Munitions identification, corrosion and chemical impact on benthic ecosystems

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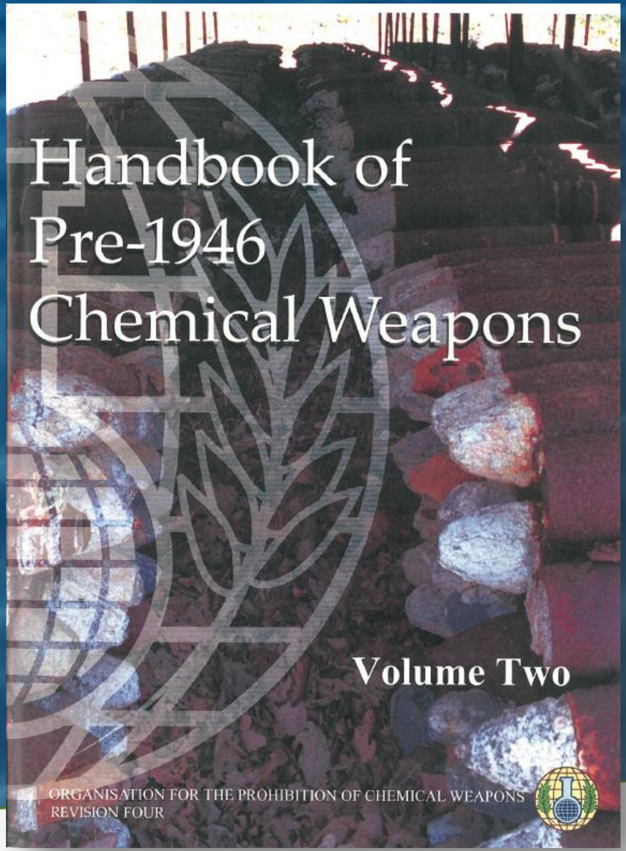
VERIFIN, University of Helsinki

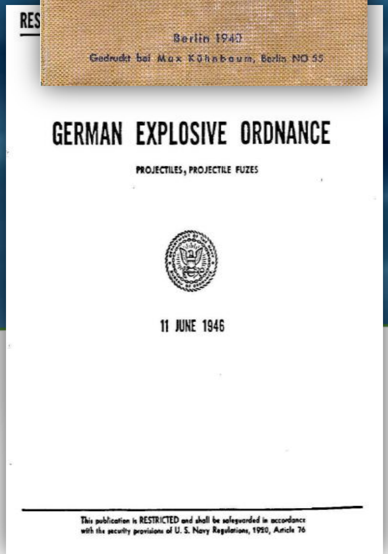
Final DAIMON Conference : Open Day
Bremerhaven 7th Feb, 2019

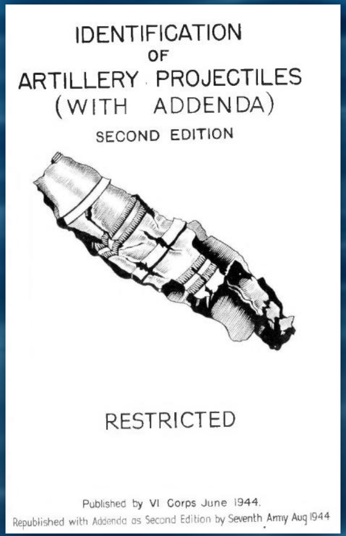
A 2.1 Examination of marine munitions' status

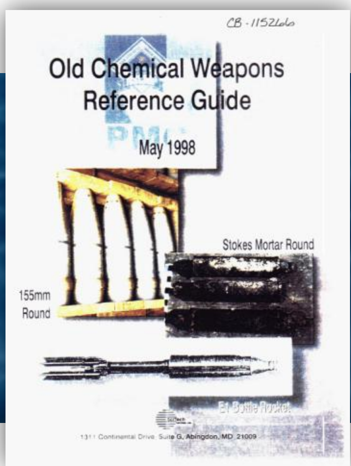
Activity 2.1.1 Identification

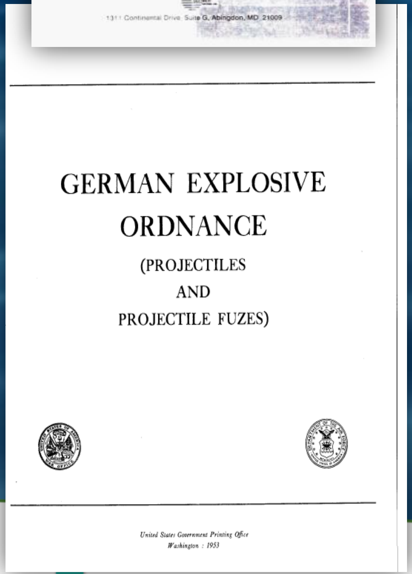
More than one source











Decision Aid for Marine Munitions

Home Jarosław Michalak

Type:	Model:	Country:
Projectile	Gr. 19 Kh.	Germany Post 1925

Description:	This projectile has two copper driving bands and a filling plug in the side. It is identical in design to the previous projectile, but is included because it shows slightly different details of construction.
Diameter:	150 mm
Length:	560 mm missing the fuze adapter
Weight:	N/A
Warefare Agent Weight:	N/A
Chemical agent:	Mustard, Mustard/Lewisite.

Additional information

File	Description
7,5-15,5 cm projectile	The document contains additional information about 7,5-15,5 cm projectiles
15 cm projectile_general_type 19	The document contains general description of German of 15 cm projectile type 19
15 cm projectile additional data	The document contains additional data about 15 cm projectiles.
15 cm projectile additional data part 2	The document contains additional data about 15 cm projectiles (part 2).
Codes and markings	German toxic chemical codes and marking system
Nomenclatures	Interpretation of German gun and munitions nomenclatures
German CWA	Summary of German Chemical Warfare Agents

The view of the detailed safety data sheet is identical for the administrator and user level (more than one source of information)

Home Jarosław Michalak

Type:	Model:	Country:
Projectile	Gr. 38 Kh. Variant	Germany Post 1925

Description:	This projectile has two copper driving bands and a filling plug in the side. The burster tube of this projectile is a variant of the normal design, going higher into the neck of the projectile. This would require a different fuze adapter as a result.
Diameter:	150 mm
Length:	550 mm missing the fuze adapter
Weight:	N/A
Warefare Agent Weight:	N/A
Chemical agent:	Assumed Mustard.

A view when the handbook of chemical weapons (OPCW) was the only source of information

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Conventional ammunition in the catalogue

Interreg Baltic Sea Region EUROPEAN UNION EUROPEAN REGIONAL DEVELOPMENT FUND

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Home Edyta Łońska

Type: Conventional contact, moored mine

Model: EMA/EMB (GU)

Country: Germany Pre 1925

Description: EMA/EMB (GU) WW1 German contact, moored mine, carried by surface vessels, with Horns. German name EMA/EMB from 1912 year.

EMA/EMB sea mine	
shape	Cylindrical
Dimensions [m]	Diameter – 0.86 Height – 1.6
Charge [kg]	150 (EMA), 220 (EMB) hexanite
Weight [kg]	460 total
characteristic	Equipped with 5 Horns total, all on upper part, one on the center
Mooring depth [m]	2 – 6 (from the surface) 130m-330m of cable
Remarks	Open anchor with mooring-hydrostat made of steel, concrete plate and oak buffers. Mines used with EMA and EMB

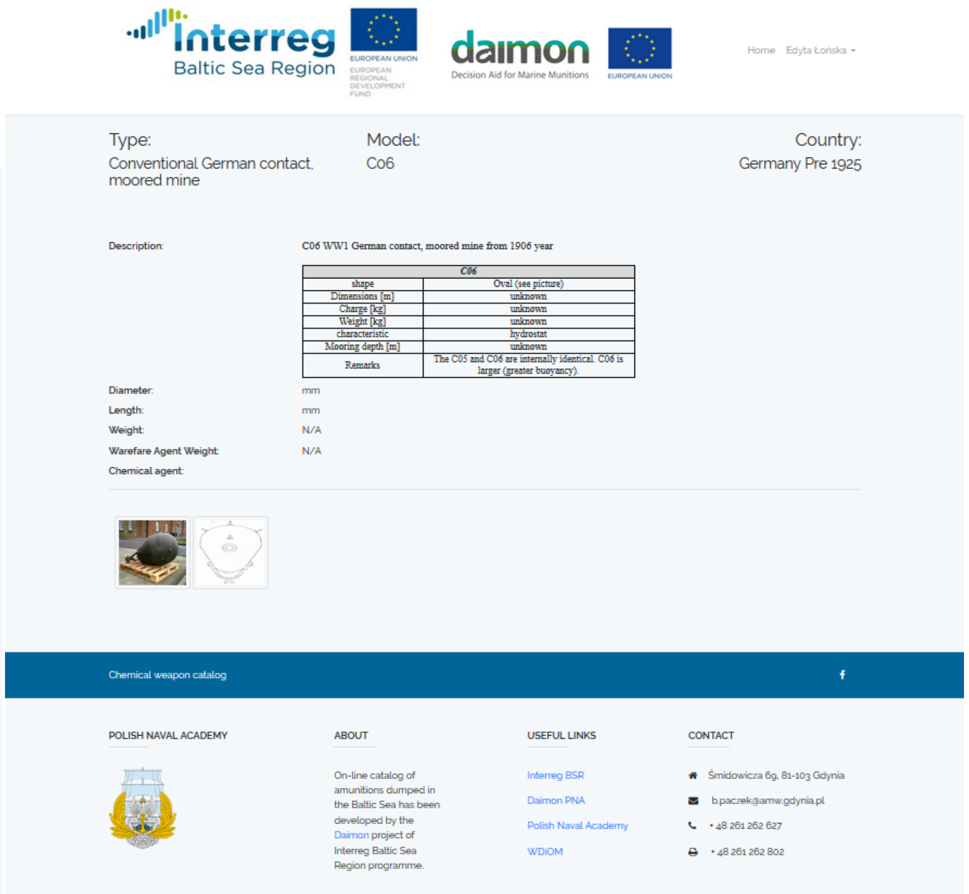
Diameter: 860 mm

Length: 1600 mm

Weight: 460

Warefare Agent Weight: 150 (EMA), 220 (EMB) hexanite

Chemical agent:



Interreg Baltic Sea Region EUROPEAN UNION EUROPEAN REGIONAL DEVELOPMENT FUND

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Home Edyta Łońska

Type: Conventional German contact, moored mine

Model: C06

Country: Germany Pre 1925

Description: C06 WW1 German contact, moored mine from 1906 year

C06	
shape	Oval (see picture)
Dimensions [m]	unknown
Charge [kg]	unknown
Weight [kg]	unknown
characteristic	hydrostat
Mooring depth [m]	unknown
Remarks	The C05 and C06 are internally identical. C06 is larger (greater buoyancy).

Diameter: mm

Length: mm

Weight: N/A

Warefare Agent Weight: N/A

Chemical agent:

Chemical weapon catalog

POLISH NAVAL ACADEMY

ABOUT

On-line catalog of amunitions dumped in the Baltic Sea has been developed by the Daimon project of Interreg Baltic Sea Region programme.

USEFUL LINKS

Interreg BSR

Daimon PNA

Polish Naval Academy

WDiOM

CONTACT

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View of conventional munitions sheet – digitalised version of traditional paper version of the „Conventional munition catalogue" prepared within DAIMON

http://dss.amw.gdynia.pl/catalog/

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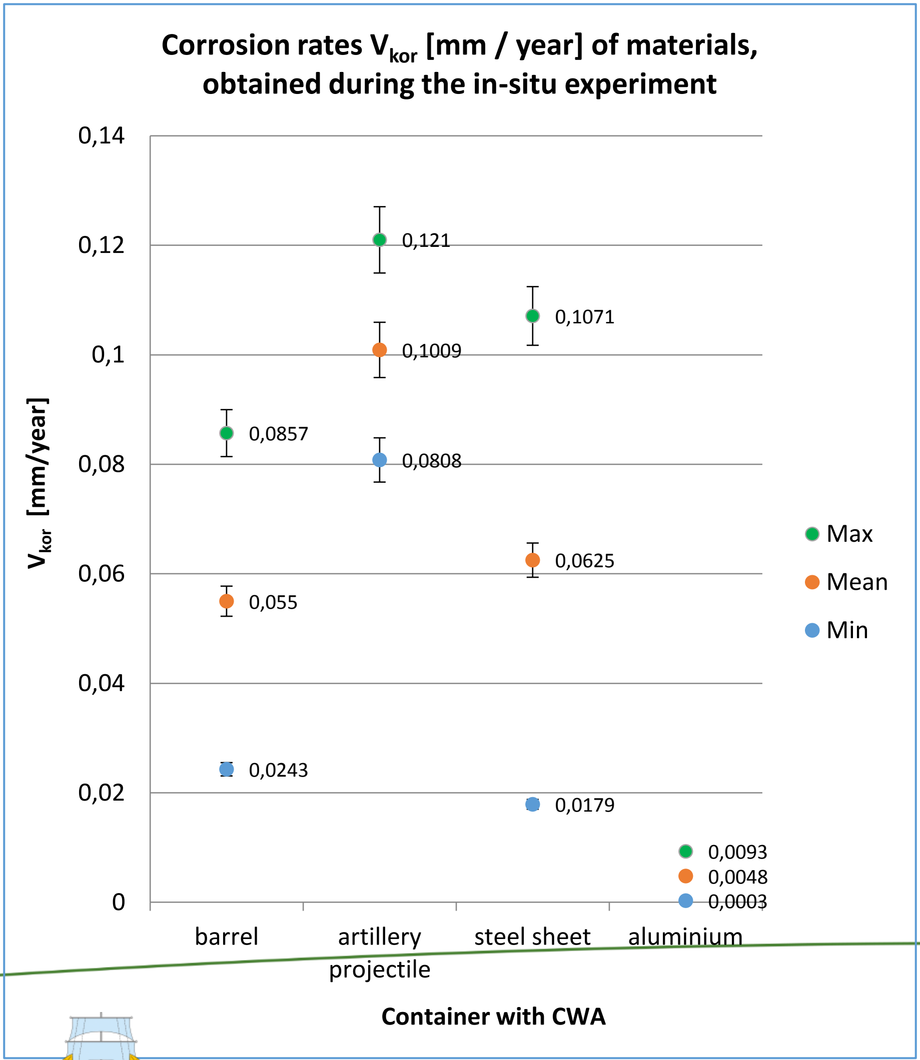
ENVIRONMENTAL EXPOSURE IN DUMPED SITES



- corrosion rate of coupons made from the barrel varies from 0.0243mm/year in the Gdańsk Deep to 0.0952 mm/year in the Bornholm Deep;
- coupons made of artillery projectile shell corrosion rate range from 0.0808 mm/year in the Słupsk Furrow to 0.1210 mm/year in the Bornholm Deep;
- steel sheet corrosion rate is in the range of 0.0179 mm/year in the Gdańsk Deep to 0.1071 mm/year in the Słupsk Furrow and 0.1002 mm/year in the Bornholm Deep;
- corrosion rate of aluminum is in the range from 0.0003 mm/year to 0.0046 mm/year.

ENVIRONMENTAL EXPOSURE IN DUMPED SITES

Assuming a 70 years' time of presence of munitions weapons in the marine environment, it can be concluded, that the thickness of the barrels that were not covered by the sediments layer decreased from 1.7 mm to 6 mm, therefore, currently regardless dumping site and environmental conditions prevailing in the these areas, the barrels are completely destroyed and unsealed, and the CWA have already been released to the marine environment.

Summarize

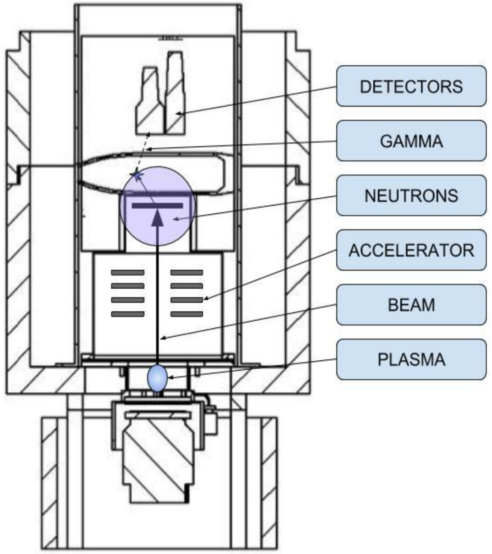
- High content of mesophilic, psychrophilic and halophilic bacteria was found in the tested samples
- The number of anaerobic bacteria was clearly lower
- The number of fungi was low
- The presence of sulfuric bacteria (SRB) was detected, their amount turned out to be high, especially when the determinations were made using a medium prepared on the basis of seawater.

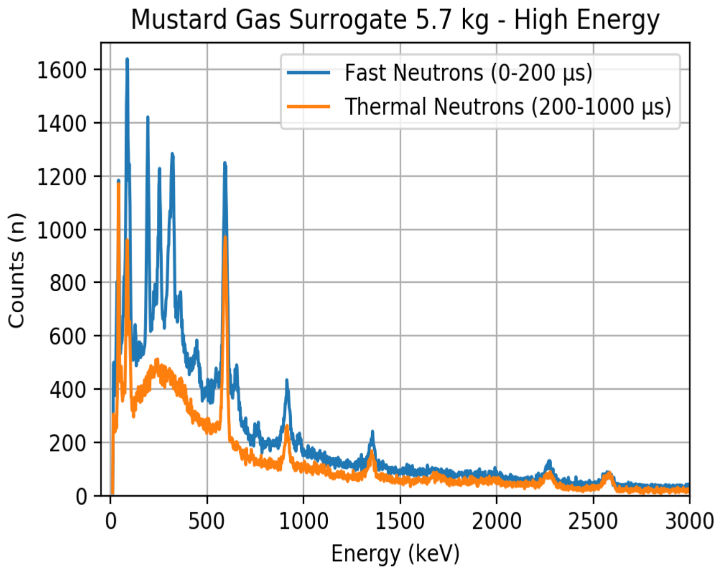
A 2.1 Examination of marine munitions' status

Activity 2.1.3 Composition

Payload identification via neutron activation analysis (NAA)

- **We have demonstrated our ability to distinguish between CWA- and HE - munitions using NAA in laboratory conditions**
- Preliminary design of a cost effective ROV -mounted **system was envisioned.**
- Work in progress: With BGO -detector we are able to measure N from HE and Fe signals in few weeks. Large LaBr detector delivery is delayed till spring. **Fast measurements soon feasible.**





Deuterium beam is accelerated and collided to deuterium atoms, resulting fusion produces neutrons. These neutrons interact with the shell and payload producing *a gamma spectrum* characteristic to a specific munition type and possibly degradation level.

A 2.2 Modelling of contamination

Activity 2.2.1 Leakage rate estimation

Aims:

- Leakage rate estimation based on corrosion estimation will be simulated using laboratory setup. (PNA)
- The experimental data will in addition to other parameters be used to establish a physical model for the leakage rate (performed by FFI).

A 2.2 Modeling of contamination

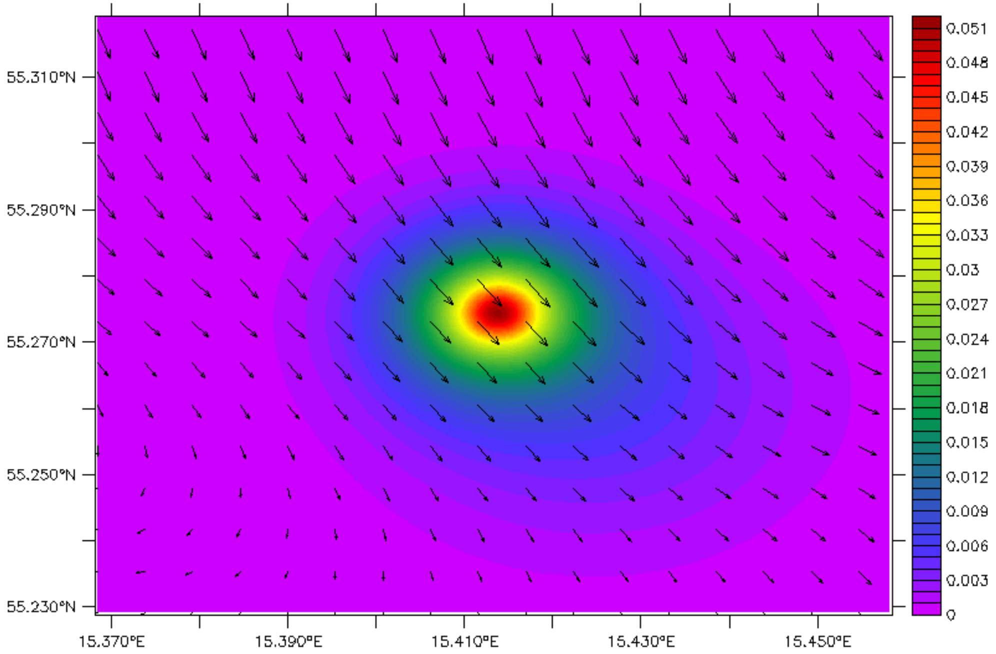
High resolution dispersion model (HRDM) has been created:

- Horizontal resolution of the model – 50 metres
- Domain size – 25x25 km
- Half-life included
- Temperature dependence of half-life included
- Direct access to the system (via internet) based on REST API has been implemented

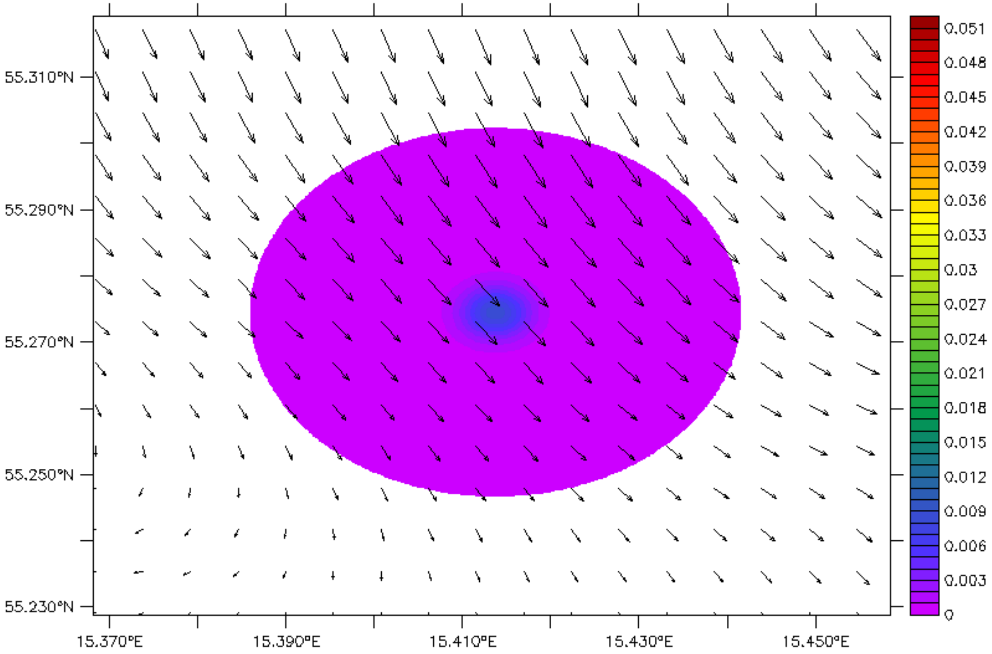
modeling of contamination

Example of simulated contamination after 5 days

Without half-life effect



With half-life effect



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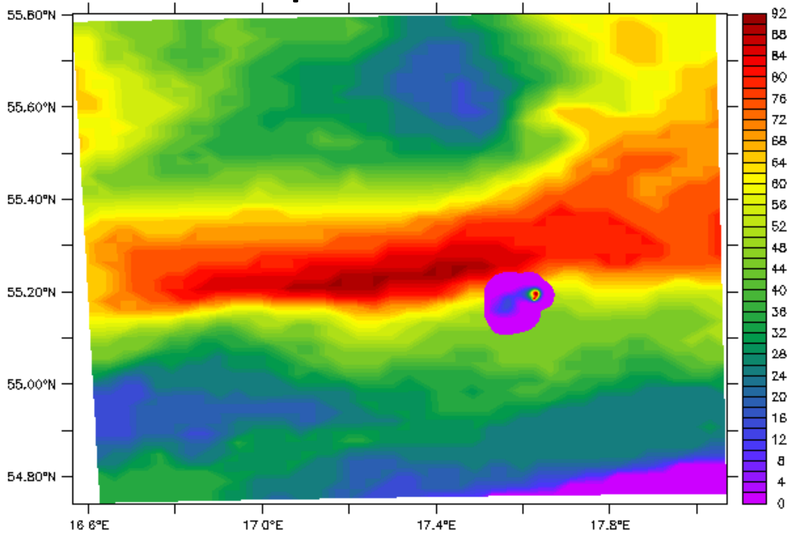
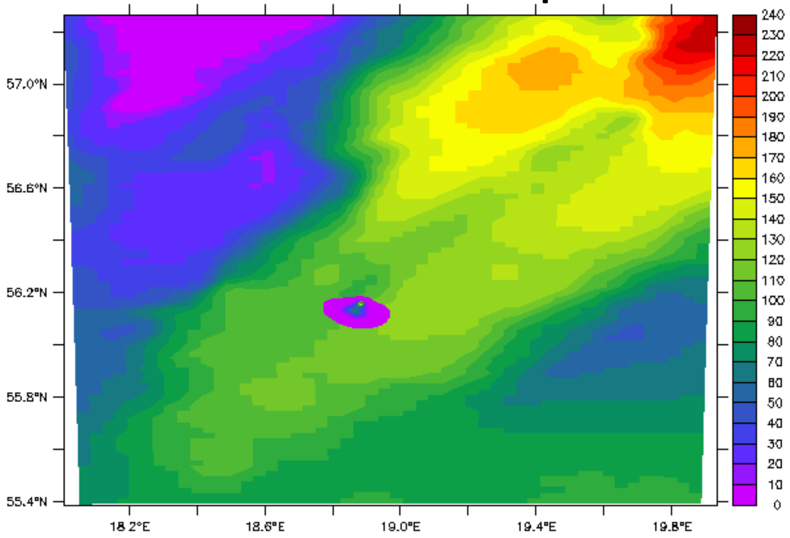
Example of results from the working system (after 5 days of integration and without half-life

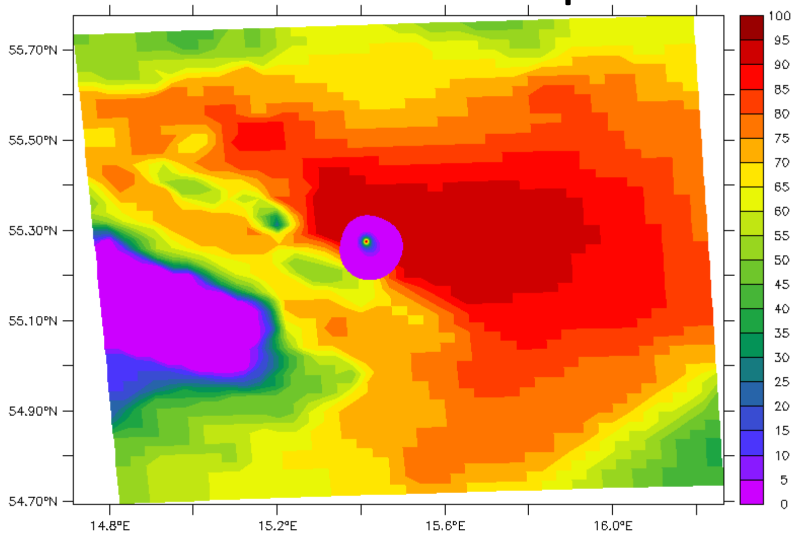
Slupsk Furrow



Gotland Deep



Bornholm Deep



More detailed information is presented on the poster

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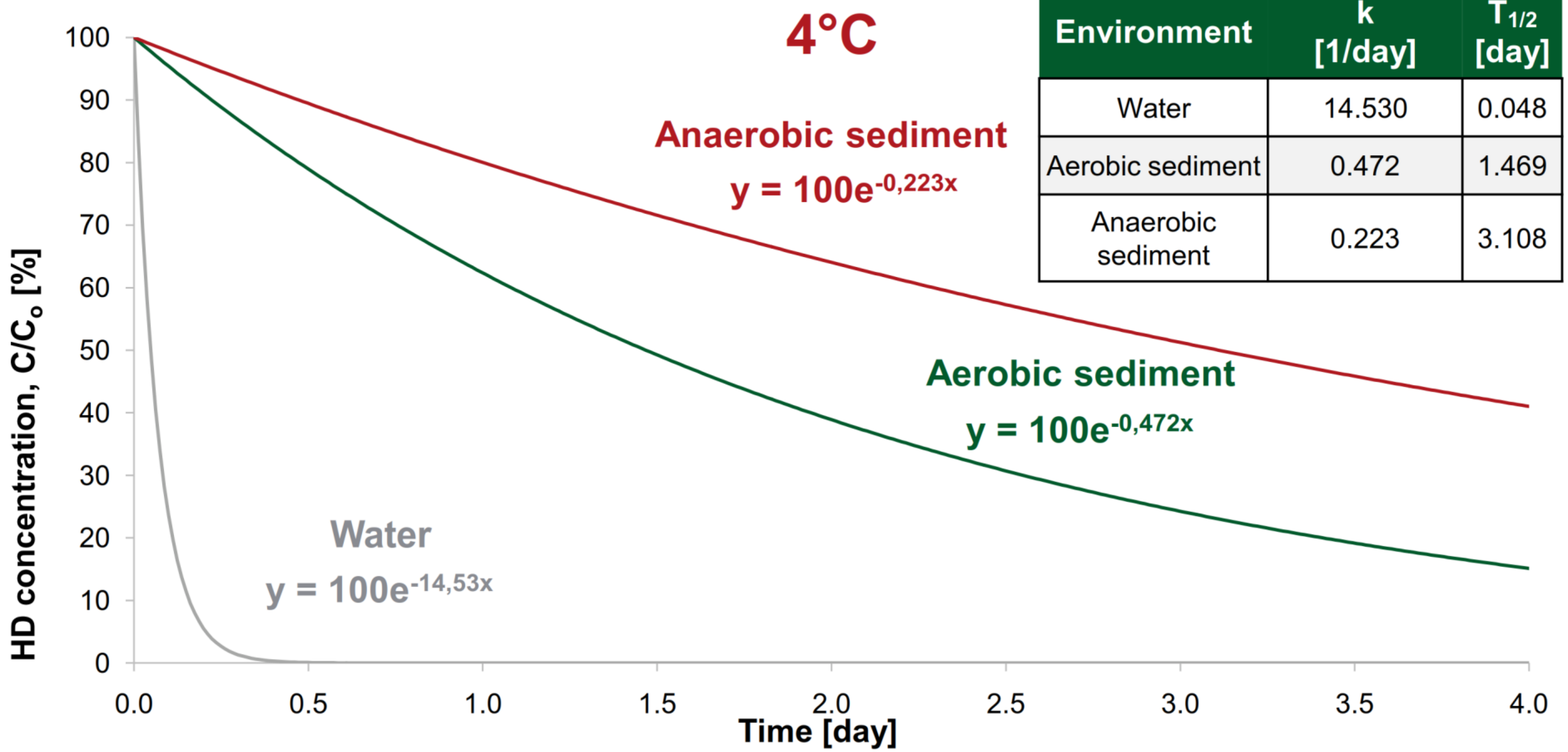
Modeling of contamination

Sulfur mustard



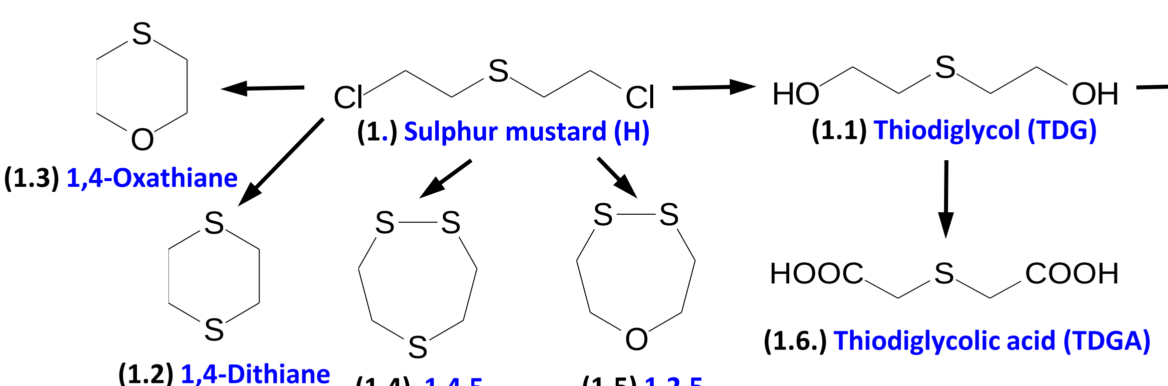
Environment	k [1/day]	$T_{1/2}$ [day]
Water	14.530	0.048
Aerobic sediment	0.472	1.469
Anaerobic sediment	0.223	3.108

Methods for determination of CWAs and explosives

- To evaluated effects of chemical and conventional munitions, method have been developed, tested, and validated:
- For determination of CWAs and related chemicals in sediments
- For toxic explosives related chemicals in sediments

Sediment samples analysis

Target chemials- CWA’s



(1.) Sulphur mustard (H)

(1.1) Thiodiglycol (TDG)

(1.1O.) Thiodiglycol sulfoxide

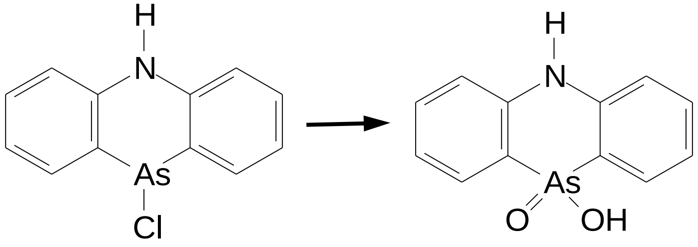
(1.3) 1,4-Oxathiane

(1.2) 1,4-Dithiane

(1.4) 1,4,5-Oxadithiepane

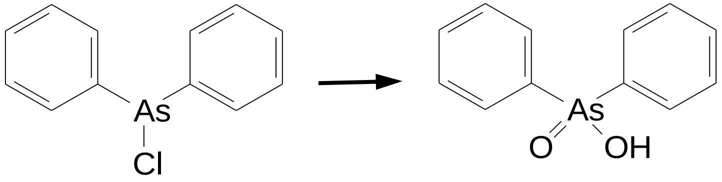
(1.5) 1,2,5-Trithiepane

(1.6.) Thiodiglycolic acid (TDGA)



(2.) Adamsite (DM)

(2.O.) 5,10-Dihydropheno-arsazin-10-ol 10-oxide



(3.) Clark I (DA)

(3O.) Diphenylarsinic acid

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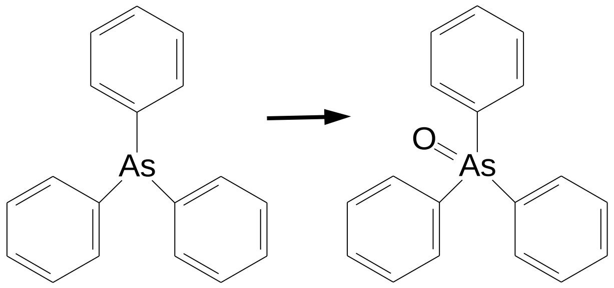
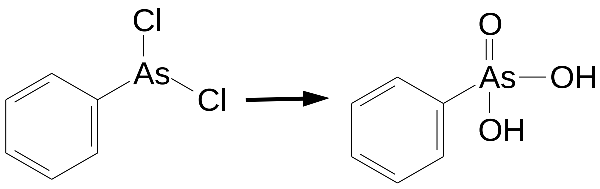
Sediment samples analysis

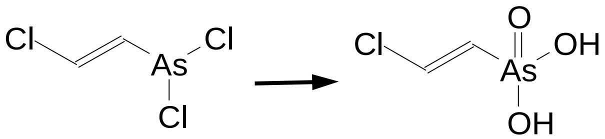
Target chemials- CWA's



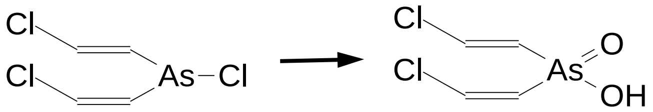
(4.) Triphenylarsine (TPA) (4O) Triphenylarsine oxide



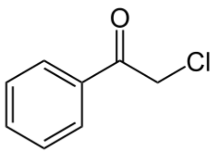
(5.) Phenyldichloroarsine (PDCA) (5O) Phenylarsonic acid



(7.) Lewisite I (L1) (7O) 2-Chlorovinylarsonic acid



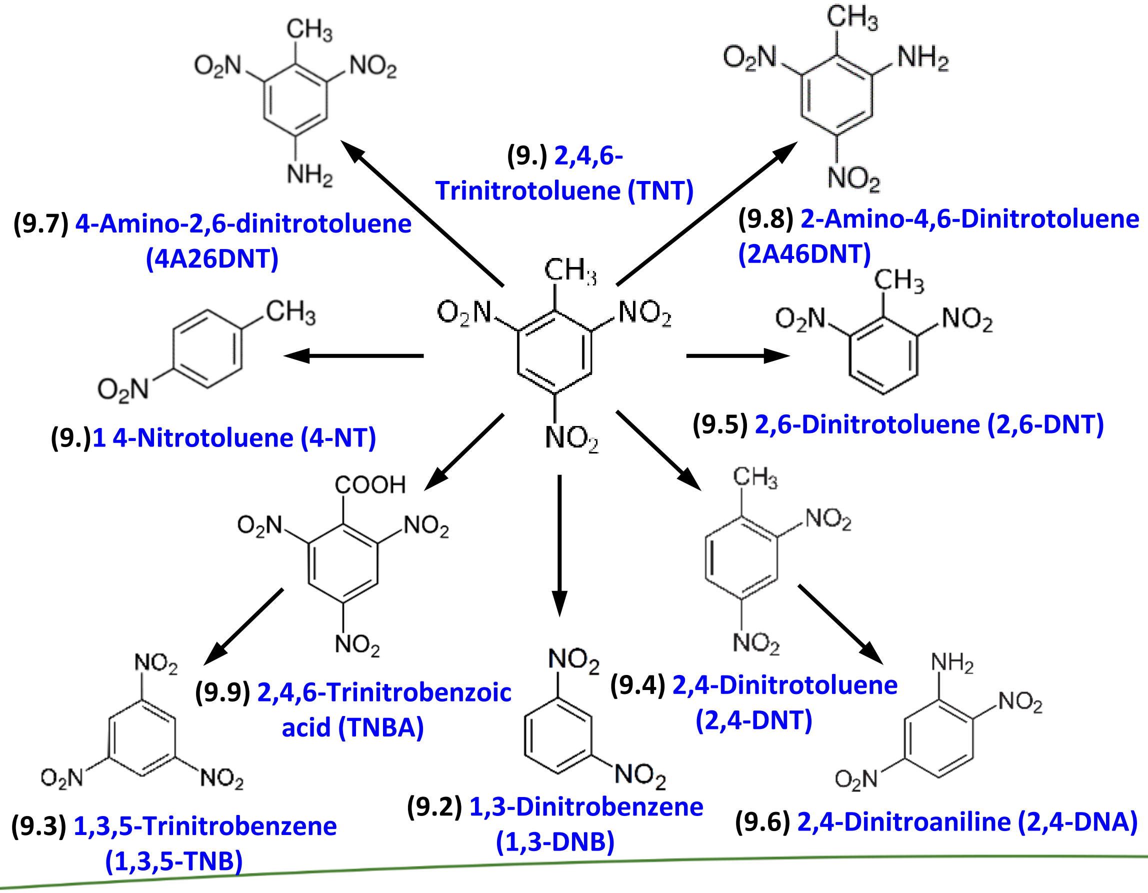
8. Lewisite II (L2) 8O Bis(2-chlorovinyl)-arsinic acid

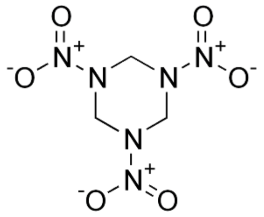


(6.) α-Chloroacetophenone (CN)

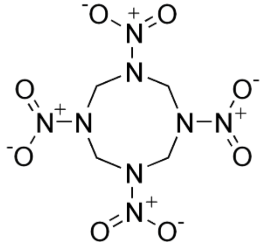
Sediment sample analysis

Target chemicals - Explosives

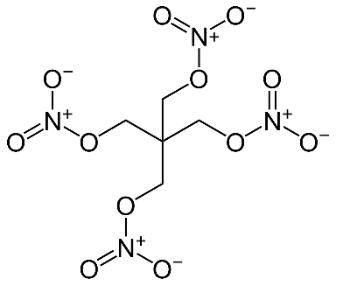




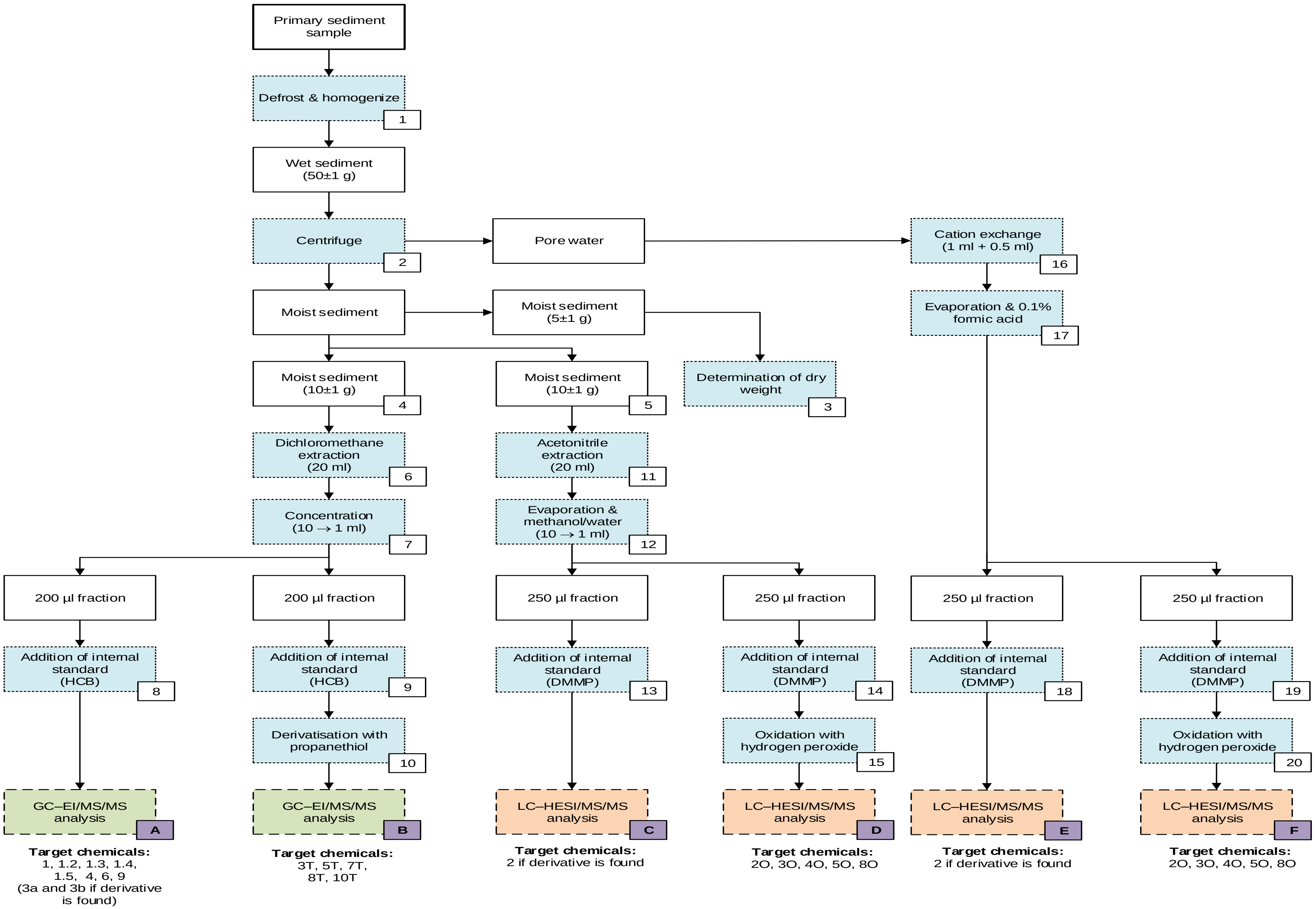
(10.) 1,3,5-Trinitro-1,3,5-triazinane (RDX)



(11.) 1,3,5,7-Tetranitro-1,3,5,7-tetrazocane (HMX)



(12.) Pentaerythritol tetranitrate (PETN)



Primary sediment sample
Defrost & homogenize
1
Wet sediment (50±1 g)
Centrifuge
2
Pore water
Cation exchange (1 ml + 0.5 ml)
16
Moist sediment
Moist sediment (5±1 g)
Evaporation & 0.1% formic acid
17
Moist sediment (10±1 g)
4
Moist sediment (10±1 g)
5
Determination of dry weight
3
Dichloromethane extraction (20 ml)
6
Acetonitrile extraction (20 ml)
11
Concentration (10 → 1 ml)
7
Evaporation & methanol/water (10 → 1 ml)
12
200 µl fraction
200 µl fraction
250 µl fraction
250 µl fraction
250 µl fraction
250 µl fraction
Addition of internal standard (HCB)
8
Addition of internal standard (HCB)
9
Addition of internal standard (DMMP)
13
Addition of internal standard (DMMP)
14
Addition of internal standard (DMMP)
18
Addition of internal standard (DMMP)
19
Derivatisation with propanethiol
10
Oxidation with hydrogen peroxide
15
Oxidation with hydrogen peroxide
20
GC–EI/MS/MS analysis
A
GC–EI/MS/MS analysis
B
LC–HESI/MS/MS analysis
C
LC–HESI/MS/MS analysis
D
LC–HESI/MS/MS analysis
E
LC–HESI/MS/MS analysis
F
Target chemicals: 1, 1.2, 1.3, 1.4, 1.5, 4, 6, 9 (3a and 3b if derivative is found)
Target chemicals: 3T, 5T, 7T, 8T, 10T
Target chemicals: 2 if derivative is found
Target chemicals: 2O, 3O, 4O, 5O, 8O
Target chemicals: 2 if derivative is found
Target chemicals: 2O, 3O, 4O, 5O, 8O

Results from LC-MS/MS analysis (78 samples)

Analyzed Chemicals: concentrations µg/kg (sediment)						
Outside code	VERIFIN code	PDCA ox	L2 ox	DM ox	DPA ox	TPA ox
C11-C57 (total of 58 samples)	R3845-R3902	No chemicals in question detected				
lb-oc-sep16-1a	R3912	ND	ND	ND	ND	ND
lb-oc-sep16-2	R3913	ND	ND	ND	ND	ND
kh-oc-sep16-1	R3914	ND	ND	ND	ND	ND
kh-oc-sep16-6	R3915	ND	ND	ND	ND	ND
kh-oc-sep16-5	R3916	ND	ND	ND	ND	ND
kh-oc-sep16-4	R3917	ND	ND	ND	ND	ND
oc-mar17-bo5-3	R3918	8	ND	35	2	ND
oc-mar17-bo2-8	R3919	138	ND	21	63	79
oc-mar17-bo5-1	R3920	5	ND	9	14	ND
oc-mar17-gd01-5	R3921	ND	ND	ND	ND	ND
oc-mar17-gd01-4	R3922	ND	ND	ND	ND	ND
oc-mar17-bo5-2	R3923	2	ND	225	6	ND
oc-mar17-bo2-3	R3924	187	ND	82	77	309
oc-mar17-gd01-2	R3925	ND	ND	ND	ND	ND
oc-mar17-bo2-7	R3926	255	ND	13	86	321
oc-mar17-bo2-5	R3927	191	ND	144	95	138
oc-mar17-bo2-6	R3928	13	ND	3	5	43
oc-mar17-bo2-4	R3929	2737	ND	157	1138	202
oc-mar17-gd01-6	R3930	ND	ND	ND	ND	ND
oc-mar17-bo2-2	R3931	5900	ND	57	2076	194

(green)	< 10 µg/kg
(yellow)	10–1000 µg/kg
(red)	> 1000 µg/kg

ND = Not detected

PDCAox = Phenylarsonic acid, L2ox = Bis(2-chlorovinyl)-arsinic acid (oxidation product of Lewisite 2), DMox = Oxidized adamsite, DPAox = Oxidation product of Clark 1 and Clark 2, TPAox = Triphenylarsine oxide

VERIFIN, University of Helsinki

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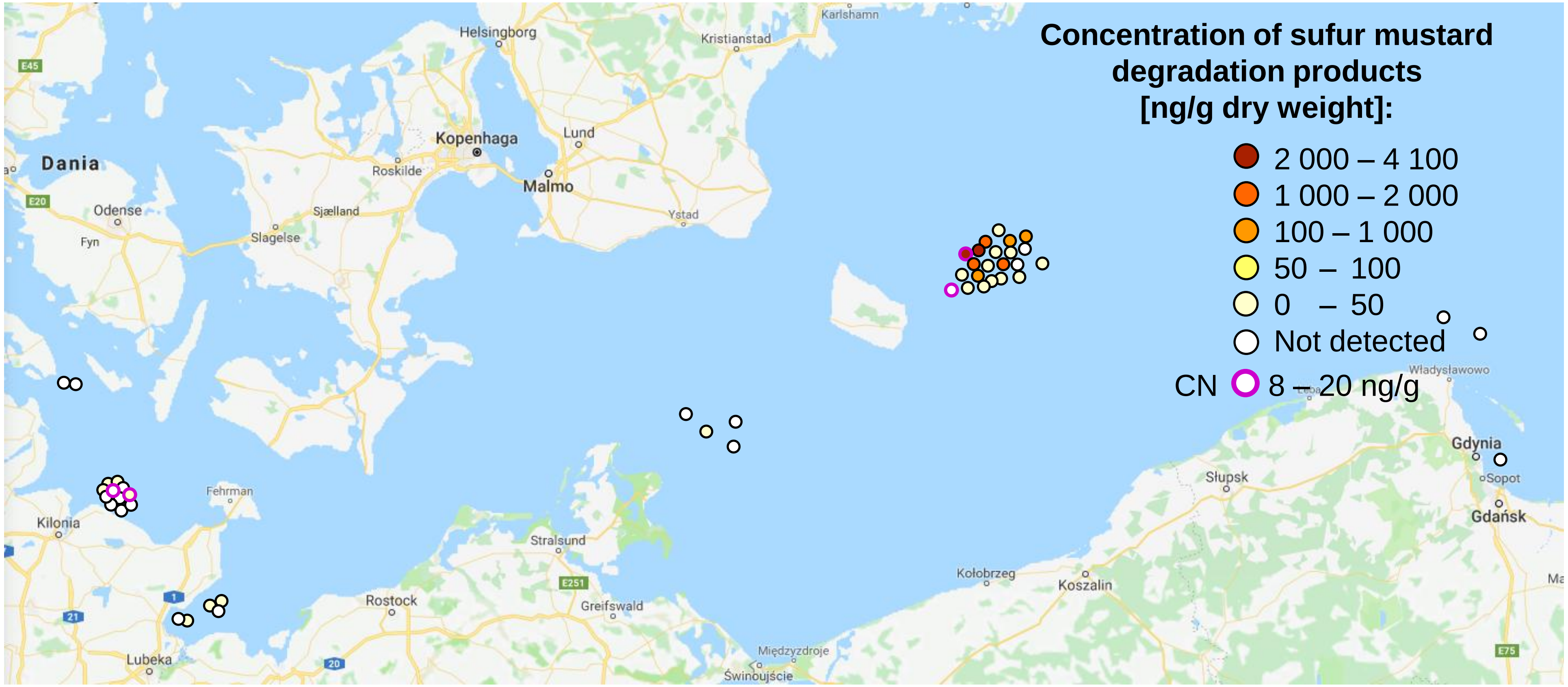
Sediment samples analysis

Sulfur mustard and its degradation products



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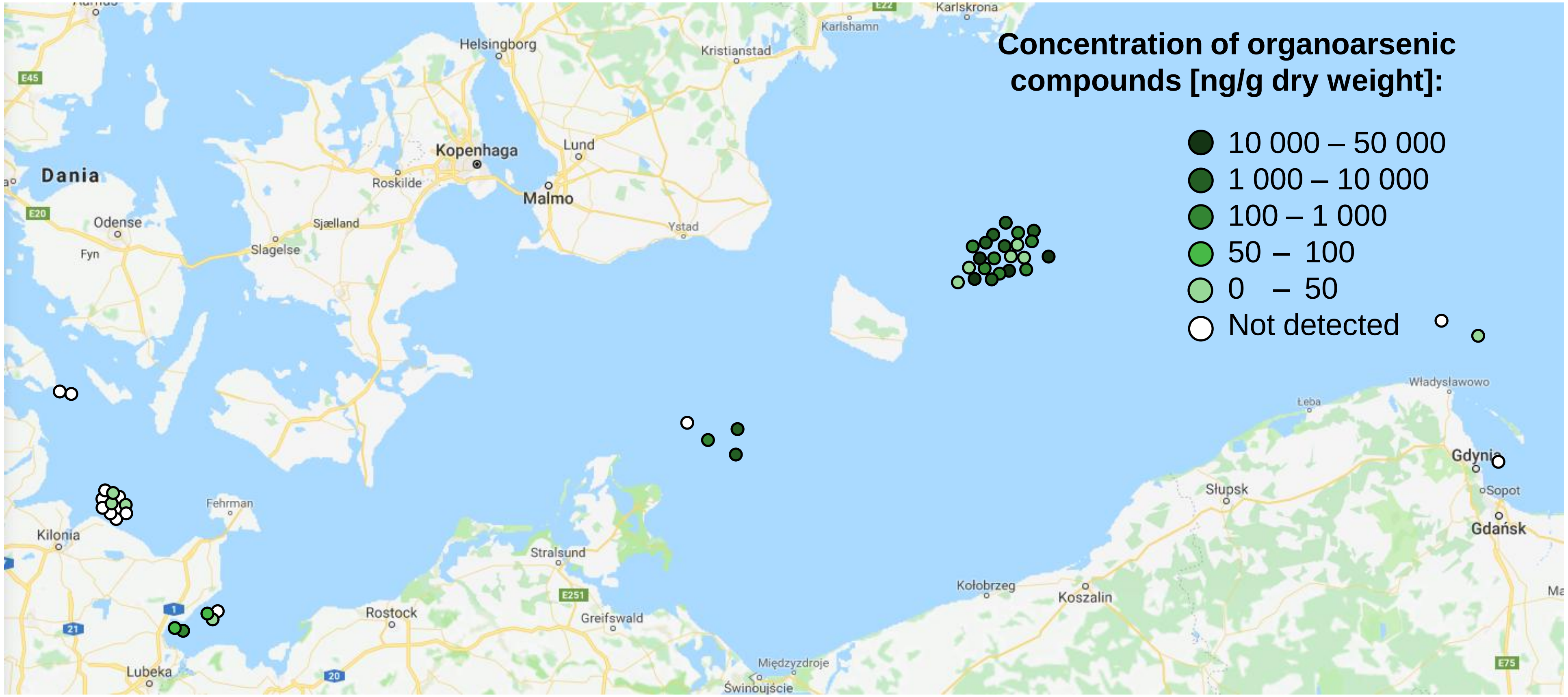
Sediment samples analysis

Organoarsenic compounds



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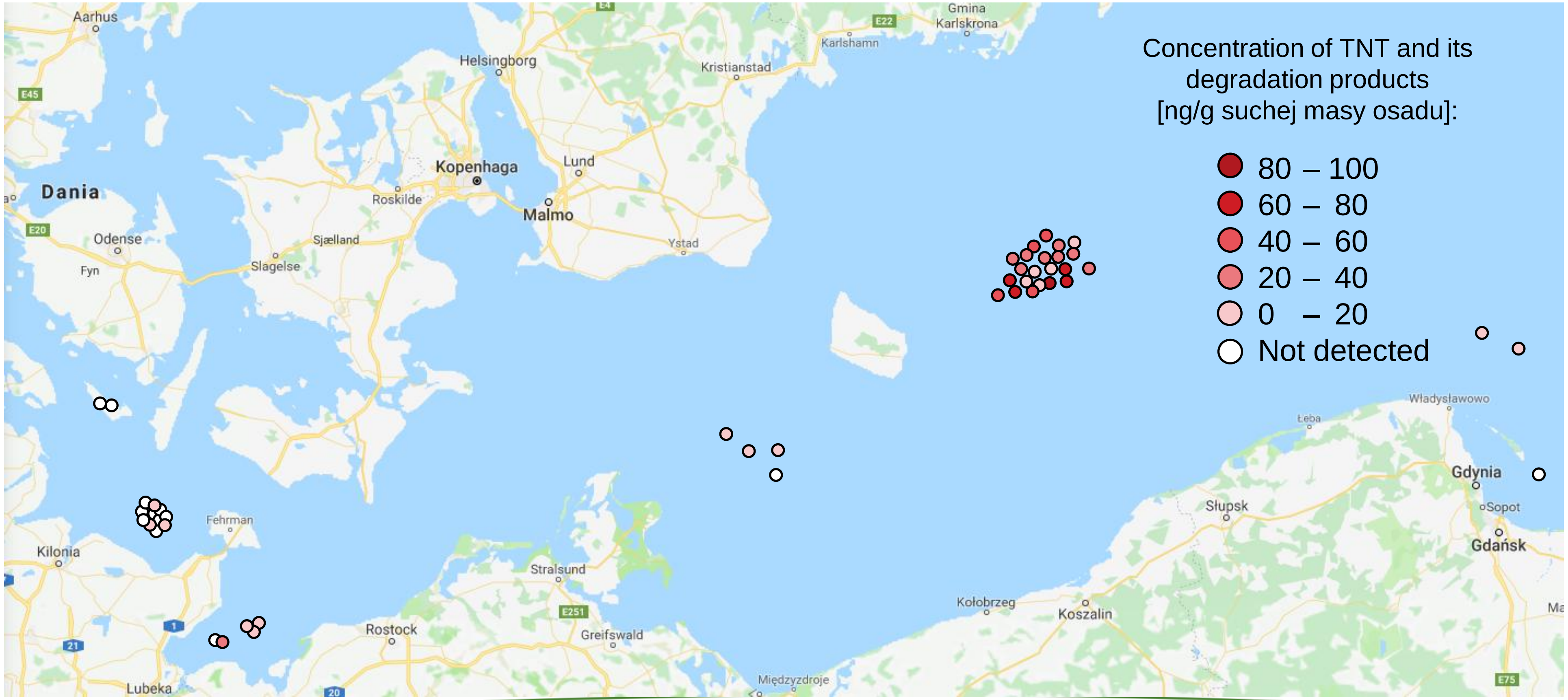
Sediment samples analysis
TNT and its degradation products



MUT, [Military University of Technology]

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New High Resolution Mass spectrometric (HRMS) approaches

Aims:

- New approaches for analysis of both CWAs and toxic explosive related chemicals on a one method using sophisticated high resolution mass spectrometry have been tested and applied in the WP3 in pilot studies

Status:

- For CWAs – selected CHEMSEA, MODUM and DAIMON samples were screened and several new chemicals were detected

  → eg. methylated phenylarsenic chemicals were found and identified using synthesized reference chemicals

- Explosives yet not studied-> will be done after sediment samples in WP3 have been analysed to find out interesting samples

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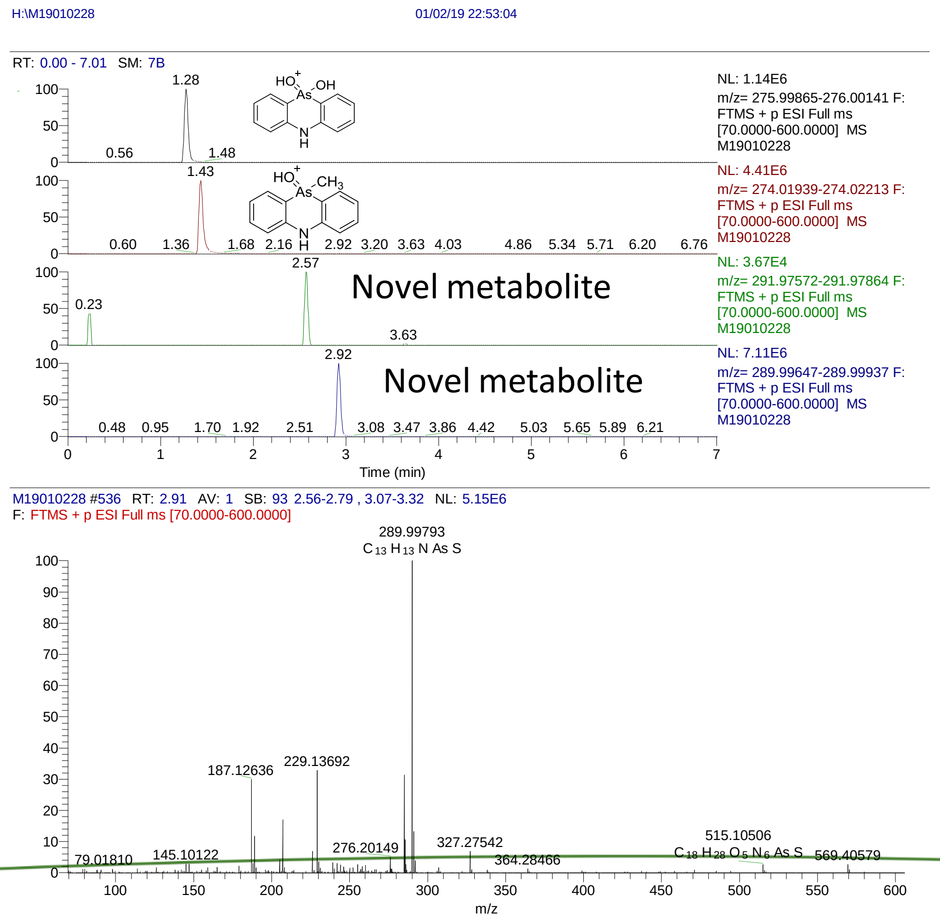
Identification of methylated CWA-related phenylarsenic chemicals from sediment



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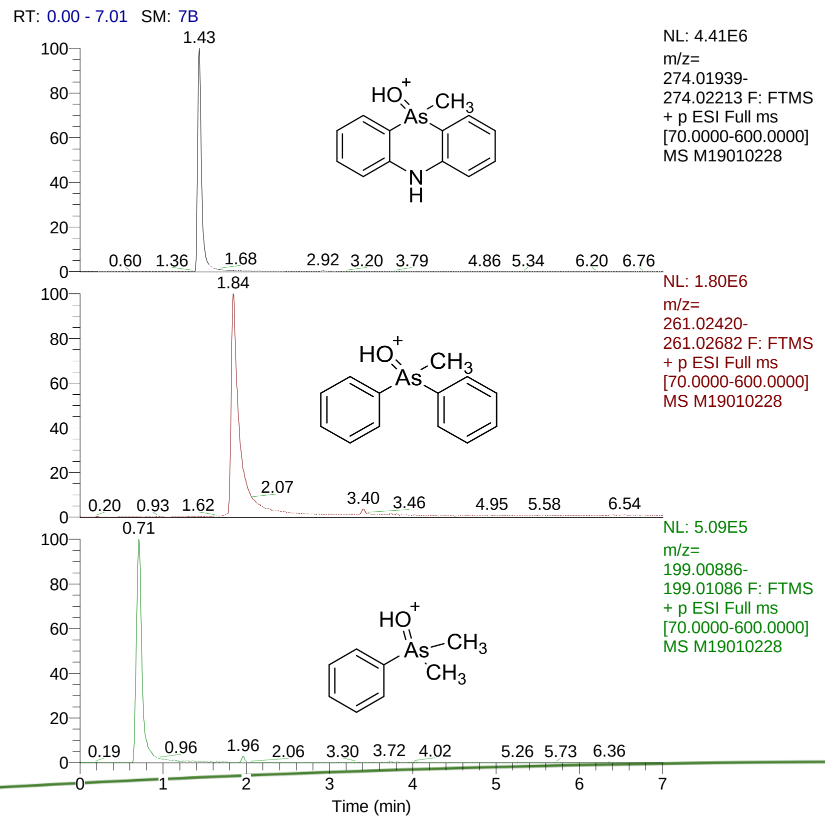
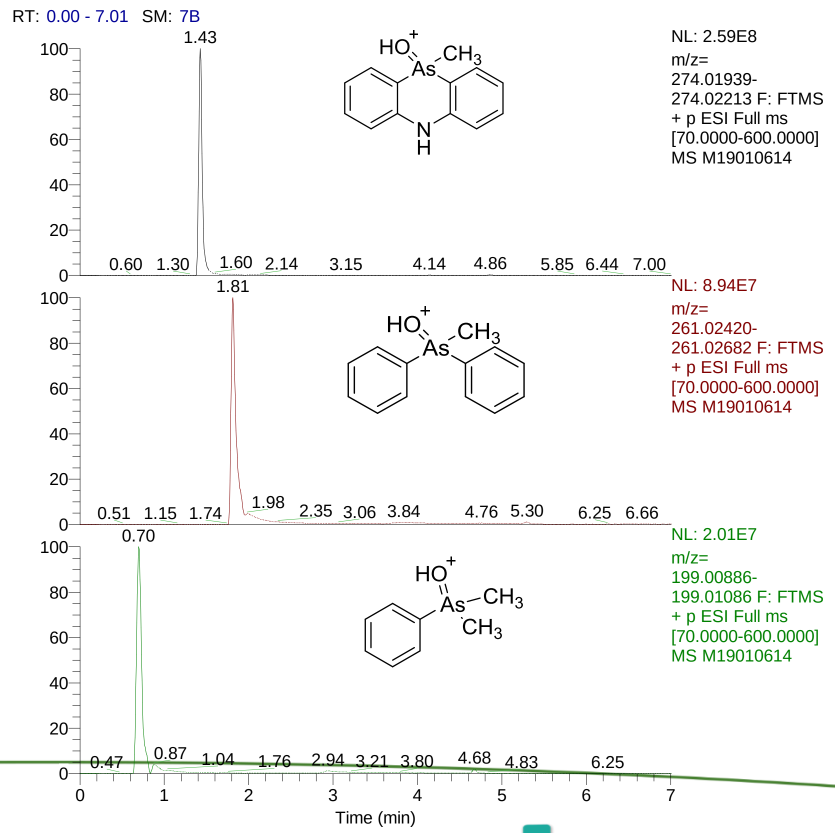
Identification based on synthetisized reference chemicals

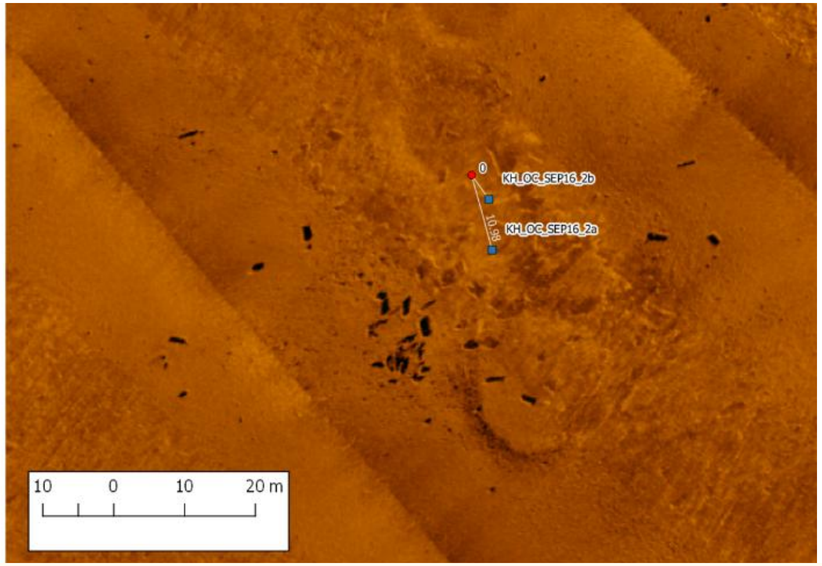
Sediment sample :

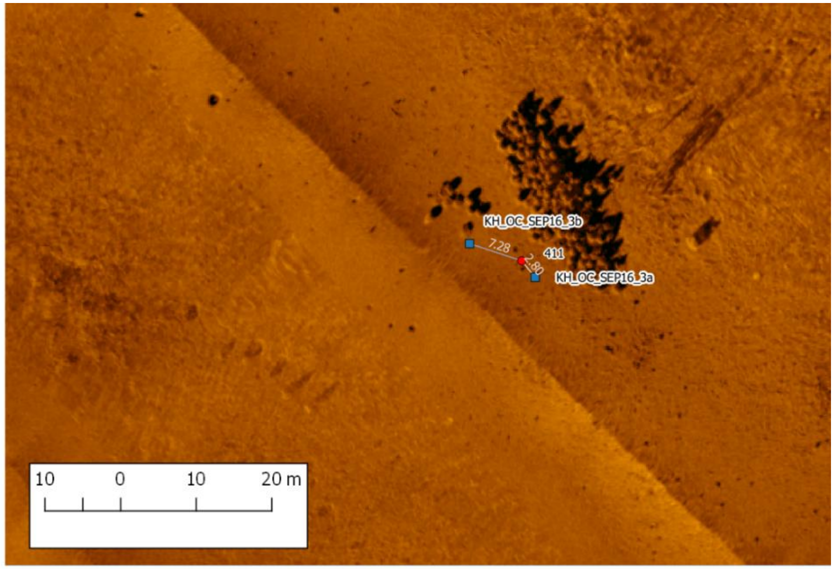


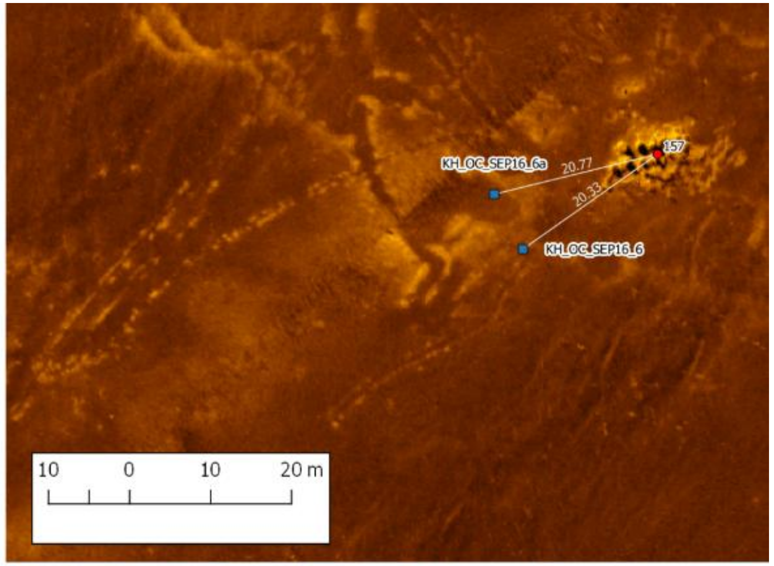
Reference standard:

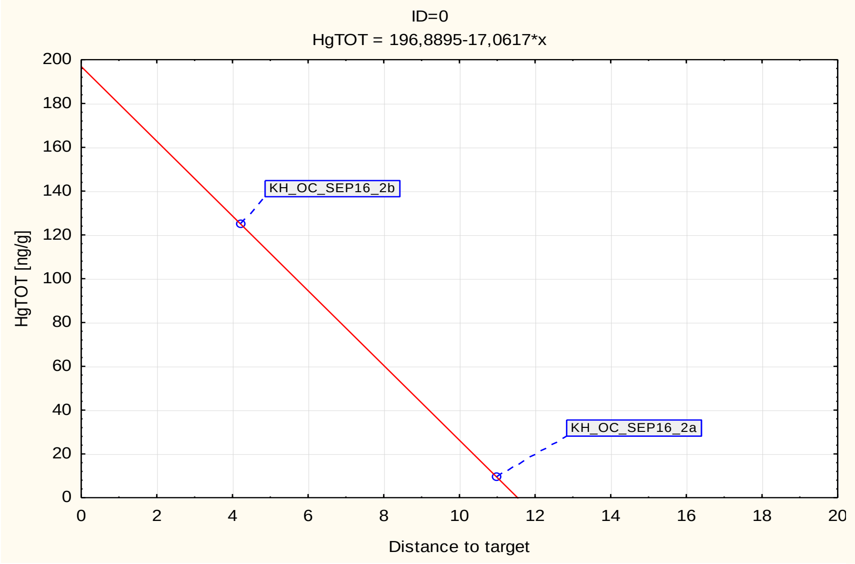


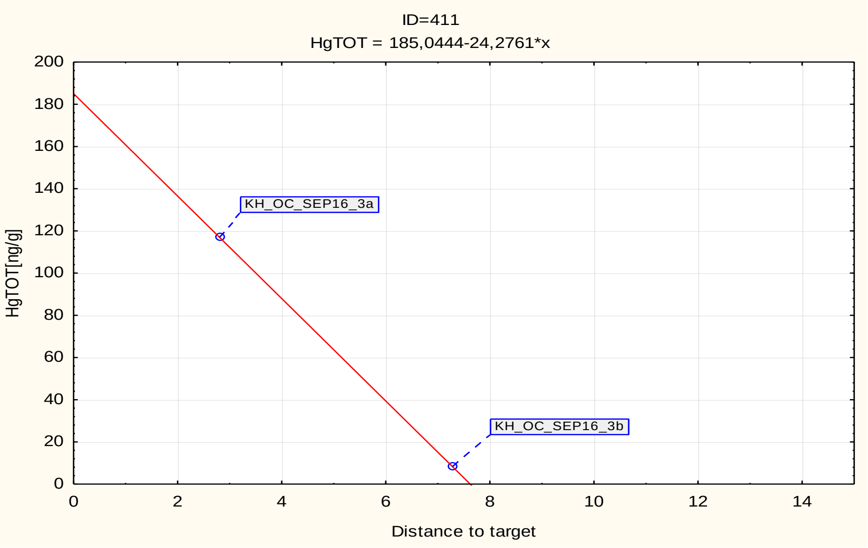
Object-by-object – drastic drop: conventional munition

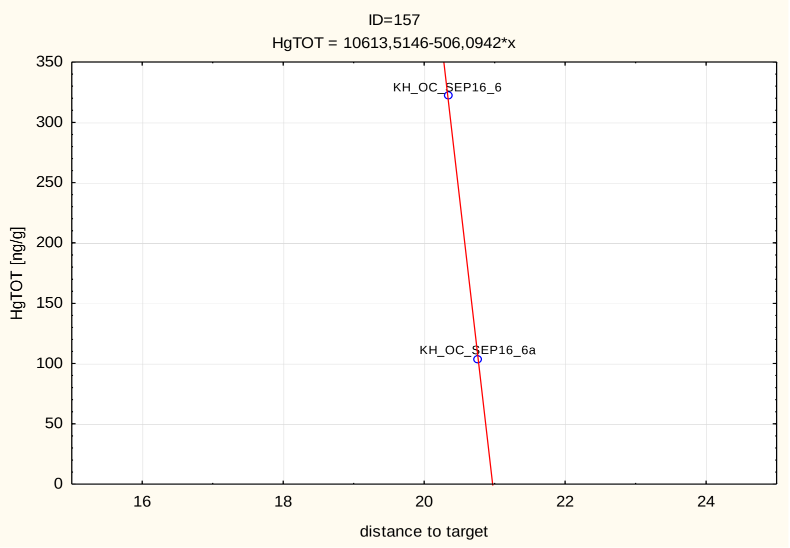




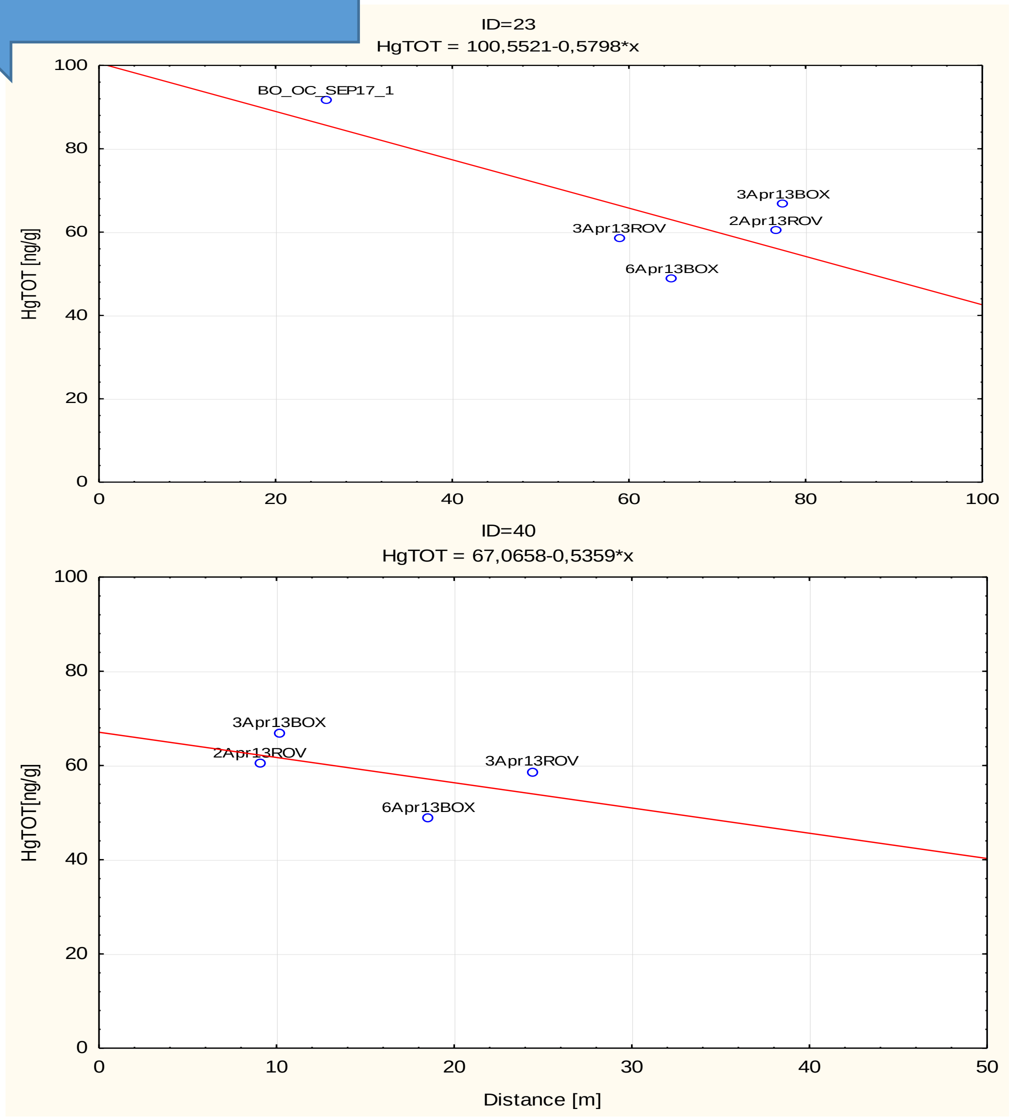


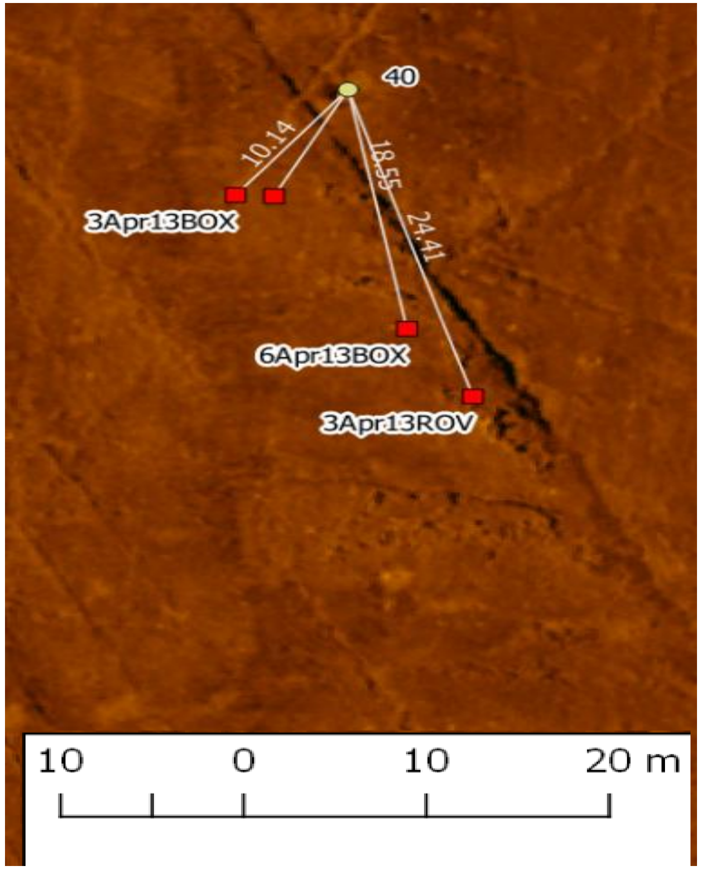






Object-by-object: CWA munition





A 2.4 Methods for measurement of warfare agents' pollution in water body

Activity 2.4.2 Passive sampling

Aims:

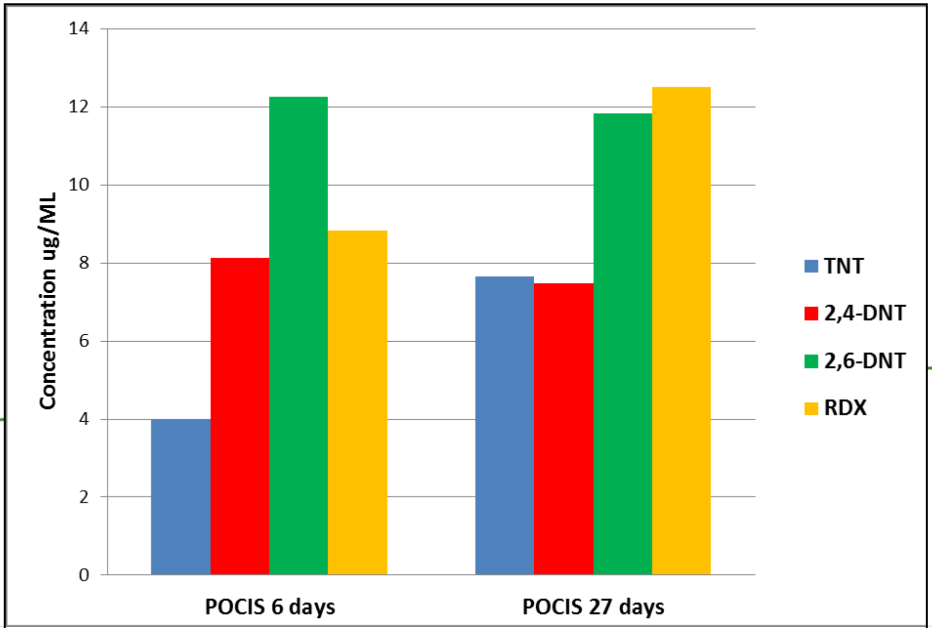
- Methods developed in WP2.4.2 will be compared with developed novel methods based upon passive samplers deployment and will be tested and applied in the WP3 in pilot studies

Status:

- *CWA:* Preliminary results for CWA presented in 4th Project Meeting in Gdynia; CWA passive samplers made available for WP3; Further tests for CWA being conducted (M.Sc. Student at VERIFIN). LC-MS results available
- FFI will write a report on passive samples for explosives and CWAs. No time for field work.

Findings

- Passive sampling is based on molecular diffusion of analytes through a diffusive surface onto an adsorbent. After sampling for days/weeks, the adsorbed analytes are desorbed off the sampler by solvent extraction.
- The POCIS adsorbent showed highest recoveries of the explosives TNT, 2,4-DNT, 2,6-DNT and RDX during laboratory experiments



- Norwegian Defence Research Establishment

Decision Aid for Marine Munitions

A 2.6 Risk categorisation procedures

Aims

Leader: Chalmers

2.6.1. Creation of lists of risk chemicals and their categorisation
  Verifin, MUT, Chalmers

2.6.2. Development of leakage scenarios and their categorisation
  FFI, Chalmers

2.6.3. Categorisation of factors affecting the spreading of the chemicals in different conditions
  IOPAS, IORAS

2.6.4. Linking of risk chemicals with their possible effects on biota
  Ecotoxdata (CWA), desktop study - Chalmers

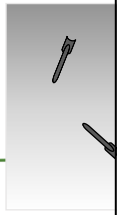
2.6.5. Development of scenarios leading to possible human exposure
  (IDUM…)

2.6.6. Building a risk categorisation procedure based on the developed lists and scenarios.
  DSS, VRAKA-CWA

VRAKA-CWA

Risk assessment model for dur ts

- Probabilistic (uncertainties) and
- Calculates the:
  - probability of a hole in a CW
  - risk by combing the probabil CWA
- Site specific indicators
  - Sea-floor oxygen concentration
  - Salinity
  - Temperature
  - Depth
  - etc.
- Activities
  - Trawling
  - Shipping traffic
  - Storms
  - etc.



VRAKA-CWA

General data

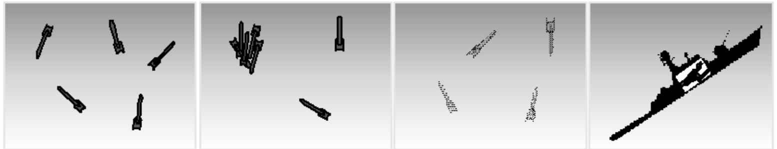
Site	
Position	
Name of assessor	
Date	

Site specific indicators	Unit	Lowest reasonable	Highest reasonable	*Min*	*Max*
Average sea-floor oxygen concentration	*ml/l*	6.8	7.4	*0*	*8*
Average sea-floor salinity	*PSU*	34	34	*1*	*35*
Average sea-floor temperature	*C*	5	7	*3*	*9*
Average sea-floor current strenght	*m/s*	0	1	*0*	*1*
Average hull thickness at construction	*mm*	0	14	*0*	*14*
Depth	*m*	190	220	*0*	*459*
Time since dumped	*years*	71	72	*0*	*100*
Bottom character	*Select*	A - Accumulation seafloor			

Activities	Unit	Lowest reasonable	Highest reasonable
Construction	*times/year*	0.01	0.1
Diving	*times/year*	0.001	0.01
Military activity	*times/year*	0.01	0.1
Shipping traffic	*times/year*	0.001	0.01
Storms	*times/year*	0.001	0.01
Trawling	*times/year*	1	2
Unstable seabed	*times/year*	0.01	0.1

Munition specific data

Arrangement of objects — *Select* — 4 - Inside a wreck

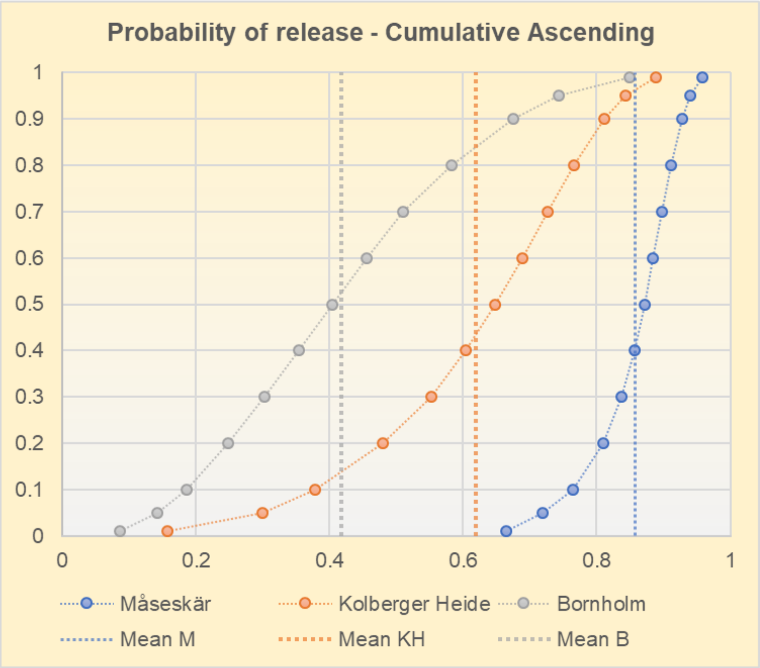


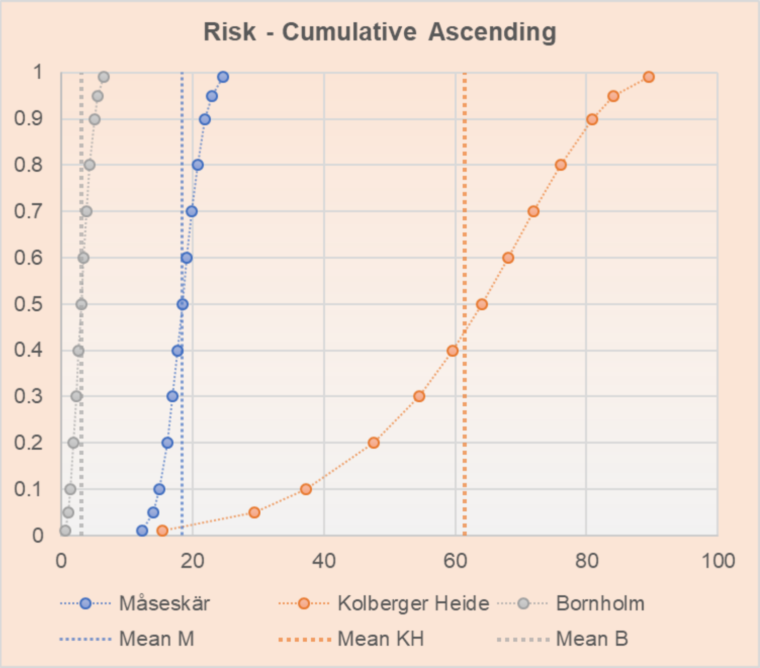
	Unit	Lowest reasonable	Highest reasonable	*Primary*	*Secondary*
Mass of toxic substance per unit	*kg*	200	300		
CWA - Toxic Unit	*Select*	Clark I		*0.41*	*0.086*

unitions

VRAKA-CWA
Practical use of results

- Evaluate and compare the risk level associated with different CWA units and areas
- Evaluate the effect of mitigation measures
- Enable well-informed decisions on how to prioritize and mitigate dumped marine munitions
- Structure and transparency
- Enable uncertainty and sensitivity analysis





WP2_ METHODS

Thank you for contribution and excellent collaboration!

- CHALMERS
- FFI
- IOPAS
- MUT
- NEUTRONGATE
- PNA
- SYKE
- TI-FI
- VERIFIN