Assessment of the environmental quality in the eastern Gulf of Finland within project Hazless (HAZardous chemicaLs in the Eastern Gulf of Finland – concentrations and impact aSSessment)

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EnviTox webinar, 13 September 2021

HAZardous chemicals in the eastern Gulf of Finland – concentrations and impact assessment

"HAZLESS" ER90

BENEFICIARIES AND BUDGET

- **Tallinn University of Technology – 214 700,00 EUR**
- Institution of Russian Academy of Sciences Saint-Petersburg Scientific-Research Centre for Ecological Safety – 152 000,00 EUR
- Zoological Institute of the Russian Academy of Sciences – 102 600,00 EUR

ASSOCIATE

- Finnish Environment Institute

BUDGET

Total: 469.300,00 EUR
Programme co-finacing: 422.370,00 EUR

DURATION

35 months
01.04.2019-28.02.2022

T06 Environmental protection, climate change mitigation and adaptation

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Cross Border Cooperation Programme

Co-funded by the European Union, the Republic of Estonia and the Russian Federation

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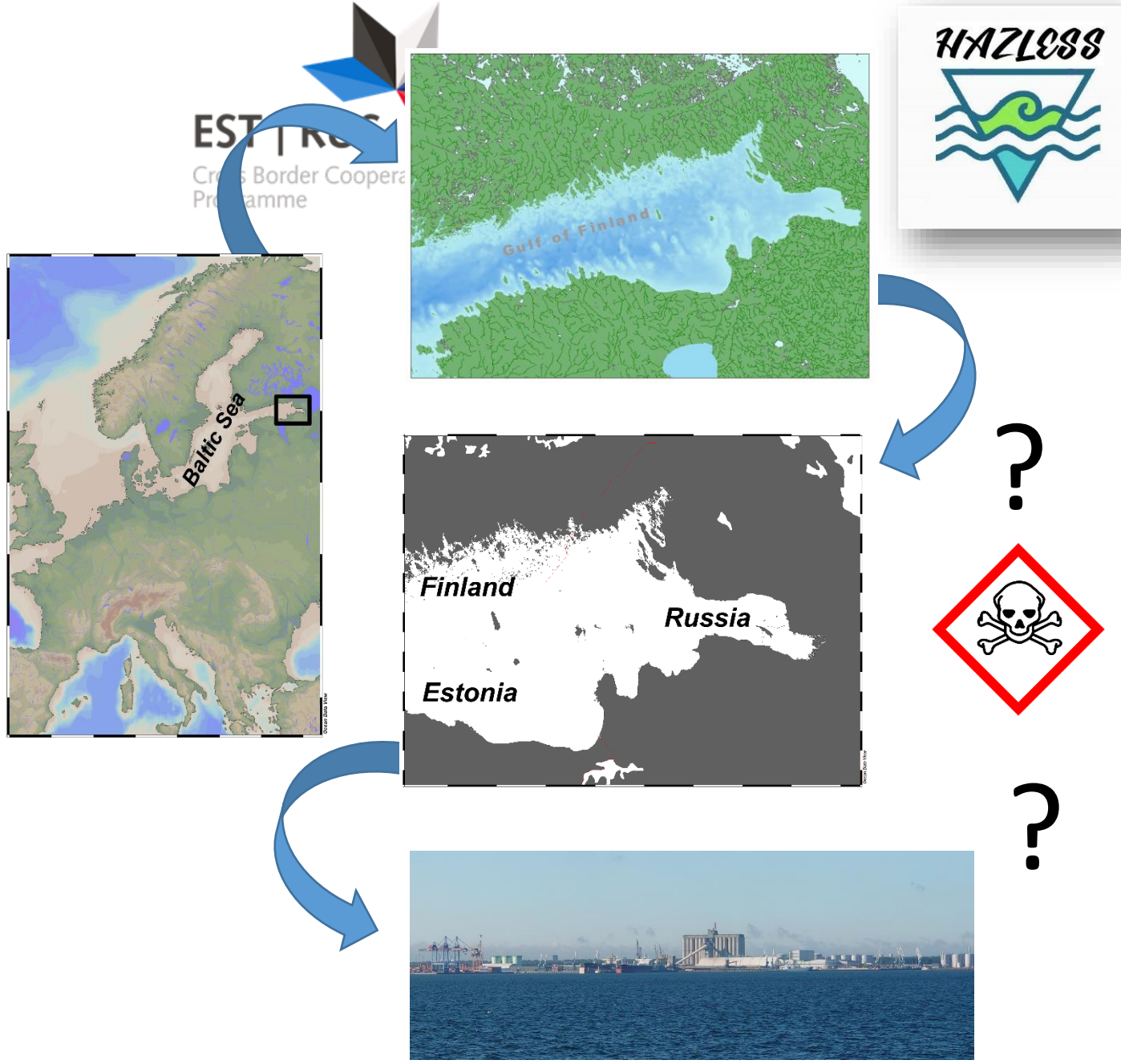
HAZLESS

The Programme web-site: www.estoniarussia.eu

BACKGROUND

- The array of cross-border stressors caused by different kind of human activities are deteriorating the Gulf of Finland (GoF)
- Environmental problems related to ecological effects of **hazardous substances** (HS), like **heavy metals, organic pollutants** and **pharmaceuticals** produce a threat to the eastern GoF environment through accumulation in the various matrices and altering biological functions of aquatic organisms
- According to the **EU Marine Strategy Framework Directive**, the evaluation of pollution indicators have to show whether the measured levels within waterbody are below the commonly agreed threshold values and subsequently meet the Good Environmental Status (GES)



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OBJECTIVES

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The overall objective:

- Adaptation and implementation of uniform biological indicators for assessment and control of environmental quality in the eastern GoF

The main outputs of the HAZLESS:

- The standard approach and strategies for transnational monitoring and assessment of emerging chemicals and harmful substances (HS) and their effects in the programme area and whole GoF

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OBJECTIVES (WP1)

- Our aim was to fulfill the existing gaps in the studies of priority substances included in the HELCOM Core Indicators list (e.g. **heavy metals**, **PAHs**, **PCBs**, **TBT**, **PFOSs** and **diclofenac**) along the eastern Gulf of Finland (GoF)
- The compilation of available data from two neighboring countries (Russia and Estonia) and collection of additional data from hotspot areas concerning the hazardous substances
- The numerical modelling of the spatial distribution of HS from different sources complement the evaluation of the comprehensive status of the GoF environment and help to assess the potential impact on the benthic organisms

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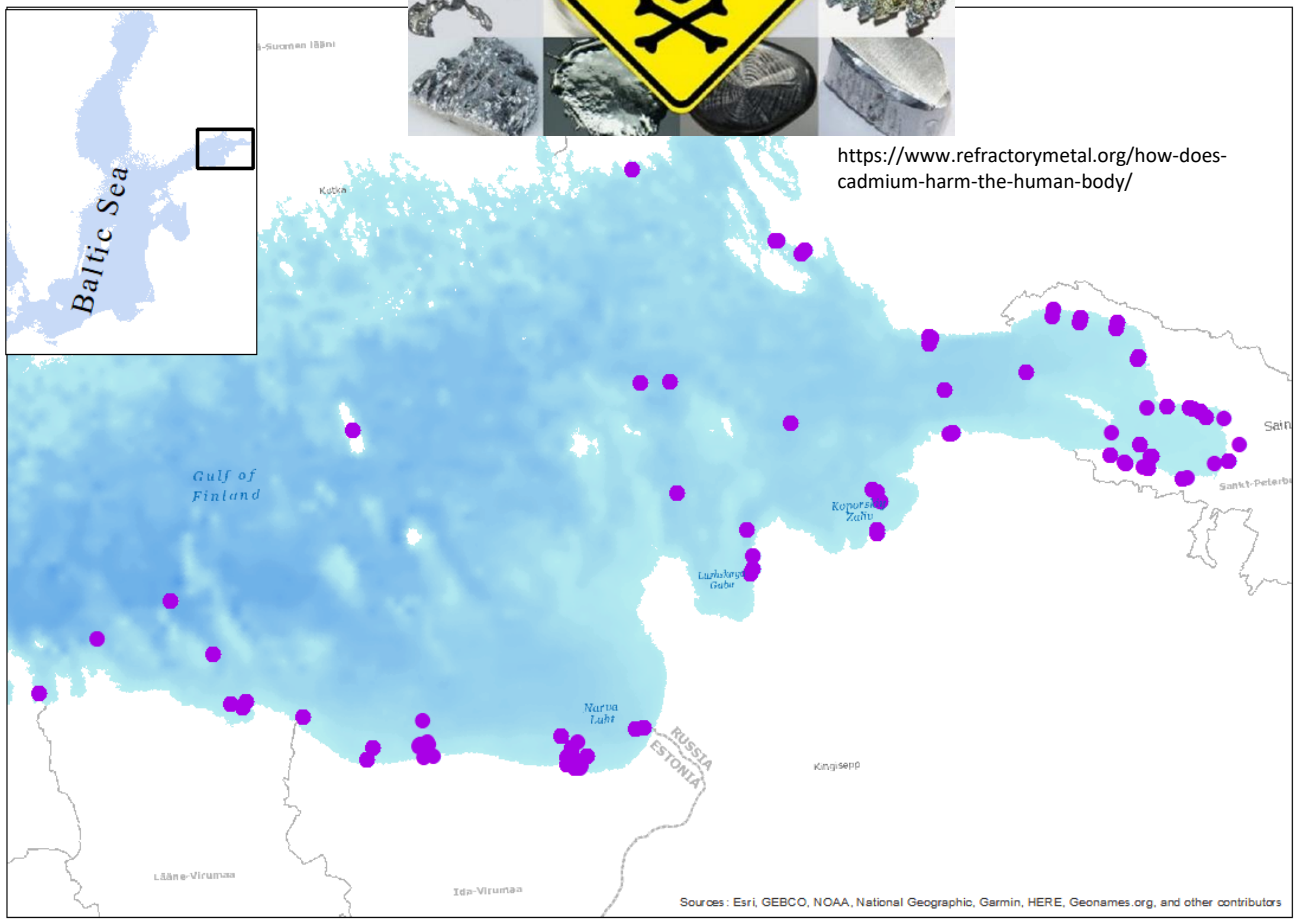
https://www.refractorymetal.org/how-does-cadmium-harm-the-human-body/



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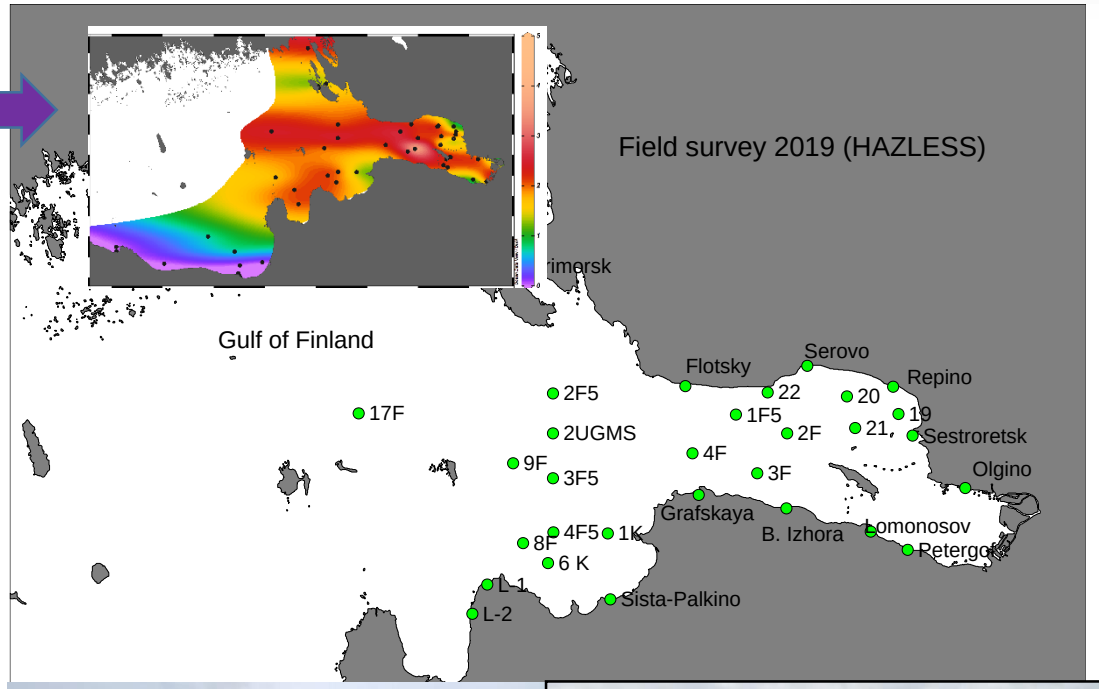
METHODS:
DATA AND SAMPLES

New data analysis



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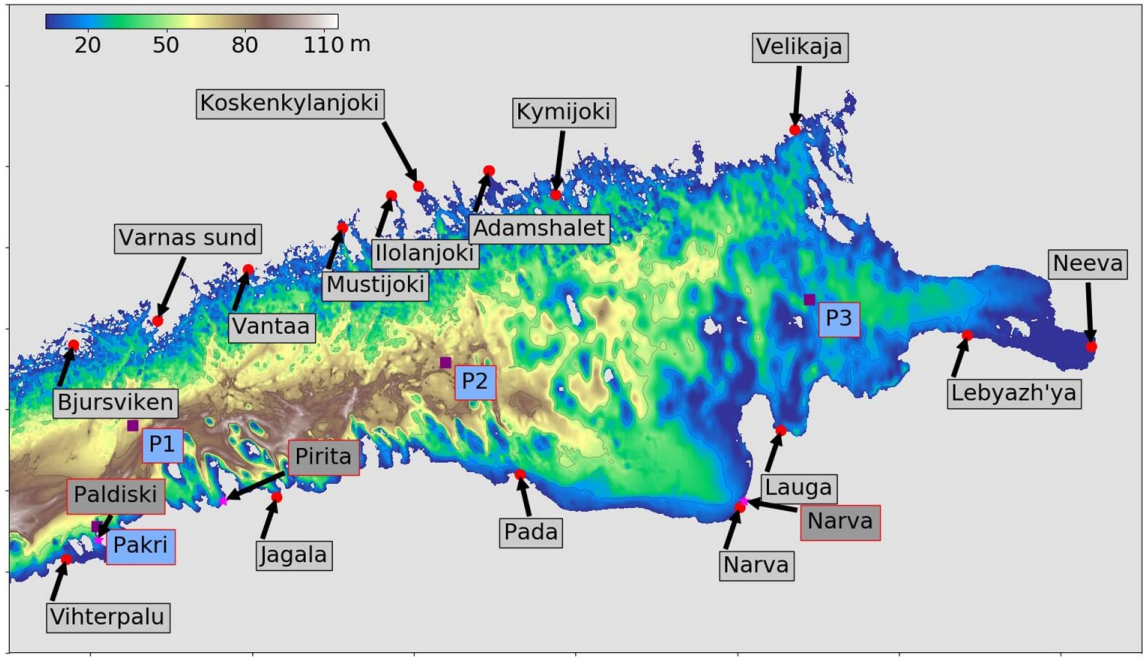
METHODS (WP1) : SIMULATION. MODEL DESCRIPTION

- Nested setup of GETM (General Estuarine Transport Model), code from IOW
- Vertical turbulence by GOTM (General Ocean Turbulence Model), SPM model from FABM
- Horizontal resolution 250 m, vertical 60 adaptive layers, outer domain with ~2 km
- Freshwater input from E-HYPE
- Atmospheric forcing HIRLAM by Estonian Weather Service



- Idealistic scenarios with different classes of SPM for possible hazardous substance transportation
- SPM classes: light (10 cm day^{-1}), medium (50 cm day^{-1}), heavy (100 cm day^{-1})

METHODS (WP2):
LABORATORY EXPOSURE STUDIES

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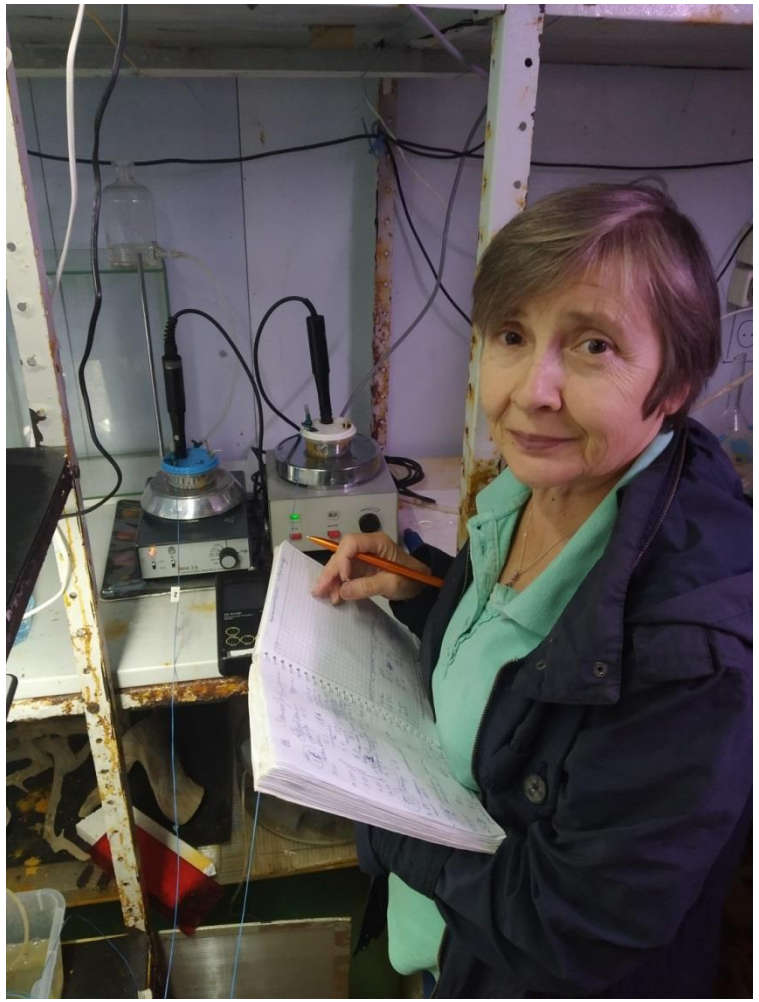
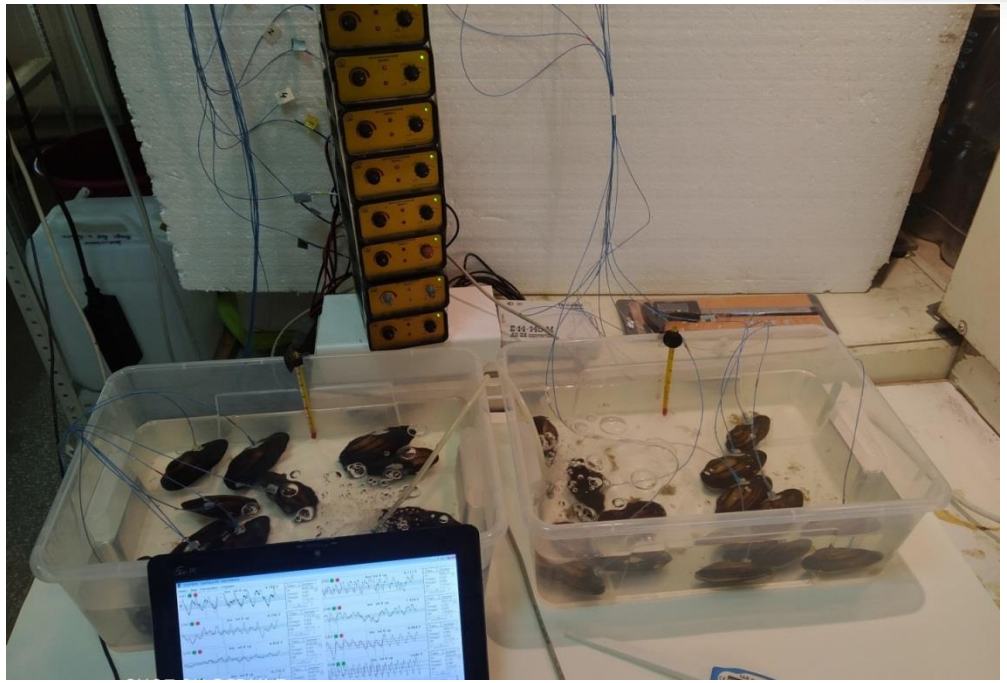


Determination of the respiratory activity



Analysis of the cardio activity of mollusks (e.g. *Limecola baltica, Anodonta anatina, Mytilus trossulus*)

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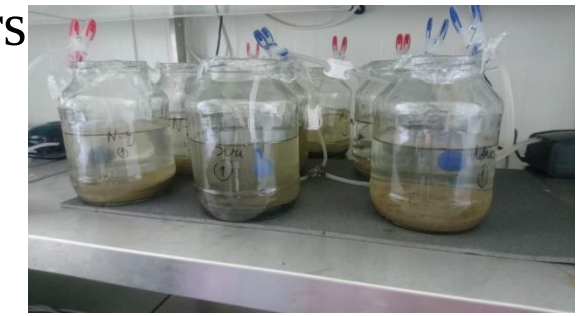
METHODS (WP3): BIOASSAYS, CAGES

- Ecotoxicological tests of sediments
- Mortality/Reproductive disorders/Biomarkers
- Amphipodes: *Monoporeia affinis*, *Pontogammarus robustoides*, *Gmelinoides fasciatus*, *Gammarus tigrinus*
- Caged mussels (*Mytilus trossulus*, *Dreissena polymorpha*, *Unio pictorum*)



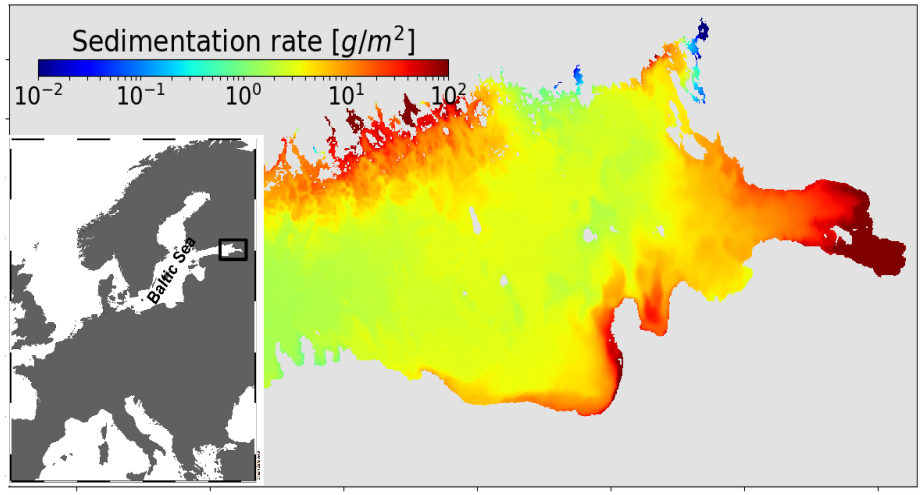
Sediment biotest

Installation of the cage

Reproductive disorders in amphipods

Samples for biomarkers

RESULTS:
POTENTIAL ACCUMULATION



Simulated suspended particulate matter sedimentation from the main river basins across the eastern GoF

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Hazardous substances in the sediments and their pathways from potential sources in the eastern Gulf of Finland

Ivan Kuprijanov [a,*], Germo Väli [a], Andrey Sharov [b], Nadezhda Berezina [c], Taavi Liblik [a], Urmas Lips [a], Natalja Kolesova [a], Jaakko Maanio [d], Ville Junttila [d], Inga Lips [a]

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ARTICLE INFO

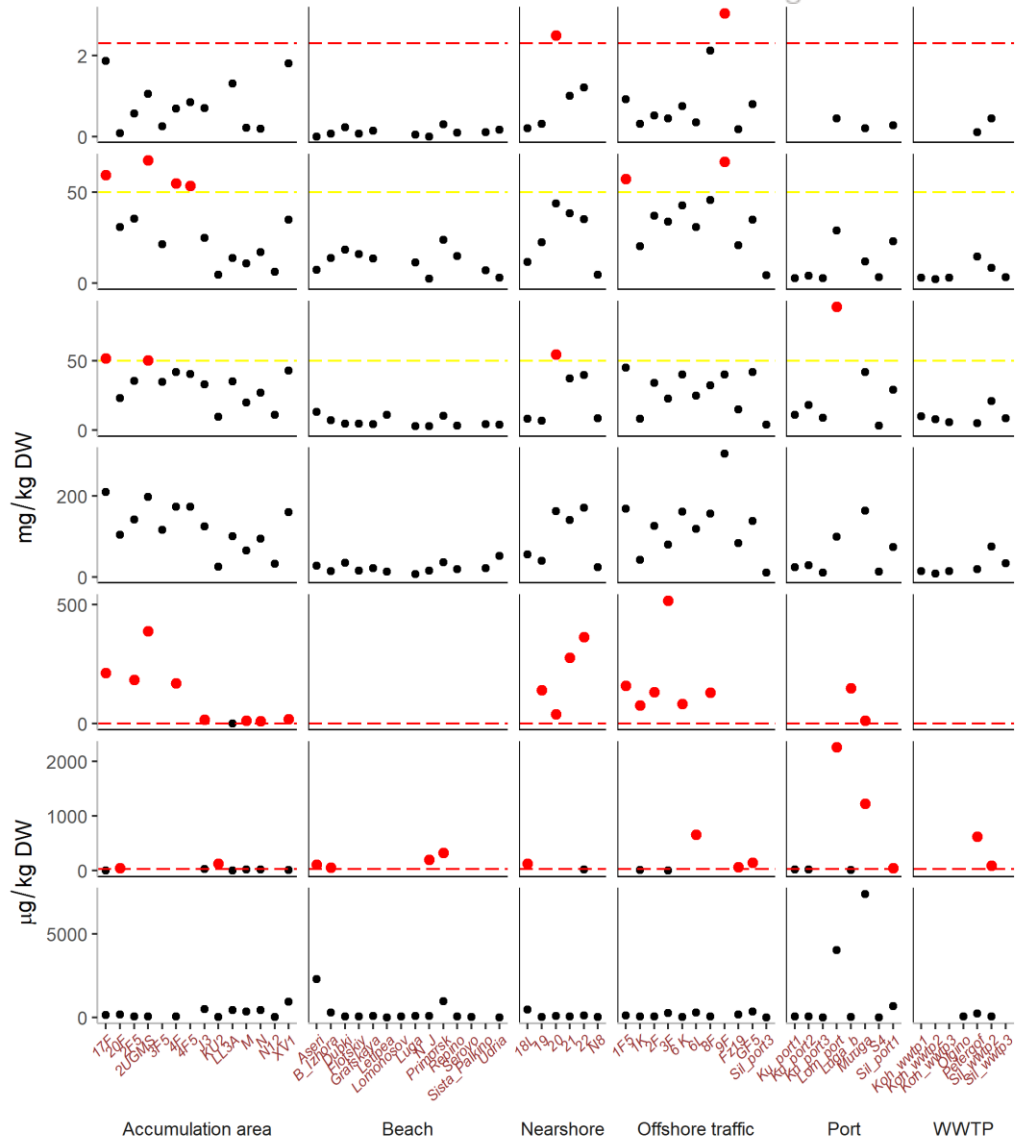
Keywords:
Organotins
PAHs
Heavy metals
Simulated accumulation
Baltic Sea

ABSTRACT

Contamination by hazardous substances is one of the main environmental problems in the eastern Gulf of Finland, Baltic Sea. A trilateral effort to sample and analyse heavy metals (HMs), polycyclic aromatic hydrocarbons (PAHs), and organotins from bottom sediments in 2019–2020 were conducted along with harvesting historical data in Russian, Estonian and Finnish waters. We suggest that the input of organotins still occurs along the ship traffic routes. The tributyltin content exceeded the established quality criteria up to more than 300 times. High contamination by PAHs found near the ports, most likely originate from incomplete fuel incineration processes. The Neva River Estuary and Luga Bay might potentially suffer from severe cadmium contamination. The high ecological risk attributed to the HMs was detected at deep offshore areas. The simulated accumulation pattern qualitatively agrees with field observations of HMs in sediments, demonstrating the potential of numerical tools to tackle the hazardous substances problems.

Kuprijanov, I., Väli, G., Sharov, A., Berezina, N., Liblik, T., Lips, U., Kolesova, N., Maanio, J., Junttila, V., Lips, I., 2021. **Hazardous substances in the sediments and their pathways from potential sources in the eastern Gulf of Finland.** *Mar. Pollut. Bull.* 170, 112642. https://doi.org/10.1016/j.marpolbul.2021.112642

RESULTS:
HELCOM INDICATORS (SEDIMENTS)



HELCOM threshold (**Cadmium**): 2,3 mg/kg dw

HELCOM threshold (**Lead**): 120 mg/kg dw

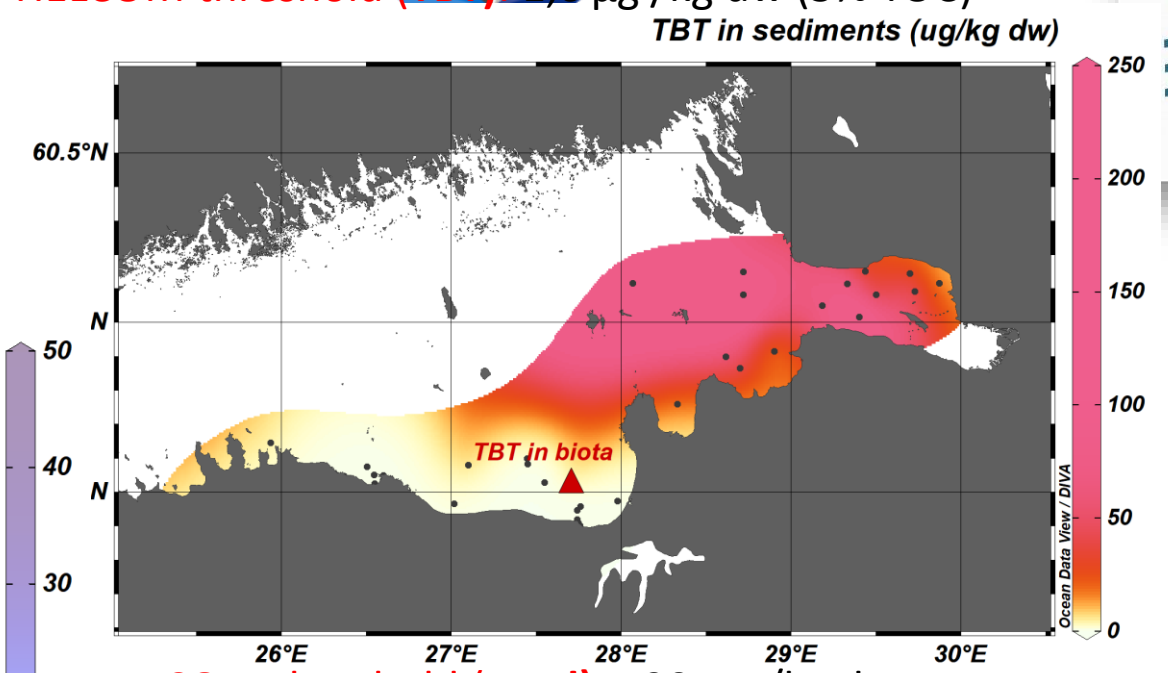
HELCOM threshold (**TBT**): 1,6 µg /kg dw (5% TOC)

HELCOM threshold (**ANT**): 24 µg /kg dw (5% TOC)

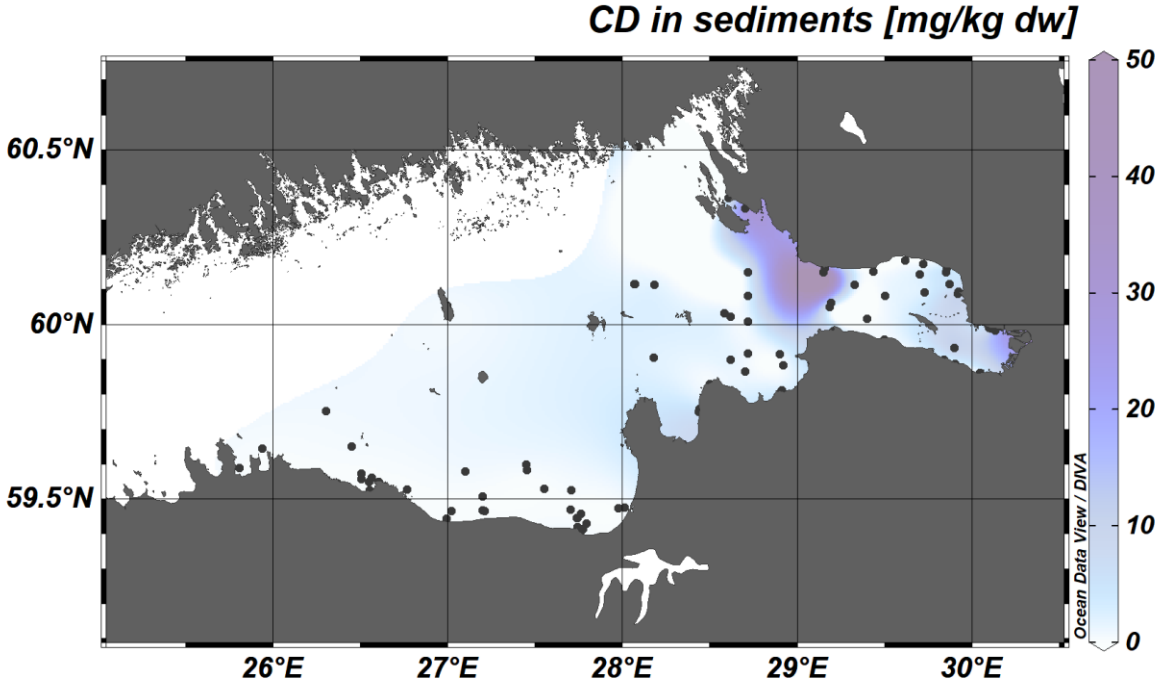
Kuprijanov, I., Väli, G., Sharov, A., Berezina, N., Liblik, T., Lips, U., Kolesova, N., Maanio, J., Junttila, V., Lips, I., 2021. **Hazardous substances in the sediments and their pathways from potential sources in the eastern Gulf of Finland.** *Mar. Pollut. Bull.* 170, 112642. https://doi.org/10.1016/j.marpolbul.2021.112642

RESULTS: DISTRIBUTION OF TRACE METALS AND TBT

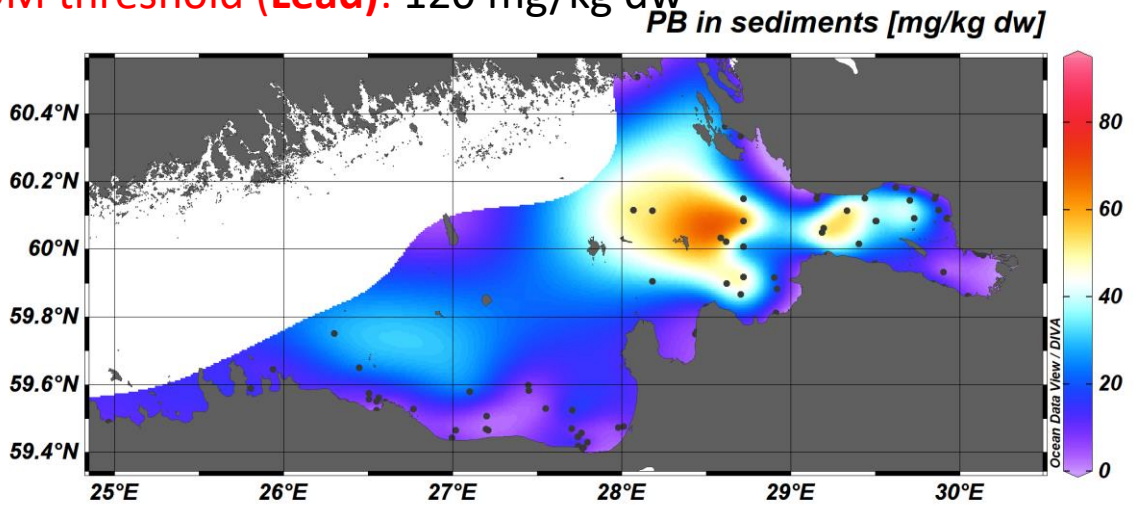
HELCOM threshold (**TBT**): 1,6 µg /kg dw (5% TOC)



HELCOM threshold (**Cadmium**): 2,3 mg/kg dw



HELCOM threshold (**Lead**): 120 mg/kg dw



Kuprijanov, I., Väli, G., Sharov, A., Berezina, N., Liblik, T., Lips, U., Kolesova, N., Maanio, J., Junttila, V., Lips, I., 2021. **Hazardous substances in the sediments and their pathways from potential sources in the eastern Gulf of Finland.** *Mar. Pollut. Bull.* 170, 112642. https://doi.org/10.1016/j.marpolbul.2021.112642

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RESULTS: PHARMACEUTICALS

7 compounds were recorded in seawater samples in a range of measured concentrations from 0.1 to 4452 ng/L :

- caffeine [81% of samples]
- carbamazepine [81%]
- ketoprofen [60%]
- diclofenac [23 %]
- ciprofloxacin, trimethoprim, and clarithromycin)
- Antibiotics were presented in trace concentrations.
- In sediment samples, 6 pharmaceuticals (0.1–66.2 ng g−1) were detected. The most common was carbamazepine (80%)

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Chernova, E., Zhakovskaya, Z., Berezina, N., 2021. **Occurrence of pharmaceuticals in the Eastern Gulf of Finland (Russia).** *Environ. Sci. Pollut. Res.* https://doi.org/10.1007/s11356-021-15250-1

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Co-funded by the European Union,

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Environmental Science and Pollution Research
https://doi.org/10.1007/s11356-021-15250-1

RESEARCH ARTICLE

Occurrence of pharmaceuticals in the Eastern Gulf of Finland (Russia)

Ekaterina Chernova[1] · Zoya Zhakovskaya[1] · Nadezhda Berezina[2]

Received: 2 March 2021 / Accepted: 28 June 2021

Abstract
The presence of substances of emerging concern—pharmaceuticals—in marine environments has been studied to a lesser extent compared to fresh and wastewaters. This is the first study of pharmaceutical distribution in the Russian part of the Baltic Sea. Among 18 pharmaceuticals previously detected in influent waters of Saint-Petersburg WWTPs, 7 compounds (caffeine [81% of samples], carbamazepine [81%], ketoprofen [60%], diclofenac [23 %], ciprofloxacin, trimethoprim, and clarithromycin) were recorded in seawater samples in a range of measured concentrations from 0.1 to 4452 ng L^{-1}. Antibiotics were presented in trace concentrations. In sediment samples, 6 pharmaceuticals (0.1–66.2 ng g^{-1}) were detected. The most common was carbamazepine (80%). The remaining compounds were located in decreasing frequency as follows: ketoprofen, trimethoprim, drotaverine, tetracycline, and ciprofloxacin. Some specific features of the Gulf of Finland affecting the distribution of pharmaceutical concentrations were highlighted—among the most important, the megapolis of St. Petersburg with its population over 5 million and freshwater input by the Neva River (high urbanization of the territory with a potent dilution factor). We discussed the suitable set of anthropogenic markers for the Russian part of the Gulf of Finland.

Keywords Pharmaceuticals · Seawater · Mass-spectrometry · Gulf of Finland · The Baltic Sea · Russia

Highlights
- Pharmaceuticals were studied in the water and sediments of the Gulf of Finland (Russian part).
- Caffeine, carbamazepine, and ketoprofen were main pharmaceuticals in seawater.
- Diclofenac was detected in 23% of seawater samples, in a range of 0.9–4.5 ng L^{-1}.
- Six pharmaceuticals in a range of 0.1–66.2 ng g^{-1} were established in sediments.
- The most common (80 %) was carbamazepine in sediments.
- Caffeine and carbamazepine are suitable anthropogenic markers for the Russian part of the Gulf of Finland.

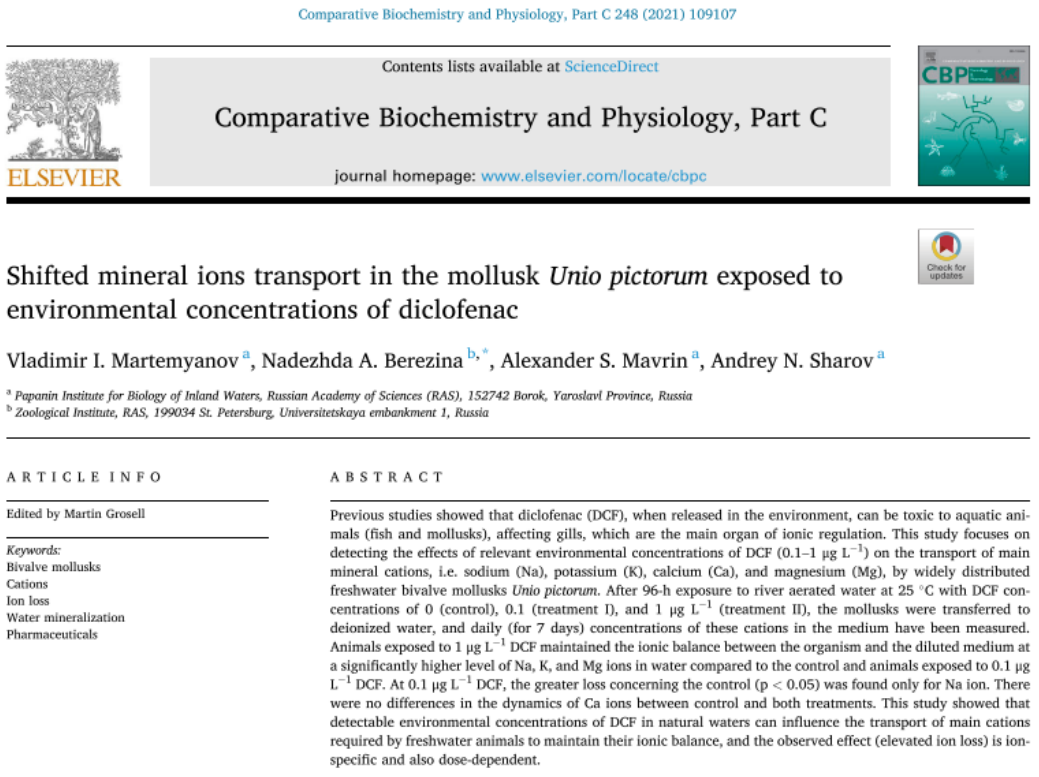
Introduction

Anthropogenic chemicals, including pharmaceuticals, represent a major cause of emerging concern. According to HELCOM (Baltic Marine Environment Protection Commission, The Helsinki Commission), the main sources of pharmaceuticals in the environment of the Baltic Sea are treated and untreated wastewaters (HELCOM 2018; Kolpin et al. 2002; Spongberg and Witter 2008). In this regard, information on the pharmaceuticals' release from WWTPs could help to predict the list of target compounds in the environment.

Pharmaceuticals are biologically active compounds; therefore, their presence in the environment, even in trace amounts, can negatively affect the state of the aquatic ecosystem

RESULTS:
EXPOSURE STUDY (DCF)

- Bivalve mollusks *Unio pictorum* exposed to **1 µg/L** DCF maintained the ionic balance between the organism and the diluted medium at a significantly higher level of Na, K, and Mg ions in water compared to the control and animals exposed to 0.1 µg/L DCF
- At **0.1 µg/L** DCF, the greater loss concerning the control ($p < 0.05$) was found only for Na ion.
- There were no differences in the dynamics of Ca ions between control and both treatments.



Comparative Biochemistry and Physiology, Part C 248 (2021) 109107

Contents lists available at ScienceDirect

Comparative Biochemistry and Physiology, Part C

journal homepage: www.elsevier.com/locate/cbpc

Shifted mineral ions transport in the mollusk *Unio pictorum* exposed to environmental concentrations of diclofenac

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[a] Papanin Institute for Biology of Inland Waters, Russian Academy of Sciences (RAS), 152742 Borok, Yaroslavl Province, Russia
[b] Zoological Institute, RAS, 199034 St. Petersburg, Universitetskaya embankment 1, Russia

ARTICLE INFO

Edited by Martin Grosell

Keywords:
Bivalve mollusks
Cations
Ion loss
Water mineralization
Pharmaceuticals

ABSTRACT

Previous studies showed that diclofenac (DCF), when released in the environment, can be toxic to aquatic animals (fish and mollusks), affecting gills, which are the main organ of ionic regulation. This study focuses on detecting the effects of relevant environmental concentrations of DCF (0.1–1 µg L^{-1}) on the transport of main mineral cations, i.e. sodium (Na), potassium (K), calcium (Ca), and magnesium (Mg), by widely distributed freshwater bivalve mollusks *Unio pictorum*. After 96-h exposure to river aerated water at 25 °C with DCF concentrations of 0 (control), 0.1 (treatment I), and 1 µg L^{-1} (treatment II), the mollusks were transferred to deionized water, and daily (for 7 days) concentrations of these cations in the medium have been measured. Animals exposed to 1 µg L^{-1} DCF maintained the ionic balance between the organism and the diluted medium at a significantly higher level of Na, K, and Mg ions in water compared to the control and animals exposed to 0.1 µg L^{-1} DCF. At 0.1 µg L^{-1} DCF, the greater loss concerning the control ($p < 0.05$) was found only for Na ion. There were no differences in the dynamics of Ca ions between control and both treatments. This study showed that detectable environmental concentrations of DCF in natural waters can influence the transport of main cations required by freshwater animals to maintain their ionic balance, and the observed effect (elevated ion loss) is ion-specific and also dose-dependent.

Martemyanov, V.I., Berezina, N.A., Mavrin, A.S., Sharov, A.N., 2021. **Shifted mineral ions transport in the mollusk Unio pictorum exposed to environmental concentrations of diclofenac.** *Comp. Biochem. Physiol. Part - C Toxicol. Pharmacol.* 248, 109107. https://doi.org/10.1016/j.cbpc.2021.109107

CONCLUSIONS (ON OUTCOMES OF WP1) :

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- Some harmful substances are banned worldwide (e.g. persistent organic pollutant **TBT**)
- Release to the environment of some contaminats significantly decreased (in case of air transported heavy metals as **Cd** and **Pb**) in the **western part of eastern GoF**
- **Except: Mercury** in sediemnts**!** ***point sources of pollution?***

But chemical residues still present and continue to affect the state of the environment through the contaminated sediments, the water column, enter sediment dwelling biota and accumulate along the trophic chain.

Persistent organic pollutants and heavy metals in accumulation areas and around centers of the maritime activity in the eastern GoF, as revealed by the environmental surveys during the last decade, might:

- Closely approach in some matrixes (e.g. **Pb** in sediments)
- While more often exceed manifold (e.g. PAH **Anthracene**, **Hg** in biota, **Pb** in biota/water, **Cd** and **TBT** in biota/sediments) of good-quality threshold set for the Baltic Sea

✓ Depending on the rate of sedimentation, HS might disperse along the shoreline in the eastern GoF much further from the initial release within river estuary systems

✓ Important to take into account the gradient structure of possible dispersion when planning monitoring activities in the eastern GoF

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Thank you for attention!

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Estonia-Russia Cross Border Cooperation Programme 2014-2020 aims to foster cross-border cooperation across the borders between the Republic of Estonia and the Russian Federation to promote socio-economic development in the regions on both sides of the common borders. The Programme web-site: www.estoniarussia.eu

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