

Integrated assessment of pollution in the Baltic Sea

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Aquatic systems are a complex and variable with multiple environmental factors acting. That is why integrated approach is needed for their ecological status assessment. HELCOM Baltic Sea Action Plan and EU Marine Strategy Framework Directive (2008/56/EC) address hazardous substances and show the need of integrated view of the situation.

The paper describes the vulnerability of the Baltic Sea ecosystem and contaminants of specific concern like heavy metals, oil hydrocarbons, polycyclic aromatic hydrocarbons, chlorinated hydrocarbon compounds, organotin compounds and others. The effects of pollutants on aquatic organisms are reviewed. Integrated assessment of the state of the aquatic environment is discussed and biological-effect methods are shown being important elements in environmental research as they can indicate links between contamination and ecological responses. The paper concludes that integrated monitoring of hazardous substances and their effects are an important step forward to reach one of the future goals – Baltic Sea life undisturbed by hazardous substances.

Key words: Baltic Sea, pollution, contaminants, biomarkers, integrated assessment

INTRODUCTION

Aquatic systems are complex and variable with multiple environmental factors. That is why any of single measures is adequate for assessing the effects of multiple stressors on biota. There is no doubt that the result of chemical analyses is an important indication whether or not organisms are exposed to pollutants at unacceptable high levels (Den Besten, 1998). However, the use of chemical criteria alone can be incomplete, as it does not include a broader ecological view (Adams, 2005).

By adoption of the Baltic Sea Action Plan (BSAP) the HELCOM countries decided to cooperate in order to build up more information on the sources of the selected hazardous substances, the extent of their occurrence in the Baltic marine environment, as well as on their biological effects (HELCOM, 2007a). Another important document – EU Marine Strategy Framework Directi-

ve (2008/56/EC) (MSFD) addresses hazardous substances, setting one of the qualitative descriptors for determining good environmental status as “Concentrations of contaminants are at levels not giving rise to pollution effects”. According to MSFD, the progress towards good environmental status will depend on whether pollution is progressively being phased out, i. e. whether the presence of contaminants in the marine environment and their biological effects are kept within acceptable limits, so as to ensure that there are no significant impacts on or risk to the marine environment. These two documents show the need of the integrated view of the situation.

THE BALTIC SEA AND ITS VULNERABILITY

The Baltic Sea is one of the largest brackish water areas in the world with a salinity varying from about 10 PSU in the south in the Baltic Proper, declining through the Bothnian Sea and reaching 2 PSU in the northern Bothnian Bay. The Baltic Sea is a very shallow water basin, with a mean

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depth of only 55 m. In spite of the comparatively small size of the sea, its various sub-basins have their own unique hydrographic characteristics. The Baltic Proper region of the sea is the largest and the deepest, with a maximum depth of 459 m. The catchment area of the Baltic Sea is approximately four times larger than the sea area itself (Kautsky, Kautsky, 2000; Myrberg, Andreev, 2003; HELCOM, 2003).

The Baltic Sea exhibits numerous important abiotic and biotic characteristics that make it exceedingly different from other European sea areas in regard to various ecological processes. The specific features of the Baltic Sea, i. e. its semi-enclosed nature, brackish water, salinity stratification, partial ice cover in winter, and large drainage area make the Baltic Sea ecosystem particularly sensitive to natural and anthropogenic impacts (Dybern, Fonselius, 1981; HELCOM, 2003; Lehtonen, Schiedek, 2006a).

Narrow Danish straits and shallow sills (Darss Sill: 18 m depth; Drogden Sill: 7 m depth) limit the water exchange of the Baltic Sea. The turnover time for the surface water layer varies widely in the different coastal areas from less than 1 day at the open coasts to 12–25 years in the more enclosed archipelagos. Deep water in the central basins tends to stagnate for periods of several years. It is estimated that a renewal of the total water mass of the Baltic Sea would take about 25–35 years (Matthäus, Schinke, 1999; Kautsky, Kautsky, 2000). Moreover, the dominating water circulation in each of the three largest basins, i. e. the Bothnian Bay, Bothnian Sea and Baltic Proper are anti-clockwise cells created by the Coriolis force due to the Earth rotation. Consequently, when a river enters the Baltic, the water turns to the right and follows the shore. This results in a longer residence time for the heavily polluted water from the large rivers entering in the south and east, which is thus kept in the Baltic Proper for a longer period than otherwise would have been the case (Kautsky, Kautsky, 2000). Thus, nutrients and hazardous substances, originated from marine and land-based sources, have a long residence time in the Baltic. Due to chemical properties most of the contaminants accumulate in sediments (Kennish, 1997; Ducrottoy, Elliott, 2008).

The positive water balance, i. e. the surplus of freshwater supply (river runoff and precipitation)

in comparison to evaporation, creates a steady outflow of brackish surface water from the Baltic. This outflow, in its turn, causes a reversal gradient current of saline water into the depth (Schulz, 1996). A permanent halocline at about 60–80 m depth prevents vertical circulation, and oxygenation of the deep water is limited to a few events of salt-water inflow. About one third of the bottom area of the Baltic Proper is without higher life due to low oxygen, therefore periodic large inflows of saline oxygen-rich water, which take place under specific weather conditions, are of vital importance for the Baltic Sea ecosystem (Ojaveer, Elken, 1997; Kautsky, Kautsky, 2000).

During 10 000 years of the history of the Baltic, the fauna and flora have been subjected to major environmental changes several times, from freshwater conditions to those of the *Yoldia* and *Littorina* Seas with higher salinity than the recent one, often referred to as the *Mya* Sea. After every disturbance, the succession had to start from almost zero, and the species composition has changed from predominantly marine to an almost completely freshwater one (Olenin, Leppäkoski, 1999). According to Dybern and Fonselius (1981), there are currently three main categories of organisms in the Baltic Sea: 1) species which belong to the North Sea ecosystems and penetrate into the Baltic Sea through the entrance sounds, 2) species from the neighboring fresh water ecosystems which invade the sea from the coastal areas, and 3) a small number of species which have survived from earlier stages of evolution of the Baltic Sea.

Since the hydrographical conditions are very peculiar and even extreme with a series of gradients (salinity, temperature, gas content, turbidity, etc.), many marine species are entirely excluded from the Baltic Sea. Other species can penetrate only to certain zones, e. g. the north–south salinity gradient restricts the northward penetration of marine organisms. Distribution of species depends on the capacity to adjust to the prevailing conditions. A change in the environmental conditions may cause a species to withdraw from an area or to spread to new areas, depending on the character of the change (Dybern, Fonselius, 1981).

Since there is a lower genetic diversity in populations and ecosystems are simple with few species and few links between them, even a relatively small environmental change may cause

a severe imbalance in the whole ecosystem. The limited number of species involved in the Baltic Sea food webs means that each individual species has a special importance in terms of the structure and dynamics of the whole ecosystem. Since most organisms of this region already live under severe physiological stress, they are sensitive to pollution. Many pollutants carried out into the Baltic Sea accumulate in organisms sometimes reaching concentrations that may become damaging for species, ecosystems or even humans (Dybern, Fonselius, 1981; Kautsky, Kautsky, 2000; HELCOM, 2003).

The Baltic Sea is surrounded by 14 densely populated and industrialized countries, where 85 million people live within the drainage area that adds a significant stress resulting from pollution. Nutrients and hazardous substances originating from cities, farmland, commercially managed forests, industrial and energy plants, transport and other human activities from the whole catchment area drain into the sea via rivers. Pollutants from an even larger area can enter the Baltic by the air transmission. Emissions and discharges from shipping and fish farms enter the sea directly. The response to nutrient enrichment results in eutrophication. The large inputs of nutrients, year after year, have resulted in increased concentrations of nitrogen and phosphorus in all basins. Nutrient enrichment may give rise to an increased rate of oxygen consumption leading to decreased oxygen concentrations and an increased frequency of oxygen depletion. Eutrophication favors growth of nuisance algae: harmful and toxic algal blooms have occurred annually in the Baltic Sea in recent years (Kautsky, Kautsky, 2000; Ærtebjerg et al., 2003; Olenina, 2003).

With its many sources of pollution and very slow water renewal the Baltic Sea is considered one of the most polluted areas in the world (Kautsky, Kautsky, 2000; HELCOM, 2003).

CONTAMINANTS IN THE BALTIC SEA

More than 40 years ago an American marine biologist Rachel Carson wrote a book "Silent Spring" (1962) where she focused on conservation and the environmental problems caused by synthetic pesticides. It became apparent to the general public that the natural environment had been seriously

affected by anthropogenic contamination. In the Baltic Sea region, in Sweden, a pesticide debate started even before "Silent Spring", after mercury-treated seed grain poisoned granivorous birds and their predators. A suspicion that such mercury might have leaked to watercourses led to the surprising discovery of high mercury concentrations in fish of inland and coastal waters. Most of this mercury was methylated and accumulated in the food chain (Elmgren, 2001).

Since then, as a result of the prohibition and strict regulation of the use of DDT, PCB, mercury and other metals in the industrialized world, as well as reduced emissions of PAHs and dioxins from combustion plants, the levels of such substances in aquatic environments have decreased. Populations of some previously affected species started to recover (Swedish EPA, 2000; Skei et al., 2000; Kautsky, Kautsky, 2000; Elmgren, 2001; Vallius, Leivuori, 2003; HELCOM, 2003, 2004, 2009). However, the fact that a certain substance is banned is no guarantee for its absence in the environment. Monitoring indicates that although the loads of some hazardous substances have been considerably reduced over the past 20–30 years, other problems still persist, and concentrations of some new substances in the marine environment have been increasing (HELCOM, 2007a). Long-range atmospheric transport of hazardous substances, unregistered use, release from imported goods, unintentional formation, former emissions of highly persistent substances as well as secondary sources like contaminated sediments, dump sites, contaminated land may all lead to contamination of the environment (Skei et al., 2000; Sternbeck et al., 2003). Another problem is that the degradation and transformation of some of these substances in the marine environment may change their structure and reactive properties. These new unknown substances could pose a considerable threat to the environment (HELCOM, 2003).

The present list of known contaminants is undoubtedly incomplete, essentially due to the shortcomings in aquatic science. Thus, for example, polychlorinated biphenyls now thought to be of very considerable significance as a coastal and oceanic pollutant have not been discovered in aquatic biota until 1966, some 37 years after their initial use by industry. And there is no doubt that new contaminants of concern will emerge as

analytical techniques improve (Phillips, Rainbow, 1994). One of the examples would be the development of sensitive and reliable methods in 1970s which made it possible to measure levels of inorganic and organic pollutants in sediments, water and organisms in the Baltic region with comparatively great accuracy (Swedish EPA, 2000).

There is still a lack of comprehensive knowledge about the impact of the most widely used chemicals and their cocktail-like combinations / mixtures on human health and the environment. Today relatively few organic pollutants are fully understood or even identified (HELCOM, 2003). Their environmental risks depend on the speciation of contaminants and their association to media and matter and by that means affect exposure. Furthermore, the risk also depends on the mobility of the substances and their pathways in food chains (Skei et al., 2000).

Let us overview the most important documents in the field of hazardous substances.

A list of eleven hazardous substances or substance groups of specific concern to the Baltic Sea was adopted in Krakow, Poland, on 15 November 2007 in accordance with HELCOM Baltic Sea Action Plan. This list contains: dioxins (PCDD), furans (PCDF) and dioxin-like polychlorinated biphenyls; tributyltin (TBT) and triphenyltin (TPhT) compounds; penta-, octa- and decabromodiphenyl ethers (pentaBDE; octaBDE and decaBDE); perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA); hexabromocyclododecane (HBCDD); nonylphenols (NP) and nonylphenol ethoxylates (NPE); octylphenols (OP) and octylphenol ethoxylates (OPE); short- and medium-chain chlorinated paraffins (SCCP and MCCP); endosulfan; mercury; cadmium.

Another important document is the Stockholm Convention on Persistent Organic Pollutants (POPs) which entered into force in 2004 (the amendment in 2009). Initially, twelve POPs and later added new POPs have been recognized as causing adverse effects on humans and the ecosystem: aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene (HCB), mirex, toxaphene, polychlorinated biphenyls (PCBs), PCDD, PCDF, and new POPs: chlordecone, alpha hexachlorocyclohexane (α -HCH), beta hexachlorocyclohexane (β -HCH), lindane, pentachlorobenzene, hexabromobiphenyl, hexabromodiphenyl ether and

heptabromodiphenyl ether, perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride, tetrabromodiphenyl ether and pentabromodiphenyl ether.

In 2008, EC directive (2008/105/EC) on environmental quality standards (EQS) in the field of water policy was adopted. This directive, also known as the Priority Substances Directive, sets limits on concentrations of 33 priority substances and 8 other pollutants in surface waters (river, lake, transitional and coastal) and confirmed their designation as priority or priority hazardous substances.

Priority Substances Directive has been transposed to Lithuanian legislation in 2010. Priority substances were added to the existing lists of substances in the Wastewater Treatment Regulation (Order of Minister of Environment No. D1-236 of 17 May 2006; amendments on 18 May 2010, Official Gazette, 2010, No. 59-2938). Wastewater Treatment Regulation contains the lists of priority hazardous substances, priority substances and the list of other controlled substances in Lithuania.

The most important substances or groups of substances which are in the lists of the mentioned documents are described below.

HEAVY METALS

Heavy metals comprise a group of elements that are potentially toxic to estuarine and marine organisms in concentrations above the threshold level. The term 'heavy metal' is used synonymously with 'trace metal' and includes both essential and non-essential trace metals (Rainbow, 1995; Kenish, 1997). Metals, at their natural concentration, play an essential role in many biochemical processes in organisms. Such concentration is called the background concentration. Any concentration lower or higher than this background can be toxic. Increased levels of metals are potentially serious, since many metals can induce biological disturbances even at relatively low concentrations (Nemerow, 1991; Kersten et al., 1994; Swedish EPA, 2000).

Two subgroups are recognized: (1) transitional metals (e. g. copper, zinc) which are essential to metabolism at low concentration but may be toxic at higher concentration, and (2) metalloids (e. g. arsenic, cadmium, lead, mercury, tin) which

generally are not required for metabolic function and are toxic at low concentration (Kennish, 1997). If there is an excess of trace metals in the aquatic environment, then living organisms are forced to take part in the cycle of these metals (Kosior et al., 2002). Heavy metals can accumulate in the marine food web up to levels which are toxic to marine organisms, particularly predators, and via food web they may also represent a health risk for humans (HELCOM, 2007b).

Heavy metal levels in aquatic environment vary with a number of factors, including type of bedrock and sediment, mineralogy, organic content, redox conditions in water and sediments, water currents, salinity, etc. (Swedish EPA, 2000). The chemistry of heavy metals is also influenced by oxygen concentrations in the water. For example, a shortage of oxygen makes cadmium and copper precipitate as sulphide compounds, and they will subsequently be deposited in sediments in this form. This means the amounts of heavy metals in the water are directly linked to the oxygen depletion associated with eutrophication (HELCOM, 2003). Heavy metals may be either dissolved in water or bound to particles. This affects the chances of organisms absorbing them from their surroundings (HELCOM, 2003).

When metals are trapped in the sediments, they become less biologically accessible and therefore less capable of affecting aquatic organisms. The accessible portion of metals varies considerably between different sediments, and may even vary within the same sediment due to fluctuations in redox conditions. The portion of metals which is incorporated in minerals can be regarded as biologically inaccessible (Swedish EPA, 2000).

Heavy metals can be transported to the sea either via rivers, run-off in coastal areas, waterborne discharges of industrial and municipal waste or by wet and dry atmospheric deposition. In the case of airborne loads, these can also originate from distant sources outside the Baltic Sea catchment area (Kennish, 1997; HELCOM, 2007b).

Once released into the Baltic Sea, heavy metals can remain in the water for very long periods. The concentrations of heavy metals in the Baltic Sea water are up to 20 times higher compared to the North Atlantic (HELCOM, 2007b). In the Baltic Sea, metal concentrations in the sediments increased from the 1950s until the 1970s. Now it seems

to be decreasing due to measures taken in the industry. Today lead concentrations are decreasing in fish, due to reduced air emissions from car traffic (Kautsky, Kautsky, 2000). However, even though the concentrations of some heavy metals have decreased in many parts of the Baltic Sea, high concentrations can still be found in certain marine organisms. 35 stations were investigated for short-term temporal trends of mercury and cadmium in fish and mussels. The analysis included stations with time series of 5–11 years. Relatively few of the locations studied showed decreasing temporal trends and a few even showed increasing concentrations of metals (HELCOM, 2010).

The most important and commonly studied heavy metals are lead, chromium, cadmium, copper, zinc, mercury and arsenic (Gerlach, 1981; Nemerow, 1991; Leivuori, 2000; Swedish EPA, 2000, HELCOM, 2010); also nickel and vanadium, which sometimes are used as markers for oil contamination (De Mora et al., 2004).

OIL

Oil has been forming from the organic remains of dead organisms over different periods in the Earth's history. These organics had been preserving till the present in fossil form in places where the absence of oxygen prevented their decomposition. As different factors influenced the formation and setting of the different sediments, the quality of petroleum is different everywhere it is found (Gerlach, 1981).

Oil contamination is usually caused by an accidental or chronic release of one of three main types of oil: crude oil, heavy fuel and diesel fuel oil (FIMR, 2007). Crude oils consisting of a complex mixture of hydrocarbon and non-hydrocarbon compounds vary widely in chemical composition and physical properties. While hydrocarbons comprise more than 75% by weight of most crude oils, non-hydrocarbons (compounds containing oxygen, nitrogen, sulfur, and metals such as copper, iron, nickel, and vanadium) can predominate in heavy crude oils (Kennish, 1997; Wake, 2005). Among heavy metals, vanadium and nickel are characteristic constituents of crude oil. Vanadium is usually associated with a high sulphur content and nickel with a low sulphur content of crude oil (FIMR, 2007).

Oil spills contaminate water by creating an oily layer. The oil spreads quickly over the sea surface, often covering extensive areas as slicks varying from micrometers to a centimeter or more in thickness. As the oil spreads and the thickness reduces, its appearance changes from the black or dark brown color of thick oil patches to iridescent and silver sheen at the edges of the slick. A common feature of spills of crude oil and some heavy fuel oils is a rapid formation of water-in-oil emulsions which are often characterized by a brown / orange color and a cohesive appearance. Oil slicks migrate downwind at 3–4% of the wind speed, spreading at a rate dependent on water temperature and composition of the oil. Light oils spread faster than heavy oils (Kennish, 1997; Stankevičius, 2008; ITOPE, 2009).

Several physical-chemical processes change the composition of oil in seawater. The main processes are evaporation, photochemical oxidation, emulsification, and dissolution. Low-molecular-weight volatile fractions evaporate, hydrocarbons undergo photo oxidation, water soluble constituents dissolve in seawater, and immiscible components become emulsified. Evaporative loss of volatile hydrocarbons removes the toxic lower-molecular-weight components during the first 24 to 48 hours of an oil spill. The loss of these volatile components substantially lowers the overall toxicity of the oil to water organisms (Kennish, 1997; Stankevičius, 2008). As the density of oil approaches that of seawater, it tends to sink. Sedimentation of oil is facilitated by the sorption of hydrocarbons to particulate matter suspended in the water column (Kennish, 1997).

Microbes play a pivotal role in the degradation of crude oil, often being the dominant factor controlling the fate of toxic hydrocarbons in aquatic environments. All together they can degrade as much as 40 to 80% of a crude oil spill. Several factors influence the biodegradation rates: oil composition, water temperature, nutrient availability, oxygen levels, and salinity (Kennish, 1997). Anaerobic conditions severely restrict microbial degradation. Investigations show that oil in sediments can persist over 30 years in concentrations of total petroleum hydrocarbons similar to those observed immediately after the spill. Such persistence of oil was attributed to the heavy contamination of the area by the spill, the high organic carbon content, and anoxic conditions in the marsh sediments that hindered microbial degradation (Reddy et al., 2002).

In the cold waters of the Baltic, where the average water temperature is only about 10 degrees, oil decomposes very slowly. Coastal areas contaminated by oil-spills need to be actively cleaned up, which is a very slow and laborious task, especially during the winter. The necessary clean-up operations may themselves unavoidably harm marine life and coastal habitats, e. g. when using oil dispersants (Riepšaitė, Stankevičius, 2005).

Oil pollution is one of the greatest hazards for the marine environment, despite weather it happens in the form of large accidents or long-term small-scale spills and leakage. Oil accidents also cause direct economic losses e. g. by affecting fish stocks and spoiling the recreational use of the sea and coastline. From an ecological point of view, damages occur at all levels of the marine food web including birds and mammals (FIMR, 2007). The most visible effects of oil-spills are caused by the oil on the surface: birds and seals are smothered, and their chances of survival are hampered by problems with their mobility or the insulating properties of their feathers or skin (HELCOM, 2003). Other aquatic organisms are also highly impacted by the spilled oil, and massive mortality of marine life including fish, worms, crustaceans, and mollusks occurring in a few days (Burger, 1994; Reddy et al., 2002).

About 10% of all oil hydrocarbons in the Baltic Sea originate from deliberate, illegal discharges from machinery spaces or cargo tanks of vessels sailing in the Baltic. Surveillance aircraft detect about 400 illegal oil discharges a year happening in the Baltic Sea (HELCOM, 2003). Long-term investigations show that there is an increase in total hydrocarbon concentrations from north to south: the Bothnian Bay towards the Bothnian Sea and further via the Gulf of Finland to the Baltic Proper. The increase is compatible with the greater number of oil spills towards the south (Pikkarainen, Lemponen, 2005).

POLYCYCLIC AROMATIC HYDROCARBONS

Polycyclic aromatic hydrocarbons (PAHs) sources can be broadly divided into two main categories: petrogenic (from fossil fuels) and pyrolytic (from incomplete combustion of organic material). PAHs are mainly produced by pyrolysis, but are also present in crude oils, coal, coal tar and various refinery products. Some PAHs have both natural and

anthropogenic origin because they are the product of both wood and fossil fuel combustion. However, the anthropogenic contribution frequently outweighs PAH input from nearly all other sources (Webster et al., 2003; Barra et al., 2006). Molecular indices, which are based on concentration ratios of selected compounds, can be used as source indicators when evaluating pyrolytic and petrogenic origin of PAH compounds (Baumard et al., 1998a; Kaag et al., 1998; Webster et al., 2003; Barra et al., 2006; Pikkarainen, 2004a, 2004b, 2008).

Polycyclic aromatic hydrocarbons are of concern due to their persistence and potential to accumulate in aquatic organisms, particularly invertebrates. The compounds range from naphthalene (C₁₀H₈, two rings) to coronene (C₂₄H₁₂, seven rings). Common PAH compounds include two-ring compounds (naphthalene); three-ring compounds (fluorene, phenanthrene, anthracene); four-ring compounds (fluoranthene, pyrene, benzo(a)anthracene); and five-ring compounds (benzo(a)pyrene, benzo(b)fluoranthene, perylene). The low-molecular-weight PAH compounds, containing two or three rings, are acutely toxic to a broad spectrum of marine organisms. Anthracene, fluorene, naphthalene and phenanthrene are examples of low-molecular-weight PAHs that tend to be toxic. High-molecular-weight PAH compounds, containing four, five, and six rings, are less toxic but have a greater carcinogenic potential. High-molecular-weight PAH compounds that are carcinogenic include benzo(a)pyrene, benzo(c)phenanthrene, dibenzo(a,i)pyrene (Kennish, 1997; Webster et al., 2003).

PAHs exhibit a wide range of physical-chemical properties (vapor pressure, aqueous solubility) that demonstrate their semi-volatile and hydrophobic character and influence their environmental fate (Barra et al., 2006). Organic contaminants in aquatic environment may exist in several forms including dissolved forms, those bound to dissolved organic matter, adsorbed to suspended particulate matter, and associated with surface sediments (Zhou et al., 1998). Due to their low water solubility and hydrophobic nature, PAHs tend to associate with particulate material. The deposition of these particles in rivers and coastal waters can lead to an accumulation of PAHs in the sediment. Accumulation of hydrophobic compounds, such as PAHs, is dependent on a sediment type; sediments

with high organic carbon content and a smaller particle size (larger surface to volume ratio) have a greater potential to accumulate PAHs compared to coarser, sandy sediments. In addition, PAHs are persistent, especially in anaerobic sediments, with the higher molecular weight PAHs being more persistent than the lower molecular weight compounds (Kennish, 1997; Webster et al., 2003).

The solubility of PAH decreases with increasing molecular weight. Thus, bioaccumulation of PAHs from sediments by marine organisms is generally greater for the lower molecular weight and more water soluble PAHs than for the higher molecular weight compounds. Different profiles of contaminants have been observed in organisms of different trophic levels. These differences were attributed to a partial biotransformation of the contaminants in the organisms of higher trophic levels (Baumard et al., 1998b).

Elevated levels of PAHs are commonly found in estuarine and coastal marine waters near heavily populated areas. Oil related activities, ballast water discharges, dredging activities and disposal, oil pollution and sewage are all potential sources of PAHs. In the marine environment the introduction of PAHs is through effluent discharges, urban run-off, atmospheric transport, and the spillage or disposal of oil and petroleum products. PAHs also have a natural origin: some are synthesized by bacteria, plants, and fungi or derive from natural products and processes, such as coal and oil, grass and forest fires emissions (Kennish, 1997; Webster et al., 2003).

Total PAH concentrations in the Baltic Sea indicate considerable pollution in some areas. Pikkarainen (2008) in her study showed that PAHs in the Baltic were pyrolytic as well as petrogenic, and diesel engine sources of PAHs, caused by steadily increasing shipping in the area, were also indicated. Fluoranthene, benzo(b)fluoranthene, benzo(g,h,i)perylene, and indeno(1,2,3-cd)pyrene dominated in the surface sediment.

CHLORINATED HYDROCARBON COMPOUNDS

In marine ecotoxicology more attention has been given to the higher-molecular-weight chlorinated hydrocarbon compounds, also known as organochlorine compounds, which are common contaminants

in estuarine and marine environments. These compounds are mainly derived from pesticides and industrial chemicals (Kennish, 1997). The chlorinated hydrocarbons are broad spectrum poisons that affect many different organisms in one area (e. g. plankton, benthic invertebrates, fish, mammals, and birds), as well as humans (Rylander et al., 1996), and thereby threatening entire communities. Their rapid distribution in marine environments is facilitated by atmospheric dispersal and deposition, current transport, and migration of animals contaminated with the organochlorines (Kennish, 1997).

Due to unique properties of chlorinated hydrocarbon contaminants – chemically stable nature, great mobility, hydrophobicity, resistance to degradation, persistence in the environment, affinity for living systems, bioaccumulative capacity, and general toxicity – they have attracted attention and were added to numerous monitoring programs (Kennish, 1997). Due to their lipophilicity, organochlorine compounds tend to concentrate in lipid-rich tissues of animals (Sole et al., 2000), and biomagnify through food webs. Hence, some marine fauna, such as mammals, situated at the uppermost trophic levels, carry very high contaminant residues (Kennish, 1997).

The half-lives of chlorinated hydrocarbon compounds typically range from months to years. The residues of the more persistent compounds, however, may be present for decades or possibly centuries, depending on temperature, light, pH, rate of microbial degradation, and other conditions. The half-life of a contaminant within an organism is in part dependent on body composition and biological functions, such as the concentration of lipids and the reproductive activity of a species (Kennish, 1997).

Most of the chlorinated hydrocarbon compounds are classified as persistent organic pollutants (POPs). According to Stockholm Convention, persistent organic pollutants possess toxic properties, resist degradation, bioaccumulate and are transported through air, water and migratory species, across international boundaries and deposited far from their place of release, where they accumulate in terrestrial and aquatic ecosystems. There have been substantial inputs of POPs into the Baltic Sea from numerous sources over the past 50 years. These sources include in-

dustrial discharges, such as the organochlorines in effluents from pulp and paper mills, runoff from farmland, special paints used on ships and boats, and dumped wastes (HELCOM, 2003). A large number of halogenated organic pollutants have been identified in the Baltic Sea and levels in some fish, e. g. herring and cod liver, were so high that recommendations were issued to restrict consumption. Joint international measures to reduce inputs to the Baltic, have resulted in a decline in concentrations of chlorinated hydrocarbons in the environment of the Baltic Sea since the 1970s. Nevertheless, these compounds are still found in all matrices of the Baltic environment (Jonsson et al., 1996; Kautsky, Kautsky, 2000; Ciereszko, 2002; HELCOM, 2003; Pikkarainen, Parmanne, 2006; Pikkarainen, 2007; Bignert et al., 2008).

Chlorinated pesticides

Chlorinated hydrocarbon pesticides are extremely harmful biocide agents, acting as a nerve poison to control population sizes of target organisms (Kennish, 1997). In the environment, the chlorinated pesticides degrade very slowly – 5 to 15 years, the half-life of DDT can even reach approx. 150 years in aquatic ecosystems (Kennish, 1997; Mulsow et al., 2002). Officially the use of chlorinated pesticides in Lithuania stopped in 1970s (Četkauskaitė, 1999).

One of the most well known and ubiquitous chlorinated hydrocarbon contaminants is **dichloro-diphenyl-trichloroethane (DDT)**, which belongs to the diphenyl aliphatics class consisting of an aliphatic or straight carbon chain, with two (di)phenyl rings attached (Kennish, 1997). Solar radiation and the metabolic activities of animals decrease the concentration of DDT in the environment (Kennish, 1997; Mulsow et al., 2002) and degrade it to DDE and DDD. Combination of DDT and its degradation products DDE and DDD is referred to as total DDT. DDD is less toxic to marine organisms than DDT or DDE, and it rarely accumulates in them. DDT is one of the most water-insoluble compounds that has been ever artificially synthesized. Its solubility amounts to approximately 6 ppb of water. In contrast, DDT is highly fat soluble. Thus, it tends to partition out of the hydrosphere into biotic compartments (Kennish, 1997).

In the Baltic Sea, there has been a significant decrease of DDT concentrations in herring muscle and cod liver since 1970s (Bignert et al., 2008), but the concentrations of DDT are still high in some bivalves and herring muscle samples from different areas of the sea (Pikkarainen, Parmanne, 2006; Pikkarainen, 2007). DDT has been completely banned since the 1980s (HELCOM, 2003).

There are eight isomers of **hexachlorocyclohexanes (HCHs)**: β -, γ -, δ -, ϵ -, η -, θ - and two forms of α -HCH. The structures of these isomers differ in the angles at which the Cl-atoms are attached to the cyclohexane. Technical HCH is dominated by α -HCH (55–80%). Lindane is a well known insecticide consisting of >99% γ -HCH and is still legally used in many countries. Upon ingestion by animals, lindane tends to be rapidly metabolized to water soluble chlorophenols and chlorobenzenes. Both α - and β - HCH are higher persistent in environment than γ -HCH. β -HCH is the isomer with the highest tendency to accumulate in humans and has a bioconcentration factor (BCF) of over 500 in comparison to 20 for α - and γ -HCH (Kennish, 1997; Sundqvist, 2009).

In recent years, in some areas of the Baltic Sea concentrations of β -HCH are generally decreasing, and are now approaching the detection limit. The concentrations of lindane have decreased significantly in all matrices except for guillemot eggs and herring (HELCOM, 2003; Bignert et al., 2008). The levels of HCHs in bivalves could be classified as high and moderate (Pikkarainen, 2007).

Several chlorinated cyclic hydrocarbons, like **endosulfan, aldrin, endrin, dieldrin**, belong to a class of compounds termed the cyclodiene pesticides. These compounds include the most toxic organochlorine insecticides, especially in terms of acute toxicity. Cyclodienes consist of chemicals developed after World War II (e. g. aldrin and dieldrin, 1948; endrin, 1951; endosulfan, 1956). All cyclodienes have low water solubility and extreme persistence. They are particularly stable in soil, and thus have been most commonly employed as soil insecticides. Some of the compounds (e. g. aldrin) are rapidly metabolized by organisms, however, their metabolites (dieldrin) are as toxic and persistent as the parent compounds (Kennish, 1997).

Endosulfan is an insecticide and a multicide applied in cultivation, e. g. fruits, vegetables, maize and rice; it is also used as a wood preservati-

ve (HELCOM, 2009). Technical grade endosulfan contains two isomers, α - and β -endosulfan, in the ratio 7:3 making up 94% of the content. Endosulfan sulphate is an oxidation product found in technical endosulfan and is also the main microbial oxidation product of α - and β -endosulfans. In the aquatic environment, endosulfan mainly adsorbs to suspended solids and deposits to sediments; however, a certain proportion is likely to remain in the water column due to relatively high water solubility (Cousins et al., 2005).

Hexachlorobenzene (HCB) is a fungicide. It was widely used as a fumigant in grain storage against fungal attacks, as soil fumigant, and as a component in wood preservatives. It is a highly persistent contaminant, largely found in estuarine and marine environments sorbed to sedimentary particles (Kennish, 1997). HCB is a dioxin-like compound resulting in dioxin-like effects in biota (Falandysz, 2000).

HCB has not been used as a pesticide in the Baltic Sea region since the early 1990s, therefore, in the Baltic there is a decrease of HCB in all fish species and in guillemot eggs (Falandysz, 2000; Bignert et al., 2008; HELCOM, 2010). Nevertheless, due to its persistence in the environment HCB can be still found in seawater, sediments (HELCOM, 2010) and fish (Pikkarainen, Parmanne, 2006).

Pentachlorophenol (PCP) is a pesticide with a broad application, wide effectiveness, and multiple modes of action. A metabolite of HCB, PCP has been used as a fungicide for wood and textile preservation, an insecticide for protection against insects, a nonselective herbicide and a pre-harvest defoliant (Kennish, 1997). PCP is highly toxic to aquatic organisms, persistent and liable to bioaccumulate (OSPAR Commission, 2001).

PCP production in Europe has been banned since the early 1980s. However, due to its persistence in the environment PCP is still found in the Baltic Sea (Sternbeck et al., 2003; Oehme et al., 2005).

Polychlorinated biphenyls (PCBs)

PCBs are a group of synthetic halogenated aromatic hydrocarbons consisting of a complex mixture of chlorinated biphenyls with a varying number of substituted chlorine atoms on aromatic rings. There are 209 possible PCB congeners. Twelve of the 209 PCB congeners have a substitution

pattern that allows the molecule to assume a planar conformation conferring a structural similarity to polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). These dioxin-like PCBs exhibit the same mode of toxicological action as PCDD/Fs (to be discussed in the next section). Physical and chemical properties of PCBs are: general inertness, thermal and chemical stability, miscibility with organic compounds, high dielectric constant, non-flammability and low cost. These characteristics enabled PCBs to be widely used wherever such properties were desirable, e. g. in dielectric fluids of transformers and capacitors, heat exchange and hydraulic fluids, lubricants, fire retardants, plastics, and other materials (Kennish, 1997; Sundqvist, 2009).

Due to highly hydrophobic character, in the environment PCBs are primarily adsorbed to particles (e. g. soil, sediment and aerosols). Furthermore, their high persistence leads to bioaccumulation in organisms. PCBs are deleterious to marine life, especially upper-trophic level organisms that tend to accumulate the compounds in their tissues. Over the period of 50 years, PCBs have become widely distributed in estuarine and marine environments and occur in nearly all marine plant and animal species (Kennish, 1997; Sundqvist, 2009).

In the Baltic Sea concentrations of polychlorinated biphenyls in sediments, bivalves and herring have decreased significantly since 1970s-80s, probably due to the effect on emissions of stricter regulations and bans in the HELCOM countries (HELCOM, 2003; Pikkarainen, Parmanne, 2006; Pikkarainen, 2007; Bignert *et al.*, 2008), **but in spite** of this fact, there is still a high degree of contamination by PCBs in some sediment and herring muscle samples (Pikkarainen, Parmanne, 2006; Pikkarainen, 2007).

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs)

Two related classes of aromatic heterocyclic compounds, the polychlorinated dibenzo-p-dioxins (PCDDs or dioxins) and polychlorinated dibenzofurans (PCDFs or furans), cause considerable biological and especially toxic impacts on aquatic organisms. Substitution with different numbers of chlorine atoms gives rise to 75 possible PCDD molecules and 135 possible PCDF molecules, which jointly are termed congeners (Sundqvist, 2009).

The PCDDs and PCDFs are hydrophobic and lipophilic compounds that resist degradation in the environment. They tend to sorb to sediments and ultimately accumulate on the sea floor, which acts as a sink for these compounds. However, in estuarine and marine environments, sediments are not the primary direct source of PCDDs and PCDFs for biota at higher trophic levels, and it appears that the food chain is the most important pathway for bioaccumulation of these compounds (Kennish, 1997).

Despite the global distribution of PCDD/Fs, they have never been intentionally synthesized. Hundreds of congeners are formed during synthetic processes such as combustion and certain industrial activities. High temperatures in combination with carbon and chlorine sources often lead to the formation of PCDD/Fs. Chemical processes producing significant amounts of PCDD/Fs include the bleaching of pulp using chlorine gas or the chemical manufacture of chlorophenols and other organochlorine chemicals (Sundqvist, 2009). PCDD/Fs may also be formed by natural biological and abiotic processes in the environment. Dioxins can be formed in peat and forest soil, presumably via the enzymatic oxidative dimerization of natural chlorophenols; even a human biosynthesis of dioxins is possible (Gribble, 2003).

In environmental samples dioxins are always found as a mixture of various congeners. The toxicity of the dioxins is very congener-specific, ranging from the most toxic 2,3,7,8-TCDD (tetrachloro-dibenzo-dioxin or the Seveso-dioxin) to congeners more than 10,000 times less toxic. In order to aggregate the results for the various congeners in a sample and get a "total" dioxin content, some international systems for calculating dioxin toxicity equivalence (TEQ) have been developed. These have been based on the assumption of similar toxic action mechanisms together with the assumption that the interactions are additive. The systems are based on a relative ranking system which gives the congeners toxicity equivalence factors (TEF) with TCDD (the most toxic) assigned a factor of 1. The quantity of each dioxin is multiplied by its TEF to normalize the amount to TCDD equivalent amount (TEQ). The results can then be simply added to give a total TCDD equivalent amount for dioxins (HELCOM, 2004). The reevaluation of TEF scale was reported by van den Berg *et al.* (2006).

Elevated levels of PCDD/Fs are present in both coastal and offshore areas of the Baltic Sea. Dioxin content in herring often exceeds the prescribed maximum limit for dioxin residues (4 WHO-PCDD/F pg/g wet weight) (Bignert et al., 2007, 2008). However, the major hotspots of PCDD/Fs are located close to the shore and have large variations in profiles, indicating that local emissions are (or have been) the major cause of pollution (Sundqvist et al., 2009). Concentrations of dioxins in fish vary regionally, and the most contaminated fish are found in the Gulf of Bothnia, including herring in the Bothnian Sea, and salmon in the Bothnian Bay. Transfers of dioxins up marine food chains can be observed in fish-eating birds and their eggs. The concentrations of dioxins in guillemot's eggs have now decreased to one third of their 1970-levels. Dioxin concentrations in sediments peaked in the 1970s, but have more recently started to decrease (HELCOM, 2003).

ORGANOTIN COMPOUNDS

Organotin compounds are substances composed of tin, directly bound to a number of organic groups. Tributyltin (TBT) is the most hazardous of all tin compounds with considerable biological effects (SOCOPSE, 2009).

In natural waters, TBT has a short residence time, with a half-life ranging from several days to weeks. Organotins are moderately hydrophobic and have a strong tendency to adsorb to sediments (Unger et al., 1996; Watanabe et al., 1997; St-Jean et al., 1999). Adsorption of TBT onto suspended particulate matter is thought to be an important removal process. On the other hand, it also means that organotins, adsorbed to suspended matter, end up in sediment (Ceulemans et al., 1998). Degradation of TBT in sediment is much slower compared to water – a half-life from one to a few years, depending on Redox conditions, water temperature, light and the presence of microorganisms (Ceulemans et al., 1998; Michel, Averty, 1999; St-Jean et al., 1999; HELCOM, 2009). The degradation of TBT in the aquatic environment follows a stepwise debutylation process to a less toxic dibutyltin (DBT) and monobutyltin (MBT) and ultimately to inorganic tin compounds. Triphenyltin (TPhT) is transformed into diphenyltin (DPhT) and further into monophenyltin (MPhT) and inorganic tin. Both TBT

and TPhT as well as their degradation products are found in the marine environment (St-Jean et al., 1999; HELCOM, 2009).

TBT is highly toxic to a wide range of aquatic species (Austen, McEvoy, 1997; Stronkhorst et al., 1999). Trisubstituted organotin compounds such as TBT and TPhT are more strongly bioaccumulated than the less lipophilic mono- and disubstituted organotins such as DBT, MBT, DPhT and MPhT. In fish and marine mammals, TBT and TPhT bioaccumulate more strongly in liver than in muscle. The majority of studies suggest that TBT is not biomagnified in aquatic food-chain. On the other hand, TPhT appears to be biomagnified fairly strongly (HELCOM, 2009).

Historically, since the early 1960s organotins have been employed as a biocide, due to its effectiveness against algae, gram-positive bacteria, fungi and certain marine organisms. Their main use was as a part of anti-fouling paints applied to ship hulls. Consequently, this led to a high contamination of sediments by organotins in harbours and shipyards as shown by different studies from all over the world (e. g. Quevauviller et al., 1989; Ko et al., 1995; Kan-Atireklap et al., 1997; Ceulemans et al., 1998; Shim et al., 1999; De Mora et al., 2003; HELCOM, 2009).

Antifouling use of organic tin compounds in all vessels was banned in the EU in 2003 (2002/62/EC). According to International Convention on the Control of Harmful Anti-Fouling Systems (AFS Convention) as of 1 Jan 2008, old paint should be removed or permanently covered. Lithuania ratified this Convention on 10 October 2006. Thus, currently in the EU the use of TBT and TPhT is assumed to be negligible.

Although the use of trisubstituted organotins in most former applications is now prohibited, small amounts of TBT are still used as a biocide (SOCOPSE, 2009). Nowadays, the main emission source of organic tin compounds is their leaching from ship hulls. Related activities that may cause emissions are sea ship traffic, leaching from contaminated harbour sediments and removal of old antifouling paints (Lilja et al., 2009). In addition, TBT occurs as an impurity in stabilizing agents containing MBT and DBT used in the manufacture of plastics (PVC, polyurethane and polyester) and the emission pathway is via the use of the products (HELCOM, 2009).

The occurrence of organotin compounds is widespread in the Baltic marine environment. Despite the legislative measures taken, the current levels of the most toxic triorganotin compounds like TBT and TPhT pose a risk to the marine environment. The highest threat caused by organotin compounds to the Baltic Sea is near harbours and shipyards. The elevated levels also occur near sea routes and at the disposal sites for dredged material. The TBT levels are high in water, sediment and biota (e. g. in mussels and fish), whereas high levels of TPhT are mainly found in fish (HELCOM, 2009).

POLYBROMINATED DIPHENYL ETHERS (PBDES)

Three polybrominated diphenyl ether (PBDE) flame retardants are available commercially, referred as penta-, octa- and decabromodiphenyl ether, but these products are actually mixtures of diphenyl ethers with varying degrees of bromination (HELCOM, 2009). Out of a total of 209 PBDE congeners Law et al. (2006) recommended eight (BDE28, BDE47, BDE99, BDE100, BDE153, BDE154, BDE183, BDE209) to be used as a minimum common congener set in determining BDEs from different matrixes. PBDEs are structurally similar to other environmental pollutants, such as dioxins and PCBs. They are lipophilic and persistent compounds and are widespread in the environment. For certain congeners, bioaccumulation has been observed (Paepke et al., 2004).

Since 2004, the production and use of decaBDE only is permitted in Europe whereas pentaBDE and octaBDE have been banned. However, stocks of PBDEs are still present in products in service and waste. PBDEs are used as flame retardants in plastics and to some extent in textile (Lilja et al., 2009).

The occurrence of BDEs is widespread in the Baltic marine environment. Penta- and octaBDE levels in the Baltic Sea have probably already decreased due to the current legislative measures. While pentaBDE and octaBDE do not seem to pose a risk to the marine environment in the western Baltic Sea, the situation may be different in the eastern part of the Baltic Sea (HELCOM, 2009).

Overall, there is a lack of information on the occurrence of PBDEs in the Baltic Sea environment.

HEXABROMOCYCLODODECANE (HBCDD)

HBCDD is an aliphatic brominated flame retardant. Technical mixture exists mainly as a combination of three different isomers, α -, β - and γ -HBCDD, which are all of environmental interest (Lilja et al., 2009; HELCOM, 2009). HBCDD has been on the world market since the 1960s. It has been used (and perhaps is still used) as a flame retardant in building insulation materials, as well as electrical and electronic equipment. The main use (90%) of HBCDD is in polystyrene. The predominant use of polystyrene is in rigid insulation panels / boards for the construction industry. The main pathways of HBCDD to the marine environment are via rivers and the atmosphere. Living organisms, especially predators, such as mammals and predatory birds are at risk via secondary HBCDD poisoning. The assessment showed that HBCDD is a persistent, very bioaccumulative and toxic substance (PBT substance). At present, information on the occurrence of HBCDD in the environment is very scarce (HELCOM, 2009).

PERFLUORINATED ALKYL SUBSTANCES (PFAS)

Perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and other related compounds belong to the chemical family called fluorinated surfactants (i. e. surface-active agent). A surfactant is a substance which, even at low concentrations, effectively lowers the surface tension of its medium by selective adsorption on the interface. In fluorinated surfactants, the hydrophobic part of the surfactant molecule contains fluorine. Perfluorinated surfactants, such as PFOS and PFOA, are fully fluorinated surfactants, where all hydrogens in the hydrophobic part of the molecule have been replaced by fluorine. Perfluorinated surfactants have a unique ability to dramatically lower aqueous surface tension, improve wetting and leveling, while remaining chemically stable under harsh use conditions. Fluorinated surfactants are stable to heat (fire resistant), acids, bases as well as reducing and oxidizing agents. Due to these unique properties, they are often irreplaceable in many applications (Poulsen et al., 2005).

The major uses for the PFOS-related substances are in providing grease, oil and water resistance to

materials such as textiles, carpets, paper and other coatings. PFOS has also been used in cleaning products, fire-fighting foams and electrical and electroplating industries. PFOA has been used in the PTFE fluoroplastics industry (Brooke et al., 2004; HELCOM, 2009).

PFOS is persistent, bioaccumulative and toxic (Brooke et al., 2004). However, when compared to typical persistent organic pollutants, some PFOS- and PFOA-related substances are much more water-soluble and slightly more volatile. Unlike most POP compounds, PFOS and PFOA do not accumulate in fatty tissues – but is more likely to bind to proteins in liver, kidney and blood plasma (Kannan et al., 2002; Poulsen et al., 2005; Law et al., 2008). Detectable concentrations of PFOS can be observed in species of higher trophic level like seals, whales, dolphins, porpoises from all over the world, including animals from locations in the Canadian Arctic, demonstrating the widespread distribution of this chemical in the environment (Law et al., 2008). **Nevertheless, water is considered to be the target matrix for PFOA (HELCOM, 2009).**

The situation regarding PFAS compounds is complicated because of the large number of substances, and it is not exactly known which substances have harmful properties (HELCOM, 2009).

NONYLPHENOLS (NP), OCTYLPHENOLS (OP) AND THEIR ETHOXYLATES (NPES & OPES)

Nonylphenol and octylphenol are organic compounds of the wider family of alkylphenols, more specifically, they are members of a group called “long-chain alkylphenols” (Lilja et al., 2009).

The name “nonylphenol” is used for a number of isomer substances having a phenol ring structure and alkyl chain of C₉H₁₉. Branched 4-nonylphenol is the most descriptive and commercially available NP. The surfactant products produced from nonylphenol are called “nonylphenol ethoxylates” (NPEs). NPEs are used as emulsifiers, dispersive agents, surfactants and / or wetting agents and are the primary source of inputs of NP and NPEs to the sea. The main users of NP and NPEs are the industrial, institutional and domestic cleaning sectors. The primary source of NP in the environment is considered to be NPEs, which can break down

into NP after being released into the environment during their production, their formulation into various other products, and the use of these products. Releases to surface water (rivers, lakes, seas and their sediments) occur via industrial and municipal waste water and waste water treatment plants, as well as via sewage sludge containing NP/NPEs (Lilja et al., 2009).

4-*Tert*-octylphenol is a high production-volume substance. It is mainly used to make phenolic resins (Brooke et al., 2005). **The remainder is converted into ethoxylates to produce surfactants.** It can also be present as an impurity in nonylphenol. Phenolic resins are used in rubber processing to make tires. Minor uses include being a component in printing inks and electrical insulation varnishes, and in production of ethoxylated resins for offshore oil recovery. Octylphenol ethoxylates are mainly used in emulsion polymerisation, textile processing, water-based paints, pesticide and veterinary medicine formulations, and to produce octylphenol ether sulphates (Lilja et al., 2009). **Octylphenol has a moderate bioaccumulation potential in aquatic biota.** When the substance is released to the environment it mainly partitions to soil and sediment (Brooke et al., 2005).

NP and OP are very toxic to aquatic organisms, especially to aquatic invertebrates and fish. In general, both substances show similar toxicity for particular taxonomic groups (Brooke et al., 2005). More data on NP/NPE and OP/OPE concentrations is needed both from discharges in the catchment area and from sea water, biota and sediment of the Baltic Sea to examine whether these substances cause harmful effects to the marine environment. While some available data indicate that levels of NP and OP in sea water and biota are not high, levels in the sediment may have adverse effects on the Baltic marine environment (HELCOM, 2009).

SHORT-CHAIN CHLORINATED PARAFFINS (SCCP OR CHLOROALKANES, C₁₀₋₁₃) & MEDIUM-CHAIN CHLORINATED PARAFFINS (MCCP OR CHLOROALKANES, C₁₄₋₁₇)

Chlorinated paraffins (CPs) are mixtures of polychlorinated *n*-alkanes. The technical mixtures are named based on chain length, C₁₀₋₁₃ are short chained chlorinated paraffins (SCCPs), C₁₄₋₁₇ are

medium chained chlorinated paraffins (MCCPs), and $C_{>18}$ are long chained paraffins (LCCPs) (Oehme et al., 2005).

SCCP as well as MCCP has been used, for example, in rubber and PVC plastics, paints and metal cutting fluids (HELCOM, 2009).

SCCPs and MCCPs are persistent, bioaccumulative and are toxic to aquatic organisms (Oehme et al., 2005). **The physico-chemical properties** of CPs (affecting their distribution in the environment) depend on carbon chain length and degree of chlorination. CPs are lipophilic with the potential to bioaccumulate. CPs have been found in aquatic biota such as plankton, mussels, crustaceans, fish, seals, whales, in fish eating birds, and in terrestrial biota such as earthworms, rabbit, moose and reindeer. CPs have the potential to biomagnify and increase in concentration with trophic level (Lilja et al., 2009). CPs have also been detected in air, water and sediments (Muir et al., 2000; Oehme et al., 2005). **The existing data** indicate that MCCP levels in fish may have adverse effects on the Baltic marine environment. Due to a wider current use of MCCP compared to SCCP, MCCP levels in fish and the sediment are higher than levels of SCCP (HELCOM, 2009). More intensive research on SCCP and MCCP concentrations in biota and sediment is needed.

PHARMACEUTICALS

Pharmaceuticals are compounds that are designed to have biological effects on humans or animals. Over 3000 chemical substances are used in human and veterinary medicines, which include, medicines used as painkillers, antibiotics, contraceptives, beta-blockers, lipid regulators, tranquilizers, and impotence drugs (HELCOM, 2010). Pharmaceuticals and their metabolites have been subjected to many years of uncontrolled emission into the environment as complex mixtures via a number of pathways; primarily from wastewater treatment plants, effluents or the land application of sewage sludge (Roberts, Bersuder, 2006). Pharmaceuticals are now recognized as relevant environmental contaminants. The examples of pharmaceuticals that have been found in the environment of the Baltic Sea are: clofibrac acid, ibuprofen, carbamazepine, gemfibrozil, diclofenac, bezafibrate, naproxen and propyphenazone, 17-alpha-ethinylestradiol (HELCOM, 2010).

Surface waters receive continuous inputs of pharmaceuticals. In addition, the substances undergo various chemical, physical and biological processes that degrade and alter them. Aquatic environment can be seen as the final sink of the most persistent compounds (HELCOM, 2010). Pharmaceuticals are a new threat to marine environment. There is a lack of information about distribution, environmental fate and effects of pharmaceuticals on biota. This group of substances is not regulated by the earlier mentioned documents, but new amendments of HELCOM and EU documents are on the way and most likely diclofenac, 17-alpha-ethinylestradiol and 17beta-estradiol will be included in the lists of priority substances.

EFFECTS OF CONTAMINANTS ON AQUATIC ORGANISMS

In their tissues marine organisms can accumulate contaminants from seawater, suspended particulate matter, sediments, with food intake, or by uptake through re-suspension of sediment material (UNEP, 1992; Sternbeck et al., 2003). The concentrations of certain contaminants in tissues are related to the concentrations in the organism's surrounding environment. This process is termed bioaccumulation, and it has been used by scientists to assess the marine contamination caused by human activities (UNEP, 1992). Many pollutants accumulate in organisms to concentrations that may become deleterious for a single species, ecosystems or even human (Dybern, Fonselius, 1981).

The widely varying conditions in different marine areas may affect the biological accessibility of pollutants. Among those conditions are salinity, temperature, changes in pH, turbidity, physico-chemical properties and substitution patterns of the individual compounds, as well as different sensitivity of various species. Different species do not bioaccumulate to the same level when they are exposed to the same concentrations of contaminant in sea water, and often have different rates of contaminant elimination. Even individuals of the same species, exposed to the same concentration of contaminants for the same period of time, might not accumulate the substances at the same rate. This is related to factors such as age, sex, size and physiological state of the individual (UNEP, 1992; Karbe et al., 1994; Kersten et al., 1994; Swedish EPA, 2000).

Different contaminants show significant differences with respect to their tendency to be bioaccumulated. Investigations by Karbe et al. (1994) show that in the sediment samples accumulation factors for metals are ranked – Mn > Pb > Hg > Cu > Cd > Fe, in the blue mussel – Hg > Cd > Cu > Pb, in hermit crab – Fe > Cu > Mn > Cd > Hg > Pb. This can be interpreted as a difference existing among metals with respect to their tendency of sorption to inorganic and organic surfaces and uptake by resorptive processes into organic matrixes. For example, the tendency of sorption to surfaces is high in case of lead and rather low for cadmium; however, the tendency for bioaccumulation as a consequence of high affinity binding to specific biochemical structures is much stronger for cadmium than for lead.

Investigations by Solé et al. (2000) indicated that bioaccumulation of organic pollutants in aquatic organisms tissue, followed the order PAHs > DDTs > PCBs > OPs (organophosphorous pesticides). Organochlorines and other organic contaminants are enriched from water to sediment and to biota as a consequence of hydrophobic / lipophilic interactions. Octanol-water partition coefficient may be used to quantify the hydrophobic properties of chemicals. The tendency to be accumulated is highest in case of the highly hydrophobic and lipophilic toxic environmental chemicals (xenobiotics) like DDT and its metabolites, as well as in case of PCBs (Karbe et al., 1994). Due to lower stability and lower partition octanol-water coefficient, OPs are more environmentally labile. In general, it has been accepted that OPs pose less risk to the ecosystem due to their low bioaccumulation factor and high biotransformation rate, which prevents their biomagnifications along the food chains. On the contrary, organochlorine pesticides and PAHs may cause chronic toxicity problems. Organochlorines, in particular, can induce negative ecological consequences to wildlife because of their biomagnifications in the top of the food webs (Solé et al., 2000). Generally, organic chemicals with octanol-water coefficient of $K_{ow} > 10^2$ have the potential to biomagnify in marine food chain and they comprise almost two-thirds of all organic chemicals used in commerce. About 40% of chemicals with these properties have a

$K_{ow} > 10^5$ and are potentially bioaccumulative because of their high degree of lipid-water partitioning (Kelly et al., 2007).

If concentrations and bioavailability are sufficiently high, negative effects in organisms can occur (Sternbeck et al., 2003). The responses of estuarine and marine organisms to contaminants are manifold, but could be generally classified into four levels of biological organization, i. e. cellular, organismal, population and community levels. The earliest detectable changes inside the cell in response to xenobiotics involve subcellular organelles such as lysosomes, endoplasmic reticulum and mitochondria (Verlecar et al., 2006).

According to Adams (2005), responses of organisms to chemical stressors are the integrated result of both direct and indirect pathways. Direct pathways operate primarily through metabolic processes, such as toxic action of chemicals at receptor sites. Indirect pathways mainly operate through effects on the food chain on habitat availability or through changes in the organism behavior (Adams, 2005).

Direct and indirect genetic effects have been also described by Medina et al. (2007). According to the authors, direct effects are related to the damage that genotoxic substances exert on the molecular structure of the genetic code (i. e. DNA). These include point mutations, chromosomal aberrations like inversions, deletions or additions, DNA adducts, DNA strand breaks, formation of micronuclei and aneugenic effects. Indirect effects are population-mediated processes when pollution decreases the genetic variability of the population.

A classic example of the effect of pollutants on marine organisms is that of tributyltin, which has been shown to induce genotoxicity, cytotoxicity, immunotoxicity and teratogenicity in some marine invertebrates (Jha, 2004). In British waters, the chemical has had a dramatic effect on the dog whelk *Nucella lapillus* which is hypersensitive to TBT. An extinction of the dog whelks now has been documented in many sites of UK, where they used to be common until the TBT paints were introduced. TBT causes the so called “imposex” effects which trigger the growth of a vas deferens and a penis in female dog whelks. These block the opening of the female genital duct so that eggs cannot be released. TBT seems to affect

the hormone system that determines the sex of prosobranch mollusks (Walker et al., 1996). Hagger et al. (2006) has provided evidence of DNA damage associated with the development of imposex in the *N. lapillus*; the masculinization of female gastropods considered to be the result of alterations to endocrine-mediated pathways. Thus, the imposex index provides an indication of the exposure of dog whelks to TBT at a site. Similar findings have been made on other gastropod species elsewhere in the world. Since 1998 imposex has been included as a biomarker in the national monitoring program in Denmark, covering both coastal and open waters in the Belt Sea, the Sound, the Kattegat and the Skagerrak. Four key species of gastropods have been selected, *Buccinum undatum*, *Neptunea antiqua*, *Hinia reticulata* and *Littorina littorea*, however, imposex development has also been found in other Danish gastropod species. The studies performed within Danish national monitoring program (NOVA) have shown that imposex is a widespread phenomenon in all regions of Danish waters (HELCOM, 2009). In addition, other considerable biological effects of TBT also exist including shell malformations of oysters, reduced resistance to infection (e. g. flounder) and effects on the human immune system (SOCO-PSE, 2009). By exposing *Mytilus edulis* to environmentally realistic concentrations of tributyltin oxide Hagger et al. (2005) showed that TBT is a cytotoxic and genotoxic compound to adult mussels. Studies of the same researchers also revealed that TBT may adversely affect marine organisms at various stages of the lifecycle and through multiple mechanisms, thus confirming that TBT has a deleterious effect to the marine environment.

At elevated levels metals act as enzyme inhibitors (Kennish, 1997). Heavy metal cations react in part specifically with cellular components to cause toxic effects. Mechanisms of detoxification are accomplished either via the high affinity of metal cations with sulphhydryl (-SH) groups of metallothionein or via their accumulation in membrane-limited granules, representing a general strategy for metal cation homeostasis (Domouhtsidou, 2004). For example, investigations show that in contaminated areas mercury may be expected to have an impact on bivalve immune

functions (Gagnaire et al., 2004). Zinc has been reported to suppress gametogenesis in *Mytilus* (Kaloyianni et al., 2005).

In regard to oil accidents, the effects are – at first – acute, causing visible damage on biota and the environment, but chronic harmful effects might also take place. Chronic contamination can provoke genetic effects in different organisms and initiate damage in the genetic structure of populations of organisms by selecting out the oil-tolerant genotypes, and, likewise, can have an effect on community structure by removing oil-sensitive species and favouring the tolerant ones (FIMR, 2007). Micronuclei test is a useful tool for oil pollution monitoring. The formation frequency of micronuclei is used for the indication of genotoxic agent action (Baršienė et al., 2004). Previous studies on biomarker responses in fish and mussels from the Lithuanian coastal area showed a significant increase of genotoxicity after an accidental oil spill in the Būtingė oil terminal (Baršienė et al., 2004, 2005, 2006a, 2006b). Increased genotoxicity and cytotoxicity levels were found at sites in the Lithuanian economic zone located close to the oil platform D-6 (FIMR, 2007). A higher frequency of micronuclei was detected in mussels from the Būtingė oil terminal and Klaipėda marine port zones in the Baltic Sea (Baršienė, Baršytė Lovejoy, 2000; Baršienė, 2002), in Mediterranean commercial port zone (Magni et al., 2006) and in the Venice Lagoon polluted by aromatic hydrocarbons (Venier, Zampieron, 2005). In different studies, a significant elevation of micronuclei levels has been described for mussels 30 days after an oil spill (Parry et al., 1997) or even eight months (Baršienė et al., 2004, 2006a).

Offshore oil industry can contaminate environment with produced water, which in addition to the remaining oil, contains other chemicals, i. e. additives used in drilling and pumping operations, as well as in the oil / water separation process (e. g. heavy metals, alkylphenols, PAHs, etc.). Investigations of Lavado et al. (2006) showed that exposure of mussels to chemicals present in produced water can lead to alterations on key biochemical pathways that could have physiological consequences for these organisms. He showed that oil and a mixture of oil and alkylphenols can affect endogenous levels of steroids in mussels.

Furthermore, studies of Stephens et al. (2000) showed that produced water chemicals can affect and induce detoxification metabolism in fish. Investigations done after the Prestige oil spill showed that activities of some oxidative stress biomarkers were significantly elevated in fish *Lepidorhombus boscii* which came from the most oil impacted area (Martínez-Gómez et al., 2006). In addition, lysosomal membrane stability was reduced in mussels from all locations in the oil spill area, indicating disturbed health (Orbea et al., 2006).

Polycyclic aromatic hydrocarbons (PAHs) are well known genotoxins and carcinogens. PAHs accumulate in tissues to high concentrations in invertebrates at the bottom of the food chains, where uptake rates greatly exceed the rates of metabolism and elimination, compared with vertebrates, where metabolism and elimination can cope with uptake (Jha, 2004). Boehm et al. (2005) have recommended using mussels (*Mytilus trossulus*) in monitoring of PAHs in marine environment, especially following an oil spill. The authors suggest to use mussels as a monitoring tool when the assessments involve food-chain effects. PAHs in the aquatic environment induce acute toxicity in organisms and the presence of PAHs in the sediments has been linked to liver neoplasms and other abnormalities in benthic fish species (Jha, 2004).

During the experiments with *M. edulis* mussels from the Baltic Sea exposed to PCB, the physiological measures (clearance rate and scope for growth) and changes in protein expression indicate the stressed state of the mussels (Olsson et al., 2004). Patterns of PCB congeners in marine organisms, capable of degrading and metabolizing some congeners, are affected by the degree and capacity of biodegradability and the storage capacity of organisms. Organisms at higher trophic levels possess mixed function oxygenase enzyme systems (MFO systems) composed of NADPH and cytochromes, which eliminate lipophilic xenobiotics by converting them to hydrophilic metabolites. In many species PCB congeners are known as MFO system inducers (Karbe et al., 1994).

Aquatic animals can enzymatically biotransform many xenobiotics. Metabolism of most xenobiotics by aquatic organisms results in their detoxi-

fication through conversion to more water-soluble and readily excretable products. Detoxification is not the only result of induction of enzymatic biodegradation pathways in living organisms; the increased reactivity of oxygenated metabolites of aromatic compounds can lead to genetic damage. Some xenobiotics, such as PAHs, organophosphorous pesticides, PCBs are enzymatically transformed to metabolites that are more toxic than the original / parent compound (Solé et al., 2000; Pikkarainen, 2008).

However, more investigations should be done to examine harmful effects of contaminants on the aquatic organisms, especially for “new emerging substances” like pentaBDE, NP, NPE, OP and endosulfan which are possible endocrine-disrupting substances (HELCOM, 2009).

BIOMARKERS

The need to detect and assess the effects of contamination at ever lower concentrations and in ever more complex mixtures has led to the development of a wide range of molecular, biochemical, sub-cellular and other indicators of exposure and effects of contaminants and other environmental stressors (CEFAS, 2000). Thus, early warning indicators – biomarkers – that respond before measurable effects on individual performance and population / community dynamics occur were established. Biomarkers indicate that organisms have been or are being exposed to certain chemicals or that organisms are suffering or likely will suffer future impairments of environmental conditions (Forbes et al., 2006).

Several definitions have been given for the term ‘biomarker’. Benford et al. (2000) presents 16 definitions of the term ‘biomarker’ appearing in the literature. In general, the definition includes almost any measurement reflecting an interaction between a biological system and a potential hazard, which may be chemical, physical or biological (WHO, 1993). Three separate terms ‘biomarker’, ‘bioindicator’ and ‘ecological indicator’ of different levels of biological organization can be defined. Biomarker is considered as any biological response to an environmental chemical at the subindividual level, measured inside an organism or in its products (urine, faeces, hair, feathers, etc.), indicating a deviation

from the normal status. The term bioindicator is defined as an organism giving information on the environmental conditions of its habitat by its presence or absence or by its behavior, and an ecological indicator is the parameter that describes the structure and functioning of ecosystems (Van Gastel, Van Brummelen, 1994).

Biomarkers can be subdivided into three classes (WHO, 1993; Van der Oost et al., 2003):

- biomarkers of exposure: cover the detection and measurement of an exogenous substance or its metabolite or the product of an interaction between a xenobiotic agent and some target molecule or cell that is measured in a compartment within an organism (e. g. acetylcholinesterase inhibition, metallothionein induction, PAH metabolites in bile (Hagger et al., 2008));
- biomarkers of effect: include measurable biochemical, physiological or other alterations within tissues or body fluids of an organism, which can be recognized as associated with an established or possible health impairment or disease. There can be physiological (feeding / clearance rate or heart rate of organisms) or sub-cellular (micronuclei and neutral red retention time) biomarkers (Hagger et al., 2008);
- biomarkers of susceptibility: indicate the inherent or acquired ability of an organism to respond to the challenge of exposure to a specific xenobiotic substance, including genetic factors and changes in receptors which alter the susceptibility of an organism to that exposure.

Biomarkers are also classified as specific or non-specific. For example, the specific biomarker metallothionein has been widely used to indicate the presence of heavy metals (Geffard et al., 2001, 2002; Geret, Cosson, 2002; Mourgaud et al., 2002; Tanguy et al., 2002; Domouhtsidou et al., 2004). Acetylcholinesterase activity is considered a specific biomarker of organophosphorus and carbamate pesticides (Bocquené et al., 1995; Bocquené, Galgani, 1998; Monserrat et al., 2001; Binelli et al., 2006). However, it should be pointed out that there is evidence to the confounding effects that some abiotic factors, like salinity or temperature, can have influence on metallothionein (Monserrat et al., 2007) and acetylcholinesterase activity (Radenac et al., 1998; Pfeifer et al., 2005). The determination of oxidative stress (DNA da-

mage, protein oxidation, lipid peroxidation) and antioxidant responses in aquatic species are non-specific biomarkers, since several pollutants can modify directly or indirectly the balance between the concentration of pro-oxidants and antioxidants (Monserrat et al., 2007). Histopathological gill changes in fishes are also non-specific to pollutant exposure (Au, 2004). The responses of general “stress biomarkers” are related to various contaminants exposure: neurotoxicity (acetylcholinesterase inhibition), lysosomal stability, immunotoxicity (macrophage activity), genotoxicity (micronuclei), oxidative stress (catalase), liver detoxification enzymes (e. g. GST) (Lehtonen, 2005).

INTEGRATED ASSESSMENT OF THE STATE OF THE AQUATIC ENVIRONMENT

Due to complexity of marine environment an appropriate number of measures are required for determining the biological significance of pollution and for understanding the cause of the observed effects. Usually only chemical criteria are used for assessing of pollution and its effects on biota (Den Besten, 1998). But relying on chemical criteria alone for assessing the effects of stressors provides an incomplete assessment of the biological and ecological condition of aquatic systems. Chemical criteria alone do not describe the influence of other environmental factors that can impair aquatic ecosystems, such as sedimentation, changes in habitat and natural flow regimes, varying temperature and oxygen regimes, and changes in ecological factors such as food availability and predator-prey interactions (Adams, 2005). In addition, contaminants in the environment can occur as a complex mixture, and the risk associated with such mixtures cannot be adequately evaluated on the basis of the effect and behavior of individual components. Since biological systems are the main target of the toxicant action, they could provide important information which is not readily available from chemical analyses (Jha, 2004). Biomarkers may be useful tools, indicating bioavailability of contaminants and their effects at the same time. Biomarkers could also be used to detect effects on the population or community level (Den Besten, 1998).

Studies of biological effects have many advantages. With the help of biological effects methods, which are usually low-cost and quick, problem areas can be identified and more detailed chemical research can be done afterwards on special areas. Numerous chemicals and their metabolites are potent genotoxins, which later can affect populations and communities. Therefore, biomarkers indicating effects of chemicals serve as early warning signals and precautionary measures can be taken before irrevocable changes would occur (Lehtonen et al., 2006).

Biological-effect methods are important elements in environmental monitoring programs. They can indicate links between contaminants and ecological responses. Biological-effect methods can be used to indicate the presence of substances, or combinations of substances of concern, but also to identify regions of decreased environmental quality or reduced ecosystem health (Thain et al., 2008).

In order to improve the assessment of the effects of chemical contaminants and their mixtures in the Baltic Sea marine ecosystem, an integrated approach is needed (Lehtonen, Schiedek, 2006b). Van der Oost et al. (2003) suggest five environmental monitoring methods which may be performed in order to assess risks of contaminants on organisms and to classify the environmental quality of ecosystems:

- chemical monitoring: measuring levels of contaminants in abiotic environmental compartments;
- bioaccumulation monitoring: measuring contaminant levels or bioaccumulation in biota;
- biological effect monitoring: the assessment of exposure and effect of contaminants using a set of biomarkers;
- health monitoring: the assessment of contaminants effect by examining the occurrence of irreversible diseases or tissue damage in organisms;
- ecosystem monitoring: the assessment of ecosystem quality by evaluation of e. g. species composition, density or biodiversity.

Thus, an integrated monitoring program is a study consisting of different monitoring activities comprising both chemical and biological measurements in environmental media or compartments (Van der Oost et al., 2003). An integrated monitoring would provide a reliable assessment

of ecosystem health of the aquatic environment and would also support political measures to be taken to improve the state of the environment (Lehtonen, Schiedek, 2006b).

CONCLUSIONS

Ecological objectives of the HELCOM Baltic Sea Action Plan are: to reach concentrations of hazardous substance close to natural levels, to ensure that all Baltic fish are safe to eat and to safeguard the health of wildlife. By signing the BSAP, HELCOM countries agreed to develop biological effects monitoring which would facilitate a reliable ecosystem health assessment (HELCOM, 2007a). Nevertheless this measure still remains to be undertaken. Biological effects monitoring is not established in some countries around the Baltic Sea. When developing biological effects monitoring, a harmonized implementation of biomarkers as an early warning system in the whole Baltic Sea should be the final aim (HELCOM, 2010).

The EU Marine Strategy Framework Directive (2008/56/EC) (MSFD) addresses hazardous substances by setting one of the qualitative descriptors for determining good environmental status as “Concentrations of contaminants are at levels not giving rise to pollution effects”. According to MSFD, the progress towards good environmental status will depend on whether pollution is progressively being phased out, i. e. whether the presence of contaminants in the marine environment and their biological effects are kept within acceptable limits, so as to ensure that there are no significant impacts on or risk to the marine environment.

The ongoing activities of HELCOM and EU are aimed at the integrated holistic assessments of the environmental state of the Baltic Sea. Whereas more scientific evidence appears the biological effects become an important issue of the environmental research. In order to achieve the objectives set by EU and HELCOM countries should look for the possibility to integrate biological effects to the Baltic Sea environmental monitoring programs. Thus, integrated monitoring of hazardous substances and their effects is an important step forward to reach one of our future goals – the Baltic Sea life undisturbed by hazardous substances.

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TARŠOS BALTIJOS JŪROJE KOMPLEKSINIS VERTINIMAS

Santrauka

Vandenų sistemos yra labai įvairios ir sudėtingos, joms turi įtakos daugybė aplinkos veiksnių, todėl norint tinkamai apibūdinti jų ekologines charakteristikas, būtinas kompleksinis vertinimas. Helsinkio komisijos Baltijos jūros veiksmų planas ir Europos Sąjungos Jūrų strategijos pagrindų direktyva (2008/56/EB) išskiria ir pabrėžia pavojingų medžiagų sukeltas problemas bei rekomenduoja atlikti kompleksinį aplinkos būklės vertinimą.

Straipsnyje apžvelgiami Baltijos jūros ekosistemos ypatumai, pabrėžiami jos pažeidžiamumo aspektai, charakterizuojami šie aktualiausi teršalai: sunkieji metalai, naftos angliavandeniliai, policikliniai aromatiniai angliavandeniliai, chloroorganiniai junginiai, organiniai alavo junginiai ir kitos teršiančiosios medžiagos. Apžvelgiamas teršalų poveikis gyviesiems organizmams, kompleksinis aplinkos būklės vertinimas bei parodoma biologinių efektų tyrimo metodų svarba vykdant aplinkos tyrimus, nes jie rodo sąryšį tarp užterštumo ir biologinio atsako. Daroma išvada, kad kompleksinė pavojingų medžiagų ir jų efektų stebėseną – svarbus žingsnis ateities tikslo link, kad Baltijos jūros aplinka nebūtų paveikta pavojingų medžiagų.

Raktažodžiai: Baltijos jūra, tarša, teršiančios medžiagos, biožymenys, kompleksinis vertinimas