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Effects of climate and anthropogenic pressures on chemical warfare agent transfer in the Baltic Sea food web

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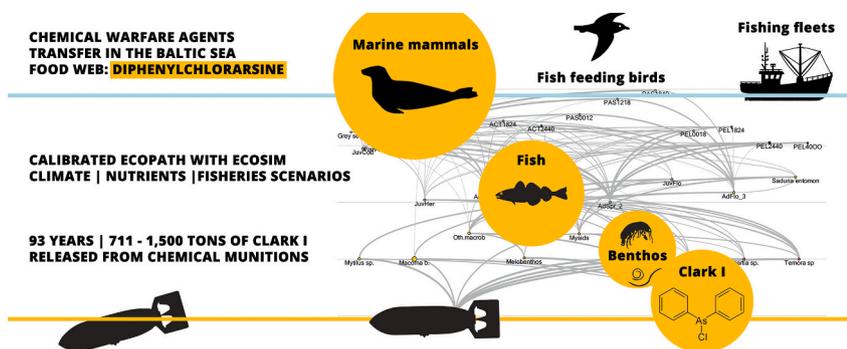
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HIGHLIGHTS

- The modelling exercise simulated potential pathways and forecasts for Clark I transfer within the Baltic Sea food web.
- Observations from the modelling timestamps covering recent times correspond with in situ detections.
- Remediation of Chemical Weapons by removal should be considered as part of the integrated management of the Baltic Sea.

GRAPHICAL ABSTRACT



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ABSTRACT

The Baltic Sea is a severely disturbed marine ecosystem previously used as a dumping ground for chemical warfare agents (CWA), which are now known to enter its food web. We have performed a modelling exercise using a calibrated and validated Central Baltic Ecopath with Ecosim (EwE) model to recreate the potential environmental pathways of the infamous Clark I (diphenylchlorarsine). Observations from modelling timestamps covering recent times correspond with in situ detections in sediments and Atlantic cod (*Gadus morhua*). Under applied modelling conditions and scenarios, there is an active transfer of Clark I from sediments through the Baltic Sea food-web. According to our results, Clark I bioaccumulates within the Baltic Sea food web exclusively throughout the detritus-based food chain. The EwE model for the Central Baltic Sea also allows the simulation of changes in the food web under multiple anthropogenic stressors and management efforts, including recommendations from the Helsinki Commission Baltic Sea Action Plan (HELCOM BSAP). Among all investigated scenarios and factors, the commercial fishing is the most impactful on Clark I accumulation rate and contamination transfer within the Baltic Sea food web. The study indicates the need to extend the existing monitoring

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approach by adding additional species representing a broader range of ecological niches and tiers within the food chains. From the environmental perspective, the remediation of Chemical Weapons by removal should be considered as part of the integrated management of the Baltic Sea.

1. Introduction

Climate change, overfishing and eutrophication directly affect the Baltic Sea's relatively simple food web and its ecosystem functioning (e.g. Meier et al., 2022; Kuliński et al., 2022; Reckermann et al., 2022). The limited water exchange with the North Sea causes long residence times for any pollutants that enter this semi-enclosed brackish waterbody (e.g. Lehmann et al., 2022). This applies to approximately 50,000 tons of chemical weapons (CW) containing up to 15,000 tons of chemical warfare agents (CWAs) that were disposed of in the Baltic Sea soon after the end of World War II (HELCOM, 2013). In 1993, the problem was brought to the attention of the Helsinki Commission (HELCOM), which formed a series of working groups focusing on dumped chemical munitions (CHEMU: 1993–95, MUNI: 2010–13, SUBMERGED: 2015- until today). In 2011, the United Nations General Assembly issued a resolution UNGA 65/149 urging cooperation in solving the problem, while the EU Parliament issued a similar memorandum in 2021. >70 years after their disposal, around the time of the estimated corrosion-driven disintegration of containers and munitions, the environmental fate of CWAs in marine ecosystems is still barely understood (HELCOM, 2024).

Potential environmental hazards linked to sea-dumped CWAs were overlooked for decades until the first large-scale investigation in 2006 by the international scientific project MERCW - Modelling of Ecological Risks related to Sea-dumped Chemical Weapons (Missiaen et al., 2010). Research was continued in CHEMSEA – (Chemical Munitions Search and Assessment), MODUM (Towards the Monitoring of Dumped Munitions Threat), and DAIMON (Decision Aid for Marine Munitions). First scientific investigations confirmed that the disposed chemical munitions are corroded and already started leaking (e.g. Missiaen et al., 2010; Beldowski et al., 2016). Sulfur mustard, arsenic-based CWAs and their transformation products have been detected in Baltic Sea sediments and their concentrations are expected to increase (Vanninen et al., 2020; Niemikoski et al., 2020a, 2020b). When exposed to aquatic conditions, CWAs may undergo transformations, including hydrolysis, oxidation, or polymerisation (Czub et al., 2020; Czub et al., 2021). One CWA of particular interest is the organoarsenic diphenylchlorarsine (DA) – also known as Clark I (Brzeziński et al., 2020). It is considered to be potentially bioaccumulating based on its high bioconcentration factor and relatively low water solubility (Sanderson et al., 2008). Diphenylchlorarsine was sea-dumped as a sole compound in original containers and with other CWAs in barrels containing technical mixtures like “Arsine Oil” or “Winterlost” (HELCOM, 2013). According to the records of the Soviet army, responsible for the disposal of Nazi Germany Chemical Warfare Materials (CWM) including chemical munitions, containers or barrels, dumped in the Baltic Sea contained from 711 to 1500 tons of Clark I (Sanderson et al., 2010). Despite its relatively fast hydrolysis into diphenylarsenic acid (DPA) in laboratory conditions, it has been observed that Clark I remains intact in marine sediments and is environmentally persistent (Nawała et al., 2021). It adsorbs on organic and mineral sediment fractions, reaching concentrations up to 16.4 mg·kg⁻¹ dry weight (Söderström et al., 2018), contributing to the total arsenic contamination of Baltic Sea sediments (Beldowski et al., 2016; Vanninen et al., 2020). Any natural or human-induced near-bottom disturbances result in sediment resuspension and, thus, the spreading of CWA, making them potentially more bioavailable (Jakacki et al., 2020). Niemikoski et al. (2020a, 2020b) detected CWA-related compounds in 14 % of 95 investigated individuals of Atlantic cod (*Gadus morhua*) caught by pelagic trawling in the primary CW dumpsite in the Baltic Sea, the Bornholm Deep. DPA was detected in 9 % of analysed muscle tissue samples and 10 % of bile samples of Atlantic cod (Niemikoski et al.,

2020a, 2020b). New findings go along with the reported higher prevalence of diseases and parasites found in cod from Bornholm Basin, when compared with other areas (Lang et al., 2018) and observed alteration in gut microbiota composition in this commercially important fish species from Bornholm Deep CW dumpsite (Wilczynski et al., 2022). Thus, it all amplifies already raised safety issues for both ecosystem and health of sea-food consumers (Greenberg et al., 2016). This demonstrates that CWAs, specifically Clark I and its transformation product, have clearly reached and affected higher trophic levels in the Baltic Sea food web. However, the trophic pathways along which pollutants from sediments reached these higher trophic levels are unknown. Furthermore, the Bornholm Deep was also the area of the recent catastrophic Nord Stream sabotage event, resulting in massive resuspension of potentially contaminated sediments (Sanderson et al., 2023).

This study aimed to fill this knowledge gap by modelling potential Clark I pathways in the Baltic Sea food web and estimating its potential bioaccumulation by accounting for uncertainties driven by climatic and ecosystem-management scenarios. The identified trophic pathways will contribute to improved monitoring strategies and enhance ecosystem-based management of the Baltic Sea. Eight different combinations of climate, nutrients and fisheries scenarios were run to the year 2100, using the calibrated Ecopath with Ecosim (EwE) model for the Central Baltic Sea for two CWA release scenarios: 711 and 1500 tons of Clark I. EwE is a well-established modelling platform used for food web modelling to answer different ecological and management questions related to the marine ecosystem (Christensen and Walters, 2004). Presented analyses enhance the general understanding and forecasting of potential environmental threats from sea-dumped munitions in general (Scharsack et al., 2021) and sea-dumped CWAs in particular by investigating contamination pathways and vectors in the Baltic Sea ecosystem and its food web. Furthermore, it creates a new foundation for existing (Beldowski et al., 2018) and upcoming monitoring strategies included within the updated HELCOM Baltic Sea Action Plan (<https://helcom.fi/baltic-sea-action-plan>) that will be essential for potential future remediation efforts.

2. Materials and methods

2.1. Study area

As a result of massive and coordinated sea-dumping, the chemical munitions can be found both at official and unofficial dumpsites, as well as along the transport routes from Wolgast harbour to dumpsites. Baltic Sea CW dumpsites are located in several deep areas of the Baltic Proper (BP), namely in the Bornholm Basin, the southern part of Gotland Basin and the Gdańsk Basin (Fig. 1). The Baltic Proper is characterised by a vertical salinity stratification caused by high riverine inflows and irregular, quasi-decadal Major Baltic Inflows (MBI), resulting in a permanent halocline at approximately 70 m depth (Leppäranta and Myrberg, 2009). Stratification and increased oxygen consumption result in deep-water hypoxia and the formation of ‘dead zones’ below the halocline (Conley et al., 2009; Carstensen et al., 2014).

Multiyear monitoring in the vicinity of submerged military objects (Czub et al., 2018) reported scarce but constant presence of Nematoda (representatives of meiofauna), adult Atlantic cod (*Gadus morhua*), and adult European flounder (*Platichthys flesus*). As mentioned, the Baltic Proper environmental conditions are characterised by sea-surface salinity gradients, high riverine inflows, large-scale inflows of oxygen-rich, saline and dense waters from the North Sea into the Baltic Sea (Conley et al., 2002; Conley et al., 2009; Mohrholz, 2018). Such large

MBI in 2014 caused a temporal recolonisation of the Bornholm Deep CW dumpsite by benthic species (Czub et al., 2018). In 2016, observations of swarms of free-swimming amphipods – most likely *Pontoporeia* sp. were the first observations of macrofaunal activity near submerged chemical munition since the beginning of the CHEMSEA project in 2011. Although not directly observed, the isopod *Saduria entomon* is known to sustain very low-oxygen conditions and is known to contribute to the Atlantic cod diet in Bornholm Basin (Dziaduch, 2011).

2.2. Food web model structure and setup

The EwE model for the Central Baltic Sea (CBS) was used to demonstrate changes in the food web (Bauer et al., 2018, 2019; ICES, 2016). It comprises 22 taxa/ecological groups and two basal resources that represent the food web of the CBS (Fig. 2): including detritus (1), phytoplankton (1), zooplankton (4), benthic invertebrates (6), fish species separated into adults (4) and juveniles (4), fish-feeding birds (1), grey seals (1), and ten fishing fleets representing three different fishing methods: active demersal (3); passive demersal (3); and pelagic (4). All CW dumpsites are located within the spatial domain of the model: ICES Sub-Divisions (SD) 25–29, excluding the Gulf of Riga. The EwE CBS model was calibrated with biomasses and catches of functional groups for 2004–2013, driven by fishing mortalities and environmental forcing. Environmental forcing was based on simulated primary production, phytoplankton biomass, water temperatures, cod reproductive volume and hypoxic bottom area to simulate the food web responses to pre-specified climate, eutrophication, and fisheries management scenarios (Table 1). The uncertainties inherent in the food web model were estimated by applying the EwE Ecosampler module (Steenbeek et al., 2018). Ecosampler assesses input parameter uncertainty on model output by applying alternate mass-balanced model parameter sets (i.e., biomass, production per biomass, consumption per biomass, catches and diet composition) using a Monte Carlo (MC) routine. We applied 2000 MC runs for each scenario.

2.3. Ecotracer – Clark I

Ecotracer is a component of the EwE package (Walters and Christensen, 2018) that solves the contaminant and biomass dynamic equations simultaneously in Ecosim and was applied within this study to investigate the bioaccumulation of Clark I. Submerged chemical munitions are located at depths exceeding 90 m, below the permanent halocline and mainly within hypoxic or anoxic waters, where the lack of oxygen strongly limits the biological activity of higher taxa. Based on the multiyear observations from the CW dumpsites from Czub et al. (2018), the potential direct absorption of this compound from the environment (Table 2) was limited to detritus, meiobenthos, adult Atlantic cod (*Gadus morhua*), adult and juvenile European flounder (*Platichthys flesus*) and *Saduria entomon* based on its reported contribution to Atlantic cod diet in Bornholm Basin (Neuenfeldt and Beyer, 2006). The remaining input data for modelling of Clark I bioaccumulation performed in our studies came from peer-reviewed literature. Due to the lack of similar marine food web modelling studies for CWAs and arsenic compounds, however, the excretion rates were adapted subjectively (Table 2), based on the existing literature on arsenic bioaccumulation levels in fish (Storelli et al., 2005; Polak-Juszczak and Richert, 2021) and input values used at bioaccumulation modelling for other persistent, highly toxic and low-water soluble compounds containing metalloids and heavy metals (Alava et al., 2018). Neither physical nor metabolic decay factors were assigned for the target phenylarsenical due to the potential adverse effects caused by both intact Clark I and any of its degradation products (Table 2). For additional validation of modelled environmental results, accumulation in detritus was recalculated based on the reported mean organic matter (OM) content in sediments from Baltic Sea dumpsites (Czub et al., 2018).

2.4. Forcing scenarios

Environmental forcing for the food web model and the projections

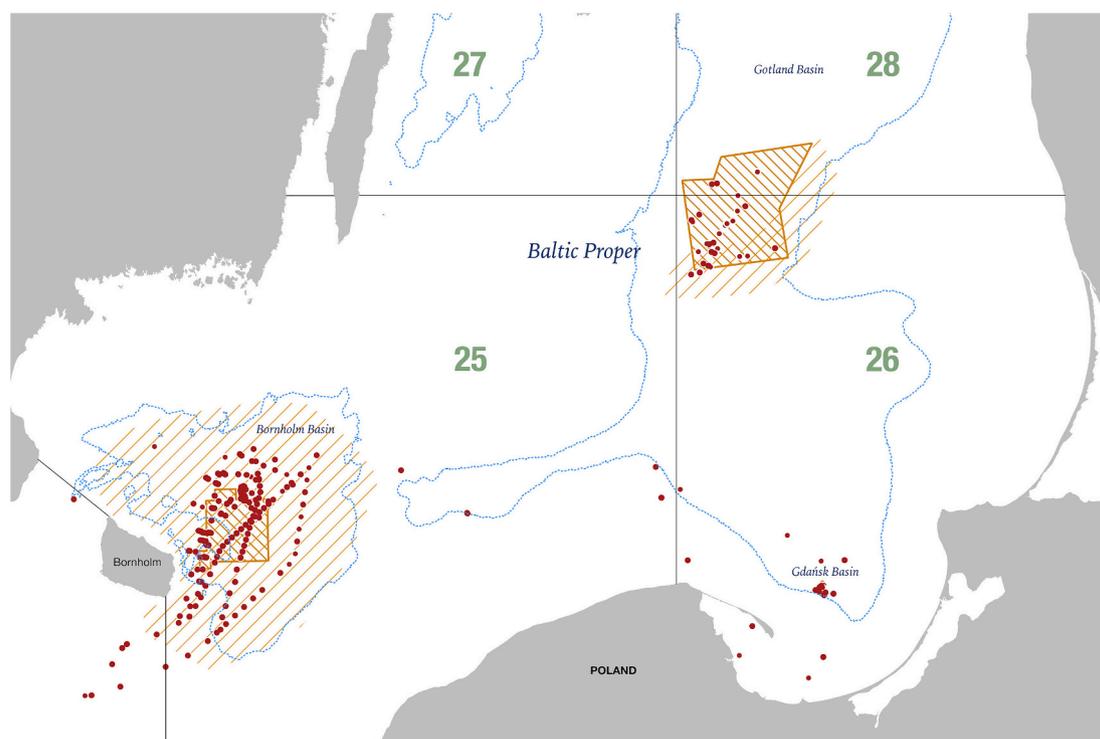


Fig. 1. Southern parts of Baltic Proper (ICES subdivisions 25–28), where Baltic Sea Chemical Weapon dumpsites (orange boxes) are located. Orange lines represent the “reported encounters with chemical warfare materials” (maps.helcom.fi). Red dots represent locations where chemical warfare agents (CWAs) have been detected in sediments (after Fauser et al., 2023). The dotted blue line illustrates the areas deeper than 70 m affected by temporary or permanent bottom water hypoxia (Czub et al., 2018).

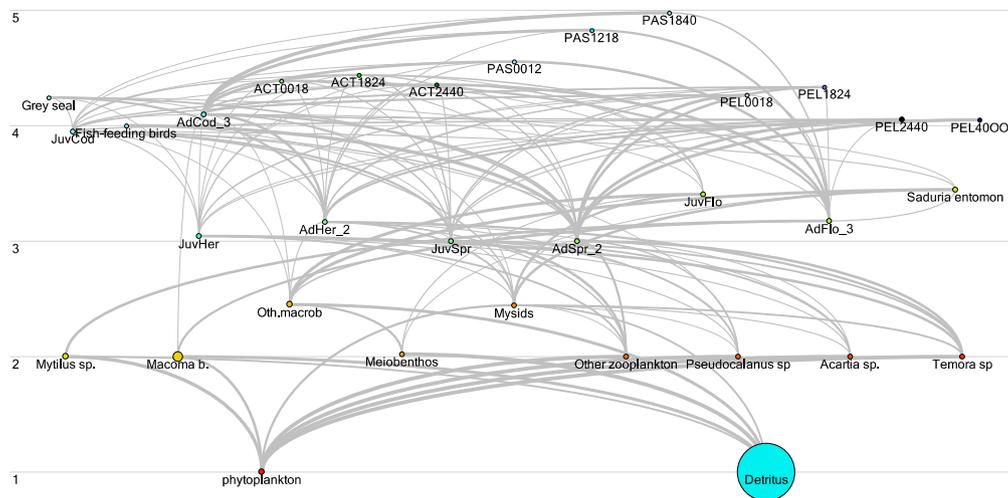


Fig. 2. Trophic diagram of the Baltic Proper food web with circles representing modelled functional groups including adult (Ad) and juvenile (Juv) groups for Atlantic cod (Cod), Atlantic Herring (Her), European sprat (Spr) and European flounder (Flo) commercial fishing fleets: ACT- active fishing gears i.e. bottom trawl, PEL- pelagic gears, PAS - passive fishing gears i.e. gillnets; while numbers are length class of vessels in metres; and edges main predator-prey relationships (based on Bauer et al., 2019): For more details on the definition of functional groups, see Tomczak et al., 2012 and Supplementary Appendix S1 at Bauer et al., 2018.

Table 1
EwE model for the Central Baltic Sea forcing scenarios.

Scenario	Abbreviation	Description
Climate	a) RCP 4.5	<u>Representative Concentration Pathway 4.5</u> : The possible range of radiative forcing values in the year 2100 (IPCC, 2021)
	b) RCP 8.5	<u>Representative Concentration Pathway 8.5</u> : The possible range of radiative forcing values in the year 2100 (IPCC, 2021)
Nutrients	c) BSAP	<u>Baltic Sea Action Plan</u> : The targets of the HELCOM BSAP are achieved (HELCOM, 2021)
	d) REF	<u>Reference</u> : Nutrient sources to the Baltic Sea ecosystem are maintained at historic (1976–2005) levels
Fisheries	e) SUS	<u>Sustainable Fisheries</u> : Fishing pressures are in accordance with the Maximum Sustainable Yield (MSY) approach outlined in the EU Common Fisheries Policy (CFP). Since presently no target fishing mortality (F) values are available for the cod stock, we applied F (FMSY = 0.3) according to the EU Atlantic cod recovery plan from 2008 (Bastardie et al., 2010). For adult herring and adult sprat, we set FMSY according to the EU Multi-Annual Plan (http://data.europa.eu/eli/reg/2016/1139/oj), i.e., FMSY = 0.22 and FMSY = 0.26, respectively.
	f) OA	<u>Open Access Fisheries</u> This scenario assumes that a largely unregulated (Open Access) fishery would be the management of choice for the future Baltic Sea. Hence, F levels were set to the historically observed maximum values, i.e., for adult cod F = 1.46, for adult herring F = 0.442 and for adult sprat F = 0.5.
Clark I	g) 711 t	<u>Conservative release</u> : Release of 711 t of Clark I (Sanderson et al., 2010) over the time of 100 years with a loading rate equal to $2.95 \times 10^{-5} \text{ t km}^{-2} \text{ y}^{-1}$.
	h) 1500 t	<u>Catastrophic release</u> : Release of 1500 t of Clark I (Sanderson et al., 2010) over the time of 10 years with a loading rate equal $6.23 \times 10^{-5} \text{ t km}^{-2} \text{ y}^{-1}$.

for nutrient and chlorophyll concentrations were based on climate and eutrophication scenarios generated by the Swedish Coastal and Ocean Biogeochemical model coupled with Rossby Centre Ocean model (RCO-SCOBI) that covers the entire Baltic Sea (Almroth-Rosell et al., 2015). RCO-SCOBI is a 3D model of the Baltic Sea with 3.7 km horizontal and 3 m vertical resolution (Saraiva et al., 2019a). The model describes the dynamics of nitrate, ammonium, phosphate, phytoplankton, zooplankton, detritus, and oxygen (Eilola et al., 2009). Climate change and biogeochemical scenarios were run with atmospheric forcing based

Table 2
Initial parameters for Ecotracer setup for the EwE model for the Central Baltic Sea (CBS).

	Direct absorption [%]	Excretion [%]
Grey seal	0	5
Fish-feeding birds	0	5
Atlantic cod (juv.)	1	25
Atlantic cod (adult.)	1	12.5
Atlantic herring (juv.)	0	25
Atlantic herring (adult)	0	12.5
European sprat (juv.)	0	25
European sprat (adult)	0	12.5
European flounder (juv.)	2	25
European flounder (adult)	2	12.5
Saduria entomon	5	50
Mytilus sp.	0	50
Macoma balthica	0	50
Other macrozoobenthos	0	50
Meiobenthos	20	80
Mysidacea	0	80
Other zooplankton	0	80
Pseudocalanus sp.	0	80
Acartia sp.	0	80
Temora sp	0	80
Phytoplankton	0	95
Detritus in sediments	95	0

Excretion – Proportion of Clark I excreted.

on three downscaled global General Circulation Models (GCMs), the Max Planck Institute Earth System Model-Low Resolution (MPI-ESM-LR), the European Countries Earth System Model (EC-EARTH), and the Hadley Center Global Environment Model v.2 - Earth System (HadGEM2-ES) (Saraiva et al., 2019b). The food web model was run with forcing derived from MPI-ESM-LR combined with RCO-SCOBI. On top of two IPCC (2021) climatic scenarios corresponding to Representative Concentration Pathway (RCP) 4.5 and 8.5, simulations reflected two nutrient loads and two fisheries scenarios, combined with two release rates of Clark I (Table 1).

2.5. Statistical analyses

Data generated in EwE were processed in R version 4.2.1. The probabilistic distributions of the Monte Carlo routine for all modelling scenarios (compare Table 1) were visually assessed in two ways: (i)

continuous accumulation and (ii) recorded at time slices (10, 30, 50, and 93 years of projections). Significant differences between probability distributions among all scenarios at the four time slices were identified using the BC - Bhattacharyya coefficient (Rauber et al., 2008). Silverman's rule of thumb was used to determine the bandwidths for the calculations of BCs. BCs range from 0 (no overlap) to 1 (complete overlap). A significance level of 0.61 was chosen since the BC for 2 normal distributions with their means 2 standard deviations apart is 0.61.

3. Results and discussion

Clark I represents a low-water-soluble contaminant residing in detritus associated with sediments. In neither of the release scenarios, its peak concentrations in sediments exceeded the highest reported values from sediment samples collected in the Baltic Sea (Söderström et al., 2018). This means that observations from modelling, including bioaccumulation rates and pathways, are plausible, at least within the local dimensions.

Across all modelled scenarios, Clark I concentrations increased linearly throughout the first half of the model period in all model compartments before reaching a plateau. The time until this plateau was reached differed between the *conservative release* (~65 years; Fig. 3) and the *catastrophic release* (~50 years; Fig. S1). Furthermore, Clark I concentrations in the *catastrophic release* exceeded the concentrations in the *conservative release* by approximately one order of magnitude. Other main patterns observed for the different climate, nutrient, and fisheries scenarios were similar for both Clark I release scenarios. Therefore, they are only described for the conservative release below due to their closer resemblance to measurements reported by CHEMSEA, MODUM and DAIMON projects.

With regard to its concentration, Clark I accumulated particularly strong in two opposing components of the food webs: (i) at the base of the food web in detritus and (ii) at the top of the food web in grey seal (Fig. 4). In absolute amount, however, the vast majority of Clark I was always within the detritus, since the total mass of detritus was >5 orders of magnitude higher than seal biomass in all scenarios (Bauer et al., 2019).

By design and definition, the RCP4.5 with BSAP under the Sustainable fisheries scenario is most favourable for the ecosystem compared to other investigated projections. Contrary to the RCP8.5 scenario, which provides higher warming, the RCP4.5 is considered relatively more realistic and possible to maintain within the upcoming decades. Regardless of the applied forcing scenario, Clark I bioaccumulates almost exclusively in food chains accommodated by benthic and demersal species (i.e., species that live and feed on or near the bottom, like cod) or those foraging on detritus-feeding species. This means that both bioaccumulation and biomagnification of Clark I in the Baltic Sea ecosystem do not depend solely on the trophic level but on the pathway along which the contaminant is transferred. Nonetheless, if a taxon is feeding on the benthic trophic pathway, the higher the trophic level of the taxon, the higher the chance that the contaminant will get biomagnified.

The type of fisheries, the implementation of BSAP and either climate scenario (RCP4.5 or RCP8.5) only slightly altered the accumulation rates across lower trophic levels, quickly plateauing and constantly overlapping during the whole run time under each forcing scenario (Fig. 3). Clark I concentrations were highest in top-level predators: grey seal and adult Atlantic cod respectively, however, they do not reach such high values in fish-feeding birds. This is because the later group's primary food source is European sprat (*Sprattus sprattus*), foraging on herbivorous zooplankton in a phytoplankton-based food chain (for details, see: ICES, 2016). Despite supported grazing by zooplankton on a planktonic fraction of detritus, the adsorbed Clark I does not accumulate in transferable levels in euphotic surface water and pelagic biomass.

There is a significant difference between the Clark I concentrations for different fishing scenarios after 30 years for the two species with the

highest trophic level: (i) grey seal and (ii) adult cod (Fig. 4). In comparison to the fisheries scenarios, climate and nutrient load scenarios seemed to play minor roles in Clark I accumulation in the Baltic Sea food web. No consistent significant differences among model scenarios were found for all model components (other than cod and seal). We detected significant differences among Clark I concentrations in detritus in the second half of the model period (Fig. 4). However, we cannot identify any meaningful pattern regarding the modelled scenarios.

The most impactful factors influencing Clark I bioaccumulation in the Baltic Sea food web in top-level predators are extensive extractions described by Open Access fisheries scenario. Fisheries have heavily exploited the BP fish resources by taking out 0.5–1 million tonnes of fish annually since the early 1960s (Bauer et al., 2019). Extensive fishing in the OA scenario clearly disturbs the ecosystem's balance, removing juvenile and adult specimens' biomasses and bioaccumulated contaminants. The mechanistic reason for the difference between the different fishing scenarios lies within the diet shifts of the two species of interest. Under the Open Access fisheries scenario, adult herring represented the majority of the diet of adult cod (~80 %). Herring, in turn, relies primarily on the pelagic trophic pathway, feeding mainly on zooplankton with some contribution of mysids and a neglectable contribution of benthic prey (<10 %) in all scenarios. Under the sustainable fishing scenario, however, cod relied on a more mixed diet with highest contributions of *Saduria entomon* to its diet (30–40 %), while herring only contributes 20–30 %. In contrast to herring, *S. entomon* relies primarily on the benthic trophic pathway and other macrobenthos comprises the majority of its diet (~60 %). The remaining diet of *S. entomon* is almost completely comprised of mysids (~40 %), while meiofauna contributes <1 %.

Similarly, the higher concentration of Clark I in grey seals under the sustainable fisheries scenario coincides with an increased grey seal predation on adult cod. Under the open access fisheries scenario cod represents only around 1 % of the diet of *H. grypus*, while it represents around 10 % of the diet under the sustainable fisheries scenario. Accordingly, the differences in Clark I accumulation under different fisheries scenarios demonstrate that the benthic trophic pathway is the channel through which Clark I can and will enter higher trophic levels and into species used for human consumption. This conclusion is further supported by the extremely low concentrations of Clark I in the exclusively planktivorous European sprat (Fig. 3).

Analyses of the arsenic contamination in fish, could therefore be a promising tool for monitoring CWA spreading and preventing potential threats to seafood consumers. Indeed, the values of measured total arsenic levels in fish from the Bornholm Deep CW dumpsite have significantly increased compared to CW-free areas. However, according to the study, they are not dangerously elevated for human fish consumption, but the trend is progressive (Polak-Juszczak and Richert, 2021). However, arsenic-based CWAs differ from other arsenic compounds, as by design, they induce severe adverse effects on human health, as either vomiting or blistering agents (Bjørklund et al., 2020). CWA in aquatic toxicity essays on crustaceans and fish clearly escape a typical trend for arsenicals (Czub et al., 2021; Wilczynski et al., 2023). Trivalent organic compounds such as phenyldichlorarsine (PDCA), Lewisite, Adamsite and Clark I are more toxic to *Daphnia magna* than many trivalent inorganic compounds (Czub et al., 2021). Although non-toxic in OECD *Daphnia magna* acute toxicity, the pentavalent degradation product of Clark I is toxic in vitro for fish (Niemikoski et al., 2021) and humans (Ochi et al., 2006; Kinoshita et al., 2006). Therefore, it is safe to say that further overlooking this threat in an already disturbed ecosystem may significantly affect future and ongoing efforts towards ecosystem restoration, including BSAP. Simultaneously, both outcomes of any improvements or continued degradation of the Baltic Sea ecosystem, together with natural processes and human activity in the region (Reckermann et al., 2022), will influence the future environmental fate and transfer of CWAs both in the environment and within the food web, especially in the higher trophic level organisms.

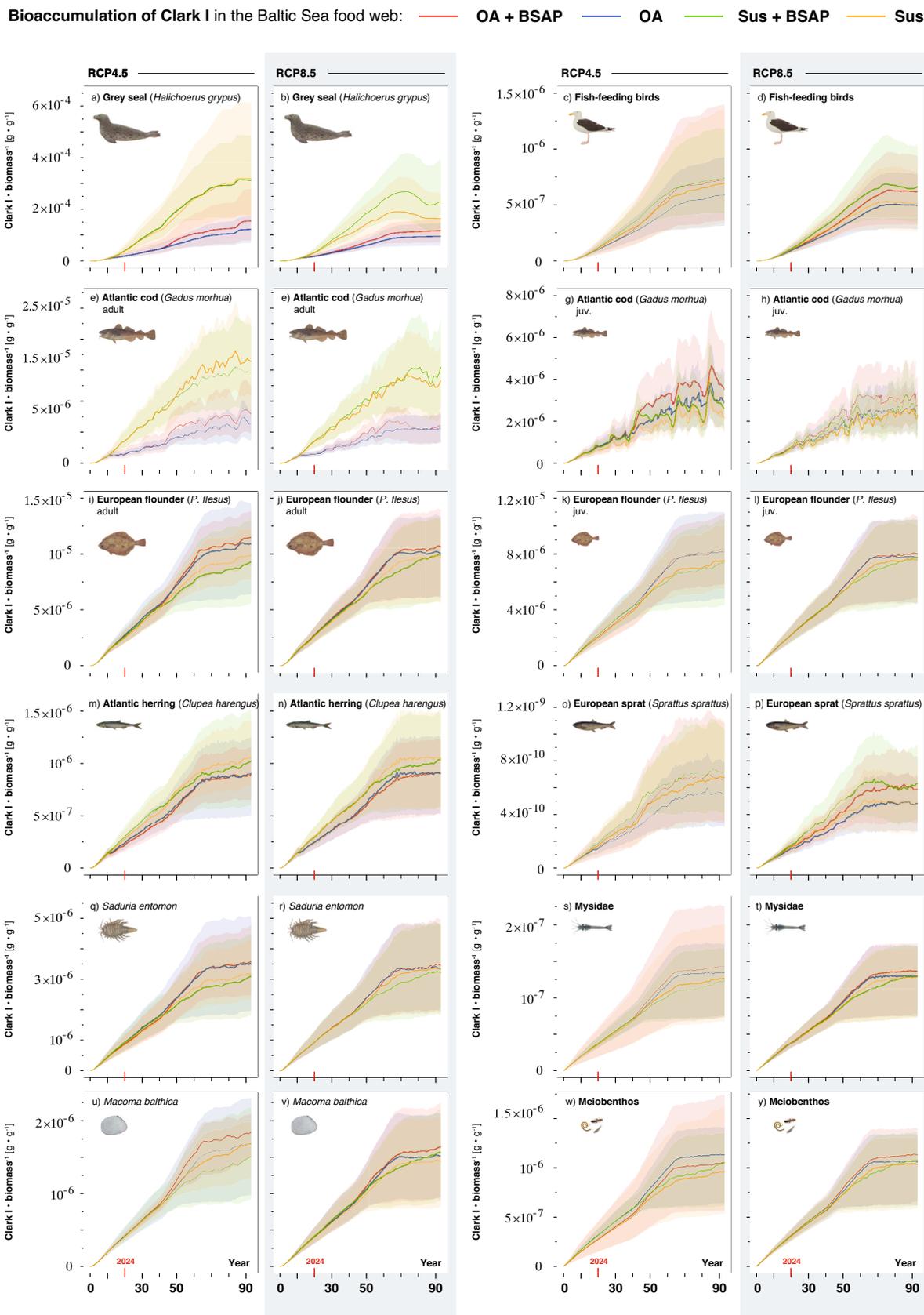


Fig. 3. Results of Clark I bioaccumulation modelling in the Baltic Sea food web at a constant release of 711 tons over 93 years. OA – Open Access Fisheries, SUS – Sustainable fisheries, BSAP – Baltic Sea Action Plan, juv. – juvenile.

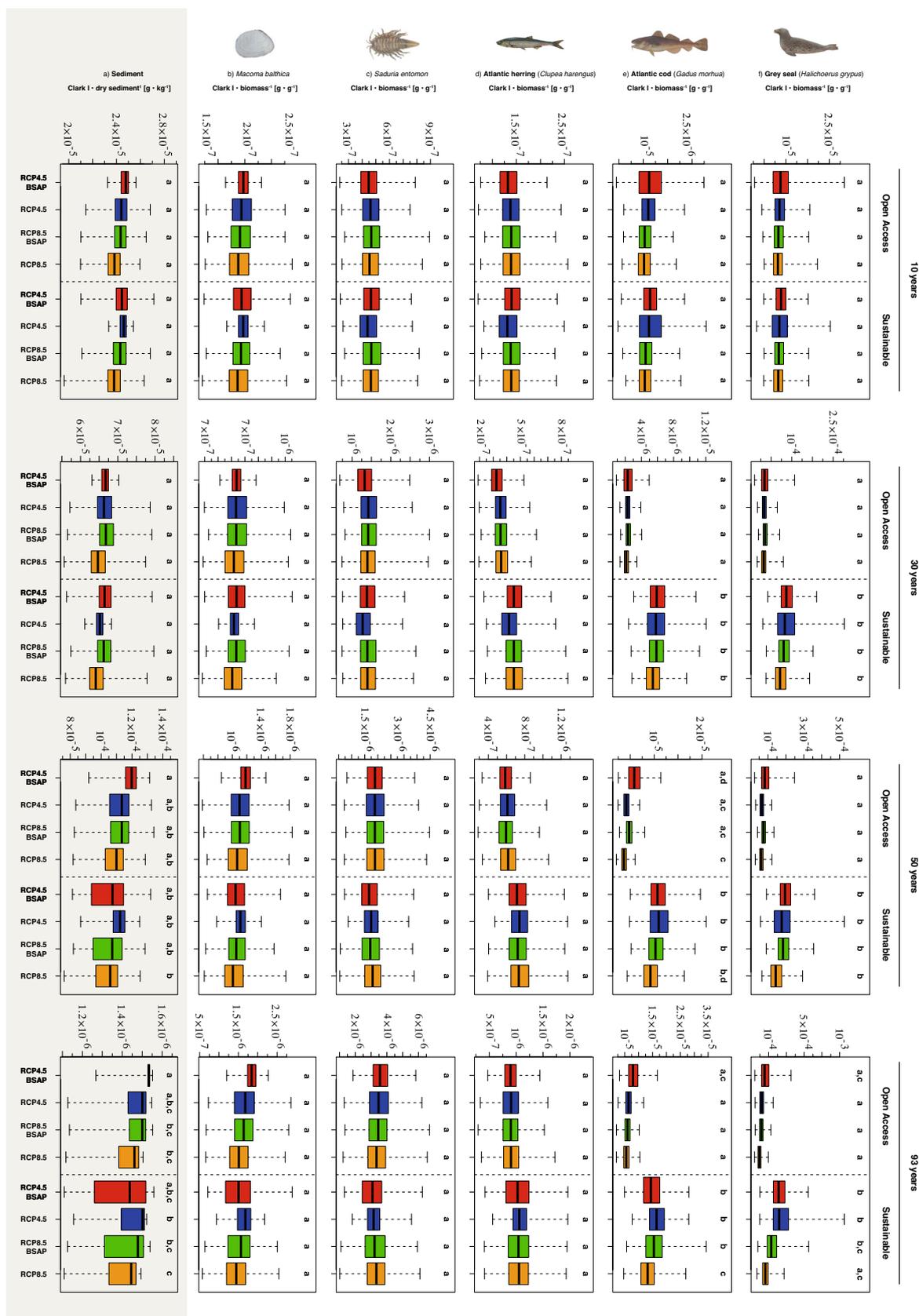


Fig. 4. Clark I bioaccumulation levels in selected taxonomic groups (g · g⁻¹) and dry sediment (g · kg⁻¹) calculated as values for detritus normalised by the % of organic matter (OM) in sediments from the Baltic Sea CW dumpsites (Czub et al., 2018).

It is also worth mentioning that besides fish species, the crustacean *S. entomon* is the only abundant large benthic predator in the Baltic Sea food web. Accordingly, only *S. entomon* is a candidate species that can lead to a long benthic trophic pathway with strong bioaccumulation of Clark I before being consumed by demersal-feeding fish species. In other ecosystems, however, where benthic diversity is higher and benthic food webs are characterised by a high number of large predators and omnivores, the potential links for Clark I to reach higher trophic levels become more numerous. Regarding the Baltic Sea ecosystem, which is very vulnerable to invasive species (Thor et al., 2023), it must be highlighted that establishing a different large benthic predator would present a new trophic pathway of CWA to high trophic levels.

During the 2014 MBI, the increased oxygen saturation and increased velocities of near-bottom current can potentially contribute to slow but constantly ongoing corrosion and disintegration of CW and CWM (Jurczak and Fabisiak, 2017; Vanninen et al., 2020; Jakacki et al., 2020). Effects of the MBI from 2014 may be among the possible explanations of the first reported detection of Clark I-related degradation products in *G. morhua* tissues (Niemikoski et al., 2020a, 2020b). Moreover, the triphenylarsine oxide (TPAO), which is an oxidation product of triphenylarsine (TPA) has also been detected within this study. Both Clark I and TPA were components of the Arsine Oil – technical mixture used in CW, and for sulfur mustard enhancement (“Winterlost”); however, TPA is still commercially available, thus can accidentally enter the Baltic Sea ecosystem. Meanwhile, the presence of Clark I in deep marine sediment and biota can be explained solely by its release from the submerged CW (Sanderson et al., 2010). Recolonisation of dumpsites by mobile macrofauna could have transferred the accumulated contamination from both detritus and meiofauna. Furthermore, higher saturation of near-bottom waters might have extended the time juvenile and adult cod specimens stay near the submerged objects, which, may serve as shelters.

The release rates of CWAs from munitions and other containers in the Baltic Sea have never been measured. However, they most likely depend on the surrounding environmental conditions as well as on the metal casing thickness and its corrosion resistance (Scharsack et al., 2021). According to numerous estimations, all barrels should now be completely corroded, aerial bombs severely corroded, while artillery projectiles can still be intact for the next decades (Jurczak and Fabisiak, 2017). Therefore, it is impossible to assess whether the “Conservative release” scenario overestimates, underestimates, or illustrates the situation in the Baltic Sea dumpsites. Furthermore, decades of documented bottom-trawling fisheries, accidents with fishermen in the Bornholm CW Dumpsite area, and hypothetically unrealistic events such as Nordstream pipelines explosions that took place approximately 15–20 km from this dumpsite might already have extensively sped up the natural corrosion, resulting in “Catastrophic release” and extending the potential area of CWA influence (Fig. 1). The major scientific outcomes were now recognised by the European Parliament in 2021, while continued investigation on underwater munitions is included within the scope of the updated HELCOM BSAP that aims in the improvement of the ecological state of the Baltic Sea in following decades. Nowadays, Baltic Proper is still under the influence of multiple significant environmental stressors, resulting in extensive hypoxia in the CW dumpsite areas. Thus, the true extent of the impact of toxic sea-dumped CWAs may be observed in the near or further future.

Currently, only Polish authorities monitor their EEZ for CWM remains, using total arsenic contamination in sediments as a proxy. At the same time, new EU projects (MUNIMAP - Marine Munition Remediation Roadmap; and MUNIRISK) are underway to develop the better approaches to meet the requirements for proper environmental risk assessments. Ideally, a well-designed monitoring strategy for CWAs transfer in the Baltic Sea ecosystem should be cost-effective and unbiased by numerous uncertainties. Up to now, only two accumulation endpoints within the Baltic Sea ecosystem have been investigated by target chemical analyses: sediments and Atlantic cod. However, it must

be underlined that at least some fraction of CWAs detected in sediments should most likely be assigned to the contamination bioconcentrated by meiofauna and Prokaryotic communities. Thus, the well-designed study of Clark I bioaccumulation by meiofaunal assemblages is critical to properly assess the entrance points of CWAs into the Baltic Sea food web. Thanks to the presented modelling exercise, we discovered three interesting contamination hotspots that are abundant and immune to applied forcing scenarios, in a way making them promising targets for CWA screening. Due to its ecology and occurrence in the cod diet, the primary target species for future monitoring should be *Saduria entomon*. Swarms of this mobile Isopoda could be collected by traps placed in neighbouring areas with submerged munitions. Due to its ecology, abundance and total biomass within the Baltic Sea food web, another promising species is *Macoma balthica*. However, selection of sampling sites should be based on the confirmed presence of oxygen in the near-bottom water, thus more likely at the official borders of the CW dumpsites. All operations should follow preliminary sea-bottom mapping for safe working conditions for any sediment sampling (Beldowski et al., 2018). *Clupea harengus* should be added to the monitoring target species lists. At the same time, *S. sprattus* could serve as validation of the modelled outcomes from this study to verify if those two food chains, detritus and phytoplankton-based, are indeed separated in terms of the influence and bioaccumulation of sediment-related contaminants.

4. Conclusions

This modelling study confirms that under applied conditions, Clark I bioaccumulates within the Baltic Sea food web exclusively throughout the detritus-based food chain. The most impactful factor on accumulation rate and contamination transfer within the Baltic Sea food web is commercial fishing, followed by climate change. Observations from modelling timestamps covering recent times correspond with in situ detections. There is an urgent need to extend the target species list in monitoring beyond analyses of CWA in sediments and *Gadus morhua*. Thus, new target species (including developing new extraction methods for chemical analyses) should be considered: *Saduria entomon* and *Clupea harengus* (i.e., Atlantic herring) as the main diet of cod under sustainable and open access fisheries scenarios, respectively, should be targeted. Additional validation of clear separation between detritus-based and phytoplankton-based food webs can be obtained by analysis of accumulation in *Sprattus sprattus*. Furthermore, the inclusion of a benthic target species with limited mobility and wide distribution in the Baltic Sea (i.e., *Macoma balthica*) will provide better understanding of the spatial extend of CWA spreading in the Baltic Sea food web.

Implementation of the BSAP and sustainable fisheries management in light of climate change will improve the Baltic Sea's ecosystem state. Our results, however, indicate that restoration efforts will amplify the potential uptake and accumulation of CWA in the Baltic Sea food web. Therefore, we strongly recommend including remediation of CW by removal as part of the integrated management of the Baltic Sea.

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CRedit authorship contribution statement

Michał J. Czub: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Data curation, Conceptualization. **Marc J. Silberberger:** Writing – review & editing, Writing – original draft, Visualization, Data curation. **Jacek Beldowski:** Writing – original draft, Funding acquisition, Conceptualization. **Lech Kotwicki:** Writing – original draft, Conceptualization. **Bärbel Müller-Karulis:** Writing – original draft, Supervision, Methodology, Data curation. **Maciej T. Tomczak:** Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data and code that support the findings of this study are available from the corresponding author upon reasonable request.

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