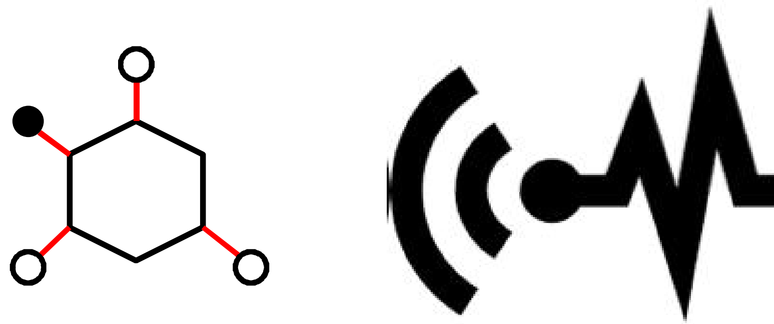
Chemical sensing and remediation: the state of the art

Dipl.-Ing. (FH) Claus Böttcher



Licence: Linkware

Introduction

- Claus Böttcher
  - Environmental Engineer
  - State* Ministry of Environment, ...
  - Managing Director of the German Program of Underwater Munitions
- Expertise
  - Crisis management & crisis communication
  - Linking stakeholders
  - Sharing information

www.underwatermunitions.de

SH Schleswig-Holstein The Government

Courtesy to

- Prof. Dr. E. Achterberg, Dr. Aaron Beck
- Prof. Dr. E. Maser, MSc. J. Strehse
- Prof. Dr. R. Schulz, Dr. O. Mudimu
- Dr. Tobias Knobloch
- Dr. H. Wackerbarth
- Dr. T. Gentz, SubSeaSpec UG
- MSc. Jann Wendt, EGEOS GmbH
- MSc. Nicolas Estoppey
- Dipl.-Ing. P. Rabenecker
- Nadine I. Goldenstein

Outline

- Introduction: the problem of munition constituents (MC) in the marine environment
- Sensors & Methodologies
  - Mass Spectrometry
  - Optical Spectrometry
  - Electrochemistry
  - Chromatography
  - Biochemistry
- What next?
- (Sources & Links)

Approaching MC

Heligoland Island,
hunting for shells filled
with the nerve agent Tabun

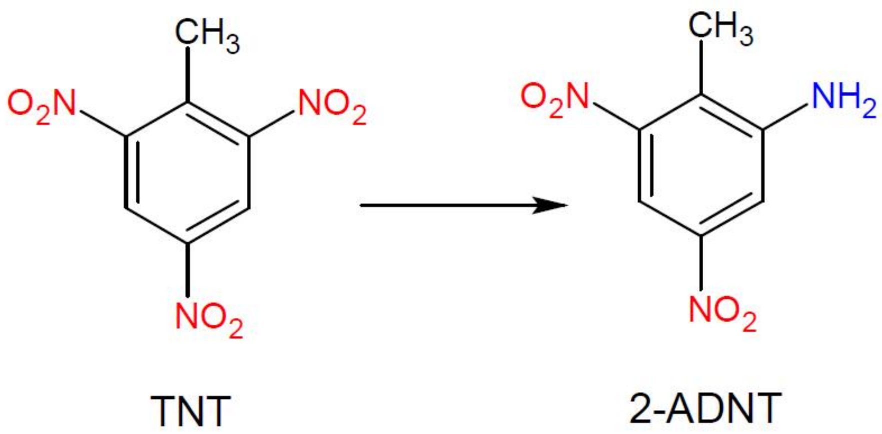
© Bundeswehr, 2008

Kolberger Heide,
passive sampling in order to monitor
consequences of blast operations

© F. Pfeiffer, 2007

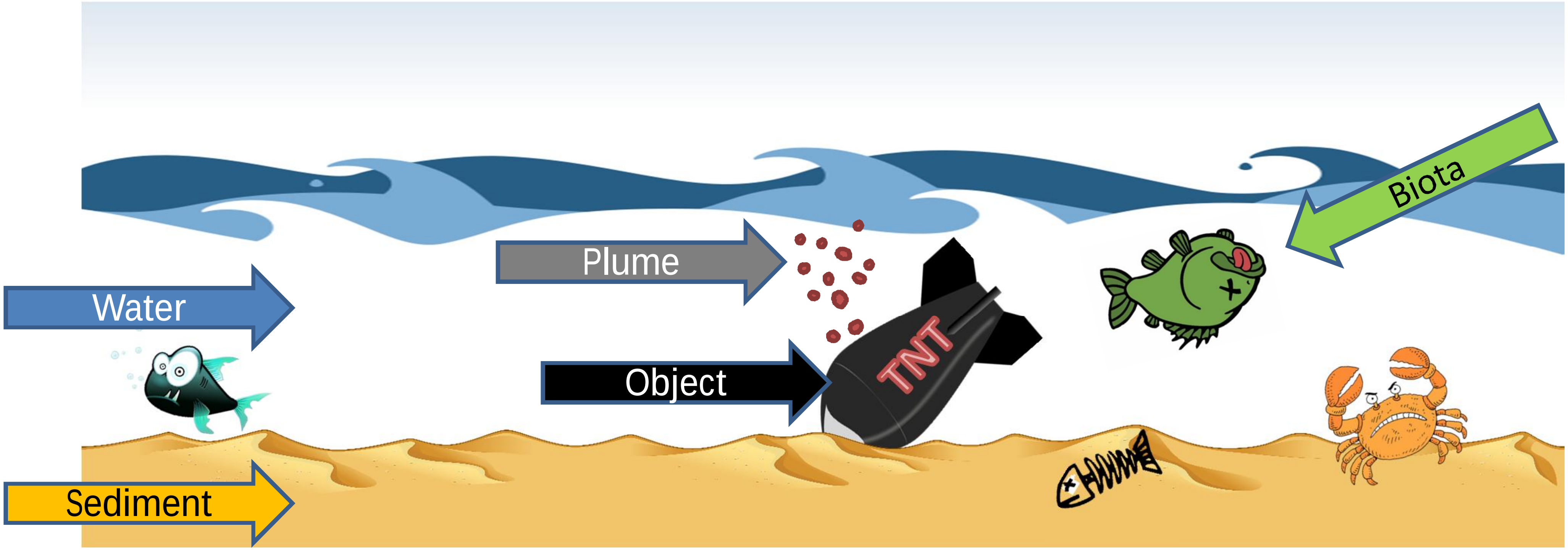
Target compounds

- All manmade, in large scale
- Transformation and metabolic products known



Beck et al., GEOMAR

Matrices

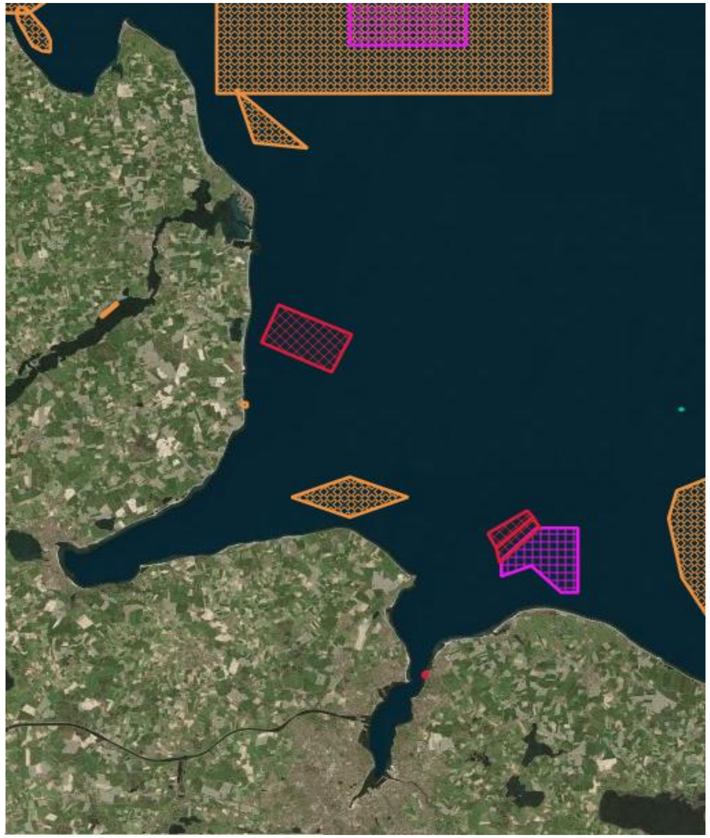


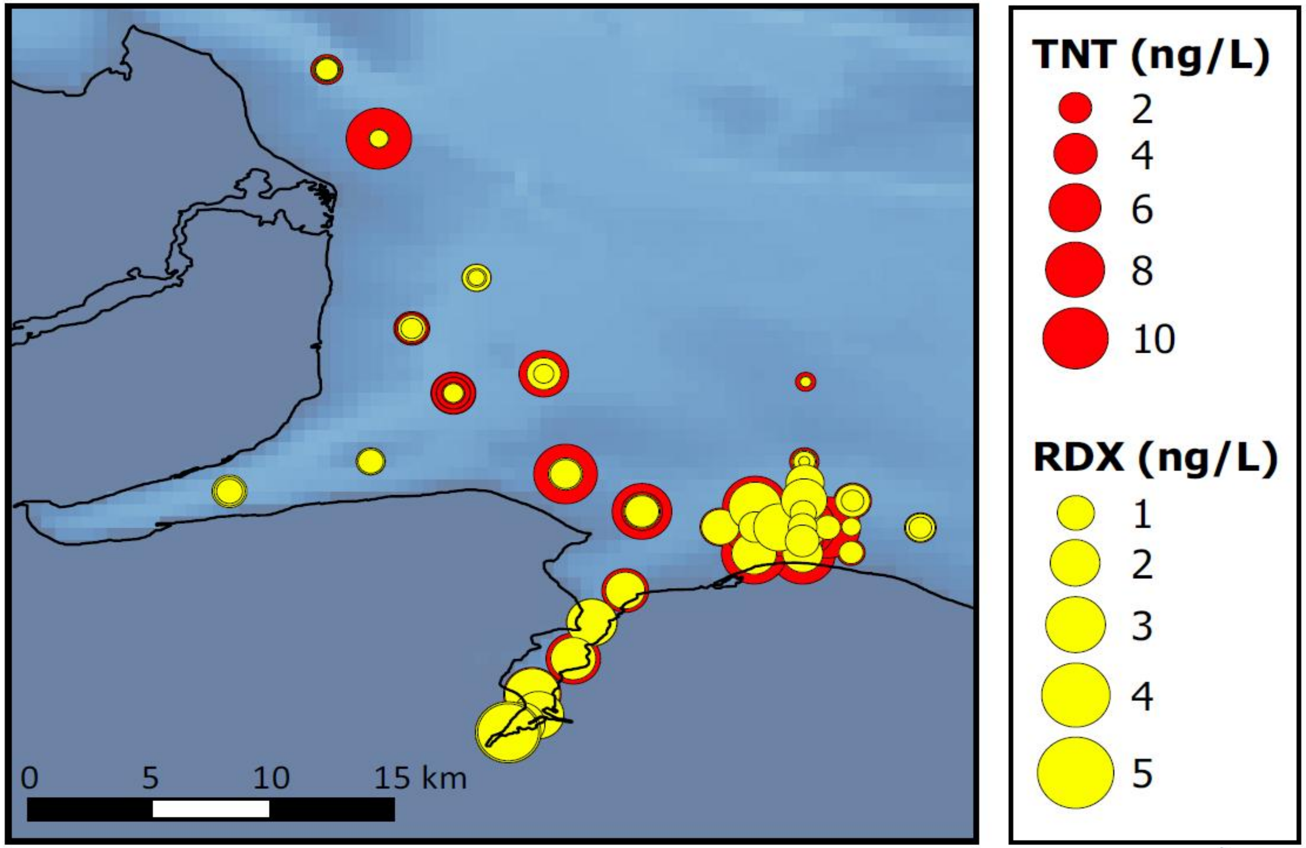
Dr. Hainer Wackerbarth, Laserlabor

Monitor pollutants

Munitions-contaminated areas in the Western Baltic Sea

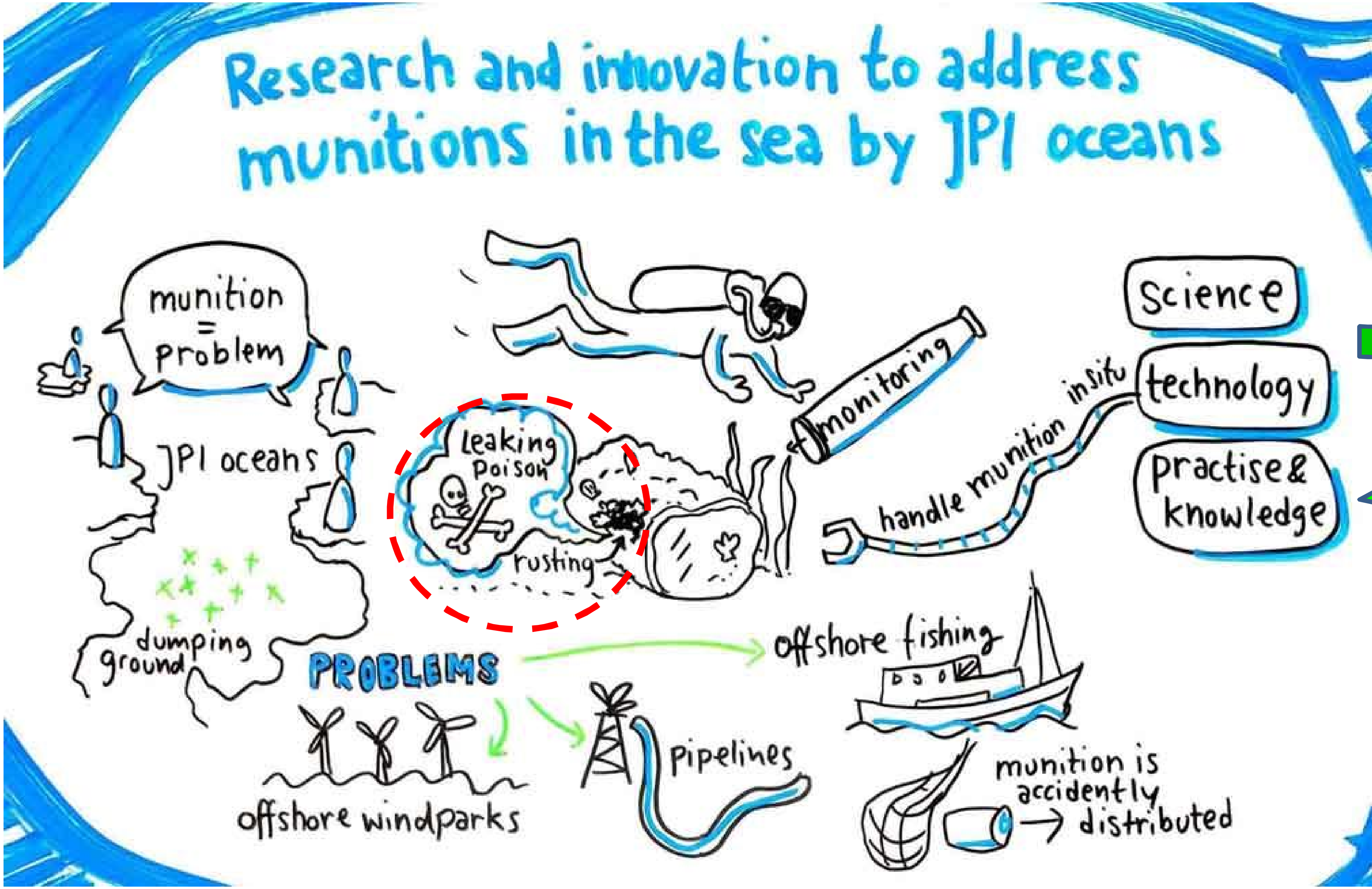
www.AmuCad.org:





(Beck et al., GEOMAR, in prep)

Gain knowledge



© www.Riesenspatz.de; HanseMesse Rostock, 2017

Chemical sensing (1/3)

- Detect munition constituents (MC)
  - Matrices: sediment, sea water, biota
- Determine type of MC
  - Identify explosive and / or chemical warfare agents
- Track towards the sources
  - Gradient of MC concentration in water column

- Measure concentration of relevant MC

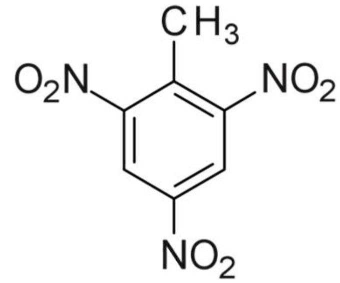
Chemical sensing (2/3)

- Offline sensor
  - Analyse fixed samples (sediment, biota, sea water)
  - Assess post-mission data
- Online sensor
  - Electric or optical sensors
  - (Near) real-time analysis
  - Quick detection: compound triggers activity

Chemical sensing (3/3)

- Obstacles, to be aware of…
- Sampling, storing and analysing MC
  - Adhesive to many polymers
  - Destroyed by UV light
  - Transformation and metabolism
  - Discuss the “non-extractable share” of MC in biota
  - ...
- Rates of release in marine waters are <u>not</u> linear

The largest share



- Introduction into the environment:
  - Production of TNT
  - Training, testing & practice
  - Military operations
  - Disposal (at sea)
  - Accidents
- Amount WW II
  - Germany: 800.000 t
  - Others: …

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Sensors & Methodologies

- Spectrometry
  - Mass (of molecules)
  - X-ray
  - Optical (Laser, UV)
- Electrochemistry
  - Electron Microscope
  - Ion analysis (IC, CE, FFE)
  - Active surface IC
- Biochemistry
  - Microfluids
  - Biomarker

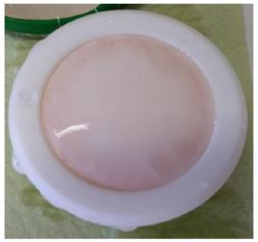
- Direct measuring
- Sampling strategies
  - Active
  - Passive
- Extraction of target MC from sample
- Assessing the results
- Conclusions and recommendations

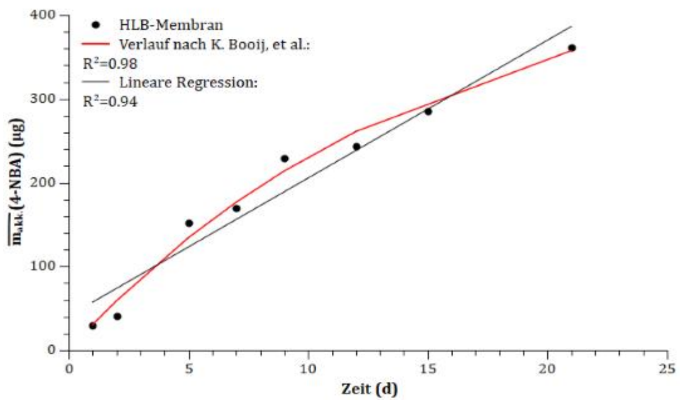
Chemical sensing

MASS SPECTROMETRY

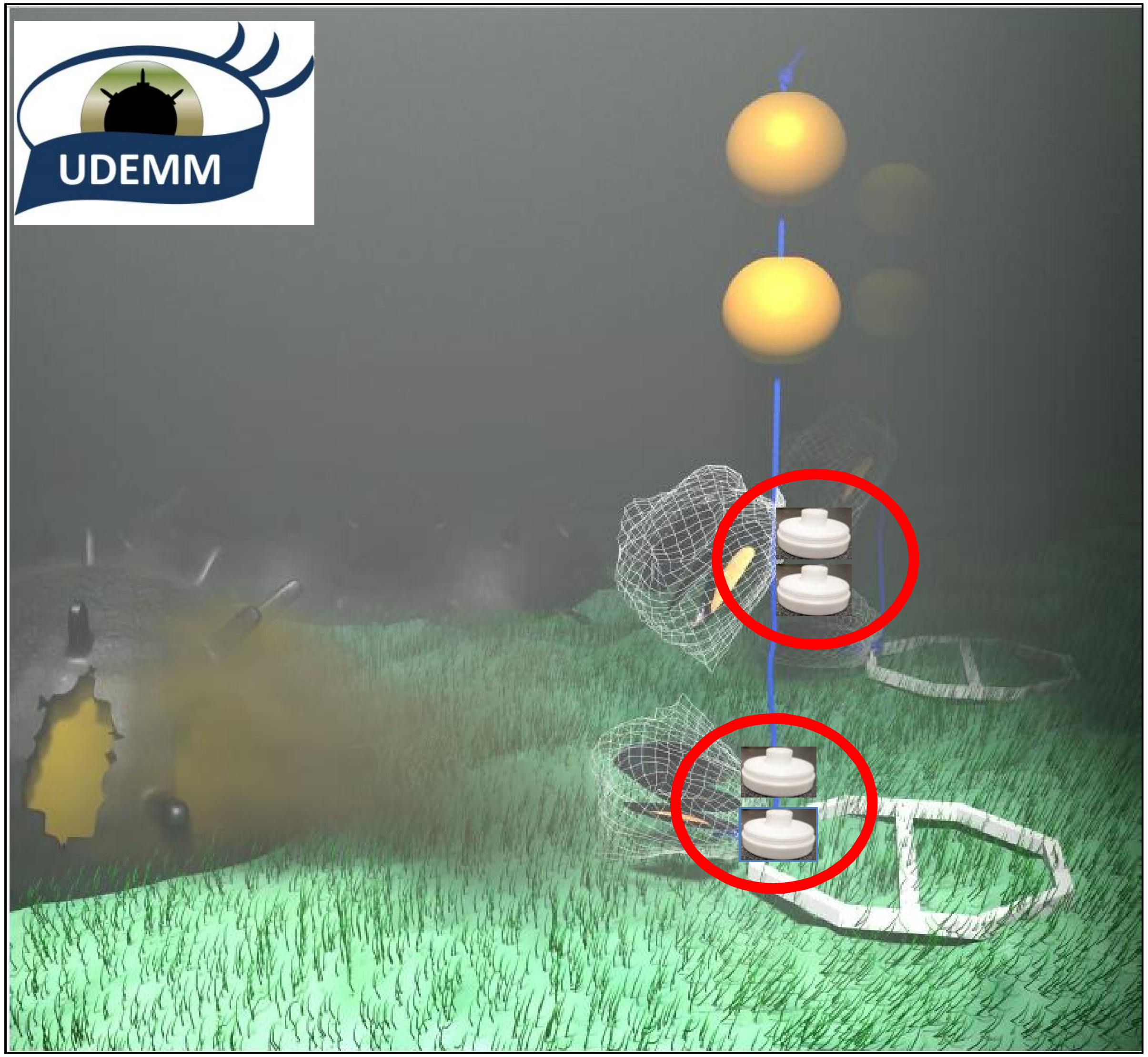
Chemcatcher®-System

Calibration in lab





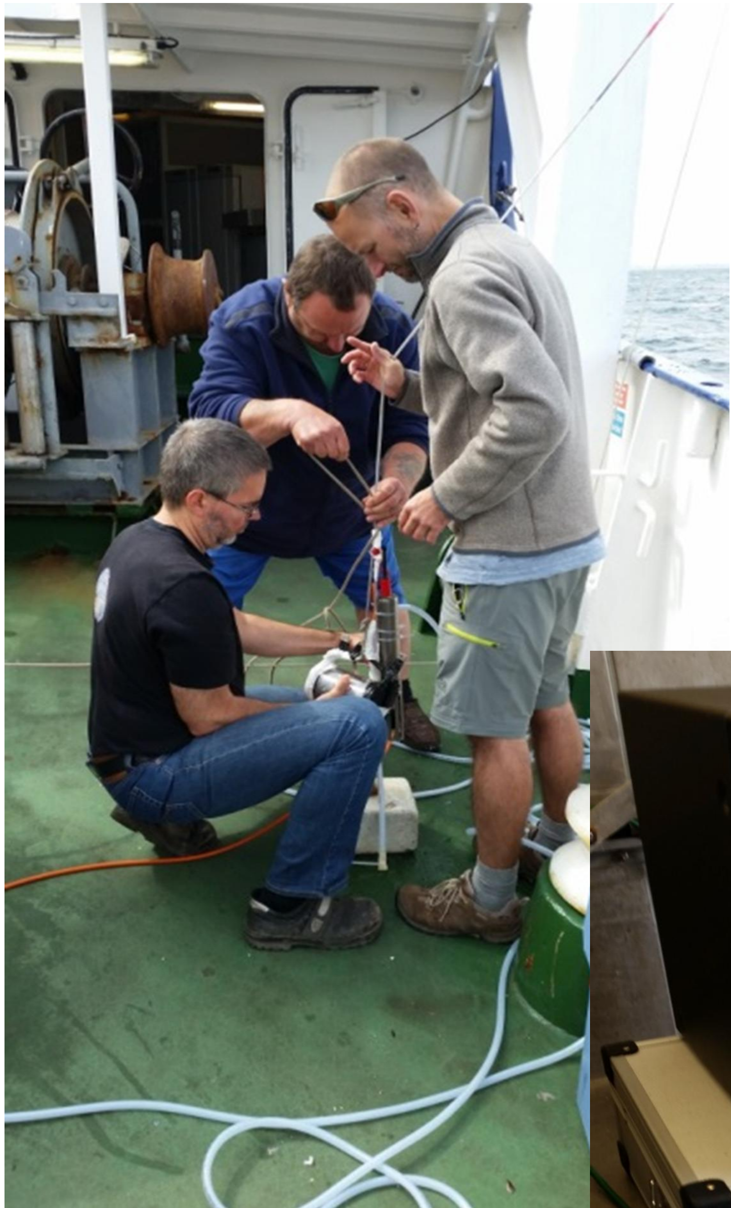
Open field experiment



© Prof. Dr. E. Maser, J. Strehse, Uni Kiel

Field sampling details (GEOMAR)

- Ultraclean double-diaphragm pump
- Camera mounted on pump tubing, in order to sample water directly adjacent to exposed munitions
- Sediment/biota collection with grab or divers



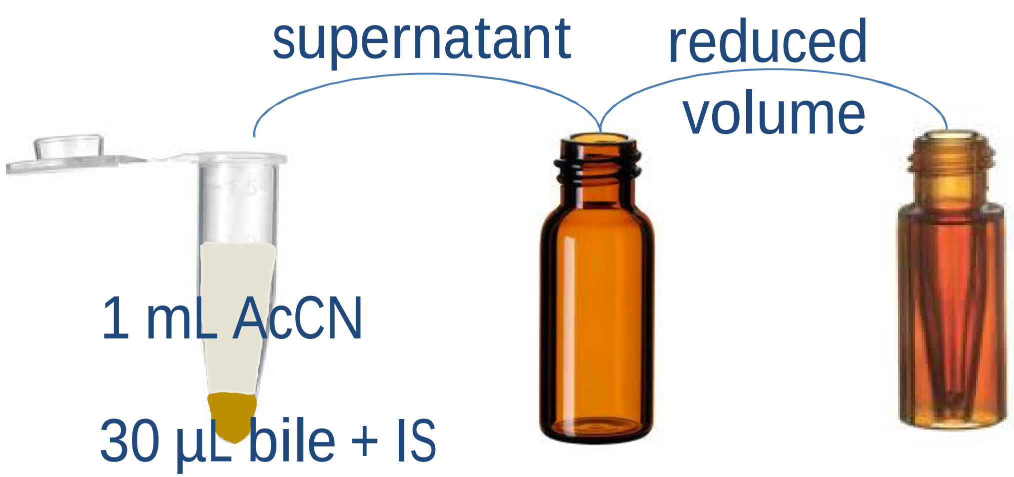
Photos: E. Maser, C. Schlosser

Preparation of bile samples and blank

- 25 µL bile/ 25 µL H_2O Eppendorf vials
- addition of internal standard (1,4-DNB)
- final concentration of 50 ng in 30 µL sample

Extraction with acetonitrile (AcCN/CH_3CN)

- reduction of supernatant to a total volume of 50 µL
- injection on HPLC-QQQ-MS



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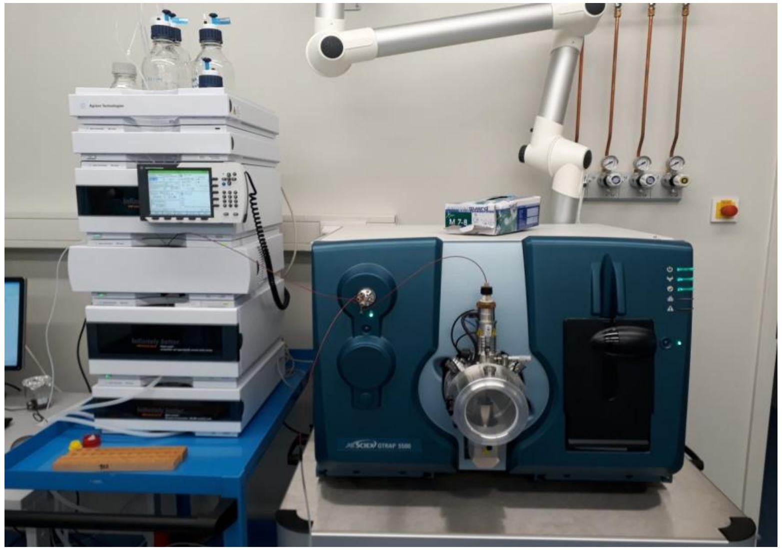

GEOMAR

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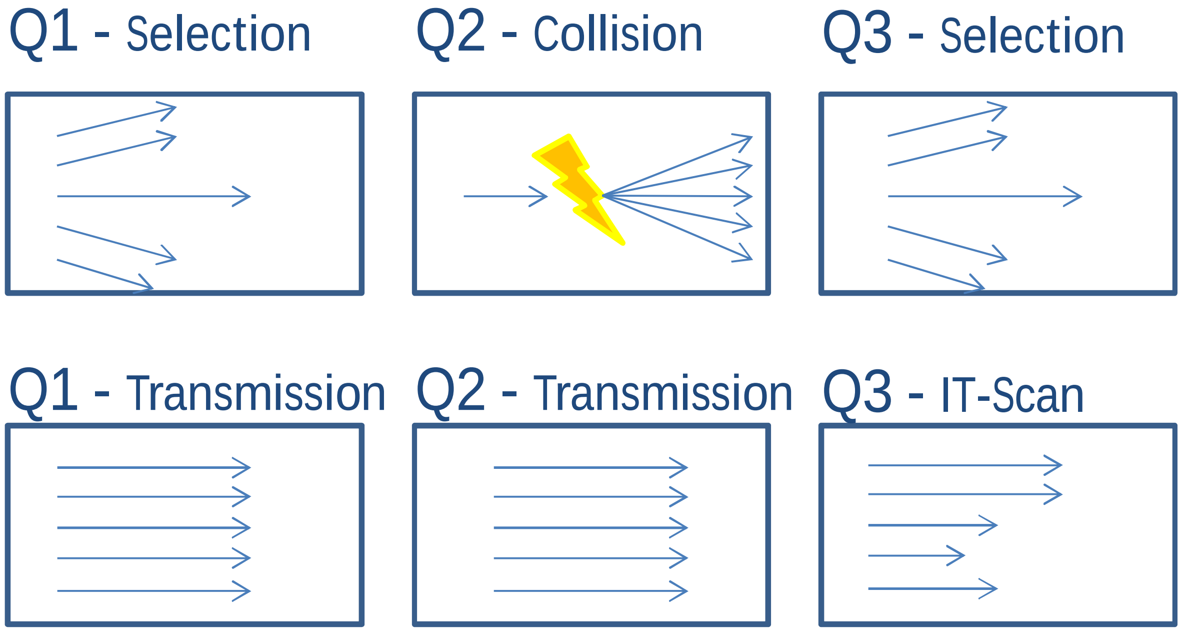
Explosives target analysis



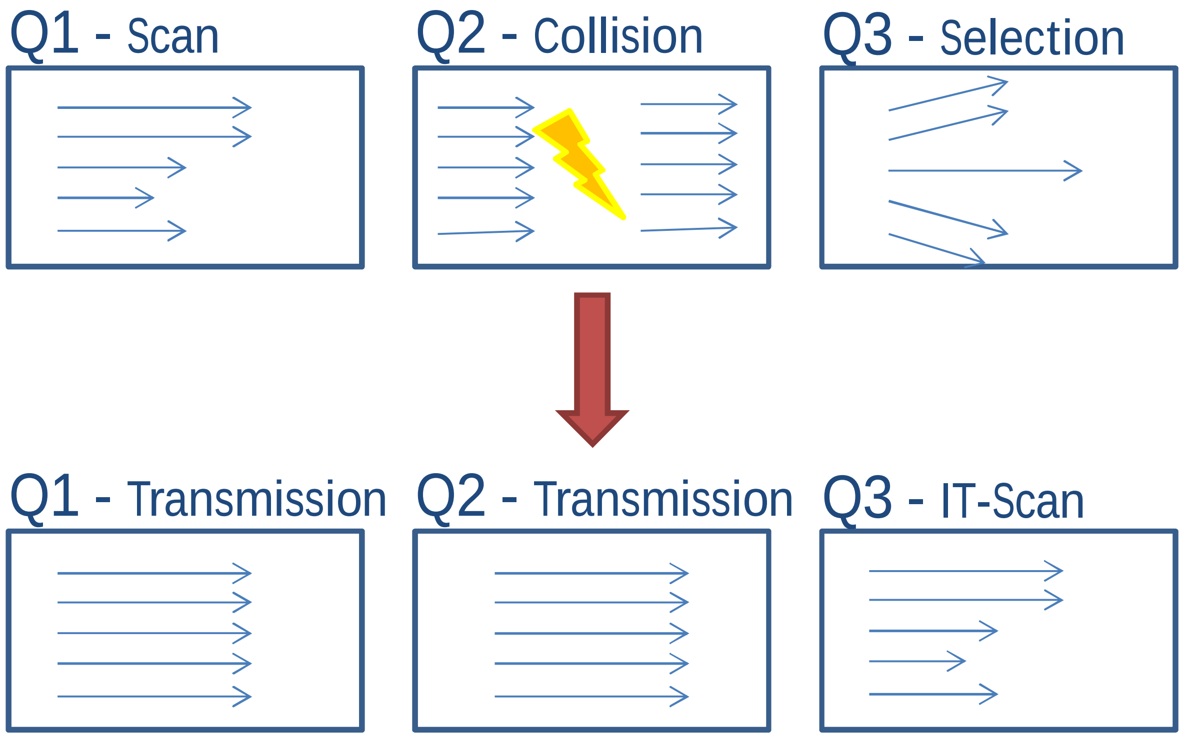
MRM - Multiple Reaction Monitoring

Sensitive target compound analysis

EMS - Enhanced Mass Spectrum

Scan of complete m/z spectrum

Screening for nitroaromatics



NL - Neutral Loss Scan

Scan of only nitro-containing compounds

EPI - Enhanced Product Ion Spectrum

Sensitive screening of nitroaromatic compounds

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Source: Nadine Goldenstein, TI-FI

Analytical method (GEOMAR): Development of a method for dissolved explosives compounds in seawater (Gledhill et al., submitted for publication)

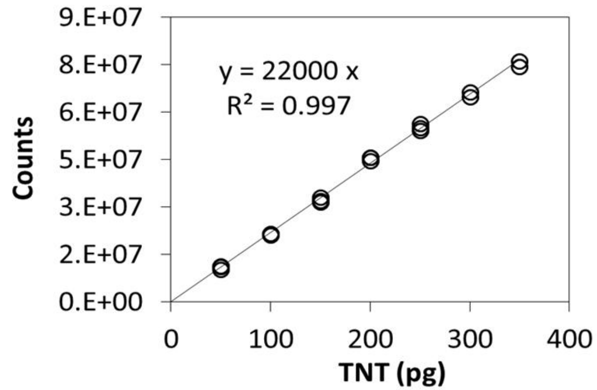
- Dissolved samples: preconcentration by solid-phase extraction
  Sediment and biota: extraction with acetonitrile, dilution/direct injection

- Analysis of TNT and breakdown products using high-performance liquid chromatography (HPLC) and heated electrospray mass spectrometry (HESI-MS)

Thermofisher UltiMate 3000

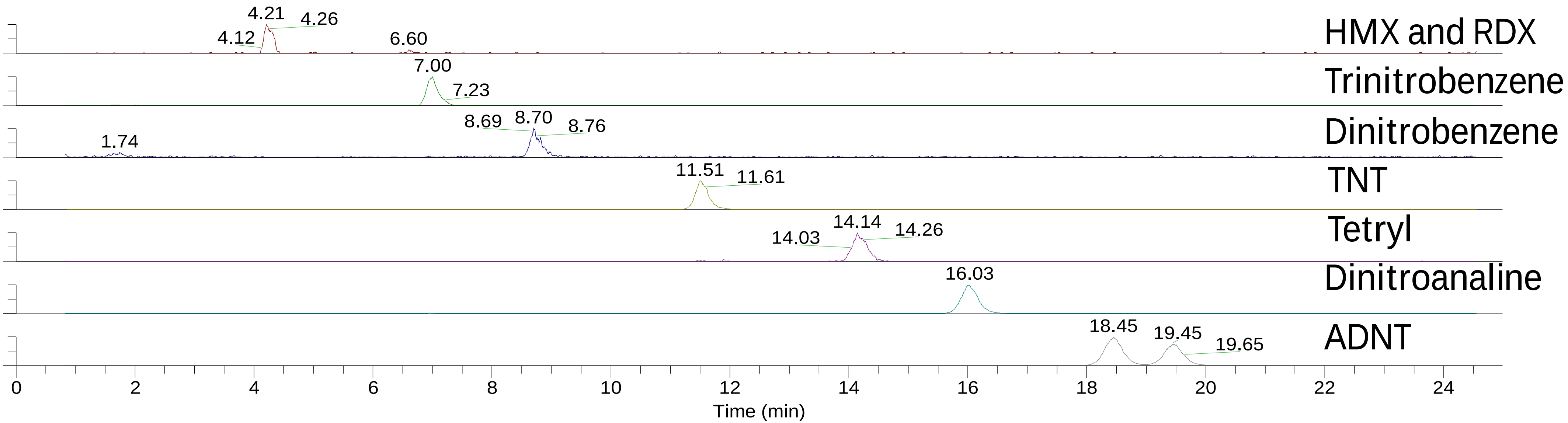
Thermofisher Q Exactive

Analytical method (GEOMAR):
Dissolved explosives in seawater, sediment, biota
Detection limits ~fg/L (10^{-15} g/L dissolved)
(Gledhill et al., submitted for publication)



Critical aspects

1. Solid-phase extraction: Seawater matrix removal, signal increase min. 1000x, isotope-labeled TNT and DNB spike
2. Liquid chromatography (HPLC): Reproducible compound separation before mass spec.
3. HESI-mass spectrometric detection: High sensitivity, unequivocal compound identification, allows use of isotope-labeled internal standards

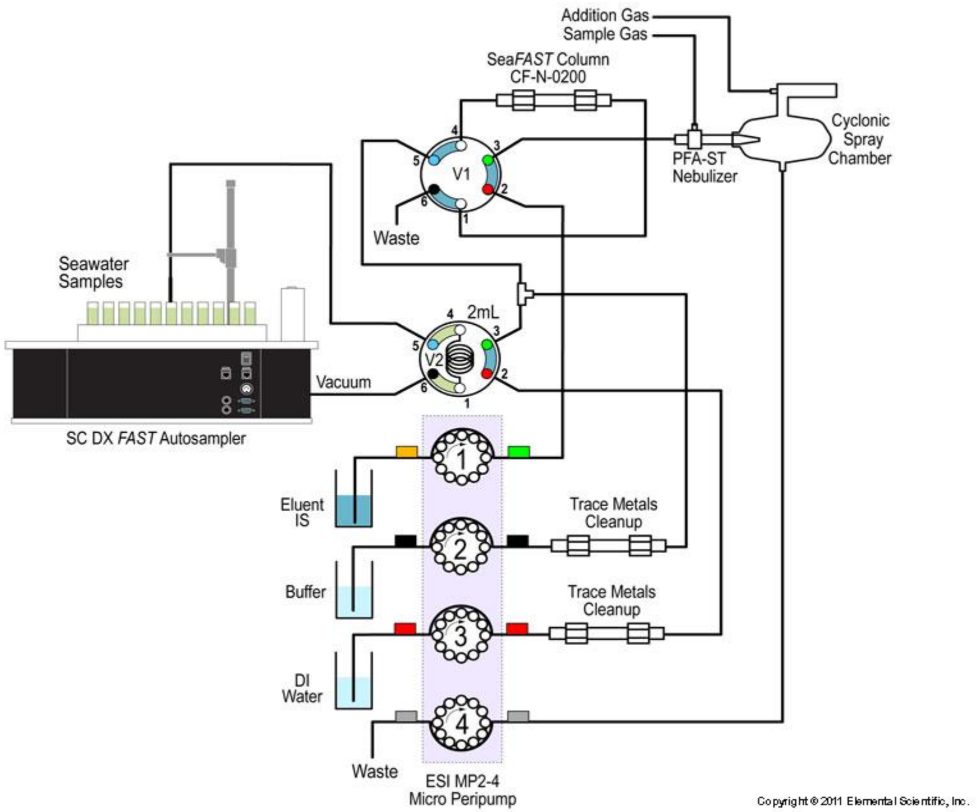


Source: Aaron J. Beck, GEOMAR

Analytical methods: Metals

- Preconcentration by solid-phase extraction
  (WAKO resin for metals, AG1-X8 for Hg)
- Analysis by inductively coupled plasma mass spectrometry (ICP-MS)

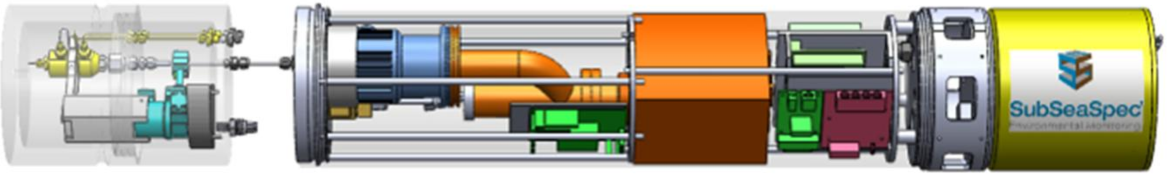
Detection limits in seawater: ng/L - µg/L



Thermo Element XR II

GEOMAR

U-Mass Spectrometer



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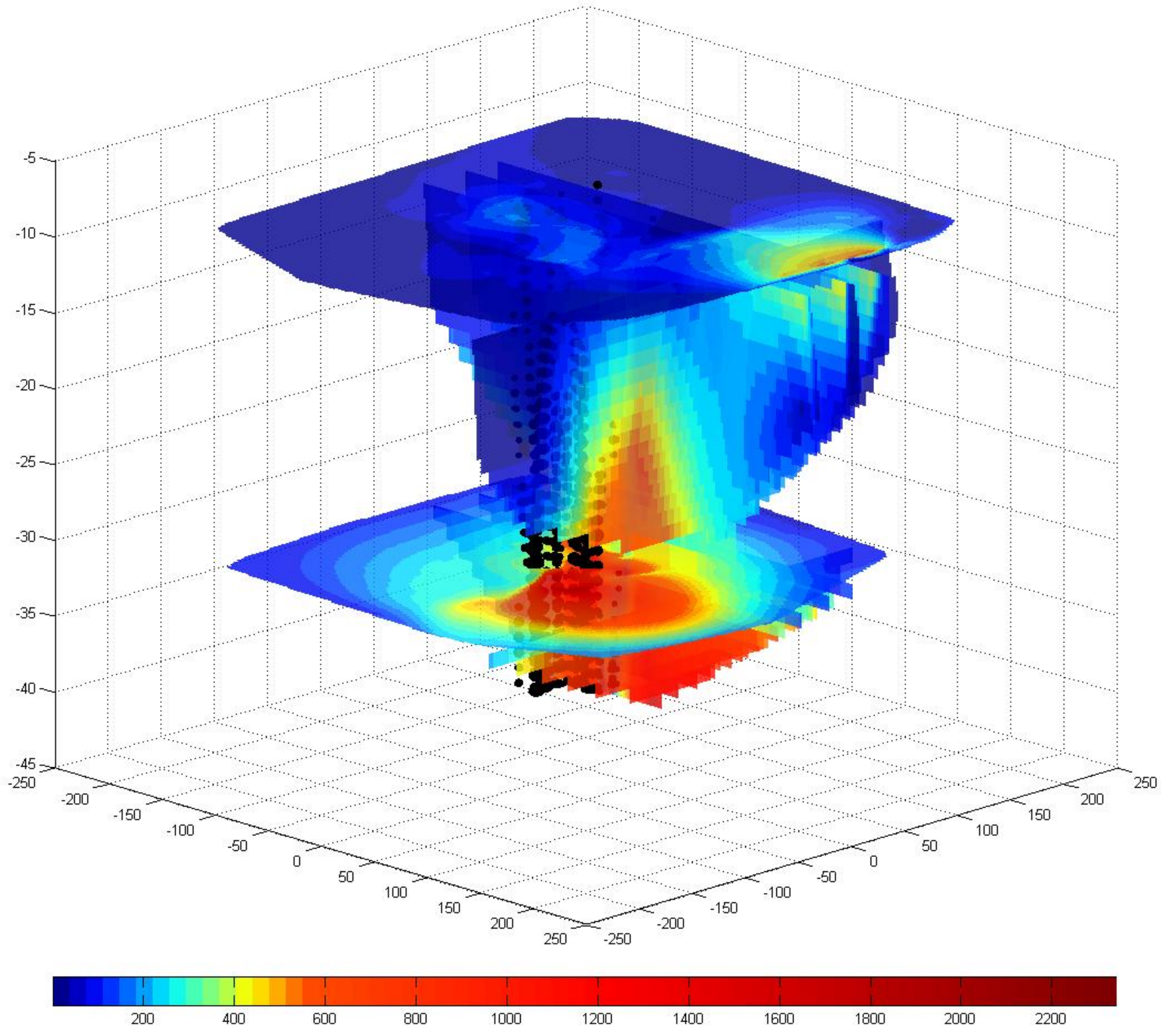
http://www.subseaspec.com

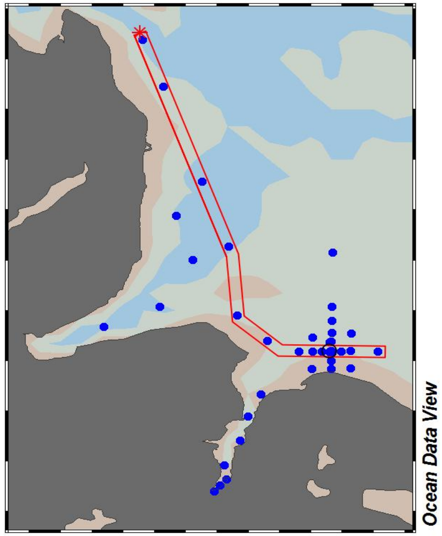
Example: Plume of CH_4

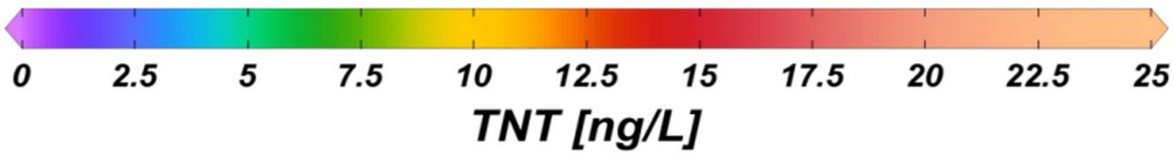


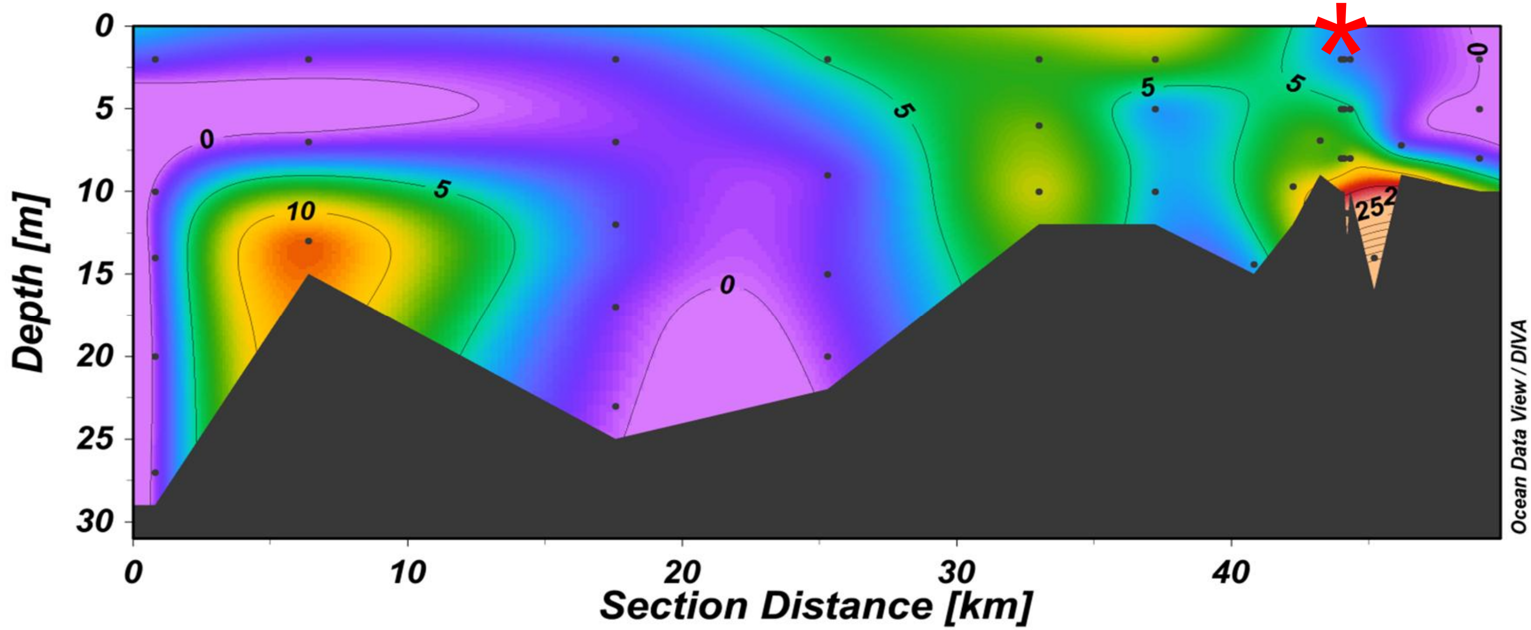
© Dr. T. Gentz, Bremerhaven

Munition compounds in water column: Depth distribution

Munitions dumpsite





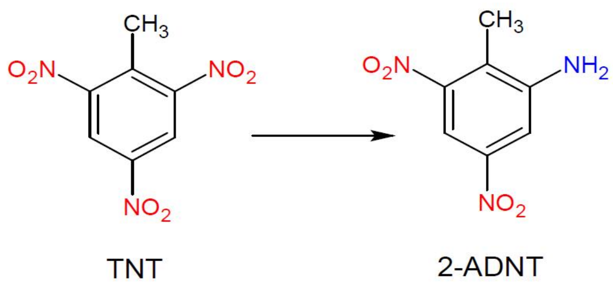


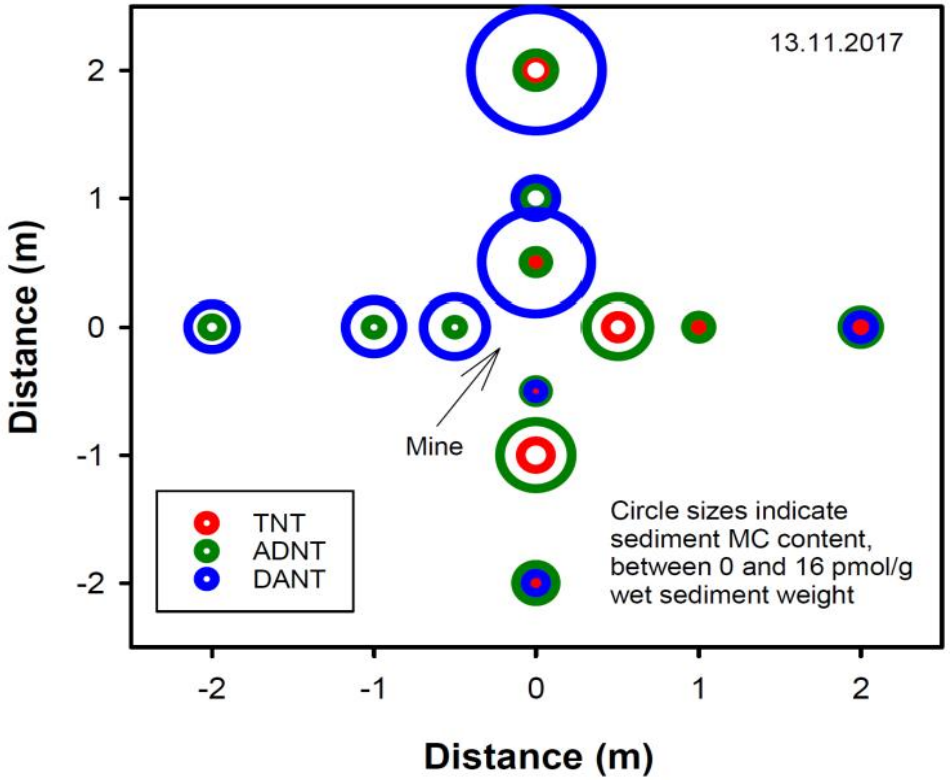
(Beck et al., GEOMAR, in prep)

TNT and degradation compounds in sediments around individual munitions in southwest Baltic Sea

Circle size indicates amount:

TNT → ADNT → DANT

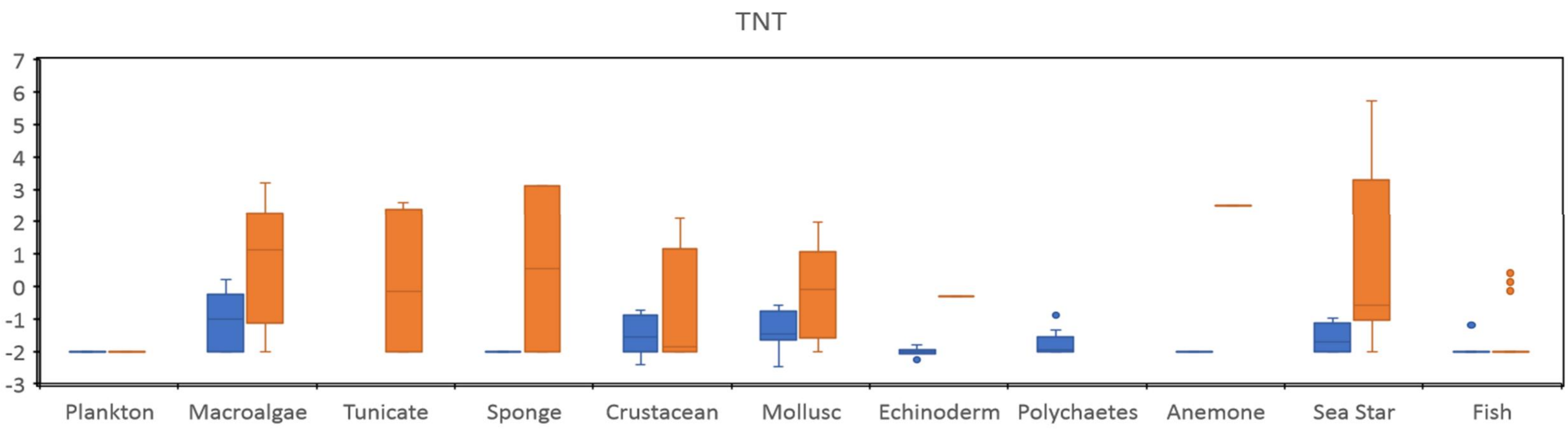




(Beck et al., GEOMAR, in prep)

TNT in biota (*log ng/g tissue*) collected in southwest Baltic Sea

Bar color:
orange samples from munitions dumpsite
blue samples away from known munitions sites



(Beck et al., GEOMAR, in prep)

Chemical sensing

OPTICAL SPECTROMETRY

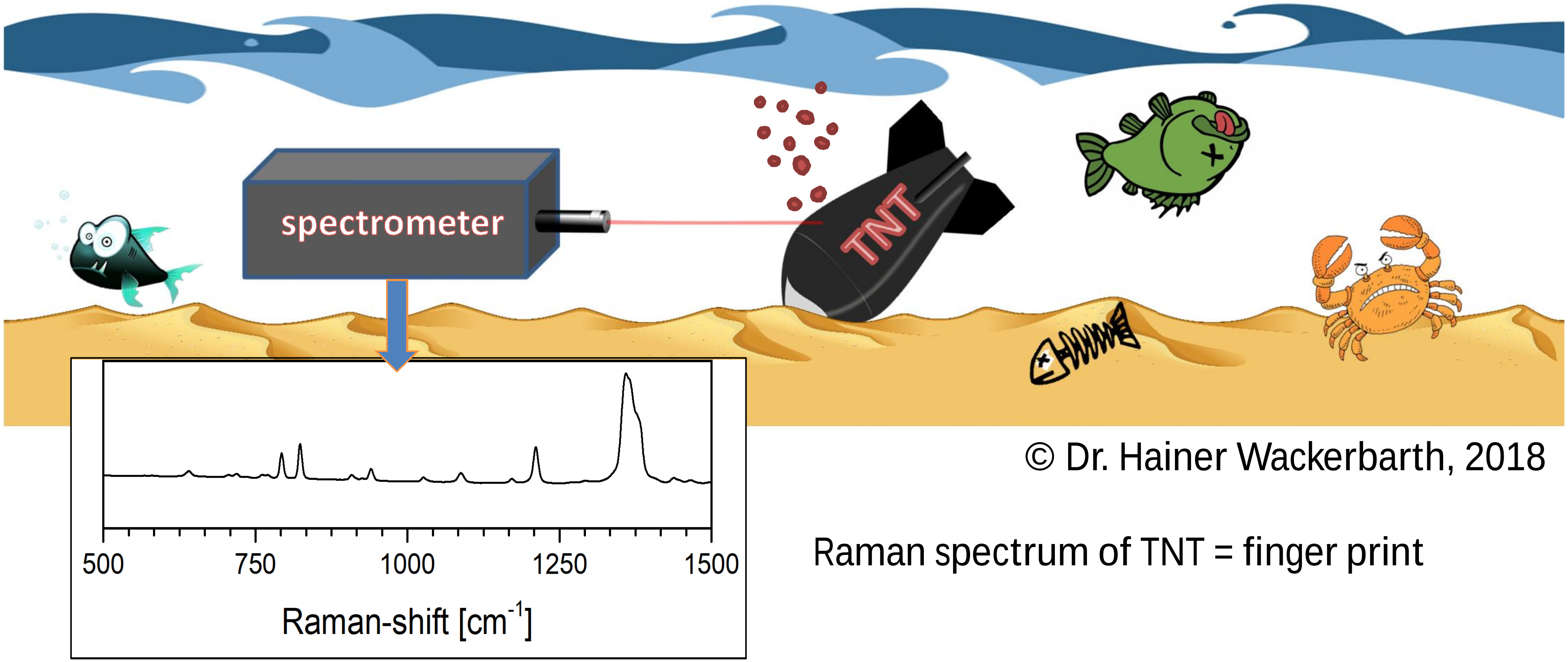
Raman spectroscopy

- Raman spectra = finger print of molecules
- Capable of detecting explosives (TNT, RDX, HMDT, Picric acid,...) and chemical warfare agents
- Water is Raman transparent (particles in the water cause trouble)
- Sample time within 5 seconds
- Suitable for undersea explosive and chemical warfare agents detection

Source: Dr. Hainer Wackerbarth, Laserlabor

Raman spectroscopy

- Suitable for undersea explosive and chemical warfare agents detection



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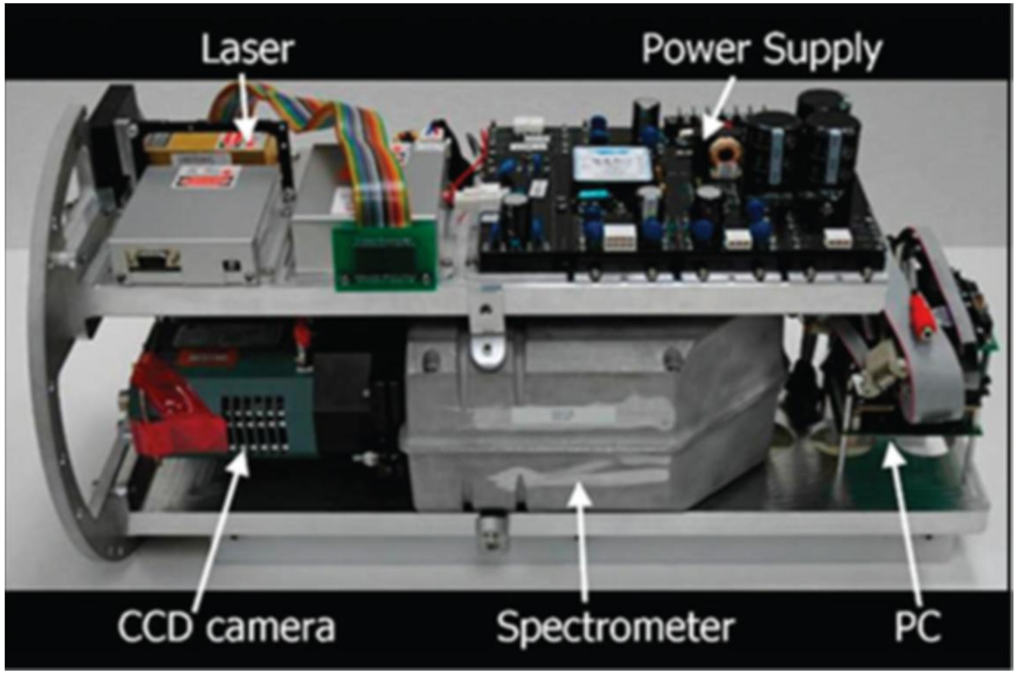
Raman spectrum of TNT = finger print

Deep Ocean Raman In-Situ Spectrometer (DORISS II)

Raman system, adapted for ROV plattform
for the exploitation of the sea ground up to 4000 m depth



Source: X. Zhang et al,
Applied Spectroscopy 2016, 66, 3, 237-249.

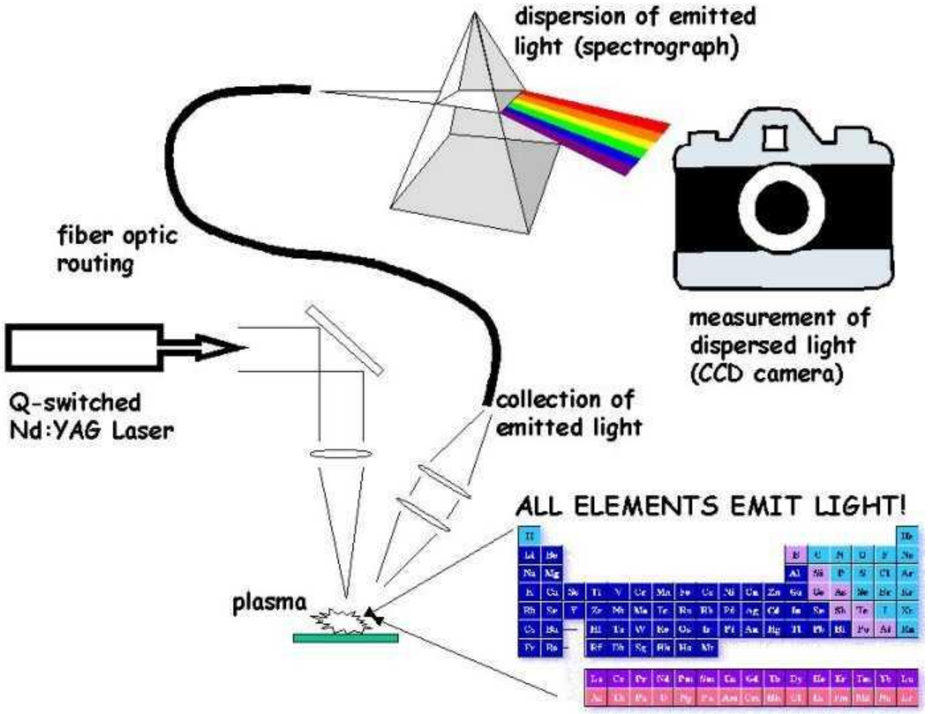
Underwater Raman Sensor for Detecting High Explosives and Homemade Explosives (HMEs)

- Results
  - 2 m detection range for most chemicals in coastal seawater
  - Ammonium nitrate (NH_4NO_3, AN) through 10 m seawater and 3 plastic bags

Form: Shiv K. Sharma et al., Hawaii, USA, supported by Office of Naval Research and NASA

Other Laser-based techniques

- Laser-induced breakdown spectroscopy (LIBS)
  - Highly energetic laser pulse induces a plasma
  - Plasma generates excited states of the elements
  - Detection of the characteristic light of the emitting elements
  - Application in undersea mining (INESC TEC) / on land for explosive detection



Disadvantage:
Sample can be ignited by the plasma
»»remote operation

Source: Wikipedia:,Courtesy of US Army Research Laboratory

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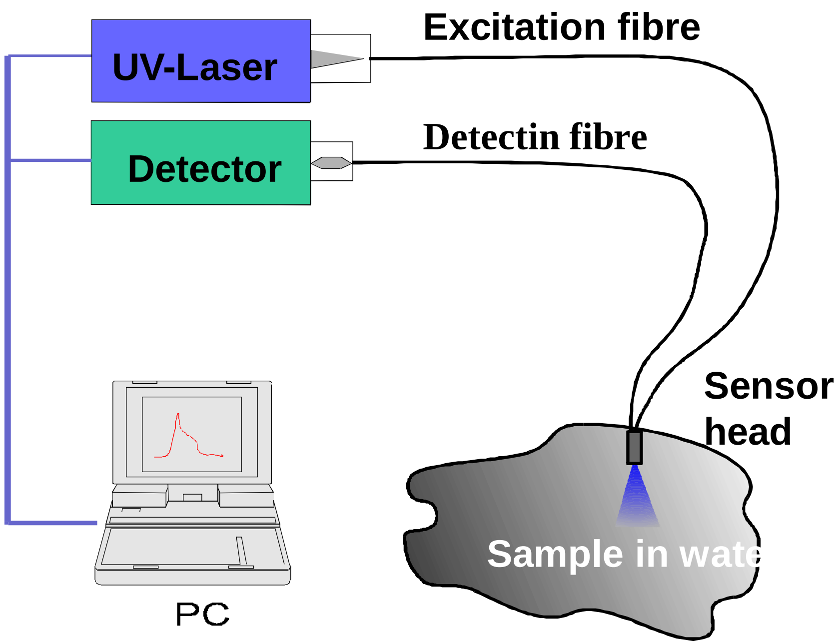
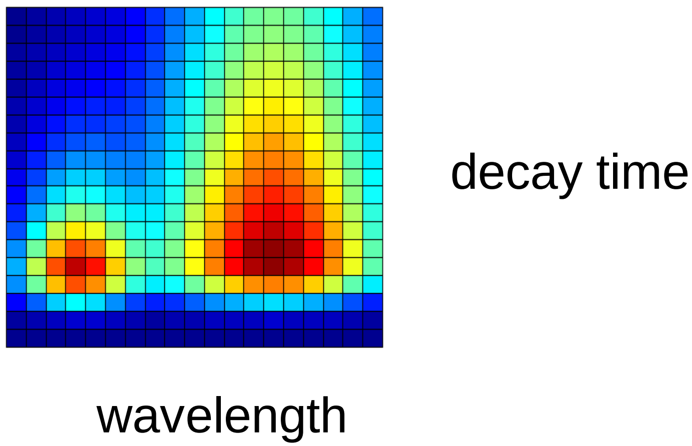
Other Laser-based techniques

- Laser-induced fluorescence
  - Excitation at 266 nm, detection of fluorescence emission and life times
  - Detection of pollutants like PAH and BTEX
  - Developed by Laser Laboratory Göttingen

Set up



Spectrum



Chemical sensing

ELECTROCHEMISTRY

Online

- Electro-chemical (FHG-ICT)

electrochemical sensor as payload aboard unmanned vehicles

- autonomous operation (AUV):
  - uses own power and neural network
- remotely operated (ROV):
  - power and communication linked to vehicle
- successfully tested with:
  - TNT, PETN in North Sea and Baltic Sea

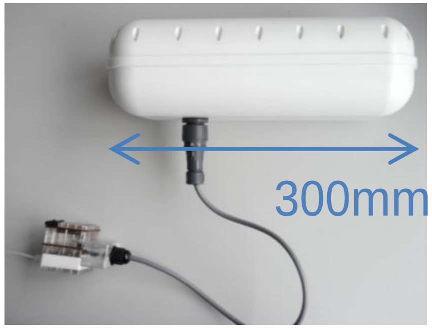
© Rabenecker, 2018

Online

- Electro-chemical (FHG-ICT)

results

  - high sensitivity – detection of 1 ng (10E-9 gram) absolute amount of explosive
  - autonomous (AUV) & remotely controlled (ROV)
  - detection successful at a distance of 1-2 m



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Chemical sensing

CHROMATOGRAPHY

Chromatography

- Ion chromatography (IC)
- Capillary electrophoresis (CE)
- Free-flow electrophoresis(FFE)

© Fraunhofer ICT

https://www.ict.fraunhofer.de/de/komp/ae/sa.html

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daimon

Decision Aid for Marine Munitions

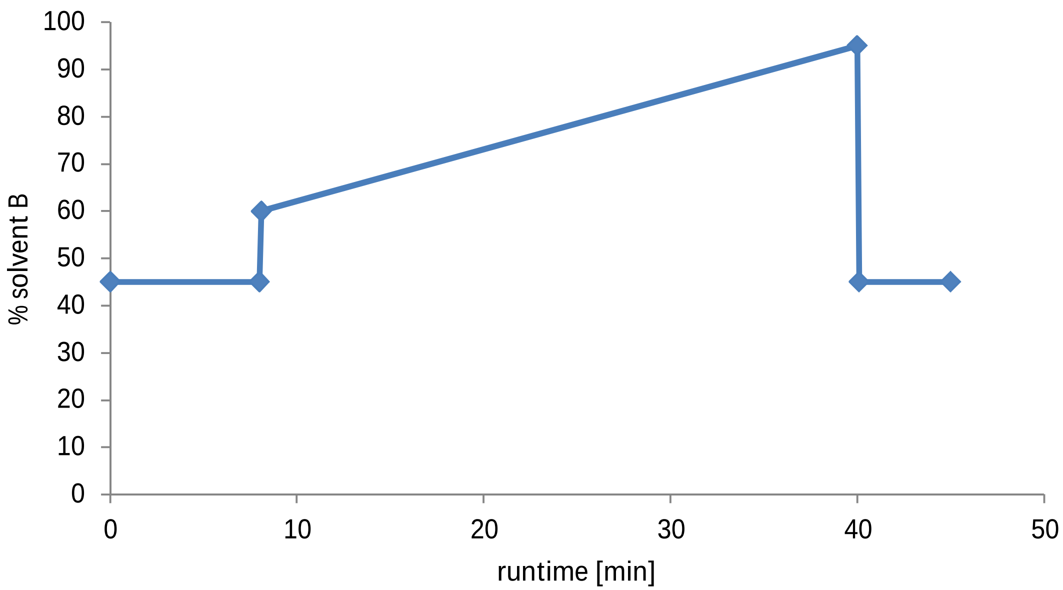
Liquid Chromatography

Liquid Chromatography

Acclaim E2 Explosives column (Thermo Fisher) @ 25°C

Eluent A: H_20 (10 mM NH_4Ac + 2.7 mL Acetic Acid, pH 4)

Eluent B: AcCN (10 mM NH_4Ac + 2.7 mL Acetic Acid)



Triple Quadrupole MS

Period 1, Experiment 1	
Experiment Type:	MRM
Num. Cycles:	1864
Polarity:	Negative
Period Cycle Time:	1297 ms
Experiment Parameters	
Parameter	Value
CAD	-2
CUR	35
GS1	60
GS2	65
NC	6
TEM	350
Mass Range Parameters	
Parameter	Value
CXP	-15
EP	-10

Name	Q1	Q3	Dwell (ms	CE	DP
HMX_1	355	46	20	-55	-60
HMX_2	342	46	20	-55	-80
RDX_1	281	46	20	-50	-40
RDX_2	267	46	20	-50	-50
TNB_1	213	183	20	-20	-50
TNB_2	213	167	20	-20	-40
1-3DNB_1	168	138	20	-20	-50
1-3DNB_2	168	46	20	-40	-40
1-4DNB_1	168	138	20	-15	-40
1-4DNB_2	138	108	20	-25	-80
NB_1	123	93	20	-20	-140
NB_2	123	108	20	-25	-50
Tertyl_1	287	241	20	-20	-50
Tertyl_2	287	213	20	-20	-50
TNT_1	227	197	20	-20	-60
TNT_2	227	210	20	-15	-40
TNT_3	226	183	20	-20	-80
2-5DNT_1	182	152	20	-15	-40
2-5DNT_2	182	122	20	-35	-130
2-4DNT_1	182	138	20	-20	-60
2-4DNT_2	182	165	20	-15	-70
NT_1	137	121	20	-20	-50
NT_2	137	108	20	-20	-50
4ADNT_1	197	120	20	-20	-90
4ADNT_2	197	167	20	-15	-90
2ADNT_1	197	120	20	-25	-70
2ADNT_2	197	167	20	-20	-70
HADNT_1	183	166	20	-20	-50
HADNT_2	183	121	20	-20	-50
DANT_1	167	137	20	-15	-80
DANT_2	167	148	20	-20	-80
TAT_1	137	93	20	-20	-30
TAT_2	137	109	20	-20	-90
TNAzoxyT_1	406	169	20	-25	-60
TNAzoxyT_2	406	360	20	-15	-80
TNAzT_1	390	344	20	-20	-50
TNAzT_2	390	197	20	-20	-50
TNBA_1	257	167	20	-20	-50
TNBA_2	257	137	20	-20	-50
DNBA_1	211	167	20	-15	-30
DNBA_2	211	137	20	-25	-30
NBA_1	167	137	20	-20	-50
NBA_2	167	123	20	-20	-50

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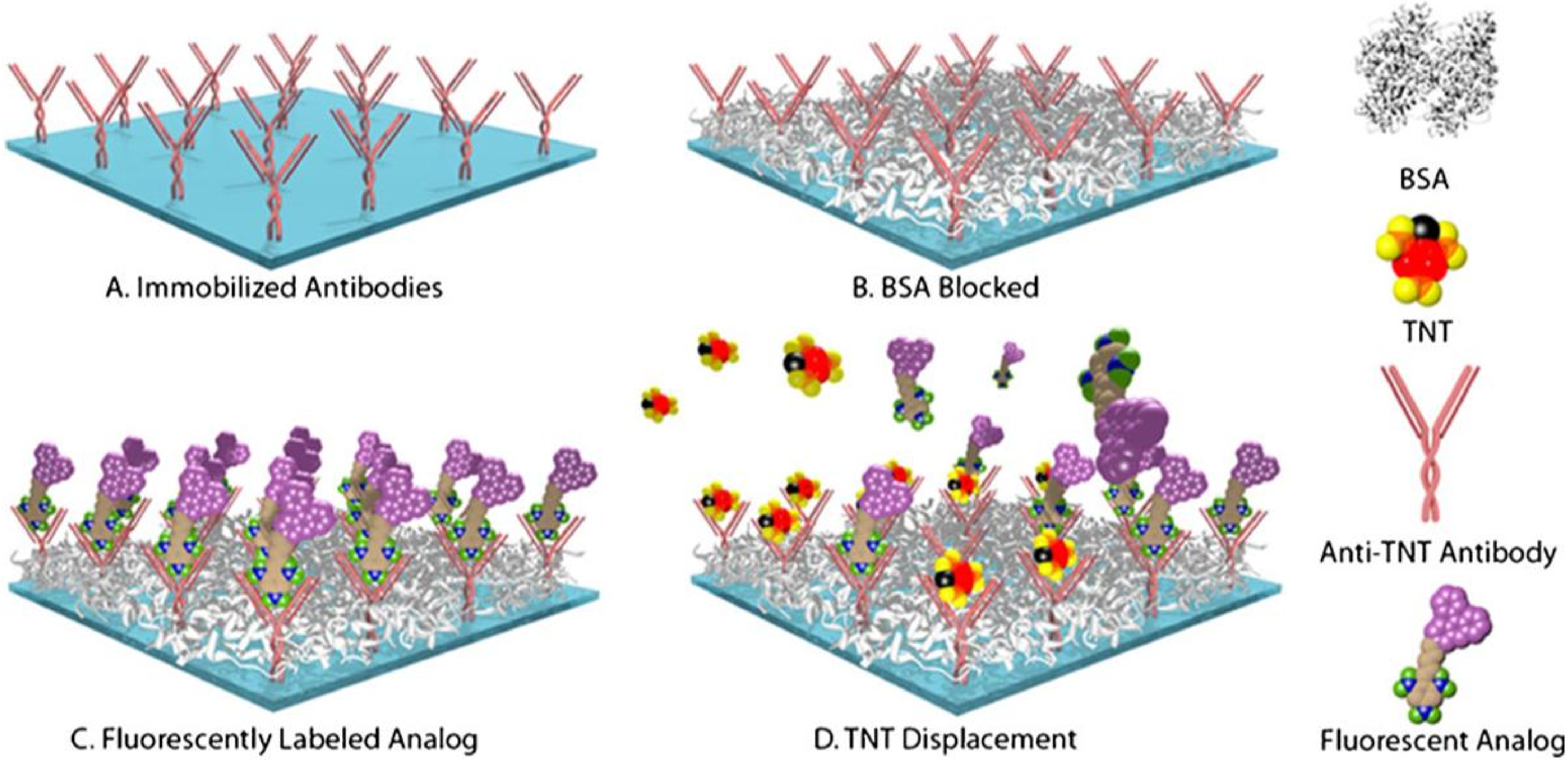
Chemical sensing

BIOCHEMISTRY

Microfluidic system (1/2)

Andre A. Adams: REMUS100 AUV with an integrated microfluidic system for explosives detection

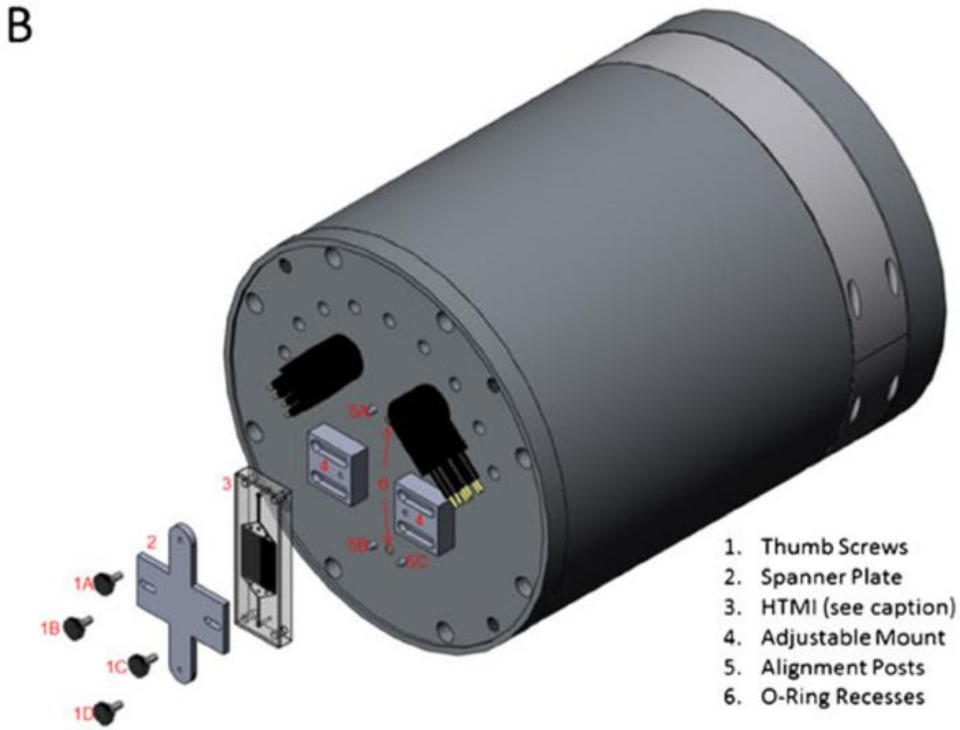


DOI 10.1007/s00216-013-6853-x

Microfluidic system (2/2)

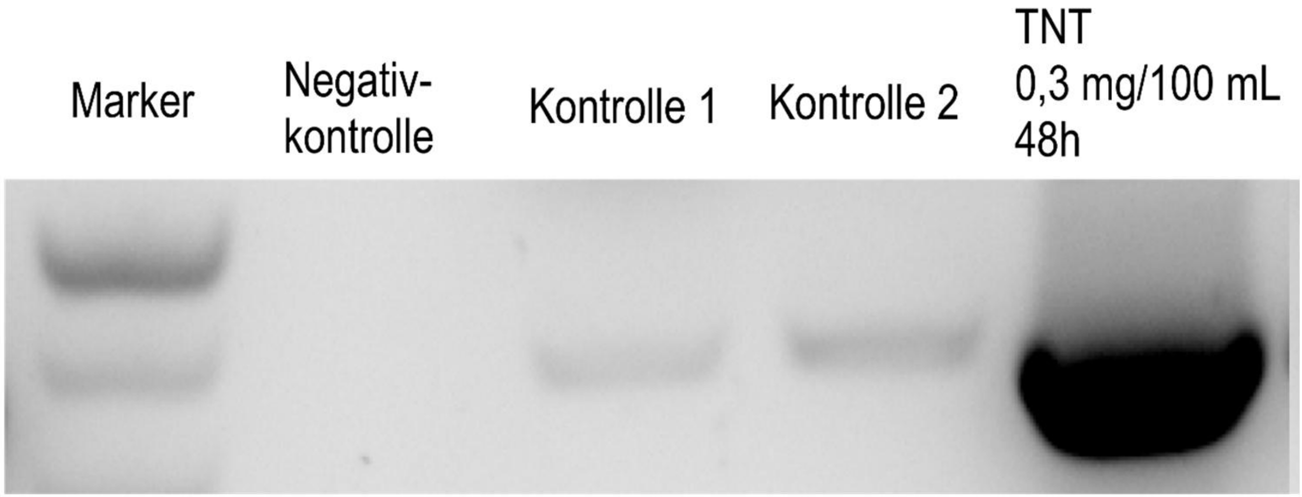
DOI: [10.1007/s00216-013-6853-x](https://doi.org/10.1007/s00216-013-6853-x)

Source: Andre A. Adams



Induced expression of the CBR1 gene in *Daphnia magna* upon exposure to TNT

(Semi-quantitative PCR)



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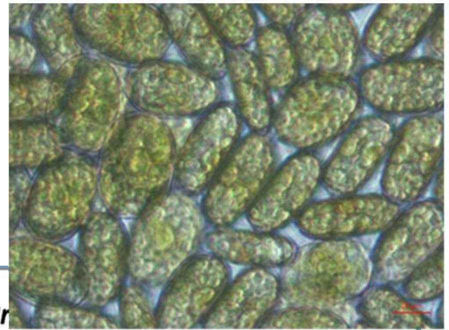
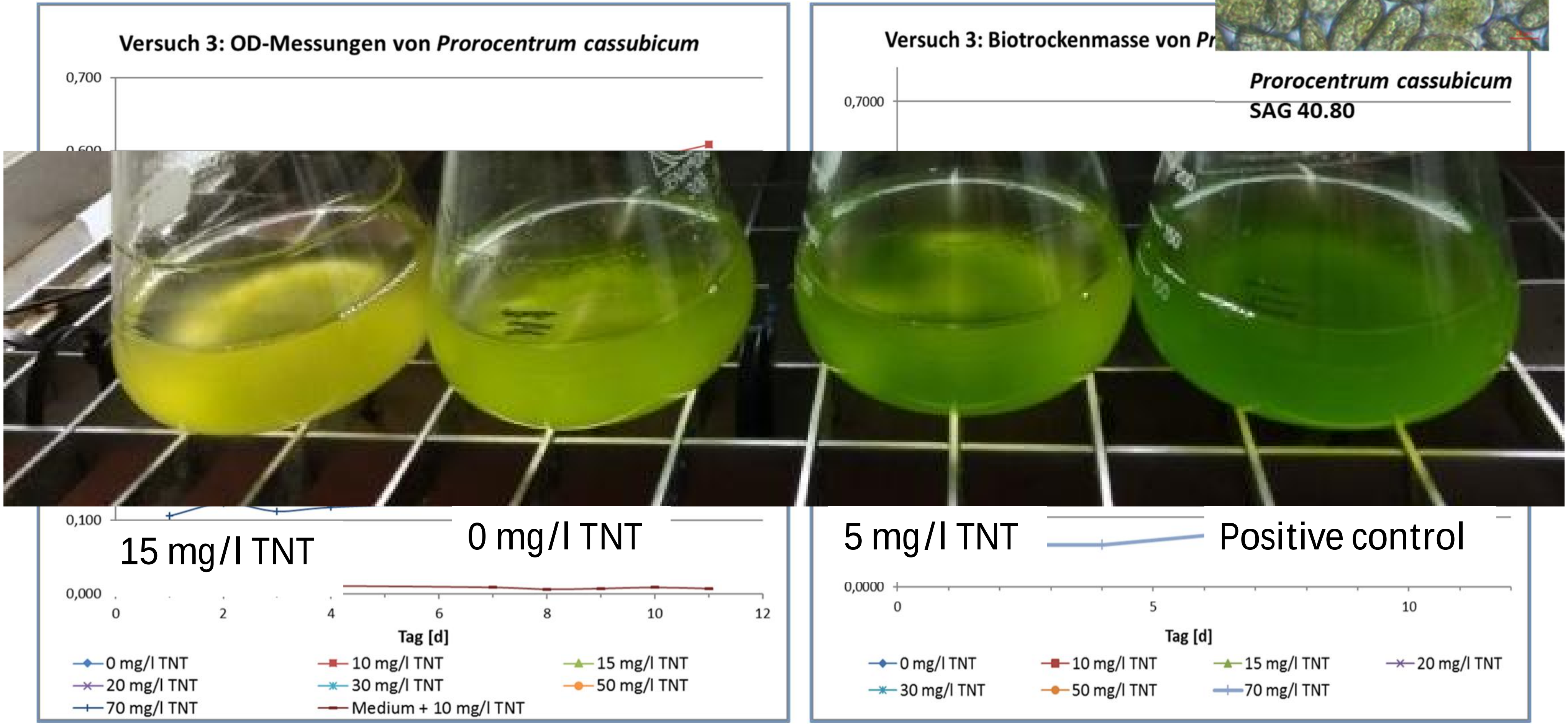
Toxic effect on microalga

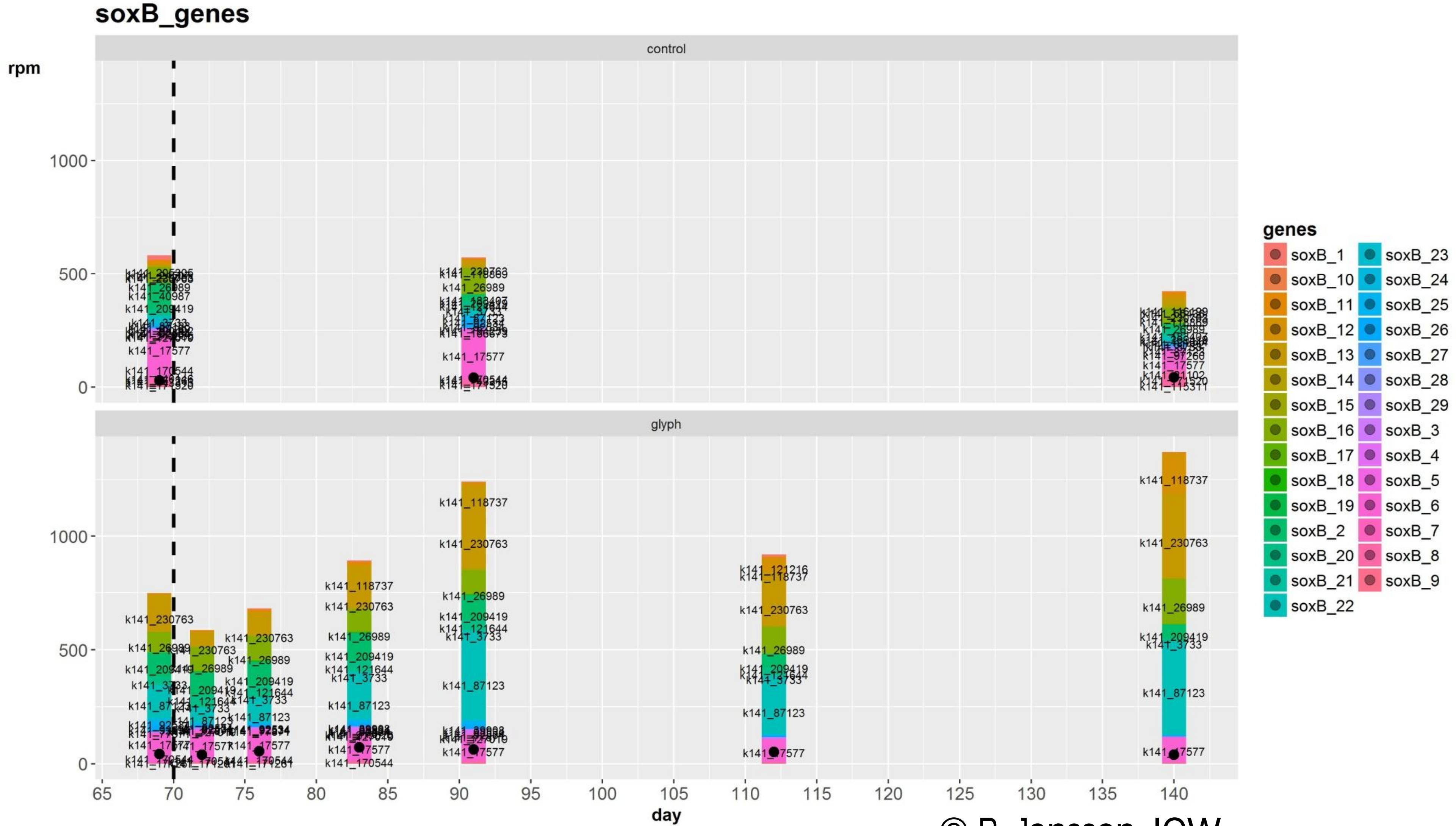
The toxic effect of TNT/STV on microalga *Prorocentrum cassubicum* was observed at concentrations of ≥30 mg/l

© Dr. Opayi Mudimu, Prof. Dr. R. Schulz, Uni Kiel





Genetic response on MC



© R. Janssen, IOW

What next?

- What appears „relevant“ regarding
  - Safety – remote sensing of MC (e.g. in-situ Neutron Gamma Radiation Spectrometry)
  - MSFD GES2020 and monitoring of MC
  - Toxicology and Detection limits (currently and in future)

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Sources & Links (1/2)

- Passive sampling
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