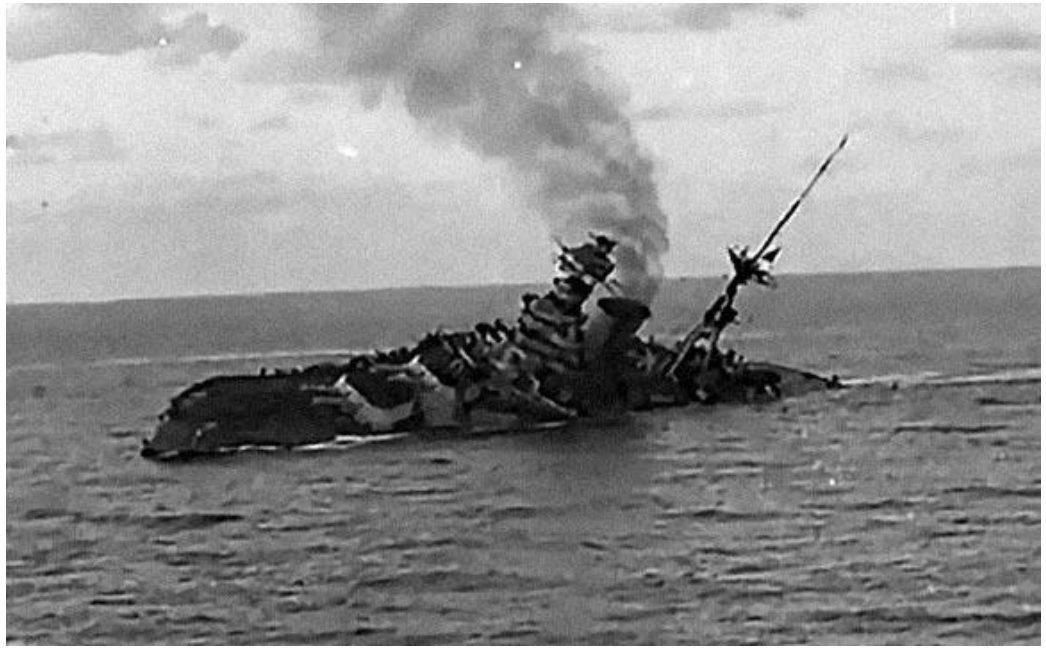
Toxicology/Kiel

UNIVERSITÄTSKLINIKUM
Schleswig-Holstein

Sea Dumped Explosive Chemicals: Analysis, Toxicity and Risk Assessment of World War Relicts

Prof. Dr. Edmund Maser

Institute of Toxicology and Pharmacology
for Natural Scientists
University Medical School Schleswig-Holstein
24105 Kiel
Germany




© picture-alliance/Everett Collection

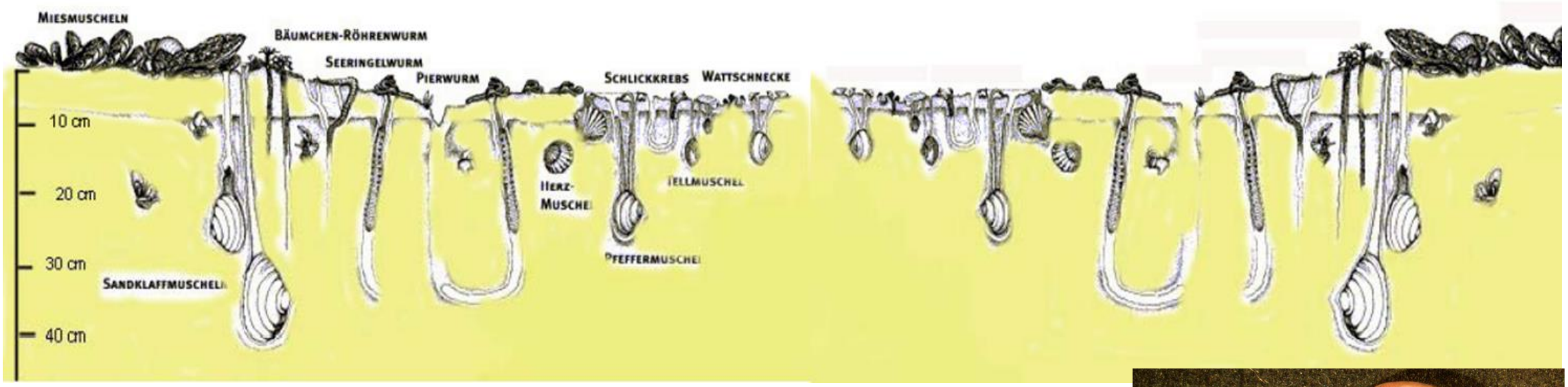

IWM

Today‘s Problems ...

Environmental damage: release of toxic chemicals from corroding ammunition vessels

Toxikologie/Kiel
UNIVERSITÄTSKLINIKUM Schleswig-Holstein

Marine habitats – origin of the marine food chain

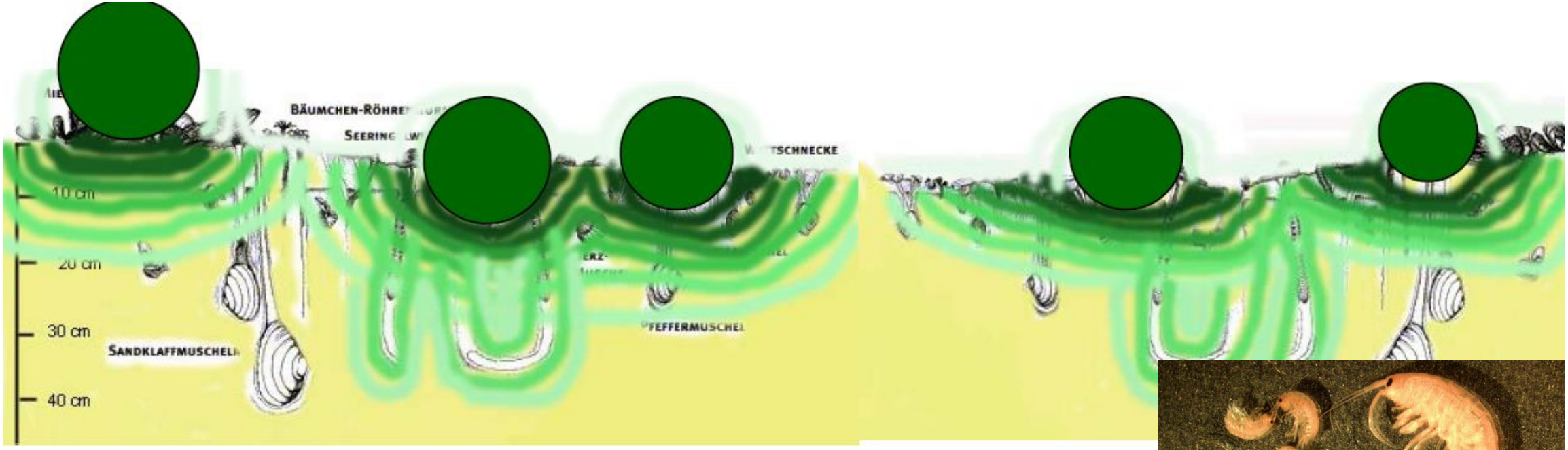


Literatur:
Munitionsbelastung der deutschen Meeresgewässer-
Bestandsaufnahme und Empfehlungen, 2011
Arbeitsgemeinschaft „Rüstungsaltlasten im Meer“
www.munition-im-meer.de

Marine habitats – origin of the marine food chain

Toxikologie/Kiel
UNIVERSITÄTSKLINIKUM Schleswig-Holstein

Anticipated distribution of toxic substances from dumped ammunition in the marine environment

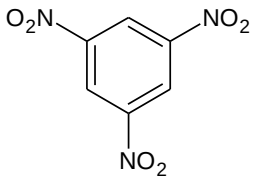


Literatur:
Munitionsbelastung der deutschen Meeresgewässer-
Bestandsaufnahme und Empfehlungen, 2011
Arbeitsgemeinschaft „Rüstungsaltlasten im Meer“
www.munition-im-meer.de

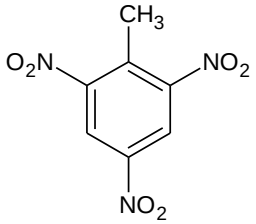
Toxicity of explosives

(Selection: Nitroaromatics)

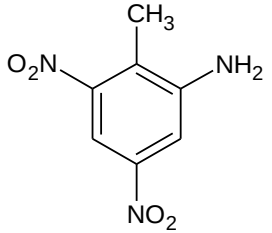
Toxikologie/Kiel
UNIVERSITÄTSKLINIKUM Schleswig-Holstein



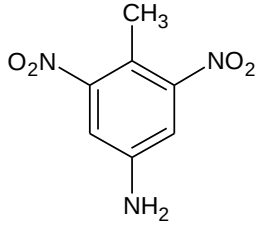
1,3,5-Trinitrobenzene



2,4,6-Trinitrotoluolene, **TNT**



2-Amino-4,6-dinitrotoluolene



4-Amino-2,6-dinitrotoluolene

Human Toxicity

- blood (anaemia)
- liver (hepatitis)
- eyes („TNT-cataract“)
- skin irritation; allergy
- nerval system

- mutagenicity: MAK-Kat. 3b
- cancerogenicity: MAK-Kat. 2

Ecotoxicity

- significant toxicity for marine plants, small crabs, mussels, worms, fish …
- entry into the food chain difficult to estimate, because too little data …

Problems to be solved:

Continuous release (corrosion) of toxic eplosives may lead to:

- intoxication of the marine ecosystem
- entry into the marine foodchain
- health risk to humans

Monitoring and risk assessment required

future ocean
KIEL MARINE SCIENCES

NORTH SEA WRECKS
EUROPEAN UNION

DAM DEUTSCHE ALLIANZ MEERESFORSCHUNG

Gefördert vom
Bundesministerium für Bildung und Forschung

UDEMM Umweltmonitoring für die Delaboration von Munition im Meer

Umwelt Bundesamt

TATTOO

JPI OCEANS

Zukunft Meer
sea our future

SH Schleswig-Holstein
Der echte Norden

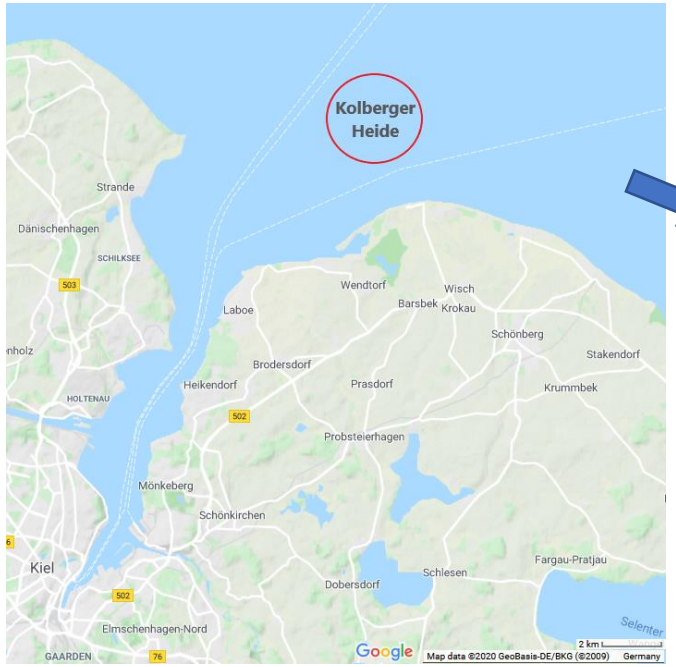
MELUND/ SH
Pilotmonitoring
Lübecker Bucht

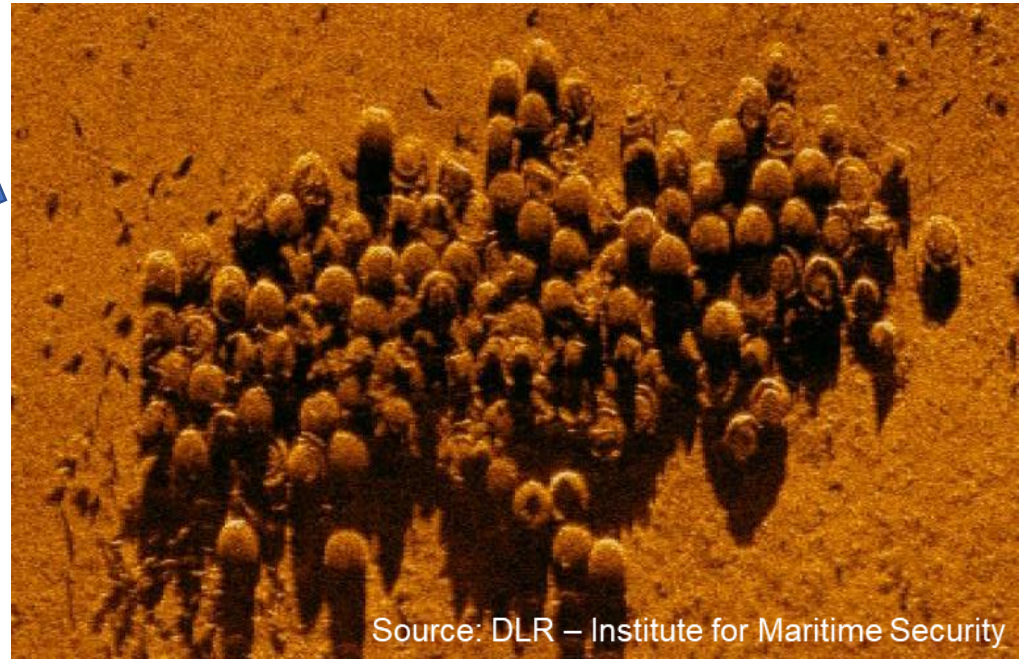
NATO OTAN S&T organization

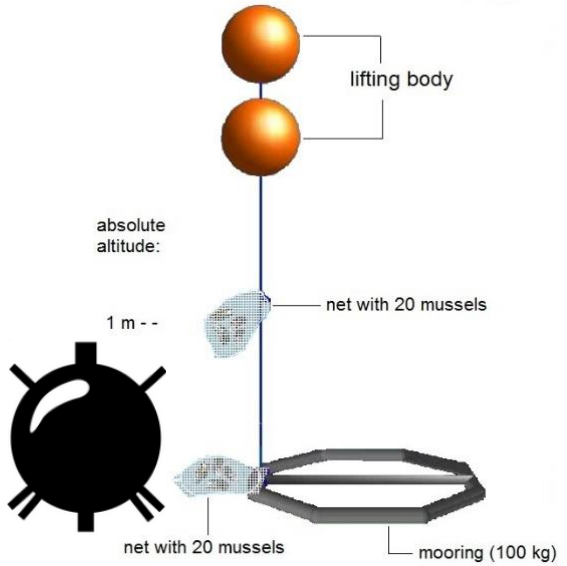
Biomonitoring by using blue mussels

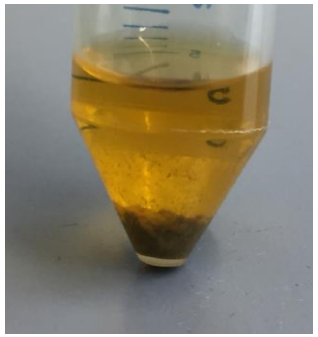
Our research approach

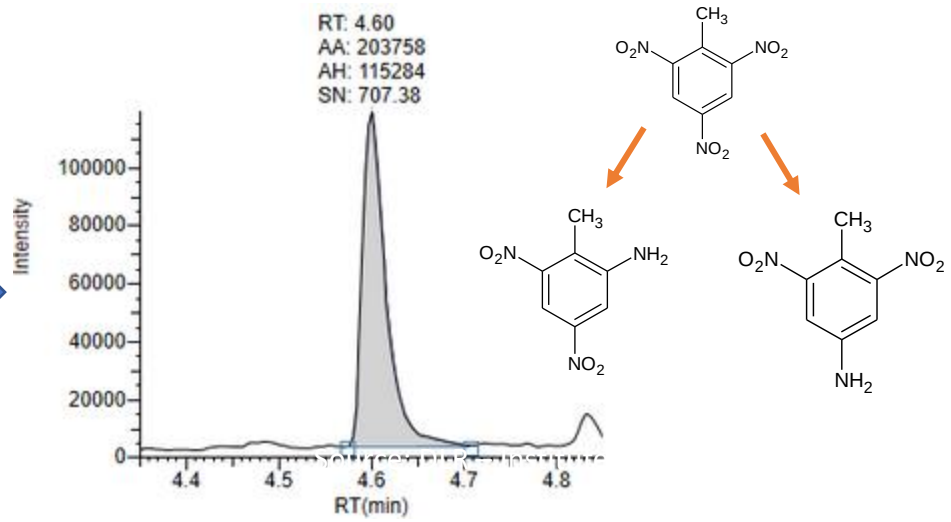
Toxikologie/Kiel
UNIVERSITÄTSKLINIKUM Schleswig-Holstein







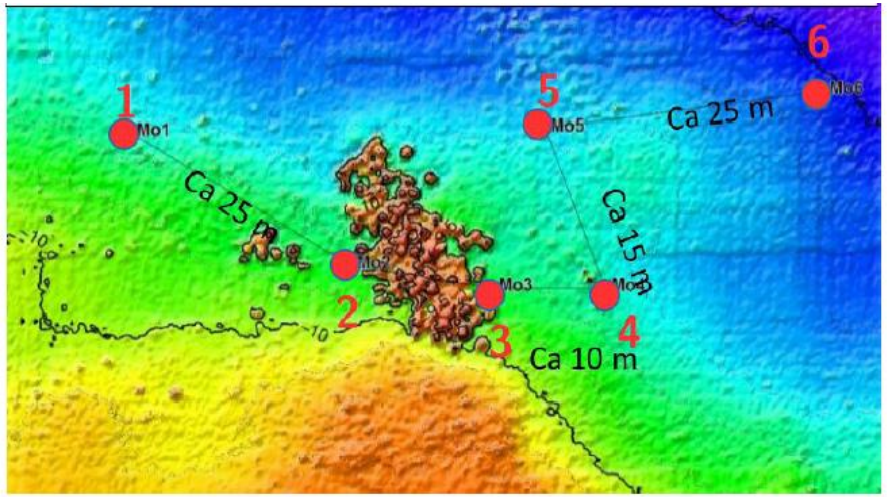




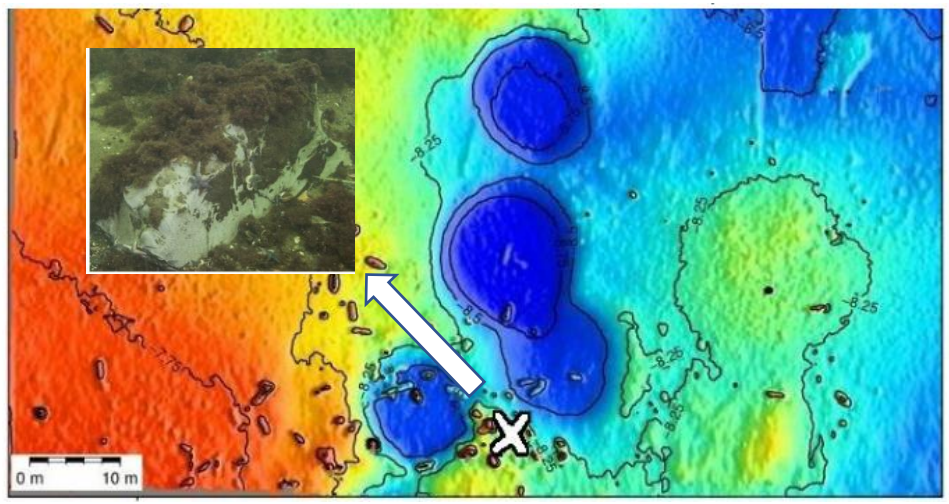
TNT and its metabolites in mussels

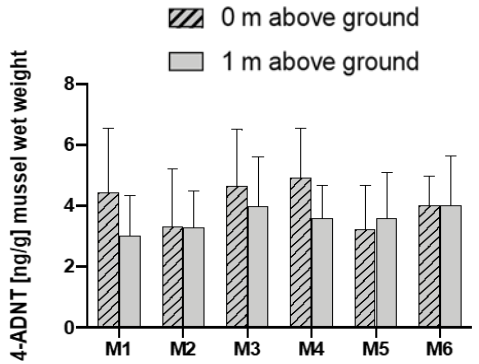
Toxikologie/Kiel
UNIVERSITÄTSKLINIKUM Schleswig-Holstein

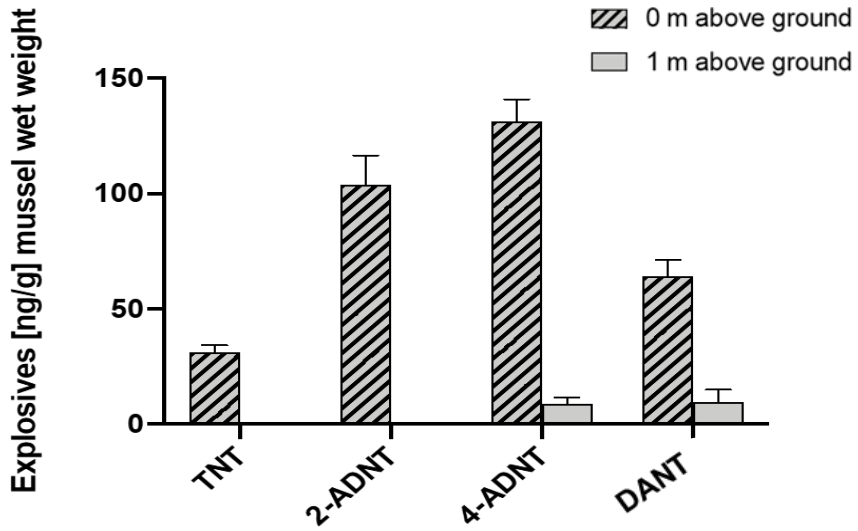
Mussels at the mine mount



Mussels at free lying TNT.



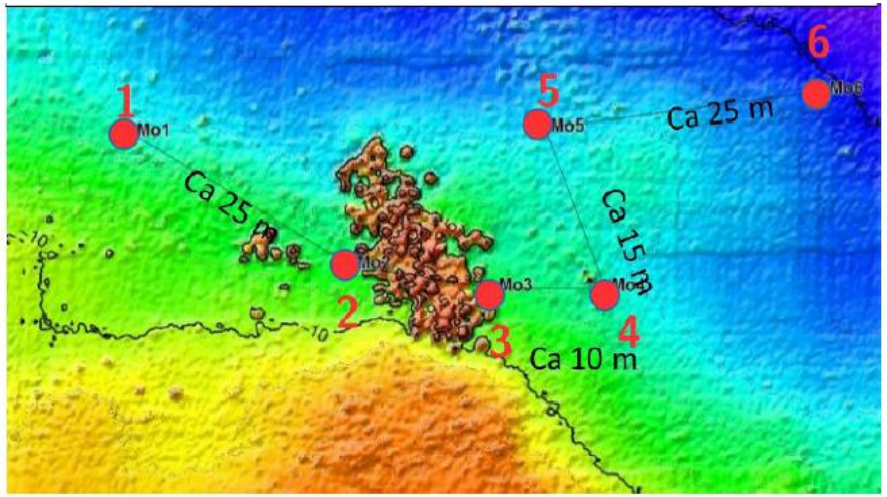




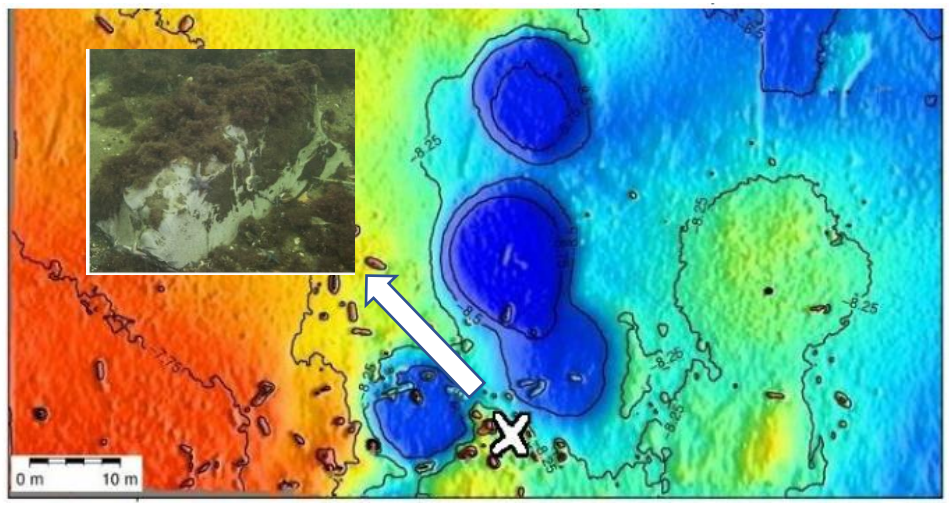
TNT and ist metabolites in mussels

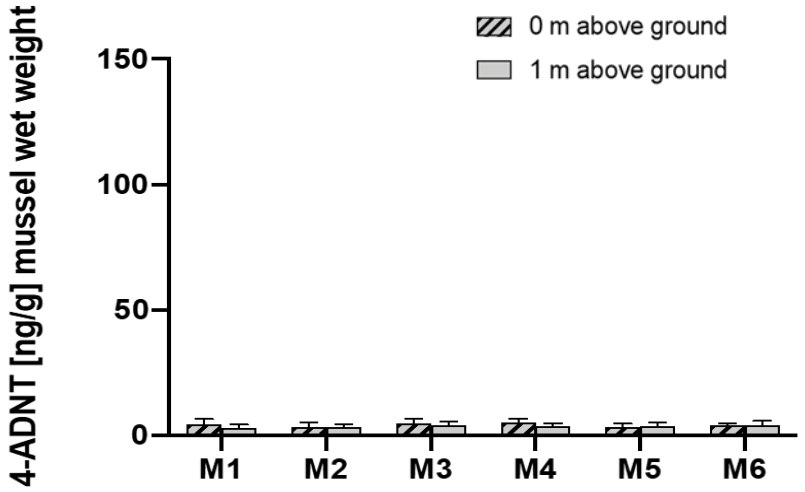
Toxikologie/Kiel
UNIVERSITÄTSKLINIKUM Schleswig-Holstein

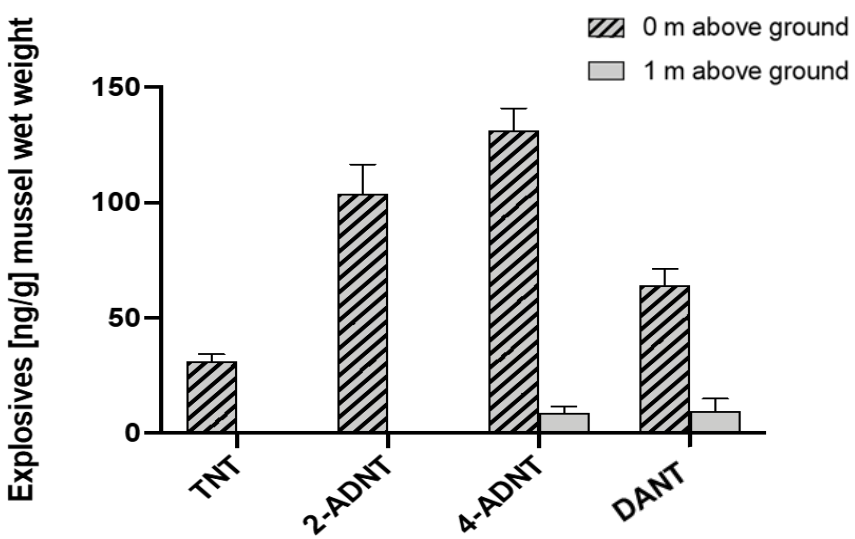
Mussels at the mine mount



Mussels at free lying TNT







Risk assessment for sea-dumped munitions

Toxikologie/Kiel
UNIVERSITÄTSKLINIKUM Schleswig-Holstein

First step required:

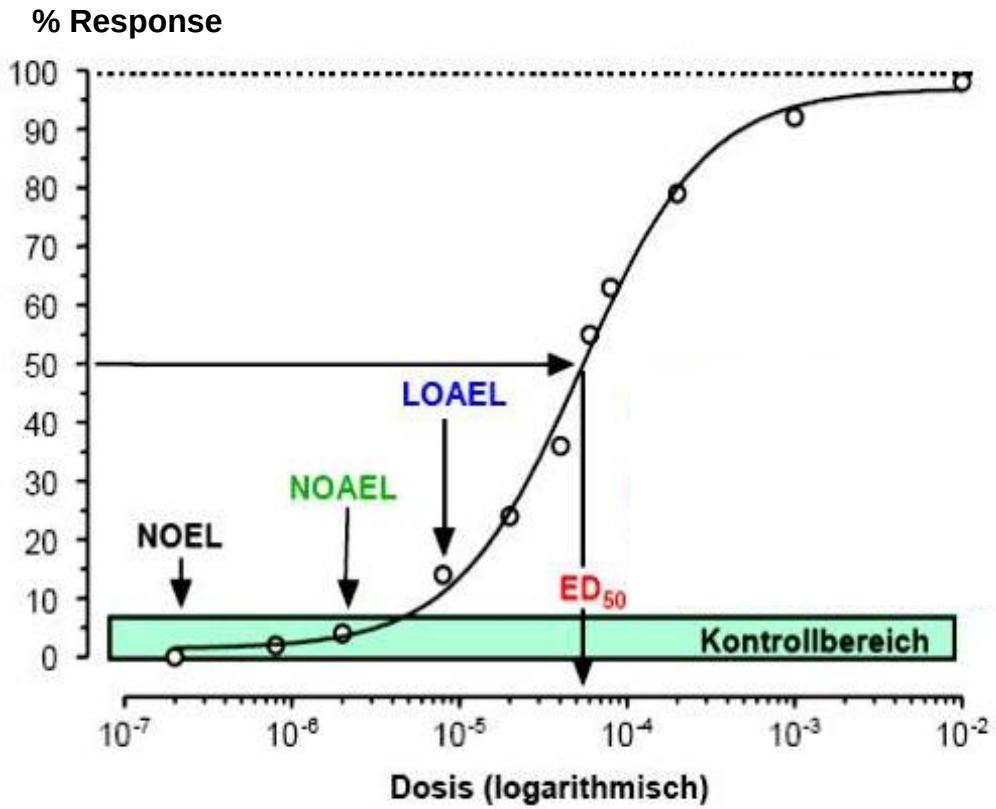
- Determination of the most sensitive endpoint (organotoxicity, immunotoxicity, cancerogenicity, reproduction toxicity, developmental toxicity, death)

For non-carcinogenic compounds:

- Dose-response calculation
- Setting of NOAEL*
  (* No Observed Adverse Effect Level)
- Safety factor: 10 x 10 = 100

For carcinogenic compounds:

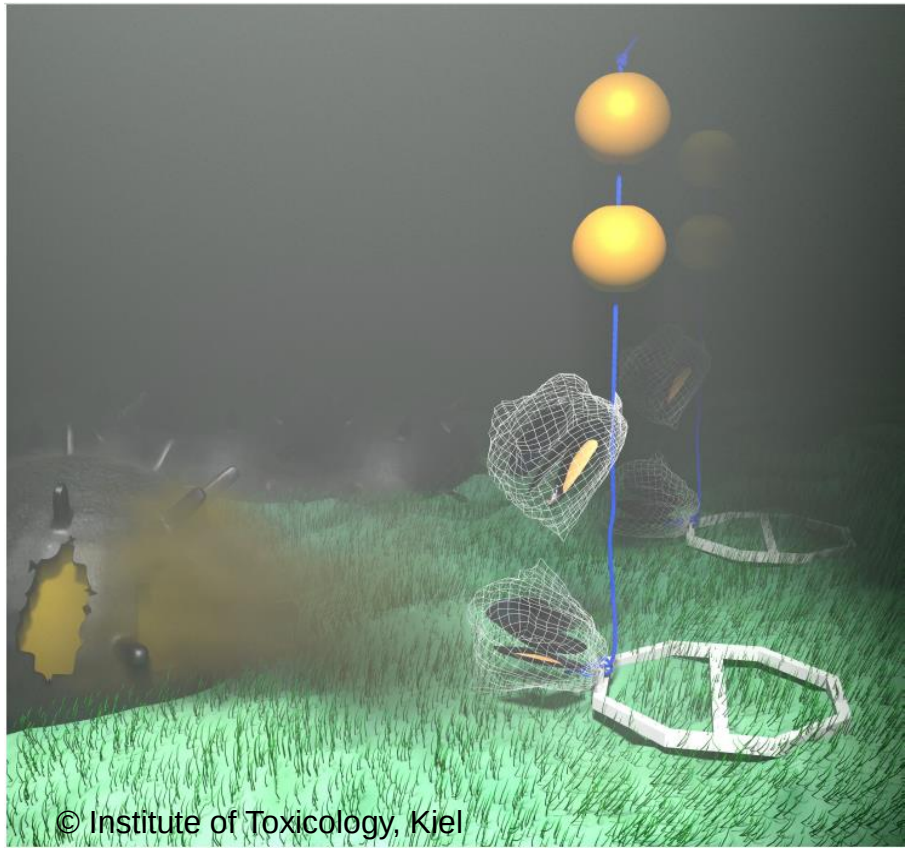
- No dose-response applicable
- Instead: BMDL, MOE
- Safety factor 10 x 10 x 100 = 10 000
  or 10 x 25 x 100 = 25 000



Risk for the human seafood consumer

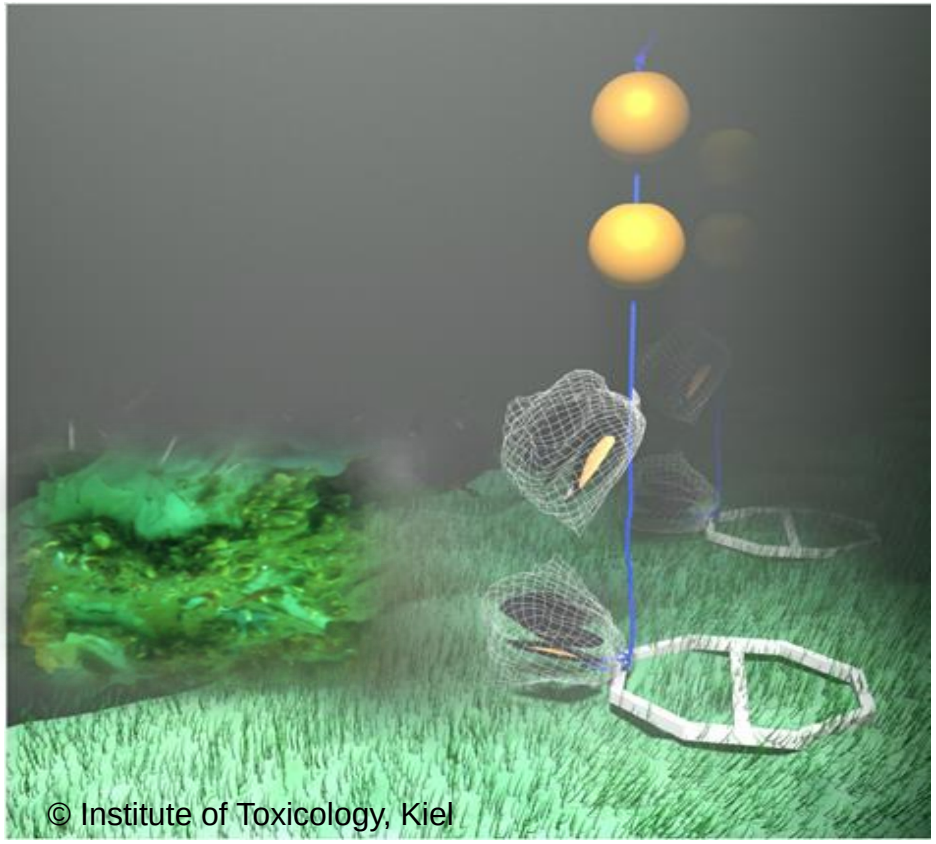
Toxikologie/Kiel
UNIVERSITÄTSKLINIKUM Schleswig-Holstein

close to corroding mines



- Mussels close to corroding mines can (still) be eaten.
- However, they show adverse health effects (oxidative stress).

at free-lying chunks of MCs after BiPs

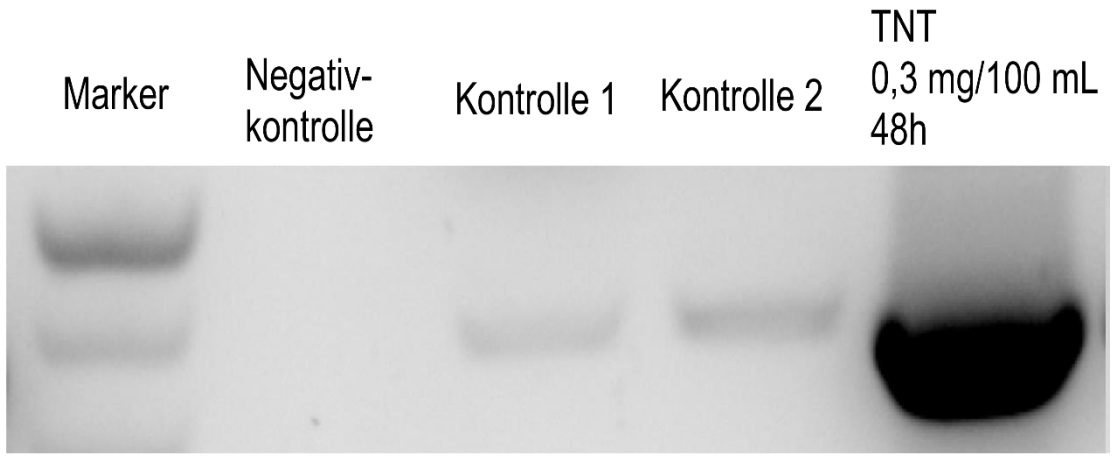


- Mussels at free-lying explosives contained 50 times higher levels of MCs.
- Consuming these mussels bears a carcinogenic risk for the consumer.

Induction of the CBR1 gene in *Daphnia magna* by **TNT**

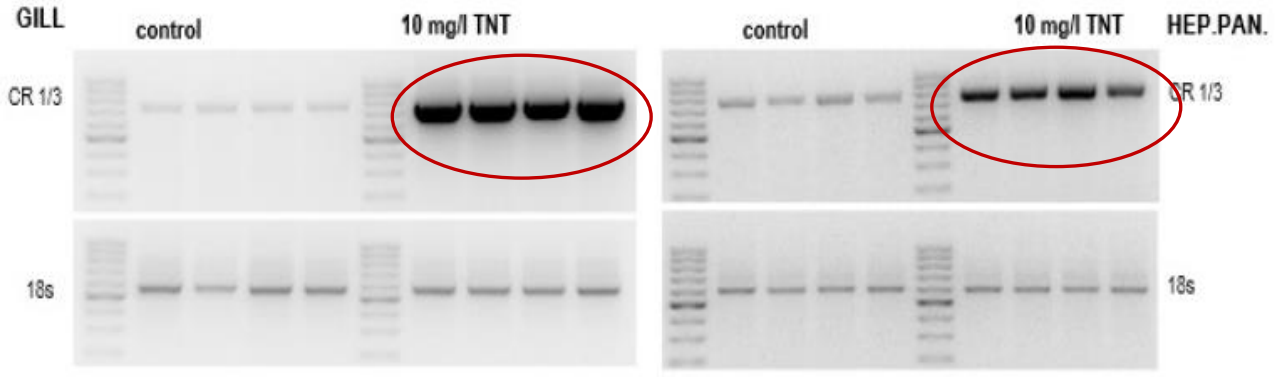
TNT
(Trinitrotoluene)

Semi-quantitative PCR:

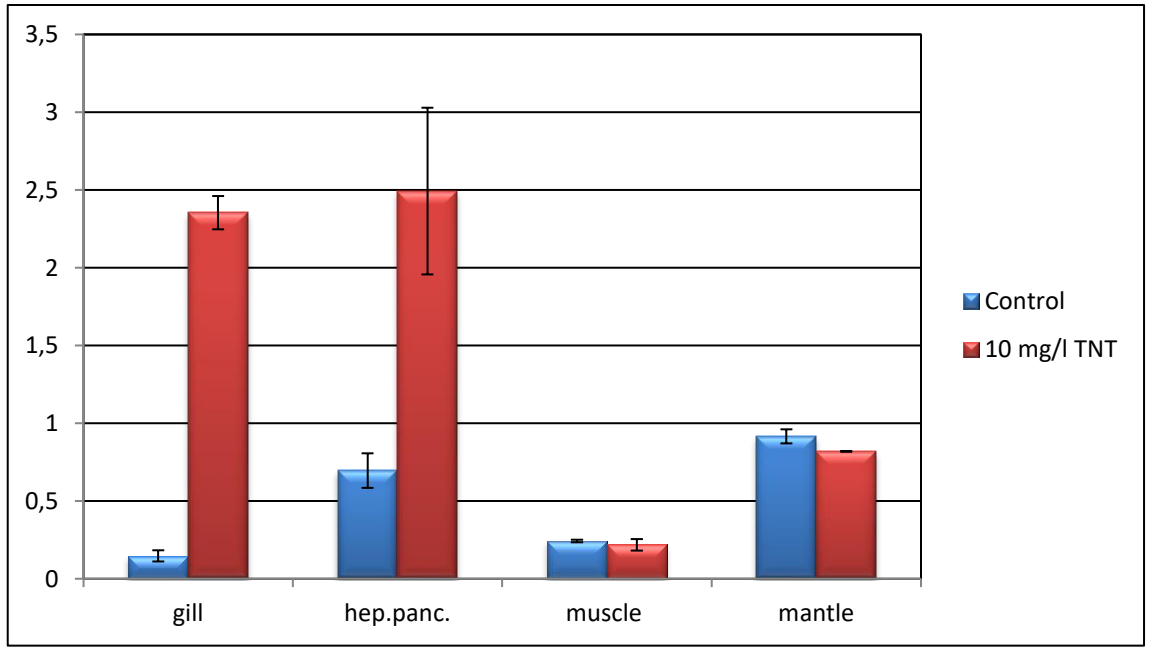


Oxidative stress marker

Induced expression of the carbonyl reductase gene in *Mytilus edulis* upon exposure to TNT



Oxidative stress marker

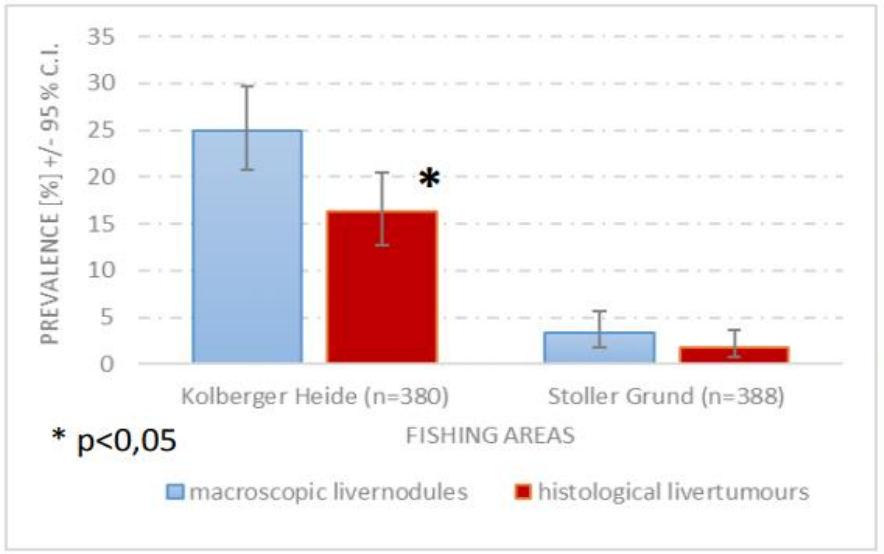


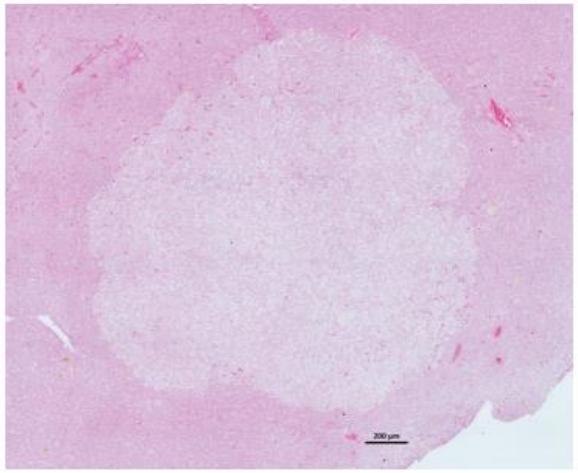
And what about fish ... ?

- Explosives were found in flatfish (dabs, plaice and flounder) near the Kolberger Heide dumping area.
- The explosives were detectable in the bile, but not in the muscle tissue (< 4 ng / g muscle).
- A toxicological risk assessment showed that there is (currently) no risk for humans as fish consumers.
- But the health of the fish was compromised: liver tumors were detected in 25%.

„Effect monitoring“ of TNT on fish:

Histological confirmation of macroscopic livertumors





North Sea wreck „SMS Ariadne“ - Fish Filet

4-ADNT ng/ml Bile
2-ADNT ng/ml Bile

Liver tumor

North Sea wreck „SMS Ariadne“ - Fish Filet

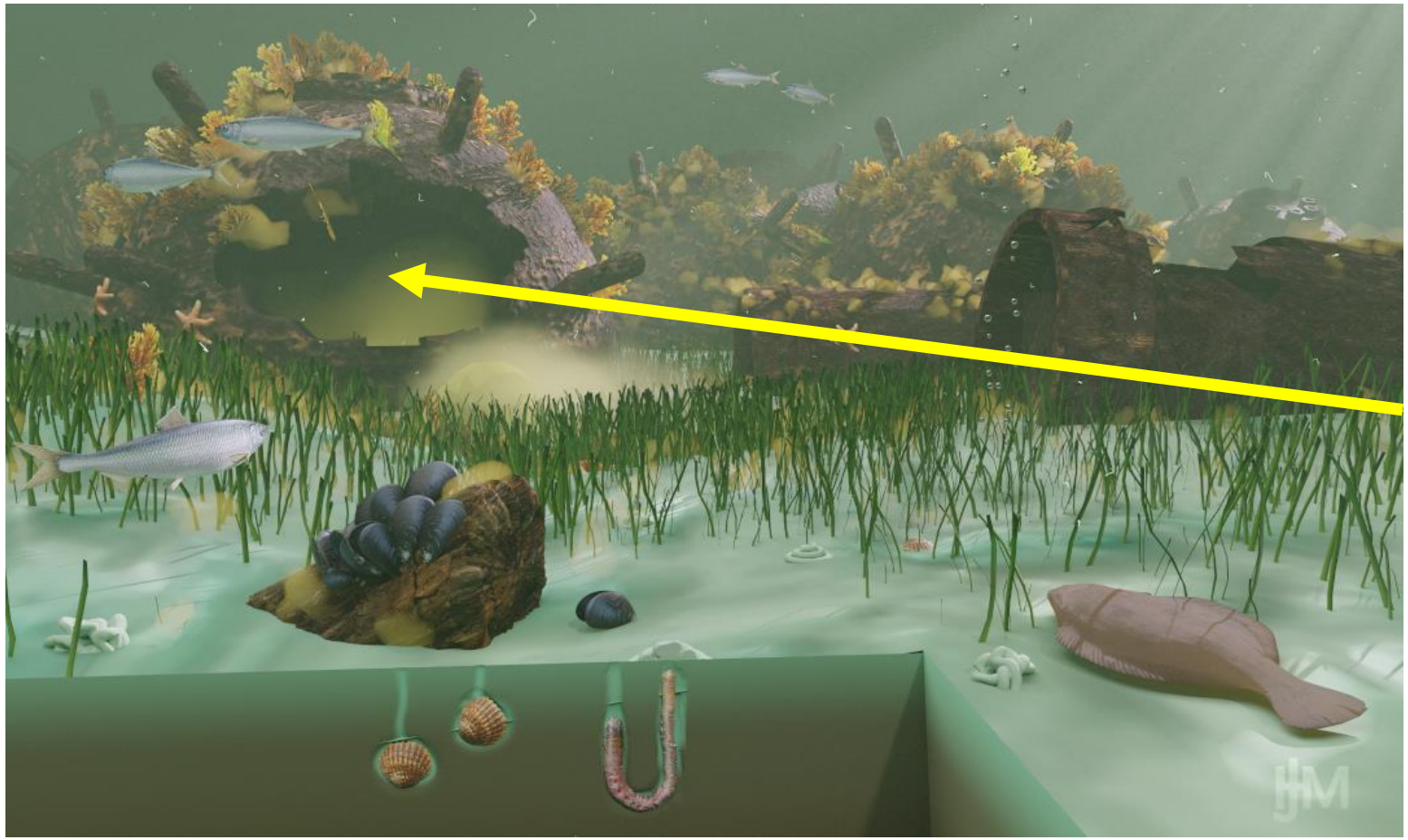
- TNT was found in fish living at the wreck “SMS Ariadne”.
- TNT was detectable in the filet (0.7 - 9.6 ng / g [d.w.]).
- A toxicological risk assessment showed that there is (currently) no risk for humans as fish consumers.
- But the health of the fish was compromised: liver tumors were detected in 60 %.

Acute toxicity determined in lab studies

Organism	Effect	TNT- Concentration
Copepods	strong increase in mortality	> 1.0 mg/L
	LC_{50}	2 mg/L
Shrimp	LC_{50}	0.26 mg/L
Mediterranean* mussels (larvae):	EC_{50}**	0.75 – 19.5 mg/L
Infant mussels	LC_{30}	1 – 1.5 mg /L
Polychaetes***	EC_{50} (oviposition)	1.8 mg/L
Fish (Flounder)		
Infant fish	All dead after 24 h	3 mg/L
Adults	LC_{50}	0.8 – 3.7 mg/L

**Mytilus galloprivincialis* ** Effect-Concentration ****Dinophilus gyrociliatus*

Munition dumping areas:
„nursery habitate“ for fish etc.?



TNT-concentration in free water directly at free-lying TNT:
3 mg/L

Fish (Flounder)	Aquarium Experiments	TNT
Infant fish	All dead after 24 h	3 mg/L
Adults	LC_{50}	0.8 – 3.7 mg/L

Conclusions

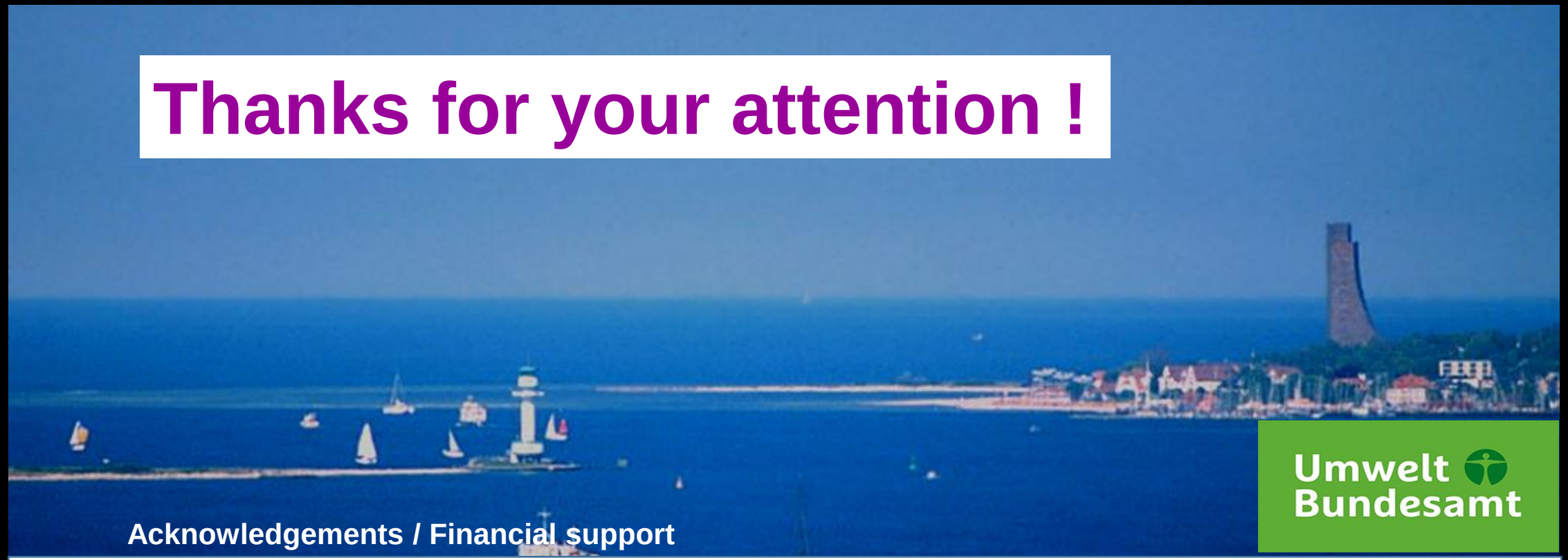
Toxikologie/Kiel
UNIVERSITÄTSKLINIKUM
Schleswig-Holstein

- Explosives from dumped munitions are toxic and carcinogenic.
- Currently, there is no acute risk for the human sea-food consumer, but ...
- Explosives endanger the marine ecology and diversity
- In principle, they may affect humans by entering the marine food chain.
- Further corrosion of the metal shells will increase the problem.
- Don‘t perform „blast in place“ operations, as these increase the problem.
- Recovery of dumped munition should begin immediately

University on the Baltic

Christian-Albrechts-Universität zu Kiel

UKSH Toxikologie/Kiel
UNIVERSITÄTSKLINIKUM Schleswig-Holstein



Thanks for your attention !

Umwelt Bundesamt

Acknowledgements / Financial support

Gefördert vom Bundesministerium für Bildung und Forschung

UDEMM Umweltmonitoring für die Delaboration von Munition im Meer

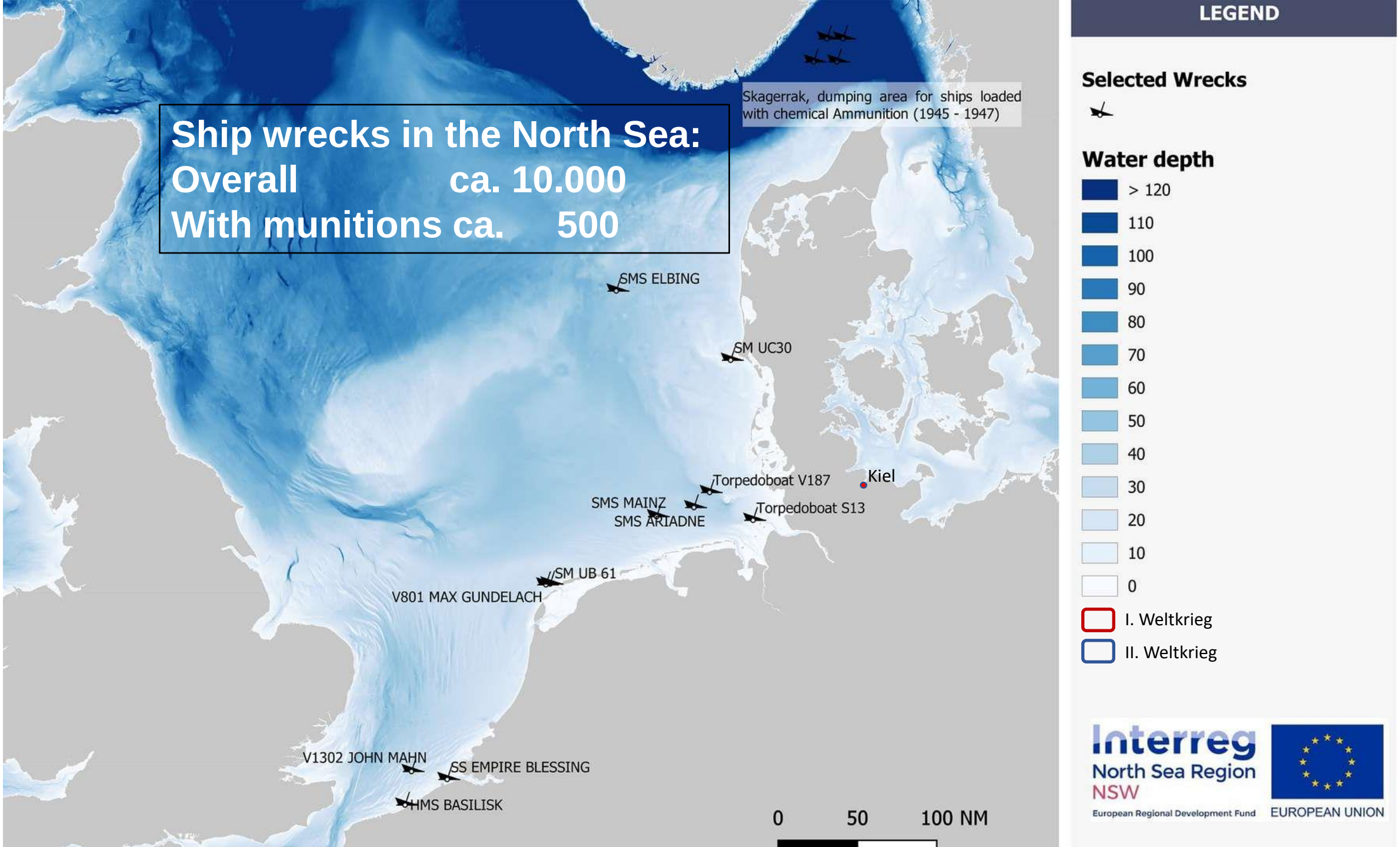
Zukunft Meer sea our future

SH Schleswig-Holstein Der echte Norden

NORTH SEA WRECKS

EUROPEAN UNION

MELUND/ SH
Pilotmonitoring
Lübecker Bucht

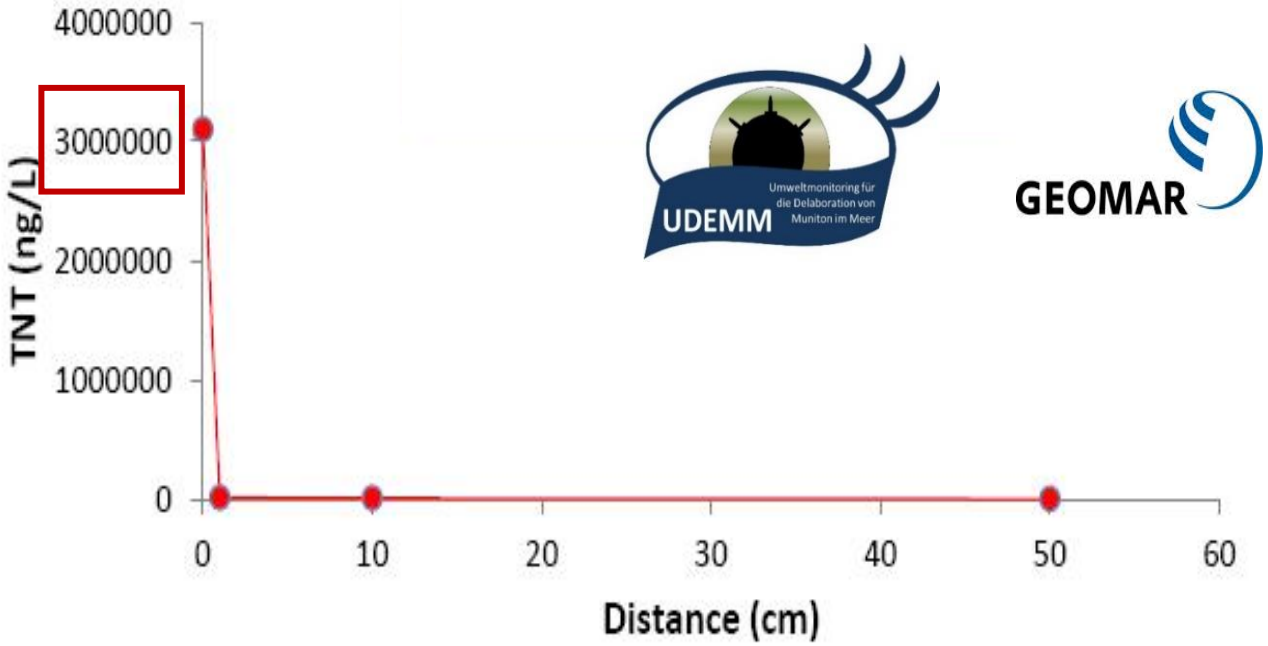

Ship wrecks in the North Sea:
Overall ca. 10.000
With munitions ca. 500
Skagerrak, dumping area for ships loaded with chemical Ammunition (1945 - 1947)
SMS ELBING
SM UC30
Torpedoboat V187
Kiel
SMS MAINZ
SMS ARIADNE
Torpedoboat S13
SM UB 61
V801 MAX GUNDELACH
V1302 JOHN MAHN
SS EMPIRE BLESSING
HMS BASILISK
0
50
100 NM
LEGEND
Selected Wrecks
Water depth
> 120
110
100
90
80
70
60
50
40
30
20
10
0
I. Weltkrieg
II. Weltkrieg
Interreg
North Sea Region
NSW
European Regional Development Fund
EUROPEAN UNION

Beside the risk of explosion or direct injury we have to face the problem with environmental ffects

Acute toxicity of TNT for fish

(lab study)

Fish (Flounder)		
Infant fish	All dead after 24 h	3 mg/L



UDEMM Umweltmonitoring für die Delaboration von Munition im Meer

GEOMAR

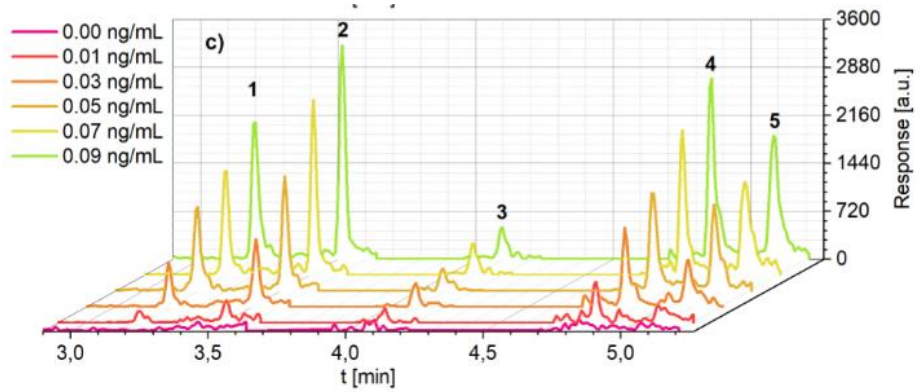
Improvement of the Limit of Detection (LoD)

toxics 16th March 2021 MDPI

Article

A Toolbox for the Determination of Nitroaromatic Explosives in Marine Water, Sediment, and Biota Samples on Femtogram Levels by GC-MS/MS

Tobias Hartwig Bünning, Jennifer Susanne Strehse, Ann Christin Hollmann, Tom Bötticher and Edmund Maser *



Instrumental:	
TNT	47 fg/µl
2-ADNT	11 fg/µl
4-ADNT	8 fg/µl
2,4-DNT	10 fg/µl
1,3-DNB	32 fg/µl

Water:	
TNT	90 pg/L
2-ADNT	60 pg/L
4-ADNT	60 pg/L
2,4-DNT	50 pg/L
1,3-DNB	200 pg/L

Sediment:	
TNT	50 pg/g
2-ADNT	30 pg/g
4-ADNT	30 pg/g
2,4-DNT	20 pg/g
1,3-DNB	100 pg/g

Mussel (Biota):	
TNT	200 pg/g
2-ADNT	40 pg/g
4-ADNT	50 pg/g
2,4-DNT	40 pg/g
1,3-DNB	30 pg/g

Bünning et al. Toxics 2021