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HAZARDOUS CHEMICALS IN THE EASTERN GULF OF FINLAND - CONCENTRATIONS AND IMPACT ASSESSMENT

Recommendations

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Sampling of sediments, water, biota

Water

The overall recommendation for the sampling in the water environment might include the following aspects. The sampling campaign should consider water layers on the surface and near the bottom, as during resuspension processes (e.g. from water circulation due to currents) in the deeper areas along the shipping routes (including harbours) and estuaries, the water layer near the bottom might contain higher concentration of pollutants. Chemical analyses conducted in the frames of the Hazless indicated that degradation products of tributyltin (TBT) might be found in the bottom water over the TBT polluted sediments near the shipping docks (at Muuga harbour) and at the offshore sediment accumulation areas (as in the case of Narva bay). Whereas the extent of contamination by organic pollutants in the water column often depends on the contamination level of the underlying sediments.

Biota

Within monitoring activities, the sampling of filter-feeding molluscs must be preferred over other organisms where possible. These sessile macroinvertebrates efficiently accumulate all kinds of pollutants from the surrounding environment, though in comparison to suspension-feeding species, deposit feeders tend to highly accumulate polycyclic aromatic hydrocarbons (PAHs) (Hickey et al., 1995). However, some PAHs tend to degrade over time after exposure event due to physiological processes within the organisms (Honda, Suzuki, 2020). It is worth mentioning that invertebrates have a lower metabolism capacity and relatively higher PAH concentrations in the body compared with fish (Dsikowitzky et al., 2016)

The heavy metals (HMs) and persistent organic pollutants (POPs) accumulate in the bodies of aquatic animals characterizing the chronic contamination from diffuse or point sources nearby. Mobile animals (crustaceans, fishes) and macroalgae might be used in environmental monitoring, but with some reservations. Algae may accumulate HMs to some extent, but for accurate assessment critical to consider rates of bioaccumulation from water/sediment (including sediment pore water). Thereby samples from different environmental matrices have to accompany the biota samples. Finally, the bioconcentration factor has to be calculated preferably, and sampling sites have to be intercompared (Gubelit et al., 2016).

The different fish species are effectively used in biomonitoring to collect information about the distribution and impact of hazardous substances in the aquatic environment. The high mobility of these organisms suggests migration over small/large areas, depending on the species and its migratory behaviour. Therefore, it is often complicated to localize the contamination source precisely, though the involvement of these vertebrate animals in the surveys is essential from the human consumption safety perspective (Food safety authority of Ireland, 2009). The POPs and HMs accumulate readily within species of bottom-dwelling (e.g. flatfish) and species with a high fat content (e.g. salmonids, river lamprey), while biomagnification is responsible for the elevated level of chemicals in the areas of chronic pollution, specifically in the vicinity of port areas, where pollutants end up in the marine environment from various diffuse sources. According to previous studies, in Narva bay, organotin compounds were elevated in herring near the port of Sillamäe and in the Muuga bay, polychlorinated biphenyls (PCBs) in flounder near the Muuga harbour (Järv, 2016).

The latest biomonitoring of commercially important fish species also revealed the high content of PCBs and dioxins within the salmon analysed from the Narva-Kunda basin (EKUK, 2020). The cadmium (Cd) content in the river lamprey samples from the Narva river exceeded the threshold level established by the national quality guidelines (EKUK, 2020). When collecting samples from fish, it is important to consider that some POPs might accumulate more intensively in specific organs than in others (e.g. PFOS bioaccumulate mainly in liver). The uneven bioaccumulation and uncertainty about the spatial distribution of pollution under investigation, might lead to a situation where alternative approaches might be implemented. The indicators of health or biological effect indicators (including PAH metabolites and multibiomarker approach) might substantially support the conventional biomonitoring data.

Large benthic macroinvertebrate species accumulate HMs directly from the surrounding environment and by biomagnification across a food chain (Lozano et al., 2010; Munoz et al., 2019). The mobile benthic organisms might host microorganisms that facilitate the biodegradation of oil products (Polyak et al., 2020), subsequently, the estimation of the abundance of hydrocarbon-oxidizing bacteria in the digestive tract might be one of the methods applied in the assessment of pollution effects. However, the effectiveness of this microbiological approach has to be evaluated systematically on different species with ecologically relevant laboratory and field effect studies.

Small crustaceans from the order *Amphipoda* are widely used in bioassay studies (Lehtonen et al., 2018). The application of sediment biotests with multiple eco-physiological endpoint measurements might be a suitable tool for pollution monitoring. Species of infauna or burrowing amphipods, when used in controlled exposure studies or collected in situ under field conditions, suit well for investigating the “cocktail effect” of multiple pollutants.

However, littoral amphipods might be successfully used in ecotoxicological exposure studies, where the impact of a specific chemical compound is in the scope of the investigation.

Sediments

Several important aspects must be considered during the sampling campaign of the bottom sediments for chemical monitoring. The variation of sediment properties might be strongly related to the capacity of the bottom environment to bind and store the contaminants. Therefore, areas of possible sediment erosion or accumulation must be identified in the study area. Fine-grained sediments (e.g. with high content of clay fraction) usually contain a higher concentration of organic matter, measured typically as the ratio of organic carbon, and are prone to developing poorer oxygen conditions in the bottom water layer, as compared to coarse-grained sediment erosion areas. The level of oxygen content, in turn, determines the temporal extent of preservation of some organic pollutants (e.g. organotins, PAHs), as aeration leads to degradation of these compounds on usually less harmful derivatives.

The application of appropriate sampling methods is also essential to consider during the planning of the sampling campaign. There was no considerable difference between the results of chemical analyses derived from samples collected by sediment corer and bottom grab at the offshore accumulation area in Narva bay. However, corer enables estimation of the historic contamination pattern by sequestering the core sample on separate layers with subsequent dating analyses. In coastal areas with shallow water, it is possible to use a sampling cylinder, which is a perfect tool when occurs visually distinguishable contamination, specifically by oil products.

The current study showed that some POPs in accumulation areas and around centres of maritime activities in the eastern Gulf of Finland can be slightly below or manifold exceed the suggested good environmental status (GES) thresholds for the Baltic Sea (Kuprijanov et al., 2021). Moreover, the high risk of contamination for the offshore eastern Gulf of Finland area and the outer Neva Estuary is confirmed by the calculated potential ecological risk index.

According to our assessment, there is evidence of continuous fresh input along the ship traffic routes and probably restricted TBT degradation at deep sediment accumulation areas. The content of TBT exceeded the GES threshold value at 60% of the sampled stations. The overall distribution pattern of TBT differs from distributions of PAHs and heavy metals, likely depending on the presence of specific diffusive sources related to maritime activities. The highest contamination by PAHs was found near the port areas, where compounds released during incomplete fuel incineration processes are likely prevailing. The situation with PAH contamination indicator in sediments – anthracene, raises the overall concern as it was detected at 52% of samples and at 29% exceeded the GES threshold, reaching extremely high values near the port areas. The spatial pattern of anthracene (ANT) distribution in the study area clearly differed from distributions of organotins and heavy metals and might be related to the point-source pollution from certain objects situated near the coast (e.g., oil storage reservoirs at the ports or harbours).

The potentially toxic heavy metals cadmium (Cd) and lead (Pb) are still traceable in significant amounts in the Neva Estuary and deep offshore areas of the eastern Gulf of Finland, while it is not a concern along the northern Estonian coast. The Pb content did not exceed the GES threshold in the study area, while Cd in sediment samples exceeded the threshold at two stations. The content of copper (Cu) in the bottom sediments may show a warning sign as its concentrations exceed (in the Neva Estuary) and approach the suggested provisional threshold levels in multiple locations across the study area. Overall, the high ecological risk of sediment contamination by heavy metals for the offshore eastern Gulf of Finland area and the outer Neva Estuary was identified from the calculated potential ecological risk index. The heavy metals had a specific distribution pattern in the study area as atmospheric deposition and waterborne inputs in different proportions are the main sources of these elements to the aquatic environment of the eastern Gulf of Finland. The simulated accumulation pattern indicates the most probable zones of riverine origin HS accumulation. Depending on the settling velocity, HS might disperse along the shoreline in the eastern Gulf of Finland much further from the initial release locations within the river estuary systems. Sedimentation of the medium size particles shows amounts growing from the outer part of the Neva Estuary to the east, highlighting the threat of increasing amounts of contaminants that are also visible from the available observations on heavy metals. This modelled gradient should be considered when planning monitoring activities in the eastern Gulf of Finland. The evidenced occurrence of periodically oxygen-depleted sediments can partly explain the presence and preservation of studied organic pollutants at the observed levels in the region. The increase of deoxygenated zones over time becomes the factor contributing to the sustainment of long-standing environmental issues regarding HS in the future as well.

The following surveys in the eastern Gulf of Finland have to focus on deeper nearshore stations for the HMs trend assessment. In addition, caution has to be taken when interpreting the results from samples taken at shallow beach areas. The continuous disturbance of the bottom surface by waves and the absence of fine sediments for pollutant accumulation might hinder the objectivity of marine pollution assessment due to high dispersion and, subsequently, low contaminant concentration. The designated polluting sites are still present in the eastern GoF basins, including the Neva estuary and Narva bay, where most of the gulf’s active municipal, industrial and agricultural hot spots release polluting substances, probably until technological changes are applied to fulfil the critical requirements for achieving GES in the marine environment (HELCOM, 2013).

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Survey of biological effects

Reproductive disorders in amphipods

We have studied the embryonic development of the sediment-dwelling amphipod *Monoporeia affinis*, which is sensitive to contaminant exposure. Therefore, the frequency of embryo aberrations in gravid females and the proportion of females carrying more than one aberrant embryo are used to detect the biological effects of chemical exposure in the Baltic Sea sediments. During the Hazless project, deep water (*M. affinis*) and shallow water (*Gammarus spp.*) amphipodes were collected and analysed for aberrated embryos. Collected data was added to the already existing dataset and used to evaluate the indicator applicability in the GoF (for *M. affinis*). The calculation of indicator preliminary thresholds for the GoF are based on available data. "Reproductive disorders in amphipods" is a supplementary indicator within the list of HELCOM biological effect monitoring indicators. During the project, we found that this indicator is applicable to the Estonian coastal waters. Specifically, based on availability of *M. affinis*, stations N8, N12 (Narva bay) and M (Käsmu bay) are the most suitable for the eastern part of the GoF (however, due to the ice cover it could be difficult to collect at station N8). Shallow water stations at Udria, Eru and Käsmu coastal waters can be considered for collecting littoral amphipods. According to the data from 2020 – the GES is not achieved for the eastern GoF. Reproductive disorders data collected during Hazless project was also provided to the HELCOM during the data call and used in HOLAS 3 assessment.

We suggest applying, for the representative assessment of the studied area, both deep water species *M. affinis* and littoral amphipods with an extent of at least 3 years of data within 6 years period. In addition to already investigated sites in the Estonian part of the eastern GoF, we propose to consider the Kunda area for sampling littoral amphipods to provide an even spatial coverage of the sampling sites. We also propose systematic intercalibration of the measurements of this indicator to ensure the quality of the assessment in the future.

Multibiomarker approach

The so-called legacy persistent contaminants (e.g. PCBs or organotins) degrade slowly in the environment and continue to exert pressure on biota. Subsequently, the diversity of genetic characteristics in exposed species is prone to decline; they experience disruption in functionality and production, and persistent cumulative pressure on higher trophic levels through biomagnification is evident. There has also been registered a shift from high concentrations of a few chemicals to low concentrations of many in the last decades (Wang et al., 2020). With the increasing knowledge of the mixture toxicity (or "cocktail") effects observed at relatively low levels of multiple contaminants, the reliability of environmental assessments based exclusively on chemical measurements is highly questionable.

In the last decades, the ecosystems of the Baltic Sea have experienced the impact of many emerging chemicals with low concentrations. However, priority contaminants continue to affect organisms on the different levels of biological organization. Within monitoring programmes conducted in the GoF, only a few biological effect indicators are implemented regularly. Both Finland and Estonia apply white-tailed sea eagle productivity monitoring. In addition, Finland assesses lysosomal membrane stability (LMS), while most other biological effect methods are implemented only on a project basis.

Based on multiple ecophysiological experiments conducted during the Hazless, it is reasonable to conclude that for reliable environmental assessment, chemical measurements should be accompanied by the estimation of the biological effect that HS contamination might trigger at the population level. The latter should be provided by the studies of the "early warning" systems for the mixture effects of contaminants implementing the multibiomarker approach (Lehtonen et al., 2016). However, the application of biochemical health indicators is related to several considerations. Firstly, the effect of contaminant on the subcellular level is species-specific, e.g. it is impossible to compare the enzymatic activity rates of acetylcholinesterase (AChE) in fish liver and mussel digestive gland on the same scale. Secondly, within the battery of biomarkers, some might more generally indicate the probable influence of the multiple specific compounds on the biochemical response. For example, the glutathione s-transferase (GST) activity rate is mostly related to the processes of removal of harmful metabolites from the cell and, therefore, might indicate the metabolization of large spectra of toxic HMs and/or POPs. However, seasonally occurring unfavourable environmental conditions such as hypoxia might modulate the enzymatic activities and change the biomarker response in the exposed biota at a similar pattern (Woo et al., 2013), which might complicate the interpretation of the survey results.

The abrupt declines in abundance of the study organisms (as happened with mussels due to the invasion of round goby in GoF (Nõomaa et al., 2022)) might distract the long-term monitoring. The application of caging might compensate for the problem of the absence of suitable organisms for biological effect study. Utilizing caging approach is possible to translocate organisms from supposedly unpolluted sites to the areas where contamination monitoring is necessary and, after deployment, conduct the analyses to reveal the exposure consequences.

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