

# Hazardous substances in the Baltic Sea

An integrated thematic assessment of  
hazardous substances in the Baltic Sea



**Helsinki Commission**

Baltic Marine Environment Protection Commission



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The natural marine environment of the Baltic Sea is susceptible to pollution by hazardous substances because natural features such as water residence times of around 30 years, shallowness, and the large catchment area predispose the Baltic Sea to the accumulation and effects of hazardous substances. The number of species inhabiting the Baltic Sea is low and the brackish water increases the natural physiological stress that many of these species, with a marine or freshwater origin, experience even in the absence of hazardous substances.

There are about 85 million people living in the Baltic Sea catchment area, in which are also located various types of industrial activities, busy traffic, and intensive farming and animal husbandry. Hazardous substances emitted or discharged by households, traffic, industries and agriculture are transported to the sea via water courses and the air. Some airborne substances can travel thousands of kilometres and their sources may be located far away from the Baltic Sea catchment area. Maritime transport and other maritime activities carried out at sea also add to the pollution burden of the sea.

The Helsinki Commission (HELCOM), which is responsible for implementing the Convention on the Protection of the Marine Environment of the Baltic Sea Area (Helsinki Convention 1992), has worked for over 30 years to reduce the pollution of the Baltic Sea. In fact, the focus of the initial Helsinki Convention signed in 1974 was largely on the prevention and elimination of pollution by hazardous chemicals. The 1970s was also the time when serious environmental problems, including collapses of seal and sea eagle populations caused by PCBs and DDTs, became obvious to the larger public. Since then, some of the focus of the HELCOM work has shifted to combating eutrophication, protecting biodiversity and ensuring the environmental safety of maritime activities. Nevertheless, hazardous substances still remain one of the four focal areas of HELCOM work and are also covered by one of the thematic segments of the HELCOM Baltic Sea Action Plan adopted at ministerial level in 2007.

This report describes and documents the degree of contamination and effects of pollution by hazardous substances in the Baltic Sea area, including

the Kattegat and Belt Sea areas. The objectives of this thematic assessment on hazardous substances are:

- To define the level of contamination and effects of hazardous substances by answering the questions: "What is the level of contamination of the marine environment caused by hazardous substances?" and "What are the effects caused by them?"
- To document the overall status of the marine environment in relation to hazardous substances using an indicator-based integrative assessment tool "CHASE".
- To document the causes of the contamination effects by describing uses, emissions, discharges, losses and inputs to the sea of hazardous substances.
- To discuss and present solutions to the pollution and contamination problem by assessing the sufficiency of existing strategies and by suggesting supplementary measures.

This report is associated with the HELCOM Baltic Sea Action Plan, which identifies pollution by hazardous substances as one of the four main issues requiring action to improve the health of the Baltic Sea. The Action Plan sets a strategic goal related to hazardous substances which is "Baltic Sea with life undisturbed by hazardous substances", and identifies a set of Ecological Objectives which corresponds to good environmental status. The Ecological Objectives are: "concentrations of hazardous substances close to natural levels", "all fish safe to eat", and "healthy wildlife and radioactivity at pre-Chernobyl levels". This thematic assessment addresses each one of the Ecological Objectives for hazardous substances, and provides an integrated overview of the status of the Baltic Sea in relation to hazardous substances and the degree to which the strategic goal has been reached.

The HELCOM Monitoring and Assessment Strategy from 2005 prompted the production of thematic assessments. According to the HELCOM Baltic Sea Action Plan, tools and methodologies need to be developed for evaluating the status of the marine environment and an integrated assessment of the occurrence and inputs, as well as uses and sources, of hazardous substances in the Baltic Sea region is required. Specifically, a Baltic Sea-wide thematic report on hazard-

ous substances was requested to be produced by 2010. This assessment is the third HELCOM thematic report defined in the Baltic Sea Action Plan (HELCOM 2007a). The previous reports were on eutrophication (HELCOM 2009a) and biodiversity and nature conservation in the Baltic Sea (HELCOM 2009b).

This thematic assessment is aimed at decision-makers, managers, scientists, educators and others interested in the environmental health status of the Baltic Sea; it includes a glossary to support readers without a professional background in marine ecology, chemistry or ecotoxicology. The assessment is supplemented by an Executive Summary.

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# 1 INTRODUCTION

This thematic report on hazardous substances is an indicator-based assessment which has been produced according to the HELCOM Monitoring and Assessment Strategy. The report is the third HELCOM thematic assessment in a series of thematic reports defined in the Baltic Sea Action Plan (HELCOM 2007a).

The status evaluations in this report cover the years from 1999 to 2007; temporal trends are presented for longer time periods as well.

This introductory chapter provides an overview of the unique nature of the Baltic Sea, the human activities taking place in the large catchment area and the resulting pollution by hazardous substances. It also presents the objectives and purpose of this report.

## 1.1 The pollution problem of the Baltic Sea

HELCOM defines substances as hazardous if they are toxic, persistent and bioaccumulate, or very persistent and very bioaccumulating. In addition, substances with effects on hormone and immune systems are considered hazardous due to the level of concern they cause. In addition to these hazardous substances, this report also concerns certain radionuclides in the sea.

Pollution is a concept which primarily addresses the act of polluting and it is defined in the 1992 Helsinki Convention as the “introduction by man, directly or indirectly, of substances or energy into the sea, including estuaries, which are liable to create hazards to human health, to harm living resources and marine ecosystems, to cause hindrance to legitimate uses of the sea including fishing, to impair the quality for use of sea water, and to lead to a reduction of amenities.”

The Baltic Sea has been exposed to an extensive use of chemicals from the very beginning of the industrialization of the region in the late 19<sup>th</sup> century and its marine environment has one of the longest histories of contamination in the world. Consequently, the Baltic has often been referred to as the most polluted sea in the world.

Natural characteristics of the Baltic Sea, namely, a long water residence time of around 30 years, a

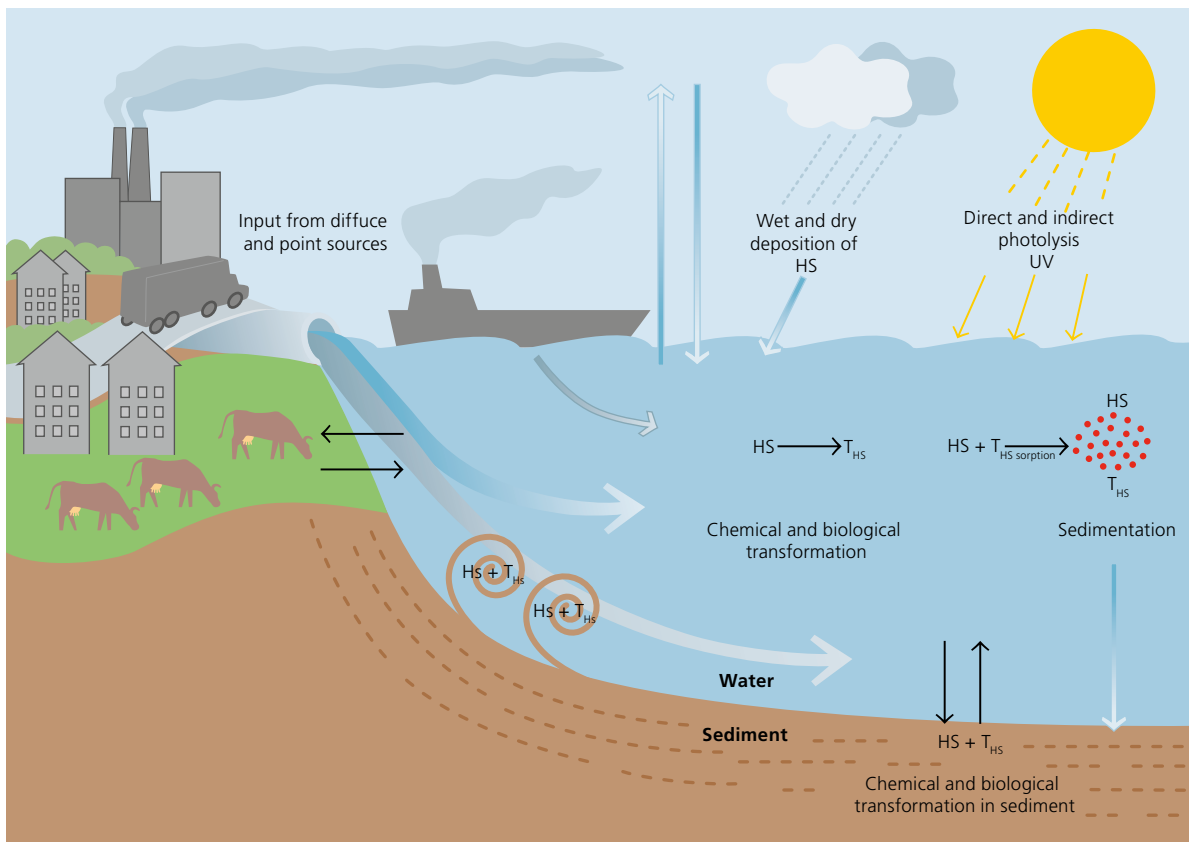
large catchment area with a population of about 85 million people and a brackish-water environment poor in species predispose the marine environment of the Baltic Sea to contamination and harmful effects caused by hazardous substances. Conditions in the different sub-regions of the Baltic Sea (**Fig. 1.1**) vary in terms of the salinity, flora and fauna, and characteristics of the seabed.

Many legal instruments have been created and applied to curb intentional pollution and to limit unintentional discharges since the increase in the awareness of the public to the environmental effects and risks of hazardous substances to human health in the 1960s.

From the very beginning, the purpose of the 1974 Convention on the Protection of the Marine Environment of the Baltic Sea (Helsinki Convention) was to prevent and abate pollution to protect and enhance the status of the marine environment. The HELCOM strategy with regard to hazardous substances has set out the objective to reduce discharges, emissions and losses of hazardous substances towards the target of their cessation by 2020, with the ultimate aim of achieving concentrations in the environment near background values for naturally occurring substances and close to zero concentrations for man-made synthetic substances (HELCOM Recommendation 19/5). Specific HELCOM recommendations along with measures based on other international agreements and, more recently, EU legislation have resulted in a significant reduction in the loading of some hazardous substances. The HELCOM Baltic Sea Action Plan, adopted in 2007, set a strategic goal related to hazardous substances which is “a Baltic Sea with life undisturbed by hazardous substances”, and identified a set of Ecological Objectives which correspond to good environmental status: “Concentrations of hazardous substances close to natural levels”, “All fish safe to eat”, “Healthy wildlife” and “Radioactivity at pre-Chernobyl levels”.

Monitoring of the marine environment and of the inputs and concentrations of hazardous substances in the Baltic Sea has been part of the activities of Helsinki Commission (HELCOM) since the late 1970s. HELCOM adopted a Monitoring and Assessment Strategy in 2005 defining indicators, thematic assessments and holistic assessments as key components of the strategy. This thematic report has been produced following that strategy.





**Figure 1.2** Conceptual model of the sources of pollution inputs to the Baltic Sea marine environment and the fate of hazardous substances (HSs) and their transformation products (T<sub>HS</sub>) (based on Dahllöf & Andersen (2009)).

to originate outside the Baltic Sea catchment area (Bartnicki et al. 2008).

In this assessment, the sources of hazardous substances are presented in substance-specific sections of **Chapter 2.2** and discussed in further detail in **Chapter 3**.

### 1.3 Objectives, scope and the basis of this assessment

This integrated thematic assessment of hazardous substances provides an overview of the status of hazardous substances in the Baltic Sea using an indicator-based assessment tool. It also provides information on the temporal development of contamination and data on the inputs and biological effects of hazardous substances.

This HELCOM integrated thematic assessment of hazardous substances is the first comprehensive attempt to compile the most recent data on hazardous substances in the Baltic Sea and to integrate

the data using an assessment tool. Assessments of hazardous substances in the Baltic Sea area have previously concentrated on specific substance groups, such as pesticides (HELCOM 2001), dioxins (HELCOM 2004b), heavy metals (HELCOM 2007b) and radionuclides (HELCOM 2009d), or have been conducted for a specific area. This assessment covers all hazardous substances for which sufficient quantities of data are available covering the Baltic Sea area. In addition, radionuclides are included in the integrated assessment as a separate component.

This HELCOM assessment on hazardous substances covers the entire Baltic Sea marine area with its sub-basins, including the Kattegat (**Fig. 1.1**). Data used in the assessment originate from national monitoring activities some of which are carried out to implement the HELCOM COMBINE monitoring programme<sup>1</sup>. In addition, separate assessment reports, HELCOM indicator fact sheets<sup>2</sup> and data from individual research

<sup>1</sup> [http://www.helcom.fi/groups/monas/CombineManual/en\\_GB/main/](http://www.helcom.fi/groups/monas/CombineManual/en_GB/main/)

<sup>2</sup> [http://www.helcom.fi/environment2/ifs/en\\_GB/cover/](http://www.helcom.fi/environment2/ifs/en_GB/cover/)

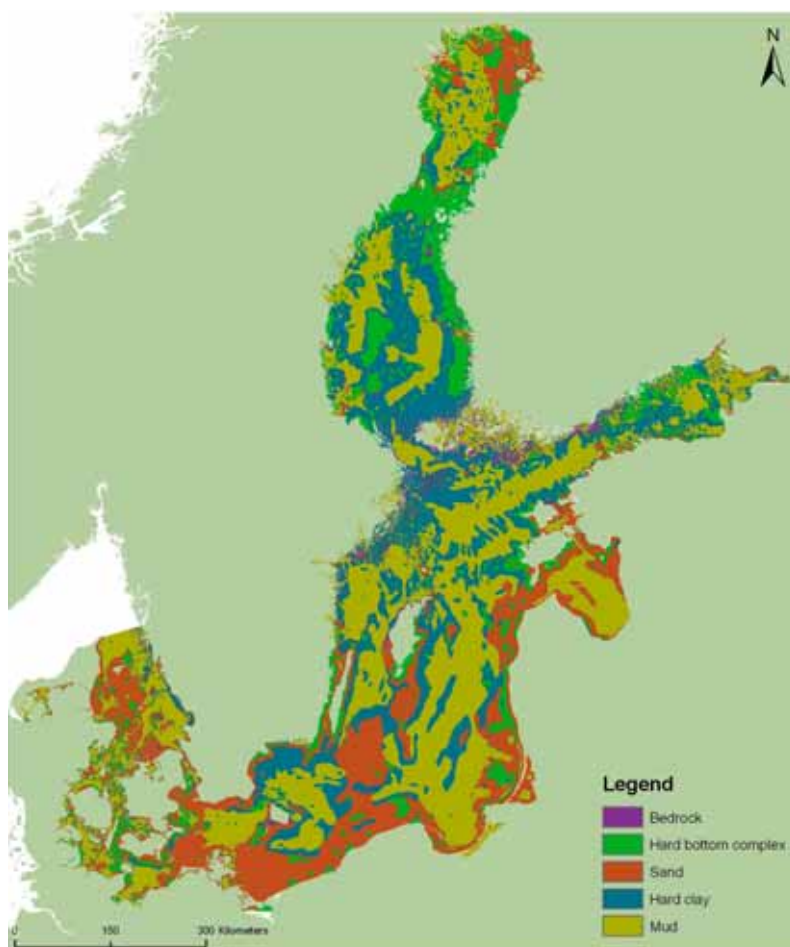
projects have been compiled into a single quantitative assessment. Measurements are primarily conducted on biota and only secondarily on surface sediments or water, because biota may describe more reliably the state of the environment. The concentrations in sediment depend on the sediment type; for example, the southern and southeastern Baltic seabed is predominantly sandy, whereas many other areas have high organic content in the sediment (**Fig. 1.3**) and thus a larger capacity to accumulate hazardous substances.

The assessment period covered is 1999–2007, with some data from 2008, and all status assessments are based on data from that time period. The time period precedes the implementation of the HELCOM Baltic Sea Action Plan (BSAP) and provides an overview of the status of the marine environment before the actions of the BSAP took

effect. In addition, long-term temporal trends are presented from varying periods of time.

This assessment also employs existing quality standards and other threshold criteria to assess whether the concentrations of hazardous substances in the marine environment and biological effects are at an acceptable or unacceptable level. A hazardous substances assessment tool CHASE has been used to integrate the status of contamination by individual chemicals and biological effects at specific sites or areas into a single status value termed the “contamination ratio”. Ultimately, the use of this integrative tool is the first step towards providing a complete overview of the status of contamination by hazardous substances and their biological effects in the Baltic Sea. The synthesis chapter links this status to existing information on the inputs and also to current international agreements and legislation for the regulation of the use and discharge of hazardous substances; it also provides recommendations for policy development and the monitoring of hazardous substances.

This assessment has linkages to the EU Marine Strategy Framework Directive (MSFD, Anon. 2008a), as hazardous substances are addressed by Annexes I and III of the Directive and they need to be evaluated in the initial assessments required by Article 8 of the Directive. This assessment will assist HELCOM EU Member Countries to implement the Directive by providing coherent Baltic-wide information on the current inputs to and status of the Baltic Sea in relation to hazardous substances. The assessment also has linkages to the EU Water Framework Directive (WFD, Anon. 2000a) and information on the comparability of the assessment approaches of the WFD with the approaches used in this assessment is provided in Annex 2.



**Figure 1.3** Composition of Baltic Sea bottom sediments (Al-Hamdani & Reker 2007).

# 2 STATUS AND TRENDS OF HAZARDOUS SUBSTANCES

The status of hazardous substances refers to the concentrations of various hazardous substances or their biological effects in the marine environment during the assessment period 1999–2007. Concentrations are data mainly from measurements in biota or sediments, and occasionally in water. Temporal trends have been presented in order to describe the change of the concentrations or biological effects over time.

**Chapter 2.1** describes the integrated status of hazardous substances in the marine environment as assessed with the CHASE assessment tool, **Chapter 2.2** presents the status and trends of individual substances and **Chapter 2.3** explains the biological effects that have been found.

## 2.1 Integrated assessment and classification of “hazardous substances status”

### 2.1.1 Methods of the integrated assessment

The hazardous substances status has been assessed and classified at 144 sites in the Baltic Sea using the HELCOM Hazardous Substances Status Assessment Tool (CHASE), which is a multi-metric indicator-based tool developed for the HELCOM integrated thematic assessment of hazardous substances in the Baltic Sea. The CHASE tool produces an integrated assessment and classification of “hazardous substances status”, which is advantageous for use in setting a baseline for the implementation of the HELCOM Baltic Sea Action Plan (HELCOM 2007a) and, in particular, for the science-based evaluation of whether the overall goal of “a Baltic Sea with life undisturbed by hazardous substances” has been achieved.

This integrated CHASE assessment of hazardous substances in the Baltic Sea is based on quality-assured monitoring data (1999–2007) on various chemicals, the radionuclide cesium-137 and certain indicators of biological effects. These data are considered in relation to the four ecological objectives in the hazardous substances segment of the HELCOM Baltic Sea Action Plan reflecting the HELCOM strategic goal for hazardous substances (**Table 2.1**).

**Table 2.1** HELCOM’s strategic goal and ecological objectives for hazardous substances (HELCOM 2007a).

Strategic goal for hazardous substances	Ecological objectives
Baltic Sea with life undisturbed by hazardous substances	Concentrations of hazardous substances close to natural levels
	All fish safe to eat
	Healthy wildlife
	Radioactivity (radionuclides) at pre-Chernobyl level

The quantification of the “hazardous substances status” is based on a Contamination Ratio (CR), which is the ratio of the current status (measurement of the concentration of a substance or biological effect) and a threshold level or quality criterion, which is used as an approximation for an environmental target for that particular substance or biological effect. The CRs of all substances or indicators within an ecological objective are integrated to yield a status classification (“high”, “good”, “moderate”, “poor” or “bad”) of that particular ecological objective. The ecological objective receiving the lowest status classification serves as the overall classification of the assessed site or area, giving the classification of the “hazardous substances status” of that site or area according to one of five classes. “High” and “good” classes indicate that areas are not disturbed by hazardous substances, while “moderate”, “poor” and “bad” indicate different degrees of disturbance by hazardous substances. See Annex 1 for a more detailed explanation of the assessment methodology.

The threshold levels used in CHASE were obtained from national legislation, international agreements or EU directives (e.g., EC Environmental Quality Standards [(Anon. 2008b)] and OSPAR Environmental Assessment Criteria [OSPAR 1997, 2004b, 2009a, 2009b]) because at the present time there are no thresholds specific to the Baltic Sea. The use of national or international threshold levels ensures compatibility with national legislation and implementation of the European Union directives. However, owing to the somewhat different composition of the species and their distribution in the Baltic Sea, some different threshold levels have been used partly based on the use of different organisms sampled for measuring the concentrations of substances. The distribution of the organisms sampled does not always cover the whole Baltic Sea or there may be other reasons for varying organisms. In addition, concentrations have been normalized to wet and dry weights, as well as lipid

weights. These differences may affect the comparison of these assessment results to those of different countries.

When interpreting the CHASE results, it is important to keep in mind that the status classifications for the different assessment units may be affected by different combinations and numbers of substances monitored and that this may affect the comparability among the assessment units. More information on the CHASE integrated assessment method is included in Annex 1.

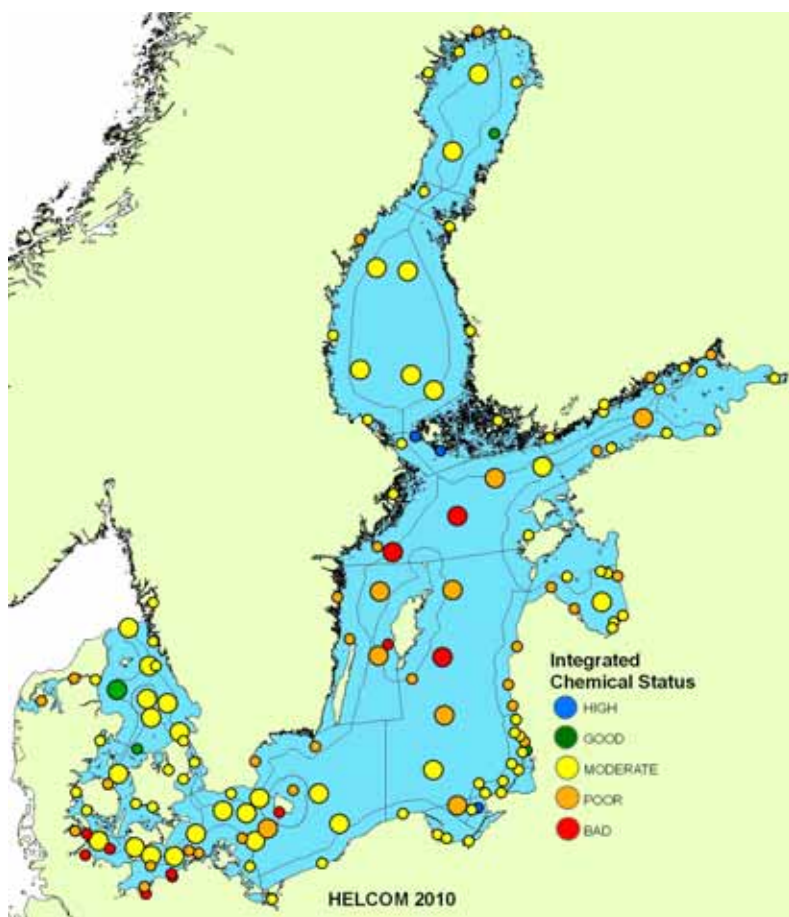
The classification results of the integrated CHASE assessments do not always give assessment results which are equivalent to the assessment results of chemical status made according to the EU Water Framework Directive (Anon. 2000a). This is due to differences in, e.g., the selection of substances, the assessment method used, and the areas assessed. See Annex 2 for further details on the relationship between the assessment approaches of the WFD and CHASE.

Altogether, 144 assessment units were analysed using CHASE: 40 of the assessment units were open-sea areas and 104 were coastal sites or areas.

### 2.1.2 Results of the integrated assessment

All open-sea areas of the Baltic Sea were classified as “disturbed by hazardous substances” and received a status classification of “moderate”, “poor” or “bad” (Fig. 2.1). The only exception was the northwestern Kattegat, which received a status classification of “good”. Open waters in the Northern Baltic Proper, Western and Eastern Gotland Basins, the Gulf of Finland and the Gulf of Gdansk received the lowest status classifications (bad or poor), while the open-sea areas in the Gulfs of Bothnia and Riga, Arkona and Bornholm Basins, and Danish open waters were mainly classified as being in moderate status.

Only six of the 104 coastal assessment units were classified as “areas not disturbed by hazardous substances” and received a status classification of good or high (Fig. 2.1). The status of coastal assessment units varied from high to bad without particular consistency. The coastal areas that received the highest status classifications were located in the Åland Islands area, in the Kaliningrad coastal area, on the Lithuanian coast, in the Kattegat and on the Finnish side of the Bothnian Bay. There was some tendency for the assessment units with the poorest status to be located either near big cities or ports (Tallinn, Klaipeda) or to be estuarine areas (Ruotsinpyhtää in the Gulf of Finland), Kvädöfjärden in the Western Gotland Basin) or coastal sites (the Kiel Bay area). The waters near large coastal cities were generally classified as having a “moderate” hazardous substances status (e.g., St. Petersburg, Helsinki, Stockholm, Riga, Gdansk and Copenhagen).

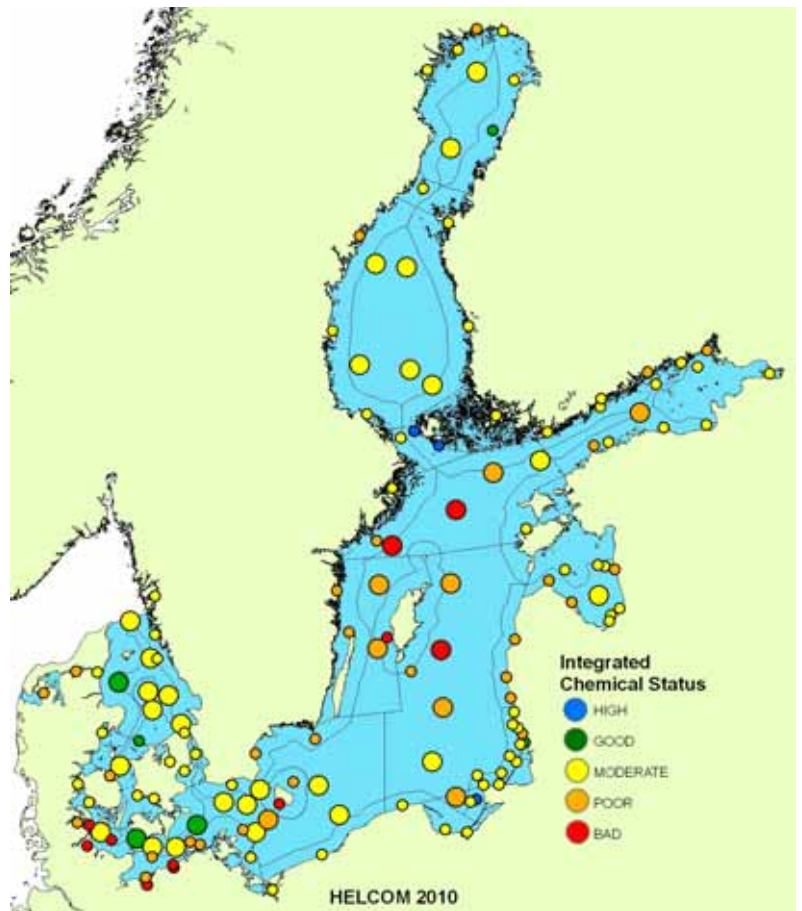


**Figure 2.1** Integrated classification of the hazardous substances status in the 144 assessment units. Blue = high status, green = good, yellow = moderate, orange = poor, and red = bad status. High and good status are equivalent to “areas not disturbed by hazardous substances”, while moderate, poor, and bad status are equivalent to “areas disturbed by hazardous substances”. Large dots represent assessment units of the open basins; small dots represent coastal assessment units which are mainly located in the territorial waters delimited by the grey line. Other grey lines represent the divisions between the sub-basins (cf. Fig. 1.1). Ecological objectives that were assessed using CHASE included all HELCOM objectives: “Concentrations of hazardous substances close to natural levels”, “All fish safe to eat”, “Healthy wildlife” and “Radioactivity at pre-Chernobyl levels”. See Annexes 1 and 2 for details.

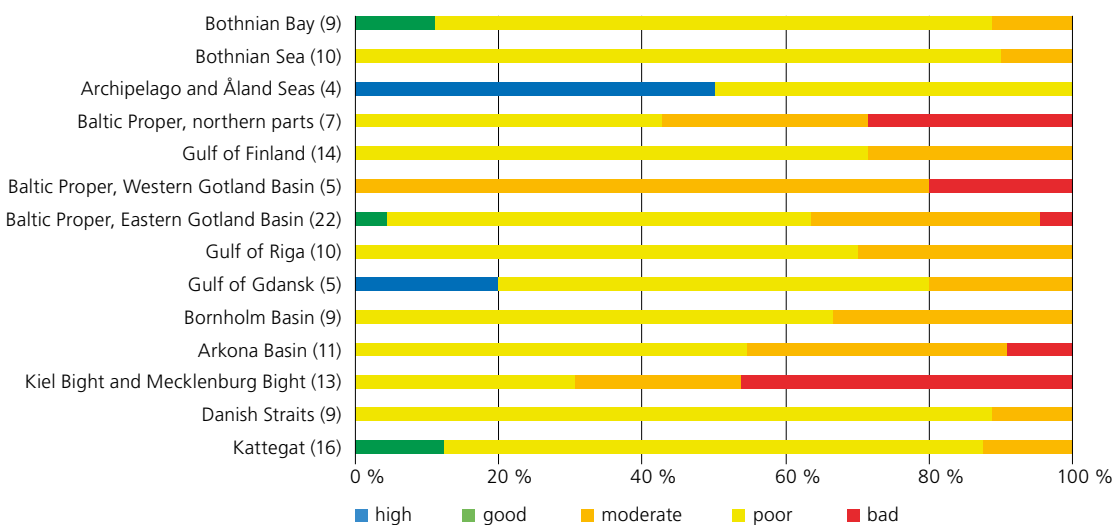
Elevated levels of radionuclides were found in the northern, eastern and central parts of the Baltic Sea, while the levels were close to pre-Chernobyl levels in the southwestern parts of the Baltic Sea. These elevated levels did not, however, affect the final status classification in those areas, as shown on the map (Fig. 2.2) with the results of the CHASE assessment carried out excluding the radionuclides. Only in two assessment units (open-sea areas “Kiel Bight East” and “Southwest Arkona Basin”) was the final classification caused by elevated levels of radionuclides (Fig. 2.2).

Although most parts of the Baltic Sea were classified as “disturbed by hazardous substances”, there were differences in the classifications between various parts of the Baltic Sea (Fig. 2.3). Generally, undisturbed areas were found at wave-exposed sites such as the Åland Archipelago and the coastal waters off Kaliningrad. The northern parts of the Baltic Proper, Western Gotland Basin as well as the Kiel Bight and Mecklenburg Bight were areas with a poorer status.

The ecological objectives that most often determined the final classification were “Concentrations close to natural levels” (in 63% of the 144 assessment units), “All fish safe to eat” (3%), “Radioactivity at pre-Chernobyl levels” (2%) and “Healthy wildlife” (1%). Altogether, for 24% of the assessment units, the final classification was determined by two different elements and for 9% of the units by three elements.



**Figure 2.2** Status classifications carried out excluding radionuclides. Only in the open-sea areas “Kiel Bight East” and “Southwest Arkona Basin” was the final classification caused by elevated levels of radionuclides. For other information, see Fig. 2.1.



**Figure 2.3** Integrated classification of “hazardous substances status” in the 14 Baltic Sea basins, with the number of assessment units indicated for each basin. Blue = high status, green = good, yellow = moderate, orange = poor, and red = bad status.



An important question is “Which substances are decisive in determining the status in the integrated classification?” PCBs, lead, mercury, cesium-137, DDT/DDE, TBT, benz[a]anthracene and cadmium were the substances most commonly observed with the highest Contamination Ratios (CR, i.e., having the highest concentrations in relation to target levels) in the assessment units classified as “moderate”, “poor” or “bad” (Table 2.1). PCBs were among the substances with the highest CRs in 20% of the units, and lead, mercury, cesium-137, TBT and DDT/DDE in 9% and cadmium in 7% of the units (Table 2.1). All common groups of hazardous substances—PCBs, dioxins, heavy metals, organometals, alkylphenols, phthalates, brominated substances, polycyclic aromatic hydrocarbons (PAHs), DDTs and chlorinated pesticides as well as the radionuclide cesium-137—were found among the substances with the highest CRs (Table 2.1).

The data in the integrated assessment were primarily from biota and only secondarily from sediment or water. Therefore, the above-mentioned decisive substances were mainly found in fish, mussels and birds and only secondarily in sediment or water samples. Data from water were only reported from eight offshore assessment units and nine coastal assessment units. There was no site where the assessment was based solely on indicators in the water phase.

Cesium-137 did not affect the final classification of the assessment units, except in two areas (cf. Figs. 2.1 and 2.2), although the substance was found in high concentrations and even with the highest CRs

in twelve assessment units (Table 2.1). The reason for this is that the indicators under each ecological objective assessed in CHASE are integrated using a method that takes into account the number of indicators in addition to the CRs (see Annex 1). Cesium-137 was always the single indicator under the ecological objective “Radioactivity at pre-Chernobyl levels”, while the other ecological objectives and especially “Concentrations close to natural levels” were always assessed with a number of indicators.

A great variety of different substances exceeded the threshold levels in the different Baltic Sea sub-basins (Table 2.2). Substances that were found to exceed threshold levels in nearly all sub-basins

**Table 2.1 Observations of hazardous substances with the highest concentrations in relation to the target level (i.e., the highest Contamination Ratio, CR) in the 137 assessment units classified as “areas disturbed by hazardous substances”. See the glossary for the abbreviations.**

	Substances with the highest CRs in 137 assessment units, number of observations	
		%
PCBs	27	20
Lead	13	9
Mercury	13	9
<sup>137</sup> Cesium	12	9
DDT/DDE	3/9	9
Tributyltin	11	8
Benz[a]anthracene	9	7
Cadmium	7	5
Dioxins/DL-PCBs	4	3
Nonylphenol	4	3
Zinc	4	3
VDSI-index	3	2
Arsenic	2	1
DEHP	2	1
HCHs	2	1
Nickel	2	1
Octylphenol	2	1
PBDE	2	1
Anthracene	1	1
Benzo[ghi]perylene	1	1
Benzo[k]fluoranthene	1	1
Copper	1	1
Fluorene	1	1
PAH-metabolites	1	1
<b>Total</b>	<b>137</b>	<b>100</b>



included PCBs, DDT/DDE, cadmium, lead, TBT and cesium-137. Mercury exceeded the threshold levels particularly in the central and northern basins,

while nonylphenol was only mentioned for the Belt Sea and Kattegat.

**Table 2.2** Distribution of the substances with the highest concentrations in relation to target levels (i.e., the highest Contamination Ratio, CR) in the 137 assessment units classified as “areas disturbed by hazardous substances” in the different sub-basins of the Baltic Sea. Numbers in parentheses indicate the number of times the substance was found having the highest CR in the assessment units of the basin. See the glossary for the abbreviations.

Baltic Sea sub-basin	Substances
Bothnian Bay	Cadmium, cesium-137 (3), BDE, DDE, DEHP and PCB
Bothnian Sea	Cadmium, cesium-137, DDE (2), dioxins (2), HCHs, lead and mercury (2)
Åland Sea and Archipelago Sea	Cesium-137 and PCB
Northern Baltic Proper	BDE*, cadmium, DDE*, lead, octylphenol, PCB (2) and TBT
Gulf of Finland	Cadmium, cesium-137, copper, DDT, lead, mercury (6), TBT and zinc (2)
Gulf of Riga	DDT (2), lead (4), PCB (3) and zinc
Eastern Baltic Proper	Anthracene, benz[a]anthracene (8), benzo[k]fluoranthene (1), cesium-137 (2), DDE (2), dioxins, mercury (3) and TBT (3)
Western Gotland Basin	DDE, dioxins, nickel and PCB (2)
Gulf of Gdansk	Benz[a]anthracene, cesium-137, mercury and PCB
Bornholm Basin	Cadmium, cesium-137, DDE (2), lead, PCB (2), TBT and zinc
Arkona Basin	Benzo[g,h,i]perylene, cadmium (2), cesium-137, DDE, lead (2), mercury, PCB (3) and TBT
Mecklenburg and Kiel Bight	Cesium-137, HCHs, lead (3), PAH-metabolites and PCB (7)
Belt Sea and the Sound	Arsenic, DEHP, nonylphenol (3), PCB (2), VDSI and TBT
Kattegat	Arsenic, BDE, fluorene, nickel, nonylphenol, octylphenol, PCB (3), TBT (3) and VDSI (2)

\*<sup>1</sup>) The substances had equal weight at the site.



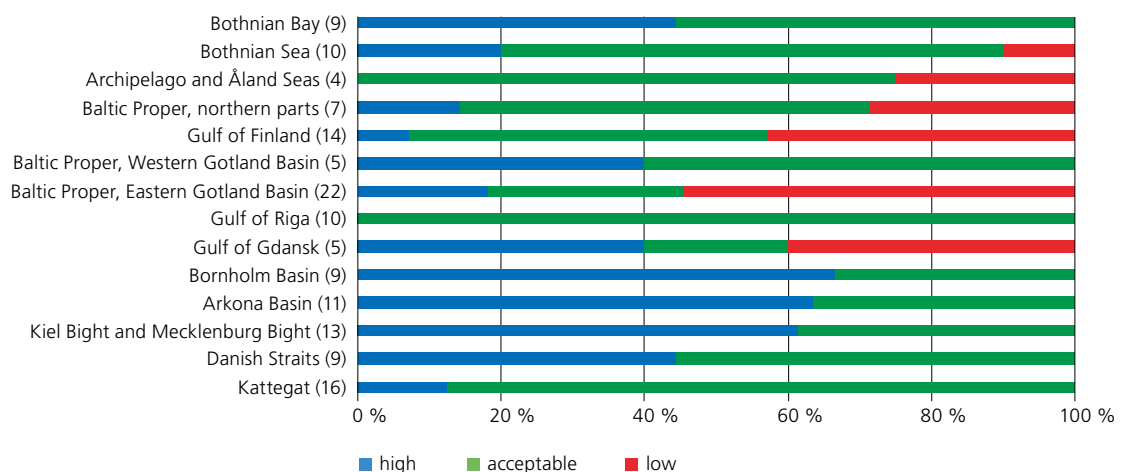
### 2.1.3 Confidence assessment of CHASE results

The accuracy of the CHASE classifications is generally considered to be good using the CHASE confidence assessment (Fig. 2.4). Altogether, the results for 119 of the 144 “assessment units” were of a high or acceptable confidence, while the remaining 25 were of a low accuracy. A spatial presentation of the confidence assessment is given in Annex 3.

In addition to the quality rating of threshold levels and data, the small number of indicators in assessment sites reduced the confidence of the CHASE classifications. It must be borne in mind that the small number of indicators or a lack of essential indicators in CHASE may lead, by pure chance, to an erroneous status of “undisturbed by hazardous substances”. In this assessment, this limitation of the assessment methodology has been avoided by manually ensuring that all six sites with good or high status had relevant indicators. This ensures that the assessment does not result in any classification of false positive status, but it does not guarantee that the assessment units would not be classified with a poorer status (i.e., poor or bad). Complete avoidance of this limitation would require a pre-defined set of substances and threshold levels in all assessment units. The detailed methods of the confidence classification are described in Annex 1.

## 2.2 Status and trends of individual hazardous substances or substance groups

A number of the substances included in the CHASE assessment that had a good geographical coverage of data for the assessment period 1999–2007 were further analysed. Information on their status and trends, uses, biological or health effects, sources and regulation is presented in this chapter. Measurements of current concentrations were related to threshold values that are either commonly agreed quality criteria or proposed levels below which toxic effects are not found in the environment. Three status classes (“good”, “moderate” and “bad”) were derived. The boundary between “good” and “moderate” status for most of the substances was the same threshold level as was used in CHASE. For brominated substances and some PCB measurements, a different threshold was used. Varying principles were used for setting the threshold between “moderate” and “bad”; however, the deviation from the “good”/“moderate” boundary was in all cases set high, at least three times the value of that boundary. In addition, long-term trends were analysed to present the temporal development of the concentrations of these substances in the marine environment.



**Figure 2.4** Provisional confidence assessment of the 144 CHASE classifications (blue = high confidence, green = acceptable confidence and red = low confidence). The principles and details are described in Annexes 1 and 3.

### 2.2.1 Status and trends of dioxins and dioxin-like compounds

Dioxins are persistent organic pollutants (POPs) that can cause severe, long-term impacts on wildlife, ecosystems and human health. The name “dioxin” refers to polychlorinated dibenzo-*p*-dioxin (PCDD) and dibenzofuran (PCDF) compounds. PCDDs and PCDFs consist of 210 congeners with one to eight chlorines, of which 17 are considered to be of toxicological importance. Some polychlorinated biphenyls (PCBs) are called dioxin-like PCBs (DL-PCBs) because they have a structure very similar to that of dioxins and have dioxin-like effects. PCDD/Fs were never produced intentionally, but they are minor impurities in several chlorinated chemicals (e.g., PCBs, chlorophenols, hexachlorophene, etc.), and are formed in several industrial processes and from most combustion processes, such as municipal waste incineration and small-scale burning under poorly controlled conditions. Formerly, pulp bleaching using chlorine gas was an important source of PCDD/Fs.

The most toxic dioxin, 2,3,7,8-TCDD, is one of the most-studied chemicals, and is used as a reference for all other related chemicals. Most of its effects are explained by its binding to the so-called dioxin receptor (AH receptor). This activated protein regulates the expression of several genes. The most relevant toxic effects of PCDD/Fs and DL-PCBs are developmental toxicity, carcinogenicity and immunotoxicity. These effects have been observed in Baltic Sea birds and mammals, as discussed in more detail in **Chapter 2.3**, although the causality of the effects of PCDD/Fs is still unclear in science.

#### Sources and deposition to the Baltic Sea

Several studies indicate that atmospheric deposition is currently the most important active source of inputs of PCDD/Fs to the Baltic Sea (SEPA, 2009a). The actual sources emitting the substances to the air which ultimately results in their deposition to the Baltic Sea, however, are not fully known. There are indications of a strong impact of long-range atmospheric transport from southwestern and southern Europe. There are also uncertainties concerning the contribution of historical emissions and secondary sources to the present status and the mechanism of PCDD/Fs accumulation in the food chain.



Gusev et al. (2007) have used data from European Monitoring and Evaluation Programme (EMEP) to illustrate the European distribution of dioxin emissions and distribution of atmospheric levels. The results show that Sweden, Norway, Finland and Iceland had the lowest average atmospheric concentrations of all EU countries in 2004. The highest level of net PCDD/F deposition flux was estimated in the southern regions of the Baltic Sea ( $0.47 \text{ ng TEQ m}^{-2} \text{ y}^{-1}$  in the Belt Sea), with the lowest level over the Gulf of Bothnia ( $0.06 \text{ ng TEQ m}^{-2} \text{ y}^{-1}$ ) (Gusev 2009b). This is consistent with the concentrations measured in the air (Sellström et al. 2009) and clearly indicates that the present atmospheric deposition is far lower in the northern regions. The deposition pattern is consistent with modelled data presented by Sundqvist et al. (2009a), who showed that atmospheric deposition is a major source for PCDD/Fs in offshore sediments of the Baltic Sea.

Modelling studies indicate that the net annual deposition of dioxins to the Baltic Sea decreased about 60% from 1990 to 2007 (Gusev 2009b).

#### Temporal and spatial trends in sediments

There are few historical sediment data (profiles) from the Baltic Sea and some data are from the late 1980s and thus unable to reveal very recent trends. All the cores, however, show a decline in surface PCDD/F concentrations compared with deeper sediments, with the highest concentrations generally dated back to the 1970s or 1960s in the northern basins, the Baltic Proper and the Kattegat – Danish straits.

Sediment surveys have revealed some major sediment contamination with dioxins in the River Kymi-joki estuary, Finland (Isosaari et al. 2002, Verta et al. 2007) and a more local contamination on the Swedish coast of the Gulf of Bothnia (Sundqvist et al. 2009b) originating from local industrial sources. Recent results from the Gulf of Gdansk do not indicate any major present dioxin pollution from the Polish territory (Niemiryzc 2008). Major data gaps are currently for the southeastern and eastern coastal regions of the Baltic Proper and the southern Gulf of Finland. According to sediment monitoring data, the dioxin-like chlorinated biphenyl, CB-118, is below the threshold level of  $0.6 \mu\text{g kg}^{-1}$  dw (OSPAR 2009a) at all sediment monitoring sites except the Åland Sea (Fig. 2.5).

#### Chlorinated biphenyl, CB-118

Surface sediments (dw)

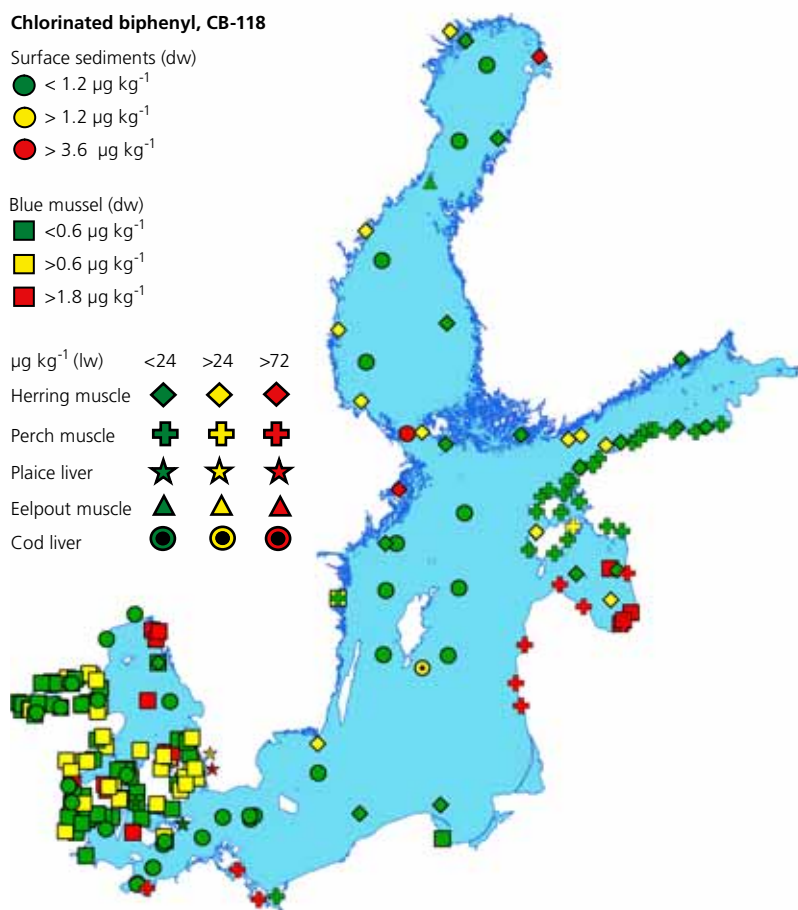
- $< 1.2 \mu\text{g kg}^{-1}$
- $> 1.2 \mu\text{g kg}^{-1}$
- $> 3.6 \mu\text{g kg}^{-1}$

Blue mussel (dw)

- $< 0.6 \mu\text{g kg}^{-1}$
- $> 0.6 \mu\text{g kg}^{-1}$
- $> 1.8 \mu\text{g kg}^{-1}$

$\mu\text{g kg}^{-1}$  (lw)

- |                | <24 | >24 | >72 |
|----------------|-----|-----|-----|
| Herring muscle | ◆   | ◆   | ◆   |
| Perch muscle   | +   | +   | +   |
| Plaice liver   | ★   | ★   | ★   |
| Eelpout muscle | ▲   | ▲   | ▲   |
| Cod liver      | ●   | ●   | ●   |



**Figure 2.5** Overall status of concentrations of the dioxin-like PCB congener CB-118 in surface sediments, blue mussels and fish. The thresholds levels of  $1.2 \mu\text{g kg}^{-1}$  dw and  $0.6 \mu\text{g kg}^{-1}$  dw for sediment and mussel, respectively, have been assessed according to the OSPAR Environmental Assessment Criteria (EACs, OSPAR 2009a). The fish criteria are EACs proposed by OSPAR (OSPAR 2009b). The red colour represents a status of high concern, which is three times the threshold level. (dw = dry weight; lw = lipid weight)

#### Spatial and temporal trends in biota

Numerous recent papers have shown differences in PCDD/F and DL-PCB concentrations in Baltic herring, sprat and salmon between the Baltic Sea basins (e.g., SCALE 2004, Lizak et al. 2007). Higher concentrations have been detected in the northern basins where dioxin and DL-PCB levels in herring exceed established maximum limit concentrations for human consumption (Fig. 2.6). Regional variation within a sub-basin has been found in the Swedish coastal region of the Bothnian Sea (Olsson et al. 2003, Bignert et al. 2006a, 2007). Since the atmospheric deposition pattern (lowest in the north) is different from concentrations in fish (generally highest in the north), other factors or sources are thus likely to be involved in determining concentrations in fish. The reasons remain unclear, but higher historical PCDD/F discharges from point sources in the northern basins have been suggested.

In general, the contribution from the DL-PCBs in total toxic equivalents (TEQ) is substantial and seems to increase the further south in the Baltic region the samples are collected (SCALE 2004). The two southeastern exceedances of threshold levels (yellow circles in Fig. 2.6) are due to DL-PCBs. Concentrations of one dioxin-like congener (CB-118) measured in different fish species (perch, herring, cod, eelpout and plaice) and blue mussels in the Baltic Sea were high compared to the ecotoxicological threshold level (Fig. 2.5). Particularly high concentrations were found in blue mussels in the Gulf of Riga and the southwestern Baltic Sea and in perch in the eastern and southern areas. Herring and plaice also had high concentrations of CB-118 at individual sites in the Bothnian Bay, the Northern Baltic Proper and the Sound (Fig. 2.5).

There is not much information about past or recent trends in PCDD/F concentrations in different fish species and generally the data do not cover past decades. The Swedish Museum of Natural History (NRM 2009) reported dioxin concentrations in the muscle of small herring collected from 1990 to 2005 at three stations on the Swedish coast that showed no indications of change during that period, but the guillemot egg data<sup>3</sup> showed a major and significant

<sup>3</sup> Common guillemot (*Uria aalge*) is a fish-feeding colony bird. One of the few colonies in the Baltic Sea breeds on the island Stora Karlsö, west of Gotland. The Swedish Museum of Natural History conducts annual monitoring of hazardous substances in guillemot eggs.

decrease since 1970 (Fig. 2.7). Szlinder-Richert et al. (2009) did not observe any decreasing trend of PCDD/F or DL-PCB from the southern Baltic Sea during 2002–2006; however, taking into account an earlier study (Karl and Ruoff 2007), they concluded that a decrease from 1999 may have occurred. Thus, a levelling of the concentrations in fish is obvious but it depends on the time scale studied and may differ in different regions.

### Human health effects and temporal trends

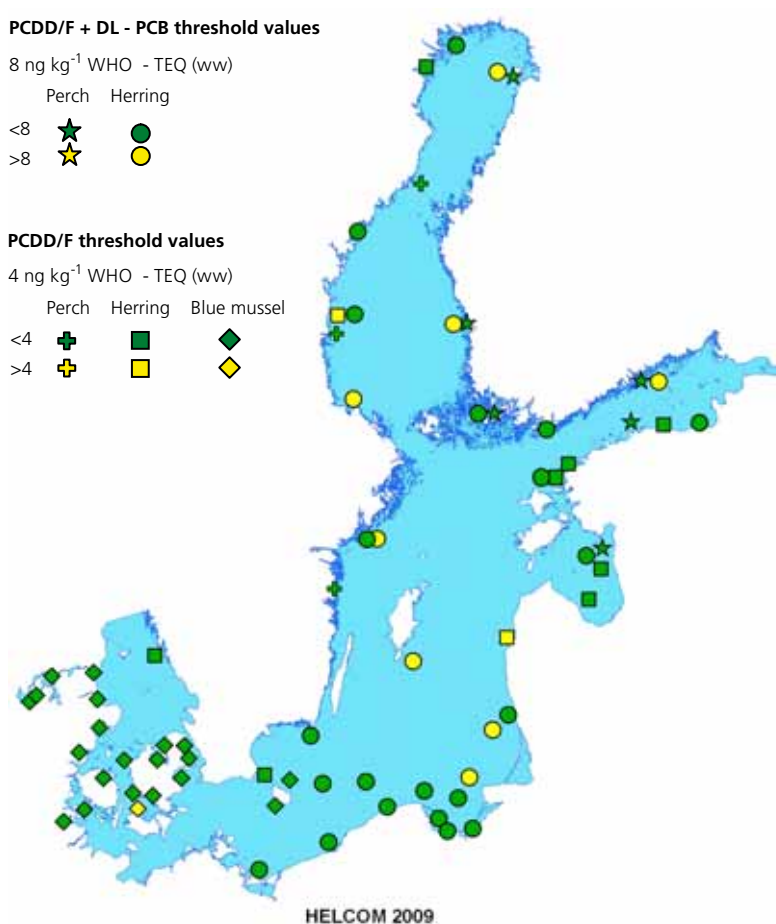
The possible health effects of PCDD/Fs and DL-PCBs are still under debate and more data and material are needed for exposure assessments. Human exposure to PCDD/Fs and DL-PCBs generally reflects the trends in the environment, although other factors may also be involved. For example, concentrations of PCDD/Fs and DL-PCBs in breast milk from women in Sweden and in Finland have decreased more rapidly than levels in fish, from a level of 100 ng kg<sup>-1</sup> to 10 ng kg<sup>-1</sup> TEQ in fat within 30–35 years (Norén and Meironyté 2000, Kiviranta 2005). This indicates the contribution from dietary changes of young women, which may partly explain the more rapidly decreasing trend of PCDD/F and DL-PCB concentrations in humans. The most relevant health impact seems to be developmental effects in children. Exposure can take place both during pregnancy and during breastfeeding. There is fairly good evidence that a real risk of several developmental effects existed during the peak periods of dioxin and PCB concentrations, i.e., until late 1980s (SCALE 2004). However, it is much less clear whether there is still a risk of those effects.

Finnish and Swedish fishermen have been observed to have higher dioxin levels than the rest of the population. Nevertheless, they also have a significantly lower coronary heart disease-related mortality rate, which is considered to be due to the positive health effects of higher fish consumption (Svensson et al. 1995, Turunen et al. 2008).

### Measures and actions

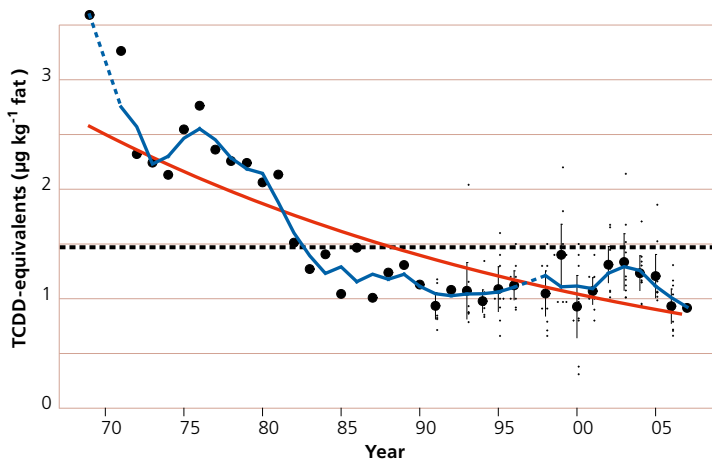
Under the Stockholm Convention, releases of unintentionally produced by-products listed in Annex C<sup>4</sup> (dioxins, furans, PCBs and HCB) are subject to continuous minimization with the

ultimate goal of elimination where feasible. The main tool for this is a National Action Plan which should cover the source inventories and release estimates as well as plans for release reductions. At the EU level, a Strategy for dioxins and PCBs was adopted in 2001. The Strategy includes actions in the area of feed and food contamination and actions related to the environment, including release reduction. Over the past decade, important legislation has been adopted to reduce the emissions of PCDD/Fs, in particular in the areas of waste incineration and integrated pollution prevention and control. Releases of POPs, including dioxins, from industrial installations are mainly regulated by the IPPC Directive (Anon. 2008c) and the Waste Incineration Directive



**Figure 2.6** Status of concentrations PCDD/Fs and dioxin-like PCBs in a low-fat fish, perch (*Perca fluviatilis*), and a fat-rich fish species, herring (*Clupea harengus*), and in blue mussel (*Mytilus edulis*) in relation to threshold levels for human consumption. The higher level (8 ng kg<sup>-1</sup> WHO-TEQ ww) refers to the sum of PCDD/Fs and DL-PCBs, whereas the lower level (4 ng kg<sup>-1</sup> WHO-TEQ ww) refers to PCDD/Fs alone. (ww = wet weight)

<sup>4</sup> Annex C in the Stockholm Convention concerns unintentional production ([http://www.pops.int/documents/convtext/convtext\\_en.pdf](http://www.pops.int/documents/convtext/convtext_en.pdf)).



**Figure 2.7** Temporal trends of TCDD-equivalents ( $\mu\text{g kg}^{-1}$  fat) in common guillemot (*Uria aalge*) eggs from Stora Karlsö in the Western Gotland Basin. The horizontal line represents the geometric mean, the red line is the trend line and the blue line the running mean smoother of the time series.

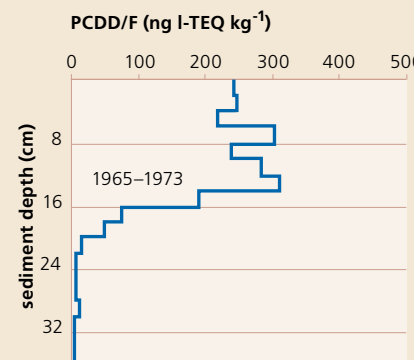
(Anon. 2000b), the former requiring Member States to establish permit conditions based on the Best Available Techniques (BAT) for a wide variety of industry sectors, and the latter setting maximum permissible limit values for PCDD/F emissions to air and water from waste incineration. The proper and timely implementation and enforcement of the IPPC Directive remain a key priority in order to ensure the necessary reduction of emissions from major industrial sources. However, at present or in the near future, non-industrial sources are likely to exceed those from industrial sources (Quaß et al. 2004).

### BOX 1: Contaminated Sediments in the River Kymijoki, Finland

The sediments in the River Kymijoki that drain into the Gulf of Finland are heavily polluted with PCDD/Fs and mercury from earlier chlorophenol, chlor-alkali, and pulp and paper manufacturing (Verta et al. 2009). A continuous transport of contaminants from the estuarine sediments is taking place to the Gulf of Finland in the Baltic Sea. The total volume of contaminated sediments in the river is estimated to reach  $5 \times 10^6 \text{ m}^3$  and hot spots with extremely high concentrations (maximum  $292\,000 \mu\text{g kg}^{-1}$  or  $1\,060 \mu\text{g I-TEQ kg}^{-1} \text{ dw}$ ) have been located immediately downstream from the pollution source in Kuusankoski, a city located about 50 km inland. Sediment contamination is accompanied by changes in benthic species assemblages, but direct effects are masked by many factors. The fish show only slightly elevated PCDD/F levels in muscle, but concentrations in the liver are an order of magnitude higher compared with reference freshwater fish. The lipid-rich fish species in the Baltic Sea have significantly higher PCDD/F concentrations than fish in the River Kymijoki.

The concentrations in human fat do not indicate high human exposure in the River Kymijoki area in general and they are lower than in coastal fishermen. The relative risk for total cancer among farmers has been shown to be marginally higher among those living close to the river compared with farmers living further away and the possibility of increased cancer risk cannot be ruled out. Human risk assessment revealed that the present probability of exceeding the WHO tolerable weekly intake of PCDD/Fs is low. The risks posed by methyl mercury exceed those from PCDD/Fs. A general

remediation plan with a cost-benefit analysis was generated for the whole river taking into account estimated risks associated with different remediation techniques. Dredging, on-site treatment, and a close disposal of the most contaminated sediments ( $90\,000 \text{ m}^3$ ) have been suggested as the first phase of the remediation and a detailed restoration plan has been prepared. Based on current knowledge, the restoration of the whole river is not feasible, considering the risk caused by contaminated sediments in the river and the costs of an extensive restoration project.



**Panel A** PCDD/F concentrations in a dated sediment core from the River Kymijoki estuary (Ahvenkoskensä) showing the highest PCDD/F deposition from the late 1960s to the early 1970s, followed by a small decrease to the surface (new) sediments. Note that the present concentration of  $200$  to  $300 \text{ ng kg}^{-1}$  (I-TEQ) (dw) is high compared with the present background concentration of about  $20 \text{ ng kg}^{-1}$  in other accumulation bottoms of the Baltic Sea.

## 2.2.2 Status and trends of polychlorinated biphenyls

Polychlorinated biphenyls (PCBs) consist of two linked benzene rings with chlorine atoms substituted for one or more hydrogen atoms (209 congeners are possible). Some are classified as dioxin-like PCBs (four non-*ortho* PCBs: CB-77, CB-81, CB-126, CB-169 and eight mono-*ortho* PCBs: CB-105, CB-118, CB-156, CB-167, CB-114, CB-123, CB-189) (Burreau et al. 2006); these were assessed in Section 2.2.1, above. This section concentrates on the other PCBs.

PCBs are synthetic chemicals and do not occur naturally in the environment. The preponderance of biomedical data from human and laboratory mammal studies as well as studies on wildlife provide strong evidence of the toxic potential of exposure to PCBs (Aulerich and Ringer 1977, ATSDR 2000). PCBs can impact human health by affecting multiple organ systems. Humans exposed to PCBs are at increased risk of cancer, infections, reduced cognitive function accompanied by adverse behavioural effects, hypothyroidism, infertility, ischemic heart disease, hypertension, diabetes, liver disease, asthma and arthritis, as well as giving birth to infants of lower than normal birth weight (Carpenter 1998, 2006). There are also indications that PCBs are associated with uterine leiomyoma development and/or growth in grey seals. In general, environmental pollution has been linked to reproductive failures in grey seals, but since the middle of the 1980s, their reproduction has normalized (Bäcklin et al. 2010).

### Sources

PCBs have been used in a wide variety of manufacturing processes especially as plasticizers and as insulators and flame-retardants. They are widely distributed in the environment through, for example, inappropriate handling of waste material or leakage from large condensers and hydraulic systems. Owing to their long-distance transport in air, PCBs now represent a global contamination problem.

### Regional differences

The congeners CB-153 and CB-180 are among the seven PCBs recommended to be analysed within the HELCOM COMBINE monitoring programme and they are also among the five most dominant

PCB congeners in the Baltic Sea (Pikkarainen 2007). For this reason, they have been used as representatives of PCB contamination in this assessment. The status of other PCB congeners was not assessed due to limited Baltic Sea-wide data.

The concentrations of CB-153 in fish and mussels were above the threshold level of 0.0025 mg kg<sup>-1</sup> ww in many regions of the Baltic Sea (EAC, OSPAR 2005) (**Fig. 2.8**). Concentrations more than three times above threshold levels were found in the Little Belt, southern parts of the Kattegat, the Sound, the Szczecin Lagoon, southern parts of the Bothnian Sea, and in the Bothnian Bay. In contrast, the concentrations of CB-180 were not found to exceed the threshold level (EAC, 0.480 mg kg<sup>-1</sup> lipid weight) (OSPAR 2009a) in any part of the Baltic Sea (data not shown). The highest concentrations of CB-180 in this assessment were found in the Pomeranian Bay, where concentrations were between 0.100 and 0.200 mg kg<sup>-1</sup> lipid weight.

### Decreasing concentrations

As a result of measures taken to reduce discharges of PCBs to the environment, concentrations of PCBs, including CB-153 and CB-180, show significant declining trends in herring, perch and blue mussels in several regions around the Baltic Sea (**Fig. 2.9**). However, only a few available data sets have time series long enough to draw statistical conclusions regarding temporal trends (Bignert et al. 2004).

The sum of seven PCB congeners (CB-28, CB-52, CB-101, CB-118, CB-138, CB-153 and CB-180) is often used to describe the PCB contamination. Decreasing trends for other PCB congeners, as well as for the sum of seven PCBs, have also been reported for some locations along the Baltic Sea (Bignert et al. 2008, GIOŚ 2007). It is estimated that levels have been decreasing by approximately 5–10% per year since the end of the 1970s (Bignert et al. 2008).

### Conventions, aims and restrictions

The Helsinki Convention (1974, 1992) has recommended special bans and restrictions on the transport, trade, handling, use and disposal of PCBs. The 1998 HELCOM Ministerial Declaration and the 1995 Declaration of the Fourth International Conference on the Protection of the North Sea called for meas-

ures to cease the inputs of toxic, persistent, and bio-accumulating substances such as PCBs to the environment completely by the year 2020. Seven PCB congeners (CB-28, CB-52, CB-101, CB-118, CB-138, CB-153 and CB-180, IUPAC) are listed as mandatory contaminants that should be analysed and reported within both the OSPAR and the Helsinki Conventions. PCBs are also included in the Stockholm Convention on Persistent Organic Pollutants. Moreover, EU Directive 96/59/EC and the Regulation (EC) No. 850/2004 on persistent organic pollutants ban the production and use of PCBs and set requirements on the disposal of PCB waste.

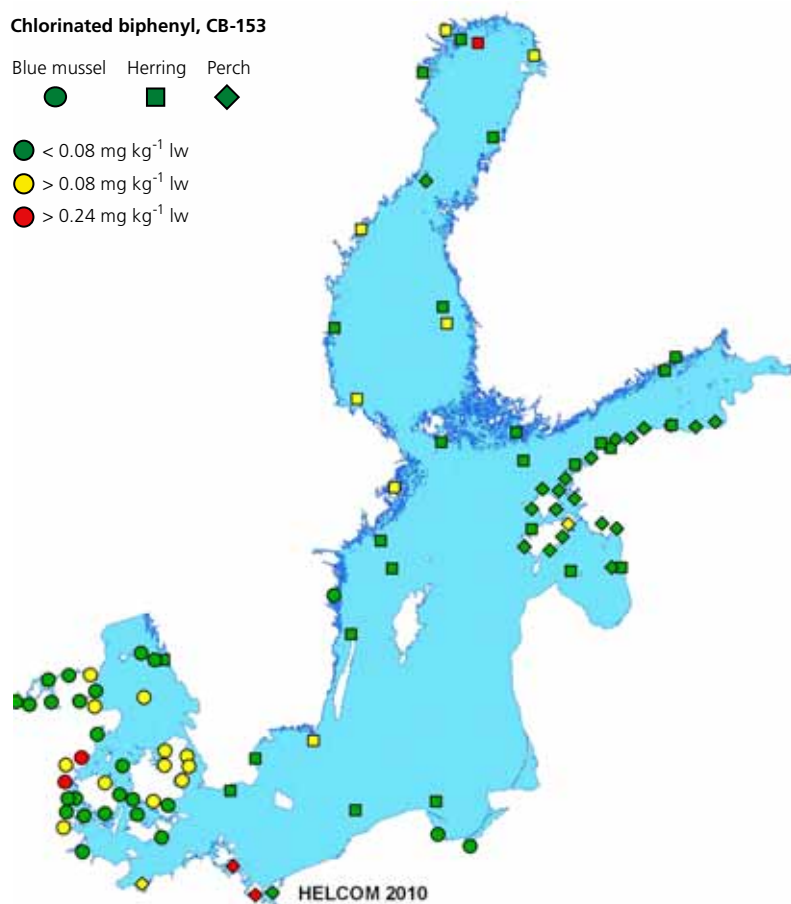
### 2.2.3 Status and trends of heavy metals

Heavy metals are elements that occur naturally in the environment. Concentrations of mercury, cadmium and lead are usually naturally very low and vary between areas of different geological origin. These metals are toxic, even at low concentrations, and have no known beneficial biological effects. Cadmium and lead concentrate in the liver where high levels can cause liver malfunction. Mercury concentrates in muscles. High metal concentrations can damage neuro-transmitters and learning capability (mercury, lead) and bones or shell strength (cadmium). In this section, special emphasis is given to mercury and cadmium, while lead is included in the integrated assessment. According to the integrated assessment, levels of lead in biota and sediment exceed the threshold levels in fish, bivalves and surface sediments in several basins of the Baltic Sea (see **Chapter 2.1**).

All metals have a concentration level above which negative effects on the most sensitive organisms can be observed. This level can be specified with Environmental Assessment Criteria (EAC) and Background Assessment Criteria (BAC). A BAC represents the low concentrations found in areas far from pollution sources, whereas an EAC indicates a level above which organisms are adversely affected by the substance (see **BOX 2**). In addition, safety levels are set separately for top predators (e.g., seals and sea eagles) (Anon. 2005) and human consumption (Anon. 2006a).

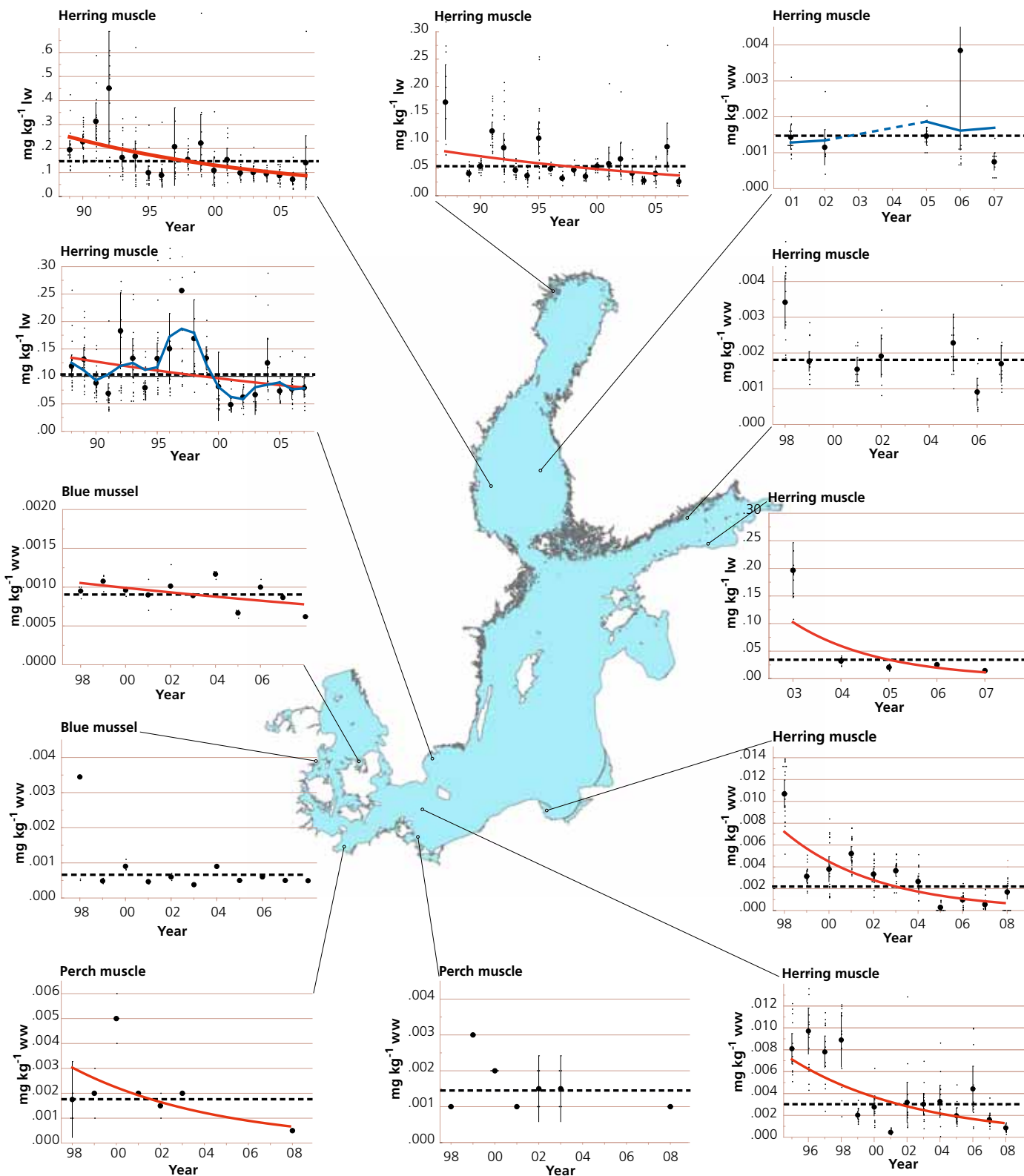
#### Where do metals come from?

The main sources of pollution by heavy metals are mines, metal smelters, coal-fired power plants and the fertilizer industry, although pulp and paper mills have also discharged large amounts of mercury into Baltic waters (SEPA 2008). In addition, methyl mercury was applied for many years as a fungicide, particularly to protect grain seeds. Thus, the main sources of cadmium and mercury are point sources and riverine runoff. Atmospheric deposition accounts for 15% for cadmium and 25% for mercury of the total inputs, whereas about half of lead originates from atmospheric emissions (Gusev 2009a, Knuutila 2009).

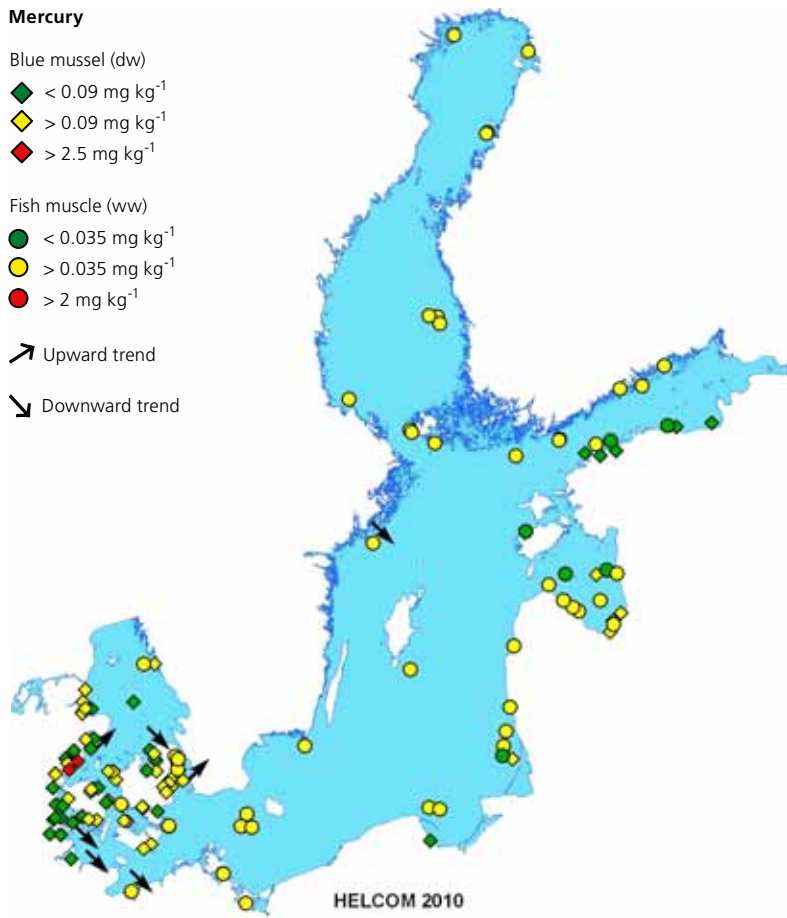


**Figure 2.8** The map illustrates the overall status of CB-153 concentrations in perch, blue mussels and herring sampled in coastal waters. The threshold level of 0.08 mg kg<sup>-1</sup> lipid weight (lw) is based on an EAC value for blue mussels and fish (0.0025 mg kg<sup>-1</sup> ww) and recalculated to fit the data set with units on a lipid weight basis. The higher threshold (0.24 mg kg<sup>-1</sup> lw) is three times the lower level to identify areas of high concern.





**Figure 2.9** Temporal trends of CB-153 concentrations in the Baltic Sea. The species investigated are herring, perch and blue mussel. Concentrations of the latter two have been measured in  $\text{mg kg}^{-1} \text{ ww}$ . Data for herring were provided on a wet weight or a lipid weight basis. Assuming a fat content of 3% (Bignert 2008), concentrations on a lipid weight basis are approximately 30 times higher than concentrations on a wet weight basis. The species and units are given for each graph separately, with year on the x-axis. Regression analyses producing statistical trends were performed for complete time series. The red line is the trendline of the measurements and the horizontal line represents the geometric mean of each time series.



**Figure 2.10** Map of the levels and temporal trends of mercury in blue mussels and fish muscle. The mercury concentrations were compared with OSPAR Background Assessment Criteria (green/yellow boundary) and Environmental Assessment Criteria or the food safety limit of the European Union (yellow/red boundary). See text and **BOX 2** for explanation. The downward and upward arrows denote decreasing and increasing trends at a level of 95% statistical probability.



In 2006, 233 tonnes of lead, 7.2 t of cadmium and 3.4 t of mercury were deposited from the atmosphere directly to the Baltic Sea (Bartnicki et al. 2008). In comparison, the waterborne loads from point and diffuse sources in 2006 were 274 t, 47.5 t, and 10.8 t for lead, cadmium and mercury, respectively (Knuuttila 2009).

The atmospheric deposition has decreased by 69% for lead, 46% for cadmium and 23% for mercury from 1990 to 2007 (Gusev 2009a). The decrease in waterborne loads was 91% for cadmium, 50% for lead and 16% for mercury during the same period (Knuuttila 2009). Significant transboundary pollution loads of waterborne heavy metals originate in Belarus, the Czech Republic and Ukraine<sup>5</sup> (HELCOM 2005).

#### The status of mercury and cadmium in the Baltic Sea

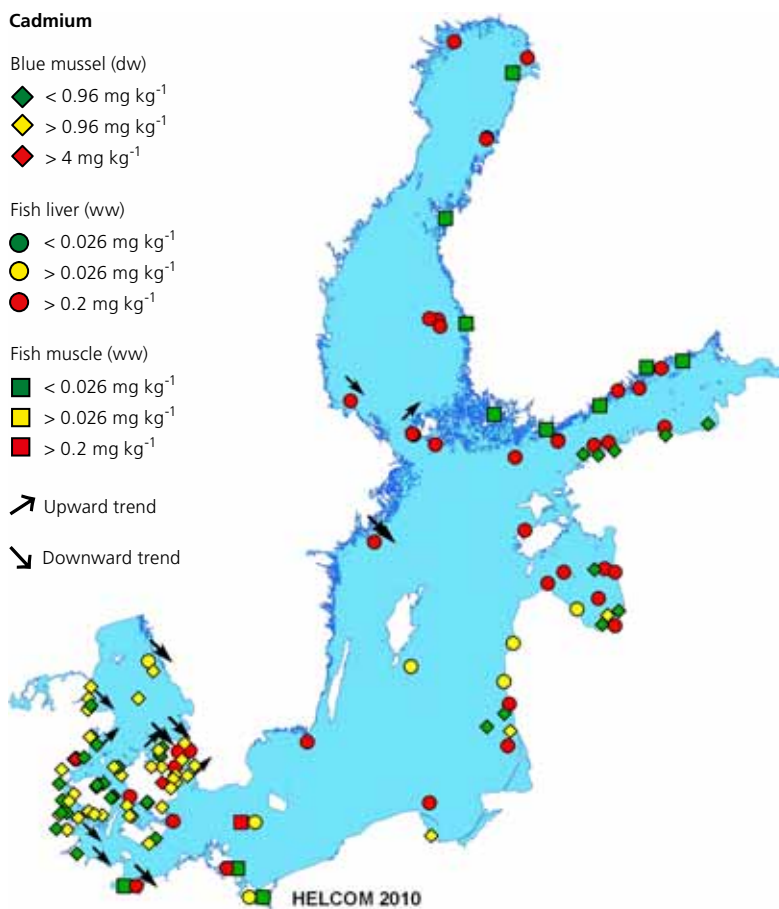
Cadmium and mercury are monitored in blue mussels (*Mytilus edulis*) from the western parts of the Baltic Sea, in the clam *Macoma balthica* on the southern and eastern coasts, and in fish in the central, northern and northeastern parts of the sea area. Monitoring of cadmium and mercury in biota is part of the HELCOM COMBINE programme.

The status of mercury and cadmium are indicated in **Figs. 2.10** and **2.11**, in which the average concentrations from the most recent three years of monitoring are compared with the OSPAR Background Assessment Criteria (BAC, see **BOX 2**). The values below the BAC indicate a low concentration of the metal. If a value is above the BAC but below the Environmental Assessment Criterion (EAC, see **BOX 2**) or food limits of the European Union, the concentration is at a level which is not expected to cause adverse effects in the environment. The concentrations above EAC or EC food limits indicate very high high cadmium and mercury levels.

<sup>5</sup> The Czech Republic contributes the largest loads of mercury (2 t), while Ukraine accounts for the most substantial loads of cadmium (3.8 t) and lead (32 t). The cadmium load from the Czech Republic is 3 t and lead load from Belarus 14 t (HELCOM 2005).

The mercury concentrations in blue mussels and fish muscle are above the threshold levels all over the Baltic Sea, indicating that mercury concentrations in biota are not near the natural background levels (**Fig. 2.11**). However, the safety limit for human food is exceeded only in blue mussels in Horsens Fjord, Denmark.

Cadmium accumulates efficiently in fish liver and the concentrations are far above the natural background levels (**Fig. 2.11**). Liver is not usually consumed by humans, but comparing with the EU food limit, 89% of fish liver assessment areas were of “high concern” (red in **Fig. 2.11**) should be viewed with caution from a human health perspective. The concentrations of cadmium in fish muscle are below the threshold level because cadmium does not accumulate in fish muscle. Blue mussels show variable concentrations of cadmium, although the majority of the sites assessed show levels higher than the estimated background concentrations (**Fig. 2.11**).



**Figure 2.11** Map of the levels and temporal trends of cadmium in blue mussels and fish liver and muscle. See explanations in **Fig. 2.10**.

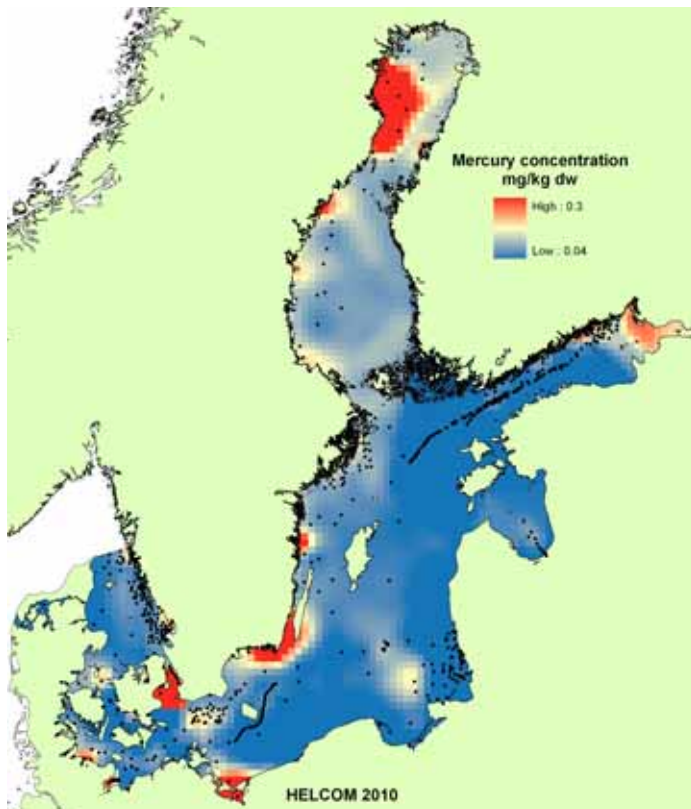
## BOX 2: Background (BAC) and Environmental (EAC) Assessment Criteria

OSPAR has developed assessment criteria for its Quality Status Reports 2000 and 2010. The Background Assessment Criteria (BAC) have been established as the median of median concentrations in mussels from different areas in the Northeast Atlantic, which are considered to be without significant anthropogenic inputs. A margin of error was added to these derived background levels based on QUASIMEME interlaboratory studies to obtain the final BAC.

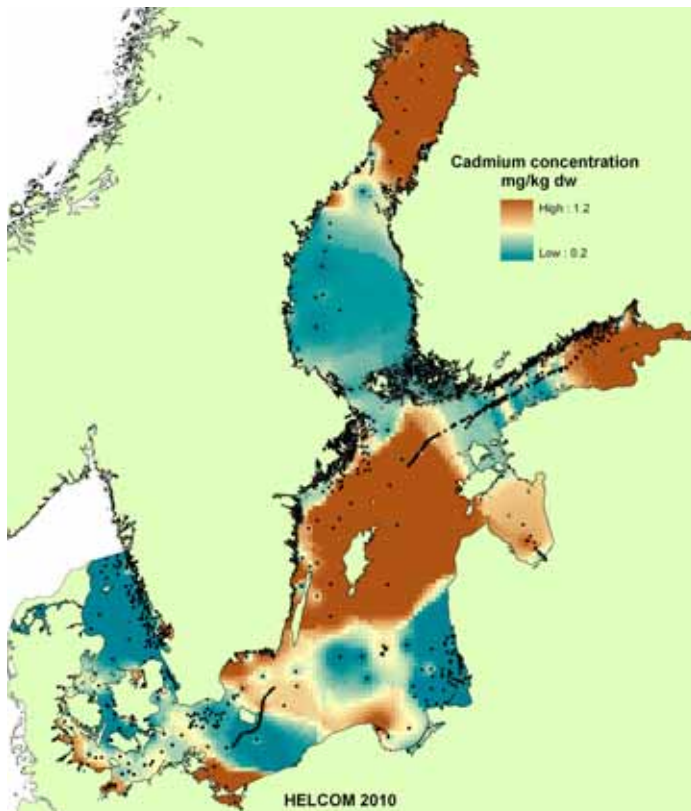
For determining Environmental Assessment Criteria (EAC), data were collected from ecotoxicological studies on several species using different endpoints ranging from cellular responses to death. The resulting concentrations were used to create lower and upper EACs, and safety factors were employed depending on the number of species and endpoints that had been used. For measured values below the high EAC, the substance could be causing chronic damage to the target

organism, whereas above the EAC acute biological effects are considered likely. In this assessment, the high EAC was used as “EAC”. Thus, values below the high EAC are considered “moderate” status and values below BAC as “good”, leaving concentrations above the high EAC as “bad”.

In the assessment of mercury and cadmium concentrations in the Baltic Sea, the OSPAR BAC concentrations for mussels were between the fifth and tenth percentile of the observed results, which is comparable to data from the OSPAR area. Hence, the BAC for mercury and cadmium were considered valid also for the Baltic Sea conditions. For fish, the BAC values for mercury and cadmium were around the tenth percentile level, whereas for lead, it was three times below the tenth percentile. Thus, for mercury and cadmium in fish, the BAC may give too positive a picture of the contamination problem.



**Figure 2.12** Concentrations of mercury in surface sediments. The scale of the colour gradient is set to vary from 0.04 to 0.3 mg kg<sup>-1</sup> dw, although higher values also are found in the contaminated areas shown on the map. The data (indicated with circles) are based on almost 2000 spatially distinct measurements from 2001–2008.



**Figure 2.13** Levels of cadmium in surface sediments. The scale of the colour gradient is set to vary from 0.20 to 1.20 mg kg<sup>-1</sup> dw, although higher values are also found in the contaminated areas shown on the map. The data (indicated with circles) are based on almost 2000 spatially distinct measurements from 2001–2008.

### Mercury contamination of fish and mussels and risks to their predators

Women in their fertile years have been warned against eating fatty fish (herring and salmon) from the Baltic Sea at least in Denmark, Finland and Sweden owing to concerns about the high levels of mercury, PCDD/Fs and DL-PCBs. For mercury, the limit has been set at 0.5 mg kg<sup>-1</sup> ww for most fish species (0.3 mg kg<sup>-1</sup> ww in flatfish) by the EU. The concentrations found in the edible parts of fish (i.e., muscle) are generally below this level all over the Baltic Sea. The EU has also set an environmental target value of 0.02 mg kg<sup>-1</sup> ww for mercury to avoid the bioaccumulation of mercury in top predators (Anon. 2008b). In this assessment, 90% of fish liver samples, 95% of fish muscle samples and almost all mussel samples exceeded this target value. However, the EU Water Framework Directive allows the addition of background concentrations to the target value (Anon. 2000a). If the OSPAR BAC level is added as a background level to the mercury target value (i.e., BAC+EU target = 0.055 mg kg<sup>-1</sup> ww), 75% of fish samples and 91% of mussel samples still exceeded the target value. Thus, even though fish (or mussels) seem to be safe to eat for humans, the risk of bioaccumulation and harmful effects in the predators of fish still exists.

### Are the Baltic Sea sediments in good condition?

The most critical heavy metals—cadmium and mercury—show high concentrations in Baltic Sea surface sediments. They also have different distribution patterns, as mercury shows more local anomalies located closer to the sources (Fig. 2.12), while cadmium as a more mobile element seems to have occupied the bottoms of larger sea areas (Fig. 2.13). High sediment mercury concentrations were found in several estuaries and particularly in the western Bothnian Bay, eastern Gulf of Finland, off southeastern Sweden and in the Sound. Cadmium concentrations were particularly high in sediments in the Bothnian Bay, eastern Gulf of Finland, Northern Baltic Proper, Western and Eastern Gotland Basins and the Pomeranian Bay. Owing to a lack of background concentrations for cadmium and mercury in sediments in the different basins, this assessment cannot evaluate the current environmental status for these metals in sediments. However, it can be estimated that the surface sediment concentrations in large areas of the Baltic Sea

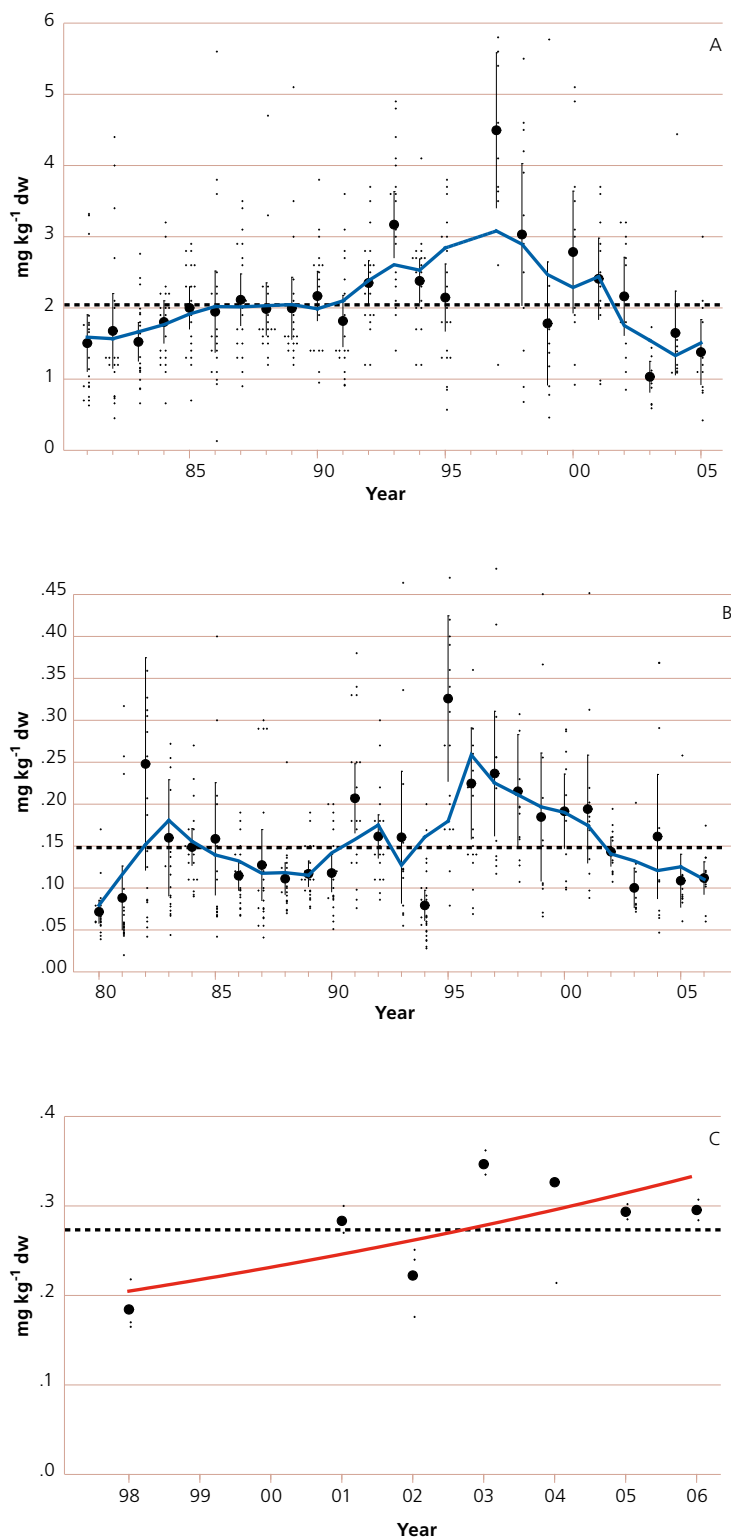
clearly exceed the threshold values for good environmental status that have been established so far<sup>6</sup>.

### Metal concentrations are not always declining over time

In the Baltic Sea, 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. The main message from this trend analysis is that relatively few of the locations studied (five for mercury and nine for cadmium) showed decreasing temporal trends and a few even showed increasing concentrations of metals (Figs. 2.10 and 2.11). The upward trends were observed in the Sound area for mercury, in the Kattegat between Denmark and Sweden for both metals, and in Åland, Finland for cadmium. Longer time series (1980–2007) from some stations, such as Landsort in the Northern Baltic Proper, showed decreasing temporal trends since the mid-1990s, whereas other stations such as in the Sound showed increasing trends over the same period (Fig. 2.14). However, it is worth noting that many of the temporal trends do not show a clear monotonic response, but rather indicate variable response curves (Fig. 2.14).

The concentrations of mercury in sediment decreased in the Bothnian Bay, Åland Sea, Eastern Gotland Basin and Kattegat between 2003 and 2008 (Swedish monitoring data, data not shown). However, at the same time concentrations seem to have increased in the Bothnian Sea, Arkona Basin and the Sound.

Sediment concentrations of arsenic, cadmium, chromium, cobalt, copper, nickel and zinc increased from 2003 to 2008 in almost all of the 17 Swedish stations monitored (data not shown). Lead concentrations decreased in the Northern Baltic Proper and the Bornholm Basin, but increased elsewhere. Although the comparison between two points in time is very uncertain, a similar message has also been received from other national sediment monitoring programmes.



**Figure 2.14** Temporal trends of concentrations (in  $\text{mg kg}^{-1} \text{ dw}$ ) of (A) cadmium and (B) mercury in fish from Landsort (Northern Baltic Proper) and (C) mercury in blue mussels from the southern part of the Sound. The horizontal dashed line shows the overall geometric mean of the data and the solid line indicates the smoothed average of the measurements (blue) or the trend (red).

<sup>6</sup> Concentrations indicating significant deviation from reference conditions in Sweden are  $0.12$  and  $0.5 \text{ mg kg}^{-1} \text{ dw}$  for mercury and cadmium, respectively (SEPA 2000). The OSPAR low EAC for mercury and cadmium are  $0.05$  and  $0.1 \text{ mg kg}^{-1} \text{ dw}$ , respectively (OSPAR 1997). The Russian criteria ( $0.5$  and  $3.0 \text{ mg kg}^{-1} \text{ dw}$  [normalized to 10% carbon] for mercury and cadmium) are in line with the other criteria.

### The ecosystem effects of cadmium, mercury and lead

Heavy metals can accumulate in the marine food web up to levels that are toxic to marine organisms and that may also be a health risk for humans. Mercury in fatty fish is considered problematic for pregnant women, as mercury can be transferred to the unborn child via the placenta. It can also be transferred to infants via breast milk. Moreover, mercury in biota occurs mainly as methyl-mercury, which is much more toxic than the  $Hg^{2+}$  ion. Both mercury and lead have been shown to decrease learning ability in children. Chronic exposure to cadmium has mainly been shown to cause kidney failure. Freshwater organisms are more susceptible to cadmium poisoning than marine organisms, which may also mean that organisms in the northern parts of the Baltic Sea may be more sensitive to high cadmium concentrations.

Once released into the Baltic Sea, heavy metals can remain in the water for long periods. The concentrations of heavy metals in Baltic Sea water are up to 20 times higher than in North Atlantic sea water.

### What measures have been put in place?

As the majority of heavy metal inputs to the Baltic Sea originate in catchment area, local and regional measures continue to be of the utmost importance. However, heavy metals are also long-range transboundary air pollutants and therefore measures addressing distant sources will be needed at European and global levels. The current measures are not sufficient to be able to reach HELCOM's objective of continuously decreasing concentrations, with the ultimate aim of achieving concentrations in the environment near background values for naturally occurring substances. The major measures to reduce the loads of heavy metals are: (1) the improvement of combustion processes of fuel and waste, (2) control of imported products, (3) reduction of crematoria emissions, (4) management of the chlor-alkali industry, and (5) restriction of cadmium in fertilizers.

Mercury and cadmium are included as priority substances under the EU Water Framework Directive (Anon. 2000a). Emissions and discharges of heavy metals from major industrial sources

are also subject to the EU Directive 96/61/EC on Integrated Pollution Prevention and Control (IPPC) (Anon. 1996), which was required to be implemented by EU Member States by October 1999, with a period of until October 2007 to bring existing installations into compliance. Mercury and other heavy metal emissions have also been reduced by the application of sector-specific EU Directives dealing with large combustion plants and waste incineration. In January 2005, the European Commission adopted a mercury strategy that envisages a number of actions to protect citizens' health and the environment, such as the reduction of EU exports and imports of mercury as well as addressing mercury storage. Recently, concern has been raised in relation to the predicted increase in the use of mercury-containing fluorescent lamps due to the EU ban on incandescent lamps.

The UN ECE Protocol on heavy metals under the Convention on Long-Range Transboundary Air Pollution (CLRTAP-HM) was adopted in Aarhus (Denmark) in 1998. Parties are obliged to reduce their emissions of mercury, lead and cadmium to levels in 1990 (or any alternative year between 1985 and 1995). There are also obligatory measures for the three heavy metals, such as the phasing out of leaded petrol or mercury in batteries and stringent limit values for point sources. The Protocol entered into force in 2003 and all HELCOM Contracting Parties, except the Russian Federation, have signed it (see also **Chapter 4**).

UNEP has adopted a global programme for mercury which has the long-term objective of facilitating national, regional and global actions to reduce, or eliminate as far as possible, uses and releases of mercury; thereby significantly reducing its adverse impacts on humans and the environment. The immediate objective of the programme is to initiate technical assistance and capacity-building activities to support the efforts of countries. A plan for global action on mercury was agreed by the UNEP Governing Council in February 2009. Governments from 140 countries decided to launch negotiations on an international mercury treaty to deal with worldwide emissions and discharges and to take accelerated actions under a voluntary Global Mercury Partnership programme whilst the treaty is being finalized.

### 2.2.4 Status and trends of TBT

The organotin compounds tributyltin (TBT) and triphenyltin (TPT) are considered to belong to the most hazardous substances that have deliberately been released into the marine environment. The clearest effects caused by TBT and TPT occur in benthic organisms such as bivalves and gastropods, which are very sensitive to effects such as shell deformation, endocrine disruption and impaired larval recruitment. For example, the so-called imposex and intersex phenomena occur widely in marine gastropods in the Baltic Sea and are specifically related to TBT pollution. This phenomenon has been detected at the extremely low TBT concentration of two nanograms per litre (2 ng l<sup>-1</sup>) (Piispanen et al., 2004) (see also **Section 2.1.2**). Although uncertainty remains, evidence suggests that the accumulation of high levels of organotins in top predators such as marine mammals might adversely affect their immune system (Santillo et al. 2001; Strand et al. 2005).

#### Sources

Most TBT and TPT leach into Baltic Sea water from maritime sources such as antifouling paints on ship hulls and TBT-contaminated harbour sediments. Consequently, especially coastal areas located near shipyards and ports (leisure boat, transport, industrial and fishery ports) contain large amounts of TBT, but elevated levels can also be found in narrow shipping lanes (Finnish Ministry of Environment 2007, Eklund et al. 2008, HELCOM 2009b, Strand 2009a).

In addition, TBT and TPT have been used as wood preservatives and previously also as an agricultural fungicide. TBT occurs as an impurity in stabilizing agents containing monobutyltin (MBT) and dibutyltin (DBT) used in the manufacture of PVC and some other plastics products (e.g., diapers). Therefore, low TBT concentrations have been found in effluents from point sources such as industry and municipal treatment plants. However, antifouling paints used on ships are generally regarded as the main source of these compounds in the Baltic Sea environment (HELCOM 2009c), see also **Chapter 3**.

#### The environmental TBT levels are of concern

Both TBT and TPT and their degradation products can still be found at significant levels in the Baltic Sea, even though organotin compounds undergo

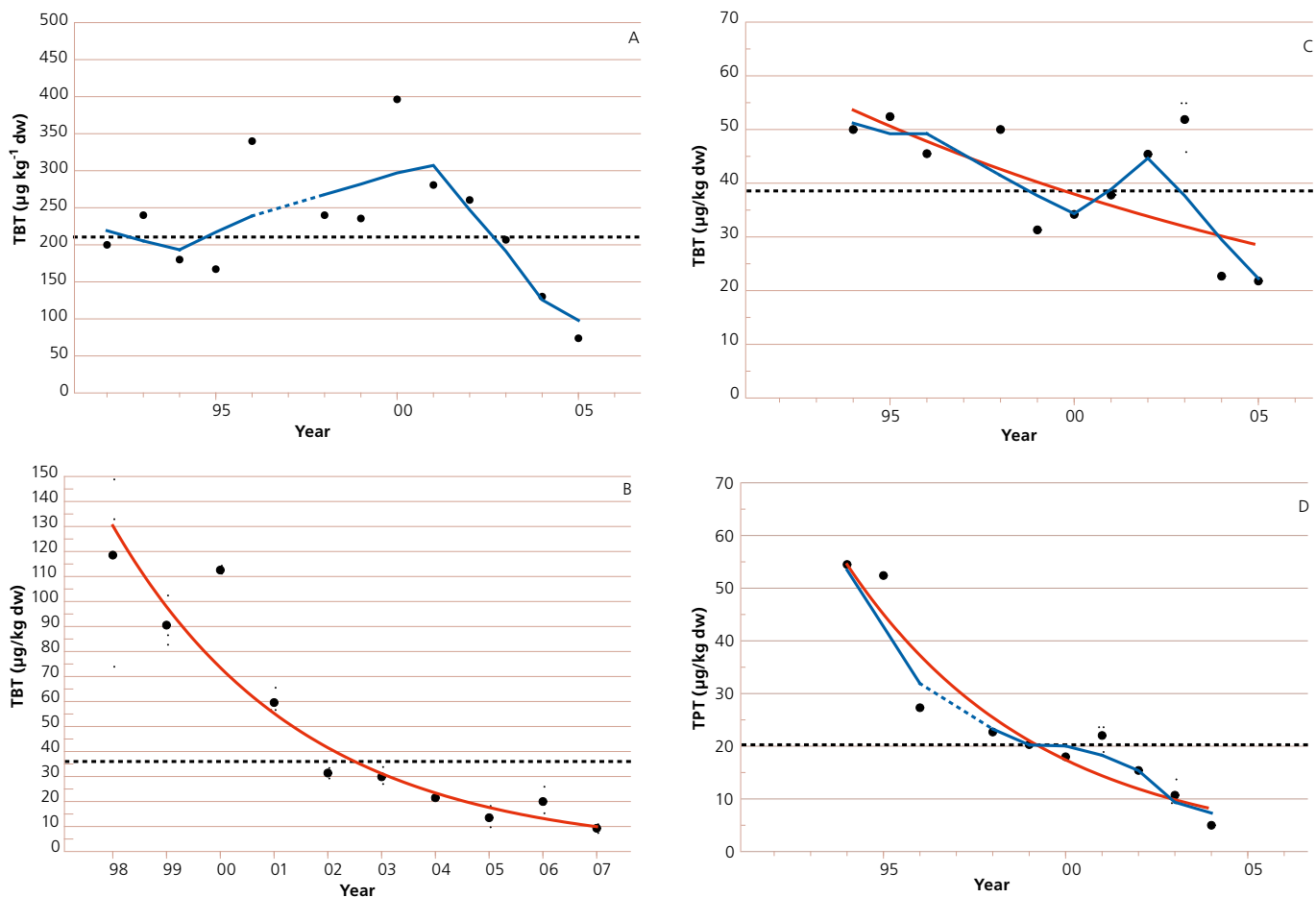


some chemical and biological transformation when released into the environment. The breakdown products DBT and MBT are less toxic than TBT. TBT and TPT adsorb strongly to suspended matter in the aquatic environment and ultimately are deposited in the sediments. Thus, benthic organisms can be exposed to very high organotin concentrations in the sediment. Furthermore, compared to their degradation in the water column, the degradation of TBT and TPT is much slower in sediments, where they can remain unchanged for years.

TBT levels in sediments and blue mussels (*Mytilus* spp.) still pose a significant environmental risk to the Baltic Sea environment (**Fig. 2.15**). The TBT levels are either of concern or even of high concern in some areas (**Fig. 2.15**). The levels are below the environmental threshold values in only 30% of the mussel samples assessed and in two of the sediment samples. These results are also in line with the TBT effects observed in benthic organisms in the region (see **Chapter 2.3**).

On the other hand, in most areas the TBT concentrations in fish are below the EU criterion for TBT in seafood<sup>7</sup> and exceed the EU criterion in 33% of the fish samples analysed. The areas affected are mainly coastal areas with dense ship traffic (**Fig. 2.16**).

<sup>7</sup> The EU food safety criterion for TBT in fish is 0.15 mg kg<sup>-1</sup> ww (Anon. 2005d).



**Figure 2.15** TBT and TPT levels have consistently decreased in blue mussels (A, B) and eelpout (C, D) since 2003, when the ban on the use of TBT as an antifouling agent began. Data for A, C and D are from the German monitoring station Darsser Ort (Rüdel et al. 2009) and for B from Århus Bight in Danish coastal waters. The horizontal lines represent the geometric mean of the time series, whereas the blue line is the smoothed average of the measurements and the red line is the trend line for the data series.

In contrast to many other hazardous organic substances, the distribution of TBT and TPT is spatially very variable, especially on a local scale. The use of this substance group as an antifouling agent on ships and smaller vessels can be seen in the concentration gradients from harbours to coastal waters and finally offshore. An exception to this general spatial trend may be the sediments in deep central parts of the Baltic Proper, where TBT seems to remain at a high level (Fig. 2.16).

#### Decreasing TBT levels in the Baltic Sea

Following the ban on the use of organotin compounds as antifouling agents, the levels of TBT in mussels and the coastal fish eelpout from the western Baltic Sea and the Belt Sea have decreased consistently during recent years. Decreasing trends have also been found for TPT in eelpout from the

German part of the Baltic Sea (Fig. 2.15 D). This indicates the importance of anti-fouling paints as a historical source of TBT, and that decreasing levels can also be expected in the years to come.

#### TBT and TPT accumulate in the food web

TBT and TPT accumulate in the food web, but a large variance in accumulation potential has been found between species, even within the same trophic level. This most likely reflects species-specific differences in their ability to metabolize and eliminate organotin compounds. Although mussels and fish are the preferred indicator species in most monitoring programmes, harbour porpoises in particular tend to accumulate more than an order of magnitude higher organotin levels compared to other organisms in the Baltic Sea (Strand et al. 2005, Strand & Jacobsen 2005). TPT levels are



about 1–13% of TBT levels in surface sediment, but fish in Finnish coastal areas show TPT concentrations mainly equal to or higher than TBT concentrations (Hallikainen et al. 2008). In Danish and German waters, TPT is also often found to accumulate in fish but generally to a lesser extent than TBT (Strand & Jacobsen 2005, Rüdell et al. 2009). There are indications of different spatial distributions of organotin compounds in the food web, sediment and mussels.

### Ban on TBT use in ships' anti-fouling paints

The 1992 Helsinki Convention bans the application of antifouling paints containing organotin compounds on pleasure craft less than 25 m in length and on fish net cages.

For commercial ships, the use of TBT in antifouling systems on ships flying an EU country flag has been banned since 2003 (Anon. 2003a). Furthermore, this EU Regulation imposes an obligation that from 1 January 2008 no ships calling at EU ports may use organotin compounds that act as biocides in their antifouling system. The Baltic Sea Action Plan extends this requirement to all ports in the Baltic Sea starting from 1 January 2010.

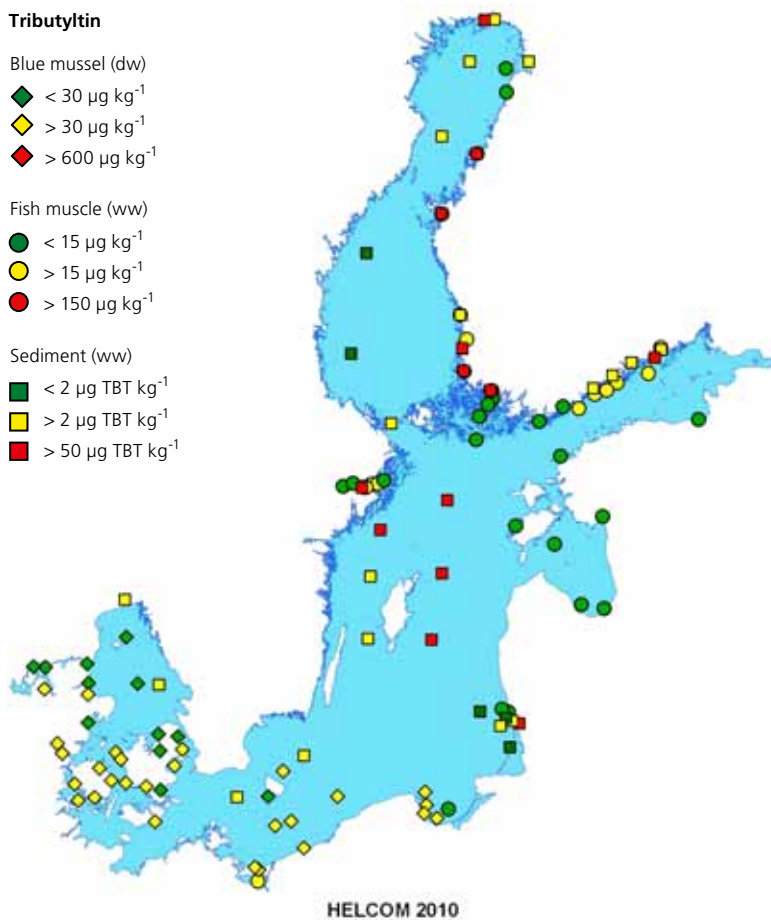
On the global level, the use of TBT in antifouling paints has been banned by the 2001 International Convention on the Control of Harmful Anti-fouling Systems on Ships (AFS Convention), which entered into force in 2008. All Baltic Sea countries except the Russian Federation have ratified the Convention.

### 2.2.5 Status and trends of organochlorine insecticides and some herbicides

Pesticides are chemicals that are widespread in the environment due to their application directly into the environment. They leach out from the soil into the aquatic environment and are transported to the sea, where they may bioaccumulate and biomagnify in food webs. DDT, HCB, lindane and endosulfan are chemicals that have been used worldwide, but are no longer used in the Baltic Sea region. DDT, HCB and lindane levels in the Baltic Sea marine environment have decreased significantly since the late 1970s and 1980s and they are still declining (HELCOM 2002a, 2003). The best-known effect of pesticides in the marine environ-

#### Tributyltin

- Blue mussel (dw)
  - ◆ < 30  $\mu\text{g kg}^{-1}$
  - ◆ > 30  $\mu\text{g kg}^{-1}$
  - ◆ > 600  $\mu\text{g kg}^{-1}$
- Fish muscle (ww)
  - < 15  $\mu\text{g kg}^{-1}$
  - > 15  $\mu\text{g kg}^{-1}$
  - > 150  $\mu\text{g kg}^{-1}$
- Sediment (ww)
  - < 2  $\mu\text{g TBT kg}^{-1}$
  - > 2  $\mu\text{g TBT kg}^{-1}$
  - > 50  $\mu\text{g TBT kg}^{-1}$



HELCOM 2010

**Figure 2.16** The status of TBT levels in the Baltic Sea assessed on the basis of measurements of TBT in blue mussels (*Mytilus* spp.), fish muscle or sediment. The yellow colour indicates that the TBT levels are of concern and red indicates high concern, whereas the green colour indicates that the TBT concentrations are below the environmental threshold values. The TBT levels in sediment and mussels have been assessed according to the OSPAR integrated assessment classes to evaluate whether the TBT levels could have severe impact on sensitive organisms in the environment, for example, by causing sterility in gastropods (OSPAR 2008). The TBT levels in fish have been assessed according to the EU quality standards for seafood for human consumption (Anon. 2005).

ment is associated with the adverse effects of DDT on the eggshell production of predatory birds and the consequent decline especially of white-tailed sea eagle populations in the northern hemisphere in the 1950s, 1960s and 1970s. The reproduction of the Baltic white-tailed sea eagle population in the 1970s was reduced to one fifth of its pre-1950 background level.

#### Selection of substances

Pesticides comprise a large number of different substances. Thus, prioritizing of pesticides for this assessment is indispensable. The ultimate criterion for selecting substances for evaluation was the

availability of monitoring data. Four substances were chosen as Primary Pesticides (**Table 2.3**) for the assessment based on:

- their monitoring data cover almost the whole Baltic Sea (DDT, HCB, HCH);
- they are “HELCOM Baltic Sea Action Plan substances” (endosulfan), “WFD Priority Hazardous Substances according to Directive 2008/105/EC amending the WFD” (HCB, endosulfan, HCH) or “WFD Other Pollutants” (DDT) according to the same Directive.

In addition, a few substances were chosen as Secondary Pesticides (**Table 2.3**) if they were WFD priority substances and monitoring data were available from at least three Baltic Sea countries.

**Table 2.3 The pesticides selected for the assessment and their classification into primary and secondary pesticides in this assessment.**

Primary pesticides	Secondary pesticides
1,1,1-trichloro-2,2-bis( <i>p</i> -chlorophenyl)ethane (DDT)	aldrin
hexachlorobenzene (HCB)	dieldrin
hexachlorocyclohexane (HCH)	endrin
endosulfan	isodrin
	atrazine
	diuron
	isoproturon
	simazine

### Sources

DDT is a persistent organochlorine insecticide which is degraded primarily to DDE (1,1-dichloro-2,2-bis(chlorophenyl)ethylene) or DDD (1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane). After 1945, DDT was used widely to control insects on agricultural crops and those carrying diseases such as malaria. The production, trade and use of DDT was banned between 1970 and 1975 in most countries bordering the Baltic Sea, especially Scandinavia and the former West Germany. DDT was no longer used in Poland by the mid-1980s and in Estonia, Latvia, Lithuania, Russia and the former East Germany by the mid-1990s. However, it is still used in some African, Asian and South American countries as an inexpensive and efficient insecticide (e.g., HELCOM 2001). In addition, there is continued leaching from contaminated soil and river sediments in some European areas (Green & Kunitzer 2003). DDT and its metabolites have been found

in the Arctic area, which indicates that it is also distributed by long-range transport (e.g., Oehme & Manø 1984, Welch et al. 1991).

Hexachlorobenzene (HCB) is a fungicide used, among others, in seed protection and wood preservation from the beginning of the 1950s. Significant sources of HCB to surface waters in the EU are the chemical industry (production of chlorinated substances such as perchloroethylene) and the metal industry, where HCB occurs as an unintentional by-product. Additionally, contaminated soil may be a significant source in some areas. The secondary aluminium industry and waste incineration are estimated to be significant sources to the air in the EU. HCB was no longer used as a pesticide in any Baltic Sea country by the early 1990s (HELCOM 2001, Anon. 2005) and its use has been banned in the Stockholm Convention.

Lindane ( $\gamma$ -HCH) was one of the most widely utilized insecticides on a worldwide scale. HCH has been used, e.g., as an insecticide and in wood treatment. Technical HCH contains various isomers: 60–75%  $\alpha$ -HCH, 15%  $\gamma$ -HCH, 7–10%  $\beta$ -HCH, 7%  $\delta$ -HCH, and 1–2%  $\epsilon$ -HCH. It came into general use in 1950. The  $\gamma$ -isomer, lindane, is the most toxic isomer of the HCHs, 500 to 1000 times more active than the  $\alpha$ -isomer. The use of technical HCH ceased in the countries around the Baltic Sea during the 1970s. Lindane was no longer used as a pesticide in the Baltic Sea countries with the exception of Russia by the mid-1990s, but it is still used in many developing countries (HELCOM 2001, Bignert et al. 2009).

Endosulfan is an insecticide and a miticide, but it has also been used as a wood preservative. The use of endosulfan has been banned in the EU as a pesticide (Commission Decision 2005/864/EC) and as a biocide since 2005, although its use decreased and even ceased already during the 1990s in some Baltic Sea countries (HELCOM 2009c). The use of endosulfan has also been restricted in Russia (PAN 2008). Endosulfan can still be used in other countries outside the EU. The most significant source of endosulfan in the EU is leaching from soil and atmospheric deposition due to its use as an agricultural pesticide outside Europe. Owing to its distribution by long-range atmospheric transport, it has been listed as a POPs substance in the Convention on Long-range Transboundary Air Pollution. This

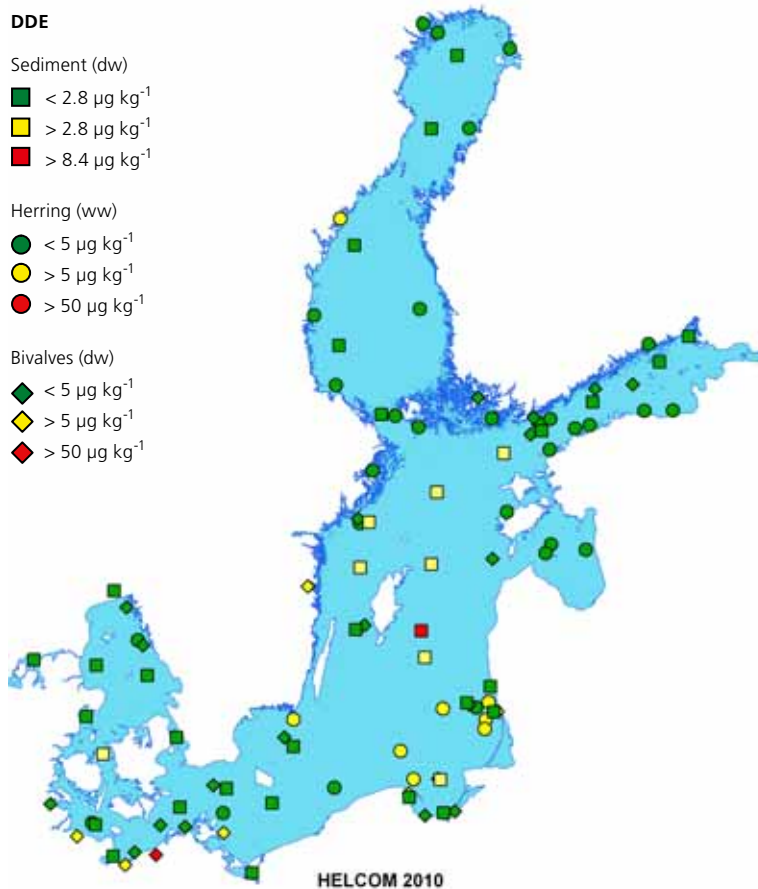
long-range atmospheric transport is assumed to be an important transportation route of endosulfan to the marine environment (OSPAR 2004a, Cousins et al. 2005).

Aldrin, dieldrin, endrin and isodrin, also known as “the drins”, have been used extensively throughout the world on a wide variety of crops and pests. The use of the drins was banned in most Baltic Sea countries by the end of the 1980s and ultimately in the whole Baltic Sea area in the late 1990s, but they are still used in a number of developing countries (HELCOM 2001). Atrazine and simazine are herbicides already banned in the EU. Diuron is a herbicide banned in the EU except for some essential uses. However, diuron is still used as a biocide, e.g., in paints. Isoproturon is a herbicide that is still permitted to be used. These herbicides may still be used in Russia.

#### Status in the Baltic Sea marine environment

This assessment is focused on the metabolite of DDT, DDE, rather than on DDT itself because DDE levels are higher than DDT (and DDD) levels in fish (e.g., Kankaanpää 2007, Szlinder-Richert et al. 2008, Bignert et al. 2009) and also in some cases in sediment (e.g., data in this study).

DDE levels in blue mussel (*Mytilus* sp.) and the Baltic clam *Macoma balthica* occasionally exceeded (seven out of 40 sampling sites) the lower threshold of  $5 \mu\text{g kg}^{-1}$  dw (EAC low, OSPAR 1997), but the higher threshold of  $50 \mu\text{g kg}^{-1}$  dw (EAC high, OSPAR 1997) was exceeded only at one site on the German coast (Fig. 2.17). DDE levels in fish muscle occasionally exceeded the lower threshold of  $5 \mu\text{g kg}^{-1}$  ww (EAC low, OSPAR 1997), especially in offshore areas of the Eastern Baltic Proper, but the higher threshold of  $50 \mu\text{g kg}^{-1}$  ww (EAC high, OSPAR 1997) was never exceeded (Fig. 2.17). DDE was found in marine surface sediment at levels occasionally exceeding (8 of 37 sites) the lower threshold ( $2.8 \mu\text{g kg}^{-1}$  dw; mean of lower and higher OSPAR 1997 criteria, Fig. 2.17) and once the concentration exceeded the higher threshold ( $8.4 \mu\text{g kg}^{-1}$  dw, Fig. 2.17) and thus was of high concern. DDT and the sum of DDTs (DDT, DDE and DDD) concentrations in sea water were lower than the respective thresholds ( $10 \text{ ng l}^{-1}$  for DDT and  $25 \text{ ng l}^{-1}$  for the sum of DDTs; AA-EQS Directive 2008/105/EC).



**Figure 2.17** DDE concentrations in surface sediment, herring (*Clupea harengus*) muscle and bivalves (blue mussels, *Mytilus* sp. and Baltic clams, *Macoma balthica*). The lower threshold level is  $5 \mu\text{g kg}^{-1}$  dw for bivalves and  $5 \mu\text{g kg}^{-1}$  ww for herring muscle (EAC low, OSPAR 1997) and  $2.8 \mu\text{g kg}^{-1}$  dw for surface sediment (mean of EAC low and high, OSPAR 1997). The higher threshold level (red) indicates a status of high concern. The higher threshold levels are  $50 \mu\text{g kg}^{-1}$  dw for bivalves,  $50 \mu\text{g kg}^{-1}$  ww for herring (EAC high, OSPAR 1997) and  $8.4 \mu\text{g kg}^{-1}$  dw (three times the lower threshold level) for sediment.

HCB levels in fish and blue mussels in the Baltic Sea were lower than the threshold ( $16.7 \mu\text{g kg}^{-1}$  ww, Anon. 2005e). HCB was not found at all in blue mussel ( $<0.3 \mu\text{g kg}^{-1}$  ww), and it was found at levels lower than the threshold in surface sediments ( $16.9 \mu\text{g kg}^{-1}$  dw, Anon. 2005) and in sea water ( $10 \text{ ng l}^{-1}$ ; AA-EQS 2008/105/EC). Nevertheless, no conclusion can be drawn on the few seawater samples, because the measurement detection limit was higher than the threshold concentration. In addition, a proper threshold for HCB in sediment is lacking, because the threshold in sediment used in this assessment is based on the equilibrium partitioning method, which has some limitations. Thus, there is a need for ecotoxicological data for sediment-dwelling organisms to enable the preparation of a reliable threshold for HCB in sediment for protection of the benthic communities of the Baltic Sea. The Dutch

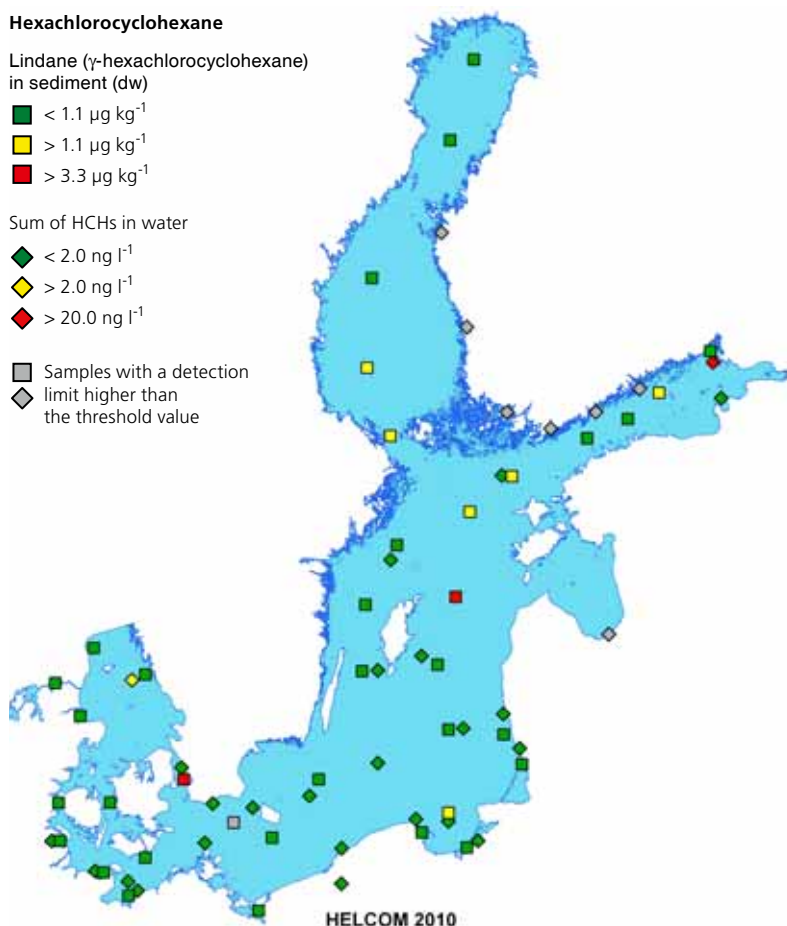
sediment risk limit for HCB is  $1.4 \mu\text{g kg}^{-1}$  dw. Even this limit was exceeded only in one sample in the German coastal waters.

HCH (sum of  $\alpha$ -,  $\beta$ - and  $\gamma$ -isomers) levels in fish and mussels were lower than the threshold ( $16.7 \mu\text{g kg}^{-1}$  ww, Anon. 2005). HCH was not found at all in blue mussels. Lindane occurred in sediment at levels occasionally exceeding (eleven out of 38 sites) the lower threshold concentration ( $1.1 \mu\text{g kg}^{-1}$  dw; Anon. 2005) and at two sites (the Sound and offshore Northern Baltic Proper) the levels were of high concern, exceeding the higher threshold ( $3.3 \mu\text{g kg}^{-1}$  dw) in the sub-basins of the Baltic Sea (Fig. 2.18). Similarly, HCH (sum of  $\alpha$ -,  $\beta$ - and  $\gamma$ -isomers) concentrations in sea water occasionally exceeded (six out of 35 sites) the threshold concentration ( $2.0 \text{ ng l}^{-1}$ ; AA-EQS 2008/105/EC) and

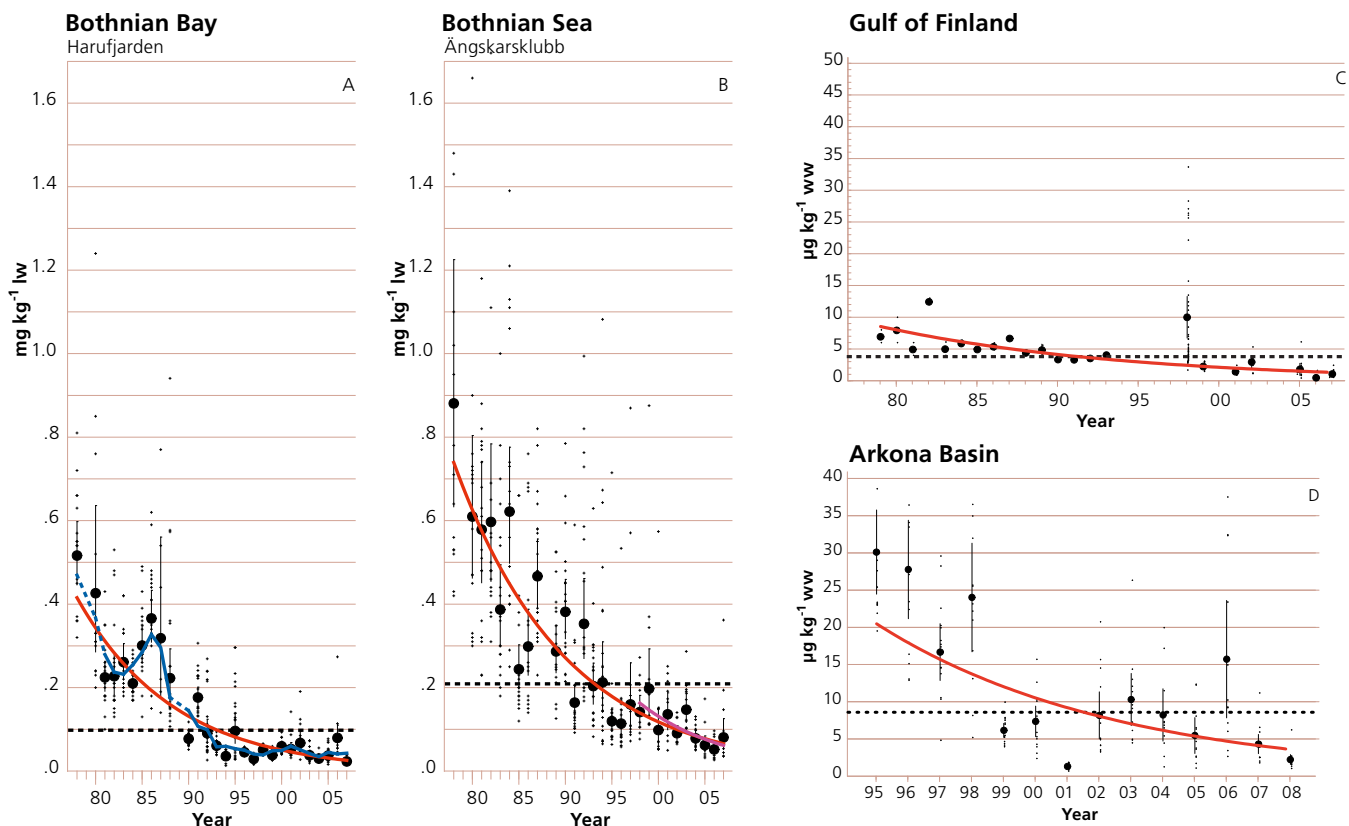
at one site the level was of high concern exceeding the higher threshold ( $20 \text{ ng l}^{-1}$ ; MAC-EQS 2008/105/EC). Nevertheless, firm conclusions could not be drawn on some water samples, because the detection limit was higher than the threshold (sites shown in grey in Fig. 2.18).

Endosulfan adsorbs mainly onto suspended particulate matter in the aquatic environment and then deposits onto the sediment. However, a certain proportion is likely to remain in the water column due to its relatively high water solubility (Cousins et al. 2005). In this assessment,  $\alpha$ - and  $\beta$ -endosulfan were not found in fish muscle, and thus the threshold concentration ( $1000 \mu\text{g kg}^{-1}$  ww, Anon. 2005) was not exceeded. However,  $\alpha$ - and  $\beta$ -endosulfan were found at low levels in surface sediments in German waters, but not in sediments in Lithuanian and Swedish areas. Levels were always lower than the threshold in sediment ( $100 \mu\text{g/kg}$  dw, lower chronic NOEC value presented in UNEP 2009). In sea water,  $\alpha$ - and  $\beta$ -endosulfan were found at low levels and always below the threshold concentration ( $0.5 \text{ ng l}^{-1}$ ; AA-EQS 2008/105/EC) in German coastal surface waters. These contaminants were not found in sea-water samples from Finnish, Lithuanian or Polish waters, but no conclusions can be drawn, because the measurement detection limit was higher than the threshold level. However, endosulfan sulphate, which is as toxic as endosulfan, was found in almost all of the fish muscle samples in the eastern Baltic Sea and off southeastern Sweden (range  $<0.010$ – $0.12 \mu\text{g kg}^{-1}$  ww) (Lilja et al. 2009). Herring had higher levels than perch or flounder. However, the observed concentrations were three magnitudes lower than the predicted no-effect concentration (PNEC) level. Endosulfan sulphate is an oxidation product found in technical endosulfan, but it is also the main microbial oxidation product of  $\alpha$ - and  $\beta$ -endosulfan (Cousins et al. 2005). A proper threshold for endosulfan in sediment is currently lacking and there is a need for ecotoxicological data for sediment-dwelling organisms to enable development of a reliable threshold for endosulfan in sediment.

Aldrin, dieldrin, endrin, isodrin, atrazine and simazine were not found in sea water and the thresholds were not exceeded (Anon. 2008b). Diuron was occasionally found in sea water (two out of eleven sites), but the threshold was not exceeded (Anon. 2008b). Isoproturon was also occasionally found in sea water (two out of eleven



**Figure 2.18** Concentrations of lindane in surface sediment and HCH (sum of  $\alpha$ -,  $\beta$ - and  $\gamma$ -isomers) in sea water. The threshold for lindane in sediment is  $1.1 \mu\text{g kg}^{-1}$  dw and for HCH in water  $2.0 \text{ ng l}^{-1}$ . The higher threshold (marked as red) for sediment is  $3.3 \mu\text{g kg}^{-1}$  dw (three times the lower threshold level) and for water  $20 \text{ ng l}^{-1}$  (MAC-EQS 2008/105/EC) and indicates a concentration of high concern. At the sites shown in grey, assessment was not possible due to the detection limits being higher than the threshold values.



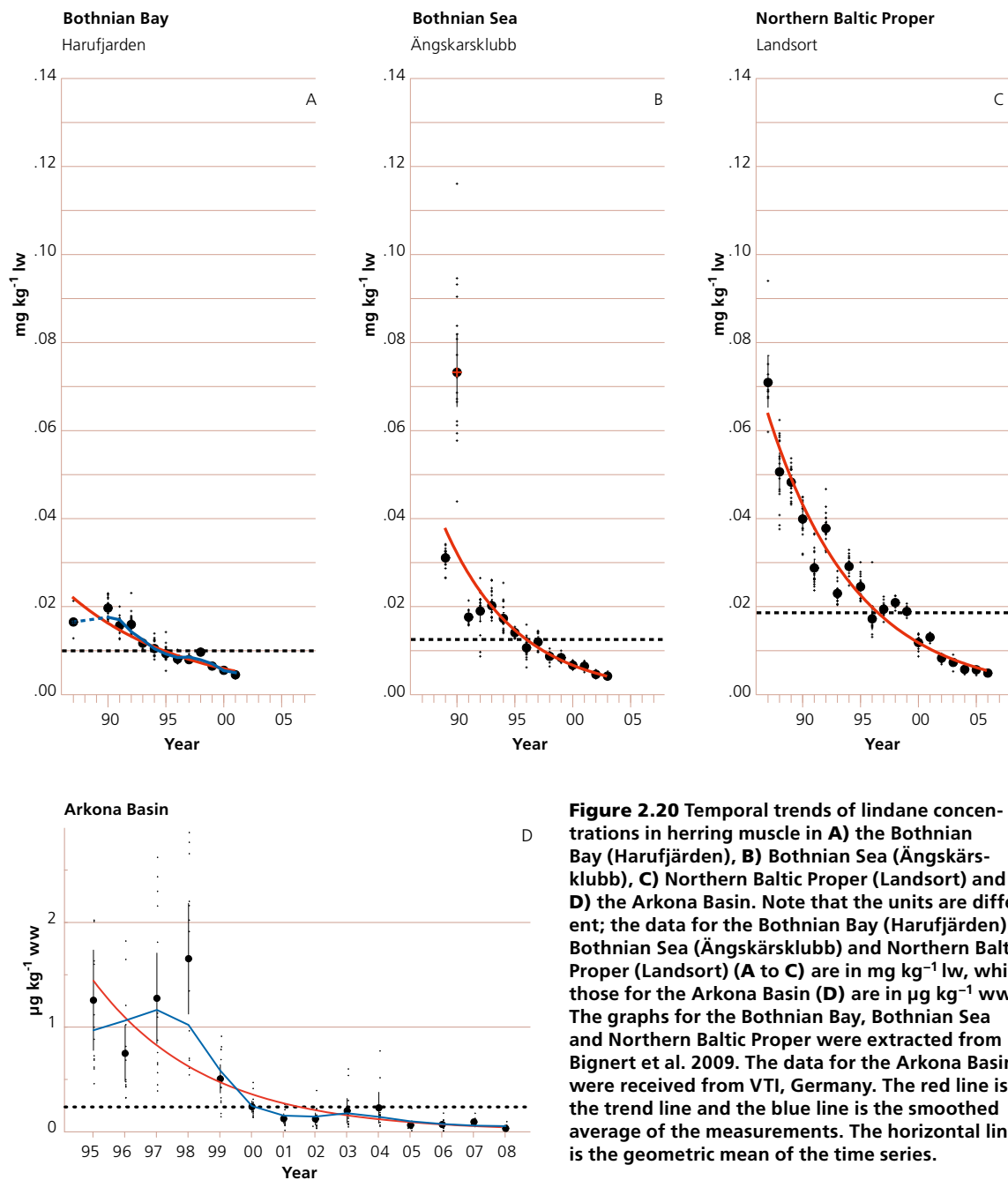
**Figure 2.19** Temporal trends of DDE concentrations in herring muscle in four sub-basins of the Baltic Sea: **A)** Bothnian Bay (Harufjärden) and **B)** Bothnian Sea (Ängskärsklubb), **C)** Gulf of Finland and **D)** Arkona Basin. Note that the units in the graphs are different; the data for the Bothnian Bay (Harufjärden) and Bothnian Sea (Ängskärsklubb) are in  $\text{mg kg}^{-1} \text{lw}$ , while those for the Arkona Basin and Gulf of Finland are in  $\mu\text{g kg}^{-1} \text{ww}$ . The graphs on the Bothnian Bay and Bothnian Sea were extracted from a Swedish report (Bignert et al. 2009), while the data for the Gulf of Finland were obtained from the ICES database. The data for the Arkona Basin were obtained from VTI, Germany. The red line is the trend line and the blue line is the smoothed average of the measurements. The horizontal line is the geometric mean of the time series.

sites), and the threshold was exceeded at one site (Anon. 2008b). Nevertheless, the data were very scarce for drawing proper conclusions.

### Temporal trends

The temporal trend of DDE concentrations in herring muscle has been declining since the end of the 1970s in all Baltic Sea sub-basins. In this assessment, temporal trends are presented for the Bothnian Bay, Bothnian Sea, Gulf of Finland and Arkona Basin in **Fig. 2.19**. The DDE level has decreased significantly at a rate of 4–11% per year since the end of the 1970s and the beginning of 1980s in most matrices analysed (herring, perch *Perca fluviatilis* and eelpout *Zoarces viviparus* muscle, cod *Gadus morhua* liver, and blue mussel *Mytilus* sp.) at several Swedish coastal sites from the Kattegat to the Bothnian Bay. From 1969–2007, the sum of DDTs in the eggs of common guillemot *Uria aalge*

showed a significant decreasing trend of 10% per year on Stora Karlsö, an island in the Western Gotland Basin. DDT has generally decreased more rapidly than the sum of DDTs, which indicates that new DDT inputs to the Baltic Sea have not taken place (Bignert et al. 2009). The sum of DDTs in herring muscle at five Finnish stations (eastern and western Gulf of Finland, Åland Sea, southern and northern Gulf of Bothnia) has declined monotonically from 1986 to 2006 and the decline has been especially significant in the Gulf of Finland and the Åland Sea (Kankaanpää 2007). A Polish study (Szlinger-Richert et al. 2008) observed downward trends of DDE in four of five fish species studied (herring, sprat *Sprattus sprattus*, flounder *Platichthys flesus* and salmon *Salmo salar*) sampled from 1995–2006 in both coastal and offshore waters in the southern Baltic Sea (e.g., Gulf of Gdansk, Eastern Baltic Proper and Bornholm Basin). The German monitoring data (VTI, unpub-



**Figure 2.20** Temporal trends of lindane concentrations in herring muscle in **A)** the Bothnian Bay (Harufjärden), **B)** Bothnian Sea (Ängskärsklubb), **C)** Northern Baltic Proper (Landsort) and **D)** the Arkona Basin. Note that the units are different; the data for the Bothnian Bay (Harufjärden), Bothnian Sea (Ängskärsklubb) and Northern Baltic Proper (Landsort) (A to C) are in  $\text{mg kg}^{-1} \text{lw}$ , while those for the Arkona Basin (D) are in  $\mu\text{g kg}^{-1} \text{ww}$ . The graphs for the Bothnian Bay, Bothnian Sea and Northern Baltic Proper were extracted from Bignert et al. 2009. The data for the Arkona Basin were received from VTI, Germany. The red line is the trend line and the blue line is the smoothed average of the measurements. The horizontal line is the geometric mean of the time series.

lished) on the sum of DDTs and DDE in herring from the Arkona Basin indicate a clear downward trend from the mid-1990s to 2008 (**Fig. 2.19 D**). However, DDE and DDT levels in blue mussels in the coastal waters of Kiel Bight and Mecklenburg-Vorpommern do not show any uniform or distinct trend. The sum of DDTs in the muscle of herring from the Estonian coastal area of the eastern and central Gulf of Finland and the Gulf of Riga decreased from 1995–1998, but thereafter the

levels increased to some extent until the year 2002 for unknown reasons (Roose & Roots 2005).

The trend of lindane concentrations in herring muscle has been declining since the end of the 1980s in the Bothnian Bay, Bothnian Sea, Northern Baltic Proper and Arkona Basin (**Fig. 2.20**). The lindane level has decreased significantly since the 1980s in most matrices analysed (herring and perch muscle, cod liver, eelpout and blue mussel) at several Swedish coastal sites from the Kattegat

to the Bothnian Bay. The decrease is in the range of 10–18% between the end of the 1980s and the present time (Bignert et al. 2009). The lindane level in herring muscle at five Finnish sites (eastern and western Gulf of Finland, Åland Sea, southern and northern Gulf of Bothnia) has declined since 1997, and since 2005 the lindane levels have been below the limit of determination ( $<0.2 \mu\text{g kg}^{-1} \text{ ww}$ ). The data for  $\alpha$ -HCH in herring muscle are rather limited, but the trend seems to be similar to that of lindane (Kankaanpää 2007). The Polish study (Szlinder-Richert et al. 2008) observed an apparent downward trend for the sum of HCHs from 1995–2006 for both coastal and offshore waters in the southern Baltic Sea (e.g., Gulf of Gdansk, Eastern Baltic Proper and Bornholm Basin) in herring and sprat (a fivefold lower level in 2006) and cod (a twofold lower level in 2006), but the decrease was less apparent in flounder and salmon. The German monitoring data (VTI, unpublished) showed that lindane levels in herring from the Arkona Basin clearly decreased within a relatively short period since the end of the 1990s. The  $\alpha$ -HCH concentration in herring showed a similar, but even more pronounced downward trend. Lindane levels in blue mussels from the Mecklenburg-Vorpommern coast exhibited a decrease at all six stations investigated between 1994 and 2001. Since 2002, lindane has been below the limit of determination ( $<0.5 \mu\text{g kg}^{-1} \text{ dw}$ ). Downward trends of lindane in the muscle of herring in Estonian coastal waters of the eastern and central Gulf of Finland and the Gulf of Riga have been observed from 1995 to 2007 (Lukki et al. 2008).

Several national monitoring reports indicate a downward trend of HCB levels in the Baltic marine environment. In Sweden, the HCB level has decreased significantly in almost all matrices analysed (herring, perch and eelpout muscle, cod liver and eggs of common guillemot) at several coastal sites from the Kattegat to the Bothnian Bay. The HCB level in blue mussels has been very low and since 2000 values have been at or below the detection limit (Bignert et al. 2009). In Finland, the HCB level in herring muscle has declined since the end of the 1990s at five sites (eastern and western Gulf of Finland, Åland Sea, southern and northern Gulf of Bothnia) (Kankaanpää 2007). HCB levels in herring from the Arkona Basin showed a decreasing trend from 1994–2008. In addition, HCB in blue mussels from German coastal areas of

Schleswig-Holstein and Mecklenburg-Vorpommern generally were below the limit of determination ( $<1 \mu\text{g kg}^{-1} \text{ dw}$ ). However, Szlinder-Richert et al. (2008) found that HCB levels did not exhibit an obvious trend from 1995–2006 in coastal and offshore waters of the southern Baltic Sea (e.g., Gulf of Gdansk, Eastern Baltic Proper and Bornholm Basin) in any of the fish species studied (herring, sprat, cod, flounder and salmon).

### Effects of pesticides on the marine ecosystem

DDT was originally used as an insecticide, but it also affects vertebrates as well as invertebrates other than those originally targeted. Owing to its persistence, DDT bioaccumulates and biomagnifies in food webs. The decline of white-tailed sea eagles (*Haliaeetus albicilla*) and other predatory birds several decades ago was associated with DDT and its metabolites such as DDE, which caused thinning of eggshells. Piscivorous seabirds and terrestrial predatory birds were most strongly affected due to their position high in the food chains. Although other contaminants such as PCBs were probably also involved, DDT contributed to a decline in many bird populations in the industrialized areas of the Northern Hemisphere during the 1950s, 1960s and 1970s. Following the bans on DDT and PCB during the 1970s around the Baltic Sea, eagle productivity began to recover in the 1980s and since the mid-1990s it has recovered largely back to pre-1950 levels (Green & Künitzer 2003, Helander et al. 2009). More detailed information on the biological effects of DDT is presented in **Chapter 2.3**.



### 2.2.6 Status and trends of perfluoroalkyl substances

Perfluoroalkyl substances (PFAs) are anthropogenic surfactants with exceptional stability and surface tension-lowering potential. Some PFAs have been manufactured for more than five decades. They are applied in industrial processes (e.g., production of fluoropolymers) and in commercial products such as water- and stain-proofing agents and fire-fighting foams. The recent development of trace chemical analytical methods for PFAs has revealed their global presence in biota and waterbodies. Exponentially increasing concentrations of some PFAs in wildlife have been reported during the 1990s (Holmström et al. 2005).

In biota, PFAs tend to accumulate in protein-rich tissues such as blood, liver and eggs. The toxicity of PFAs has mainly been studied in mammals. Toxic effects include weight loss, liver enlargement, immunotoxicity and a number of developmental effects such as post-natal mortality. The consumption of contaminated fish from the Baltic Sea has been suggested to contribute significantly to human blood levels of PFAs (Falandysz et al. 2006). The production and use of perfluorooctane sulfonate (PFOS), one of the major PFA representatives, have been regulated in some countries (e.g., Canada and the EU), but large-scale PFOS production continues in other parts of the world. Based on mammalian toxicity data, the OSPAR Commission (OSPAR 2005, 2006) suggested a predicted no-effect concentration (PNEC) for effects through the food chain of 0.067 mg PFOS kg<sup>-1</sup> food. However, so far no formal or legally binding threshold values have been defined for PFOS or any other PFA in the environment.

#### Sources and transport pathways to the Baltic Sea environment

The pattern of environmental PFA contamination varies greatly between geographical locations, suggesting multiple emission sources. These include primary emissions of PFAs to air and water from their industrial production and application as well as secondary emissions from consumer products or sewage treatment plant effluents. The picture is complicated by the fact that a number of volatile so-called PFA precursor compounds are industrially produced as well. These compounds can undergo long-range atmospheric transport

and subsequently be transformed to PFAs in the environment. This process has been suggested to be important for PFA transport to remote regions such as the Arctic. Contamination in more densely populated areas, such as the Baltic Sea, is believed to be predominantly a result of direct emissions of PFAs and their transport through waterbodies.

#### Current concentrations in Baltic Sea biota, water and sediment<sup>8</sup>

**Biota.** PFAs have been analysed in blue mussels (*Mytilus* spp.), various fish species, eider duck (*Somateria mollissima*), common guillemot (*Uria aalge*) as well as grey, harbour and ringed seals (*Halichoerus grypus*, *Phoca vitulina*, *Phoca hispida botnica*) from the Baltic Sea. Due to the large inter-annual and inter-species variability of results, as well as the different analytical methods and tissue types (blood, liver, muscle, egg) applied in the studies, it is difficult to derive spatial or temporal trends from the diverse literature and screening data. Distinct case studies of spatial and temporal trends of PFAs in the Baltic are therefore presented in this report.

In general, PFOS is the predominant PFA in biota, with the highest levels in marine predatory birds and mammals (**Fig. 2.21**). Several hundreds to one thousand µg kg<sup>-1</sup> ww of PFOS have been found in the livers of grey seals (Southern Baltic Proper and Bothnian Sea; Nordic Council of Ministers, 2004), harbour seals (Great Belt and the Sound; Nordic Council of Ministers, 2004) as well as ringed seals (Bothnian Bay; Kannan et al., 2002) (**Fig. 2.21**). In the eggs of common guillemots (Western Gotland Basin), PFOS concentrations were greater than 1000 µg kg<sup>-1</sup> ww (Holmström et al. 2005). Long-chain perfluorinated carboxylates (PFCAs) also tend to accumulate in the same tissues, however, at levels one to two orders of magnitude lower than PFOS.

Compared to marine mammals and seabirds, levels in fish are generally considerably lower with some exceptions. For example, the liver of pike (*Esox lucius*) from the Gulf of Finland (close to Helsinki and Espoo) contained 200 to 550 µg PFOS kg<sup>-1</sup> ww, as well as up to 140 µg kg<sup>-1</sup> ww of PFOSA, a non-persistent precursor compound of PFOS (Nordic Council of Ministers, 2004). Additional hot spots seem to be the mouth of the river Oder in the

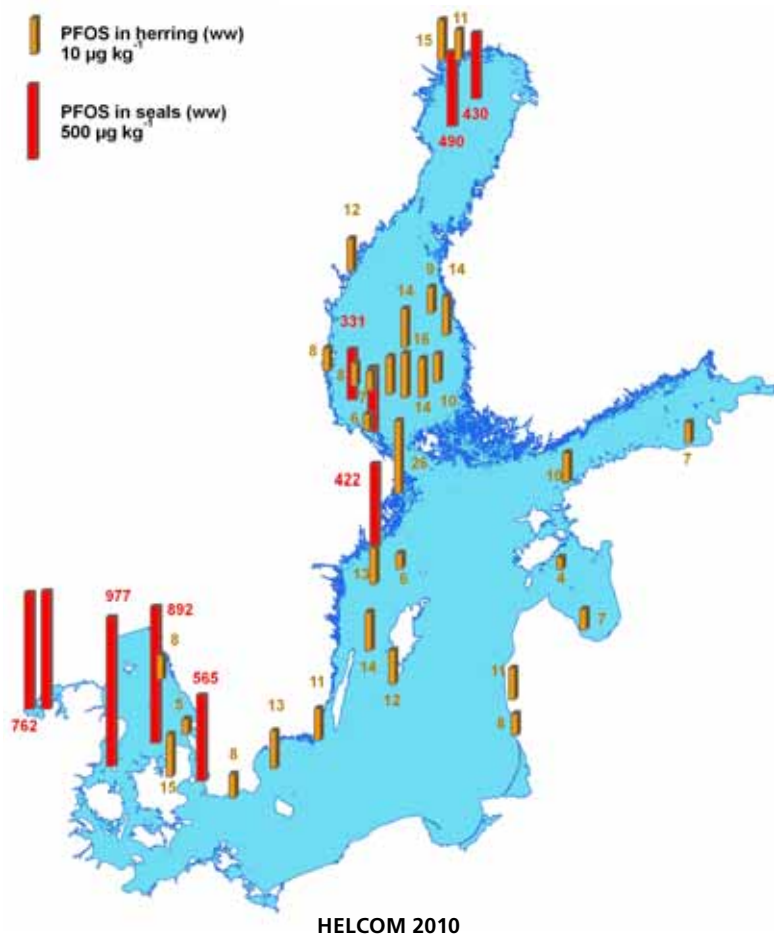
<sup>8</sup> All samples discussed hereafter have been collected between 1996 and 2009.



Bornholm Basin (coast of Poland; Lilja et al. 2009), the Hanö Bight (Bornholm Basin, coast of Sweden; SEPA, 2006) and the Kattegat (Nordic Council of Ministers, 2004). In all these regions, fish liver values of around  $60 \mu\text{g PFOS kg}^{-1} \text{ ww}$  have been observed (perch, cod, eelpout, respectively). Thus, the proposed PNEC level could be exceeded in the liver of fish near major coastal cities and inflows of large European rivers. In regions less affected by anthropogenic pollution, typical PFOS levels in fish liver were in the range  $1\text{--}20 \mu\text{g kg}^{-1} \text{ ww}$ . However, for wildlife or general human consumption, whole body or muscle concentrations would be more relevant as food matrices, which so far have not been found to exceed the PNEC value for PFOS. Compared to liver, PFOS concentrations in muscle were lower, typically in the range  $<1$  to  $5 \mu\text{g kg}^{-1} \text{ ww}$  (Berger et al. 2009b). In blue mussels from the Kattegat, Great Belt and the Sound, PFOS was below the detection limit of  $0.2 \mu\text{g kg}^{-1} \text{ ww}$  (NERI 2007).

PFOS data on Baltic Sea herring liver are reviewed in **Fig. 2.21**. The data originate from three different studies (Berger et al. 2009a, Lilja et al. 2009, Nordic Council of Ministers 2004) with distinct differences in sampling years, number of individuals per sample and analytical methodologies, thus hampering the comparability between studies. Despite these confounding factors, the distribution of PFOS in herring liver was found to be quite homogeneous throughout the Baltic Sea (around  $10 \mu\text{g kg}^{-1} \text{ ww}$ ), which probably is a result of the extraordinary persistence of the compound and its use for more than three decades. A somewhat higher level of  $26 \mu\text{g kg}^{-1} \text{ ww}$  was found along the Swedish coast of the Northern Baltic Proper, reflecting the proximity of the city of Stockholm (**Fig. 2.21**). Again, PFCA levels were typically one to two orders of magnitude lower, with a dominance of long-chain compounds with an odd number of carbon atoms (C9, C11, C13).

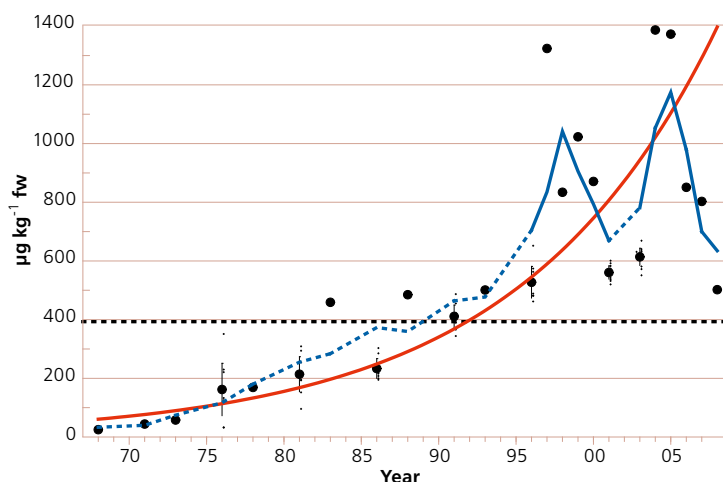
**Water.** Only a few measurements of PFAs in Baltic Sea surface water exist (Nordic Council of Ministers 2004, Theopald et al., 2007, Lilja et al. 2009). They were mostly performed in potentially affected coastal areas. Perfluorooctanoate (PFOA) and PFOS dominated the water samples. Concentrations of PFOA were determined in the range  $<1 \text{ ng l}^{-1}$  (Little Belt, Kiel Bight, Mecklenburg Bight, Arkona Basin) up to  $4\text{--}7 \text{ ng l}^{-1}$  (Little Belt, the Sound, coast of Poland, Gulf of Finland). PFOS was found at levels



**Figure 2.21** Perfluorooctane sulfonate concentrations in herring liver and livers of grey seals (Southern Baltic Proper and Bothnian Sea), harbour seals (Great Belt and Sound) and ringed seals (Bothnian Bay). The bars illustrating concentrations in seals are shown on a different scale from that used for herring. The numbers indicate the actual concentrations ( $\mu\text{g kg}^{-1} \text{ ww}$ ). Results from four different studies are shown (Berger et al. 2009a, Kannan et al. 2002, Nordic Council of Ministers 2004, Lilja et al. 2009). Samples from the different studies were collected in different years (1996–2008) and analysed applying different methods. Therefore, they are not fully comparable.

below or around  $1 \text{ ng l}^{-1}$  for all locations mentioned, with the exception of single measurements of  $2.9 \text{ ng l}^{-1}$  (coast of Poland) and  $22 \text{ ng l}^{-1}$  close to Helsinki (Gulf of Finland). Further away from the coast in the Arkona Basin, PFOA and PFOS levels were  $<0.5 \text{ ng l}^{-1}$ .

**Sediment.** Limited data exist for PFA concentrations in Baltic Sea sediments (Nordic Council of Ministers 2004, SEPA 2006, NERI 2007, Theobald et al. 2007). PFOS and/or PFOA were occasionally detected, but consistently at levels below  $1 \mu\text{g kg}^{-1} \text{ dw}$  or  $\text{ww}$ . The highest levels reported so far have been from the Gulf of Finland close to Helsinki (PFOS  $0.9 \mu\text{g kg}^{-1} \text{ ww}$ ), close to Stockholm (PFOS  $0.6 \mu\text{g kg}^{-1} \text{ ww}$ ) and along the coast of Poland (PFOS and PFOA both around  $0.6 \mu\text{g kg}^{-1} \text{ dw}$ ).



**Figure 2.22.** Temporal trend of PFOS concentrations ( $\mu\text{g kg}^{-1}$  fw) in common guillemot eggs from Stora Karlsö in the Western Gotland Basin. The horizontal line represents the geometric mean, the red line is the trend line and the blue line the running mean smoother of the time series.

#### Spatial trends in liver of herring along the Swedish Baltic Sea coast

Within the Swedish EPA environmental monitoring programme, herring liver samples have been collected along the entire Swedish coastline and analysed annually since 2005. The distribution of PFOS did not show appreciable variations along the Swedish coast (see **Fig. 2.21** and discussion above). On the other hand, PFOSA showed higher concentrations in the Kattegat and the Sound (up to  $10 \mu\text{g kg}^{-1}$  ww) compared to the Swedish east coast ( $1\text{--}3 \mu\text{g kg}^{-1}$  ww), possibly reflecting a current source.

Among the PFCAs, the C9 perfluorononanoate (PFNA) and C11 perfluoroundecanoate (PFUnA) compounds dominated in herring liver. PFNA showed higher levels along the quite densely populated Swedish coast of the Northern Baltic Proper and the Western Gotland Basin ( $4\text{--}6 \mu\text{g kg}^{-1}$  ww) compared to the remote Bothnian Sea and Bothnian Bay ( $1\text{--}3 \mu\text{g kg}^{-1}$  ww) and the Kattegat and Sound ( $<1 \mu\text{g kg}^{-1}$  ww). PFNA is produced deliberately and therefore originates mainly from direct sources (production and use of consumer products) and waterborne transport to remote locations with corresponding dilution effects. In contrast, PFUnA was more evenly distributed along the entire coastline ( $1\text{--}4 \mu\text{g kg}^{-1}$  ww). PFUnA is an unintentional by-product and its presence in the environment is probably due to both direct sources (impurities in PFOA and PFNA production) and indirect sources (airborne precursors).

#### Temporal trends of PFAs in common guillemot eggs from the Western Gotland Basin

PFAs have been analysed retrospectively in the eggs of common guillemot from the Western Gotland Basin on the island Stora Karlsö in a time series starting in 1968. A significant increasing trend was observed for PFOS in eggs, with an increase of 7–10% per year (**Fig. 2.22**, Holmström et al. 2005). This corresponds to 25–30 times higher levels in the early 2000s as compared to the late 1960s. Due to relatively high interannual variations after 1996, the future trend for PFOS in the Baltic marine environment cannot be predicted. However, the running mean smoother (blue line in **Fig. 2.22**) suggests that concentrations may have started to level off after 1997. On the other hand, the trend lines for C<sub>9</sub>–C<sub>13</sub> PFCAs showed an exponential increase up to 2007 (Berger et al. 2008).

#### Measures to reduce contamination by PFAs

Due to their concentrations and/or temporal trends, PFOS, PFOA and PFNA are currently the PFAs of most concern in the Baltic Sea environment. These compounds originate predominantly from direct emission sources, such as industrial production and application. The leading PFA manufacturers in Europe and North America have already agreed to take measures to significantly reduce emissions (Prevedouros et al. 2006). It remains to follow up on whether these measures show a positive effect on environmental levels. A greater challenge for the future may be to control emissions from new PFOS manufacturers in South-east Asia (Ministry of Environmental Protection of China 2008). PFOS was recently added to the Stockholm Convention and within the EU its use has already been limited (see **BOX 4** on page 80 and **Chapter 4.2.4**).

#### 2.2.7 Status and trends of some brominated flame retardants

Polybrominated diphenylethers (PBDEs) are used as an additive flame retardant (BFR) in plastics, textiles and electronics. Three types of polybrominated diphenylether (PBDE) products are produced with varying degrees of bromination: penta-BDE, octa-BDE and deca-BDE products. The main components of penta-BDE are referred to as lower-brominated BDEs and octa-BDE and deca-BDE as higher-brominated BDEs. The penta-BDE product

mainly contains six BDE congeners (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153 and BDE-154). The octa-BDE product mainly contains BDE-183, a hepta-BDE, and octa-BDEs, nona-BDEs and deca-BDE. The deca-BDE product contains mainly deca-BDE and some nona-BDEs. Penta-BDE has been identified as a priority hazardous substance under the EU Environmental Quality Standard Directive (Anon. 2008b).

Hexabromocyclododecane (HBCDD) is used as a flame retardant in polystyrene-based insulation products employed in the building and construction industry and in high-impact polystyrene in electrical or electronic parts. It is also used in textiles for furniture, mattress ticking and for seating in vehicles. Commercial HBCDD products are mixtures mainly of three isomers ( $\alpha$ -HBCDD,  $\beta$ -HBCDD,  $\gamma$ -HBCDD). A typical ratio in technical products is: 10–13%, 1–12% and 75–89%, respectively. HBCDD is lipophilic and persistent, and bioaccumulates in the food web. The European Chemical Agency has recently identified HBCDD as one of 14 substances of “Very High Concern”. However, there are currently no restrictions on the production and use of HBCDD.

PBDEs have negative effects on the behaviour and learning of mice and rats after prenatal exposure (Viberg 2004, Viberg et al. 2006, 2007, Costa & Giordano 2007). Effects on thyroid hormone transport and metabolism have also been reported (Legler 2008). Laboratory exposure studies of environmentally relevant doses of lower brominated BDEs in birds (American kestrels) have shown immunosuppression, oxidative stress, effects on thyroid homeostasis and decreased vitamin A and E levels (Ferne et al. 2005a, 2005b). Observational studies also report reduced eggshell thickness and reproductive success in American kestrels (Ferne et al. 2009).

The effects of HBCDD include an increase in liver weight in rats, as well as an increase in pituitary and thyroid weight and an effect on the thyroid hormone axis (van der Ven et al. 2006). Developmental and neurotoxic effects such as changes in spontaneous behaviour and learning and memory defects have also been indicated (Eriksson et al. 2006).

### Sources

PBDEs are emitted to the environment from the production and use of flame-protected materials and from waste sites. The use of the penta- and octa-BDE products has been banned in the EU since 2004, but they are still found in imported products. Deca-BDE is still in use but has been restricted in the EU since 2008 (Anon. 2002).

PBDEs mainly spread to the Baltic Sea environment by diffuse distribution via the atmosphere and rivers. The environmental distribution differs between the lower-brominated BDEs and the higher-brominated BDEs. Higher-brominated BDEs have low water solubility and are mainly distributed in the sediments. They are not easily transported from the sediment and suspended particulate material to marine organisms. Deca-BDE is thus found only in very low concentrations in fish, in contrast to the lower-brominated BDEs which are commonly found in marine organisms.

HBCDD leaches easily into the environment. It can be released during the entire life-cycle of a product, from production and use to waste disposal. HBCDD mainly spreads to the environment by diffuse distribution via the atmosphere and rivers. For further information, see HELCOM 2009c.

### Status in biota

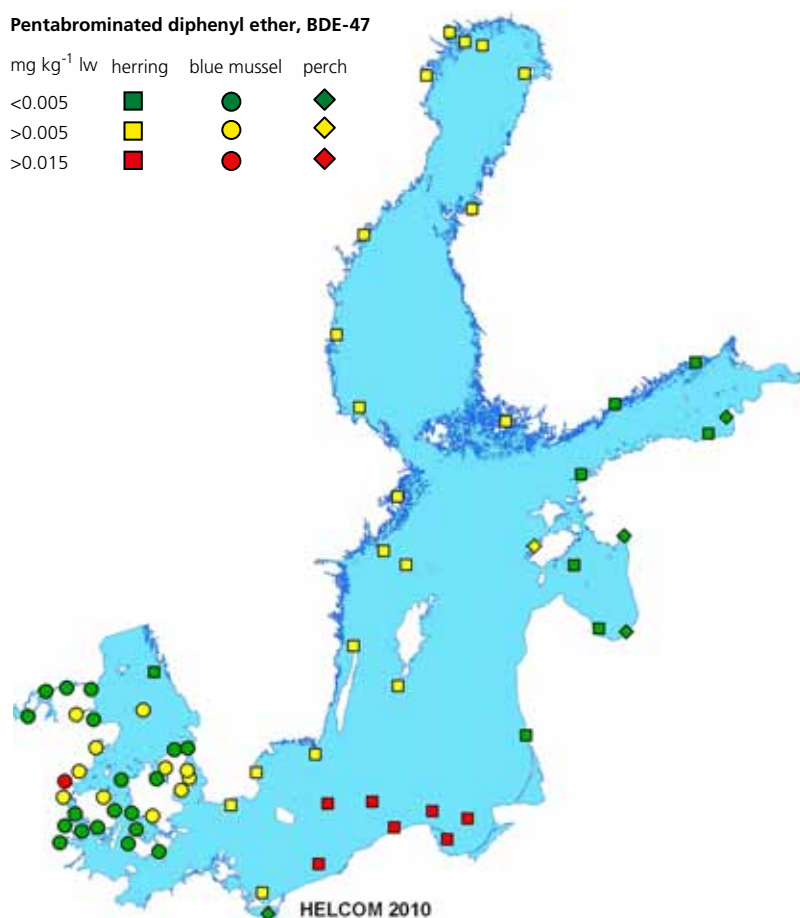
To assess the penta-BDE contamination in marine organisms in the Baltic Sea region, BDE-47 was chosen as a representative for the lower-brominated BDE group. Due to the lack of formally adopted threshold levels or even publications regarding biological thresholds for PBDE, this study has evaluated concentrations of BDE-47 in relation to a concentration at the lower end of the concentration gradient in the Baltic Sea, i.e., 0.005 mg kg<sup>-1</sup> lw. Thus, exceedances of the threshold do not necessarily indicate ecotoxicological concern.

The concentrations of BDE-47 varied throughout the Baltic Sea. In the eastern part (Gulf of Finland and Gulf of Riga), concentrations were below the threshold level (**Fig. 2.23**, green). Levels were moderate in the Bothnian Bay and along the Swedish east coast (**Fig. 2.23**, yellow). In the southern regions outside the coast of Poland, levels were more than threefold higher than the threshold level (**Fig. 2.23**, red). Along the Danish

coasts and the Swedish west coast, concentrations were good to moderate, with higher levels in the Little Belt.

In marine top predators, PBDE concentrations indicate a cause for concern. For example, white-tailed sea eagles in the Baltic Sea (Nordlöf et al. 2007) have BDE concentrations (sum of four BDEs with four to six bromines) up to four times higher than the reported effect levels in exposed American kestrels, which were causing adverse effects (Ferne et al. 2005a, 2005b, 2009).

Deca-BDE has generally not been analysed in fish from the Baltic Sea or has been found in very low concentrations. However, Burreau et al. (2004) reported relatively high levels (median  $48 \mu\text{g kg}^{-1}$  lw) in roach from the Archipelago Sea (Åland). Deca-BDE was also found in perch ( $1.3 \mu\text{g kg}^{-1}$  lw) and pike ( $1.7 \mu\text{g kg}^{-1}$  lw) from the same area.



**Figure 2.23** Status of BDE-47 concentrations in herring and perch muscle and in blue mussel. The threshold value was set at  $0.005 \text{ mg kg}^{-1} \text{ lw}$  and a large deviation from the threshold (three times the threshold) is indicated by the red colour.

HBCDD concentrations in herring muscle were found to exceed the threshold value<sup>9</sup> at all monitoring stations near the Swedish coast from the Bothnian Bay to the Kattegat (data not shown). In contrast, HBCDD did not exceed the threshold level in the muscle of flounder and perch in the coastal waters of Lithuania, in the Gulf of Riga, in the Gulf of Finland or in Szczecin Lagoon (Lilja et al. 2009).

### Status of PBDEs in sediment

Relatively few studies have reported PBDEs in marine sediment from the HELCOM region (see HELCOM 2009c). In a Danish study, deca-BDE was reported to be the dominant BDE congener compared to lower-brominated congeners. The highest concentrations of deca-BDE ( $21 \mu\text{g kg}^{-1}$  dw) were found in Copenhagen harbour (Christensen & Platz 2001). The Copenhagen harbour region exhibited BDE-47, BDE-99, BDE-100 and BDE-154 concentrations of 0.24, 0.76, 0.17 and  $0.08 \mu\text{g kg}^{-1}$  dw, respectively, which were among the highest in the southwestern Baltic Sea<sup>10</sup>.

The highest levels of penta-BDE were found in the Limfjord, Denmark. The Swedish sediment monitoring programme, covering 16 stations in the coastal and offshore areas of the Baltic Sea, showed that concentrations of BDE-47, BDE-99 and BDE-100 were clearly the highest in the Kattegat ( $0.44$ ,  $0.62$  and  $0.08 \mu\text{g kg}^{-1}$  dw, respectively, at station Fladen, SGU 2003).

### Temporal trends

Several time series of BDE-47 concentrations in herring muscle tissue from the Bothnian Sea, the Baltic Proper and the Kattegat showed significant decreasing trends, with half-lives in the herring populations of about 6–8 years, exemplified in **Fig. 2.24**.

Time series of HBCDD from monitoring sites along the Swedish coasts showed no significant trends in herring muscle tissue (**Fig. 2.25**), whereas a clear increasing trend of about 3% per year ( $p < 0.001$ ) was detected in eggs from common guillemot (*Uria aalge*) collected from Stora Karlsö in the Western Gotland Basin (**Fig. 2.26**).

<sup>9</sup> Swedish criterion  $0.5 \mu\text{g kg}^{-1}$  lw.

<sup>10</sup> BDE-47:  $0.27 \mu\text{g kg}^{-1}$  dw, BDE-99:  $1.16 \mu\text{g kg}^{-1}$  dw, BDE-100:  $0.3 \mu\text{g kg}^{-1}$  dw, BDE-154:  $0.2 \mu\text{g kg}^{-1}$  dw (Danish sediment monitoring programme 2007).

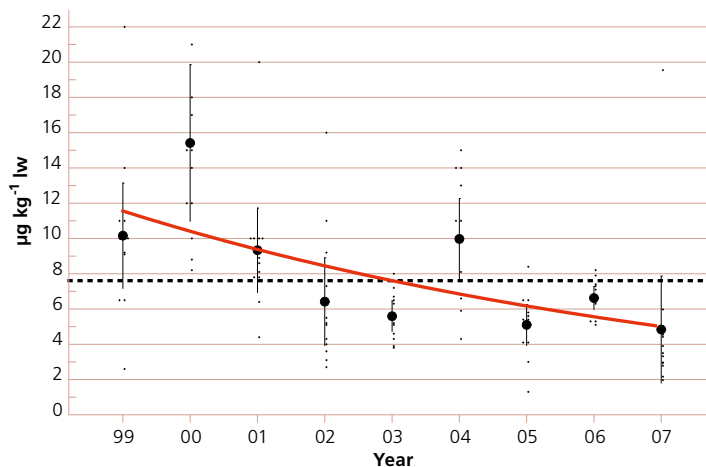
### 2.2.8 Status and trends of polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are widespread environmental contaminants that originate from pyrolytic and petrogenic sources. They are also formed in natural processes (diagenetic and biogenic compounds). PAHs make up a broad group of compounds that are composed of two to six fused benzene rings. Among them, 16 PAHs are recommended as priority pollutants by the United States Environmental Protection Agency (U.S. EPA), the WFD and MSFD. PAHs are non-polar, lipophilic and relatively persistent compounds. Due to these properties, they tend to accumulate in the fatty tissues of marine organisms, although large differences are found between species.

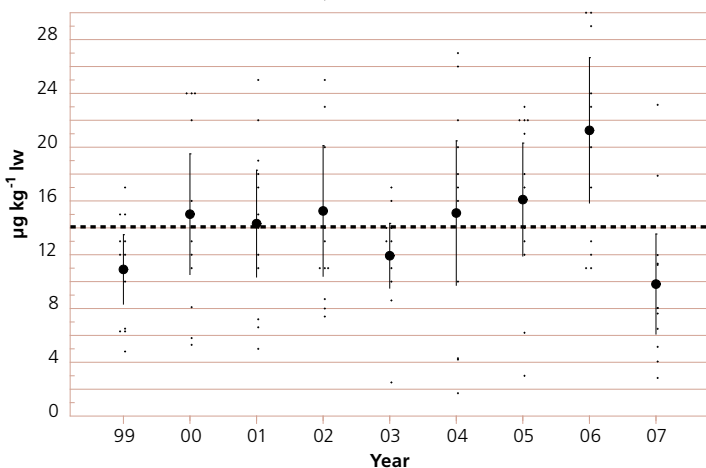
PAHs are generally considered to be toxic to aquatic organisms owing to their mutagenic and carcinogenic effects (White 1986). Benzo[a]pyrene, dibenzo[a,h]anthracene and benzo[b]fluoranthene have been recognized as carcinogenic agents to humans or experimental animals (Table 2.4). While PAHs can be weakly carcinogenic or non-carcinogenic, they can modify the carcinogenic activity of other PAHs in complex mixtures (Marston et al. 2001). Therefore, the synergistic effects of PAHs can be larger than the total levels of PAHs would indicate. Higher concentrations of PAHs are also harmful to the reproduction of fish and can damage cellular membrane structures (Knutzen 1995). When PAHs are exposed to sunlight, the mechanism known as phototoxicity is involved, producing reactive and toxic photo-modification products.

#### Sources of PAHs in the Baltic Sea

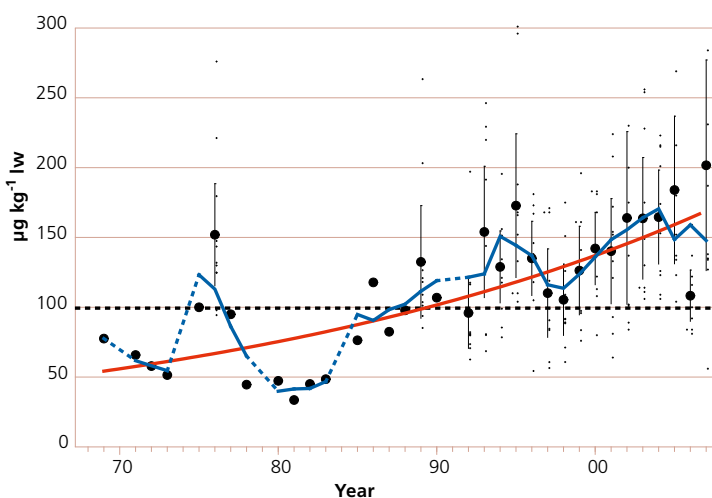
Anthropogenic PAH sources in the marine environment include the release of crude oil products (petrogenic source) and all types of incomplete combustion of fossil fuels—coal, oil and gas or wood and waste incineration (pyrolytic sources) (Neff 2004). Some PAHs are formed naturally, but the majority of PAHs in the marine environment come from anthropogenic activity. Each source generates a characteristic PAH pattern, enabling distinction of the sources in a sample; concentration relationships of individual PAH compounds can be used to reveal the sources of the PAH compounds (Baumard et al. 1998, Sicre et al. 1987, Yunker et al. 2002).



**Figure 2.24** The temporal trend of BDE-47 concentrations ( $\mu\text{g kg}^{-1}\text{ lw}$ ) in the muscle of herring from Landsort, Northern Baltic Proper. The red line is the trend line of the measurements and the horizontal line is the geometric mean of the time series.



**Figure 2.25** The temporal trend of HBCDD concentrations ( $\mu\text{g kg}^{-1}\text{ lw}$ ) in the muscle of herring from Landsort, Northern Baltic Proper. The horizontal line is the geometric mean of the time series.



**Figure 2.26** The temporal trend of HBCDD concentrations ( $\mu\text{g kg}^{-1}\text{ lw}$ ) in eggs of common guillemot from Stora Karlsö, Western Gotland Basin. The red line is the trend line and the blue line is the smoothed average of the measurements. The horizontal line is the geometric mean of the time series.

**Table 2.4** Characteristics of the 16 priority polycyclic aromatic hydrocarbons. The environmental assessment criterion (EAC) is according to OSPAR (2009a). The carcinogenicity status is assigned by the International Agency for Research on Cancer (IARC); the lower the value, the greater the carcinogenicity\*. The  $K_{OW}$  value refers to the bioaccumulation potential of the compound; the higher the value, the greater the potential to bioaccumulate.

Name of the compound	Number of rings	EAC in mussels $\mu\text{g kg}^{-1}$ dw	EAC in sediment $\mu\text{g kg}^{-1}$ dw 2.5% C	Carcino-genicity (IARC)	Log $K_{OW}$
Naphthalene	2	340	160	2b	3.37
Acenaphthylene	3	—	—	—	4.07
Acenaphthene	3	—	—	3	3.98
Fluorene	3	—	—	3	4.18
Phenanthrene	3	1700	240	3	4.45
Anthracene	3	290	85	3	4.45
Fluoranthene	4	110	600	3	4.90
Pyrene	4	100	665	3	4.88
Benz[a]anthracene	4	80	261	2b	5.61
Chrysene	4	—	384	2b	5.16
Benzo[b]fluoranthene	5	—	—	2b	6.04
Benzo[k]fluoranthene	5	—	—	2b	6.06
Benzo[a]pyrene	5	600	430	1	6.06
Dibenz[a,h]anthracene	5	—	—	2a	6.84
Indeno[1,2,3-c,d]pyrene	6	—	240	2b	6.58
Benzo[g,h,i]perylene	6	110	85	3	6.50

\*) The International Agency for Research on Cancer has classified carcinogens into groups. Group 1 includes substances that have been proven to cause cancer in humans. Group 2a indicates that the substance is probably carcinogenic to humans. Group 2b means that carcinogenic effects have been shown on experimental animals. Group 3 indicates that the substance is not classifiable in respect of its carcinogenicity to humans (according to IARC classification).

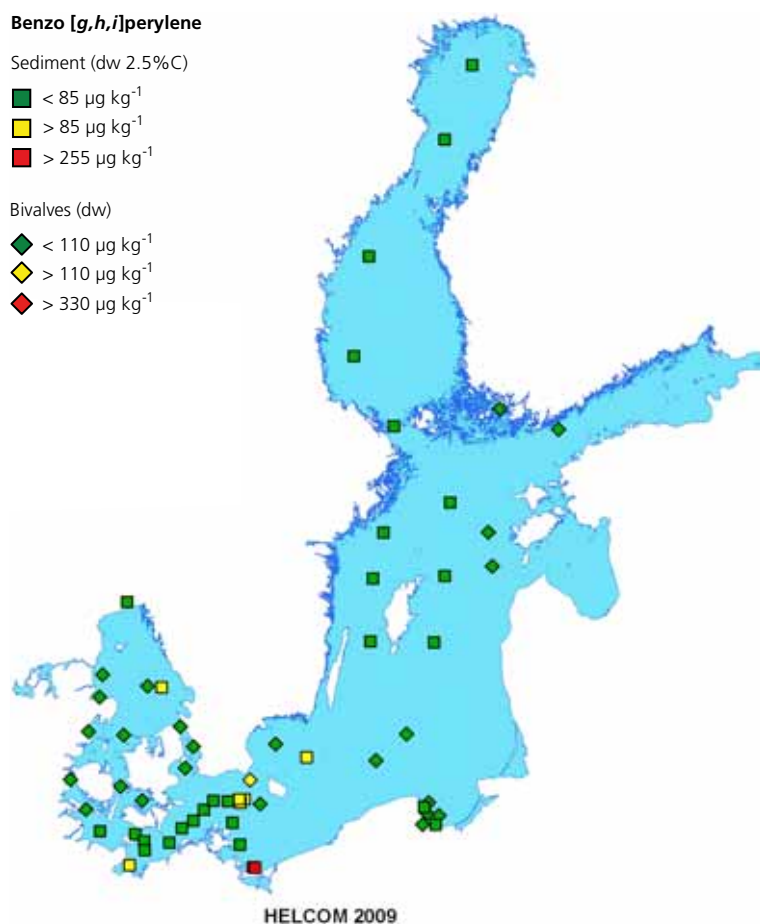
#### Benzo [g,h,i]perylene

Sediment (dw 2.5% C)

- < 85  $\mu\text{g kg}^{-1}$
- > 85  $\mu\text{g kg}^{-1}$
- > 255  $\mu\text{g kg}^{-1}$

Bivalves (dw)

- ◆ < 110  $\mu\text{g kg}^{-1}$
- ◆ > 110  $\mu\text{g kg}^{-1}$
- ◆ > 330  $\mu\text{g kg}^{-1}$



**Figure 2.27** Map of the status of benzo[g,h,i]perylene concentrations in bivalves (blue mussel *Mytilus* sp. and clam *Macoma balthica*) and surface sediments in relation to the threshold values (EAC, OSPAR 2009a).

In this assessment, seven different molecular indices calculated from both sediment and biota showed that pyrolytic sources predominate in the Baltic Sea PAH contamination. However, in the Gulf of Finland and some areas in the western Baltic Sea (Sound, Belt Sea and Kattegat), molecular indices indicated a significant contribution of petrogenic PAHs. This may indicate that atmospheric deposition combined with shipping activities is the main source of PAHs in these areas. The dominance of pyrolytic sources could be surprising in view of the heavy maritime traffic and illegal oil discharges. On the other hand, no reliable information is available on the airborne deposition of PAHs onto Baltic Sea surface waters (Pikkarainen 2004).

#### Status of PAHs in the Baltic Sea marine environment

The widespread occurrence of the 16 PAH compounds in the Baltic Sea ecosystem (sediments, biota and water) has been relatively well-documented in national monitoring programmes and

a number of scientific papers (Witt 1995, Kowalewska & Konat 1997, Rantamäki 1997, Baumard et al. 1999, Pikkarainen 2004, Lubecki et al. 2006). However, the coverage of monitoring data is much better for the western part of the Baltic Sea than for the remaining sea areas. Moreover, the matrix of sampling and the sampling years vary among the Baltic Sea countries. In this assessment, special emphasis has been given to three compounds: benzo[a]pyrene, benzo[b]fluoranthene and benzo[g,h,i]perylene.

The highest levels of PAHs were observed in lagoon areas (e.g., Szczecin lagoon), in the vicinity of harbours (e.g., port of Copenhagen) and in accumulation areas (e.g., Arkona Deep and Gdańsk Deep). In general, the concentrations of low molecular weight PAHs such as fluoranthene and phenanthrene in Baltic biota and sediments do not exceed the OSPAR toxicity threshold values in any of the sub-regions (OSPAR 2009a). The high molecular weight compound benzo[a]pyrene, which has been shown to be highly toxic, carcinogenic and mutagenic, was below the threshold values in both sediment and bivalves in the entire sea area.

The other compound assessed, benzo[g,h,i]perylene, is a 6-ring compound, which has not been proven to be carcinogenic to humans, but as a high molecular weight PAH it is highly lipophilic and bioaccumulating, and may cause adverse effects on reproduction. Benzo[g,h,i]perylene is present in high concentrations in Baltic Sea sediments, often exceeding the threshold values (Fig 2.27). In bivalves and sediments, it was found to exceed the threshold value in the southern and southwestern sea areas.

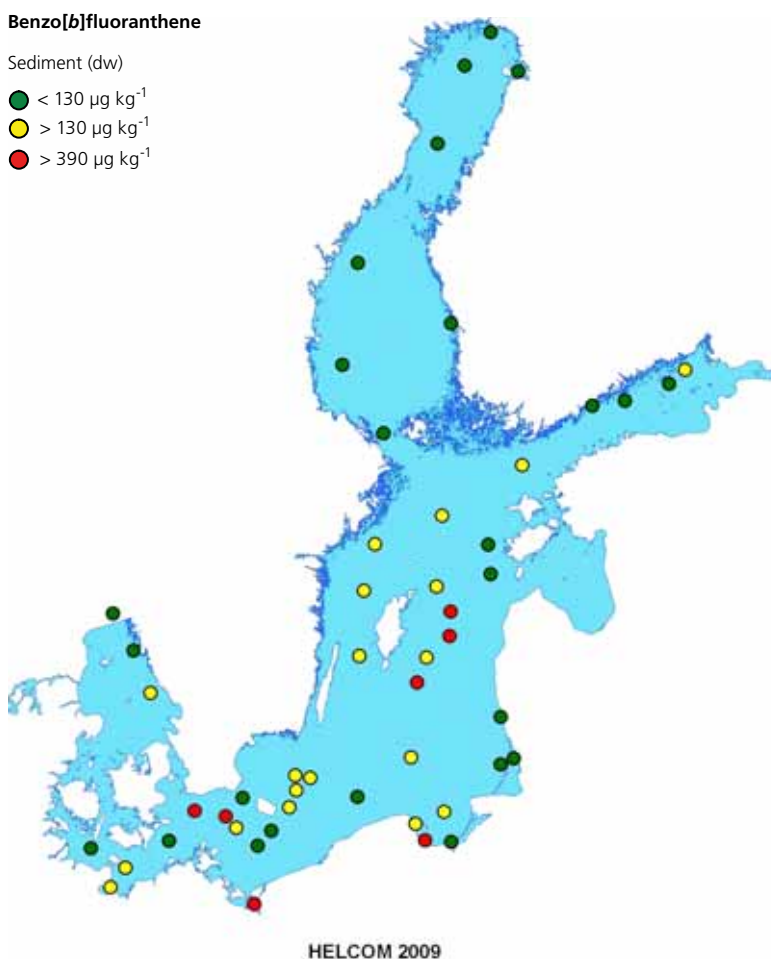
Benzo[b]fluoranthene, another high molecular weight PAH with carcinogenic effects, was found to exceed the threshold values in sediments in all basins except the Bothnian Sea and Bothnian Bay (Fig 2.28). However, the threshold value for benzo[b]fluoranthene<sup>11</sup> is not normalized to sediment carbon and therefore the spatial comparison may be misleading due to the different seabed characteristics (see Fig. 1.3).



#### Benzo[b]fluoranthene

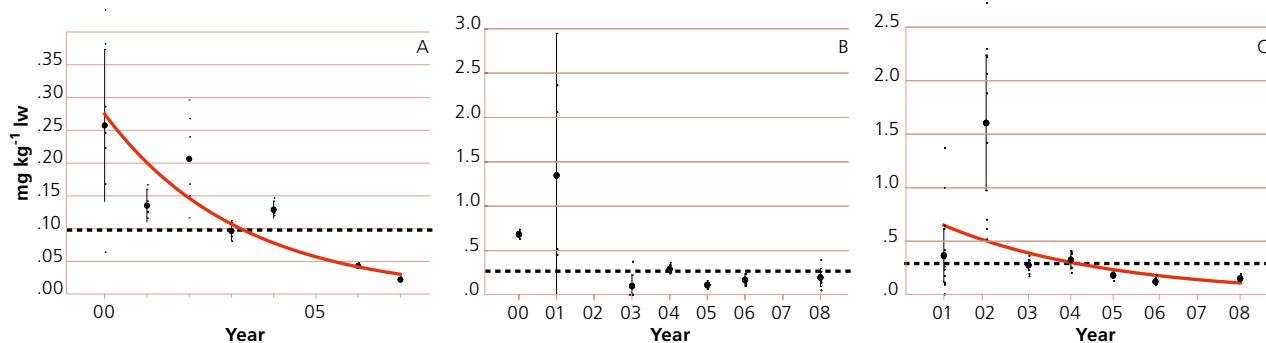
Sediment (dw)

- < 130  $\mu\text{g kg}^{-1}$
- > 130  $\mu\text{g kg}^{-1}$
- > 390  $\mu\text{g kg}^{-1}$



**Figure 2.28** Map of the status of benzo[b]fluoranthene concentrations in surface sediments in relation to the threshold value of 130  $\mu\text{g kg}^{-1}$  dw (U.S. EPA T20 value to indicate the boundary of a 20% probability to observe toxicity). The red colour refers to a status of high concern, given as three times the threshold value.

<sup>11</sup> The threshold is 130  $\mu\text{g kg}^{-1}$  dw and is based on the T20 value, which indicates a 20% probability of observing toxicity in an amphipod species (U.S. EPA).



**Figure 2.29** Temporal trends of benzo[a]pyrene concentrations ( $\text{mg kg}^{-1}$  lipid) in blue mussels (*Mytilus* spp.) from **A)** Århus Bight, **B)** Great Belt and **C)** the Sound area.

### Temporal trends

Temporal trends of PAH concentrations in biota and surface sediments cannot be assessed in the majority of the Baltic Sea area due to temporally and spatially fragmented data sets. Most of the information is available for the PAH group as a whole. Thus far, taking into account data from 1999 to 2008, temporal trends for individual PAHs have been determined using Danish national monitoring data. Examples of temporal trends of benzo[a]pyrene concentrations in blue mussels collected from Århus Bight, the southern Sound and the Great Belt area are presented in **Fig. 2.29**. Benzo[a]pyrene concentrations in mussels from Århus Bight and the Sound were characterized by a statistically significant decrease, while mussels from the Great Belt show relatively constant concentrations over time. However, it is difficult to detect and interpret temporal variations without long time series and case studies, including examination of environmental conditions.

### 2.2.9 Status of substances not monitored on a regular basis

A number of studies have been carried out in the Baltic Sea to determine the presence of chemicals that are not monitored on a regular basis. This section assesses the results of screening data, with special emphasis on nonylphenol (NP), octylphenol (OP), bisphenol A, short-chain chlorinated paraffins, phthalates and pharmaceuticals.

#### Data availability from screening projects

Several hazardous substances have been recognized as persistent, bioaccumulating and toxic, but there are very few data to assess their status in the marine environment. From 2000–2007,

Sweden screened the occurrence of approximately 200 substances in the Baltic (Sternbeck & Österås 2009). The substances screened included, for example, pharmaceuticals, biocides, phthalates, phenolic compounds, antibacterial agents, flame retardants and a variety of high-volume chemicals. Of these substances, 45 organic pollutants were detected in biota, sediment or surface water in the Baltic Sea.

The HELCOM SCREENING project (2008–2009) carried out a screening study of substances identified in the Baltic Sea Action Plan (Lilja et al. 2009). The project concentrated on the eastern Baltic Sea, with an additional reference station in southeastern Sweden (Utlängan). There were eight substance classes studied with altogether 47 substances or isomers.

#### Contamination of the so-called reference areas

The results of the screening studies showed that relatively high concentrations of several hazardous substances were found in areas that had originally been chosen as reference areas and initially considered to be unpolluted. The substances that were found in the “reference areas” were generally those with PBT properties (persistent, bioaccumulating and toxic) and known to be subject to long-distance atmospheric transport. However, there were also some exceptions: substances such as triclosan, bromophenols, pentachlorophenols and diethylhexyl adipate. These substances were detected in fish from reference locations, although there had so far been no indication of their bioaccumulation or capability for long-distance transport (**Fig. 2.30**). This may indicate that hazardous substances are more widespread than predicted



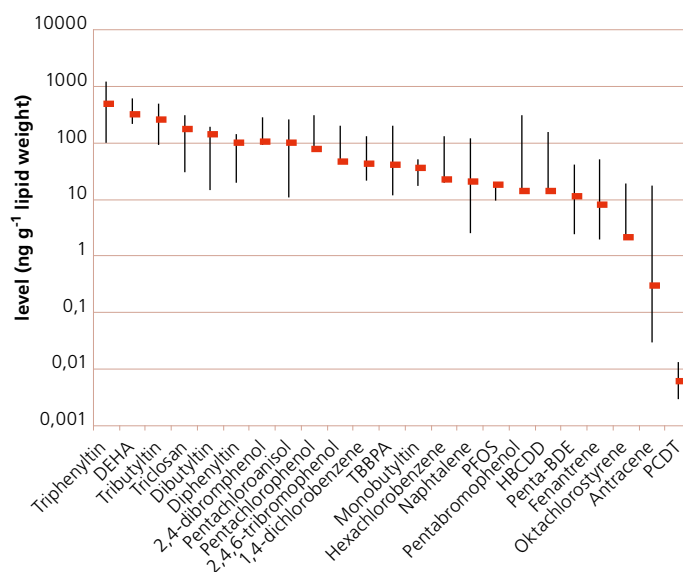
or that further research needs to be done on the long-distance transport of these substances.

Another striking result was that only a few substances had higher levels in the so-called “affected areas” compared to the reference locations. The substances that showed high concentrations near anthropogenic sources included tributyltin (TBT), triphenyltin (TPT) and polychlorinated dibenzothiophenes (PCDT) (Sternbeck & Österås 2009). Moreover, the concentrations of tetrabromobisphenol A (TBBPA) and triclosan were so high that adverse environmental effects are possible. The status of TBT and TPT is discussed in Section 2.2.4, above.

### Status of chlorinated paraffins

Chlorinated paraffins (CPs) are mixtures of polychlorinated n-alkanes. CPs are lipophilic and considered persistent, bioaccumulating and toxic to aquatic organisms. Short-chain chlorinated paraffins (SCCP) are classified as a priority hazardous substance group in the EU Water Framework Directive (Anon. 2000a). Information regarding the use of CPs in HELCOM countries is limited, but indicates a decreasing use of SCCPs due to their substitution by medium-chain chlorinated paraffins (MCCP), for which the trend of use is increasing (HELCOM 2009c). SCCP and MCCP were found at low concentrations in the liver of fish from the eastern Baltic Sea, Szczecin Lagoon and southeast coast of Sweden (SCCP: 5.2–62  $\mu\text{g kg}^{-1}$  ww; MCCP: 3.9–15  $\mu\text{g kg}^{-1}$  ww) (Lilja et al. 2009) (**Fig. 2.31**). Previous studies in the liver of flounder in Kiel Bight and the southwestern Baltic Sea have shown SCCP concentrations of 99–221  $\mu\text{g kg}^{-1}$  ww and MCCP concentrations of 31–206  $\mu\text{g kg}^{-1}$  ww (Oehme et al. 2005, Reth et al. 2005). All of the SCCP concentrations are two orders of magnitude lower than the proposed PNEC level, whereas the highest MCCP concentrations exceed the PNEC of 170  $\mu\text{g kg}^{-1}$  ww (Anon. 2005).

Some of the difficulties of finding hazardous substances in the environment are related to their chemical properties. Fish is an appropriate matrix for monitoring most of the above-mentioned substances, whereas nonylphenol, octylphenol and their ethoxylates should be monitored in water or preferably sediment because they are metabolized in fish.



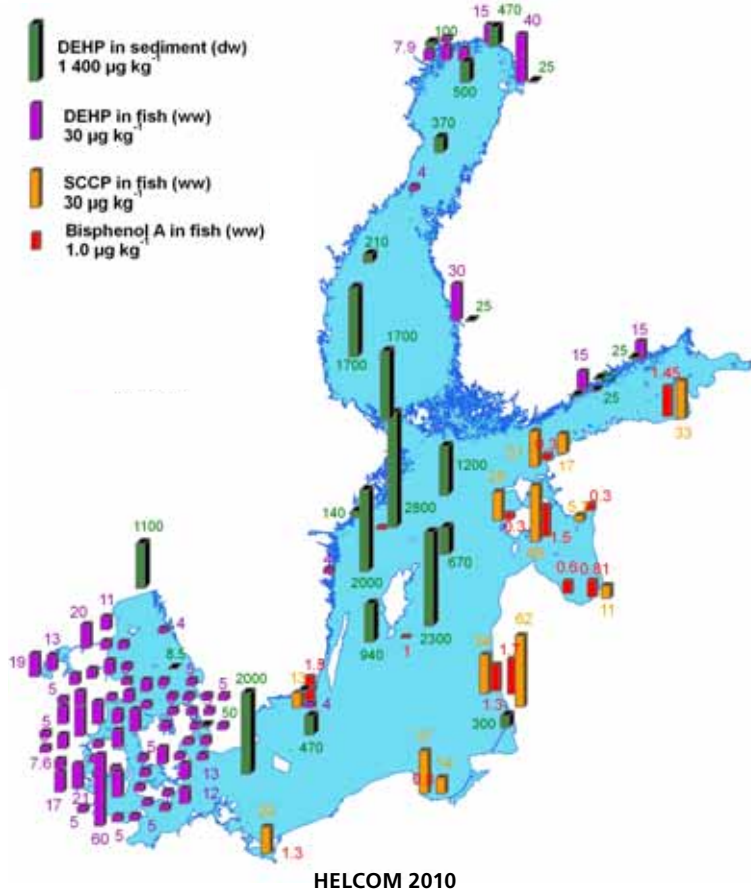
**Figure 2.30** Concentrations of the most commonly observed substances in the muscle of fish in background areas in the Baltic Sea. Note the logarithmic scale on the vertical axis (modified from Bignert et al. 2006b).

### Status of phthalates

Phthalates are primarily used as plasticizers and, from a global perspective, they are the most commonly used plasticizer. Low levels of phthalates can be found almost everywhere. They reach the environment via leakage from waste deposits and effluents from sewage treatment plants. This continuous leakage and exposure is a warning signal as they have been shown to have effects on the human reproductive system of both males and females.

There are continuous losses of phthalates to the environment, but the pattern of environmental levels seems to reflect the consumption pattern five years ago. This may be explained by the large amounts of diethylhexyl phthalate (DEHP) still present in the technosphere (Palm Cousins et al. 2007). Therefore, further studies will be needed to show the distribution of presently used phthalates in the environment. DEHP bioaccumulates, but the uptake in biota seems to be limited. This is probably due to its preference to bind to particles in water.

Based on the low concentrations in the air in reference areas, it has been considered that the long-range transport of phthalates is negligible. On the other hand, concentrations of DEHP close to sources are so high that biological effects are possible. **Figure 2.31** shows the concentrations of DEHP in Baltic Sea surface sediments and biota.



**Figure 2.31** Concentrations of bisphenol A, short-chain chlorinated paraffins (SCCP) and diethylhexyl phthalate (DEHP) in fish muscle and blue mussels as well as DEHP in surface sediments. The bars are in different scales and therefore one measurement bar for each of the substances is shown as a reference.



Sediment levels were especially high in the Bothnian Sea, Baltic Proper and Arkona Basin (**Fig. 2.31**). DEHP levels in mussels and fish were high in coastal areas, particularly near cities. However, PNECs for sediment and biota were not exceeded in any area (Anon. 2005).

After 2000–2001, a shift in the use of phthalates took place as DEHP was replaced by di-isononylphthalate (DINP) and di-isodecylphthalate (DIDP). DIDP and DINP account for the majority of the phthalate use within the EU today (Palm Cousins et.al. 2007), but there were no data to assess their status in the Baltic Sea environment in this assessment.

#### Status of bisphenol A

Bisphenol A is one of the world's most commonly used chemicals. It is used primarily in the production of polycarbonate plastics and epoxy resins. It is used in many plastic materials, such as water bottles, medical equipment and household appliances. Losses to the environment are probably derived from the processing industry and from the use and degradation of various products.

Bisphenol A is an endocrine disruptor, which can mimic the body's own hormones and may lead to negative health effects. The main source of human exposure is most likely via direct exposure and the use of, for example, plastic bottles containing bisphenol A.

Bisphenol A can be toxic to aquatic organisms. The levels in the environment are generally low, but the recent HELCOM screening found concentrations in fish that may cause adverse effects.

As a water-soluble compound, bisphenol A would not be expected to readily bioaccumulate in fish, which indicates that ongoing discharges maintain the observed high concentrations in the Baltic Sea. The bisphenol A concentrations in fish in Estonia, Latvia, Lithuania, Poland and southeastern Sweden ranged between 0.6 and 3.9  $\mu\text{g kg}^{-1}$  ww in herring, perch and flounder (**Fig. 2.31**).

#### Status of nonylphenol

The term "nonylphenol" can apply to a large number of isomeric compounds. Nonylphenols

(NP) are or were recently used in the paint and plastics industry, the production of washing agents and in the production of nonylphenol ethoxylates (NPE). The main environmental recipients are surface waters that receive municipal and industrial wastewater and soil due to the recycling of sewage sludge (HELCOM 2002b). Atmospheric depositions of NP and NPE are also significant. Nonylphenol has been shown to be toxic to aquatic organisms and to have anti-estrogenic effects. Since January 2005, an EU Directive has restricted the use of nonylphenol and nonylphenol ethoxylate by banning their use in cleaning products at concentrations  $>0.1\%$  (Anon. 2003b).

Releases of NP from production processes are estimated to be very low. Thus, very little NP enters the environment directly. The primary source of NP found in the environment is considered to be NPEs, which can break down into NP in wastewater treatment plants or in the environment.

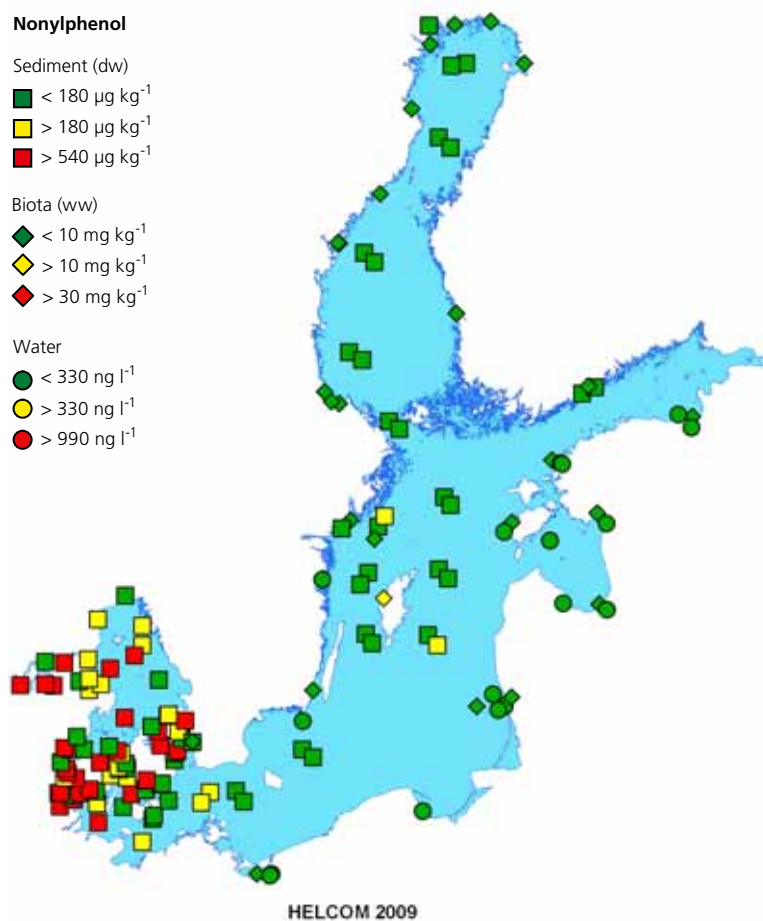
Nonylphenol levels in biota are not high. At the station Utlängan in southeastern Sweden, a sample of flounder liver contained  $23 \mu\text{g kg}^{-1}$  ww 4-iso-nonylphenol and another flounder liver sample near Klaipeda, Lithuania, contained  $12 \mu\text{g kg}^{-1}$  ww (Lilja et al. 2009). Other NP measurements in the HELCOM screening project and all NPE measurements were below the detection limit (Lilja et al. 2009). The PNEC concentration for the protection of predators from secondary poisoning has been estimated at  $10 \text{ mg kg}^{-1}$  ww. PNECs for water and sediment are  $330 \text{ ng l}^{-1}$  (EC 2008) and  $180 \mu\text{g kg}^{-1}$  dw (Anon. 2005), respectively. The concentrations measured in water were below the PNEC (ranging between 13 and  $66 \text{ ng l}^{-1}$ ) (HELCOM 2009c). Sediment measurements showed that concentrations of 4-iso-nonylphenol or unidentified NPs in the surface sediment exceeded the PNEC level<sup>12</sup> in the Northern Baltic Proper and the southwestern Baltic Sea (Fig. 2.32).

### Status of octylphenol

Octylphenols (OPs) are used in the production of detergents and, in lesser quantities, in other applications such as pesticides. Losses of octylphenols to the environment probably occur from the processing industry and from the use of various

products. Octylphenols are not broken down effectively in sewage treatment plants and releases of the substance occur primarily to land and water.

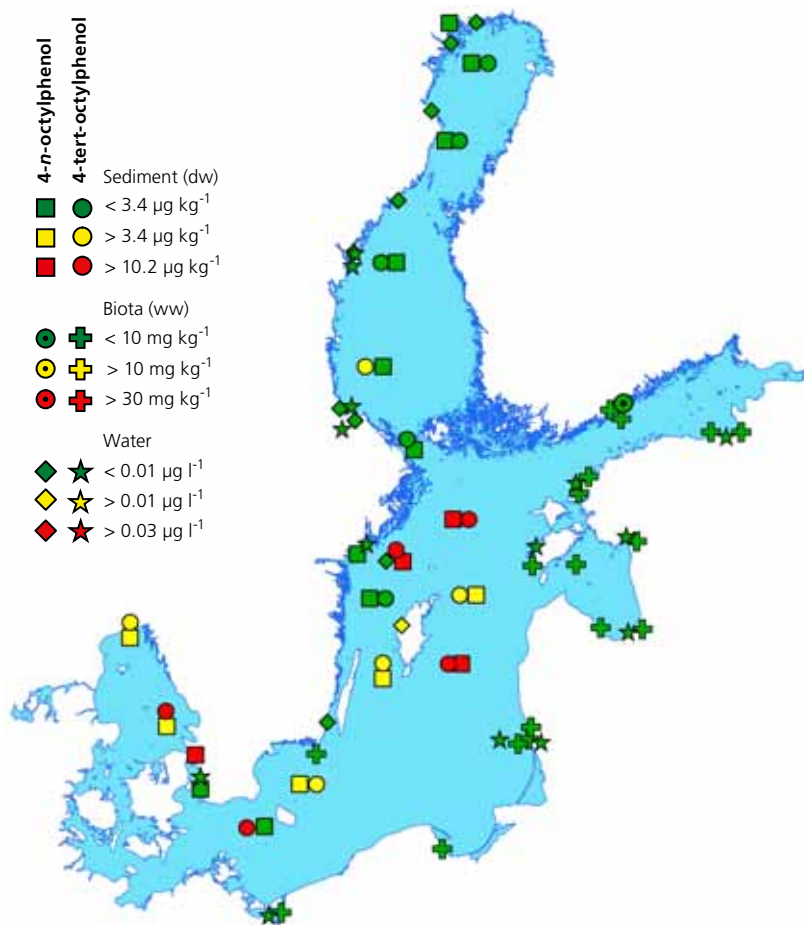
Octylphenols are very toxic to fish and other aquatic organisms and they have anti-estrogenic effects. They are not readily biodegradable and require months or even longer to degrade in surface waters or in soils and sediments. Octylphenols bioconcentrate and bioaccumulate in aquatic organisms and birds, and concentrations measured in biota have been found that are ten to one thousand times greater than concentrations in the surrounding environment. However, the concentrations of 4-tert-octylphenol and octylphenol ethoxylates (OPEs) in fish muscle samples from Estonia, Latvia, Lithuania, Poland and southeastern Sweden were all below the detection limit (Lilja et al. 2009). Finnish fish samples near wastewater treatment plants in the Helsinki region showed concentrations from  $<1$ – $355 \mu\text{g kg}^{-1}$  ww (Londesborough et al., unpublished).



**Figure 2.32** Status of nonylphenol concentrations in sediment, biota and water. The threshold concentrations for sediment, biota and water are given according to Anon. (2005) and the EU Priority Substance Directive (Anon. 2008b).

<sup>12</sup> The 4-*n*-nonylphenol concentrations were lower than the PNEC at all sites measured (Anon. 2005).

Concentrations of octylphenol in surface sediment were very high, with 50% of 4-*n*-octylphenol levels and 65% of 4-*t*-octylphenol levels exceeding the threshold concentration for the substance<sup>13</sup> (Swedish monitoring data 2003). The deep sediments in the Northern Baltic Proper contained levels 30 times higher than the threshold concentration (Fig. 2.33 and HELCOM 2009c). However, octylphenol was found in only one water sample from Lithuania (1.2 ng l<sup>-1</sup>) (Lilja et al. 2009).



**Figure 2.33** Status of octylphenol concentrations in sediment, biota and water. The threshold concentrations for sediment and biota are from Anon. (2005) and for water from the EU Priority Substance Directive (Anon. 2008b).

### Pharmaceuticals – A new threat to the marine environment

Pharmaceuticals are compounds that are designed to have biological effects on humans or animals. It has been estimated that over 3000 chemical

substances are used in human and veterinary medicines. These include, for example, medicines used as painkillers, antibiotics, contraceptives, beta-blockers, lipid regulators, tranquilizers, and impotence drugs.

In the course of the past decade, pharmaceuticals have become recognized as relevant environmental contaminants. Surface waters receive continuous inputs of pharmaceuticals, but the substances also undergo various chemical, physical and biological processes that degrade and alter them. Marine waters can be seen as the final sink of the most persistent compounds. At present, little is known about the environmental fate, possible accumulation and effects on biota of pharmaceuticals.

Hormonal contaminants are known to interfere with the normal functioning of the endocrine system. There are also indications that pharmaceuticals may alter the behaviour of aquatic organisms at very low concentrations (<10 ng l<sup>-1</sup>). Little is known of the development of microbial resistance to antibiotics in aquatic ecosystems or the synergistic effects of different chemicals sharing common mechanisms of action.

Rivers in Baltic Sea countries have been shown to contain up to  $\mu\text{g l}^{-1}$  concentrations of pharmaceuticals. It is therefore to be expected that these substances will be transported to the Baltic Sea. The substances will also be discharged to the Baltic Sea in the effluents of wastewater treatment plants situated at the coast. There are few data on the occurrence of pharmaceuticals in the Baltic Sea. Oxazepam (a benzodiazepine) has been detected near the coast of Stockholm at concentrations of 15–20 ng l<sup>-1</sup> (Woldegiorgis et al. 2007). 17 $\alpha$ -ethinylestradiol (EE2, active hormone in contraceptives) has been detected along with several other pharmaceuticals off the coast of Germany (Fig. 2.34. and Table 2.5). Higher concentrations were measured close to coastal areas where the impact of wastewater effluents was more prominent. Baltic Sea salmon has been found to contain EE2 at a concentration of 0.90  $\mu\text{g kg}^{-1}$  ww (Andersson et al. 2006). In a Swedish screening study, the antibiotic substance ciprofloxacin was found in three out of five fish samples, with an average concentration of 6  $\mu\text{g kg}^{-1}$  ww (Sternbeck & Österås 2009). Seventeen other antibiotics were

<sup>13</sup> The PNEC is 3.4  $\mu\text{g kg}^{-1}$  dw for 4-*n*-octylphenol and 4-*t*-octylphenol (Anon. 2005).

**Table 2.5** Pharmaceuticals in the coastal Baltic Sea off Germany, according to Beck et al. (2009), and effects at environmentally relevant concentrations.

	Therapeutic use	Concentrations, ng l <sup>-1</sup> (min–max)		Effect in the aquatic environment	References for the effects
		Wismar Bay	Darss Peninsula		
<b>Clofibrac acid</b>	Metabolite of fibrates (lipid regulators)	0.11–0.37	0.07–0.09	Adverse effects on reproductive system of fish	Runnalls et al. 2007
<b>Ibuprofen</b>	Anti-inflammatory	0.07–0.14	<detection limit–0.03	Behavioural effects on crustacean	De Lange et al. 2006
<b>Carbamazepine</b>	Antiepileptic	2.6–6.8	0.93–4.2	Adverse effects on mussels	Martin-Diaz et al. 2009
<b>Gemfibrozil</b>	Lipid regulator	0.1–0.13	0.03–0.04	Bioconcentration and adverse effects on fish and mussels	Fent et al. 2006 Canesi et al. 2007
<b>Diclofenac</b>	Anti-inflammatory	0.08–0.39	<detection limit	Interferes with osmoregulation of crabs	Eades & Waring 2009
<b>Bezafibrate</b>	Lipid regulator	0.19–0.26	<detection limit–0.03	Adverse effects on immune system of mussels	Canesi et al. 2007
<b>Naproxen</b>	Anti-inflammatory	0.35–0.45	<detection limit		
<b>Propyphenazone</b>	Analgesic	0.12–0.20	0.09–0.19		

also measured, but the concentrations were below the detection limits of 2–41 µg kg<sup>-1</sup> ww.

Environmental impacts of *human* pharmaceutical products are not a criterion for refusal of marketing authorization. However, environmental risks of *veterinary* pharmaceutical compounds are part of the analysis of environmental risks and benefits; environmental risks that are too great may lead to refusal of the marketing permission. At present, there are no regulations for the monitoring of pharmaceuticals in the aquatic environment or limit values for treated wastewaters.

### 2.2.10 Status and trends of radioactive substances

The Baltic Sea is the regional sea in the world with the highest concentrations of cesium-137 (<sup>137</sup>Cs) due to radioactive fallout from the Chernobyl accident. The Baltic Sea ranks third in the world with respect to strontium-90 (<sup>90</sup>Sr) in sea water; only the Irish Sea and the Black Sea show higher levels. In 1990, average concentrations of <sup>137</sup>Cs in fish from the Baltic Sea were similar to those in the Irish Sea, about four times higher than in the Black Sea and about 30 times higher than in the Mediterranean Sea. Concentrations of radionuclides in the Baltic Sea have been presented in the recent HELCOM thematic assessment on radioactivity (HELCOM 2009d).



**Figure 2.34** Range of concentrations of EE2 (17 $\alpha$ -ethinylestradiol) off the coast of Germany, Baltic Sea (Beck et al. 2005). Site 1: 2.1–17.9 ng l<sup>-1</sup>, Site 2: below detection limit to 14.1 ng l<sup>-1</sup>, Site 3: below detection limit to 3.9 ng l<sup>-1</sup>, Site 4: 1.6–3.0 ng l<sup>-1</sup>, Site 5: 1.7–3.2 ng l<sup>-1</sup>

### Inputs of radionuclides to the Baltic Sea

The most significant source of man-made radioactivity in the Baltic Sea is the fallout from the accident at the Chernobyl nuclear power plant in 1986. The radionuclide <sup>137</sup>Cs dominated in the fallout and the second most significant radionuclide was <sup>134</sup>Cs. The total input of <sup>137</sup>Cs from Chernobyl to the Baltic Sea has been estimated

at 4700 TBq and the post-Chernobyl river discharges of  $^{137}\text{Cs}$  to the Baltic Sea were estimated at 300 TBq.

The second most important source of radionuclides is the global fallout from atmospheric nuclear weapons tests carried out during the late 1950s and early 1960s. The predominant radionuclides in the global fallout were  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$ . During the late 1990s, the decay-corrected amounts of  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  in the Baltic Sea from the nuclear weapons tests were evaluated at 800 TBq and 500 TBq, respectively.

The corresponding decay-corrected total inputs of  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  to the Baltic Sea in the late 1990s, originating from nuclear reprocessing plants in Western Europe, have been estimated at 250 TBq and 40 TBq, respectively. At present, these sources have been reduced to minor importance due to a significant reduction of discharges in recent years.

The predominant radionuclide in discharges from the nuclear power plants and research reactors in the Baltic Sea region is tritium ( $^3\text{H}$ ). Total discharges of  $^3\text{H}$  from these local sources have amounted to 3200 TBq and those of other beta-gamma-emitting radionuclides were about 24 TBq until the end of 2006. The total discharges of alpha-emitting radionuclides have been 0.005 TBq.

For  $^{137}\text{Cs}$  in the Baltic Sea, the main sources are fallout from Chernobyl (82%) and the nuclear weapons test fallout (14%). For  $^{90}\text{Sr}$ , the main source of contamination is fallout from nuclear weapons tests (81%), while the proportion from Chernobyl fallout was smaller (13%).

#### **Cesium and strontium in sea water**

At present,  $^{137}\text{Cs}$  is the main indicator with respect to man-made radioactivity in Baltic sea water. The highest concentrations of approximately  $80 \text{ Bq m}^{-3}$  during 1999–2006 were found in the Baltic Proper and the Bothnian Sea. The general trend is steadily decreasing, with effective half-lives in the range of 9–15 years. It is estimated that the pre-Chernobyl target value of  $15 \text{ Bq m}^{-3}$  will be reached between 2020 and 2030. The inventory of  $^{137}\text{Cs}$  in Baltic sea water in 2006 is estimated at 870 TBq.

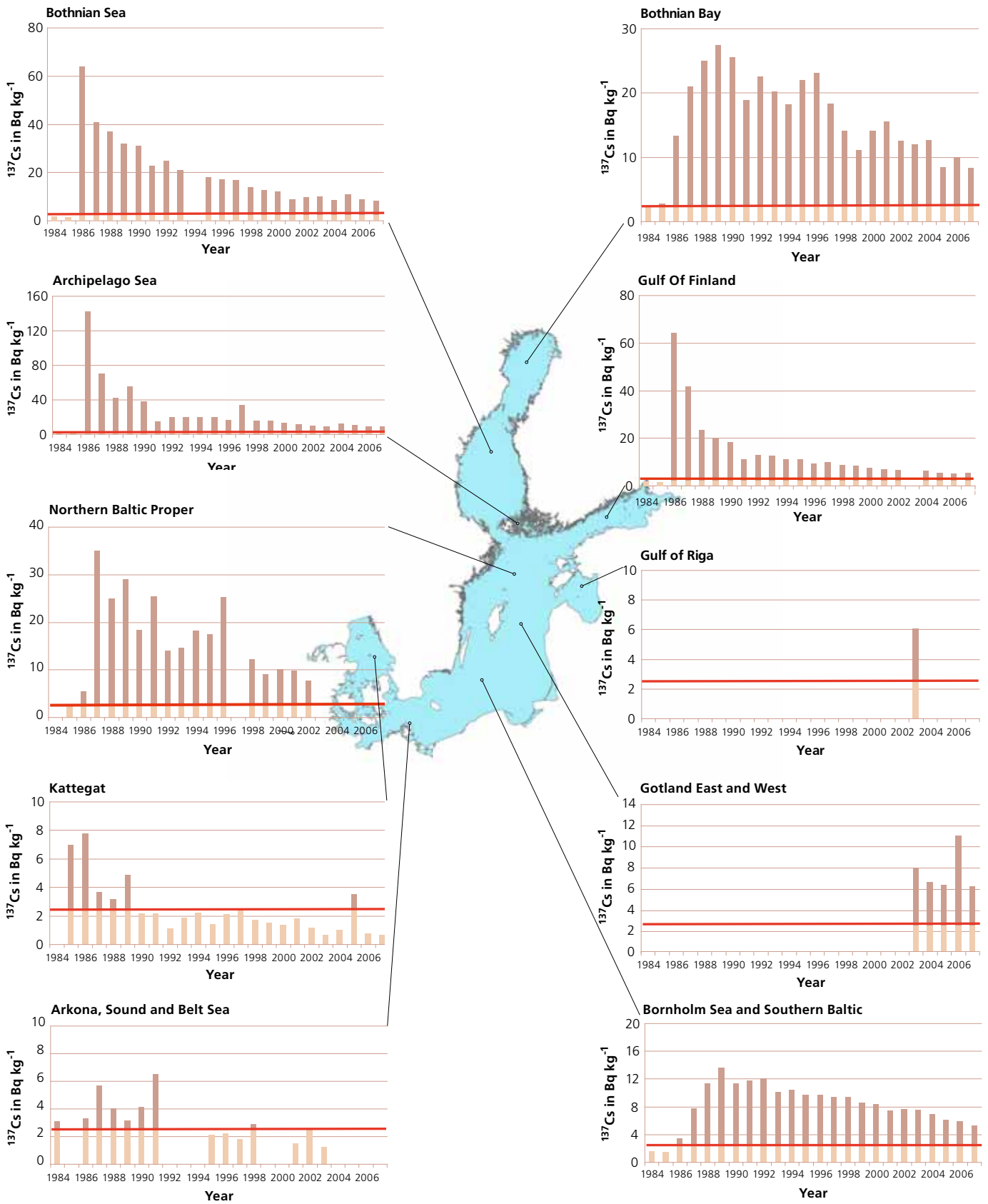
During 1999–2006, concentrations of  $^{90}\text{Sr}$  in Baltic sea water varied between 5 and  $15 \text{ Bq m}^{-3}$  in surface and near-bottom water. The lowest concentrations were found in the Kattegat in near-bottom water, where only  $2 \text{ Bq m}^{-3}$  of  $^{90}\text{Sr}$  was found. The  $^{90}\text{Sr}$  inventory in the Baltic Sea was about 200 TBq in 2006, which was half of the inventory in 1985, the year before the Chernobyl accident. The  $^{90}\text{Sr}$  concentrations in sea water decrease slowly with time and behave differently from  $^{137}\text{Cs}$ . Strontium-90 is more soluble in water and its effective half-life in Baltic sea water is longer than that of  $^{137}\text{Cs}$ , around 20 years during 1987–2006.

#### **Radionuclides in sediments**

Most of the radioactivity in the sediments of the Baltic Sea originates from naturally occurring radionuclides. The total amounts in the 0–10 cm sediment layer were estimated to be roughly about 8500 TBq for  $^{40}\text{K}$  and about 420 TBq for  $^{226}\text{Ra}$ . Although there are considerable amounts of long-lived man-made radionuclides in the Baltic Sea sediments, the levels are low and are not expected to cause harmful effects to man or wildlife. The total amounts of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  in Baltic Sea sediments are estimated at 26 TBq and 2100–2400 TBq, respectively. The transfer of  $^{137}\text{Cs}$  continues by sedimentation from the water column to deeper sediment layers, thus reducing its availability for biological uptake. This trend is further amplified by the radioactive decay of  $^{137}\text{Cs}$ , which has a half-life of 30 years.

#### **Radionuclides in fish**

From 1999–2006, the dominant man-made radionuclide in Baltic Sea fish with regard to activity concentrations was  $^{137}\text{Cs}$ . By the end of this period, mean values of  $1\text{--}10 \text{ Bq kg}^{-1}$  ww were found in marine roundfish (cod, herring, whiting) in various Baltic Sea basins, while freshwater pike in Finnish coastal areas showed values of  $10\text{--}25 \text{ Bq kg}^{-1}$  ww due to its higher concentration factors (**Fig. 2.35**). In marine flatfish (plaice, flounder, dab), slightly lower mean values were found than in marine roundfish. Concentrations of man-made radioactivity in fish show generally decreasing trends (**Fig. 2.35**).



**Figure 2.35**  $^{137}\text{Cs}$  activity concentrations (in  $\text{Bq kg}^{-1}$  ww) in herring muscle from 1984–2006, as annual mean values by basin. The target value has been calculated as the average of the pre-Chernobyl (1984–1985) activity concentrations.

## 2.3 Biological effects of hazardous substances: status and trends

Once introduced into the environment, anthropogenic hazardous substances have the potential to interact with various components of the ecosystem. Persistent organic pollutants (POPs) bioconcentrate in organisms directly from the water via body surfaces, bioaccumulate from food, and

**Table 2.6. Biomagnification factors in Baltic Sea pelagic food chains (predator/prey relations). Concentration in organism/concentration in food; all normalized to lipid content. Values >1 indicate biomagnification.**

Compound	Zooplankton/ phytoplankton	Mysids/ zooplankton	Herring/ mysids	Seal/ herring
PCB-153*	0.85	1.73	3.33	
p,p-DDE*	0.66	3.78	3.04	
Octachlordane*	0.22	1.19	4.25	
ΣPCBs**				<12
ΣDDTs**				<9
ΣChlordanes**				<26

\*Nfon et al. 2008

\*\*Strandberg et al. 1998

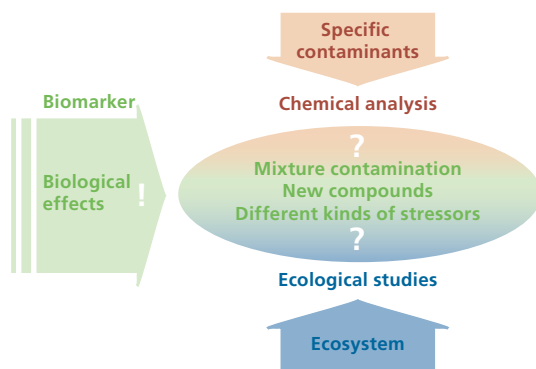
biomagnify along the trophic chain from bacteria to predators. Thus, although concentrations of hazardous substances in water may be below the detection limit, they may reach harmful levels in predators at the high level of the food web, including seals, harbour porpoise, some species of fish and birds, and ultimately, man. Examples of the biomagnification of some organic pollutants in the Baltic Sea pelagic food chains are shown in **Table 2.6**. Lower trophic levels may also be at risk due to the introduction of more water soluble compounds (e.g., pesticides, PAHs, metals, pharmaceuticals,

etc.), many of which do not biomagnify but nevertheless are known to be harmful to organisms.

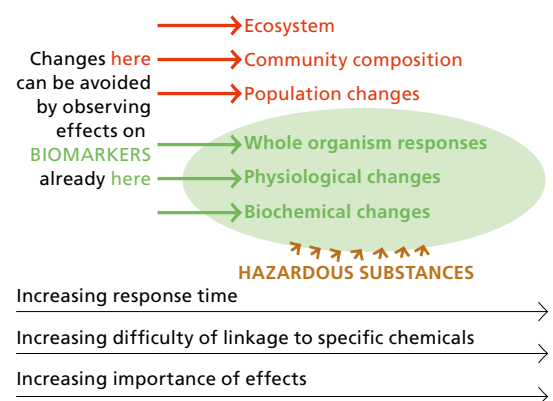
Chemical analysis of tissue concentrations of hazardous substances gives information on the levels of single substances. However, these levels do not provide information on the effects of the mixture of compounds that the marine organisms are exposed to in their habitats, or on the synergistic effects due to other abiotic or biotic stressors. Thus, the assessment of biological effects and the application of so-called biomarkers in indicator species representing different trophic levels serve as a tool to provide realistic evidence for the impact of hazardous substances under specific environmental conditions (**Fig. 2.36**).

Hazardous substances can cause harmful effects on organisms at molecular, cellular, tissue and organ levels (**Fig. 2.37**). These alterations may ultimately affect populations through reduced fitness, pathological disorders or by disturbing reproduction, but such causality has been shown only by indirect evidence (**Fig. 2.50**; Helander et al. 2009, Bergman (2007). Alterations in population size and/or structure—especially of key species—can markedly change community structures and thus affect whole ecosystems and their function. Following this scheme, an environmental monitoring strategy to observe early effects (biomarkers) can be predictive for later responses at higher levels.

At present, the monitoring of biological effects in the Baltic Sea is conducted in national monitoring programmes and some time series are available (reproduction of the white-tailed eagle, health



**Figure 2.36** Diagram showing the integrating role of biological effects within the impact assessment of environmental pollution.



**Figure 2.37** Conceptual model of the biomarker approach in environmental monitoring. Modified after Walker et al. (2001).

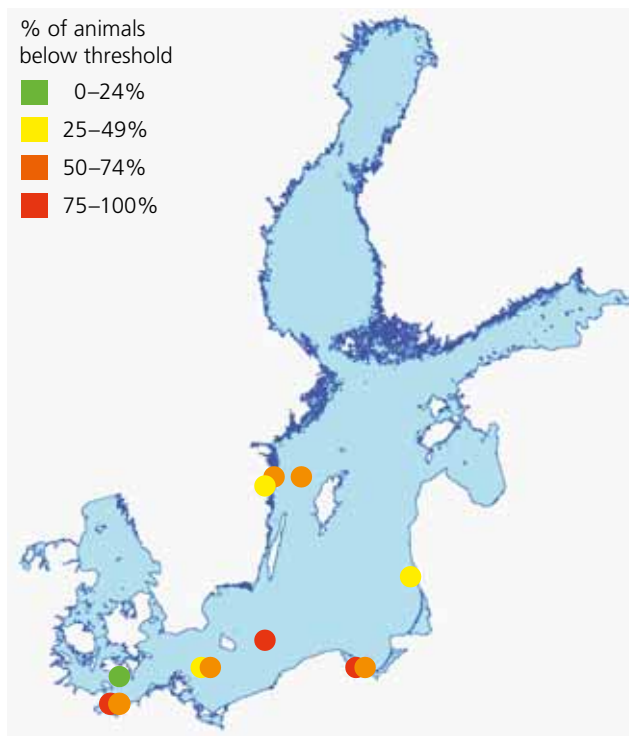


of seals, fish diseases, embryonic aberrations in crustaceans, imposex in snails and EROD activity in fish). In addition, large international research projects have been targeted to develop and apply biomarkers of exposure and effects of toxicants (e.g., the EU project BEEP, the BONUS+ projects BEAST and BALCOFISH). This chapter presents examples of the status (research projects) and trends (national monitoring programmes) of biological effects monitoring at various trophic levels using endpoints at different biological levels.

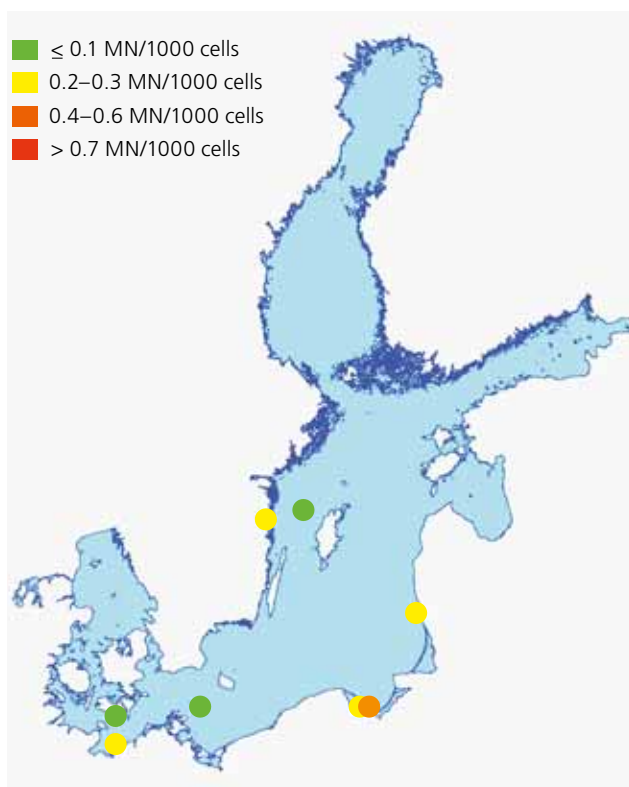
### 2.3.1 Early warning responses

The ability to detect adverse effects at an early stage in individuals, i.e. before damage in populations occurs, is one of the major challenges in marine environmental monitoring. This so-called biomarker approach was applied in comprehensive field studies during the EU project Biological Effects of Environmental Pollution in Marine Coastal Ecosystems (BEEP) also in the Baltic Sea region (see Lehtonen et al. 2006).

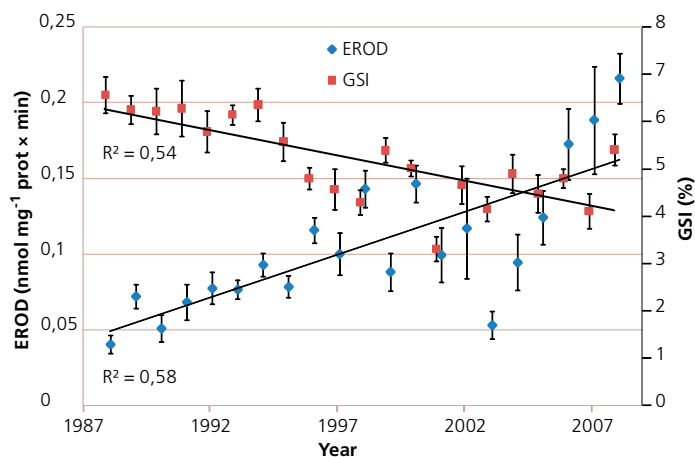
One of the early toxic effects detectable in organisms is damage to biological membranes, leading to strong alterations in the cellular functional capability. This has been measured using the lysosomal membrane stability (LMS) test. LMS is an integrative parameter that reflects the combined impact of a mix of contaminants due to its responsiveness to most contaminant classes. It is already being applied as a first-tier screening parameter in the monitoring programme in the Mediterranean Sea (Viarengo et al. 2007, UNEP 2007). Thresholds for LMS have been defined for mussels and fish, characterizing the different stages of toxic cell damage (Broeg et al. 2005, Broeg & Lehtonen 2006, ICES 2008a). The "non-disturbed status" is defined as low LMS index values, which are rarely found in the Baltic Sea (see one site in **Fig. 2.38**). Results of LMS measured in flounder (*Platichthys flesus*) collected from different sites in the southern Baltic in 2001 and 2002 document marked effects in coastal and harbour areas (**Fig. 2.38**). In addition, individuals collected from an open-sea site close to the main dumping area of WWII chemical weapons exhibit strong toxic effects. LMS, as a biomarker of general toxicity, can be used as a powerful tool to detect risk areas where pollutant effects, once detected, will need to be further characterized and their causes identified.



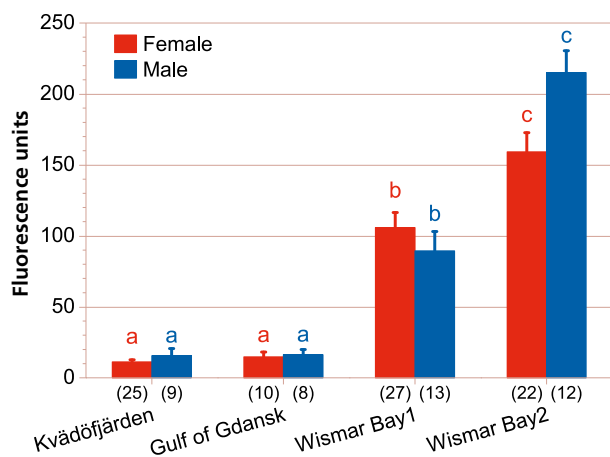
**Figure 2.38** Lysosomal membrane stability in flounder (*Platichthys flesus*) from different areas of the southern Baltic Sea in autumn 2002.



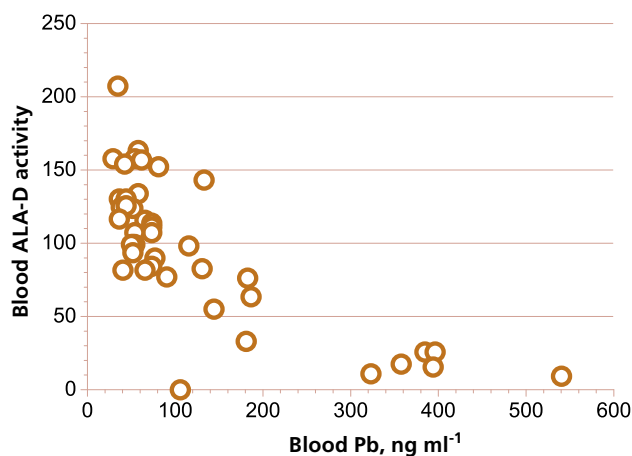
**Figure 2.39** Frequency of micronuclei (MN) in the red blood cells of flounder (*Platichthys flesus*) from different areas of the southern Baltic Sea in autumn 2002.



**Figure 2.40** EROD activity and GSI level in perch (*Perca fluviatilis*) at the Kvädöfjärden monitoring site on the coast of the Swedish Baltic Proper from 1988–2008. Increased EROD activity and reduced GSI level indicate a poorer state of the environment.



**Figure 2.41** The presence of PAH metabolites measured as the total fluorescence (mean  $\pm$  S.E., at the excitation/emission of 341/383 nm) of bile in female and male eelpout sampled in autumn at four locations in the Baltic Sea. The different letters above the bars indicate significant ( $p < 0.05$ ) differences between the areal means among the sexes. Redrawn from Vuorinen et al. 2006.



**Figure 2.42** Relationship between  $\delta$ -aminolevulinic acid dehydratase (ALA-D) activity and lead concentration ( $\text{ng ml}^{-1}$ ) in the blood of common eiders at five locations in the Finnish archipelago (best fit:  $\ln \text{ALA-D} = 8.4 - 0.92 \ln \text{blood Pb}$ ,  $r = -0.69$ ,  $p < 0.001$ ,  $n = 42$ ). Redrawn from Franson et al. 2000b.

The micronucleus (MN) test is a widespread indicator of genotoxic damage caused by various chemical agents. Micronuclei are produced from chromosome fragments or entire chromosomes that lag in cell division owing to a missing or damaged centromere, or a defect in cytokinesis (Fenech et al. 2003). In the Baltic Sea, higher frequencies of MN have been identified, e.g., in the red blood cells of flounder collected from coastal and harbour areas compared to more offshore areas (**Fig. 2.39**).

Ethoxyresorufin-*O*-deethylase (EROD) is a biotransformation enzyme, which is the most common biomarker used to indicate exposure to planar aromatic compounds such as dioxins, PCBs and PAHs. In perch (*Perca fluviatilis*), a four-fold increase in EROD activity and a concurrent approximate 30% reduction in the gonadosomatic index (GSI) have been recorded at a long-term monitoring site (starting in 1988) in Kvädöfjärden, on the Swedish coast of the Baltic Proper (**Fig. 2.40**). The reduction in GSI is associated with reduced reproductive capacity. The hypothesis that perch in this area are exposed to increasing levels of one or several environmental contaminants is supported by temporal trends that have also been observed in other biomarkers, such as increased activity of glutathione reductase (GR) in the liver (indication of oxidative stress), increased number of white blood cells (immunological response) and increased levels of inorganic ions in blood plasma (SEPA 2009b). Similar temporal trends have also been observed in the Bothnian Bay (SEPA 2009c), suggesting that the problem is not only of a local nature.

Among the most contaminant-specific biomarkers are biliary PAH metabolites in fish, measured as individual metabolites or total fluorescent aromatic compounds (FACs), and  $\delta$ -aminolevulinic acid dehydratase (ALA-D) activity in blood to detect lead poisoning, both of which have been successfully used also in the Baltic Sea (e.g., Vuorinen et al. 2006, Kammann 2007, Franson et al. 2000b). In Wismar Bay, heavily polluted from industrial and domestic sources as well as from ship traffic, the levels of bile FACs in eelpout (*Zoarces viviparus*) were highly elevated compared to the reference area (Kvädöfjärden) or the Gulf of Gdansk (**Fig. 2.41**). In common eiders (*Somateria mollissima*) from the Finnish archipelago,

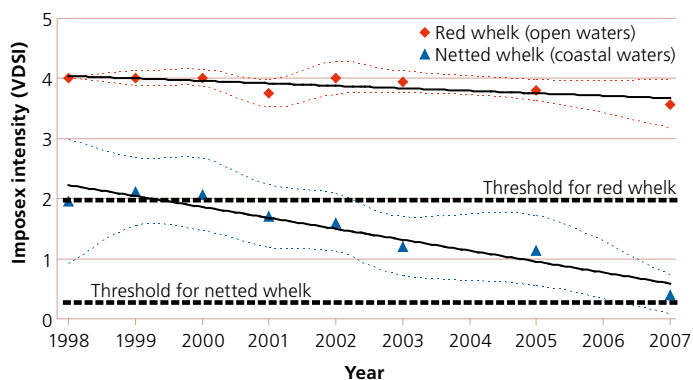
the blood ALA-D activity was determined to correlate negatively with the lead concentration in blood (Fig. 2.42). Apparently the highest lead concentrations were derived from ingested lead shots (Franson et al. 2000a), but the concentrations mainly demonstrated environmental lead pollution, because a distinct decreasing gradient from eastern to western locations was detected (Franson et al. 2000b).

### 2.3.2 Individual health and reproductive disorders

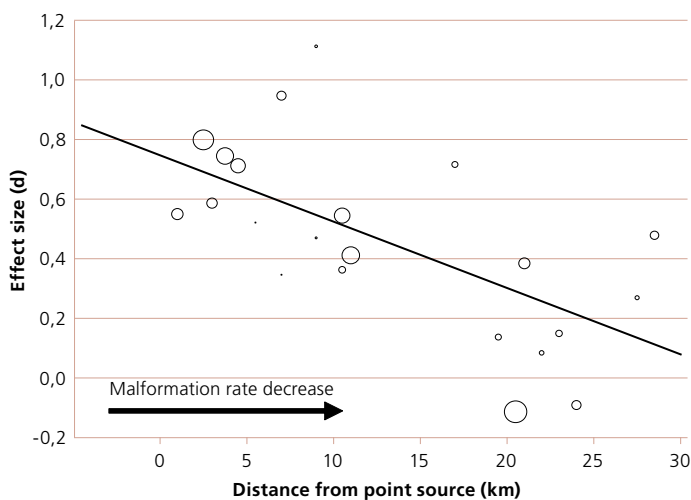
Imposex and intersex in certain species of marine snails (Prosobranch gastropods) are signs of endocrine disruption and are widely used as specific biomarkers for TBT contamination (OSPAR 2008, Strand 2009a, 2009b). Ship traffic is regarded as the main source of TBT in the Baltic (see also Section 2.2.4). Imposex refers to the development of male sexual characteristics superimposing female characteristics, while intersex refers to the transformation of female sexual characteristics towards those of a male. The different stages of imposex are classified using a *vas deferens* sequence index (VDSI).

The red whelk (*Neptunea antiqua*) represents a very sensitive species with regard to imposex because high levels occur even in non-coastal areas. In the Belt Sea area (Denmark), 100% of the red whelks have developed imposex and about 10% of the individuals were regarded as sterile due to a severe imposex development stage (Strand 2009a). Similar to TBT levels, the levels of imposex have also declined during recent years owing to the ban on the use of TBT as an antifouling agent on ship hulls. This trend is particularly clear in the netted whelk (*Hinia reticulata*) from coastal waters, whereas the trend is not completely clear in the more long-living red whelk in the open-sea areas of the Belt Sea (Fig. 2.43). In low-salinity regions of the Baltic Sea, imposex has also been found in the mud snails *Hydrobia ulvae* (Gercken & Sordyl 2007, Magnusson 2008).

Adverse effects of various hazardous substances on the reproduction of the soft-bottom amphipod *Monoporeia affinis* are visible as malformed embryos in the Baltic Sea (Sundelin & Eriksson 1998, Sundelin et al. 2008). This variable has been

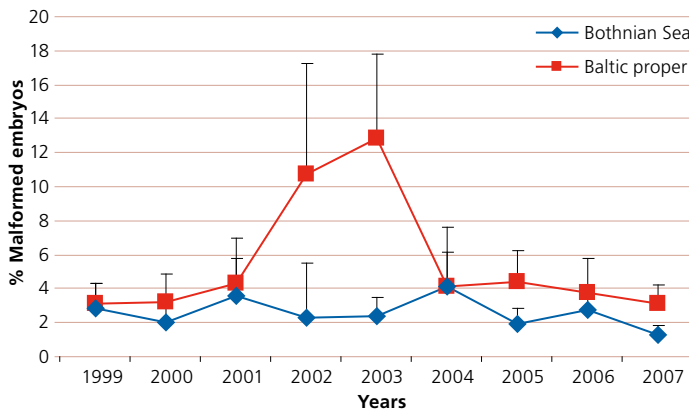
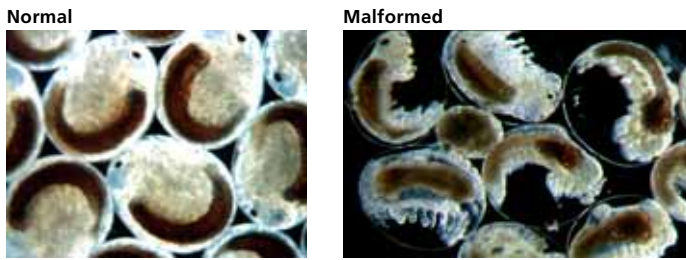


**Figure 2.43** Temporal trends of imposex levels (intensity classified as VDSI with 4.0 as the maximum value) in two marine snail species, the netted whelk (*Hinia reticulata*) and the more sensitive red whelk (*Neptunea antiqua*) from coastal and open waters in the Danish part of the Belt Sea (Strand 2007). Threshold values for imposex in the two species are shown for comparison (OSPAR 2008). Symbols denote median values and broken lines show 95% confidence intervals.



**Figure 2.44** The proportion of malformed embryos in the amphipod *Monoporeia affinis* increases with decreasing distance from the point source, suggesting that there is a strong relationship between the emission sources studied and the malformation rate. The analysis includes results from a total of 24 sampling stations from six regional studies at polluted recipient sites. Results have been transformed into “effect sizes” in order to make the studies comparable (mean-centred and scaled with 1/SD).

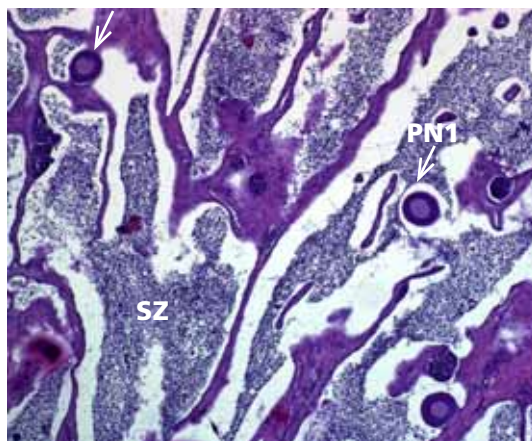
used in various types of industrial recipient areas as part of effects monitoring, and a strong relationship between distance from the source and malformation rate has been observed (Fig. 2.44). The method was included in the Swedish national monitoring programme in 1994, with five stations in the Bothnian Sea and nine in the Baltic Proper. Generally, the embryonic malformation rate is higher in the latter area, indicating a higher level of sediment-associated contaminants (Fig. 2.45, see also Chapter 2.2).



**Figure 2.45** Percentage of malformed embryos in the amphipod *Monoporeia affinis* collected from stations in the Bothnian Sea and the Baltic Proper. The malformation rate increased between 2001 and 2004 in the Baltic Proper for unknown reasons. Variance is given as upper 95% confidence intervals.



**Figure 2.46** Example of two-headed malformed eelpout larvae (Photo: Jakob Strand).



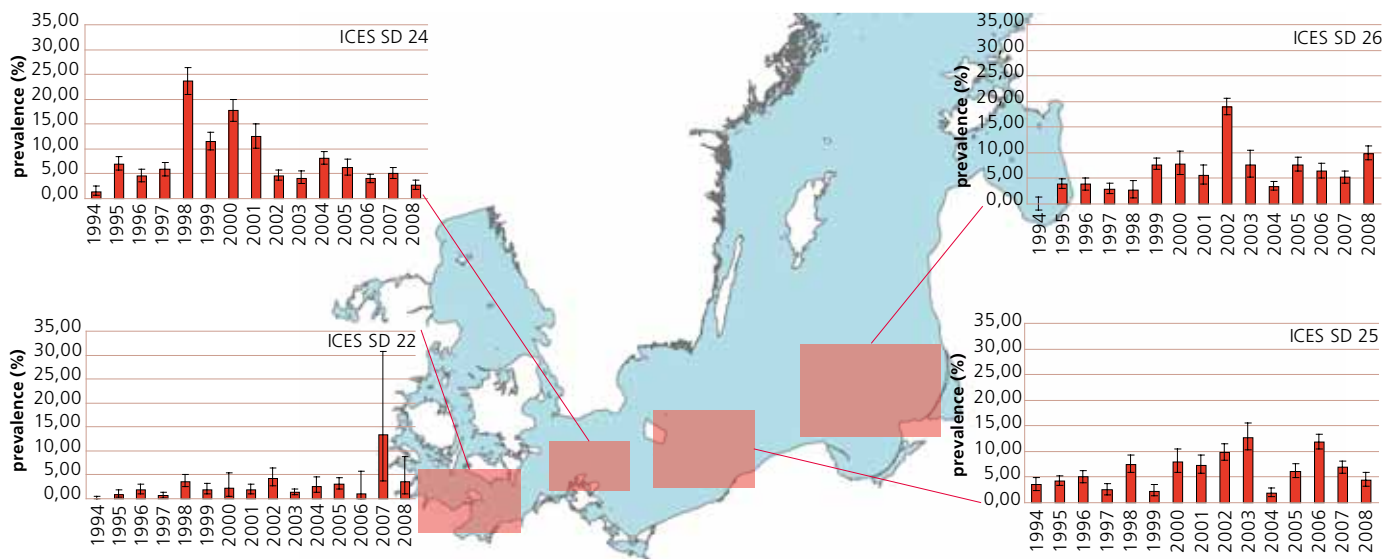
**Figure 2.47** Intersex in eelpout male testis. PN: primary oocyte, SZ: spermatozoans (Photo: Jonna Tomkiewicz).

Effects on the reproduction of the viviparous fish eelpout (*Zoarces viviparus*) have been measured in coastal areas of Sweden, Denmark, Germany and Poland. These measurements are now included in national monitoring programmes. The presence of abnormal development of embryos and larvae in eelpout broods is used as an indicator of impaired reproduction because chronic exposure to various contaminants has the potential to induce adverse developmental effects in fish (Fig. 2.46). In some areas that are known to be more polluted, malformed larvae are found in more than 80% of the eelpout broods (Vetemaa et al. 1997, Strand et al. 2004, Gercken et al. 2006). Other studies on endocrine disturbances in eelpout carried out in German and Danish coastal waters have also recorded a widespread occurrence of intersex, i.e., primary oocyte development, in the testes of more than 25% of the males studied (Fig. 2.47) (Gercken & Sordyl 2002, Gercken & Sundt 2007, Strand et al. 2009). A skewed sex ratio with a prevalence of females in eelpout broods was observed close to an effluent output site of a Swedish pulp mill (Larsson et al. 2000).

Diseases in wild Baltic Sea fish have been monitored on a regular basis since the beginning of the 1980s as a component of national environmental monitoring and assessment programmes. Within these programmes, significant alterations in the disease prevalence are used as a general ecosystem health indicator, reflecting the effects of environmental change, including anthropogenic impacts, on the disease resistance of wild fish. The fish diseases cannot be directly linked to any specific compound, but they are probably caused by multiple stressors in the environment.

Temporal changes in the prevalence of one of the most conspicuous diseases of Baltic cod (*Gadus morhua*), the bacterial skin ulcer disease, are shown in Figure 2.48. Over the period 1994–2008, there was a marked fluctuation in prevalence, with maximum values of 23.6% in 1998 (ICES Subdivision 24) and 18.9% in 2002 (ICES Subdivision 26), respectively. For some periods, there is an indication of upward or downward trends.

The reproductive disorder of salmon (*Salmo salar*), the M74 syndrome, which is manifested as high mortalities of yolk-sac fry and which threatened the existence of salmon in the Baltic Sea during its

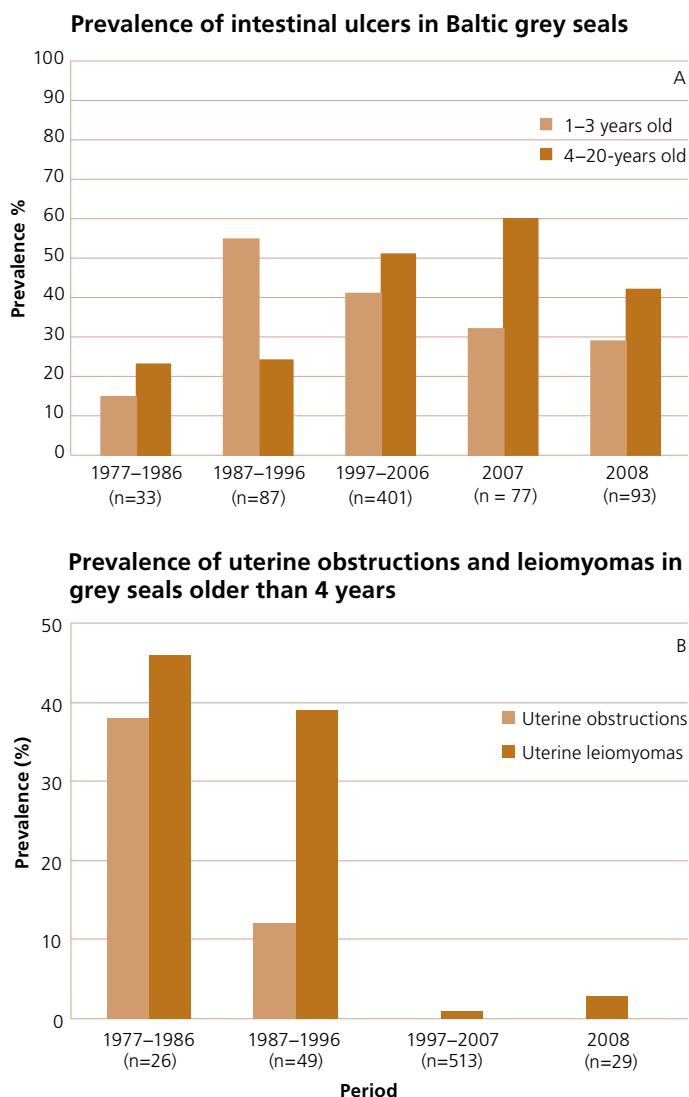


**Figure 2.48** Prevalence ( $\pm$  95% C.I.) of acute skin ulcers in Baltic cod (*Gadus morhua*) from ICES Subdivisions 22, 24, 25 and 26 in the period 1994–2008 (data from December surveys) (T. Lang, unpublished data).

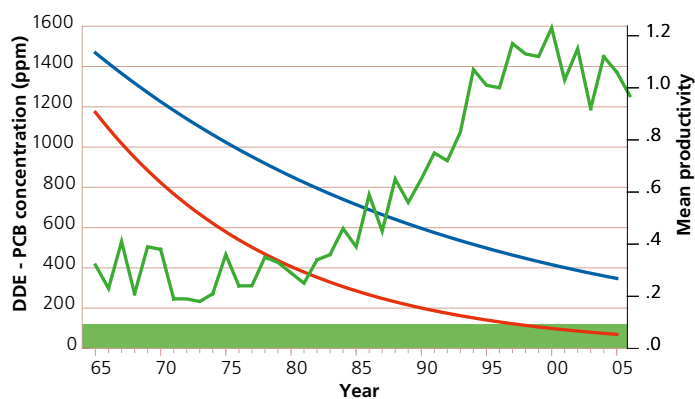
very high prevalence in the 1990s, has been statistically related to high concentrations of dioxins and DL-PCBs in the muscle of female salmon (Vuorinen et al. 1997, 2002), but the cause-effect relationship is not clear.

The prevalence of intestinal ulcers in immature Baltic grey seals (*Halichoerus grypus*) has increased since the middle of the 1980s, and ten years later the prevalence also increased in mature grey seals (Fig. 2.49A). In the young age group, ulcer preva-

lence decreased somewhat during the 2000s but still remains at a high level. Even though there is no certainty regarding the cause of the increased ulcer formation (Bergman 1999, Bäcklin et al. 2009), PCBs are suspected to be associated with interrupted pregnancies and uterine obstructions in both ringed and grey seals as well as with uterine leiomyomas in the latter (Bergman & Olsson 1985, Bäcklin et al. 2003, Bredhult et al. 2008), and thus probably contributed to the observed small number of Baltic seals in the 1970s. Since the mid-



**Figure 2.49** Prevalence of **A)** intestinal ulcers and **B)** uterine obstructions and leiomyomas in the Baltic grey seal (*Halichoerus grypus*) during different periods from 1977–2008.



**Figure 2.50** Mean productivity (green line) vs. egg lipid concentrations of DDE (red line) and PCBs (blue line) of the white-tailed sea eagle (*Haliaeetus albicilla*) on the Swedish Baltic Sea coast from 1965–2005 (Helander et al. 2002, 2008). The area below a previously determined lowest estimated effect level (LOEL) for DDE is marked green. Mean productivity is the mean number of nestlings in all occupied nests.

1980s, increases in population sizes of grey seals have been recorded and no uterine obstruction has been observed in Swedish waters since 1997 (Bergman 2007, Bäcklin et al. 2009) (**Fig. 2.49B**). The occurrence of uterine leiomyomas has also decreased since the 1990s (Bredhult et al. 2008).

A significant phenomenon considered to be directly related to elevated levels of hazardous substances, especially DDT and PCBs, has been the disturbances observed in reproduction and health status of the white-tailed sea eagle (*Haliaeetus albicilla*). Reproduction in the Baltic eagle population in the 1970s was reduced to one fifth of the pre-1950 background level due to a severely reduced hatching success, which led to a diminished population size (Helander et al. 2009). The subsequent recovery correlates with reductions in environmental concentrations of organochlorine compounds resulting from bans on the use of DDT and PCBs during the 1970s around the Baltic Sea (**Fig. 2.50**). Since the mid-1990s, eagle productivity has largely returned to pre-1950 levels and the population on the Swedish Baltic coast has increased at a rate of 7.8% per year since 1990 (Helander et al. 2009). However, signs of an improvement in productivity could only be seen after the residue concentrations of DDE in the eggs declined to below 400 mg kg<sup>-1</sup>. Based on productivity and egg residue concentrations measured in 82 individual females between 1965 and 1997, a lowest observable effect level (LOEL) for DDE of approximately 100–120 mg kg<sup>-1</sup> has been estimated. The further positive development of productivity from 1998–2005 continues to support the estimated LOEL.

In another case, exceedingly high chick mortalities have led to the population decline of the nominate lesser black-backed gull (*Larus fuscus fuscus*) in the Gulf of Finland, which has been associated with the very high concentrations of organochlorines observed in the liver of the chicks (Hario et al. 2004).

# 3 POLLUTION SOURCES

Hazardous substances are either naturally occurring substances, such as heavy metals, or intentionally or unintentionally formed anthropogenic compounds. Intentionally synthesized substances are used by humans either as such or as components of other products. Some substances such as dioxins are formed unintentionally, for example, in combustion processes, while others are formed through transformation or metabolism. Heavy metals, radioactive substances and some organic compounds occur naturally, but become hazardous when they accumulate from anthropogenic sources to high enough concentrations.

Hazardous substances from sources on land are transported to the Baltic Sea via waterborne and airborne pathways (Fig. 3.1). These land-based sources include point sources, such as industrial facilities, municipal wastewater treatment plants and large waste disposal sites, and diffuse sources, such as losses from household uses of chemicals or the use of pesticides. In addition, heavy metals, certain organic compounds and radioactive substances occur in nature and contribute to the natural background concentrations. Large proportions of the substances that originate from the land-based sources are transported to the sea via watercourses. These substances also include

substances deposited from the air onto the land or inland waters. Transformation processes and the retention of substances take place during their transport to the sea.

Emissions to the air originate from numerous sources, such as transportation, combustion of wastes and fossil fuels, industrial emissions, spraying of pesticides and even small-scale combustion of wood in households. Substances emitted to the air can travel long distances before being deposited as either wet or dry deposition to the sea. Some emission sources are located in distant areas outside the Baltic Sea catchment, while others such as ship emissions originate at sea.

HELCOM monitoring programmes provide regular information on the waterborne and airborne inputs and sources to the Baltic Sea of selected heavy metals and some organic substances. Data on sources and inputs of hazardous substances are, however, scarce especially with regard to “new” substances. Case studies under the Control of hazardous substances in the Baltic Sea region (COHIBA) project are being conducted in the Baltic Sea countries in order to evaluate the sources of the eleven substances of specific concern to the Baltic contained in the Baltic Sea Action Plan (BSAP).

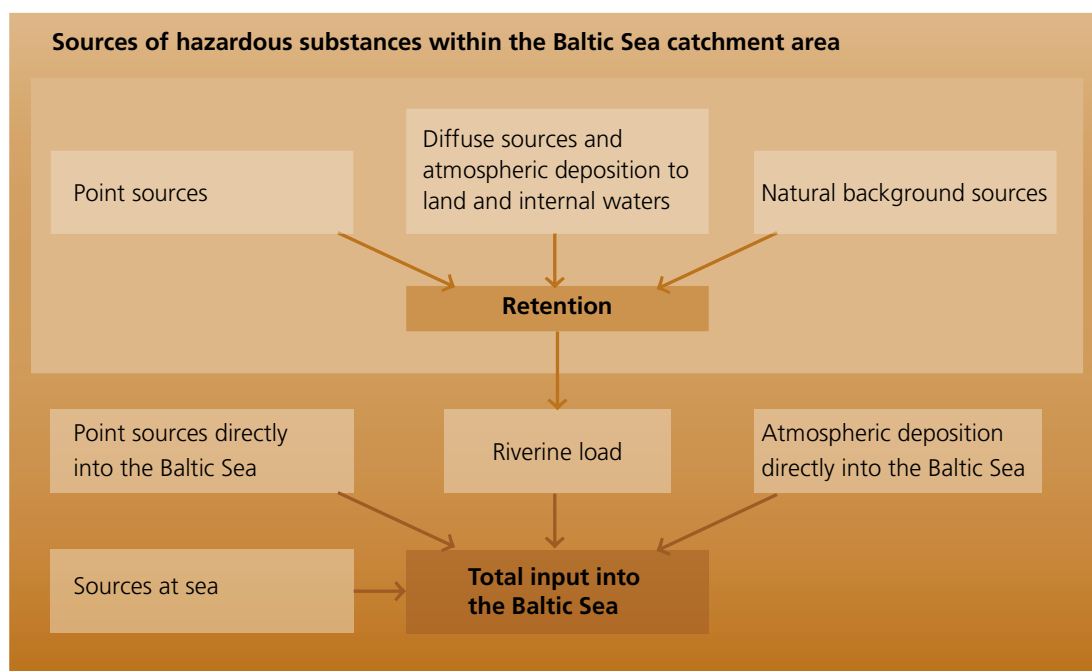
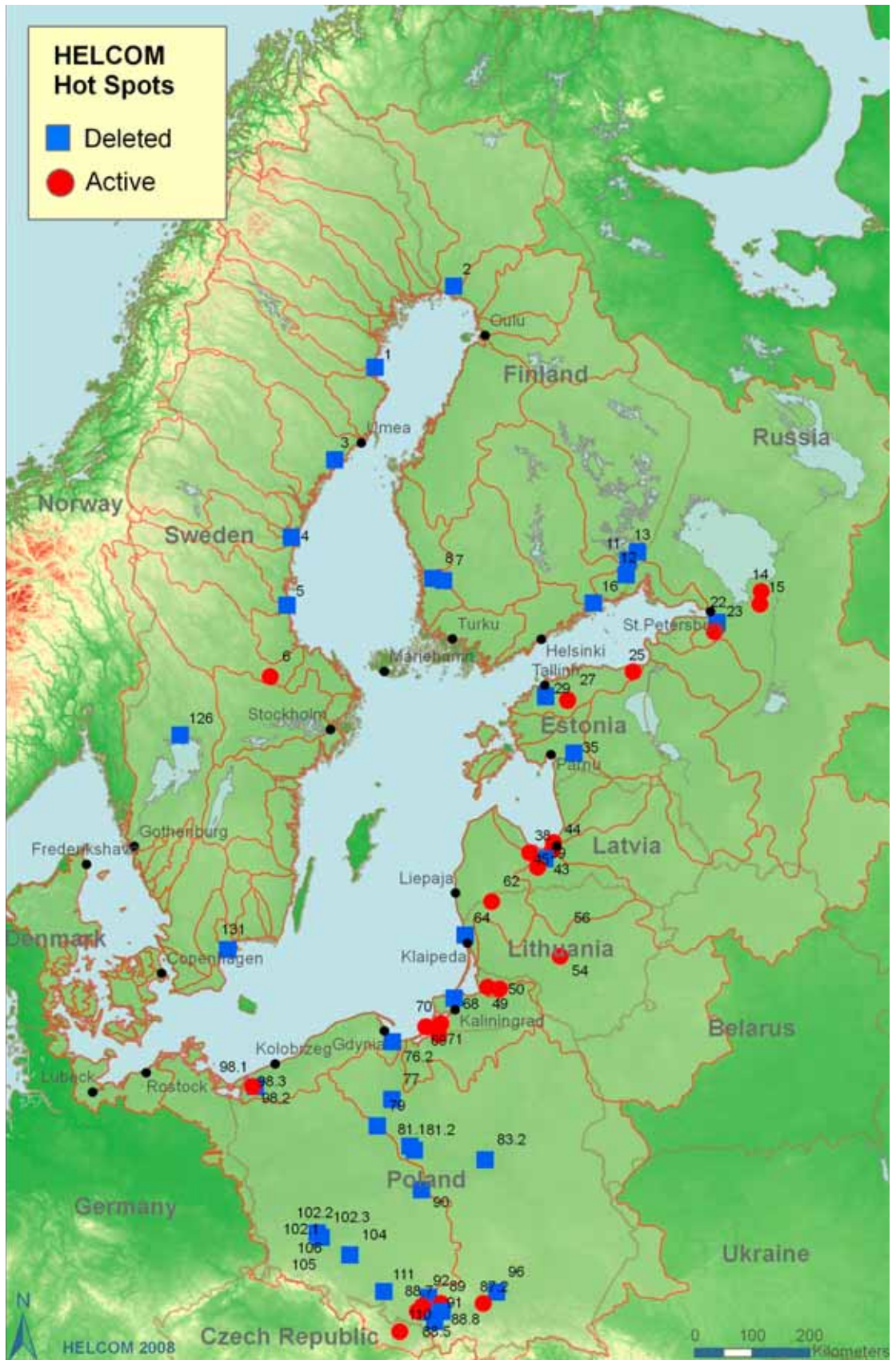


Figure 3.1 Conceptual model of the sources of inputs of hazardous substances to the Baltic Sea.



**Figure 3.2** HELCOM Industrial hot spots in the Baltic Sea catchment area in 2009. The numbers refer to the list on the HELCOM website\*.

\*) [http://www.helcom.fi/projects/jcp/hotspots/en\\_GB/hotspots/](http://www.helcom.fi/projects/jcp/hotspots/en_GB/hotspots/)



## 3.1 Land-based point-source pollution

Point-sources on land include, *inter alia*, various kinds of industrial sources as well as municipal sources. In addition, this section contains information on the sources of radioactivity to the Baltic Sea, most of which also have a point-source origin.

### 3.1.1 Industrial sources

Industrial sources include a great variety of different kinds of production facilities with a multitude of different types of substance discharges, losses and emissions. Some of the different types of industrial sectors with emissions of hazardous substances that operate in the Baltic Sea catchment area include: waste incineration, metallurgical production, power production, the mineral industry, textile industry, chemical industry, refineries, pulp and paper, wood preservation and asphalt processing.

The forest industry has been an important source of dioxins. Chlorophenol and chlor-alkali paper and pulp production, in which chlorine was used in large quantities for pulp bleaching until the early 1990s, used to be an important source of dioxins, but many of these facilities have been phased out, at least in Finland and Sweden (HELCOM 2004b).

In 1990, Prime Ministers of the Baltic Sea countries adopted the Baltic Sea Declaration, under which

a high-level task force developed the Baltic Sea Joint Comprehensive Environmental Action Programme (HELCOM 1990). The Baltic Sea JCP aimed at reducing pollution inputs to the Baltic Sea and chose to focus on a set of point-polluters, “hot spots”, in the Baltic Sea catchment area.

Originally 132 hot spots and 31 sub-hot spots were identified within the Baltic Sea catchment area, 47 of which were priority sites where investments would result in a significant reduction of the pollution load (**Fig. 3.2, Table 3.1**). Fifty industrial hot spots were on the original list of hot spots. By 2009, 89 hot spots and sub-hot spots had been deleted from the list as a result of investment activities, clean-up efforts and cessation of operation.

Between 1991 and 1998, discharges of wastewater from all industrial hot spots decreased by 50%, with the largest reductions reaching 75% at eleven hot spots. During this time period, discharges of chlorinated compounds (AOX) and heavy metals decreased by 83% and 62%, respectively (HELCOM 2002b). Air emissions of heavy metals from the HELCOM hot spots decreased 61% during the same time period. The reduction of AOX from pulp and paper mills was particularly large in the Nordic countries (Huuska & Forsius 2002). In the early 1990s, the St. Petersburg metal plating industry consisted of about 300 plants and was the single largest polluter of metal effluents to the Baltic Sea, with a 20% share of the total loading to the sea (HELCOM 2004a). In 1991, only

**Table 3.1 HELCOM Hot Spots related to industry and hazardous waste in the Baltic Sea catchment area in 2009.**

	Current Industrial Hot Spots	Current Industrial Priority Hot Spots	Deleted Industrial Hot Spots	Original Industrial Hot Spots
Belarus	2	0	0	0
Czech Republic	2 *	1	0	3 *
Denmark	0	0	0	0
Estonia	4	1	5	9
Finland	0	0	7	7
Germany	0	0	0	0
Latvia	6	5	1	7
Lithuania	4	1	9	13
Poland	12	12	27	39
Russia	16	10	13	29
Slovakia	0	0	0	0
Sweden	1	0	6	7
Ukraine	1	1	0	1
<b>Total</b>	<b>48</b>	<b>31</b>	<b>68</b>	<b>115</b>

\*) One Hot Spot shared with Poland.

about 90 plants had any kind of pre-treatment of wastewaters. Between 1991 and 1995, the discharge of heavy metals was reduced significantly (Huuska & Forsius 2002). After several national and international projects, all large galvanic plants obtained local wastewater treatment facilities and recycling of galvanic effluents. Some of the galvanic plants were able to reduce their discharges by 99% (HELCOM 2004a). By 2002, the heavy metals in St. Petersburg wastewater had been reduced as follows: Cu 87%, Zn 56%, Ni 80%, Cr 95%, Pb 93% and Cd 97%. New techniques replaced the use of cadmium, mercury, nonylphenol ethoxylates, cyanides and chlorinated organic pollutants. On the other hand, the economic recession during the 1990s in the so-called transition countries at that time caused more than one hundred plants to be shut down for economic reasons.

### 3.1.2 Wastewater treatment plants and municipal storm waters

Wastewater treatment plants (WWTPs) filter out several contaminants and prevent them from entering the sea, but due to their high discharge volumes and low removal efficiency for some contaminants, they can be seen as point polluters (HELCOM 2009c). Tributyltin (TBT), pentabrominated diphenylether (penta-BDE), nonylphenols (NP) and octylphenols (OP) have been found at high concentrations in treated wastewater from several WWTPs around the Baltic Sea (HELCOM 2009c). In addition, wastewater treatment plants are major point sources of a wide array of pharmaceutical substances, such as analgetics, antibiotics, anti-inflammatory drugs, anti-depressants, anti-psychotics and sedatives. Wastewater treatment processes have not been designed to break down pharmaceuticals. These substance groups have recently been addressed in Swedish screening studies (Woldegiorgis et al. 2007, Sternbeck & Österås 2009) and have been found in wastewater from the city of Stockholm (Cajsa Wahlberg, unpublished results from Stockholm Vatten); they are also discussed in **Section 2.2.9**.

Some screening studies show that industrial and municipal storm waters contain very high TBT levels (Sternbeck et al. 2006, Strand et al. 2007), whereas storm waters from motorways and industrial areas and leachates from landfills contain high concentrations of nonylphenols and octylphenols

(HELCOM 2009c). In this assessment, it has been shown that alkylphenols and penta-BDEs occur at high concentrations at some of the stations measured, indicating that all sources of these substances should be identified and managed.

### 3.1.3 Sources of radioactive substances

Radioactive substances occur naturally in the environment. Naturally occurring radioactive substances originate mainly from the elements of which the Earth was originally formed and partly from the Earth's atmosphere by cosmic radiation from outer space. Examples of the former are isotopes of uranium (U), thorium (Th) and potassium (K) with half-lives comparable to the age of the Earth, i.e., billions of years. Examples of the latter are tritium ( $^3\text{H}$ , super heavy hydrogen) and carbon-14 ( $^{14}\text{C}$ ) with half-lives of 12 yr and 5700 yr, respectively. The long-lived isotopes  $^{235}\text{U}$ ,  $^{238}\text{U}$  and  $^{232}\text{Th}$  are transformed by radioactive decay into a series of decay products, which are also radioactive and therefore contribute an additional number of radioactive substances to the environment; these decay products include radium-226 ( $^{226}\text{Ra}$ ) and polonium-210 ( $^{210}\text{Po}$ ) with half-lives of 1600 yr and 140 days, respectively. Therefore, the marine environment contains a number of naturally occurring radionuclides. One cubic metre of seawater typically contains 1000 Bq  $^3\text{H}$ , 4 Bq  $^{14}\text{C}$ , 40 Bq  $^{238}\text{U}$ , 4 Bq  $^{226}\text{Ra}$ , 4 Bq  $^{210}\text{Po}$  and 12 000 Bq  $^{40}\text{K}$ .

The occurrence of man-made radioactive substances in the Baltic Sea arises from four main causes. From 1950–1980, the United States and the Soviet Union carried out atmospheric nuclear weapons tests which peaked in the 1960s causing radioactive fallout on the northern hemisphere. This pollution is declining but still noticeable in the sea and on land. The accident at the Chernobyl nuclear power plant in 1986 caused heavy pollution in the zone near the power plant and considerable fallout over the Baltic Sea. The European facilities for reprocessing used nuclear fuel, Sellafield in the UK and La Hague in France, discharge radioactive substances to the sea; this radioactivity is transported by sea currents to the North Sea from where a small proportion enters the Baltic Sea. In addition, authorized discharges of radioactivity to the sea from the routine operation of nuclear installations (nuclear power plants and

nuclear research reactors) in the Baltic Sea region provide small contributions.

The levels of naturally occurring radionuclides in the Baltic Sea remain constant and present no risk to man or the environment. The dominant man-made radionuclide in the Baltic Sea is cesium-137 ( $^{137}\text{Cs}$ ), which mainly arises from fallout from the Chernobyl accident. Cesium-137 is being slowly transported from the Baltic Sea to the North Sea via the Kattegat. Minor amounts of other radionuclides from European facilities for the reprocessing of spent nuclear fuel are transported in the opposite direction. Routine discharges of radioactivity from nuclear power plants in the Baltic Sea area are small and detectable only locally. The three dumping sites with five officially confirmed dumpings of radioactive waste performed in the late 1950s or early 1960s in the Baltic Sea show negligible doses to man (HELCOM 2009d). Non-nuclear facilities such as hospitals and research laboratories discharge short-lived radionuclides to the environment, but they have no significant effects on the ecosystem or human health.

## 3.2 Diffuse land-based pollution

Information on the diffuse waterborne inputs of hazardous substances from land is somewhat scattered. In this section, information is provided on riverine inputs of persistent organic pollutants and heavy metals, on pesticides, and on losses from various types of goods, articles and materials.

### 3.2.1 Riverine inputs of POPs and heavy metals

Rivers are one of the main pathways of contaminants from diffuse sources as well as inland point sources to the Baltic Sea. Heavy metals in the Baltic Sea enter largely via riverine inputs (**Fig. 3.3**). In 2006, about 85% of cadmium, 75% of mercury and 50% of lead inputs entered the Baltic Sea via rivers or as direct waterborne discharges. The remainder arrived via atmospheric deposition. Due to incomplete data sets, it is difficult to assess temporal trends of riverborne heavy metal inputs. However, it is quite clear that lead inputs from Poland and Sweden have decreased significantly, cadmium inputs from Germany and Lithuania



have decreased, and mercury inputs from Russia, Finland, Sweden, Denmark, Germany and Poland have decreased (Knuuttila 2009).

The River Neva, which discharges to the Gulf of Finland, has the largest river basin catchment area of the Baltic Sea (17% of the whole catchment) (**Table 3.2**). The Gulf of Finland also has two other large catchment areas: Velikaya (3%) and Kymijoki (2%). The cadmium inputs via the River Neva were clearly the largest of all the rivers, (**Fig. 3.4**). Concentrations of heavy metals in Estonian and Latvian rivers were generally close to natural levels, but in the rivers flowing to the central Gulf of Finland, the concentrations of several metals have recently been found to be higher, classifying them as in a “moderate or bad environmental status” (Roose & Roots 2005). The main sources of heavy metals in Estonia are overflows from municipal and industrial wastewater plants and storm waters.

The River Kymijoki is a major source of mercury and dioxin to the Gulf of Finland. The input of dioxins during the 1970s and 1980s from pulp and paper mills in the River Kymijoki catchment area has polluted the sediments in the river and its estuary area (Salo et al. 2008). The use of chlorine gas in bleaching no longer occurs in Finland or Sweden (HELCOM 2004b).

**Table 3.2** The ten largest river catchment areas around the Baltic Sea.

River	Catchment area km <sup>2</sup> (%)	Baltic Sea sub-basin
1. Neva	285 063 (17%)	Gulf of Finland
2. Vistula	192 196 (12%)	Gulf of Gdansk
3. Oder	130 708 (8%)	Bornholm Basin
4. Nemunas	95 380 (6%)	Eastern Gotland Basin
5. Daugava	90 073 (5%)	Gulf of Riga
6. Velikaya	56 348 (3%)	Gulf of Finland
7. Göta	54 000 (3%)	Kattegat
8. Kemijoki	51 921 (3%)	Bothnian Bay
9. Tornionjoki	40 345 (2%)	Bothnian Bay
10. Kymijoki	37 352 (2%)	Gulf of Finland

The largest riverine inputs of PCBs to the Gulf of Finland enter from the Okhta River, Chernaya River and Sestroretsk in the Russian territory (Roose & Roots 2005). The annual Estonian riverine input of PCBs was approximately 332 kg in 2003 (Roose & Roots 2005).

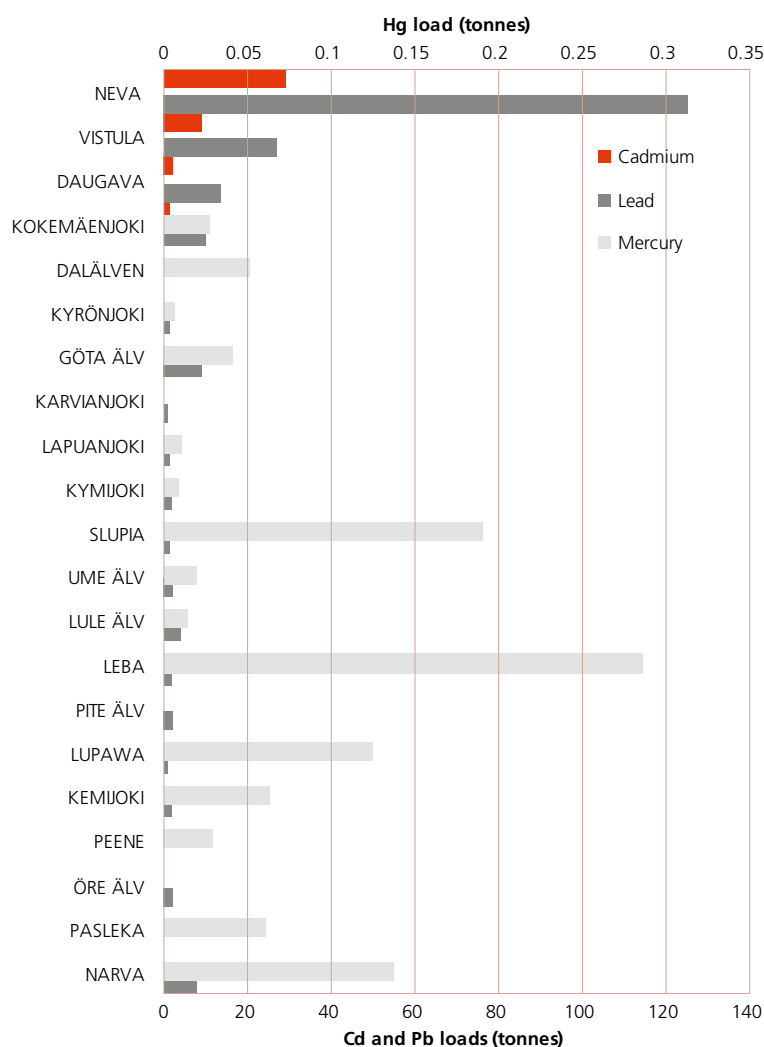
The River Vistula has the second largest catchment, covering 12% of the Baltic Sea catchment area. It carries large amounts of pesticides, alkylphenols, metals, detergents, PAH compounds and aromatic amines, originating from agriculture, wastewater treatment plants and several industrial complexes in the area (Galassi et al. 2008). The contaminants from the Vistula River are deposited as sediments in the Gdansk Deep (Sapota 2006).

The River Oder is the only large river flowing into the Bornholm Basin, the deepest part of which is a sink for organic pollutants from the Oder and the Szczecin lagoon (Sapota 2006). The catchment area of the River Oder is the third largest in the Baltic Sea (8%, **Table 3.2**). The fourth largest catchment, covering 6% of the Baltic Sea catchment area, is for the River Nemunas, which is the major river flowing into the Eastern Gotland Basin. A significant part of its waters originate from Belarus. The River Daugava is the main source of pollution inputs to the Gulf of Riga and has the fifth largest catchment area in the Baltic Sea (Nordic Environmental Research Programme 1999).

The Arkona Basin, Mecklenburg Bight, Kiel Bight, Little Belt, Great Belt and the Sound have very small catchment areas and no large rivers. However, the Kattegat, receives drainage from three large river catchments, the Göta, Lagan and Gudenå, as well as from the Danish fjords Limfjord, Mariager fjord, Roskilde fjord, Randers fjord and Odense fjord.

### 3.2.2 Pesticides in the catchment area

Pesticides typically originate from land-based sources. In the marine environment, they are mainly found near river mouths and urban areas (Galassi et al. 2008). A Russian study on the riverine discharges of pesticides concluded that the Russian Federation has particularly discharged DDT and its derivative DDE to the Baltic Sea (Zhulidov et al. 2000). On the other hand, concentrations of pesticides in Estonian river water and sediment



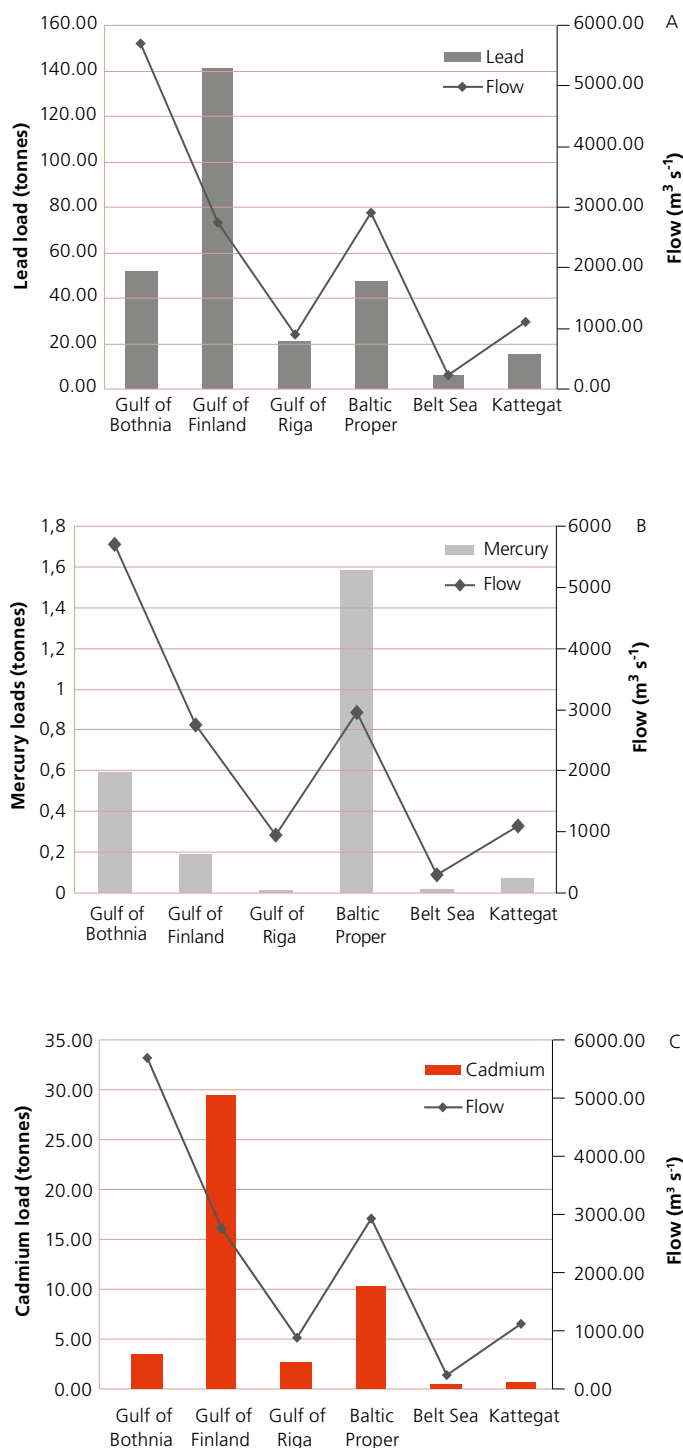
**Figure 3.3** Riverine inputs (tonnes) of cadmium (Cd), lead (Pb) and mercury (Hg) to the Baltic Sea in 2006 (unpublished data from HELCOM PLC 5). Note that data on the load of mercury from River Vistula is lacking.

are below target levels (Roose & Roots 2005) because the use of pesticides decreased sharply in the early 1990s. Estimates of the annual Estonian riverine inputs of DDT and HCHs were 2.8 kg and 47.5 kg, respectively, in 2003. Poland covers 20% of the catchment area but has almost 50% of the agricultural land in the Baltic Sea catchment area. Pesticides such as DDT and its degradation products have been found in large quantities in the Gulf of Gdansk, which may indicate a quite recent origin of pollution in the area (Galassi et al. 2008). DDT was banned in 1996 in Poland. Belarus is the only country in the Baltic Sea catchment area in which many pesticides have not been banned, but it is not known whether they are still used or their amounts. Because Belarus covers 5% of the whole catchment area, its impact on the riverine input of pesticides to the eastern and southeastern Baltic Sea may be significant.

### 3.2.3 Losses from various types of goods, articles and materials

An area that definitely needs more attention is the diffuse losses from various goods, articles and materials. There are presently several research programmes being conducted in the Baltic Sea region, but the quantities of such losses are still a matter of great uncertainty. It has been estimated that leakage from products is the main pathway for brominated substances (PBDEs and HBCDD), fluorinated substances and nonylphenols (HELCOM 2009c). PBDEs are used as flame retardants in furniture, which have a half-life of use of 10 years. During that time, about 0.39–0.54% of PBDEs volatilize (EU-RAR 2000). In many countries, HBCDD is used as a flame retardant primarily to produce polystyrene (for use as building insulation), but it is also used in electrical products and textiles. Fluorinated compounds are used in the impregnation of textiles, leather, paper and cardboards, but also in cleaning products. Nonylphenols have been used extensively in the plating industry and cleaning products, and they also leak to the environment from waste sites (HELCOM 2009c).

The brominated flame retardants PBDEs can be used as an example to illustrate a product-based emission source to the marine environment. Penta-BDE and octa-BDE have probably entered the Baltic Sea area as additives to various forms of plastic polymers and textiles. There were previously also



**Figure 3.4** Total waterborne inputs of **A)** lead, **B)** mercury and **C)** cadmium to the Baltic Sea sub-basins in 2006 (Knuuttila 2009). The flow ( $m^3 s^{-1}$ ) indicates the average annual riverine inflow entering each sub-basin. The mercury load from River Vistula has been removed due to unreliable monitoring data.

historic point sources such as within the Swedish textile industry. The concentrations of octa-BDE and penta-BDE in eggs of common guillemot (*Uria aalge*) have been measured establishing a time series from 1969. **Figure 3.5** shows the concentrations of penta-BDE in guillemot eggs from 1969 to 2005. The downward trend starting in the mid-1980s coincides with the voluntary phase-out of PBDEs in Germany and Sweden. The EU banned the use of penta-BDE and octa-BDE in 2004. Electronic products on the Swedish market were virtually free from the substances in 2008 (unpublished data, pers. comm. Christina Larsson, Swedish Chemicals Agency).

In contrast, HBCDD has not showed the same pattern, and the concentration is still increasing in common guillemot eggs (**Fig. 2.26**). The EU risk assessment of HBCDD indicates that the emissions used to be heavily dominated by the release from one single company and this production site in Aycliffe, UK has now been closed. The industry

initiative VECAP<sup>14</sup> has also implemented a voluntary programme with major emissions reductions on the agenda. HBCDD is, however, still frequently used as an additive to insulation materials in Eastern Europe, which might explain the continued upward trend for HBCDD. Based on the experience of the losses of hazardous substances from household products, it is important to take action not only on emissions from point sources, but also on the use of substances within articles.

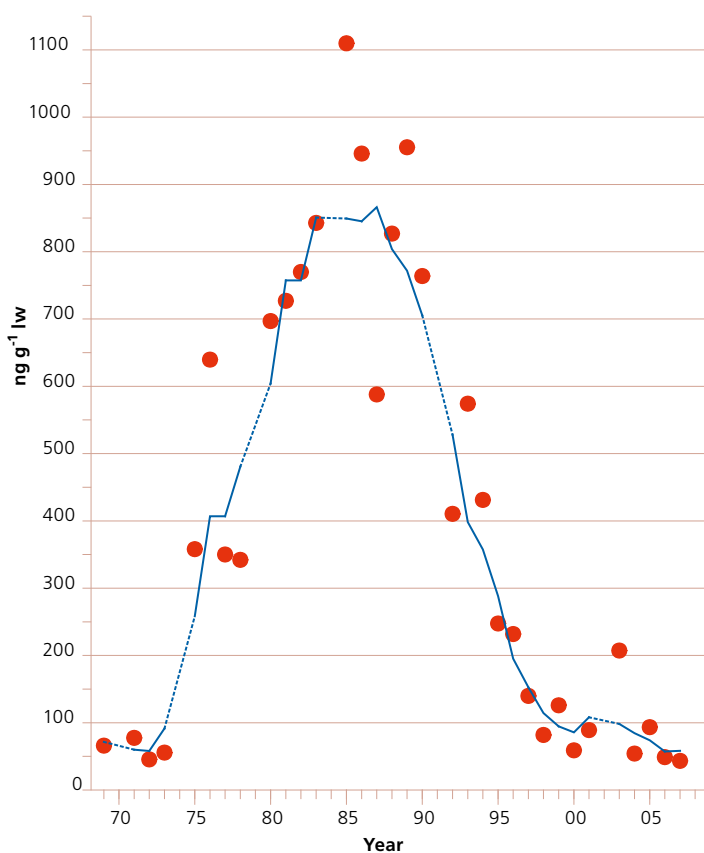
### 3.3 Pollution from sources at sea

This section presents information on the sources of pollution at sea, including shipping activities, harbours and marinas, oil platforms and contaminated sediments.

#### 3.3.1 Shipping

The Baltic Sea is one of the most crowded shipping areas in the world. Shipping of a wide array of cargo types, including chemicals and oil, occurs in almost every part of the sea area (**Fig. 3.6**). In 2008, more than 170 million tonnes of oil was transported via the Great Belt, twice as much as in 2000. Further increases in oil shipments are predicted. Hazardous substances from shipping reach the environment through atmospheric emissions from combustion, leaking from anti-fouling paints, and intentional or accidental spills of oil and hazardous substances.

Tributyltin (TBT) is the organotin biocide component in anti-fouling paints that were widely used on ships to protect their hulls from fouling organisms (all kinds of sessile algae, crustaceans and molluscs). At present, the use of TBT is banned under international law in many countries' waters and ports, including all Baltic Sea countries except the Russian Federation. According to a rough estimate, a large container ship with a hull area of 6900 m<sup>2</sup> contributed approximately 276 g TBT daily to the Baltic Sea (Haskoning 2002). The Finnish Ministry of Environment (2007) has estimated that a total of 50 tonnes TBT (3.6 tonnes per year) had been released from ship hulls to the



**Figure 3.5** Temporal trends of concentrations of the pentabrominated diphenylether BDE-47 in eggs of common guillemot (*Uria aalge*) from 1969 to 2007 on Stora Karlsö, an island in the Western Gotland Basin.

<sup>14</sup> Voluntary Emissions Control Action Programme ([www.vecap.info](http://www.vecap.info))

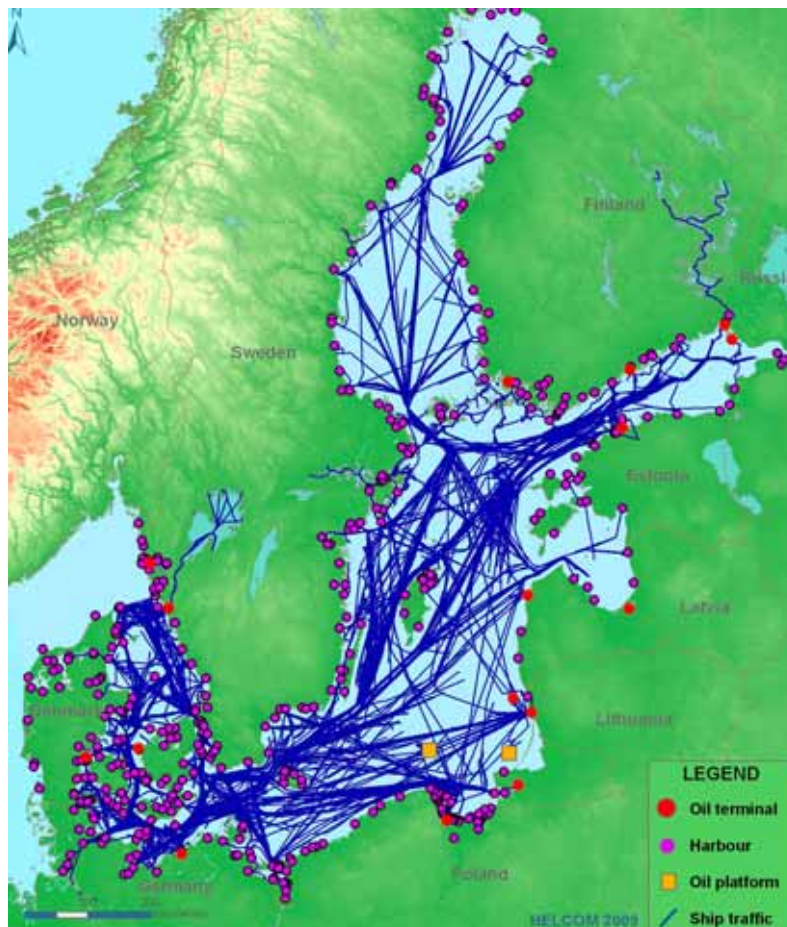
Finnish coastal waters from 1992–2005. Currently, organotin compounds have been substituted by other toxic booster biocides in combination with copper as antifouling agents in ship paints and they are generally regarded as less persistent and consequently having less environmental impact on non-target organisms. However, copper concentrations have been found to increase in the Baltic Sea environment (see **Section 2.2.3**).

The legislative framework to ban TBT use in anti-fouling paints is in place, and the efforts should focus on its full enforcement in the entire Baltic Sea region. First of all, Russia should ratify the Convention on the Control of Harmful Anti-fouling Systems on Ships as soon as possible. Secondly, monitoring and control of ships' compliance with the regulations should be given priority. Based on the results of the port State control, namely a list of non-compliant ships, HELCOM will develop a monitoring system to enable the detection of such ships entering the HELCOM area.

Last but not least, the Contracting Parties should promote the development of effective, environmentally friendly and safe TBT-free antifouling systems to ensure that TBT is not substituted by other hazardous substances.

The continuing illegal oil discharges observed in the Baltic Sea (**Fig. 3.7**), as well as shipping accidents resulting in oil spills and other pollution (**Fig. 3.8**), are a significant source of heavy metals and PAH compounds to the offshore and coastal environment. Particularly in the Arkona Basin and the Sound, the areas of heavy ship traffic, PAH compounds show high concentrations in surface sediments, sometimes exceeding the threshold concentrations of acceptable contamination levels. On a positive note, the amount of oil discharged illegally has decreased substantially, and currently the majority of spills found are smaller than 100 litre<sup>15</sup>.

All HELCOM countries are parties to MARPOL 73/78 and its Annexes I and II. To enforce the regulations, regular sea surveillance is carried by the Contracting Parties, using both aircraft and satellite observations. Additionally, the HELCOM Automatic

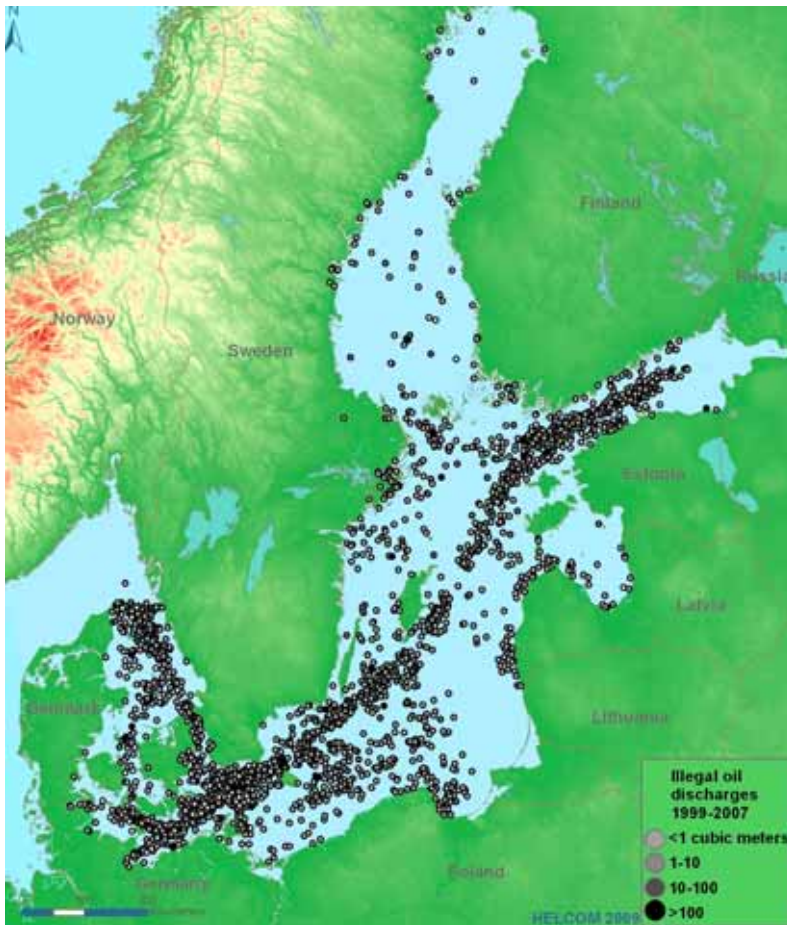


**Figure 3.6 Shipping routes, harbours, oil terminals and oil platforms in the Baltic Sea.**

Identification System for ships, combined with the oil drift forecasting tool SeaTrackWeb, increases the likelihood of identifying illegal polluters. All single-hull tankers entering the Baltic Sea are automatically detected by a HELCOM prevention and monitoring system, and they are further checked to determine that they are not violating the regulations banning the carriage of heavy grade oil by single-hull ships.

The number of deliberate, illegal discharges of oil from ships annually observed by national surveillance planes as well as satellites over the Baltic Sea area has decreased by more than 55% since 1999. The size of the spills is decreasing as well. However, more than 200 spills are still detected every year. Most parts of the Baltic with regular traffic zones are covered by national aerial surveillance, but some Contracting Parties still do not carry out surveillance flights in accordance with the HELCOM requirements. There is also a need to

15 HELCOM Indicator Fact Sheet on illegal oil spills (2009): [http://www.helcom.fi/environment2/ifs/ifs2009/en\\_GB/illegaldischarges/](http://www.helcom.fi/environment2/ifs/ifs2009/en_GB/illegaldischarges/)



**Figure 3.7** Illegal discharges of oil from ships in the Baltic Sea, 1999–2007. The oil discharges are detected by aerial surveillance. The territorial waters of the Russian Federation are not included in the data.

ensure a certain proportion of flight hours for the detection of polluters in darkness, when deliberate discharges are more likely to occur, which means that aircraft should be properly equipped to detect oil at night or in poor visibility.

### 3.3.2 Harbours and marinas

Harbour sediments contain very high concentrations of TBT, heavy metals, PAHs and other contaminants originating from anti-fouling paints and various harbour activities. TBT was introduced in anti-fouling paints in the 1960s, and in the 1980s it was discovered that TBT has severe side effects on the ecosystem. In this assessment, TBT concentrations in surface sediments were found to be well above threshold levels all over the Baltic Sea. The Finnish Food Safety Agency screened for TBT concentrations in coastal fish (perch, pike, pikeperch, burbot) and found that fish in areas close to old and current harbours are unsafe to eat; their TBT

concentrations were as much as three times higher than the quality standard (Anon. 2005, Hallikainen et al. 2008).

The high contamination in coastal areas is found not only near harbours, but also in marinas (Finnish Ministry of Environment 2007, Eklund et al. 2008, HELCOM 2009c). The marina areas are commonly used as service areas for small boats where the scraping of old anti-fouling paint and repainting have occurred. Because of the adverse effects of TBT on marine invertebrates, such use has been widely banned for small boats (<25 m) since the late 1980s within the EU (Santillo et al. 2001) as well as in HELCOM Contracting Parties since the entry into force of the 1992 Helsinki Convention in 2000. Despite this, a recent Swedish study of small-vessel marinas found TBT concentrations comparable to those in large harbours (Eklund et al. 2008).

### 3.3.3 Oil platforms

The discharges associated with the offshore exploitation of oil usually include polycyclic aromatic hydrocarbons (PAHs) and heavy metals. There are only two oil platforms operating in the Baltic Sea: “Baltic Beta” located 70 km north of the Hel Peninsula, Poland, and D-6 located 23 km off the Curonian Spit, in the southeastern part of the Baltic Sea (Fig. 3.6). All process and household wastes from Platform D-6 are collected in containers and transported by vessels onshore for further treatment. The company operating the platform conducts environmental monitoring, including satellite observations for spills of oil, as well as water quality.

According to the monitoring near D-6, concentrations of heavy metals (copper, mercury, lead and chromium) are within acceptable limits, whereas PAH compounds have locally high concentrations. Concentrations of benz[a]anthracene and chrysene were  $>35 \text{ ng l}^{-1}$  and benzo[a]pyrene was  $3\text{--}10 \text{ ng l}^{-1}$  (Lukoil 2006), which exceed the acceptable limits of  $1.2 \text{ ng l}^{-1}$  for benz[a]anthracene and  $0.05 \text{ ng l}^{-1}$  for benzo[a]pyrene in sea water (Anon. 2008b, ICES 2008b).

Because of the abundant historical and current illegal and accidental oil discharges from ships to the sea, it is difficult to distinguish the impact of operating oil platforms from the oil contaminants originating from ships. In addition, oil entering the



Baltic Sea from coastal point sources and through rivers, e.g., from refineries, may have contributed to PAH concentrations in sea water.

According to HELCOM requirements, discharges of “black” chemicals from offshore platforms were banned from 2008, and discharges of “red” chemicals and oil-containing water are banned from 2010 (previously, the oil content of discharged production and displacement water was not to exceed 15 mg l<sup>-1</sup>). “Black” chemicals include very harmful substances categorized as “X” under Annex II to MARPOL 73/78. “Red” chemicals include harmful substances categorized as “Y” under Annex II to MARPOL 73/78 as well as 12 additional hazardous substances.

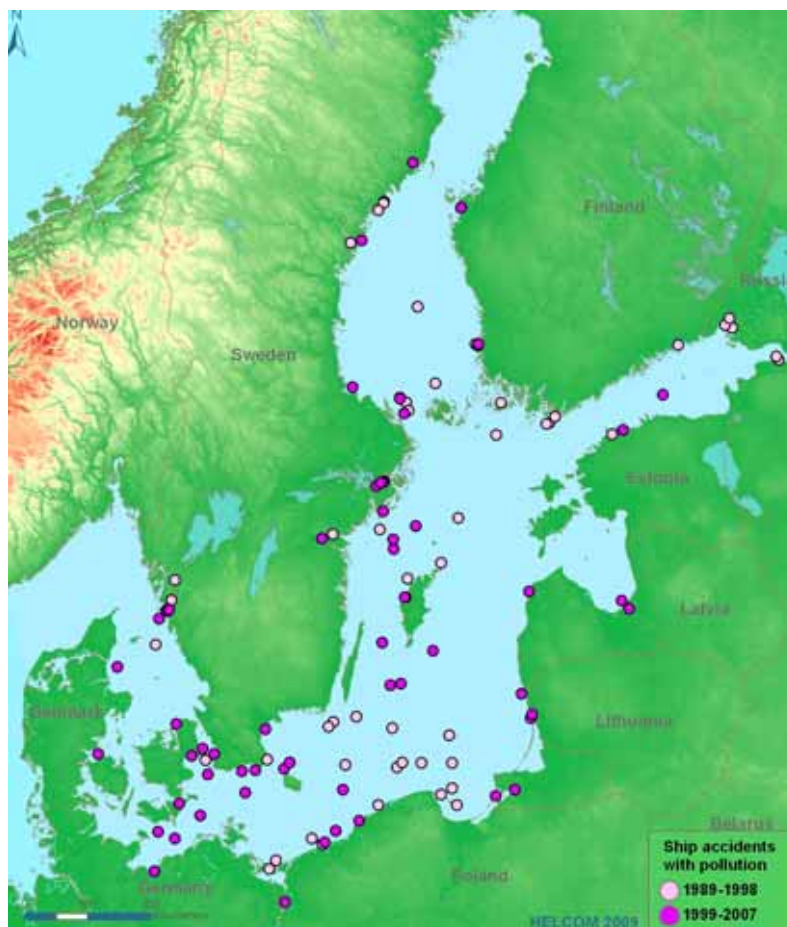
### 3.3.4 Contaminated sediments as a source of pollution

#### Estuarine sediments

Sediments act as a sink for hazardous substances as long as they are not disturbed physically (e.g., dredging or hydrographic changes) or by biophysical disturbances (bioturbation by organisms). Disturbance of contaminated sediments may result in the resuspension of hazardous substances and increase their availability to chemical and biological processes.

Contaminated estuaries are easily recognized from the status maps in **Chapter 2**. For example, the Vistula Lagoon is a HELCOM hot spot owing to pollution by chemicals from the River Vistula. The River Oder flows into the Szczecin Lagoon, which is heavily polluted due to riverine discharges, but also by coastal point sources of pollution. Another example is the estuary of the River Kymijoki in the Gulf of Finland, where the long history of chlorine contamination from pulp and paper mills has resulted in highly toxic estuarine sediments (**BOX 1**, on page 20).

Many historical and present point polluters have been located along rivers in the Baltic Sea catchment area. Depending on the river flow and the geomorphology of the estuary, discharges of hazardous substances may have been retained in the river estuary and estuarine sediments, in particular. Estuarine sediments are frequently disturbed by dredging, such as for harbour maintenance, maintenance of navigation channels and coastal con-



**Figure 3.8** Shipping accidents resulting in pollution in the Baltic Sea.

struction works. Other construction activities, such as the construction of pipelines or windmills, may also reactivate the contaminants in the sediments.

#### Disposal of dredged sediments

The Helsinki Convention generally prohibits dumping, but the disposal of dredged material is allowed through a permit system which is accompanied by requirements for HELCOM Contracting Parties to report to the Helsinki Commission on the nature and quantities of the material disposed. Reporting requirements and guidelines for permitted disposals include the need for information on the contamination level of the materials disposed at sea.

During 2003–2007, seven of the nine countries reported that they did not dump dredged material that exceeded national threshold concentrations for hazardous substances. According to the reports by Finland, Germany and Sweden, some of the disposed dredged material contained tributyltin



**Figure 3.9** Known disposal sites for dredged material in 2003–2007 and the confirmed dumping sites of World War II chemical munitions.

or its derivatives and polychlorinated biphenyls. Russia reported that in one site in the Neva Bay disposed dredges spoils contained high amounts of cadmium, mercury and zinc. The dumping sites reported are shown in **Figure 3.9**. Although the concentrations measured in dredged material did not exceed national standards, many of the maximum concentrations were above the international quality standards defined for good environmental status. For example, in the Kattegat and on the Latvian coast, the reported mercury, lead, cadmium or other metal concentrations in the disposed material were very high.

#### Dumped chemical munitions

Dumped chemical munitions can cause a severe threat to the marine environment. With relative certainty, around 40 000 tonnes of chemical munitions were dumped in the Helsinki Convention area at the end of World War II. It is esti-

mated that the chemical munitions contained no more than 13 000 tonnes of chemical warfare agents. Most of the agents were mustard gas (approximately 7000 tonnes), but also about 3400 tonnes of arsenic-containing chemicals were dumped in the area. This figure does not take into account the dilution and degradation that have taken place since then. In addition, around 34 000 tonnes of chemical munitions—containing about 12 000 tonnes of chemical warfare agents—were dumped east of Bornholm and near Gotland in 1947 and 1948, 200–300 tonnes of chemical munitions residues, discovered after 1952 in the former GDR, were dumped east of Bornholm and unconfirmed reports suggest that about 55 000 tonnes of chemical munitions were dumped southwest of Rønne (Bornholm) in 1946 and 1956 (HELCOM 1994). The dumping area in the Skagerrak just outside the HELCOM area includes 20 000 tonnes of chemical munitions, e.g., mustard gas (HELCOM 1994).

It is known that the sites in the Bornholm Basin and the eastern Baltic Proper contain mustard gas, sternutators, lachrymators and suffocating agents (**Fig. 3.9**) (HELCOM 1995). Although almost all warfare agents have broken down at varying rates into less toxic, water-soluble substances, some compounds show an extremely low solubility and slow degradability (viscous mustard gas, Clark I and II, and Adamsite). However, as these compounds cannot occur in higher concentrations in the water, a wide-scale threat to the marine environment from dissolved chemical warfare agents can be ruled out. The biological effects of chemical warfare agents were discussed in the HELCOM report on dumped chemical munitions (HELCOM 1994).

A recent EU-funded research project, Modelling of Ecological Risks Related to Sea-Dumped Chemical Weapons (MERCW), analysed sulphur mustard and its degradation products; Tabun; -chloroacetophenone; Adamsite and its degradation products; Clark I and Clark II and their (identical) degradation products; phenyldichloroarsine and its degradation products; phenylarsonous acid and its degradation product; trichloroarsine and its degradation products; triphenylarsine and chlorobenzene from the Bornholm dumping site. No intact warfare agent chemicals—sulphur mustard, Tabun,  $\alpha$ -chloroacetophenone, Adamsite, Clark I,

**Table 3.4 Results of the analysis of chemical warfare agents in the Bornholm Basin.**

Sediment samples		
Warfare agent or its derivative	Concentration	Number of samples in which found (total 68)
Degradation products of sulphur mustard	1.6 µg kg <sup>-1</sup>	1 sample
Degradation products of Adamsite	0.4–130 µg kg <sup>-1</sup>	37 samples
Degradation products of Clark I	2–16000 µg kg <sup>-1</sup>	31 samples
Degradation products of phenyldichloroarsine	0.3–1200 µg kg <sup>-1</sup>	45 samples
Degradation products of trichloroarsine	280 µg kg <sup>-1</sup>	1 sample
Triphenylarsine	2–180 µg kg <sup>-1</sup>	16 samples
Chlorobenzene	3–18 µg kg <sup>-1</sup>	8 samples

Pore water samples		
Warfare agent or its derivative	Concentration	Number of samples in which found (total 4)
Degradation products of Clark I	13–780 µg l <sup>-1</sup>	3 samples
Degradation products of phenyldichloroarsine	14–230 µg l <sup>-1</sup>	3 samples

Clark II or phenyldichloroarsine—were found in the analysis. **Table 3.4** shows the results of the study. In only nine of 68 sediment samples, was no target chemical found. The results showed that the area is contaminated with arsenic-containing degradation products of Adamsite, Clark I, phenyldichloroarsine and trichloroarsine. Only one finding of mustard gas-related chemicals was made. Triphenylarsine and chlorobenzene are lipophilic and thus less water soluble. Heavy metal analysis of the sediment samples found arsenic concentrations from <8 mg kg<sup>-1</sup> to 210 mg kg<sup>-1</sup>. The nine samples with the highest concentrations (over 45 mg kg<sup>-1</sup>) were all taken within the primary dump site.

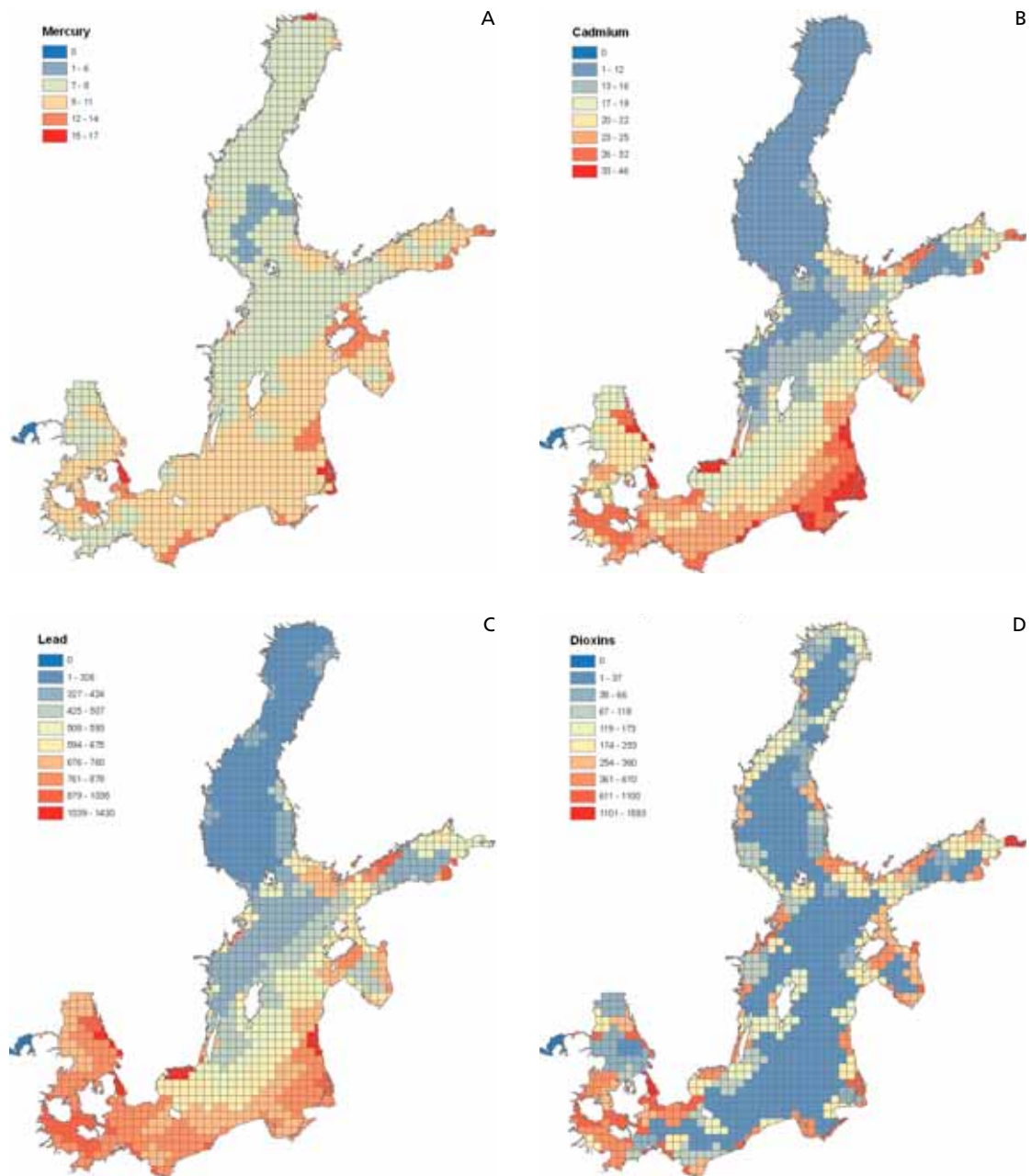
### 3.4 Emissions to air and atmospheric deposition of hazardous substances to the Baltic Sea

All heavy metals and POPs can be carried via atmospheric transport to the Baltic marine environment. Specific estimates of atmospheric deposition onto the Baltic Sea are available for cadmium, mercury, lead, and dioxins and furans, as provided by the European Monitoring and Evaluation Programme (EMEP). Assessments of other substances cover larger EMEP areas.

#### 3.4.1 Heavy metals

The atmospheric deposition of heavy metals to the Baltic Sea represents approximately half of the total inputs to the sea. The Belt Sea and Kattegat are especially exposed to airborne deposition (**Fig. 3.10A–C**). The total annual atmospheric deposition of heavy metals to the Baltic Sea decreased from 1990 to 2006 by 45% for cadmium, 24% for mercury, and 66% for lead (Gusev 2009a), which reflects the reductions in their emissions (Gusev 2009d). While cadmium and lead showed the steepest decline in the Gulf of Finland sub-basin (67% and 74%, respectively), the greatest decline of mercury (37%) occurred in the Belt Sea area (Gusev 2009a). Since Poland, Russia and Germany are the largest sources of these metal depositions, it is clear that the industrial restructuring and international and national investments in cleaner technology in Russia, Poland and the Baltic countries have contributed to the decreased levels, but much of the reductions certainly originate from economic turn-overs in the catchment area.

The greatest reductions in the emissions of cadmium occurred in Estonia (88%) and Lithuania (90%). Mercury showed the steepest decline in Latvia (92%) and Germany (85%), while the lead reduction was the greatest in Sweden (96%) and Denmark (95%). Despite the large reductions, this assessment showed unacceptable levels of cadmium and mercury contamination in surface



**Figure 3.10** Maps of the atmospheric deposition of **A)** mercury, **B)** cadmium, **C)** lead (in  $\text{g km}^{-2} \text{yr}^{-1}$ ) and **D)** atmospheric deposition of dioxins and furans ( $\text{pg m}^{-2} \text{yr}^{-1}$ ) to the Baltic Sea (average over the years 2005–2007, data from EMEP in 2009).

sediments, fish and mussels. However, the temporal trends show that the investments and reductions are already having a positive effect.

### 3.4.2 Dioxins and furans and other POPs

Dioxins and furans are formed in waste incineration and particularly in all kinds of combustion processes and therefore atmospheric deposition is their main pathway to the Baltic Sea. In addition

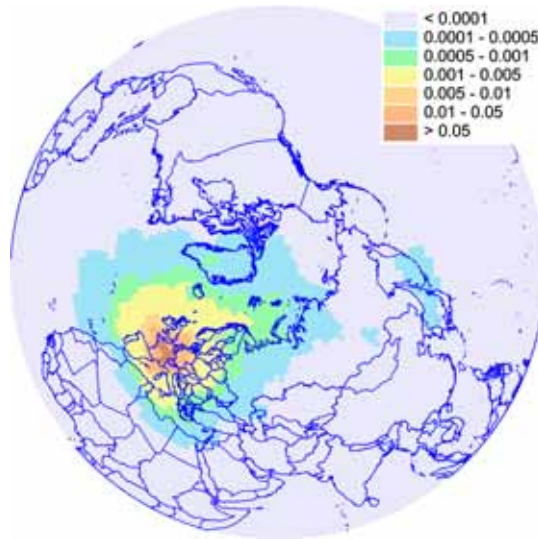
to household combustion, a significant source is iron sintering (Sundqvist et al. 2009b). Due to their formation during incomplete burning, dioxins can also form naturally in small amounts. The net annual deposition of dioxins and furans (PCDD/Fs) to the Baltic Sea decreased from 1990 to 2007 by 62% (Gusev 2009b). The change in deposition was quite similar between the basins and varied from 51% to 68%. The largest deposition occurred in the Belt Sea ( $470 \text{ pg TEQ m}^{-2} \text{yr}^{-1}$ ), whereas the smallest was found



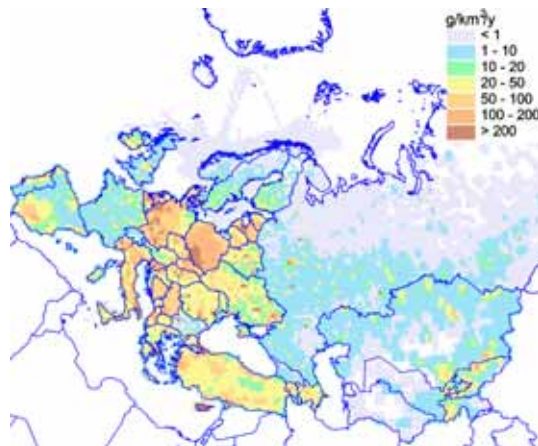
in the Gulf of Bothnia ( $60 \text{ pg TEQ m}^{-2} \text{ yr}^{-1}$ ) (Fig. 3.10D). Annual emissions of dioxins and furans in HELCOM countries (1.4 kg TEQ in 2006) decreased from 1990 to 2006 by 21% (Gusev 2009c). The most significant reductions in PCDD/F emissions were noted for Denmark and Finland, with more than a 50% reduction. Nevertheless, the concentrations of dioxins and furans in biota were high in the central and northern sea areas (see Section 2.2.1).

Modelled concentrations of HBCD in the air were relatively high in the Baltic Sea region (Fig. 3.11). Emissions of benzo[a]pyrene in 2007 were relatively elevated in the central, southern and eastern parts of Europe in relation to other areas, and in the Baltic Sea region they were especially elevated in the southern areas (Fig. 3.12, Gusev et al. 2009).

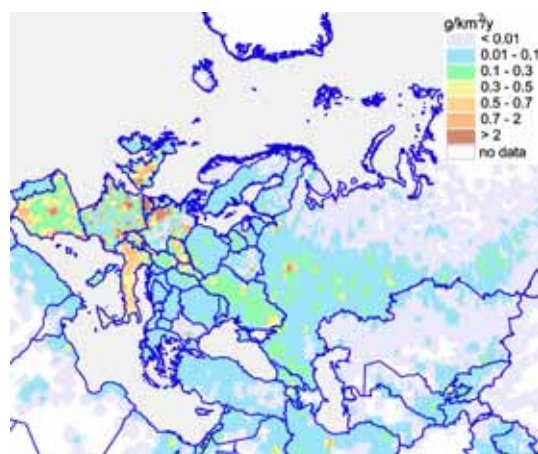
The most significant levels of PCB-153 emission fluxes in 2007 in the Baltic Sea region were from Lithuania and Germany (Fig. 3.13).



**Figure 3.11** Map of the spatial distribution of HBCD concentrations (relative units, annual means) in the above-ground air in the Northern Hemisphere calculated using the MSCE-POP model (relative units, Gusev et al. 2009).



**Figure 3.12** Map of the spatial distribution of benzo[a]pyrene emissions in 2007 over the EMEP grid with a resolution of  $50 \times 50 \text{ km}^2$ , in  $\text{g km}^{-2} \text{ yr}^{-1}$  (Gusev et al. 2009).



**Figure 3.13** Map of the spatial distribution of PCB-153 emissions over the EMEP grid in 2007 with a resolution of  $50 \times 50 \text{ km}^2$ , in  $\text{g km}^{-2} \text{ yr}^{-1}$  (Gusev et al. 2009).

# 4 OBJECTIVES AND STRATEGIES

This chapter outlines the environmental objectives and management actions related to hazardous substances that are of concern for the marine environment of the Baltic Sea and have been agreed in national and international frameworks.

## 4.1 Why do we care? – A healthy wildlife and safe food

Once released into the Baltic Sea, hazardous substances can remain in the marine environment for decades and accumulate in marine food webs up to levels that are toxic to marine organisms. Levels of some hazardous substances in the Baltic Sea exceed concentrations in the Northeast Atlantic by more than 20 times. Hazardous substances can cause adverse effects on the ecosystem, such as

- impaired general health status of animals,
- impaired reproduction of animals,
- increased pollutant levels in fish used as human food.

Contaminant concentrations in some Baltic fish species consumed by humans exceed the limit values for maximum levels set by the EU. Certain contaminants may be hazardous because of their effects on human hormone and immune systems, as well as their toxicity, persistence and bioaccumulating properties. In particular, substances that are persistent and bioaccumulate may cause hazards to humans.

Already the 1974 Convention on the Protection of the Marine Environment of the Baltic Sea Area (Helsinki Convention) called for the Contracting Parties to take action to counteract the introduction, whether airborne, waterborne or otherwise, into the Baltic Sea of hazardous substances as specified in Annex I of the Convention.

The revised 1992 Helsinki Convention presents the prevention of pollution as one of the fundamental principles and obligations:

*“The Contracting Parties shall individually or jointly take all appropriate legislative, administrative or other relevant measures to prevent and eliminate pollution in order to promote the ecological restoration of the Baltic Sea Area and the preservation of its ecological balance.” (Article 3, paragraph 11)<sup>16</sup>*

According to the 1992 Convention, the prevention of pollution shall be based on the precautionary principle, best environmental practice, and best available technology (BAT) in order to diminish hazards to marine ecosystems, living resources and human health in the Convention Area.

The vision of a healthy Baltic Sea ecosystem is the basis for all actions in the Baltic Sea Action Plan (BSAP) adopted in 2007 (HELCOM 2007a). The concept of a healthy ecosystem is defined in this context with the four goals of the BSAP:

- (1) life undisturbed by hazardous substances,
- (2) the sea unaffected by eutrophication,
- (3) towards favourable conservation status of Baltic Sea biodiversity, and
- (4) environmentally friendly maritime traffic.

Under each of these four segments, there are a number of objectives that define in more detail the desired ecological status or, in the case of maritime activities, the kind of measures that are urgently needed in order to reach the overall vision. The ecological objectives for the hazardous substances segment are: (1) concentrations of hazardous substances close to natural levels, (2) all fish safe to eat, (3) healthy wildlife, and (4) radioactivity at pre-Chernobyl level.

The ecosystem approach to the management of human activities implemented through the BSAP recognizes that humans are an inseparable part of the ecosystem, as is demonstrated, for example, by the ecological objective “all fish safe to eat” (HELCOM 2007a). Therefore, the monitoring of seafood safety is included in this assessment. Hazardous substances may also result in indirect undesirable impacts on habitats and food-web deterioration. Thus, biological effects caused by hazardous substances are an important indicator for a healthy ecosystem.

## 4.2 International regulatory framework for hazardous substances

Environmental pollution cannot be reversed without international cooperation because pollutants disperse beyond national boundaries. During recent decades, several important steps have been

<sup>16</sup> [http://www.helcom.fi/Convention/en\\_GB/convention/](http://www.helcom.fi/Convention/en_GB/convention/)

### BOX 3: HELCOM Recommendations on hazardous substances, their production, use and after-use management.

Recommendation number and title	Eleven substances of specific concern in the BSAP
6/4 Dentistry	Hg
9/4 Leaded gasoline	
13/1 Disposal of dredged spoils	
13/2 Industrial connections to municipal sewerage systems	Dioxins
14/3 Glass industry	Dioxins
14/5 Batteries	
15/4 Maritime pollution prevention	
16/4 Pulp and paper industry	SCCP
16/7 Leather industry	SCCP
17/6 Fertilizer production	Hg, Cd
17/8 Kraft pulp industry	SCCP
17/9 Sulphate pulp industry	SCCP
18/2 Offshore activities	Hg, Cd
19/5 Objective for hazardous substances	All
19/17 Pollution from offshore units	
20/2 Pesticide use	
20/4 Anti-fouling paints	TBT, TPT
23/4 Mercury in products	Hg
23/5 Urban stormwater treatment	
23/6 Chloralkali industry	Hg
23/7 Metal surface treatment	NP/NPE, Hg, Cd
23/8 Discharges of oil refineries	
23/9 Hard coal cookeries	
23/10 Production of pesticides	
23/11 Chemical industry	Hg, Cd
23/12 Textile industry	NP/NPE, OP/OPE, Hg, Cd
24/2 Batteries containing Cd, Pb and Hg	Cd, Hg
24/4 Iron and steel industry	Hg, Cd
24/5 Proper handling of waste/landfilling	
25/1 Elimination of PCBs and PCTs	Dioxins
25/2 Effective use of BAT in industry	Dioxins
27/1 Incineration of waste	Dioxins, Hg, Cd
29/1 Emissions from Crematoria	Hg
28E/8 Emissions from small-scale combustion	Dioxins

taken in international fora and in national legislation to ban dangerous or harmful substances and to regulate the use and management of several substances in order to reduce emissions and discharges of harmful pollutants and to decrease inputs of hazardous substances into the Baltic Sea. Among the most significant measures are the shift to unleaded fuel in the 1990s and the ban on dangerous pesticides such as DDT.

In order to be effective, ecological objectives must be measurable preferably through quantitative

indicators with target levels. Although there are a number of international conventions which deal either directly or indirectly with the chemical status of the marine environment, only a few measurable objectives have been defined.

#### 4.2.1 Helsinki Convention and HELCOM Recommendations

The 1974 Helsinki Convention banned the use of DDT and its derivatives DDE and DDD for all final uses except drugs, and PCBs and polychlorinated

terphenyls (PCTs) for all uses, except in existing closed system equipment until the end of service life or for research, development and analytical purposes. The Convention, however, allowed other “noxious” substances and materials listed in Annex II to be introduced into the marine environment of the Baltic Sea area subject to special prior permits given by appropriate national authorities. This annex included heavy metals such as mercury and cadmium, some POPs, oil, polycyclic aromatic hydrocarbons, pesticides and radioactive materials.

Article 5 of the revised Helsinki Convention of 1992 provides that the Contracting Parties undertake to prevent and eliminate pollution of the marine environment of the Baltic Sea area caused by harmful substances from all sources. Annex I of the Convention sets criteria for the identification and evaluation of harmful substances that cause pollution. The Annex also provides a list of substances for which the Contracting Parties should give priority when taking preventive measures.

Article 6 together with Annex III of the 1992 Helsinki Convention prescribes principles and obligations concerning pollution from land-based sources.

HELCOM’s overall objective (the HELCOM Strategy) was defined in HELCOM Recommendation 19/5 from March 1998. The overall objective is to prevent pollution of the Convention Area by continuously reducing discharges, emissions and losses of hazardous substances towards the target of their cessation by the year 2020, with the ultimate aim of achieving concentrations in the environment near background values for naturally occurring substances and close to zero for man-made synthetic substances. The objective defines substances as hazardous if they are toxic, persistent and bioaccumulating (PBT-substances), or very persistent and very bioaccumulating (vPvB). Moreover, substances that affect hormonal and immune systems are also considered hazardous substances and are of equal concern. The HELCOM Strategy with regard to hazardous substances lists substances of concern, from which HELCOM has selected 42 hazardous substances for immediate priority action. That list has been further condensed and the HELCOM Baltic Sea Action Plan focuses on eleven substances of specific concern to the Baltic Sea.

Currently, the HELCOM Strategy on hazardous substances is under revision and will be updated to reflect recent changes in global and European approaches to hazardous substances.

To establish the rules for specific substances and the limitation of their inputs into the marine environment, HELCOM has agreed on a wide array of recommendations to ban, reduce or manage in an environmentally friendly manner several hazardous substances and/or groups of substances in the Convention Area (**BOX 3**). Although the recommendations are not legally binding on the Contracting Parties, they set focus on the problem areas of different sectors and gaps in legislation, and point them out to the policy-makers. Moreover, many of the recommendations have paved the way for new national laws, directives of the European Union or international conventions.

#### 4.2.2 HELCOM Baltic Sea Action Plan

According to the HELCOM Baltic Sea Action Plan, adopted in 2007, the overall HELCOM goal concerning pollutants is to achieve a Baltic Sea with life undisturbed by hazardous substances. This goal is described by four ecological objectives.





### **Ecological objective “Concentrations of hazardous substances close to natural levels”**

The status of the first objective is primarily measured in relation to five contaminants or contaminant groups (cadmium, mercury, dioxins/furans/dioxin-like PCBs, tributyltin and PFOS). The primary target for these indicators is decreasing trends of their concentrations in fish and mussels. The ultimate target for metals is concentrations close to background levels and for organic pollutants concentrations close to zero. For mercury and dioxins (including furans and dioxin-like PCBs), there are also intermediate targets: 0.5 mg kg<sup>-1</sup> ww and 8 ng kg<sup>-1</sup> ww in fish muscle, respectively. The intermediate target levels are the same as the maximum permitted concentrations in fish for human consumption of the European Union (Anon. 2006a).

### **Ecological objective “All fish safe to eat”**

The ecological objective “All fish safe to eat” refers not only to fish consumed by humans but also to fish consumed by other predators in the Baltic marine ecosystem. The status of the ecological objective is measured by the concentrations of mercury, cadmium and dioxins/furans/dioxin-like PCBs in edible fish. The primary target is a decreasing trend in concentrations and the ultimate target is either a close-to-zero concentration (organic pollutants) or a concentration close to natural levels (heavy metals). In addition to the primary and ultimate targets, intermediate targets have been set. For mercury and dioxins, they are the same as for the objective “Concentrations close to natural levels”, and cadmium has an intermediate target of 0.05 mg kg<sup>-1</sup> ww. The target level for cadmium is the maximum permitted concentration of cadmium in fish for human consumption in the European Union (Anon. 2006a). In principle, this objective is not valid only for human beings but also for all fauna or wildlife in the Baltic Sea. In practise, the risk assessment of top predators via secondary poisoning is dealt with through the Ecological objective “Concentrations of hazardous substances close to natural levels”.

### **Ecological objective “Healthy wildlife”**

The HELCOM objective on healthy wildlife has not been clearly defined. The Baltic Sea Action Plan indicates that suitable indicators would be the reproduction of white-tailed sea eagles, fish health

and seal health. The first two indicators do not have target levels, but the target for seal health is defined as a “normal level” in a set of reproductive and pathological indicators.

### **Ecological objective “Radioactivity at pre-Chernobyl levels”**

The objective “Radioactivity at pre-Chernobyl levels” is defined by the activity of the radionuclide cesium-137 in water, sediment and fish muscle. Cesium-137 is the isotope that originates mainly from the Chernobyl accident and causes the bad status in this ecological objective. Although the primary target “decreasing concentration trend” is based on the natural half-life of the isotope, the ultimate target defines the desirable status, which is 14.6 Bq m<sup>-3</sup> for water, 1640 Bq m<sup>-2</sup> for sediment, 2.5 Bq kg<sup>-1</sup> ww for herring muscle and 2.9 Bq kg<sup>-1</sup> ww for flatfish muscle.

## **4.2.3 Directives and regulations of the European Community**

General awareness about the impacts of toxic chemical substances within the European Community has to a large extent been driven by the need to prevent the exposure of the population to hazardous chemicals in case of industrial accidents. Since the Seveso accident in 1976, the prevention of chemical pollution and later the assessment of risks to human health and the environment have gradually been integrated into the common European law. The intensified use of chemicals has led to a further understanding of the need for comprehensive chemical management.

Current EU legislation addresses the chemical status of the marine environment through horizontal legislation that focuses on the quality of the marine environment, the main legislative instruments being the Water Framework Directive (WFD) and the Marine Strategy Framework Directive (MSFD), and controls the inputs of hazardous substances under framework legislation such as the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) regulation (Anon. 2006b) and use- or input-specific regulations.

The WFD aims to achieve “a good surface water chemical status” in all bodies of surface waters in the EU by 2015. The WFD and the recently adopted

## BOX 4: Examples of EU regulations on specific hazardous substances

Dioxins	<ul style="list-style-type: none"><li>• POPs regulation 850/2004/EC, Dioxin strategy from 2001.</li><li>• 2008/1/EC (Integrated Pollution Prevention and Control Directive).</li><li>• 2000/76/EC (Waste Incineration Directive).</li></ul>
Organostannic substances	<ul style="list-style-type: none"><li>• 2002/62/EC: prohibiting the marketing and use of organostannic compounds in anti-fouling systems for all ships, irrespective of their length.</li><li>• From 1 January 2008, ships bearing an active TBT coating on their hulls will no longer be allowed in Community ports (782/2003/EC). Moreover, biocide use of all organic tin compounds was banned in autumn 2006 (98/8/EC) and the pesticide use of triphenyltin already in 2002 (91/414/EC).</li></ul>
Penta-BDE	<ul style="list-style-type: none"><li>• Total ban on pentabrominated diphenylethers (penta-BDE) since August 2004 (2003/11/EC).</li><li>• 2002/95/EC (RoHS Directive) from July 2006 prohibits new electrical and electronic equipment placed on the market to contain penta-BDE, Cd and Hg with some exceptions.</li><li>• 2002/96/EC (WEEE Directive): imposes responsibility for the disposal of waste electrical and electronic equipment on the manufacturers of such equipment.</li></ul>
Endosulfan	<ul style="list-style-type: none"><li>• Banned in the EU in plant protection products since 2005 (7864/2005/EC).</li></ul>
SCCP	<ul style="list-style-type: none"><li>• Limitations on marketing and use; banned in metal-working fluids and leather finishing at concentrations more than 1% (2002/45/EC).</li></ul>
OP/OPE	<ul style="list-style-type: none"><li>• Indirectly banned as a detergent (2004/648/EC).</li></ul>
NP/NPE	<ul style="list-style-type: none"><li>• Restrictions on the marketing and use of nonylphenols (NP) and nonylphenol ethoxylates (NPE) (2003/53/EC). NP and NPE banned at concentrations more than 0.1% since 1 January 2005 in industrial and institutional cleaning, domestic cleaning, textiles and leather processing, emulsifier in agricultural teat dips, metal working, manufacturing of pulp and paper, cosmetic products, other personal care products, co-formulants in pesticides and biocides.</li></ul>
PFOS	<ul style="list-style-type: none"><li>• Restrictions on the marketing and use of perfluorooctane sulfonate (PFOS) (2006/122/EC). PFOS is partly banned as a substance or constituent of preparations at concentrations more than 0.005% by mass and in semi-finished products or articles more than 0.1% by mass from 27 June 2008.</li></ul>

Priority Substance Directive (Anon. 2008b) give environmental quality standards (EQS) for 33 priority substances. The MSFD is built on the same rationale as the WFD, but aims for a good status of the marine environment by 2020. Good chemical status as defined in the WFD is assessed using the environmental quality standards with the aim of reducing the concentrations of all 33 priority substances to below the defined levels.

The REACH regulation controls the placement of chemicals on the market and their use, and therefore has an indirect but very significant influence on the status of the marine environment. It is complemented by the Regulation for Classification, Labelling and Packaging of Substances and Mixtures, which incorporates the classification criteria and labelling rules agreed at the UN level in the Globally Harmonized System of Classification and Labelling of Chemicals (GHS). Substance-specific

restrictions are applied both through framework regulations as well as sectoral legislation that is currently under revision. New chemicals (introduced to EC market before 18 September 1981) face the advance approval process before being introduced to the human use in the EC area.

### 4.2.4 International conventions

#### The Stockholm Convention

The Stockholm Convention on Persistent Organic Pollutants (POPs)<sup>17</sup> came into force in 2004. The objective of the Convention is to protect human health and the environment from persistent organic pollutants and it requires contracting parties to take measures to eliminate or reduce the release of POPs into the environment. All HELCOM countries except

<sup>17</sup> <http://chm.pops.int/>

the Russian Federation have ratified, accepted or accessed to the Stockholm Convention (**Table 4.1**). Of these countries, all except Estonia have elaborated and submitted their national plans for implementation of the Convention.

The Convention prohibits the use, import and export of the following substances: aldrin, chlordane, dieldrin, endrin, heptachlor, hexachlorobenzene (HCB), mirex, toxaphene and polychlorinated biphenyls (PCBs) by 2025. In addition, the production and use of DDT must be restricted. Article 5 of the Convention contains a minimum set of measures to reduce the unintentional release of dioxins, furans, PCBs and HCB. The Convention also has provisions for the management of wastes containing POPs.

The measures include: preparation and implementation of an action plan, promotion of feasible reduction measures, promotion of substitutes for materials or processes that release dioxins, furans, PCBs and HCB, and promotion of best available techniques and best environmental practices. The fourth meeting of the Conference of the Parties to the Stockholm Convention in 2009 adopted amendments to Annexes A, B and C of the Convention. These amendments will enter into force on 26 August 2010. The amendments cover the listing in these Annexes of, e.g., lindane, perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride, and certain penta- and tetra-BDE congeners to prevent their use in commercial products.

### International Convention on the Control of Harmful Anti-fouling Systems on Ships

HELCOM recommended a ban on the retail sale or use of organotin-containing paints for pleasure boats or fish net cages already 20 years ago (HELCOM Recommendation 20/4). This Recommendation was followed by changes in the Helsinki Convention to ban the use of organotin compounds in antifouling paints on pleasure craft less than 25 m in length and on fish net cages. Organotin compounds are also listed in Appendix 3 of HELCOM Recommendation 19/5 as a substance for immediate priority action.

Global regulations on TBT in antifouling paints used on sea-going ships were not developed until

2001. The 2001 International Convention on the Control of Harmful Anti-fouling Systems on Ships (AFS Convention) came into force on 17 September 2008. The Convention bans the application or re-application of organotin compounds that act as biocides in anti-fouling systems. Following a proposal by any Party to the Convention, it can be amended to include other substances used in anti-fouling systems that have adverse effects in the environment or on human health.

According to the HELCOM Baltic Sea Action Plan, all HELCOM Contracting Parties should ratify the AFS Convention by 2008–2009, and by the beginning of 2010 all of these countries except Russia had done so (**Table 4.1**).

Additionally, Regulation (EC) No 782/2003 of the European Parliament and of the Council of 14 April 2003 on the prohibition of organotin compounds on ships imposes an obligation that as of 1 January 2008 no ships calling at EU ports may use organotin compounds that act as biocides in their anti-fouling system (Anon. 2003a). The BSAP extends this requirement to all ports in the Baltic Sea starting from 1 January 2010.

**Table 4.1 Status of signing (S), accession, acceptance or ratification (X) by HELCOM Contracting Parties of the international conventions or their protocols regulating inputs of hazardous substances into the marine environment of the Baltic Sea as of the beginning of 2010.**

S – Signature X – Accession, acceptance or ratification	Stockholm Convention on POPs	Convention on the Control of Antifouling Systems of Ships	Conv. On Long Range Transboundary Air Pollution (CLRTAP)	CLTRAP POPs Protocol	CLTRAP HM Protocol	London Convention 72	London Convention Protocol 96	MARPOL 73/78 (Annex I/II)
<b>Denmark</b>	x	x	x	x	x	x	x	x
<b>Estonia</b>	x	x	x	x	x			x
<b>Finland</b>	x	x	x	x	x	x		x
<b>Germany</b>	x	x	x	x	x	x	x	x
<b>Latvia</b>	x	x	x	x	x			x
<b>Lithuania</b>	x	x	x	x	x			x
<b>Poland</b>	x	x	x	s	s	x		x
<b>Russian Federation</b>	s		x			x		x
<b>Sweden</b>	x	x	x	x	x	x	x	x

### **UNECE Convention on Long-Range Transboundary Air Pollution and the Protocols on POPs and Heavy Metals**

The United Nations Economic Commission for Europe (UNECE) Convention on Long-Range Transboundary Air Pollution (CLRTAP) came into force in 1983 and aims at reducing air emissions of contaminants by specific measures. Protocols to the UNECE CLRTAP on persistent organic pollutants and heavy metals entered into force on 23 October 2003. All HELCOM Contracting Parties have ratified this Convention (**Table 4.1**) and they have also ratified the protocols, except for the Russian Federation and Poland, which have not signed or ratified, respectively, the protocols.

The Protocol on POPs covers 23 pesticides, industrial chemicals and by-products or contaminants, including all Stockholm Convention substances (prior to the 2009 additions). The Protocol includes provisions for dealing with POPs-containing wastes. It also obliges Parties to reduce their emissions of dioxins, furans, PAHs and HCB below their levels in 1990 (or an alternative year between 1985 and 1995). In addition, it establishes specific limit values for the incineration of municipal, hazardous and medical wastes. The protocol's objective is to phase out the use and production of POPs. For example, hexachlorobutadiene, pentachlorobenzene and polychlorinated naphthalenes are scheduled for an immediate phase-out.

The Protocol on Heavy Metals targets three particularly harmful metals: cadmium, lead and mercury.

According to one of the basic obligations, Parties will have to reduce their emissions of these three metals below their levels in 1990 (or an alternative year between 1985 and 1995). The protocol aims at cutting emissions from industrial sources (iron and steel industry, non-ferrous metal industry), combustion processes (power generation, road transport) and waste incineration. It also introduces measures to lower heavy metal losses from other products, such as mercury in batteries, and proposes the introduction of management measures for other mercury-containing products, such as electrical components (thermostats, switches), measuring devices (thermometers, manometers, barometers), fluorescent lamps, dental amalgam, pesticides and paint.

### **Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter**

The London Convention (Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter, 1972) regulates the deliberate disposal of wastes at sea by dumping or incineration. The Convention entered into force on 30 August 1975 and was the first major global initiative designed to protect the marine environment from the unregulated dumping of waste. Currently, 77 countries are Contracting Parties to the Convention. All Baltic Sea countries except for Estonia, Latvia and Lithuania have ratified the Convention (**Table 4.1**).

In 1996, a new London Convention Protocol was signed and is currently undergoing the process of ratification. The single most significant effect of the Protocol will be to move away from a list of materials which may not be dumped at sea to a restricted list of materials which may be considered for disposal at sea, all others being prohibited. In addition, before a decision is taken on the disposal at sea of any waste, a rigorous assessment will need to be undertaken in each case to ensure that this is the best practical environmental option.

### **The International Convention for the Prevention of Marine Pollution from Ships – MARPOL 73/78**

The International Maritime Organization (IMO) is the global regulator of shipping, and its main task



has been to develop and maintain a comprehensive regulatory framework for shipping, including in relation to environmental concerns.

The MARPOL Convention—the International Convention for the Prevention of Marine Pollution from Ships—is the most important instrument for the protection of the environment from shipping. It is a combination of two treaties adopted in 1973 and 1978, respectively, and updated by amendments through the years.

The Convention includes regulations aimed at preventing and minimizing pollution from ships, both accidental pollution and that from routine operations. The Convention includes six technical Annexes, two of which relate to hazardous substances: Annex I covering pollution by oil and Annex II dealing with pollution by chemicals. All HELCOM Contracting Parties are parties to MARPOL 73/78 and its Annexes I and II (**Table 4.1**).

Annex I regulates operational discharges of oil from tankers and makes it mandatory for new oil tankers to have double hulls. It also contains a phase-in schedule for existing tankers to be fitted with double hulls. The Baltic Sea, due its vulnerability to pollution by oil, has been designated a special area, meaning that discharges of oil or oily mixtures from ships have been prohibited completely, with minor and well-defined exceptions.

Annex II specifies discharge criteria and measures for the control of pollution by noxious liquid substances carried in bulk. About 250 substances were evaluated and included in the list appended. The discharge of their residues is allowed only to reception facilities until certain concentrations and conditions are complied with. To uphold this prohibition, MARPOL 73/78 and HELCOM require all ships, with a few exceptions, to deliver to a port reception facility, before leaving the port, their ship-generated wastes and cargo residues that cannot be legally discharged under MARPOL 73/78. To further encourage delivery, the countries bordering the Baltic Sea have agreed that ships should not be charged for using such reception facilities under the “no-special-fee” system. Costs are recovered instead from general harbour fees or general environmental fees.

#### 4.2.5 Other national objectives and legislation

##### General information concerning environmental legislation and legislation on chemicals in Finland

The Finnish National Programme on Dangerous Chemicals was published in 2006. The programme takes into account the effects on consumers, public health, workers' health and safety, and the effects on the environment during the entire lifecycle of chemicals. The five priority areas identified are:

- A high level of protection of health and the environment under the REACH regulation will be achieved, the provisions of the regulation will be effectively implemented and the new data gathered in the implementation of the regulation will be utilized.
- Adequate data on exposure and emissions of chemicals dangerous to human health and the environment must be provided for risk assessment and risk management activities.
- Companies must have sufficient know-how of and tools for chemical risk management and must apply them to ensure a high level of protection.
- Sufficient data on chemicals in products and manufactured goods must be provided and the risks from these chemicals must be controlled during the entire lifecycle of the products and goods.
- Finland has actively participated in the work to minimize by 2020 significant adverse effects of chemicals globally in accordance with the Johannesburg objectives.

The main legislative requirements for chemicals are set at the EU level. Two national acts, the Chemicals Act and the Environmental Protection Act, implement the EU directives or designate the control authorities and punishments for EU regulations. They also include basic principles for chemical users and manufacturers which form a certain safety net for chemicals handling. These principles include the duty to exercise caution, the duty to obtain information, the substitution principle, the polluter pays principle, the principle of best available technique, and absolute prohibitions on soil contamination and groundwater pollution. In addition, the Environmental Protection Act and Decree specify the industrial and other sectors that require an environmental permit. The scope also covers

plants smaller than those covered by the IPPC Directive. Hazardous substances, especially those belonging to the substance groups listed in the IPPC Directive, need to be taken into consideration within the environmental permitting system.

According to the general principles, sufficient care and caution shall be exercised in the manufacture, import and other handling of chemicals in order to prevent harm to health and the environment, taking into consideration the amount and dangerous character of the chemical. Manufacturers and importers of a chemical shall obtain such information on the physical and chemical properties and on the effects on health and the environment of the chemical that is adequate for assessing the health and environmental risks and for labelling the chemical. The manufacturers or users of chemicals shall select the chemical or method for use which causes the least risk, whenever possible.

#### **Lithuanian national legislation**

The main Lithuanian law with a focus on water is the Law on Water. The law is from 21 October 1997; essential amendments to this law, especially for the full implementation of the WFD, took place on 25 March 2003 and the most recent amendments were made on 17 December 2009. Details for monitoring are regulated in the Law on Environmental Monitoring of 20 November 1997 (most recent amendments on 4 May 2006). For some regulations under the Law on Water that deal with the control of pollution by hazardous substances, there are specific provisions by Orders of the Minister of Environment, e.g., Order of the Minister of Environment No. 457 on the Approval of the Regulation for the Determination of the Environmental Quality Objectives of 15 September 2003 (most recent amendments on 9 June 2009). The Programme for the Reduction of the Discharges of Dangerous Substances into Water Bodies, approved by the Order of the Minister of Environment No. D1-71 of 13 February 2004 (most recent amendments on 20 May 2008), includes a list of substances that may be discharged by certain types of industries. The lists of priority hazardous substances, hazardous substances and other substances that are under control in Lithuania were fixed in the Order of the Minister of Environment No. D1-236 of 17 May 2006 on Wastewater Treatment Regulation (most recent amendments

took place on 29 December 2009). According to the Wastewater Treatment Regulation, economic entities that discharge their wastewater into the sewerage systems must determine which hazardous substances and priority hazardous substances are present in the wastewater and at what concentrations. The Regulation also provides a list of parameters to be controlled according to the type of industry. Furthermore, economic entities must make an inventory of dangerous substances applicable to their industrial sector and present this inventory in the application for an IPPC permit (Order of the Minister of Environment No. 80, Integrated Pollution Prevention Control of 27 February 2002; most recent amendments took place on 25 January 2010). The frequency of monitoring hazardous substances by industries is set in the IPPC permit. If the maximum allowable concentrations of these substances are exceeded, reduction programmes should be prepared and implemented.

#### **Polish national regulations on hazardous substances**

Except the directly binding EU legal regulations, as for example European Community Regulation on chemicals and their safe use REACH, there are several national regulations which deal with ban of the usage and limiting emission of hazardous substances.

For example marketing of cadmium is regulated by:

- the Act of 24 April 2009 on batteries and accumulators, which describes requirements for entering the market of batteries and accumulators, the rules for collecting, processing, recycling and disposal of spent batteries and accumulators,
- Regulations of the Minister of Economy of 27 March 2007 on detailed requirements regarding the use in electrical and electronic equipment of certain substances that might adversely impact on the environment,
- Regulation of the Minister of Agriculture and Rural Development dated 19 October 2004 on implementation of certain provisions of the Law on Fertilizers and Fertilization, which defines the limit value of pollutants, including cadmium in mineral fertilizers.

Occurrence of mercury in environment is regulated through several regulations based on ecological quality standards set up by EU law. However limitation and prohibition of usage is reflected for

example in Regulations of the Minister of Economy of 27 March 2007 on detailed requirements regarding the use in electrical and electronic equipment of certain substances that might adversely impact on the environment and the Act of 24 April 2009 on batteries and accumulators.

Ban the use and marketing of endosulfan in Poland is introduced by Regulation of the Minister of Agriculture and Rural Development dated 28 June 2006 changing the regulation on the list of active substances according to which use in pesticides is prohibited.

Usage and marketing of brominated diphenyl ethers are regulated through Regulation of the Minister of Economy of 27 March 2007 on the detailed requirements for the restriction on the use of electrical and electronic equipment for certain substances which could negatively impact on the environment.

Ban the use and limiting use of nonylphenols is regulated by Regulation of the Minister of Health dated 30 March 2005 on the list of substances prohibited or permitted with restrictions for use in cosmetics and graphic logos appearing on the packaging of cosmetic products (Annex for a list of substances prohibited for use in cosmetic products).

Occurrence of dioxins, furans and dioxin like polychlorinated biphenyls is regulated by Regulation of the Minister of Environment dated 24 July 2006 on conditions to be met for the introduction of sewage into the water or soil and on substances particularly harmful to the aquatic environment however use and handling of above mentioned substances is introduced by Regulation of the Minister of Economy dated 24 June 2002 on requirements for the use and handling of substances posing a particular threat to the environment and the use and cleaning of installations or devices, which have been or are used for substances posing a particular threat to the environment.

Organotin compounds are limited as well in the market is regulated by Regulation of the Minister of Agriculture and Rural Development dated 12 February 2008 on the permissible levels of pesticide residues in feed materials and compound feed as in environment through Regulation of the Minister of Environment dated 24 July 2006 on condi-



tions to be met for the introduction of sewage into the water or soil and on substances particularly harmful to the aquatic environment.

#### **Russian national legislation**

In 2002, a new federal law on "environmental protection" was adopted in Russia. The new legislation aims to develop a modern national system of technology standards based on best available technologies (BAT). This system will result in a more efficient process for granting permits to industrial enterprises and will ultimately lead to better environmental protection. The law introduces a concept of technology standards based on allowable discharges and emissions of substances and microorganisms into the environment per unit of production. The technology standards are considered to be strict.

On 1 July 2003, the Federal Law on Technical Regulation went into effect in Russia. The development of this law was mainly initiated owing to the accession of the Russian Federation to the World Trade Organization (WTO). The Federal Law seeks to harmonize the Russian system of standards with the international system. The negotiations on Russia's accession to the WTO reached its final stage at the time that the EU tightened its chemical manage-

ment legislation by the introduction of the REACH system. New technical regulations are being drafted in Russia and many of them are directly associated with the modernization of the chemicals industry. However, many of the technical regulations still have to be developed (Eco-Accord 2006).

The Federal Law on Safe Management of Pesticides and Agricultural Chemicals is in force. The Law regulates the fulfillment of state management functions in the sphere of safe handling of pesticides and agricultural chemicals, and the development, production, sale, storage, transportation, use, neutralization, recycling, destruction, advertising, import and export of pesticides and agricultural chemicals. However, it is not yet supported by relevant regulations on procedures of state testing and registration of pesticides, on state control of production, transportation, storage and elimination of pesticides, or on rehabilitation of storage facilities contaminated by pesticides.

In general, Russian legislation on environmentally safe management of chemical products lacks a comprehensive risk assessment of the environmental hazards of substances due to the general “acute” toxicity approach, which does not allow proper evaluation of potential impacts on marine ecosystems.

Further harmonization of the legal framework with regard to hazardous substances is needed and HELCOM provisions should be well-utilized for this purpose.

### **General information concerning environmental legislation and legislation on chemicals in Sweden**

Sweden has a long history of environmental legislation and legislation on chemicals. In 1999, the Swedish Environmental Code came into force. The Code replaces fifteen previous Acts that were repealed on its entry into force on 1 January 1999. With its related Ordinances and rules, the Environmental Code covers a very wide field. Altogether the Code’s system of rules comprises thousands of provisions. The Code is a framework law, which means that its rules do not generally specify limit values for various operations and that it does not go into detail in relation to striking a balance between various interests. The rules are often made more specific by regulations issued by central

government agencies in the environmental sector such as the Swedish Environmental Protection Agency and the Swedish Chemicals Agency.

The Environmental Code is the integrated body of environmental legislation enacted in Sweden. Its rules relate to many issues, for example, the management of land and water, environmentally hazardous activities and chemical products, among others.

To conduct more environmentally hazardous operations, permits must be obtained from environmental courts or county administrative boards. The supervisory authority in each municipality also has an important role in protecting human health and the environment from damage and detriment.

The general purpose of the Code is to promote sustainable development that will ensure a healthy and sound environment for present and future generations.

The Swedish Parliament has adopted fifteen national environmental quality objectives which describe environmental states that are a precondition for sustainable development. According to the Parliament, it should be possible to achieve these objectives within one generation or by the year 2025.

In the Code, the so-called general rules of consideration comprise several fundamental principles and must *always* be complied with and applied to all operations and measures covered by the provisions of the Code, for example, the handling of chemical products and the conduct of environmentally hazardous activities.

Specific rules on chemical products are found in chapter 14 of the Environmental Code. Of particular interest for chemicals and for chemical products is one of the rules for consideration: “the product choice principle”. This principle states that the use or sale of chemical products that may involve hazards to human health or the environment should be avoided if other, less dangerous products can be used instead. The product choice principle should always be applied where there is a choice. There is a strong link between the principle of “the knowledge requirement” and the principle that “the best available technology” should be used. The product choice principle applies particularly to persons who use or sell chemical products.



# 5 SYNTHESIS AND SUGGESTIONS FOR FUTURE WORK

In this chapter, the findings presented in the previous chapters are summarized and analysed to provide an overview of the contamination status of the Baltic Sea, its underlying reasons and recommendations for the improvement of the status.

## 5.1 Conclusions on the status, trends and biological effects of hazardous substances

### 5.1.1 Integrated assessment of the status of hazardous substances in the Baltic Sea

According to the results of the CHASE assessment, the entire Baltic Sea was an area with a high contamination level in 1999–2007 because 137 out of the 144 areas assessed were classified as being “disturbed by hazardous substances”. All open-sea areas of the Baltic Sea except the northwestern Kattegat were classified as being “disturbed by hazardous substances” (Fig. 2.1). Similarly, 98 of the 104 coastal assessment units were classified as being “disturbed by hazardous substances”, leaving only seven units with a status “undisturbed by hazardous substances”.

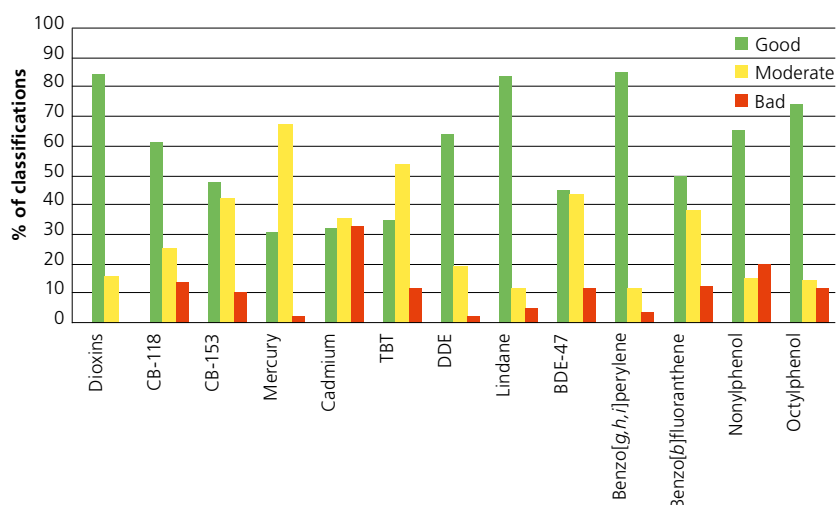
The main basin of the Baltic Sea (Northern Baltic Proper, Western and Eastern Gotland Basins) together with the Kiel and Mecklenburg Bights were the most contaminated areas (Figs. 2.1 and 2.3). In the main basin, the eight open-sea areas with bad or poor status were most contaminated with PCBs and benz[a]anthracene, i.e., they were the substances with the highest contamination ratios (Table 2.2). Other substances with high contamination ratios were TBT, mercury, DDE and dioxins. In the coastal sites of the Kiel and Mecklenburg Bights with bad or poor status, PCB compounds were the substances with the highest contamination ratios. Other substances were lead, HCH and PAH metabolites.

The status classifications of coastal areas were highly variable, but there was a certain tendency for the waters near larger cities (Tallinn, Rostock, St. Petersburg, Helsinki, Gdańsk and Stockholm) to be classified as having a moderate or poor status. The coastal assessment unit of Stora Karlsö in the Western Gotland Basin was classified as having a bad status based on contaminants (mainly dioxins

and lead) in the eggs of common guillemot (*Uria aalge*). The common guillemot feeds on fish, which results in bioaccumulation of contaminants to the birds and their eggs. These data from guillemot eggs from Stora Karlsö feature a number of representative long-term temporal trends (see Chapter 2.2) and allow for setting threshold values based on known historical measurements of contaminants.

Throughout this assessment, substances such as PCBs, lead, DDE, cadmium, mercury, TBT, and dioxins as well as brominated substances, for example, BDE appear as contaminants with the highest concentrations in relation to the threshold levels. In the CHASE assessment, countries had the option of carrying out the coastal assessments using any threshold values they wished, whether national or international, while the status maps on different substances presented in Chapter 2 were based on harmonized threshold values. Nevertheless, the overall result is largely the same and the above-mentioned substances appear with the greatest numbers on the list of substances that were decisive in determining the status in the integrated classification of CHASE (Table 2.1) as well as among the substances with the largest fractions of moderate or bad status classifications (and the least good) on the various status maps presented in Chapter 2 (Fig. 5.1).

The integrated assessment did not include certain hazardous substances that were presented in Chapter 2 owing to a lack of threshold levels.



**Figure 5.1** Percent distribution of the different status categories of the different substances, as presented on the maps in Chapter 2. Key: green = good, yellow = moderate, red = bad status. CB-118 = Chlorinated biphenyl congener 118, CB-153 = Chlorinated biphenyl congener 153 and BDE-47 a lower brominated diphenylether.

Such substances were, for example, all perfluorinated alkyls, bisphenol A and pharmaceutical substances. However, their concentrations in the marine environment are high and increasing (**Sections 2.2.6 and 2.2.9**). Our understanding of their environmental fate is poor, and as long as we do not understand their spatial distribution, main sources and transport mechanisms, it is difficult if not impossible to suggest targeted measures to improve the situation.

### 5.1.2 How far are we from reaching a Baltic Sea with life undisturbed by hazardous substances?

This assessment covers an eight-year time period before the agreement on the Baltic Sea Action Plan. Therefore, the results of this assessment serve as a baseline for the implementation of the BSAP actions. However, this assessment also shows how far we are from reaching the BSAP objectives.

The assessment shows that there is still a lot of work to be done in order to reach the goal of the Baltic Sea Action Plan of a Baltic Sea with life undisturbed by hazardous substances, although there are

encouraging signs of decreasing trends of certain substances and improving health status of some top predators. A number of indicators and targets were identified in the BSAP and the following evaluation makes use of those indicators and targets.

#### Ecological objective “Concentrations of hazardous substances close to natural levels”

This ecological objective is still to be reached. The primary target of decreasing trends has been fulfilled to some extent, but the ultimate status target of concentrations in biota close to natural levels is still to be reached for all indicators.

There are indications that the primary trend objective has been reached for dioxins, furans and dioxin-like PCBs. Temporal trend data on dioxins, furans and dioxin-like PCBs indicate their decrease in common guillemot eggs since 1970, a levelling off in fish and a decline of PCDD/F in the sediments since the 1960s or 1970s, but the overall data availability was poor and did not allow a comprehensive assessment. There are also some signs of decreasing trends of TBT concentrations. Temporal trends of tributyltin in this assessment



mainly concerned Danish and German waters, but they indicated decreasing trends of TBT in mussels and fish. For PFOS, the target of a decreasing trend has not been reached but only one time series was available. It showed a significant increasing trend of 7–10% per year for PFOS in eggs of the common guillemot from the Island of Stora Karlsö (Western Gotland Basin) since 1968.

The short-term trend analyses of mercury and cadmium in biota indicated that few locations showed decreasing trends and some even showed increasing concentrations. For cadmium and mercury, the concentrations in biota were largely above the threshold levels and therefore the ultimate target of concentrations close to background levels was not reached in 1999–2007 (Figs. 2.10 and 2.11). The only areas with low mercury concentrations were found in the Gulf of Riga, the Estonian coast of the Gulf of Finland, one site in the Gulf of Gdansk and in Danish waters (Fig. 2.10). Concentrations of cadmium in fish liver and blue mussel mostly were in a “moderate” or “bad” status. The only areas with low levels of cadmium in fish liver or muscle and blue mussel were found in the Lithuanian offshore waters, Finnish coastal waters and Danish waters. Although most of the concentrations of dioxins and dioxin-like compounds were classified as “good”, the concentrations exceeded the threshold levels in many cases in the Gulfs of Bothnia and Riga, and the Baltic Proper (Figs. 2.5 and 2.6). The ultimate target of concentrations close to zero was not reached anywhere except in the Kattegat. However, very high concentrations of dioxins and dioxin-like compounds yielding a status classification of “bad” were not observed. The target of TBT concentrations close to zero was not reached because TBT levels in sediments and blue mussels were still of concern or of high concern in most areas of the Baltic Sea (Fig. 2.16). PFOS levels in marine predatory birds, mammals and in fish were elevated, which implies that the ultimate target of concentrations close to zero was not reached (Fig. 2.21).

#### Ecological objective “All fish safe to eat”

The primary target of a decreasing trend of cadmium, mercury and dioxins in the edible parts of fish seems to have been reached for dioxins or dioxin-like compounds, but for mercury and cadmium the target was not reached.

The intermediate targets of the Baltic Sea Action Plan for cadmium, mercury and dioxins are the threshold levels for food consumption. Regarding the intermediate targets, mercury levels found in edible parts of fish were generally below the threshold levels and thus the intermediate target of the BSAP was reached. Cadmium concentrations above the threshold levels were found in several parts of the Baltic Sea and hence the intermediate target was not reached for the Baltic Sea as a whole. Dioxins and dioxin-like compounds were below the threshold levels for food consumption that were used as intermediate targets, especially in the Gulfs of Finland and Riga and the southern Baltic Sea, but exceeded the threshold levels in many cases in the Gulf of Bothnia and the Baltic Proper (Fig. 2.6).

The ultimate target of concentrations of dioxins and dioxin-like PCBs close to zero in edible fish was nearly reached for dioxins and dioxin-like PCBs in the Kattegat, whereas the ultimate targets for mercury and cadmium of levels close to background concentrations were not reached because the majority of cadmium and mercury samples exceeded the quality criteria for the marine environment (see Section 2.2.3).

#### Ecological objective “Healthy wildlife”

This assessment showed that the health of the Baltic Sea wildlife is improving in terms of the health of predatory birds and seals, but there are no signs of improvement in fish health and lower trophic levels are also still impacted by hazardous substances. Predatory birds, seals and fish were suggested as descriptors of this ecological objective in the BSAP.

A recovery of the reproduction and health status of the white-tailed sea eagle (*Haliaeetus albicilla*) has taken place since the late 1960s, and since the mid-1990s eagle productivity has largely returned to pre-1950 levels. This recovery correlates with reductions in environmental concentrations of organochlorine compounds owing to bans on the use of DDT and PCBs around the Baltic Sea enacted during the 1970s (Fig. 2.50). However, it may be noted that the predatory birds have also received extra feed devoid of hazardous substances which has helped the recovery.

Since the mid-1980s, increases in the population sizes of Baltic grey seals (*Halichoerus grypus*) and ringed seals (*Phoca hispida botnica*) have been recorded. PCBs are suspected to have been associated with interrupted pregnancies and uterine obstructions in both ringed and grey seals as well as with uterine leiomyomas in the latter, and thus probably contributed to the small number of Baltic seals in the mid-20<sup>th</sup> century. No uterine obstructions have been observed since 1997 and the occurrence of uterine leiomyomas has also decreased (**Fig. 2.49B**).

The various types of data presented in relation to fish diseases do not allow any decisive conclusions on the health status of fish populations, but there are discouraging rather than encouraging signs in the current health status, and fish populations in the coastal areas clearly suffer more from pollution than in the open-sea sites (**Figs. 2.38** and **2.39**). In perch (*Perca fluviatilis*), a four-fold increase in EROD activity, indicating exposure to compounds such as dioxins, PCBs and PAHs, was observed between 1988 and 2008 in Kvädöfjärden on the Swedish coast of the Baltic Proper (**Fig. 2.40**). An integrative parameter of the impact of a combination of contaminants and general toxicity, the lysosomal membrane stability (LMS) test measured in flounder (*Platichthys flesus*), indicated marked impacts in coastal and harbour areas in the southern Baltic Sea and the Baltic Proper, as well as in an open-sea site close to the main dumping area of WWII chemical munitions (**Fig. 2.38**). The poorer status of the coastal sites was confirmed with another indicator of genotoxic damage measured in flounder, the micronucleus (MN) test (**Fig. 2.39**). Diseases in wild Baltic Sea fish have been monitored on a regular basis since the beginning of the 1980s in some HELCOM Contracting Parties. Over the period 1994–2008, there was a marked fluctuation in the prevalence of bacterial skin ulcer disease in cod in the southern and south-eastern Baltic Sea.

Lower trophic levels showed reproductive disorders in Baltic Sea organisms such as marine snails and eelpout (*Zoarces viviparus*). Imposex in snails is specifically related to endocrine disruption caused by TBT pollution. Reproductive disorders in eelpout such as embryo aberrations and intersex are responses to a combination of environmental stressors, including estrogenic compounds.

### Ecological objective “Radioactivity at pre-Chernobyl levels”

This assessment shows that the primary target of decreasing trends of the radionuclide cesium-137 in water, sediment and fish muscle has been reached in all parts of the Baltic Sea and for all compartments of the ecosystem (e.g., **Fig. 2.35** for <sup>137</sup>Cs in fish).

As for the ultimate target, the assessment indicates that the pre-Chernobyl levels of cesium-137 (14.6 Bq m<sup>-3</sup> for water, 1640 Bq m<sup>-2</sup> for sediment, 2.5 Bq kg<sup>-1</sup> ww for herring muscle and 2.9 Bq kg<sup>-1</sup> ww for flatfish muscle) have not been reached in the Baltic Sea area, except in the Belt Sea and Kattegat for <sup>137</sup>Cs in herring muscle (**Fig. 2.35**) and sediments (see also HELCOM 2009d). The total amount of <sup>137</sup>Cs in Baltic Sea sediments was estimated at 2100–2400 TBq, but the transfer of <sup>137</sup>Cs continues by sedimentation from the water column to the deeper sediment layers, thus reducing its availability for biological uptake. Overall, the levels of long-lived man-made radionuclides in Baltic Sea sediments are low and are not expected to cause harmful effects to man or wildlife although their total amounts are considerable. For cesium-137 in water, it has been estimated that the pre-Chernobyl target value of 15 Bq m<sup>-3</sup> will be reached between 2020 and 2030.

## 5.2 Suggestions for future work

### 5.2.1 Proposals for the management of chemicals

It is often tempting to think that hazardous substances degrade in nature and that expensive management measures will not be needed. This assessment clearly shows that inputs that primarily took place decades ago are still obvious in the Baltic Sea, as is demonstrated by undesirable concentrations of PCBs, DDT and TBT. This finding carries three messages: (1) contaminants discharged into the Baltic Sea environment are quite persistent, (2) sediment disturbances may create further contamination in the food web, and (3) some contaminants in biota pose a health risk for humans in the area. In the light of these messages, there is a critical need to implement the measures that have already been agreed and to plan for future measures.

The following measures have been identified as necessary and potential actions to improve the state of the marine environment:

- Bans of substances in products and processes in cases where alternative solutions exist (e.g. brominated flame retardants in plastics and building material, mercury in measuring instruments). As the first step information about substitutes or alternative techniques should be shared among HELCOM countries followed by the introduction of HELCOM recommendations and measures.
- HELCOM measures against the use and releases of mercury should be analysed and, if necessary, strengthened bearing in mind the agreement included in the Baltic Sea Action Plan on the application of strict restrictions on the use of mercury in products and processes and supporting the work towards further limiting and, where feasible, totally banning mercury in products and processes. This issue should be reviewed at the HELCOM 2010 Ministerial Meeting.
- Consideration should be given to strengthening the restrictions on the use and releases of octylphenols (OP) and octylphenol ethoxylates (OPE) because this assessment shows their abundant presence in the marine environment especially in the Northern Baltic Proper (**Fig. 2.33** and **Table 2.2**) and bearing in mind that the Baltic Sea Action Plan includes an agreement to initiate adequate measures, such as the introduction of use restrictions and substitutions in the most important sectors identified by the Contracting Parties, if relevant assessments show the need to do so.
- The sufficiency of measures taken since 2008 against the use and releases of nonylphenols (NP) and nonylphenol ethoxylates (NPE) should be analysed bearing in mind that the Contracting Parties agreed to start by 2008 to work for strict restrictions on their use in the whole Baltic Sea catchment area of the Contracting Parties.
- The introduction of HELCOM measures against the use and releases of chlorinated paraffins (SCCP, MCCP), hexabromocyclododecane (HBCDD), perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and brominated diphenylethers (penta-BDE, octa-BDE and deca-BDE) should also be considered, provided that measures in other fora are not sufficient. The HELCOM Contracting Parties should also cooperate to obtain more stringent measures under other international regulatory frameworks.



- Enhancement of the implementation of the Helsinki Convention and HELCOM recommendations with regard to dredging and the disposal of dredged material in order to minimize the resuspension of hazardous substances (e.g., TBT, TPT, PAHs, PCBs and heavy metals) from bottom sediments. Dredging of contaminated sediments should be performed as infrequently as possible and in an environmentally acceptable manner. Research initiatives concerning improved procedures for the handling of dredged materials should be supported and the results should be reflected in relevant HELCOM recommendations.
- A wide network of boat hull washing sites should be introduced in coastal areas in order to reduce the use of anti-fouling agents (e.g., copper) and environmental awareness should be raised with regard to washing boat or ship hulls instead of using anti-fouling agents.
- HELCOM Contracting Parties should cooperate towards the implementation of a strong system of compliance monitoring for the IMO anti-fouling convention.
- Control of imported consumer products and articles containing PFOS, PFOA and TBT must be strengthened in order to reduce the “substance flow” to the Baltic Sea area.
- Proper handling measures should be implemented for wastes and contaminated areas such as landfills or industrial areas and for the treatment of leachates from landfills and storm water originating from waste-sorting sites.
- In relation to the control and treatment of urban runoff (i.e., storm water), urban planning and major construction works should include the use

of technical solutions for the proper handling of storm water such as pre-sedimentation dams and local infiltration (e.g., restoration of wetlands). Local authorities and water administrations should introduce programmes to restrict the discharge of hazardous substances to municipal wastewater systems. The substitution of hazardous substances with safer alternatives should be applied before being allowed to connect to the municipal wastewater treatment system.

- The discharge of persistent compounds such as alkylphenols and fluorinated compounds (PFOS, PFOA) should first of all be reduced through substitution of these compounds with less hazardous substances because wastewater treatment plants are not adapted for the elimination of very persistent substances.
- Enhanced municipal wastewater treatment may contribute to reduced discharges of pharmaceuticals and hazardous substances, but upstream precautionary measures are normally more cost-efficient.
- Industries with large discharges should, as a part of the permit procedure, be requested to introduce enhanced wastewater treatment measures.
- This assessment shows that cadmium is of high concern for the Baltic Sea marine environment and, therefore, strict restrictions on the content of cadmium in fertilizers should be introduced.
- Emission limit values should be introduced for dioxins from small-scale combustion activities and uncontrolled backyard burning of waste should be banned.
- Enhanced research should be conducted on the long-range airborne transport of dioxins and emission limit values should be introduced for dioxins from industrial combustion in the Baltic Sea catchment area and beyond.
- Increased efforts should be made to trace other sources of airborne deposition of dioxins and reduce their emissions.

### 5.2.2 Suggestions for monitoring and assessment of contaminants and their effects

HELCOM Monitoring and Assessment Group MONAS should be strengthened with regard to its activities concerning hazardous substances, possibly through the establishment of a specific expert group on hazardous substances. Such a group should provide the expertise needed to develop an annually updated core set of indicators for hazard-

ous substances, as well as updates to this thematic assessment and pollution load compilations with the aim of preparing a Baltic-wide substance-flow analysis for each substance. Similarly, the expert group should be responsible for developing, together with appropriate load or emission experts in the HELCOM Land-based pollution Group LAND and HELCOM MARITIME Group, a full management scheme for the hazardous substances of primary importance.

The monitoring and compilation of information concerning the inputs of pollutants should be strengthened. Pollution Load Compilations should cover the waterborne inputs of all heavy metals with alerting levels (for cadmium, mercury, lead, copper, zinc, nickel and chromium) in addition to oil and, as far as possible, also POPs and pharmaceutical residues. In addition to monitoring, screening studies and modelling should be employed to enable better links to be established between the inputs, status and effects of hazardous substances in the sea.

It should be considered whether the reports of EMEP to HELCOM on the annual atmospheric deposition to the Baltic Sea should also cover other substances with a capacity for long-range atmospheric transport, such as aromatic hydrocarbons and polychlorinated biphenyls. The monitoring and compilation of atmospheric pollution loads carried out in cooperation with EMEP currently cover cadmium, mercury, lead and dioxins/furans, and prior to 2004 also lindane.

Monitoring of the concentrations of hazardous substances in the marine environment should be strengthened as it is not at a satisfactory level in all HELCOM Contracting Parties. This was also reflected in the provisional confidence assessment of the 144 CHASE classifications, in which particularly the Eastern Gotland Basin, Gulf of Gdansk and the Gulf of Finland showed the lowest accuracies of the assessment results due to, *inter alia*, deficiencies in the quantity and quality of monitoring data. It must be noted that no data were submitted for this report by the authorities of the Russian Federation and the few data for Russian waters were mainly obtained through Lukoil's web pages for the Kaliningrad region. Data from the Polish coastal waters were also largely fragmentary. Poor monitoring or, alternatively, insufficient reporting of the monitoring data to the international community is in great

contrast to the fact that these countries are the two largest emitters of, e.g., cadmium, mercury, dioxins and dioxin-like substances and lead to the Baltic Sea (Gusev 2009c, 2009d, Knuuttila 2009).

The development of HELCOM biological effects monitoring to facilitate a reliable ecosystem health assessment is a measure which was agreed in the Baltic Sea Action Plan, but still remains to be undertaken. The risk of the occurrence of unobserved impacts and subsequent biological damage exists with the current monitoring strategy strongly focused on late responses observed at high biological levels such as top predators, reproductive disorders, population declines and community structures. 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, with careful consideration of the specific sub-regional conditions. Comparable approaches are already part of the monitoring strategies for other European convention sea areas i.e., the Mediterranean Sea (MEDPOL) and the Northeast Atlantic (OSPAR) (UNEP 2007, OSPAR 2010).

Regular and targeted monitoring as well as ecotoxicological research on the less well-known substances should be a high priority for the future. Many of the substances that are already rather well known and managed show decreasing trends in the Baltic Sea, while many newer substances, as for example those presented in **Sections 2.2.6** and **2.2.9** are both poorly investigated and a potentially increasing threat to the marine environment. Some of these substances possess unique physico-chemical properties. For example, PFOS and PFOA are both hydrophobic and oleophobic, and extraordinarily strong surfactants as well as extremely persistent. Pharmaceuticals, on the other hand, may be quickly chemically transformed, but persistent metabolites could still exhibit adverse effects in exposed ecosystems. Challenges encountered with such special characteristics are quite new to environmental chemists and managers. Environmental behaviour and fate as well as possible ecotoxicological threats are poorly understood and cannot be deduced from concepts developed for lipophilic POPs or metals. Additionally, the data base for emerging contaminants in the Baltic Sea environment is very weak and very few temporal trend studies are available for these substances. Understanding the sources and transport pathways of new chemicals is, however, highly dependent on

sufficient and accurate monitoring data. Without this understanding, it will not be possible to take efficient measures to reduce the emissions and risks associated with emerging chemicals.

The HELCOM ecological objective “Healthy wildlife” should be defined in a wider sense than what was included in the Baltic Sea Action Plan. In addition to the health status of predatory birds, seals and fish, biological effects in organisms at lower trophic levels should also be included. The quality of the environment depends to a great extent on the health of habitat-forming species, among others.

The use of an integrative assessment tool such as CHASE represents a major step forward. However, there is room for improvement; the CHASE tool is only as good as the data and resources that are made available to it. In particular, the comparability of assessment units should be improved by including harmonized sets of indicators under each assessment unit. Hence, CHASE should be seen as a first step in a process leading to further development of both indicator fact sheets as well as an improved assessment tool.

To enable a proper assessment of hazardous substances in the Baltic Sea, scientifically justified threshold values, harmonized across the Baltic, need to be developed. Such a need exists especially for TPT in biota and sediments, as well as for PFOA in marine water, sediment and biota. In addition, a proper threshold for PFOS, NP, OP, HCB and endosulfan in sediment is lacking; there is a need



for ecotoxicological data for sediment-dwelling organisms in order to develop reliable thresholds in sediment. The thresholds for dioxins and dioxin-like compounds used in this assessment were those developed for human consumption and it may be that they do not correctly reflect the risk of those substances for the organisms of the Baltic Sea; therefore, development of environmental thresholds should be considered for dioxins and dioxin-like compounds.

Most of the EU Priority Substances do not have quality standards for measurements in sediment or biota, as quality standards have mainly been defined for the water phase. By using other target values, this assessment showed that some of the Priority Substances have high concentrations in the Baltic Sea; particularly, PCB, tributyltin (TBT), mercury and cadmium showed high concentrations in fish, mussels and sediment all over the sea area.

### 5.3 Perspectives

The management of hazardous substances affecting the Baltic Sea marine environment needs to take into account climate change. It is already having an impact on the Baltic Sea region as a whole and on the marine environment of the Baltic Sea, in particular. Increased precipitation is likely to increase losses of certain hazardous substances, such as pesticides, from the catchment area and increase their waterborne input. A prolonged growth season in the region is foreseen to increase the use of pesticides, which also causes an increased risk for the marine environment. Furthermore, physical changes such as decreased water salinity and increased water temperature are likely to increase the vulnerability of

many Baltic Sea organisms to the effects of hazardous substances simply by increasing the physiological stress that they experience in their habitat.

We cannot change the fact that the seas act as ultimate sinks for chemical wastes created by humans, whether arriving via rivers, the atmosphere or by direct discharges, but we should be able to slow down the rate of pollution. An increased resource use among the 85 million people living in the catchment area of the Baltic Sea also increases the use of chemicals. People living in distant countries also contribute to the pollution burden via long-range transport of heavy metals and persistent organic pollutants. New chemicals are introduced for human use daily and we still know too little about many of the chemicals already in use not to speak of the cocktail effects of the chemicals found in the marine environment. Whether we will be able to slow down the rate of pollution, while maintaining the present lifestyle, remains a key question.

Although the primary focus of the 1974 Helsinki Convention was largely on the prevention of pollution by hazardous substances, this assessment is the first comprehensive report on the contamination status of the Baltic Sea. This report provides evidence that the management actions taken in the past have been effective and concentrations of earlier pollutants are decreasing. It also shows that we are still far from a Baltic Sea with life unaffected by hazardous substances and that there are new threats caused by emerging, poorly known substances. We need to take all the necessary actions and probably even more to guarantee our grandchildren a Baltic Sea which is no longer called the world's most polluted sea.





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- ALA-D –  $\delta$ -aminolevulinic acid dehydratase activity
- Anthropogenic – Effects, processes or materials resulting from human activities.
- Background Assessment Criteria (BAC) – BAC are used by OSPAR for defining concentrations of pollutants in mussels collected from areas in the Northeast Atlantic considered to be without significant anthropogenic inputs. See also **BOX 2**
- BALCOFISH – Integration of pollutant gene responses and fish ecology in Baltic coastal fisheries and management (BONUS project 2009–2011).
- BAT – Best available technique
- BDE – Brominated diphenyl ether
- BEAST – Biological Effects of Anthropogenic Chemical Stress: Tools for the Assessment of Ecosystem Health (BONUS project 2009–2011).
- BFR – Brominated flame retardants
- Biota – Biota is the total collection of organisms of a geographic region or a time period.
- Bioaccumulation – Bioaccumulation refers to the accumulation of substances, such as metals, pesticides, or other organic chemicals in an organism. Bioaccumulation occurs when an organism absorbs a toxic substance at a rate greater than that at which the substance is lost.
- BONUS – Baltic Organisations Network for Funding Science EEIG
- BSAP – HELCOM Baltic Sea Action Plan adopted in 2007 at ministerial level (HELCOM 2007a).
- Cd – Cadmium
- C.I. – Confidence interval
- Congener – A term for many variants or configurations of a common chemical structure.
- Contamination – Contamination is the presence of a minor constituent in another chemical or mixture, often at the trace level. In chemistry, the term usually describes a single chemical, but in specialized fields the term can also mean chemical mixtures, even up to the level of cellular materials. In environmental chemistry, the term is in some cases virtually equivalent to pollution, where the main interest is the harm done on a large scale to humans or to organisms or environments that are important to humans.
- Contamination ratio (CR) – The ratio between the measured contamination status and the threshold value for contamination.
- Convention on Long-range Transboundary Air Pollution (CLRTAP) – Is a convention for international cooperation to solve transboundary air pollution problems.
- CPS – Contracting Parties (e.g. of HELCOM)
- DBT – Dibutyltin (see also TBT)
- DDD – 1,1-dichloro-2,2-bis(p-chlorophenyl)ethane
- DDE – 1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene
- DDT – 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane
- DEHP – bis(2-ethylhexyl) phthalate
- Detection limit – The lowest quantity of a substance that can be distinguished from the absence of that substance with a predetermined confidence.
- DIDP – di-isodecylphthalate
- DINP – di-isononylphthalate
- DL-PCBs – Dioxin-like polychlorinated biphenyls
- dw – dry weight
- Ecological objective – A definition of the condition of the ecosystem reflecting good environmental or ecological status.
- Ecotoxicological Assessment Criterion (EAC) – See **BOX 2** for explanation.
- EE2 – 17 $\alpha$ -ethinylestradiol, an active hormone in contraceptives
- EMEP – European Monitoring and Evaluation Programme (EMEP) is a scientifically based and policy-driven programme under the Convention on Long-range Transboundary Air Pollution (CLRTAP) for international cooperation to solve transboundary air pollution problems and EMEP MSC-E – Is the eastern Meteorological Synthesizing Centre of EMEP.
- EROD – Ethoxyresorufin-O-deethylase, a biotransformation enzyme
- EQS – Environmental Quality Standard
- FAC – Fluorescent aromatic compounds
- GSI – Gonado-somatic index
- HBCDD – Hexabromocyclododecane
- HCB – Hexachlorobenzene
- HCHs – Hexachlorocyclohexane
- HELCOM – Helsinki Commission, the body responsible for the implementation of the Helsinki Convention.
- IUPAC – International Union of Pure and Applied Chemistry (<http://www.iupac.org/>)
- Hg – Mercury
- JCP – Joint Comprehensive Environmental Action Programme of HELCOM
- lw – lipid weight
- MBT – Monobutyltin (see also TBT)
- MCCP – Medium-chained chlorinated paraffins
- MSFD – EU Marine Strategy Framework Directive (Anon. 2008a)

- ng – Nanogram.  $10^{-9}$  gram
- NP – Nonylphenol
- NPE – Nonylphenoethoxylate
- OP – Octylphenol
- OPE – Octylphenol ethoxylate
- OSPAR – OSPAR is the organization by which fifteen Governments of the western coasts and catchments of Europe, together with the European Community, cooperate to protect the marine environment of the North-East Atlantic by implementing the 1992 Convention for the Protection of the Marine Environment of the North-East Atlantic.
- PAHs – polycyclic aromatic hydrocarbons
- Pb – Lead
- PBDE – Polybrominated diphenyl ethers (PBDEs)
- PBT-properties – Substances that have PBT-properties are *Persistent* (long-lived), *Bioaccumulate* in organisms and are *Toxic*
- PCBs – Polychlorinated biphenyls (PCBs)
- PCDD/F – “Dioxin” compounds, i.e., chlorinated dibenzo-*p*-dioxin (PCDD) or dibenzofuran (PCDF) compounds. A group of about 210 different congeners of the dioxin family.
- PCDT – Dibenzothiophenes
- PCT – Polychlorinated terphenyl
- Petrogenic – Of petrochemical origin.
- PFAs – Perfluoroalkyl substances. Chemicals consisting of a (often hydrophilic) head group and a carbon chain in which all hydrogen atoms were replaced with fluorine.
- PFCAs – Perfluorinated carboxylates. A group of PFAs containing a carboxylate (or carboxylic acid) head group.
- PFNA – Perfluorononanoate. A PFCA representative with 9 carbon atoms.
- PFOA – Perfluorooctanoate. A PFCA representative with 8 carbon atoms.
- PFOS – Perfluorooctane sulfonate. A PFA representative with 8 carbon atoms and a sulfonate head group.
- PFOSA – Perfluorooctane sulfonamide. A non-persistent PFOS precursor compound.
- PFUnA – Perfluoroundecanoate. A PFCA representative with 11 carbon atoms.
- Pharmaceutical – A chemical produced industrially (medicinal drug), which is useful in preventive or therapeutic treatment of a physical, mental, or behavioural condition.
- PNEC – Predicted no-effect concentration. The highest concentration in an exposure medium, which presumably does not lead to effects on the exposed organism.
- Pollution – Introduction by man, directly or indirectly, of substances or energy into the sea, including estuaries, which are liable to create hazards to human health, to harm living resources and marine ecosystems, to cause hindrance to legitimate uses of the sea including fishing, to impair the quality for use of sea water, and to lead to a reduction of amenities (Article 2 of the Helsinki Convention).
- POP(s) – Persistent organic pollutant(s)
- Pyrolytic – Resulting from decomposition or transformation of a compound caused by heat.
- REACH – The EU regulation on Registration, Evaluation, Authorisation and Restriction of Chemicals. It entered into force on 1st June 2007. It streamlines and improves the former legislative framework on chemicals of the European Union (EU).
- SCCP – Short-chained chlorinated paraffins
- S.D. – Standard deviation
- S.E. – Standard error
- Surfactant – Surfactants are wetting agents that lower the surface tension of a liquid, allowing easier spreading.
- TBBPA – Tetrabromobisphenol A
- TBT – Tributyltin
- Technosphere – The part of the physical environment affected through building or modification by humans.
- TEQ, Toxic Equivalent – Dioxins and dioxin-like PCBs are chemicals with different degrees of dioxin-like toxicity. The use of toxic equivalency factors allows concentrations of the less toxic compounds to be expressed as an overall equivalent concentration of the most toxic dioxin, 2,3,7,8-TCDD. These toxicity-weighted concentrations are then summed to give a single concentration expressed as a Toxic Equivalent (TEQ).
- Top predator – An animal that has virtually no predators of their own, residing at the top of the food chain.
- TPT – Triphenyltin
- VDSI-Index – A *vas deference* sequence index, an index used for classifying different stages of imposex.
- WFD – Water Framework Directive (Anon. 2000a)
- ww – wet weight (or fresh weight)
- WWTP – Wastewater treatment plant

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## Classification of the hazardous substances status with CHASE

The integrated assessment of the status of the Baltic Sea marine environment in relation to hazardous substances was performed using the HELCOM Hazardous Substances Status Assessment Tool (CHASE). HELCOM has also used similar assessment tools to assess the status of eutrophication (e.g., HEAT, see HELCOM 2009a for more information) and biodiversity (e.g., BEAT, see HELCOM 2009b for more information). The benefit of using integrative tools is to obtain a larger picture by using numerous indicators, which often describe the environment from very different aspects. Because the results of individual indicators are not seen in the end result, HELCOM publishes the background material with all the indicators and their values used in the assessment in a separate technical background report.

The assessment of hazardous substances is not limited to the concentrations of hazardous substances alone, but views the "hazardous substances status" of the environment from the ecosystem perspective in which all organisms, including humans, are part of the ecosystem. Thus, the integrated assessment has been organized according to the Baltic Sea Action Plan (BSAP) (HELCOM 2007a). BSAP has four ecological objectives for hazardous substances: (1) concentrations of hazardous substances close to natural levels, (2) all fish safe to eat, (3) healthy wildlife and (4) radioactivity at pre-Chernobyl levels.

The integrated assessment provides an overall status for the assessed site. The status is assessed according to five classes: bad, poor, moderate, good and high. The classifications of bad, poor and moderate status indicate an environmental state which is "disturbed by hazardous substances". The classifications of good and high status indicate an environmental state "undisturbed by hazardous substances". Thus, this classification system is basically binomial (undisturbed/disturbed) and is based on the threshold value (management status), which defines the boundary between moderate and good status. Further classification is based on statistics and is intended to show deviation from the boundary.

## Structure of the assessment tool CHASE

The assessment tool CHASE is a multi-metric tool, which integrates the results of an unlimited number of indicators. Indicators have been classified under four quality elements, named according to the four BSAP objectives (1) concentrations of hazardous substances close to natural levels, (2) all fish safe to eat, (3) healthy wildlife and (4) radioactivity at pre-Chernobyl levels.

Thus, the first element relates to concentrations of hazardous substances in the environment in general, the second element relates to concentrations of hazardous substances in seafood, the third element relates to biological indicators of the effects of hazardous substances, and the fourth element relates to concentrations of radionuclides.

The CHASE tool gives each element a status (bad, poor, moderate, good or high) and the final status is defined as the lowest status of the four elements. Thus, the final classification is based on the "one out, all out principle". Moreover, the approach adopted gives equal weight to all the elements, i.e., the objectives of BSAP.



### Calculation of the status

The CHASE tool is based on a simple scheme, whereby each indicator/substance is assessed against a threshold level and the results of the indicators are then combined to obtain the status for each element. The measurement of each indicator is divided by the threshold level, producing a so-called “contamination ratio” (CR). The higher the “contamination ratio”, the lower is the status of that indicator. In effect,  $CR > 1.0$  indicates moderate or worse status for the given indicator/substance.

Hazardous substances and their biological effects are never independent of each other. Synergistic effects are poorly understood, but it is well-known that several smaller stressors add up to effects that would not be expected from these individual stressors alone. Thus, the integration of the indicators must take into account all the other indicators. In the CHASE tool, CR values are summed within an element and then divided by the square root of the number of indicators. As a result, the status is not totally dependent on the number of indicators in the element, it does not give much weight to several low-CR indicators and it does not “mask” individual indicators with high CR values. In practice, the resulting status thus takes into account the few high CR values but does not add up to a value

that is too high. This can be seen in the following explanatory cases:

*Example 1:* The element consists of ten indicators, eight of which have CR values less than 0.5, one indicator has CR 0.78 and one has CR 2.58. The integration gives the result 1.30, thus taking into account the several low CR values, which indicate good or high hazardous substances status. However, one indicator clearly exceeds the threshold level, which is taken into account in the final status of that element (i.e., moderate status).

*Example 2:* The element consists of 23 indicators, 20 of which have CR values well below 0.5, two indicators have CR 0.58 and 0.77 and one indicator has the value 1.04. The result is 0.97 and thus the status is good.

Indicators in the elements 1, 2 and 4 (see above) are all based on a *positive response* (i.e., increasing values indicate decreasing status). However, the indicators in the element 3 may also have negative response. To take this into account, CHASE has a + / - selection for each indicator.

### Arriving at the five classes

The primary classification in the CHASE tool is based on the threshold level, which defines a moderate or good status for each element. This boundary is ecotoxicologically justifiable (if the threshold is based on ecotoxicology). The further classification is not intended to be understood strictly as an ecotoxicological status of the environment, but rather as a deviation from the boundary condition.

Moderate status is defined as a CR sum value  $> 1.0$ . Poor status is assigned for a CR sum value  $> 5.0$  and bad status is reached at a value of 10.0. At the opposite end, a high status is a CR sum value  $< 0.5$ .

### Selection of indicators and threshold values

The selection of indicators for CHASE was based on two primary criteria: (1) an indicator must have a threshold level which is preferably ecotoxicologically or statistically justified, and (2) an indicator must reliably describe the status of hazardous substances in the Baltic Sea. In addition, the following criteria were set: (3) a substance cannot be entered into an element more than once, and



(4) the indicators under elements 1 and 4 are to be based on measurements primarily from bivalves, secondarily from fish, and thirdly from sediment. Water-based indicators are to be used only if other measurements are not available. In the seafood element (element 2), the compound can be entered even though it has been used under element 1, because the data and threshold levels in this element differ from those in element 1.

Despite many available scientific effects studies, relatively few compounds have quality criteria which are agreed widely or have been formally adopted. In CHASE and the assessment of the individual substances, thresholds were taken from directives of the European Union, from working groups under the EU Water Framework Directive, from OSPAR, NOAA and the U.S. EPA. In case of heavy metal concentrations and concentrations of POPs in sediments, some thresholds were taken from the Swedish EPA and the Russian Federation. In case of biological effects indicators, thresholds were produced within scientific studies. In addition, countries were given the choice to use national threshold levels in coastal CHASE assessments and Germany and, to some extent, Lithuania and Sweden used this opportunity. It is acknowledged that the OSPAR, EU, U.S. EPA and NOAA criteria are not specific to the Baltic Sea and future work should concentrate on developing criteria for the Baltic Sea.

### Selection of data

This assessment used data from the following sources:

- National monitoring programmes (data from countries or from the ICES database)
- National screening studies
- Scientific projects (quality-assured data)
- Peer-reviewed scientific publications

If no other data were available, non-assured data were used (e.g., environmental monitoring by private corporations), but this resulted in a low confidence in the confidence assessment (see below).

The assessment period was 1999–2007 and the following rules were set for data management:

- If data were available from several years' time span, they were to be tested for temporal trends. In case of no clear trend, a median of the data was to be taken.
- If there was a time trend, the latest year was to be taken or, ideally, the latest year from logarithmically transformed data.
- Data can be used from individual samplings and even from one year's sampling.

### Confidence assessment of the results

The great heterogeneity in the data sources, time spans, amount and quality of indicators used, and quality of threshold levels made it necessary to carry out an estimate of the quality of the assessment results. This was conducted for each CHASE assessment unit by the experts performing the assessment by applying the rules presented in the table below.

Rules for the confidence assessment in CHASE		
Confidence	Threshold	Status data
<b>Low</b>	Statistical No ecotoxicology	Single measurement Rough transformation
<b>Moderate</b>	From different regions Normalization problems Methodological uncertainty	Data from one year Several values <DL Transformation not adequate
<b>High</b>	Published in peer-reviewed journal Sound science Acceptable methodology	Median over years Time trend acknowledged

The CHASE tool allows experts to choose three quality scores for both the thresholds and the data: low, moderate and high. The confidence is first calculated for each indicator by giving values between 0% and 100% for the low, moderate and high scores and by taking an average of the two percentage values. The confidence of an element is taken as the average of the indicator confidence values. Moreover, the final confidence is the average of the four elements' values. If the assessment has only one element, the confidence rating is reduced by 25%, i.e., one level lower.

## **Assessment of the “integrated status of hazardous substances” sensu the HELCOM BSAP vs. assessment of “chemical status” sensu the EU Water Framework Directive**

It should, as a precautionary note, be mentioned that the HELCOM assessment methodology differs from the assessments of “chemical status” produced by EU Member States under the Water Framework Directive (WFD). Differences to be highlighted include: (1) the CHASE tool includes a suite of matrices (biota, sediments, water, as well as biological effects), while the WFD-related assessments focus only on water, (2) CHASE makes use of all available data on hazardous substances and radioactive substances following the HELCOM Baltic Sea Action Plan and being monitored in a specific area, while the WFD focuses on so-called priority substances, which include a total of 33 substances identified to be of special interest, (3) CHASE covers the entire Baltic Sea area, while WFD-related assessments cover national waters up to the outer limit of territorial waters, (4) CHASE has five classes while the WFD-related assessment only has two classes, and (5) CHASE applies harmonized assessment principles across the entire Baltic Sea, while the WFD-related assessments are conducted from a national perspective.

The CHASE tool also makes use of a ‘one out, all out’ principle among the four HELCOM ecological objectives in the hazardous substances segment of the HELCOM Baltic Sea Action Plan. Furthermore, there might be differences in spatial and temporal resolution compared to national WFD-related assessments.

Given the differences mentioned above, the HELCOM assessment arrives at a classification that is not directly comparable to the assessment made by EU Member States with regard to the ‘chemical status’ of their coastal and transitional waters. This is not necessarily a disadvantage as the HELCOM assessment is likely to hold a higher confidence than the WFD-related assessments. Additionally, trans-national application of a common assessment tool on data from an entire regional marine area provides a unique possibility to compare across sub-regions despite well-justified variations in monitoring activities.

Hence, the application of the CHASE tool should be seen as a strengthening of this integrated thematic assessment. CHASE is providing, for the first time, not only a Baltic Sea-wide integrated assessment of the degree of disturbance by hazardous substances, but also a science-based foundation for improving monitoring activities and targeting of Baltic Sea-wide and basin-specific management actions through its confidence assessment.

## Confidence of the integrated assessment of the status of hazardous substances

A confidence assessment is an inseparable part of the HELCOM integrated assessments. All components of the integrated assessment need to be evaluated and scored (high, acceptable or low). Moreover, the principles of evaluation must be common to all authors of the assessment in order to ensure a harmonized confidence assessment. The principles and methods of the confidence assessment are presented in Annex 1 of this report, whereas this Annex will concentrate on the results of the confidence assessment.

### Confidence of the offshore assessment units

None of the offshore assessment units had low quality, i.e., a “low” score in the confidence assessment. However, only six of the 40 units had “high” quality (**Figure A1**). The “acceptable” quality of the 34 units was primarily determined by the short time spans of the data in the integrated assessment, as most of the indicators were based on sediment data from only one year. However, the assessment units were assessed “acceptable” also due to the lack of high-quality threshold values in the Gulf of Riga, Gulf of Finland, Bothnian Sea (eastern units), Arkona Basin, Mecklenburg and Kiel Bights, Belt Sea and Kattegat.

### Confidence of the coastal assessment units

The 104 coastal assessment units had confidence ratings from low to high. In 26 units, the results of the integrated assessment were rated as low quality for three reasons: low-quality thresholds for indicators, small number of indicators (lack of data) and low-quality data (based on occasional measurements). The confidence assessment results are presented for each country in **Figure A2** and in the text below.

#### Denmark

All of the coastal assessment units had high or acceptable quality in Denmark. The number of indicators was large and three or four CHASE quality elements had indicators at all the sites. Moreover, the data in the indicators were medians over a sufficient time span. The large amount of data allowed the use of indicators with adequate threshold levels.

#### Estonia

About half of the Estonian assessment units were of low quality. The reason for the low quality was the lack of high-quality threshold values for the indicators. The monitoring programme has several stations, samples are taken from fish and bivalves and measurements are made for 5–10 substances. Moreover, in several cases medians were taken over 2 to 4 years. However, many of the substances are metals, for which there is a general lack of reliable threshold values. The Estonian assessments lacked indicators for element 3 “Healthy wildlife”.

#### Finland

All the Finnish assessment units were rated as acceptable or high quality. The assessments consisted of relatively few selected indicators which had high-quality threshold levels. Moreover, the data covered a sufficient time span. None of the Finnish sites had indicators for element 3 “Healthy wildlife”.

#### Germany

Most of the German assessment units had high quality, the rest being of acceptable quality. The indicators covered a sufficient time span and also covered element 3 “Healthy wildlife”. Germany was the only country applying its own criteria for all the indicators; in many cases the threshold levels were stricter than in the assessment in general.

#### Latvia

Latvia did not assess its coastal waters but provided the HELCOM Secretariat with the data available for the assessment. The Latvian monitoring programme has several stations with 5–10 substances measured per station. The indicators in CHASE cover a 1- to 4-year time span, but consist predominantly of metals. Metals have poor threshold levels currently available, which resulted in several low quality assessments. Moreover, many of the Latvian assessments did not include indicators for other quality elements than element 1 “Concentrations close to natural levels”, which affected the confidence rating of the units. Thus, 40% of the units had low quality in the integrated assessment.

### Lithuania

All except one of the Lithuanian assessment units had high or acceptable quality in the integrated assessment. This was mainly because data for several indicators had high-quality threshold levels. The lack of carbon-normalized sediment data limited the number of indicators, but that did not reduce the confidence of the assessments.

### Poland

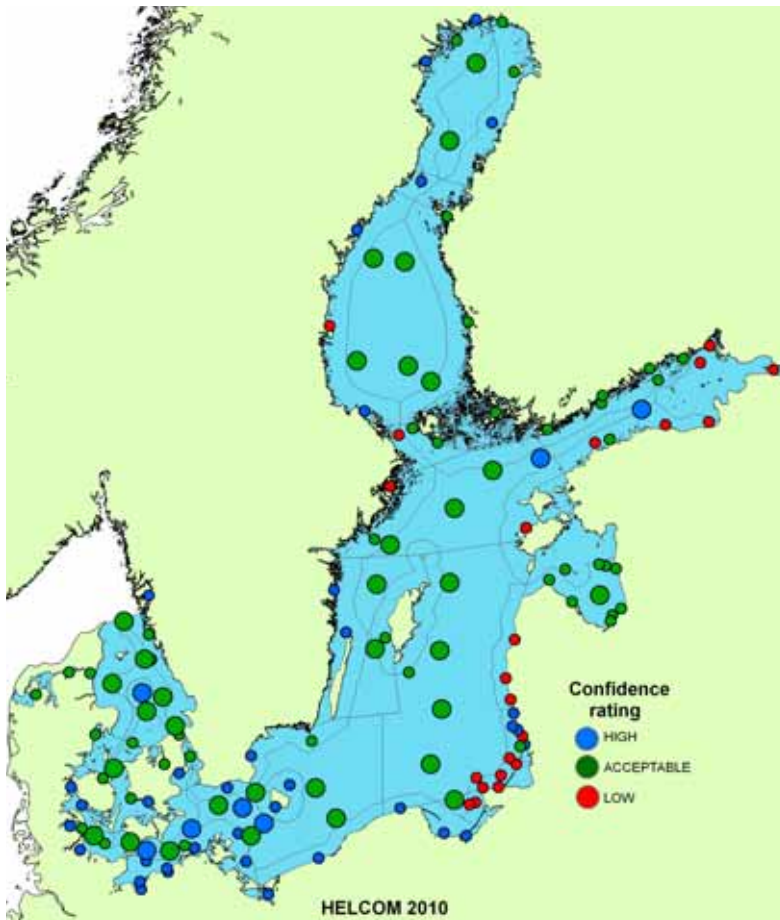
All of the assessment units in the Polish coastal waters were of high quality. Although the assessments contained indicators with weak threshold levels, the majority of indicators had good quality thresholds. Moreover, many of the coastal sites had one or two indicators in element 3 “Healthy wildlife”.

### Russia

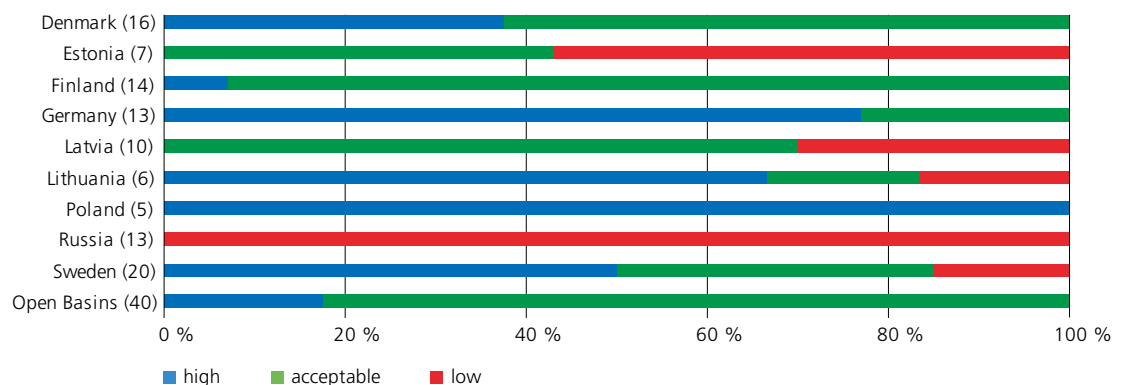
The Russian Federation did not provide data for the integrated assessment. The assessments in CHASE were made by the HELCOM Secretariat on the basis of fragmented reports. Because of this uncertainty, all the data were of moderate quality at best. Some medians over a 4-year time span were derived from the environmental monitoring at the D-6 oil platform off Kaliningrad. All the assessment units included indicators in element 1 only, as the other elements lacked indicators. This reduced the quality of the integrated assessment.

### Sweden

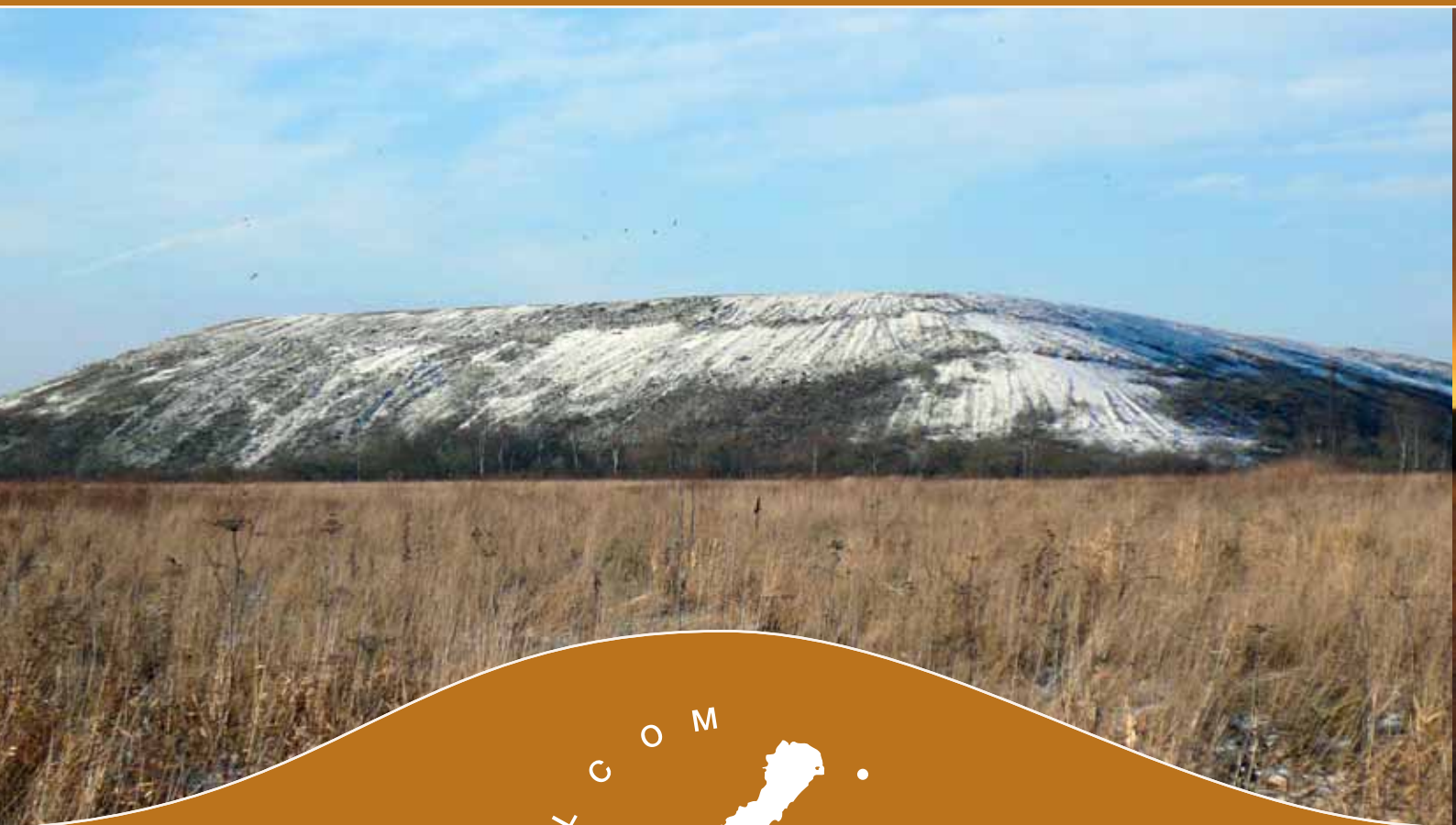
For the coastal assessment in Sweden, three sites were of low quality, with the rest of acceptable or high quality. The Swedish indicators cover a sufficient time span, enabling a high quality rating for the indicators. In three stations on the eastern coast, only the first element had indicators, which resulted in a reduced quality of the assessment.



**Figure A1** Results of the confidence assessment for the integrated assessment of the status of hazardous substances in the Baltic Sea using the assessment tool CHASE. Open sea assessment areas are indicated with large circles while the coastal assessment sites are indicated with small circles.



**Figure A2** Confidence ratings per country. Key: blue = high, green = acceptable, and red = low.



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