Interreg Baltic Sea Region

EUROPEAN UNION
EUROPEAN REGIONAL DEVELOPMENT FUND

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Decision Aid for Marine Munitions

EU STRATEGY FOR THE BALTIC SEA REGION
FLAGSHIP

Bioeffects, impact assessment and toolbox

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Finnish Environment Institute

Final project meeting/Open Day
Bremerhaven, February 4, 2019

THÜNEN SYKE AWI UNIVERSITY OF HELSINKI VERIFIN FINNISH INSTITUTE FOR VERIFICATION OF THE CHEMICAL WEAPONS CONVENTION FFI IBPAN

The Issue

Are dumped war materials causing harm to the Baltic Sea ecosystem?

- munitions containing chemical warfare agents (CWA)
- conventional munitions containing toxic explosives (e.g., TNT, RDX, HMX)
- **toxicity** (effect thresholds)
- exposure → **biological effects on local biota**
- evidence of exposure
  - **bioaccumulation** (parent compounds, metabolites/degradation products)
  - **effects at different biological levels**
    - ✓ molecular/biochemical
    - ✓ cellular
    - ✓ tissue (pathology)
    - ✓ physiology
    - ✓ reproduction
    - ✓ behaviour

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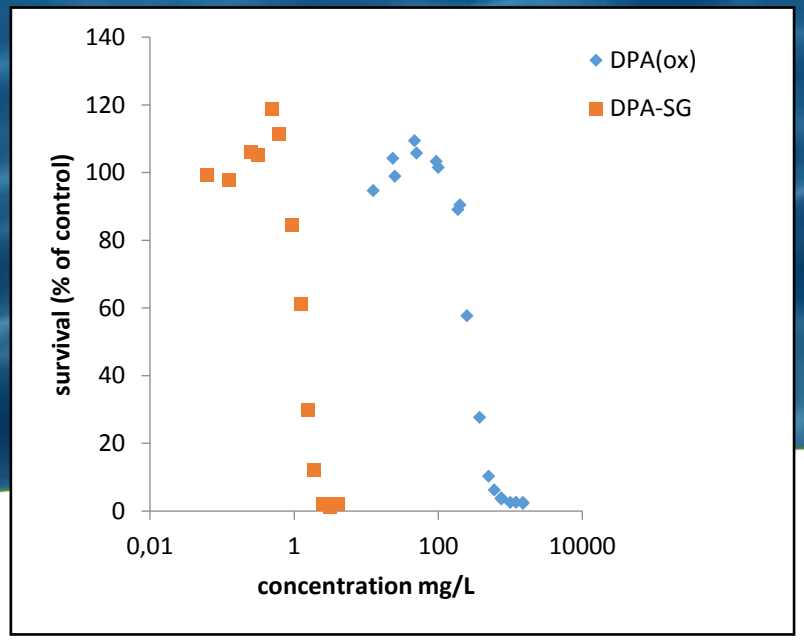
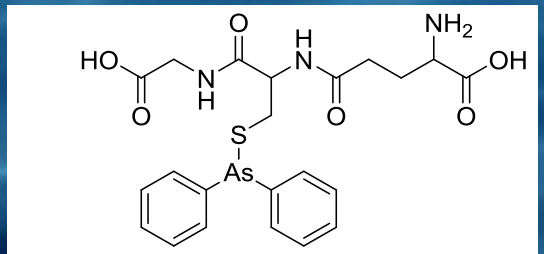
Toxicity threshold studies

Toxicity of CWAs: oxidized form and metabolite of Clark I/II

- *in vitro* studies with fish hepatocytes showed that DPA[ox] forms a glutathione conjugate (DPA-SG)
- the main metabolite two orders of magnitude toxic than the DPA[ox] itself
- other novel metabolites of DPA[ox] were also identified using high resolution mass spectrometry





DPA-SG, glutathione conjugate of DPA[ox]

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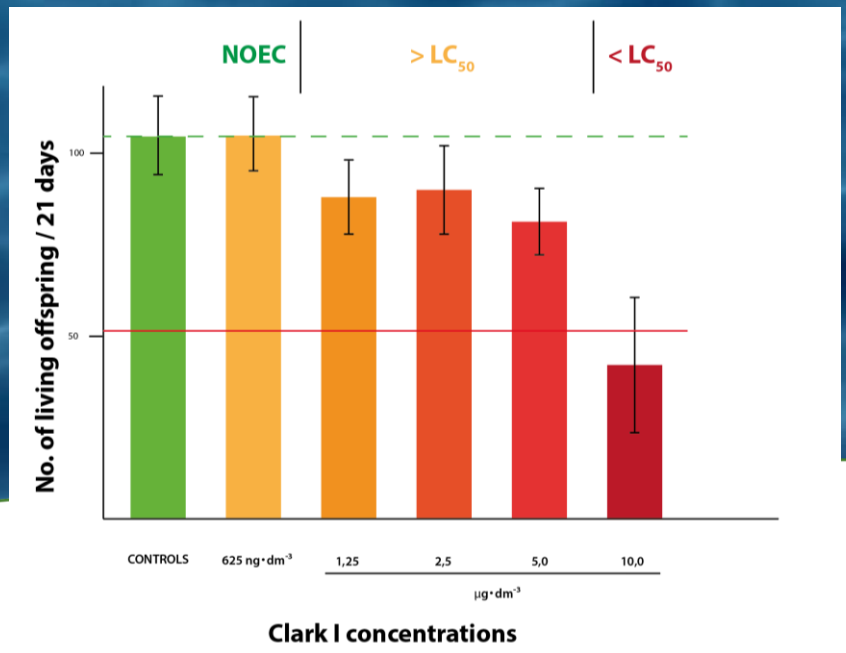
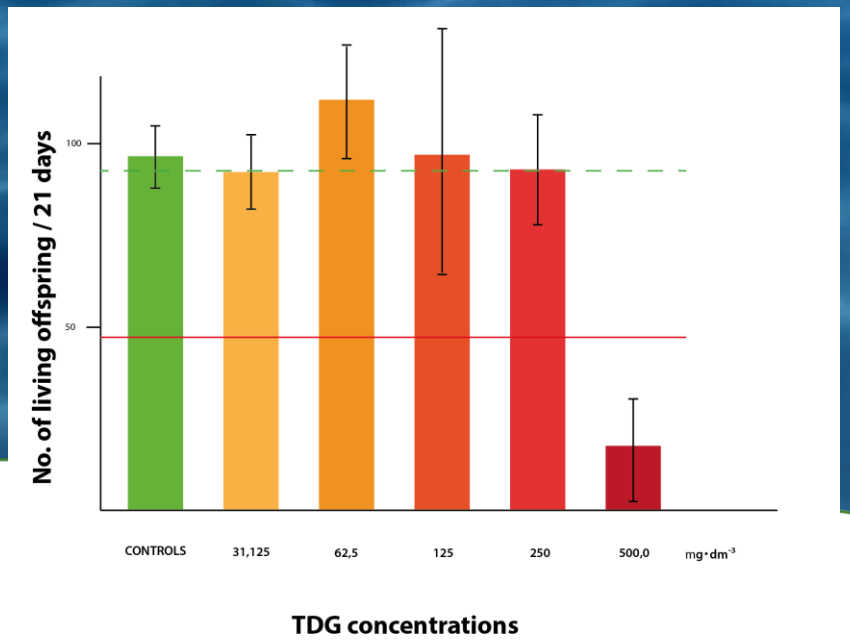
Toxicity threshold studies

Toxicity of CWAs: Clark I and thiodiglycol (TDG)

- 21-day reproduction test with the water flea (*Daphnia*)
- **Clark I** toxic at environmentally realistic concentrations (NOEC 625 ng l^{-1})
- **TDG (mustard gas hydrolysation product)** toxic threshold very high (250-500 mg l^{-1})

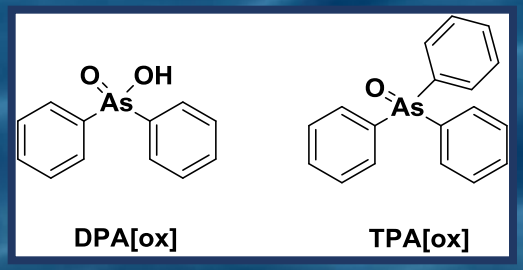




Bioaccumulation

CWAs in biota

- sampling in Bornholm, Måseskär and Skagerrak dumpsites (175 individuals in total)
- trace amounts of phenylarsenic CWAs were detected from marine biota samples for the first time
    - 25 % of analysed muscle tissue samples contained CWAs



- chemicals were analysed as their oxidation forms
  → total CWAs concentrations in marine biota remain still unknown

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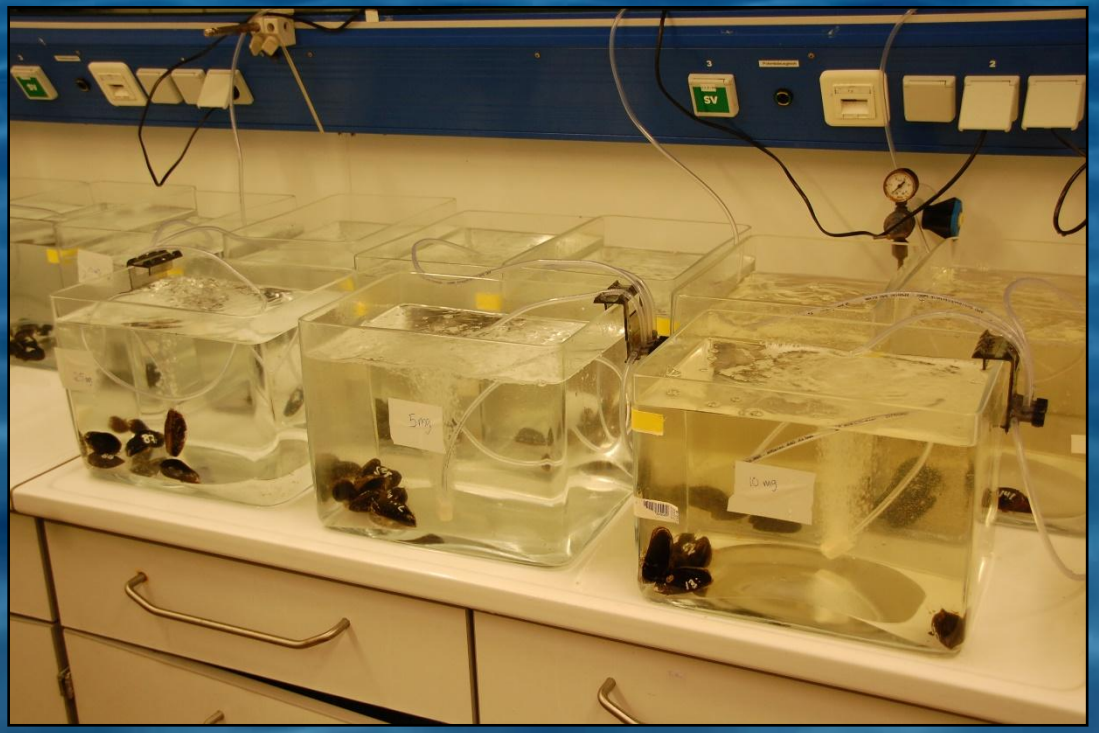
Bioeffects

Laboratory exposure of mussels to TNT

Acute (96 h) and chronic (21 d) laboratory toxicity tests



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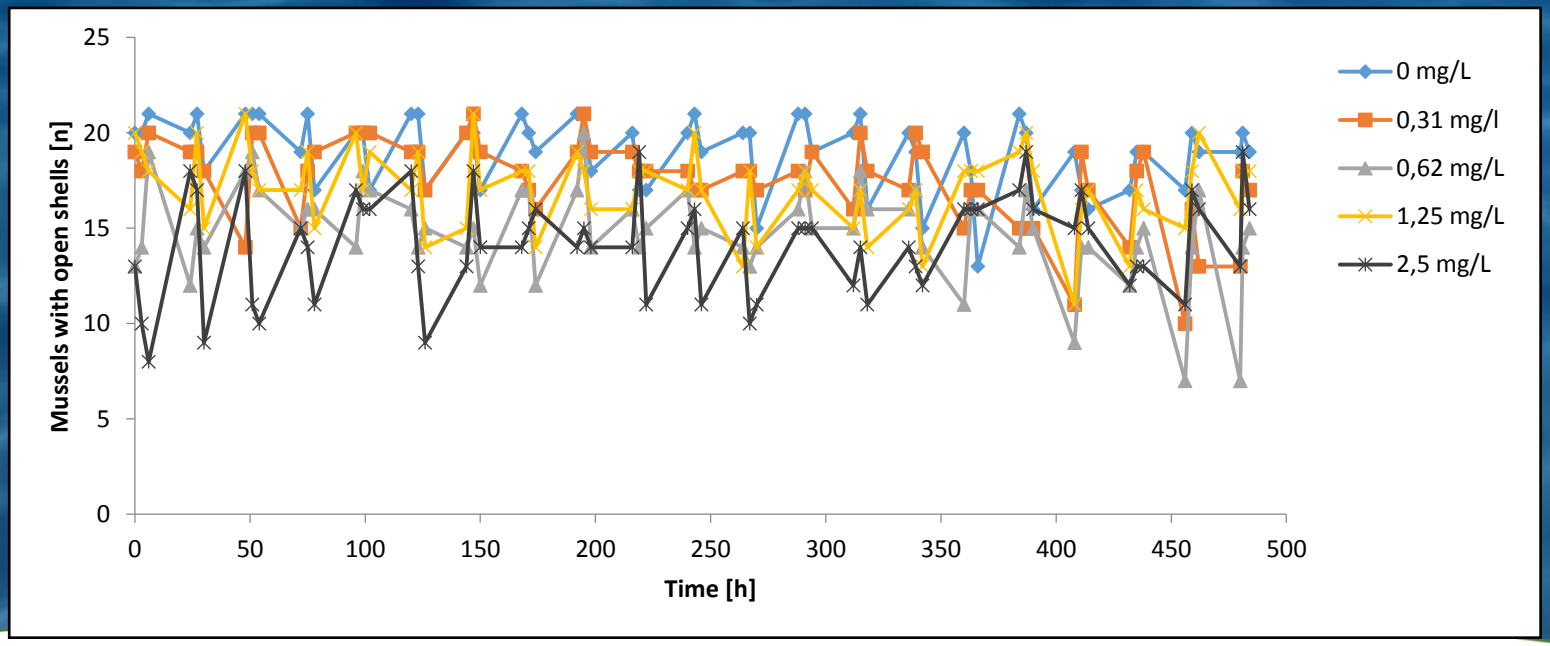
Bioeffects

Laboratory exposure of mussels to TNT

21-day experiment

Shell closure
(behavioural response)



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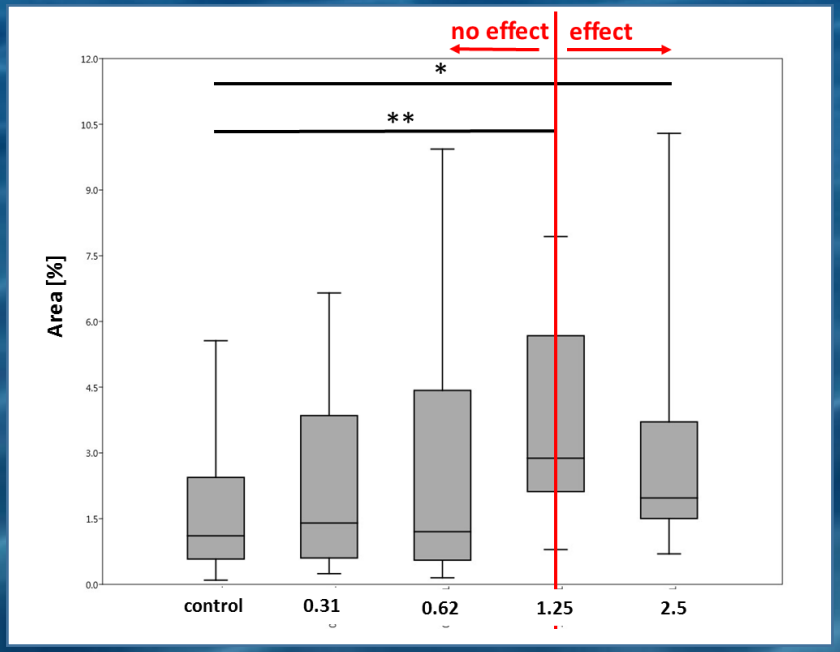
Contact: Matthias.Brenner@awi.de

Bioeffects

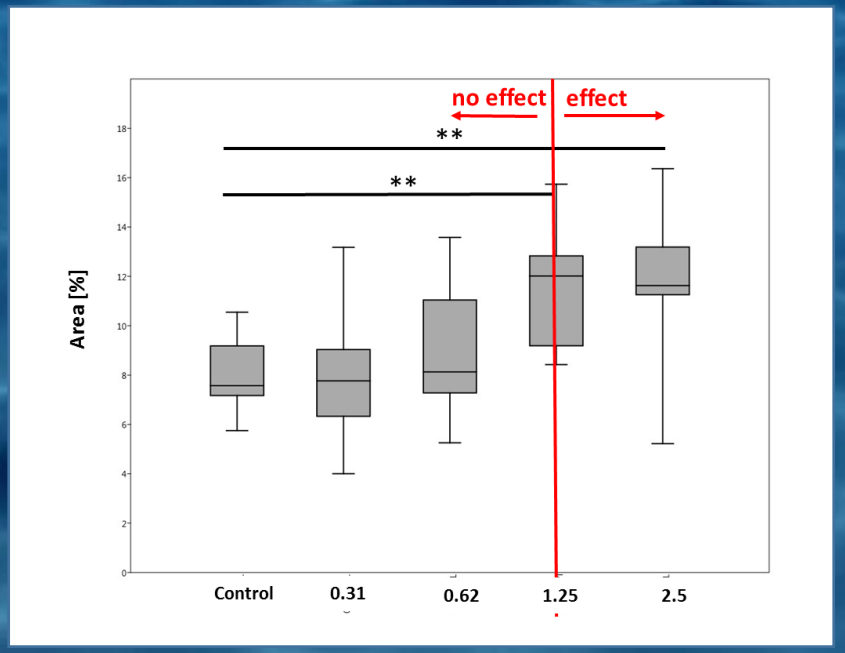
Laboratory exposure of mussels to TNT

21 day exposure

Lipofuscin accumulation
(metabolic end product of peroxidation processes)



Neutral lipid accumulation
(connected to exposure to organic pollutants)



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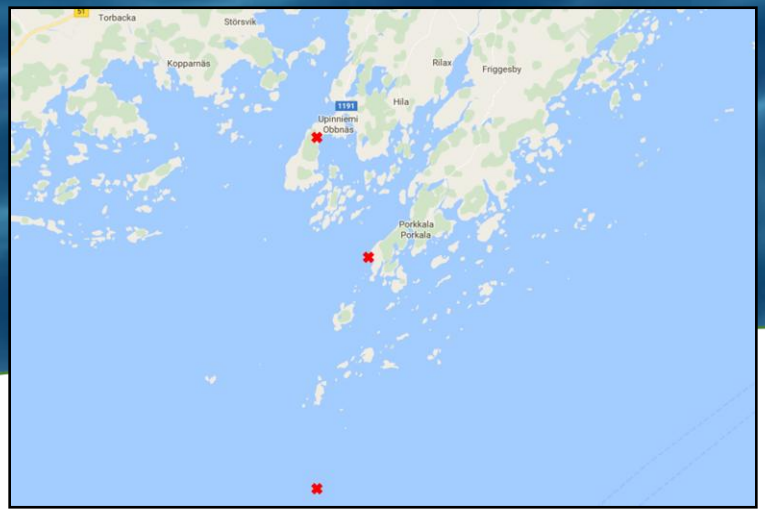
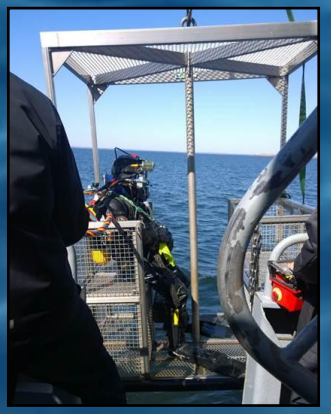
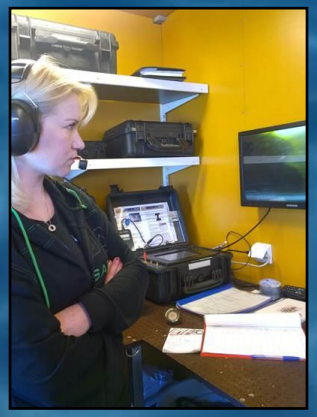
Bioeffects

Field studies: field-collected and transplanted mussels in target areas

- WWII wreck “M451“ in the Gulf of Finland
- Finnish Navy divers collected mussels growing on the wreck and on top of the depth charges before the deactivation operation
- reference samples from a nearby coastal area







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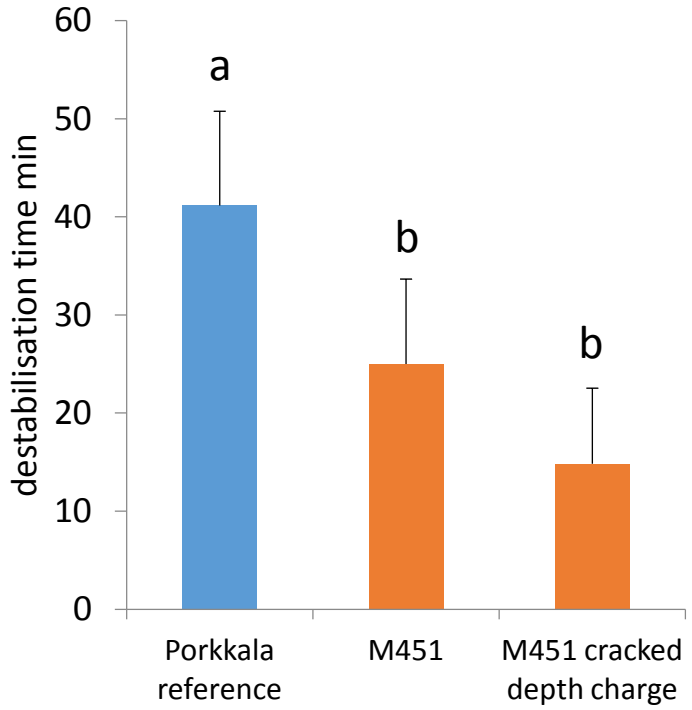
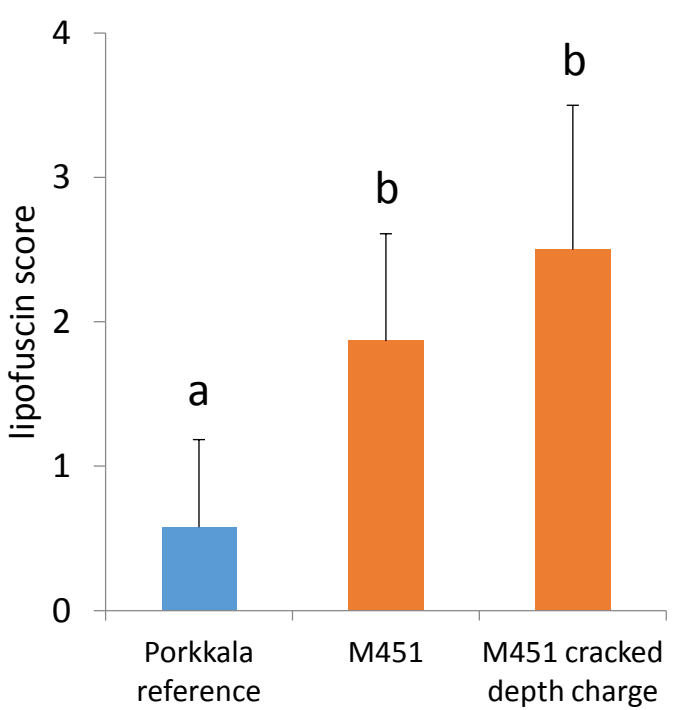
Bioeffects

Field studies: field-collected and transplanted mussels in target areas

Lysosomal membrane stability
(cytotoxicity, general stress)



Lipofuscin accumulation
(metabolic end product of peroxidation processes)



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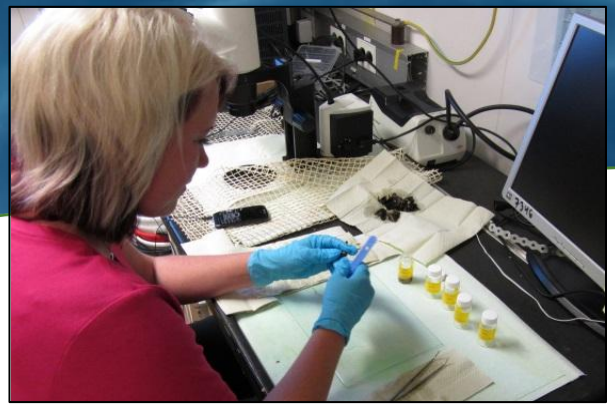
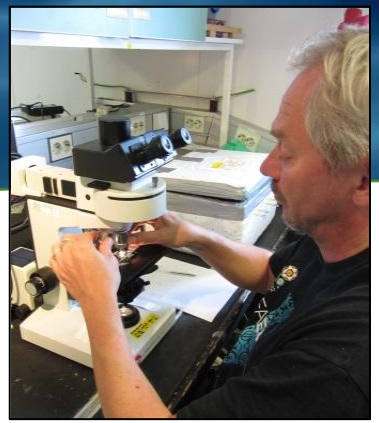
Field studies: field-collected and transplanted mussels in target areas





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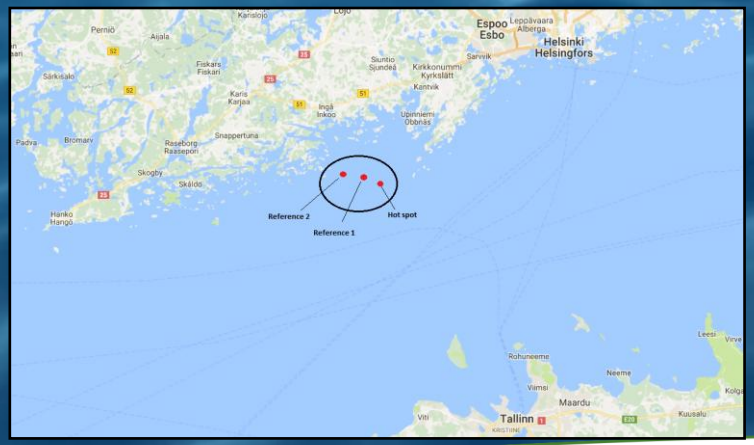
Bioeffects

Field studies: field-collected and transplanted mussels in target areas

Mussel caging experiment

- a large (ca. 350 kg) sea mine in the Gulf of Finland
- one cage close to the mine (20 m) and two reference cages 1 and 2 nm from the “hot spot”



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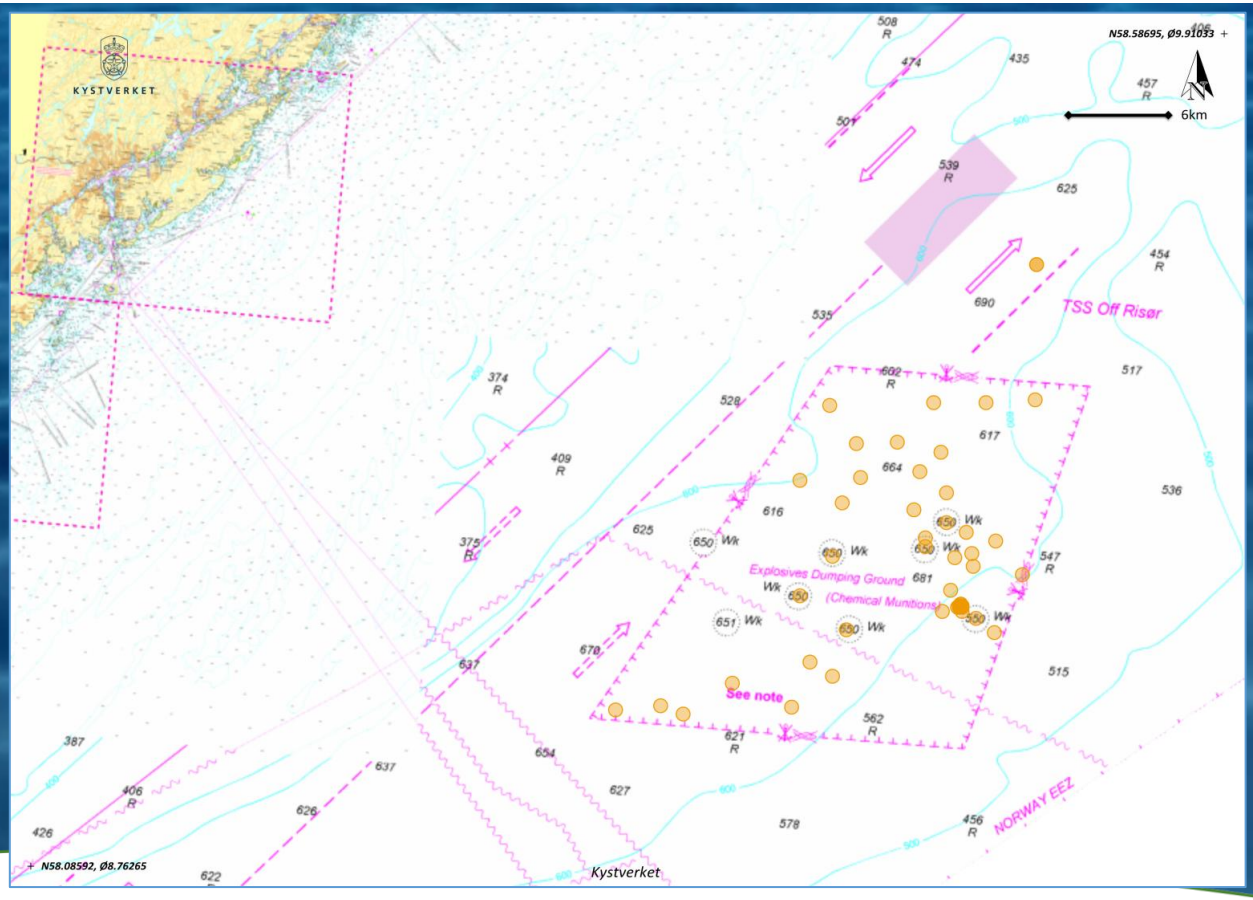
Bioeffects

Field studies: hagfish in Skagerrak near a CWA dumpsite



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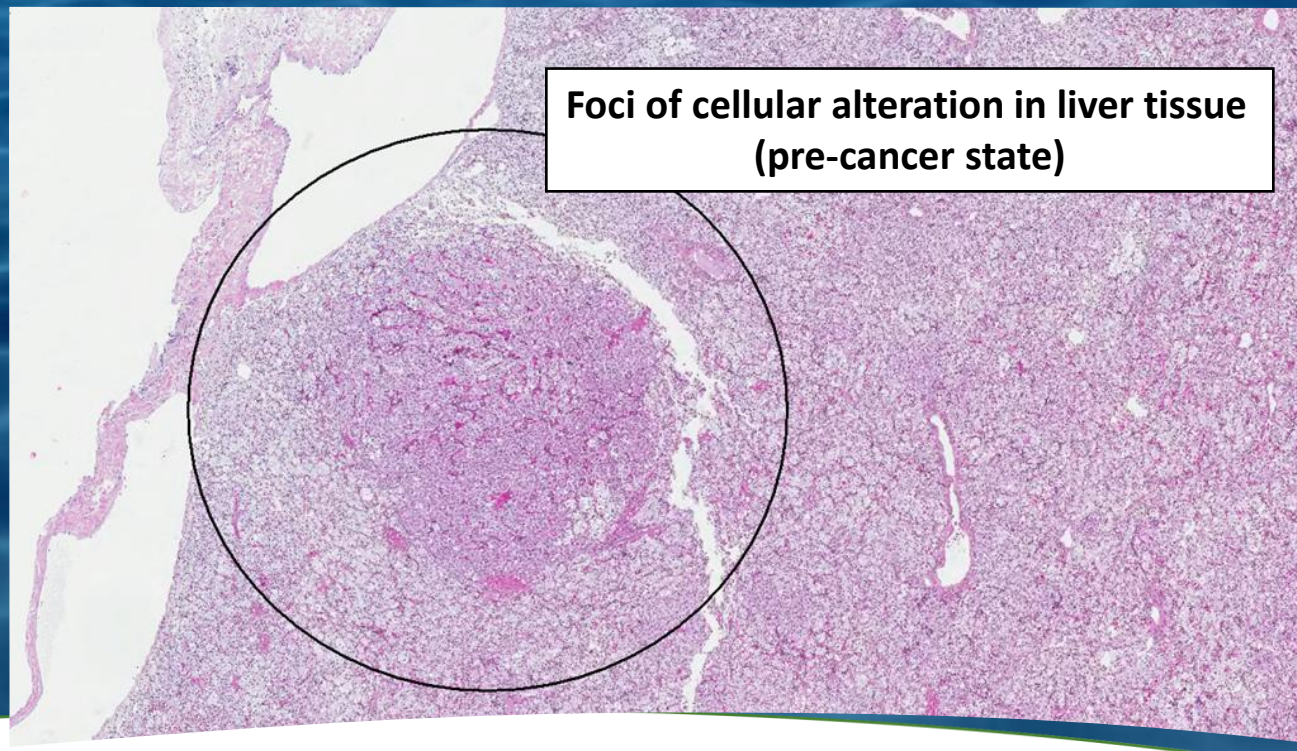

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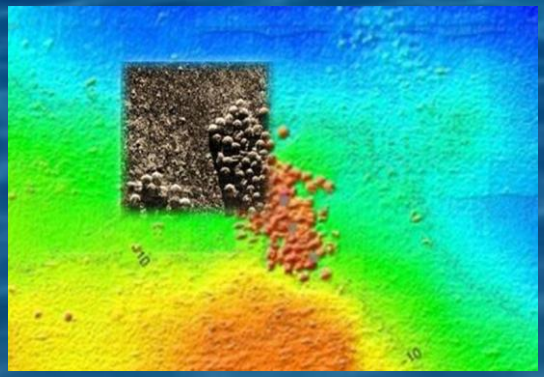
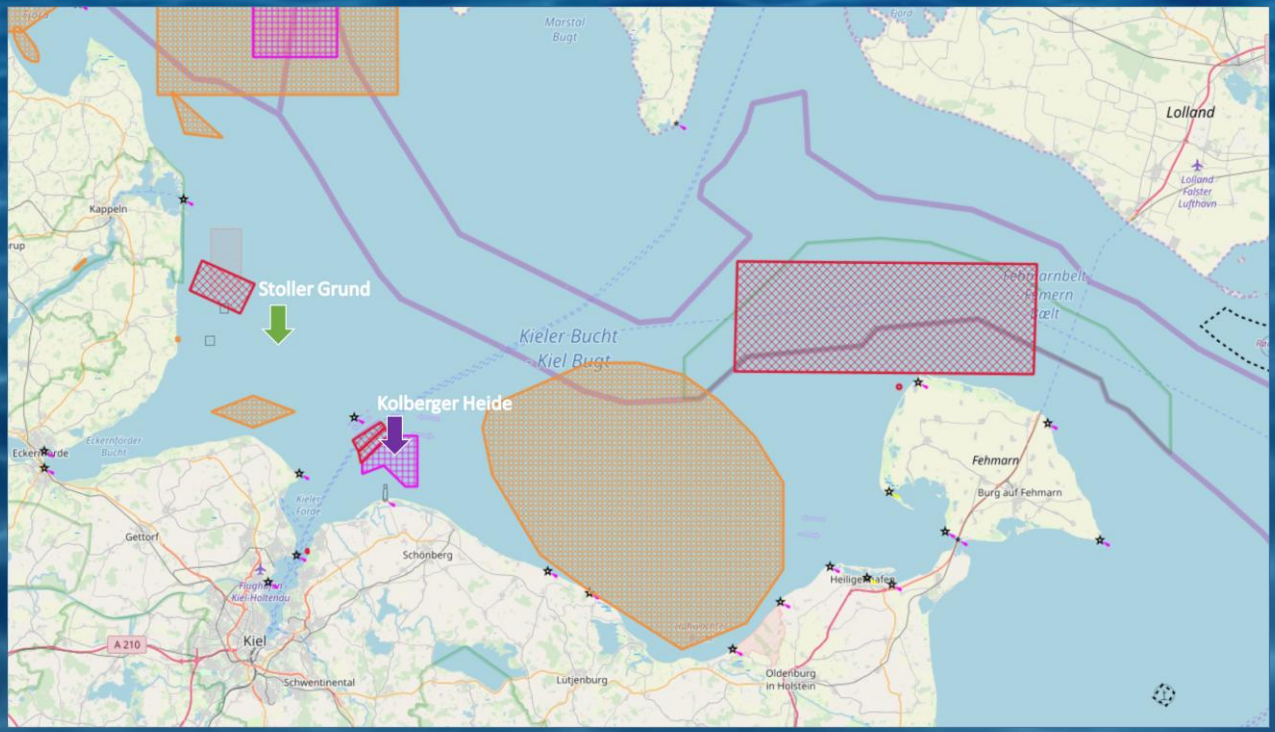
Bioeffects

Field studies: flatfish in Kolberger Heide sea mine dumpsite





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Bioeffects

Field studies: flatfish in Kolberger Heide sea mine dumpsite

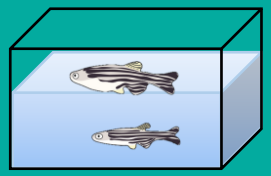
Metabolism of explosives in-vitro

Detection of metabolites in wild fish

Laboratory

Field

Genotoxicity of explosives and metabolites



Identification of malignant liver tumors in wild fish

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The Toolbox

From suspicion to decision

The case

- For a given geographical maritime area there is suspicion that dumping of munitions took place in the past.

The concern

- Do these munitions and their toxic chemical components pose a threat to marine organisms in their habitat?

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The Toolbox

From suspicion to decision

The questions

- munitions present?
- hazardous substances released to the environment?
- biological effects?
- overall, a reason of concern?
- actions recommended?

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The Toolbox

From suspicion to decision

The solution

- apply the DAIMON Toolbox because it provides
  - concept & strategy
  - selection of appropriate methods
  - method description (fact sheets)

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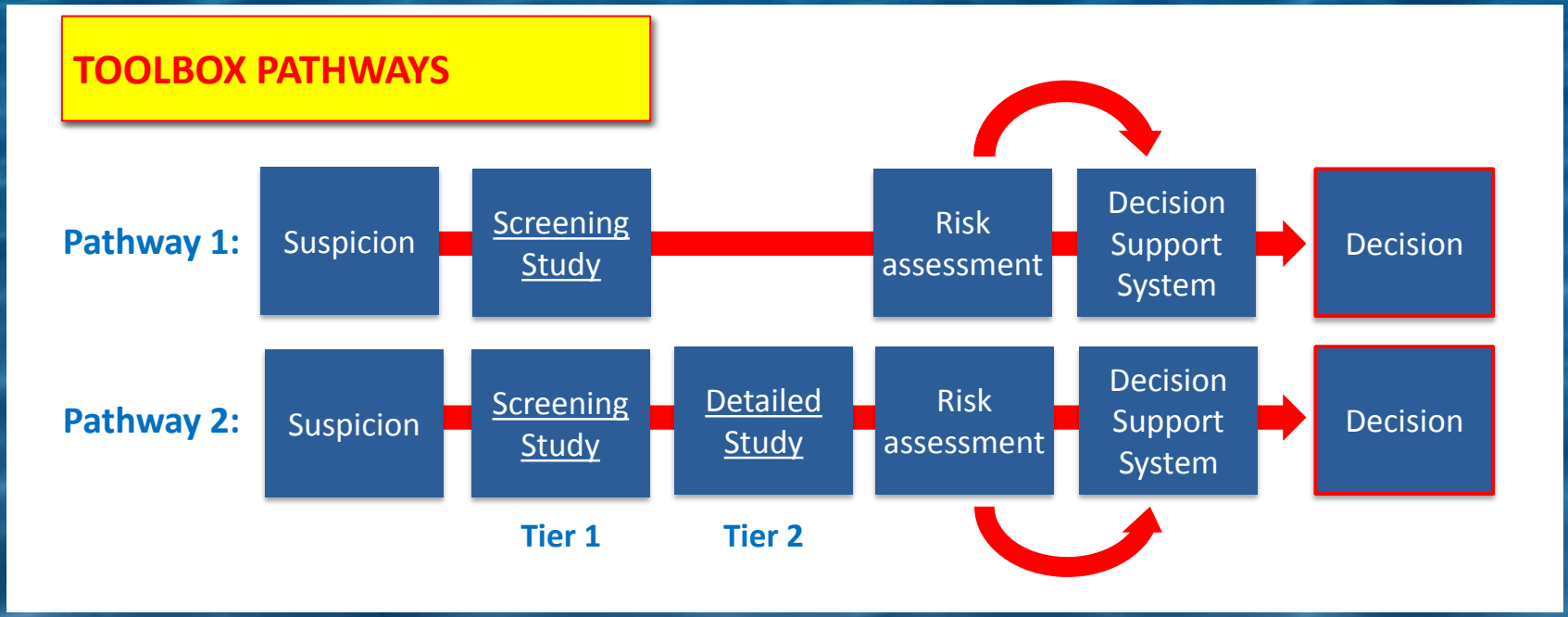
The Toolbox

From suspicion to decision



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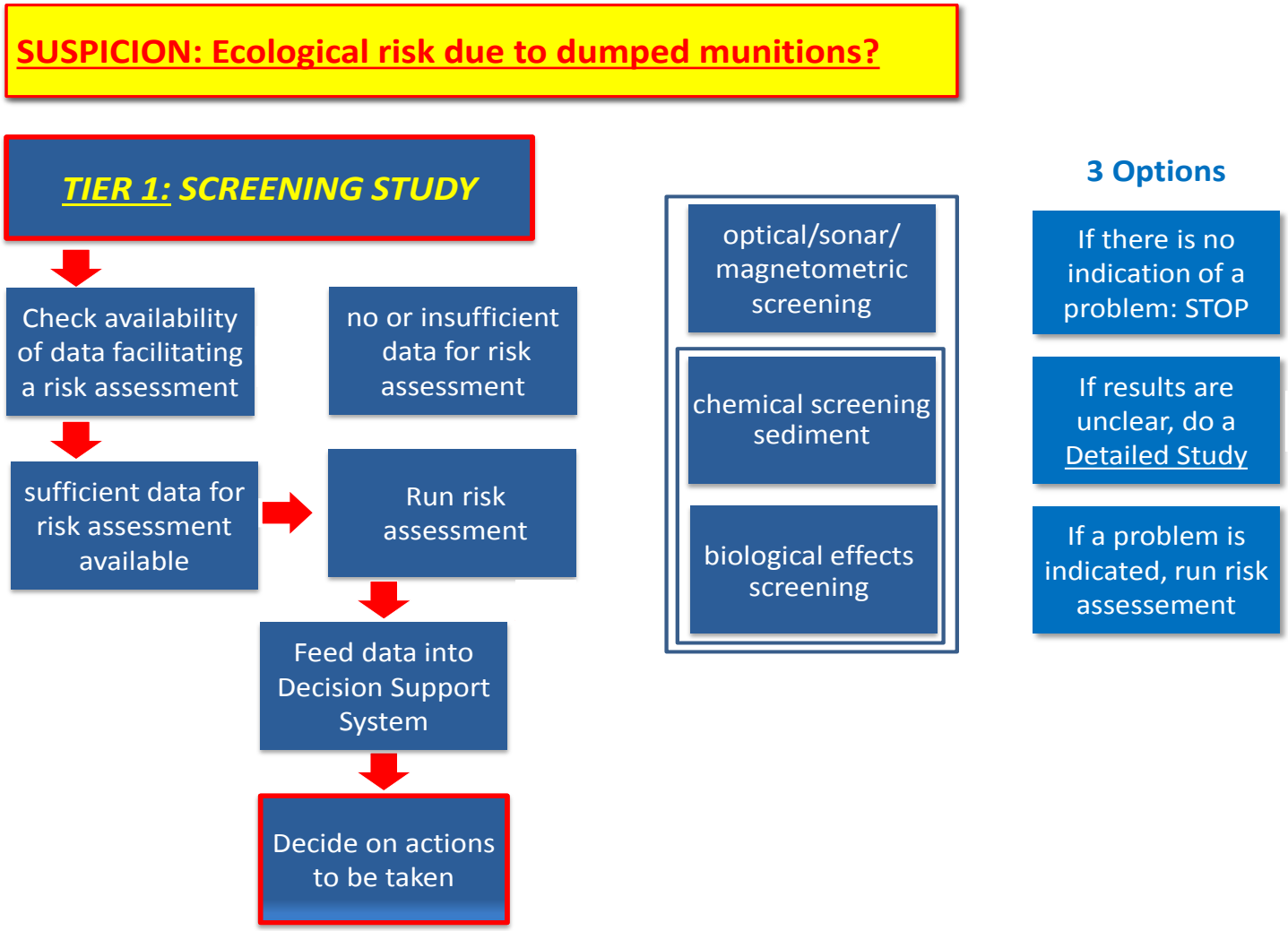
From suspicion to decision



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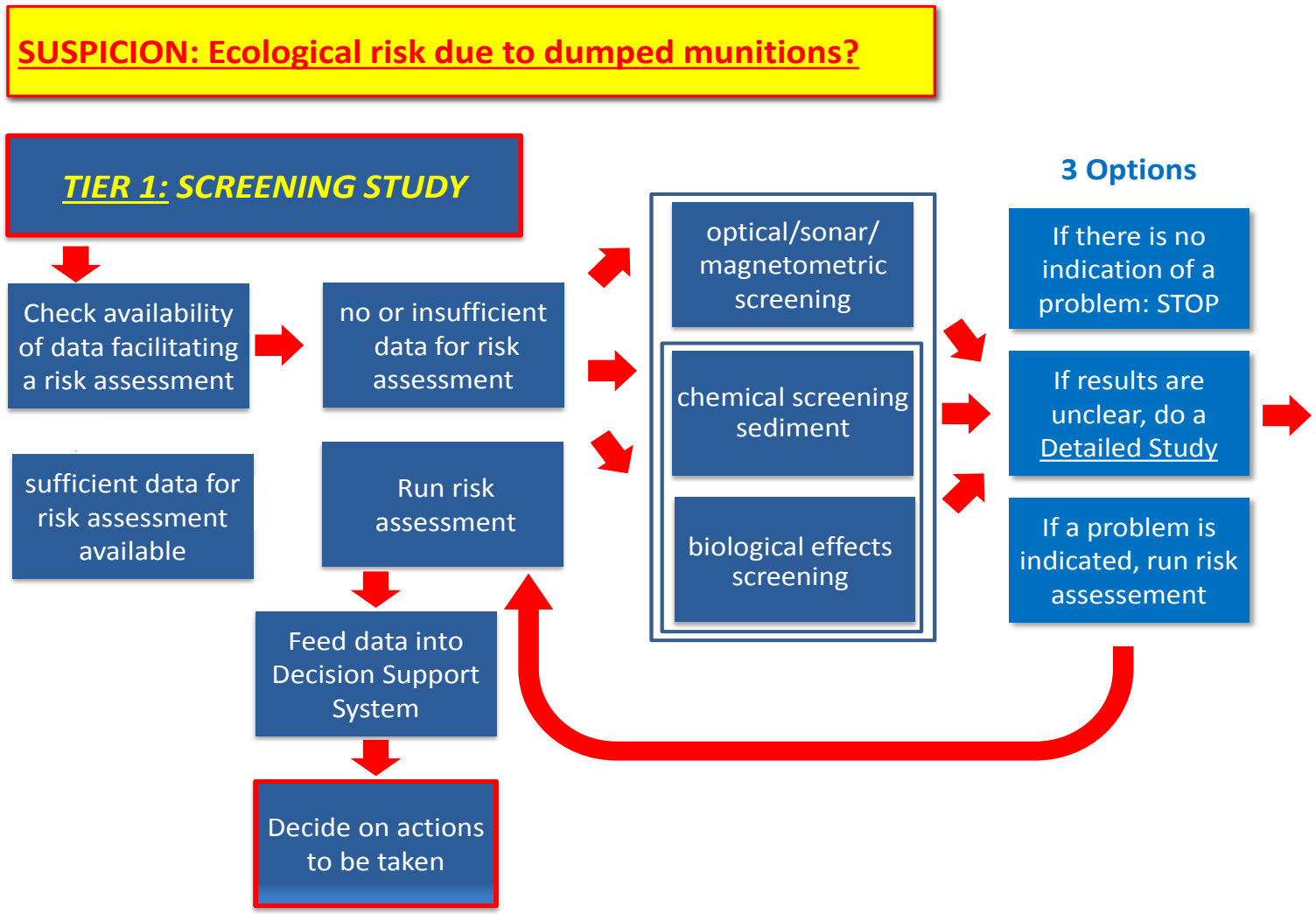
From suspicion to decision



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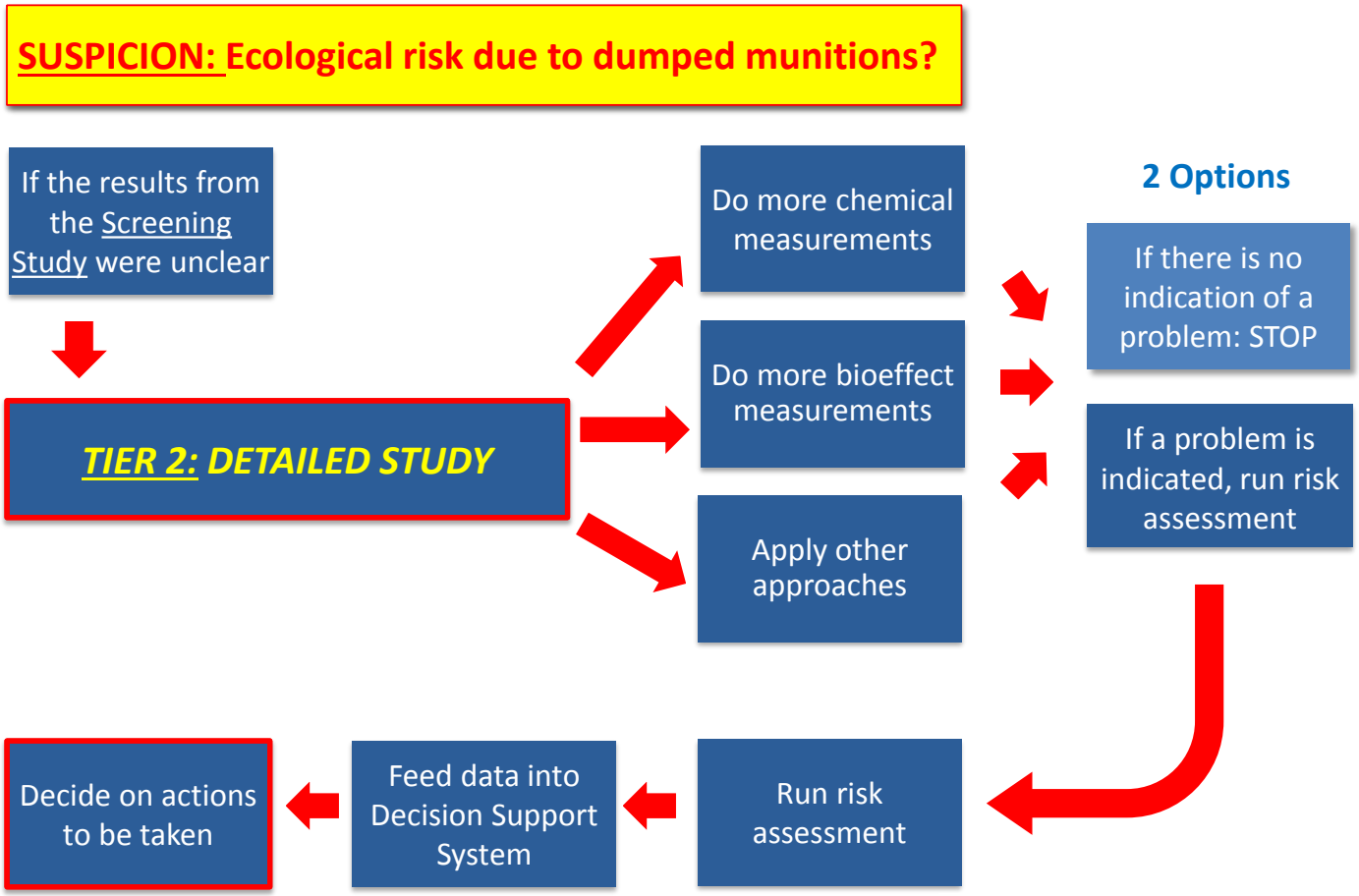

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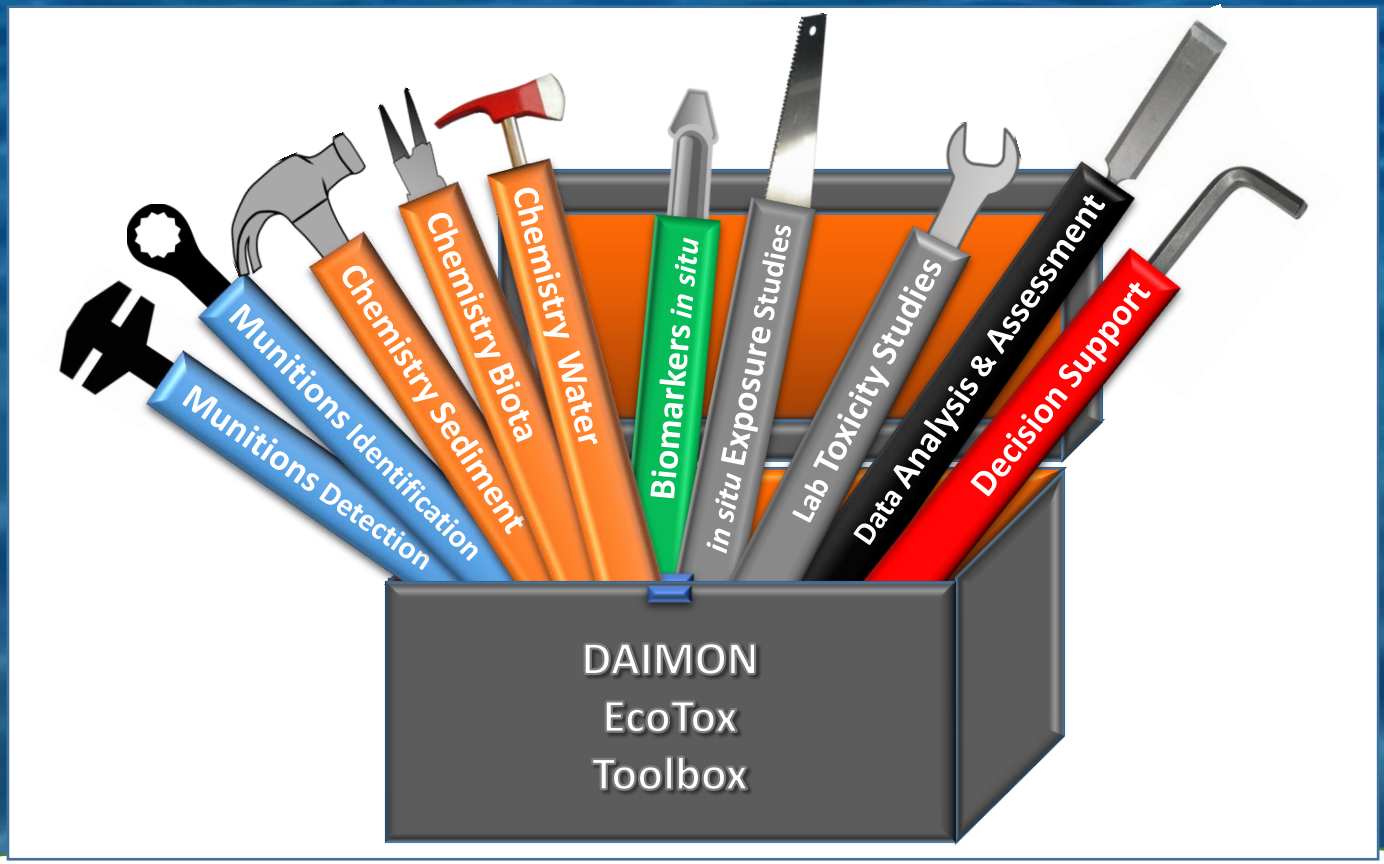
From suspicion to decision



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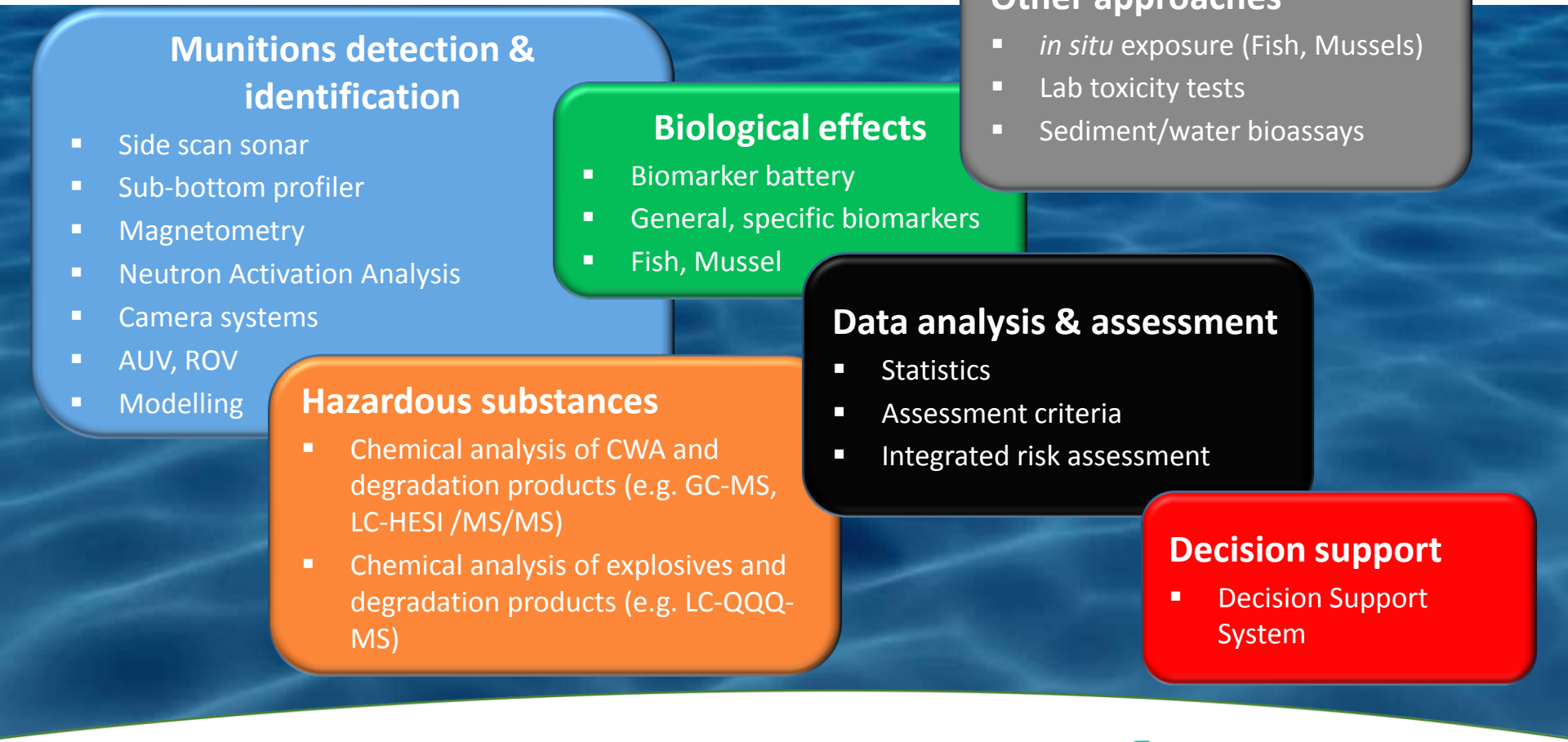
The Toolbox

From suspicion to decision



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Thank you for your attention!