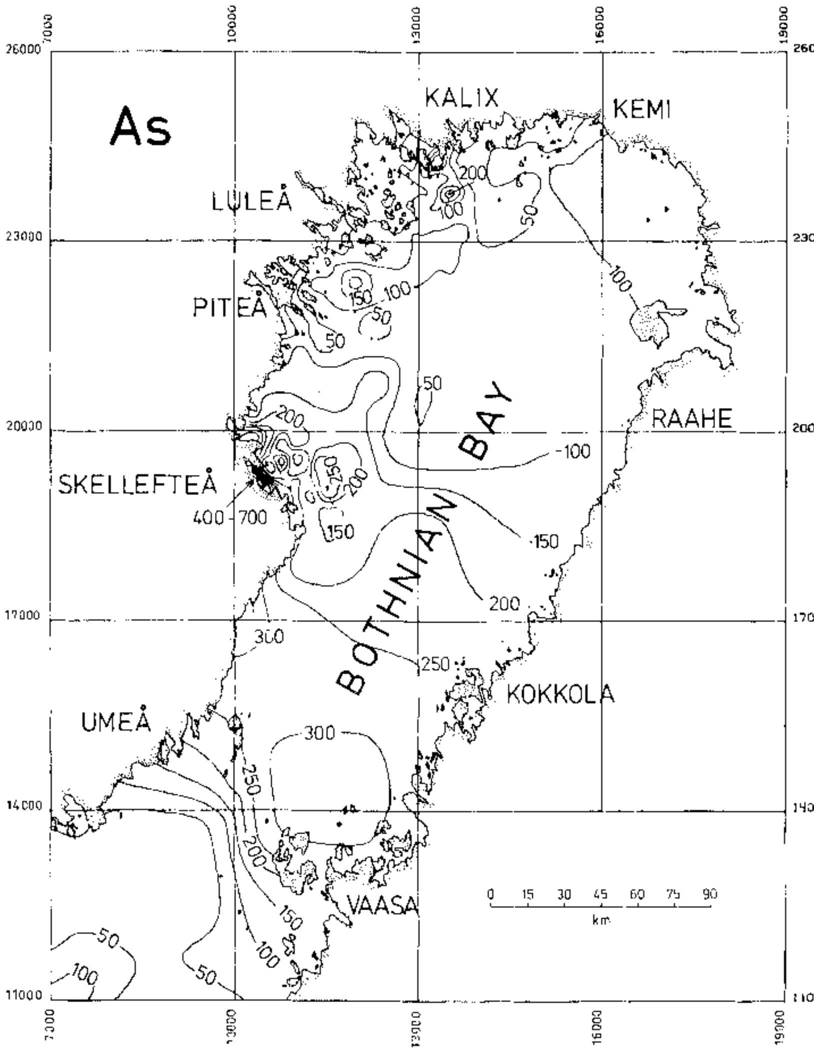


Figure 8 Arsenic in the Gulf of Bothnia (ppm) from Hallberg 1979. Skellefteå has a large gold mining industry.

7.3.10 Conclusions and recommendations

The background and overall aim of this desktop based screening report was to assess if the observed OAs could have other sources than CWAs. There are at least two important aspects to this: the quality (could they have other sources), and secondly the quantitative: would these sources amount to anything comparable to the CWA source? We set up three aims of the study in the first section of the report (p. 3), which are addressed in the below and in Table 6. In section 2.0 (Approach) we highlighted five research areas that we would address to derive the overall conclusions relative to the overall aim of the report. The responses to these are illustrated in the figures 3-8 and accompanying text. Below are the conclusions based on the findings from section 3 of the report.

The review of the available literature suggests that the vast majority of the arsenic that enters the Baltic Sea from all sources will be in an inorganic form rather than an organic form. This is partly due to the lack of biological function of the metal even though some organisms can immobilize arsenicals in an organic complex.

There are multiple diverse continuing sources of arsenic to the Bornholm Deep dumpsite region. The major source is the terrestrial environment with direct and indirect pathways with river transport making the largest contribution and the atmospheric fallout of dusts also significant. The basement geology does not appear to make any significant contribution in this location.

Some pathways were identified during this study for which no data were available at the time of review; these include the disposal of waste from sources other than chemical weapons and the bottom transport of particulate matter from outside of the dumpsite.

The data suggest a deposition of arsenic to the 800 km^2 extended dumpsite (Sanderson et al. 2010) of around 11 tonnes per year. This is based on realistic sedimentation rates and particle concentrations with an increase in the accretion rate since this is a muddy zone where sediments are accumulating rather than eroding. This value of 11 tonnes can be compared to the total of 1000 tonnes of arsenic deposited during the disposal of the chemical weapons.

The amount of arsenic deposited as CWA is roughly equivalent to around 100 years' worth of annual deposition although the data from VERIFIN suggest the arsenic is constrained to a relatively small number of hot spots and the arsenic has not been distributed within the sediments to any great extent. This is in contrast to the annual deposition which would have a homogeneous distribution over the entire 800km^2.

There is the potential for microbial transformations of inorganic arsenic within the sediments; this may lead to the formation of organic arsenic compounds similar to the degradation products of some of the CWA (namely TCA). There is no evidence of microbial production of compounds in chemical weapons themselves. The most likely organic compounds to be formed by the *in situ* microbial assemblage will be related to the TCA degradation products.

Of the compounds of interest detected in the extended dumpsite region, the TCA degradation products were more frequently found outside the dumpsite (Sanderson et al. 2012) and they were also measured at higher concentrations at these external sites. This pattern of occurrence may be indicative of an alternative source unrelated to CWA and may be part of a natural microbial pathway.

Degradation products of PDCA and DM were found at equal concentrations both inside and outside of the dumpsite although the detection frequency was greater inside the designated box. All other compounds of interest were found at a higher concentration and at high frequencies inside the designated dumpsite rather than outside it (Sanderson et al. 2012). These data may support potential non-CWA sources for the oxidation products of PDCA; PDCA-ox; TCA; DM. The other compounds are likely to have solely CWA sources. This is summarised in Table 6.

Table 6 Likely formation and sources for compounds of interest in the Bornholm Deep extended dumpsite area. This is the result of screening and expert judgment but will have uncertainties due to the absence of data at this time.

Compound	Abiotic production	Biotic Production	Alternate anthropogenic (non-CWA) sources
DM	÷	÷	+
DM[ox]	÷	÷	÷
PDCA	÷	÷	+
PDCA[ox]	÷	÷	+
TCA	÷	?	+
TCA degradation	÷	+	÷
Compound + degradation products			
DA	÷	÷	÷
L1	÷	÷	÷
L2	÷	÷	÷
TPA	÷	÷	÷

+ = Yes; ÷ = No; ? = maybe.

From the above it is clear that from a qualitative point of view it seems like that DM; PDCA and TCA could have other sources than CWA – primarily anthropogenic but also natural (TCA). However, the annual quantities seem significantly lower than from the CWA point sources – however, these sources are continual over potentially very many years. Moreover, it is important to note the patchy detection of the compounds, and that some of these compounds are found as or more frequent out-side the dump site as inside and at comparable mean concentrations (bullets 7 & 8 above). There are still some uncertainties remaining which would require additional experimental work to elucidate (see section 4.1).

7.3.11 Recommendations and analytics

There are some obvious data gaps regarding the sources and pathways of arsenic in the Baltic Sea. However, the screening completed here has indicated that these may not greatly enhance our conclusions regarding the potential for other non-CWA sources of arsenic. What is lacking, however, are data on the context and specific transport pathways from known sources. We hosted the workshop on July 4th and also toured the laboratories at DCE-AU and found that the labs are equipped and adequate for the remaining potential analyses needed.

Context. The studies to date have been conducted solely in the vicinity of the designated CWA disposal site. These data do not provide information about the quantity of similar compounds at other sites in the Baltic Sea which may have been derived from alternative sources. In this regard, there is a known significant point source of inorganic arsenic in the Gulf of Bothnia (Figure 8) and the local conditions may favour the microbial production of organic derivatives. The current flow in the Baltic Sea is such that materials would be transported from this location towards the dumpsite. To provide the best possible chance of determining the contribution of remote non-CWA sources, a surface sediment sampling campaign is recommended to characterize the environmental conditions (what conditions may lead to the formation of these compounds?) and the full suite of CWA and their degradation products through established LC-MS/MS methods along a transect from the Gulf of Bothnia to the designated dumpsite.

To conduct such a study, surface sediments and cores would be collected at several locations (~100 based on the detection frequency of compounds in the VERIFIN data) in the Baltic Sea with good spatial coverage. Cores would be taken in the soft sediments to determine the vertical distribution which would show if arsenic was entering the sediments from the water column or vice versa. Surface sediments would be collected from several grab samples at each location and pooled to avoid the patchy nature of the distribution shown in the VERIFIN data. All chemical analyses would be conducted using standard LC-MS/MS methods.

Sediment Deposition. Published data suggest an annual deposition of around 15 mg of arsenic (in many different chemical forms) per square meter of the seafloor in the Bornholm Deep. This arsenic will originate from non-CWA sources although there is a small potential for localized resuspension of deposited sediments if disturbed. To determine the non-CWA derived arsenic deposition to the site, near bottom suspended sediment traps could be deployed which would intercept depositing material raining out of the water column. These sediment traps can collect sediment for specified periods (*e.g.* monthly) and then rotate a new sampling jar into position and continue to collect for extended periods. Samples could be analysed for all potential CWA compounds and their degradation products through LC-MS/MS together with total and inorganic arsenic to provide real measures of the deposition rate and arsine speciation to this area. This will unambiguously show if CWA and their degradation products are depositing in the dumpsite from external sources.

A small number of samplers would be deployed from a ship in the dumpsite and in similar depositional areas near Bornholm Island. These would be recovered after an appropriate period of time and the samples analysed as before for inorganic and organic arsenic compounds.

7.3.12 References

Andreae, M.O. & Froelich, P.N., 1984. Arsenic, antimony and germanium biogeochemistry in the Baltic Sea. Tellus, 36B, 101-117

DHI. 2010-12: Danish Hydraulic Institute. Monitoring of benthic fauna and chemical warfare agents in Sweden and Denmark. Nord Stream PO 10-1149. (2010) Doc. No.: G-PE-EMS-REP-188-M10FR1IN-A. & Monitoring of Benthic Fauna and Chemical Warfare Agents in Sweden and Denmark, Nord Stream Project No 10-1149, Doc. No.: G-PE-EMS-MON-188-M11DENIN-A, Monitoring of Benthic Fauna in Danish Waters in 2011, Final Report for 2011). & Monitoring of Benthic Fauna and Chemical Warfare Agents in Sweden and Denmark, Nord Stream Project No 10-1149, Doc. No.: G-PE-EMS-MON-188-M11DENIN-A, Monitoring of report for Benthic Fauna in Danish Waters in 2012.

Emelyanov, E.M., 1996. Chemical Components and Elements in the Suspended Matter and Sediments of the Western Baltic. Baltica 9, pp. 5-15.

EMEP/EEA, 2011. Emission inventory guidebook 2009 for international navigation, national navigation, national fishing. Available at: http://www.eea.europa.eu/themes/air/emep-eea-air-pollutant-emission-inventory-guidebook/emep

E-PRTR, 2013. The European Pollutant Release and Transfer Register. http://prtr.ec.europa.eu/

Fauser, P., Sanderson, H., Hedegaard, R.V., Sloth, J.J., Larsen, M.M., Krongaard, T., Bossi, R., Larsen, J.B., 2013. Occurrence and sorption properties of arsenicals in marine sediments, Environmental Monitoring and Assessment 185 (6), pp. 4679-4691.

Garnaga, G., Wyse, E., Azemard, S., Stanekvicius, A., de Mora, S., 2006. Arsenic in Sediments from the Southeastern Baltic Sea. Environmental Pollution 144, pp. 855-861.

Hallberg, R., 1979. Heavy Metals in the Sediments of the Gulf of Bothnia Ambio, Vol. 8, No. 6, pp. 265-269.

Hempel, M., Daus, B., Vogt, C., Weis, H., 2009, Natural attenuation potential of phenylarsenicals in anoxic.

Groundwaters. Environmental Science and Technology 43, 6989–6995Huang, J.-H., Scherr, F., Matzner, E. (2007) Demethylation of dimethylarsinic Aaid and arsenobetaine in different organic soils. Water Air Soil Pollutio 182:31–41.

IPCS, 2001. International Programme on Chemical Safety (IPCS), Environmental Health Criteria 224, Arsenic and arsenic compounds, World Health Organization, Geneva.

Li, C.L., Kang, S.C., Zhang, Q.G., Gao, S.P., Sharma, C.M. (2011). Heavy Metals in Sediments of the Yarlung Tsangbo and its Connection with the Arsenic Problem in the Ganges-Brahmaputra Basin. Environmental Geochemistry and Health 33(1), pp. 23-32.

Kristiansen, S.M., Nørnberg, P., Ramsay, L., 2005. Arsenic in Danish drinking water – an underestimated traceelement (Arsen i dansk drikkevand – et undervurderet sporstof in danish), Geologisk nyt (4), pp. 22-24.

Sanderson, H., Fauser, P., Thomsen, M., Vanninen, P., Soderstrom, M., Savin, Y., Khalikov, I., Hirvonen, A., Niiranen, S., Missiaen, T., Gress, A., Borodin, P., Medvedeva, N., Polyak, Y., Paka, V., Zhurbas, V., Feller, P., 2010. Environmental hazards of sea-dumped chemical weapons. Environmental Science and Technology, Volume 44, Issue 12, 15 June 2010, pp. 4389-4394.

Sanderson, H., Fauser, P., Thomsen, M., & Larsen, J.B., 2012. Weight-of-evidence environmental risk assessment of dumped chemical weapons after WWII along the Nord-Stream gas pipeline in the Bornholm Deep. Journal of Hazardous Materials, Volume 215-216, 15 May 2012, pp. 217-226.

Schnoor, J.L., 1996. Environmental Modeling – Fate and Transport of Pollutants in Water, Air and Soil. A Wiley-Interscience Series of Texts and Monographs. John Wiley & Sons, Inc.

Slyemi, D., Bonnefoy, V., 2012, How prokaryotes deal with arsenic. Environmental Microbiology Reports, 4, 571–586

Stoeppler, M., Burow, M., Backhaus, F., Schramm, W., Nürnberg, H. W., 1986. Arsenic in seawater and brown algae of the Baltic and the North Sea. Marine Chemistry 18(2-4), pp. 321-334.

Tarvainen, T., Albanese, S., Birke, M., Ponavic, Reimann, C., 2013. Arsenic in agricultural and grazing land soils of Europe. Applied Geochemistry 28, pp. 2-10.

Turpeinen, R., Pantsar-Kallio, M., Kairesalo, T., 2002. Role of microbes in controlling the speciation of arsenic and production of arsines in contaminated soils . The Science of the Total Environment 285, 133-145.

Tijhuis, L., Brattli, B., Sæther, O.M. (2007) Levels of trace metals and sequential extraction of arsenic in topsoil and sand from sandboxes at playgrounds in Oslo, Norway. Trace Metals and other contaminants in the environment. (9) pp. 269-295.

Uddin, A., Shamsadduha, M., Saunders, J.A., Lee, M.K., Ahmed, K.M., Chowdhury, M.T. (2011). Mineralogical Profiling of Alluvial Sediments from Arsenic-Affected Ganges-Brahmaputra Floodplain in Central Bangladesh. Applied Geochemistry 26(4), pp. 470-483.

US EPA, 2004. Understanding Variation in Partition Coefficient, Kd, Values, Volume III: Review of Geochemistry and Available Kd Values for Americium, Arsenic, Curium, Iodine, Neptunium, Radium and Technetium. United States Environmental Protection Agency . Office of Air and Radiation. Interagency Agreement No. DW89937220-01-7.

US EPA, 2012. Arsenic compounds. Available at:
http://www.epa.gov/ttnatw01/hlthef/arsenic.html

VERIFIN, 2010. 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, Kostiainen and Vanninen.

VERIFIN, 2011: VERIFIN, Finnish Institute for Verification of the Chemical Weapons Convention. Report on chemical analysis of sea-dumped chemical warfare agents in sediment samples. VER-MS-0245. By: Söderström, Taipalus, Hakala, Kostiainen, Isomaa, and Vanninen.

VERIFIN, 2012: VERIFIN, Finnish Institute for Verification of the Chemical Weapons Convention. Report on chemical analysis of sea-dumped chemical warfare agents in sediment samples, 2012 report. VER-MS-J151. By: Martin Söderström, Annette Pettersson, Olli Kostiainen, Ullastiina Hakala, Jere Häyrynen, Keijo Isomaa, Maaret Karjalainen, Matti Kuula, Terhi Taure and Paula Vanninen.

Waeles , M., Vandenhecke, J., Salaün, P., Cabon, J.-Y., Riso, R., 2013. External sources vs internal processes: What control inorganic As speciation and concentrations in the Penzé estuary? Journal of Marine Systems 109-110, pp. 5261-5272.

[Blank page]

ENVIRONMENTAL ASSESSMENTS OF SEA DUMPED CHEMICAL WARFARE AGENTS

CWA report

This is a report on the information gathered during work related to sea dumped chemical warfare agents. It mainly reviews the work conducted in relation to the installation of the two Nord Stream gas pipeline from 2008-2012. The focus was on the weight-of-evidence risk assessment of disturbed CWA residues in connection with the installation of the pipelines. Novel exposure and toxicity assessments are presented and the risk is assessed. The overall conclusion is that there is a negligible acute added CWA risk towards the fish community from the installation of the pipelines.

ISBN: 978-87-7156-181-4
ISSN: 2245-0203