HAZARDOUS AND RADIOACTIVE SUBSTANCES IN DANISH MARINE WATERS

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PREFACE

The objective of this assessment report is to describe the degree of contamination from hazardous and radioactive substances and their temporal trends, as well as the effects of some of these hazardous substances, in the Danish marine environment. The assessment is based on existing information, primarily data collected via national and regional Danish monitoring activities until 2005.

The assessment report has been written in order to fulfil Danish reporting obligations in relation to the OSPAR Trend Assessment on Dangerous Substances.

CHAPTER 1

defines hazardous substances and describes in general terms their fate in the marine environment, as well as effects that can be induced. The concepts of risk assessment and the use of biomarkers are also discussed.

CHAPTER 2

focuses on the hazardous substances included in the Danish National Aquatic Monitoring and Assessment Program 1998-2005 (NOVA and NOVANA) and related activities. These include heavy metals, polyaromatic hydrocarbons, organohalogen compounds, anti-fouling compounds, and a number of other organic substances, as well as some biological effects of hazardous substances.

CHAPTER 3

describes the status and trends for radioactive substances in Danish marine waters, which is based on the long-term monitoring and assessment work co-ordinated by the Radiation Research Department of Risø National Laboratory.

CHAPTER 4

contains a summary of the present state of the marine environment with respect to hazardous substances, as well as a discussion of future management, assessment, and monitoring practices in relation to hazardous substances in the marine environment.

A map of the Danish marine waters and the locations mentioned in the assessment can be found at page 106. The background documents, references, as well as suggestions for further reading have been compiled at the end of the report, together with a glossary and list of abbreviations in order to assist readers without a professional background in ecotoxicology or marine ecology.

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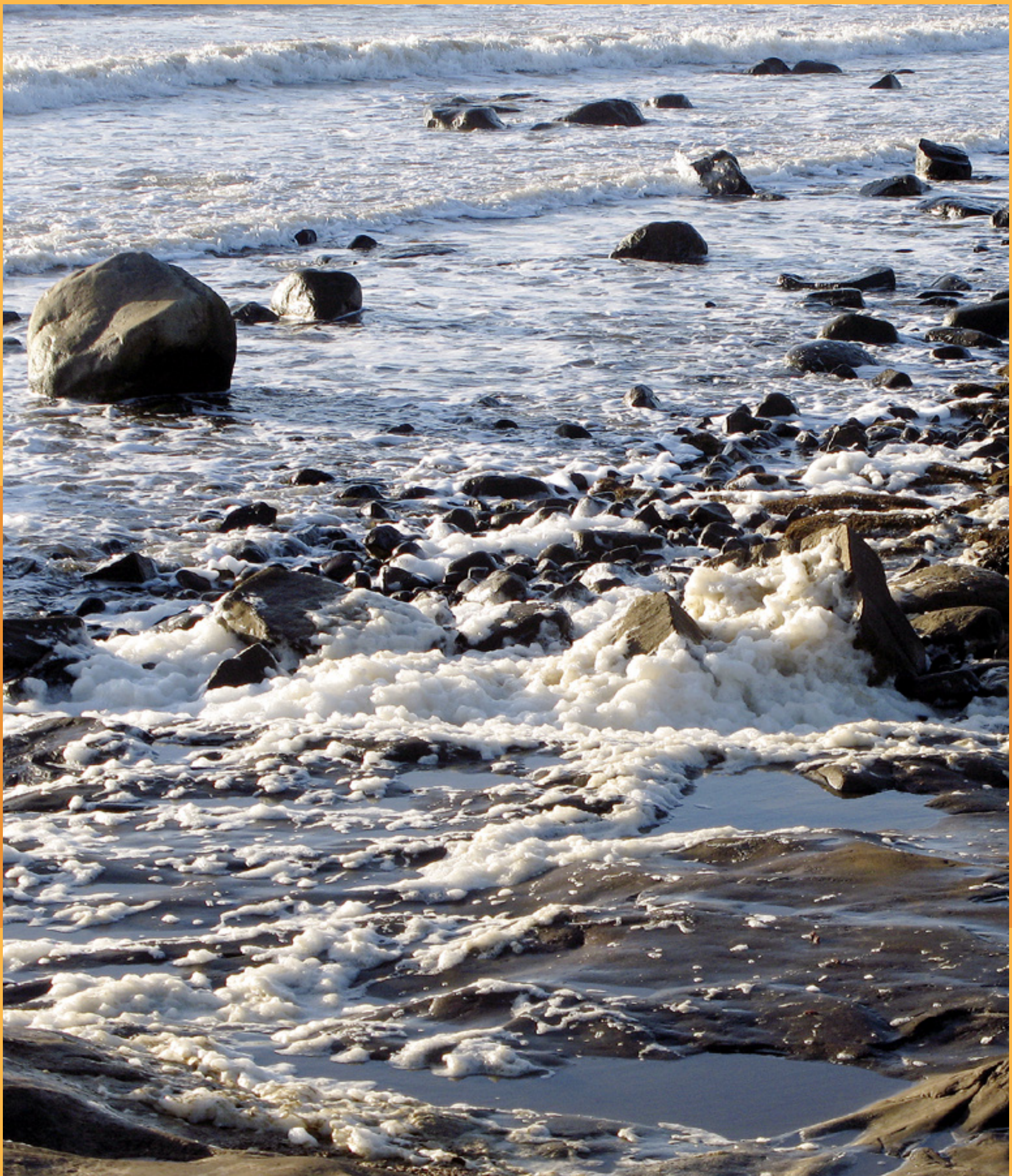

Photo: DMU/Ingela Dahllöf

Introduction

1

Hazardous substances are chemicals introduced through human activity that can have a negative effect on the marine ecosystem. Heavy metals and some organic compounds occur naturally, but they are considered hazardous substances when found in higher concentrations compared to natural background levels. There are thousands of substances that are classified as hazardous substances, and here they are grouped together according to their chemical similarity, or area of use. The following groups have been and remain the focus of the national marine monitoring programme in Denmark and constitute the main subject of this report:

Heavy metals and trace metals

occur naturally in the environment, but increased inputs from human activities have raised concentrations above background levels. Trace amounts of certain metals such as copper and zinc are important micro-nutrients for plants and animals, but are toxic at higher concentrations.

Polyaromatic hydrocarbons (PAHs)

are derived from crude oil products and from combustion of both oil products, including petrol, and organic material such as wood and household waste. Some PAHs are formed naturally, but the majority of PAHs in the marine environment come from anthropogenic activity.

Organohalogen compounds

such as the chlorinated compounds PCB and DDT are persistent and readily bioavailable. PCB, although banned, is still used in Denmark in older installations, whereas DDT has been phased out. Newly developed halogenated aromatic hydrocarbons include brominated flame-retardants. Dioxins and furans are chlorinated compounds formed during combustion that are also readily bioavailable and persistent.

Anti-fouling agents or booster biocides

are toxic substances that are used together with the biocide copper to protect ship hulls and marine installations from fouling by marine organisms. Fouling increases fuel consumption, causes corrosion, and disrupts the function of mechanical installations, as well as contributes to the spreading of invasive non-native marine species.

RADIOACTIVE SUBSTANCES

occur naturally in the environment and originate both from the time of the formation of the earth, and from the bombardment of the earth by cosmic radiation producing radionuclides in the atmosphere. Man-made radioactive substances are also introduced into the environment as a result of military activities, as well as from nuclear power stations.

OTHER GROUPS OF CHEMICALS

are also presented such as plasticizers, detergents, additives in detergents and cosmetics, as well as chemicals used for surface treatments. These chemicals all occur on the OSPAR List of Chemicals for Priority Action, or the OSPAR Substances of Possible Concern, but data from the Danish marine environment are scarce.

OSPAR COMMISSION

FOR THE PROTECTION OF THE MARINE ENVIRONMENT OF THE NORTH-EAST ATLANTIC

The 1992 OSPAR Convention is the current instrument guiding international cooperation on the protection of the marine environment of the North-East Atlantic. It combined and up-dated the 1972 Oslo Convention on dumping waste at sea and the 1974 Paris Convention on land-based sources of marine pollution.

The work under the convention is managed by the OSPAR Commission, made up of representatives of the Governments of 15 Contracting Parties and the European Commission, representing the European Community .

The work under the Convention is guided by the Ministerial Declarations and Statements made at the adoption of the Convention and at the Ministerial Meetings of the OSPAR Commission. The work applies the ecosystem approach to the management of human activities. It is organised under six strategies:

- Protection and Conservation of Marine Biodiversity and Ecosystems
- Eutrophication
- Hazardous Substances
- Offshore Oil and Gas Industry
- Radioactive Substances
- Monitoring and Assessment

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HELCOM
Baltic Marine Environment Protection Commission

The Helsinki Commission, or HELCOM, works to protect the marine environment of the Baltic Sea from all sources of pollution through intergovernmental co-operation between Denmark, Estonia, the European Community, Finland, Germany, Latvia, Lithuania, Poland, Russia and Sweden.

HELCOM is the governing body of the ”Convention on the Protection of the Marine Environment of the Baltic Sea Area” - more usually known as the Helsinki Convention.

HELCOM’s vision for the future is a healthy Baltic Sea environment with diverse biological components functioning in balance, resulting in a good ecological status and supporting a wide range of sustainable economic and social activities.

In pursuing this objective and vision the riparian countries have jointly pooled their efforts in HELCOM, which is works as:

- an environmental policy maker for the Baltic Sea area by developing common environmental objectives and actions;
- an environmental focal point providing information about (i) the state of/trends in the marine environment; (ii) the efficiency of measures to protect it and (iii) common initiatives and positions which can form the basis for decision-making in other international fora;
- a body for developing, according to the specific needs of the Baltic Sea, Recommendations of its own and Recommendations supplementary to measures imposed by other international organisations;
- a supervisory body dedicated to ensuring that HELCOM environmental standards are fully implemented by all parties throughout the Baltic Sea and its catchment area; and
- a co-ordinating body, ascertaining multilateral response in case of major maritime incidents.

For three decades HELCOM has been working to protect the marine environment of the Baltic Sea. This work has been driven by the specific environmental, economic and social situation in the Baltic region and the specific sensitivity of the Baltic Sea. The work of HELCOM has led to improvements in various fields, but further work is still needed.

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1.1

INPUT TO THE MARINE ENVIRONMENT

Photo: DMU/Britta Munter

The marine environment receives hazardous substances irrespective of where the discharge takes place (Figure 1.1). This is particularly true for Danish waters where the shallow Danish fjords and coastal waters, such as the Belt Seas and the Sound, primarily are affected by local input and shipping activities.

The more open waters such as the Baltic Sea, the Skagerrak, and the Kattegat receive input from many countries through riverine discharge, land runoff, atmospheric deposition, and an intense shipping traffic.

The Skagerrak is also a depositional area for input from the eastern North Sea, and the North Sea itself is affected by inputs from major European rivers, atmospheric deposition, shipping, and offshore industrial activities such as oil exploration and exploitation.

Hazardous substances may be released to the atmosphere through combustion and through direct emissions such as the spraying of pesticides. Sewage-treatment plants, industries, and stormwater runoff from towns are considered point sources from which hazardous substances reach the marine environment through watercourses, such as rivers and streams. Diffuse sources include runoff of atmospheric deposition on land, pesticides from agricultural activities, and emissions from traffic. Harbours, shipyards, and commercial activities such as oil exploitation and fish farms represent direct discharges from point sources to the marine environment. Diffuse direct emissions and discharges occur through shipping activities where the combustion of fuel and release of oil products and anti-fouling substances are the main sources. A special case is dredged harbour sediment that is deliberately dumped in an area away from the actual source.

Most substances that enter the marine environment adsorb to particles and organic matter in the water column and only a fraction can be found as truly dissolved. The substances may also be transformed by biological and chemical processes, creating metabolites of the original substance, processes that occur both in the water column as well as in the sediment. Adsorbed substances ultimately sink through the water column down to the sediment where they degrade more slowly than in the water column, leading to higher concentrations of hazardous substances in the sediment. Hazardous substances can also be released from the sediment and temporarily returned to the water column through resuspension by strong winds and currents, or through changed oxygen conditions. Over time, most hazardous substances are buried in the sediment, which makes it possible to follow trends in contamination in sediment cores (Figure 1.2). ■

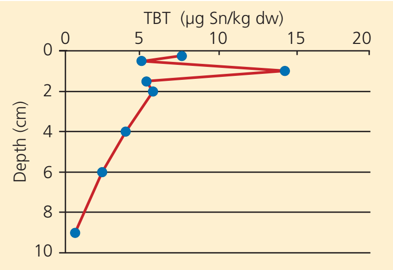


Figure 1.2
Depth profile of tributyltin (TBT) concentrations (measured as elemental tin (Sn) on a dry weight basis (dw)) in a sediment core from the Sound with a sedimentation rate of 1–2 mm/year (Jacobsen, 2000).

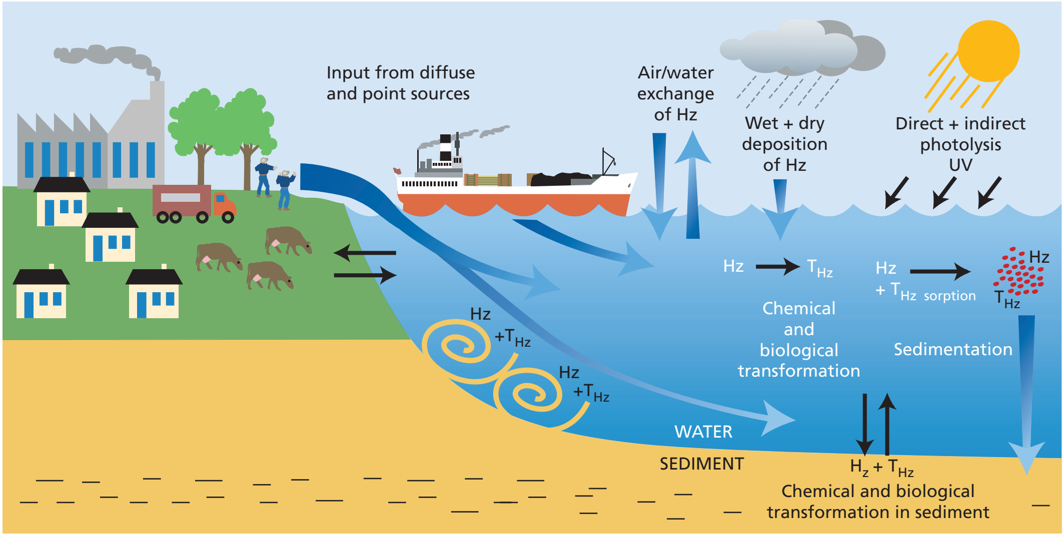


Figure 1.1
Fate of hazardous substances (Hz) and transformation products (T_{Hz}) of hazardous substances in the marine environment. Blue arrows indicate transport of substances and black arrows indicate transformation processes. After Swarzenbach *et al.* (1993).

1.2

FATE OF HAZARDOUS SUBSTANCES IN THE MARINE FOOD WEB

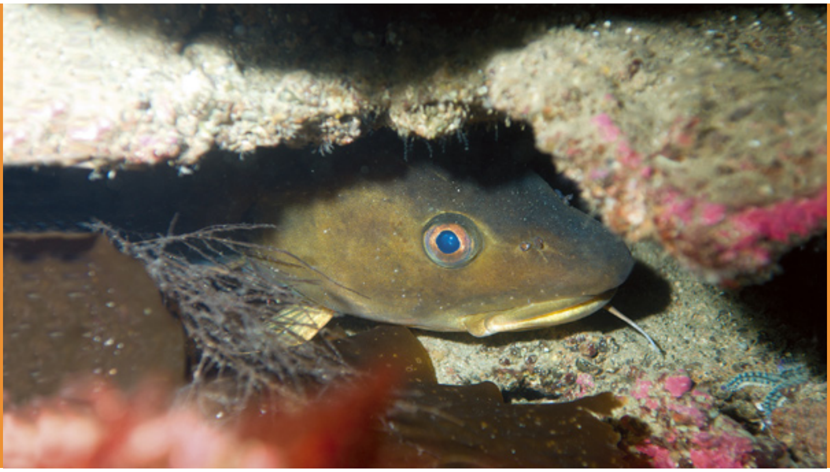


Photo: DMU/Karsten Dahl

The exposure of pelagic organisms to hazardous substances can take place either passively through the diffusion of dissolved compounds from the water phase into cells or through the ingestion of food particles (Figure 1.3). The particle-bound hazardous substances that sink out of the water column to the sediment become accessible to sediment-dwelling organisms, and because sediment-dwelling organisms are part of the food resource for many fish species, the hazardous substances may be transferred back to the pelagic food chain again.

A hazardous substance is said to bioaccumulate when the concentration in an organism is higher than that in the surrounding environment such as water or sediment, and biomagnified if the concentration is higher in a predator compared to its prey. Whether a specific substance is bioaccumulated and biomagnified depends on the target species and its ability to metabolize and/or excrete the substance; this may differ even between species within a group at the same trophic level. Measuring the concentration of a substance in different marine organisms gives an indication of whether bioaccumulation and biomagnification occurs. Many of the lipid-soluble, persistent substances are biomagnified through the food web (Figure 1.4).

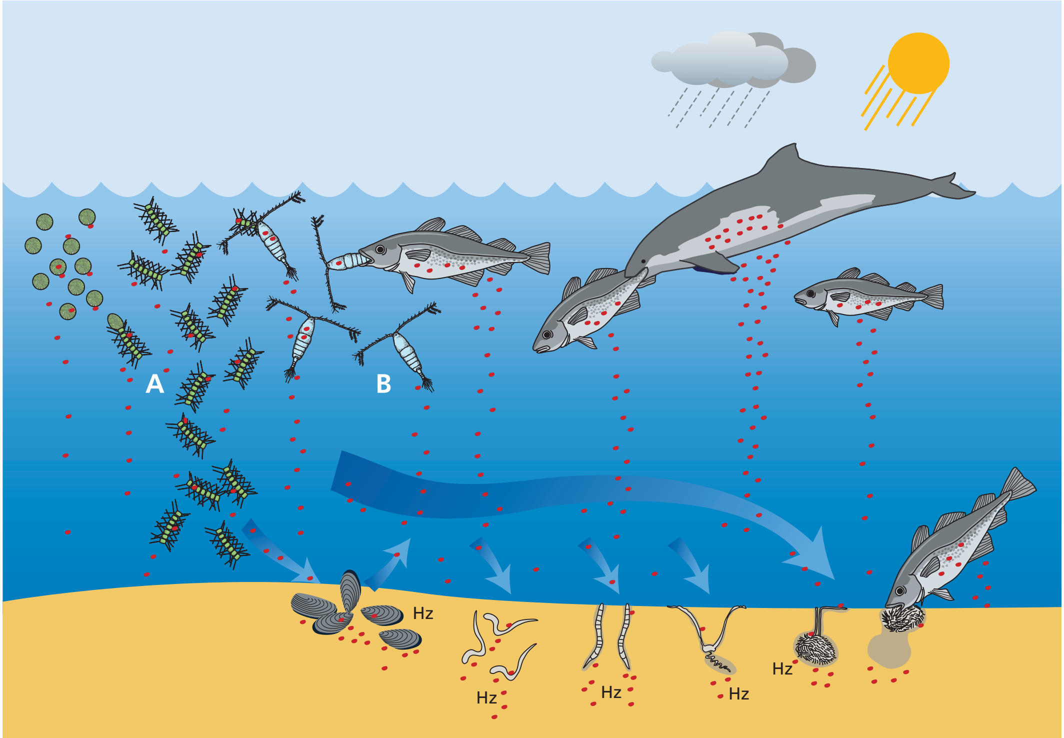


Figure 1.3
Transport of hazardous substances and transformation products (•) through the food web. Algae (**A**) represent the trophic level of primary producers, zooplankton (**B**) the trophic level of herbivores, fish and marine mammals the trophic level of predators. Sediment-dwelling organisms also include deposit-feeders that consume organic matter produced in the water column (Redrawn with permission from Ida-Maja Karle). The relative sizes of the organisms in this diagram have been changed to enhance clarity: the sizes of algae, zooplankton, and sediment dwellers have been magnified greatly in relation to those of the fish and the marine mammal.

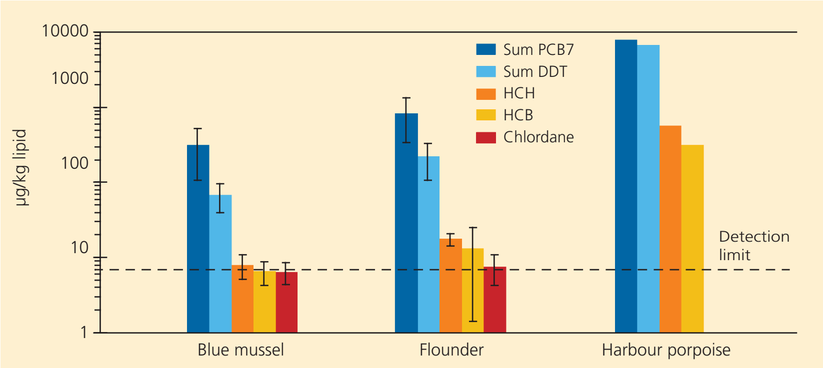


Figure 1.4
Organochlorine compounds in organisms at three different trophic levels in the marine food web (HCH = hexachlorocyclohexane; HCB = hexachlorobenzene).

1.3 EFFECT OF HAZARDOUS SUBSTANCES IN THE MARINE ENVIRONMENT

Photo: DMU/Britta Munter

Hazardous substances can have a variety of long-term effects on the different organisms in the marine environment. Such effects may include hormonal disturbances that affect reproduction, effects on the immune system which increase susceptibility to diseases, effects on metabolic processes influencing growth and general fitness, or effects on behaviour such as changes in habitat selection or prey avoidance. Furthermore, the same substance can induce different effects depending on the type of organism.

We often do not become aware of the effects of hazardous substances in the marine environment until they affect human health, economic interests, or higher animals. One of the most drastic examples of effects on humans is the Minamata incident in Japan, where mercury was dumped by the local industry into the bay (National Institute for Minamata Disease). The mercury accumulated in fish and shellfish, which were used for consumption by the inhabitants of Minamata. The result was severe neural disorders in both adults and children, as well as deformations in newly born children. The Minamata disaster led to restrictions around the world on the human intake of mercury and other hazardous substances from fish. In Denmark, the EU recommendations concerning the quantity of fatty fish that pregnant women may consume with respect to the intake of mercury and dioxins are applied.

An example of the economic impact of hazardous substances was the decline in oyster farming in France in the late 1970s, owing to shell deformation and reduced reproduction of the oysters (Alzieu *et al*., 1981). This problem was eventually traced to the presence of TBT-based anti-fouling paints on boats in local marinas and harbours, and ultimately led to a ban on the use of TBT for boats smaller than 25m. The declines in the populations of white-tailed eagles and of seals in the Baltic Sea area, caused by the polychlorinated aromatic compounds DDT and PCB in the period following 1950, are examples of the effects of marine pollution becoming evident on higher animals. DDT was shown to cause shell thinning of bird eggs, and PCB is known to disrupt the development of early life-stages. The breeding success of both eagles and seals has gradually improved as a result of the ban on the use of DDT, PCB, and other persistent hazardous substances (Tidlund & Brenner, 1998).

Before these obvious effects can be seen, hazardous substances are likely to have affected the base of the marine food web, such as bacteria, algae, zooplankton, and fish. These effects are more difficult to detect directly in the marine environment because the abundance and productivity of these organisms are dependent on several factors such as nutrient and food availability, light penetration, and physical conditions. Interactions between the different trophic levels also make it difficult to assess what is a direct or an indirect effect, but with respect to ecosystem health both types of effects are equally important. The ecological structure and processes in the marine ecosystem may thereby have been affected for a long time before the effects become evident in higher organisms. ■

Photo: DMU/Jonas Teilmann

1.4 RISK ASSESSMENT AND CLASSIFICATION OF CONTAMINATION LEVELS

Photo: DMU/Britta Munter

Risk assessment is used to determine whether a certain contaminant has the potential to impact the marine environment, and therefore should be monitored and eventually regulated. The basis of risk assessment is the comparison of concentrations measured in the environment to known effect concentrations derived from laboratory experiments. There are several ways to assess effect concentrations, ranging from theoretical calculations based on chemical properties (QSAR – Quantitative Structure-Activity Relationships) (Vighi et al., 2001), to controlled experiments in the laboratory and field. Effect concentrations in the laboratory are determined by exposing organisms to a concentration gradient and comparing the response to a non-exposed control in a dose-response experiment. The most common effect concentrations used are: No Observed Effect Concentration (NOEC), Lowest Observed Effect Concentration (LOEC), the effect concentration at which the function of 50% of the organisms is affected (EC50), and the concentration that causes the mortality of 50% of the organisms (LC50, L = lethal) (Figure 1.5).

Several assumptions should be fulfilled in order to validate effect concentrations that are determined experimentally for use in relation to the marine environment. First, the species tested should be ecologically relevant in that they occur in the local environment and represent the most sensitive species; second, the time frame of impact should reflect the exposure pattern in the environment; and third, both direct and indirect effects should be assessed. In most cases these assumptions are not fulfilled, which is the reason why safety factors are applied that aim to protect at least 95% of the species present. Such a strategy is employed in the OSPAR ecotoxicological assessment criteria (EAC) (OSPAR, 1998), which are used in the OSPAR Joint Assessment and Monitoring Programme (OSPAR, 2003a) to assess the risk of impact from hazardous substances to marine areas with respect to the degree of contamination. EACs are derived for water, sediment and mussle tissue concentrations. When establishing EACs, the contaminant should have been tested on at least three different species representing three different trophic levels, for example, algae, copepods, and fish (Figure 1.3). If information on direct environmental effect levels is available, it can also be included in the assessment. Within the OSPAR framework, the concentration for an EAC is determined from published effect concentrations divided by a factor of 10 to 10,000 depending on whether the value is a NOEC or a LC50. The reliability of an EAC for a given contaminant increases with both the number of studies and the number of marine organisms included in the assessment. If the concentration of a substance in the environment exceeds the EAC, it indicates cause for concern. However, concentrations below EACs do not necessarily imply a safe situation, since the background information might be insufficent at the time when the EACs are established. There is therfore an ongoing revision of the EACs when new important information is available.

Classification of contamination can also be based on measured concentrations, as is the case in Norway and Sweden. These classification methods do not necessarily take into account the concentrations at which the substance can be expected to have an effect, but rather the statistical distribution of the contaminant concentrations. The Norwegian system consists

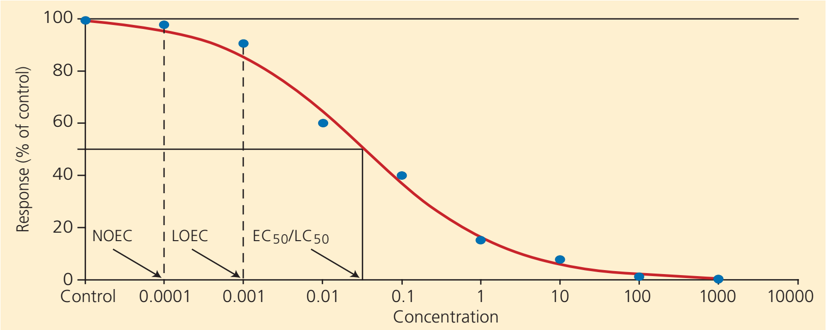


Figure 1.5

A dose-response curve with the response of the effect on the y-axis as % of the unaffected control, and the log-distributed concentration of the substance on the x-axis. NOEC – No Observed Effect Concentration, LOEC – Lowest Observed Effect Concentration, EC_{50} or LC_{50} - the concentration at which the effect (E) or lethality (L) is 50% of the control.

Table 1.1
Quality criteria for hazardous substances in sediments. The Norwegian and Swedish quality criteria are mainly based on statistical distributions of hazardous substances, whereas the OSPAR EACs are derived from ecotoxicological data. The OSPAR EACs are provisional, which means they should be used for guidance and not for final classification.

	Norway	**Sweden**	**OSPAR EAC**
	Quality Class I (mg per kg dry weight)	Reference Quality (mg per kg dry weight)	(provisional) (mg per kg dry weight)
Copper (Cu)	<35	15	5-50
Cadmium (Cd)	<0.25	0.2	0.1-1
Lead (Pb)	<30	25	5-50
ΣPCB	<0.050	0	0.001-0.01
Benzo[a]pyrene	<0.005	0	0.1-1
TBT	–	0	0.000005-0.00005

of five classes where Class I represents areas with only diffuse contamination, and Class V represents highly impacted areas (SFT, 1993). The Swedish system also consists of five classes (Naturvårdsverket, 1999), where Class I represents background levels for heavy metals, and is set to be zero for anthropogenically derived hazardous substances. No corresponding classification exists as yet in Denmark, but the EU Water Framework Directive requires that such a classification be implemented; this is discussed further in Chapter 5. A comparison of contaminant levels representing the highest environmental class for some hazardous substances is given in Table 1.1.

In this report, the concentrations of hazardous substances found are compared to either the OSPAR EAC-values, where applicable, or to the Norwegian classification system. Either comparison is used in order to facilitate comparison with other marine areas, and should not be interpreted as a classification of the Danish marine environment.

1.4.1 BIOMARKERS FOR THE DETECTION OF EFFECTS IN THE MARINE ENVIRONMENT

Another way to assess the effects of hazardous substances is through the use of biomarkers. Biomarkers are biochemical or physiological responses to hazardous substances in organisms living at a site, or transplanted to a site of interest. There are two groups of biomarkers: one group that contains biomarkers specific for the effects of a compound or group of compounds, and a second group that includes biomarkers that integrate the effects of many hazardous substances (Table 1.2). Examples of specific biomarkers are imposex and intersex in marine gastropods, which are biomarkers for tributyltin (TBT) contamination. Imposex and intersex were the only biomarkers used in the Danish Monitoring Programme NOVA (1998-2003); they are described in more detail in Chapter 2.7.1. The specific biomarkers can also be used to indirectly assess the concentration of a contaminant if there is a known dose-response pattern, which is the case with imposex (OSPAR, 2003b). This is especially useful where the limits of detection for the chemical analysis are higher than the levels at which effects are induced. One example of such a biomarker is imposex for snails, which can be used for assessing the effect level of TBT.

There are two issues that must be kept in mind when interpreting the results from biomarkers, as illustrated

Table 1.2
Some examples of techniques recommended by ICES for biological effects monitoring programmes at the national or international level (ICES, 2004).

Method	Organism	Substances addressed	Biological significance
AChE inhibition	Fish Bivalves	Organophosphates and carbamates or similar molecules. Possibly algal toxins	Measures exposure
Metallothionein induction	Fish Bivalve	Measures induction of metallothionein protein by certain metals (e.g., Zn, Cu, Cd, Hg)	Measures exposure and disturbance of copper and zinc metabolism
EROD or P4501A	Fish induction	Measures induction of enzymes which metabolize planar organic contaminants (e.g., PAHs, planar PCBs, dioxins)	Possible predictor of pathology through mechanistic links. Sensitive indicator of past and present exposure
ALA-D inhibition	Fish	Lead	Index of exposure
PAH bile metabolites	Fish	PAHs	Measures exposure to and metabolism of PAHs
Lysosomal stability	Fish Bivalves	Not contaminant-specific but responds to a wide variety of xenobiotic contaminants and metals	Measures cellular damage and is a predictor of pathology. Provides a link between exposure and pathological endpoints. Possibly, a tool for immunosuppression studies in white blood cells
Reproductive success of eelpout (*Zoarces viviparus*)	Fish	Not contaminant-specific but responds to a wide variety of xenobiotic contaminants and metals	Measurement of reproductive success of females and deformities in larvae Provides a link between exposure and effects on a population level
Vitellogenin induction	Fish	Oestrogenic substances	Measures feminization of male fish and reproductive impairment
Intersex in gastropods	Gastropods	Specific to organotins	Reproductive interference in coastal (littoral) waters
Imposex in gastropods	Gastropods	Specific to organotins	Reproductive interference in estuarine and coastal littoral waters (*Nucella*) and offshore waters (*Buccinum*).

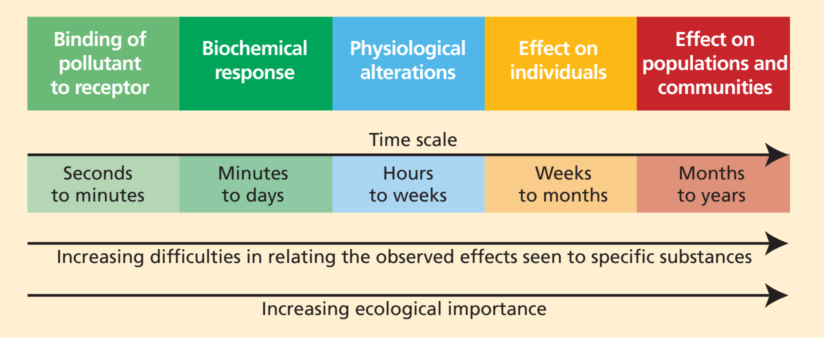


Figure 1.6
Relationship between biochemical, physiological, individual, and population responses to hazardous substances (Adapted from Peakall, 1992).

in Figure 1.6. First, a biomarker response may not necessarily imply that there will be negative biological/environmental effects on ecosystem function and structure. The biomarkers will thereby have the function of an early warning signal of potential risks. Second, the response of a biomarker may be difficult to relate either to a specific group of compounds, or to the general contamination level, since the causality between dose and response as well as the time frame of impact are not fully established. These issues can be resolved, but only through a large body of research and long-term evaluation of the biomarker in use, in conjunction with chemical analyses.

In the new Danish monitoring programme NOVANA (2004–2009), three more biomarkers have been introduced: reproductive success of eel-pout (*Zoarces viviparus*), lysosomal stability in mussel haemolymph, and EROD activity, an enzymatic activity biomarker for exposure to PAHs and PCB-like substances. All of these biomarkers are described in Chapter 2.8.2. Reproductive success and lysosomal stability are general biomarkers in that they integrate the effects of many types of hazardous substances, and can be used to assess changes in contamination level over time.

Photo: DMU/Ingela Dahllöf

Photo: DMU/Ingela Dahllöf

2

HAZARDOUS SUBSTANCES: STATUS AND TEMPORAL TRENDS

The monitoring of marine contaminants has for several years focused on contaminant levels in sediment and biota samples (OSPAR, 2000b; HELCOM, 2002). The accumulation of contaminants in sediment and biota can provide stronger evidence of the general concentration levels in a restricted area, and can be regarded as a time-integrated measure of contaminant levels, whereas concentrations in seawater vary more both day-to-day and season-to-season. In addition, lower detection limits can more easily be achieved for hydrophobic compounds such as organochlorines in sediment and biota, owing to their high affinity to particulate organic matter, and their high bioaccumulation potential. This makes determination of environmentally relevant concentration levels easier and more reliable.

The status of contaminant levels and temporal trends reported here are based on results from the Danish National Monitoring and Assessment Programme for the Aquatic Environment 1998–2003 (NOVA 2003). The results and experience from NOVA have formed the basis for the present monitoring and assessment programme, NOVANA, which runs from 2004 to 2009. ■

2.1 MONITORING OF HAZARDOUS SUBSTANCES


Photo: DMU/Britta Munter

A monitoring programme of heavy metals in fish had been initiated in relation to OSPAR in 1979, but it was first with the national programme NOVA in 1998 that a more comprehensive monitoring started, including both organic substances and heavy metals in sediment and mussels. The national monitoring programme is divided into two parts: the coastal waters, under the responsibility of the regional councils, and open waters, under the responsibility of the National Environmental Research Institute (NERI) (Figure 2.1). In NOVA, the regional stations were chosen to represent gradients from point sources such as towns and harbours. Some councils extended the geographical coverage by adding regional stations or relocated some of the transect stations to other fjords during the last years of NOVA. The open-water stations were chosen to represent diffuse contamination or background levels. In the present monitoring programme NOVANA, one NOVA station from each region has been retained in order to maintain the time series, whereas the regions can chose to place the remaining stations in different locations each year in order to determine spatial variation. For the open waters, most of the NOVA stations are also used with in NOVANA.

Hazardous substances were measured annually in mussels, which allowed both for temporal trend analysis and the detection of special events. Blue mussel (*Mytilus edilus*) was the preferred indicator organism, as it is stationary, have a widespread geographical distribution, and is used in many national monitoring programmes, thus facilitating comparison between regions and countries. Concentrations measured in blue mussels integrate an exposure time span of weeks to months. Due to the widespread use of the blue mussel in monitoring, it is also included in classification systems such as OSPAR EACs and the Norwegian and Swedish systems (see Chapter 1.3.1). The blue mussel cannot be found in some coastal areas in Denmark, so the soft-shell clam (*Mya arenaria*) is used instead. A limited comparison of the bioaccumulation potential between the two species of shellfish has been performed, but a more extensive comparison is needed to be able to translate assessment criteria from blue mussel to soft-shell clam. The monitoring of hazardous substances in flatfish such as plaice (*Pleuronectes platessa*) and flounder (*Platichthys flesus)* is also performed on an annual basis. Concentrations in fish are integrated over a larger geographical area

Photo: DMU/Jens Larsen

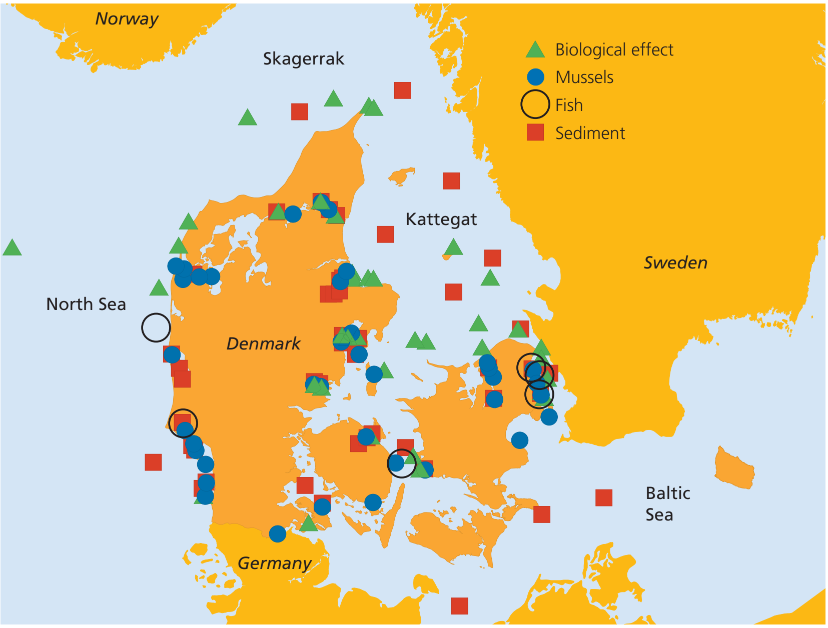


Figure 2.1
Map of monitoring stations for hazardous substances during NOVA.

than in mussels, owing to their migration pattern. Sediment was sampled twice during NOVA where the top centimetre was used, which usually integrates five to ten years of inputs depending on the sedimentation rate in the area. Contaminant levels in sediments can also be classified in the same manner as contaminant levels in mussels (see section 1.4).

The data presented in this report have all passed the extensive quality control assessment of the analyses following the NOVA guidelines. The requirements placed by the Danish Environmental Protection Agency (EPA), who listed the laboratories approved for analyses of the different matrices, based on their submission of quality assurance (QA) data and results from intercalibrations. For the marine matrices, participation in intercalibration exercises under the European scheme QUASIMEME, or formal accreditation was the standard. For analyses of some substances for which the quality control criteria cannot be met, the Danish EPA appointed laboratories. Quality data are reported annually by the laboratories and only analyses that pass the standards set in the NOVA guidelines are reported to the marine database MADS (http://www.dmu.dk/Vand/Havmiljoe/MADS), where all results from NOVA and NOVANA can be found.

The hazardous substances determined in NOVA and related activities were mainly chosen to comply with programmes under international conventions such as the Helsinki Convention (HELCOM), the OSPAR Convention (OSPAR), as well as EU and national regulations (Appendix I). Some hazardous substances on the OSPAR List of Chemicals for Priority Action and List of Substances of Possible Concern were determined once or twice during the period to evaluate their presence and concentration levels in order to assess whether the substances should be included in future monitoring. There are a few substances such as mercury, cadmium, lead, PCBs, and PAHs that are mandatory in Danish monitoring under the OSPAR Coordinated Environmental Monitoring Programme (CEMP) and more substances and measurements of biological effects will be added to this list with time.

In this chapter, the description of the geographical distribution of hazardous substances is based on NOVA data from 2003 for those substances that have been monitored on a regular basis, and where concentrations were above the detection limit. Temporal trends cover at least the five years of the NOVA period (1998–2003) for mussels, and 20–25 years for heavy metals in fish. For substances that were part of screening activities, the main results are given. The average concentration and concentrations ranges for substances included in the regular monitoring activities are given in Appendix I.

The brief information on the toxicology of the different substances is derived from HELCOM and OSPAR background papers on hazardous substances and the references provided therein. A list of the background papers is given under "Where can I read more" page 98.

Photo: DMU/Britta Munter

2.2 HEAVY METALS


Photo: Lone Reersø Hansen

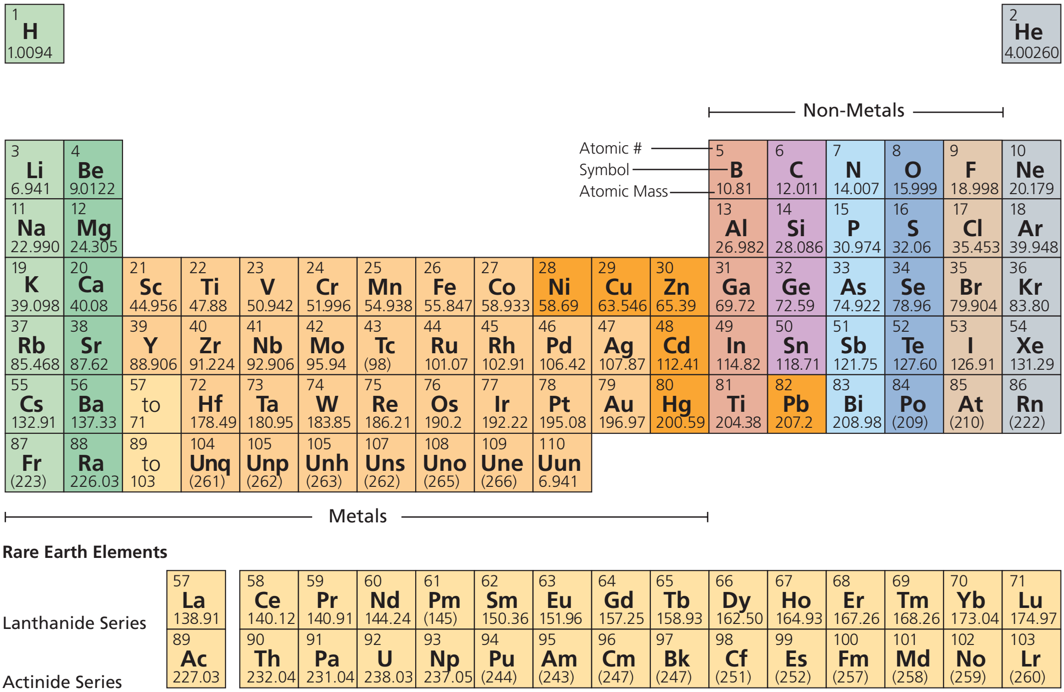
Accidental copper-spills in Roskilde Fjord.

Heavy metals comprise the group of non-degradable elements between copper and mercury in the periodic table of elements, and include metals such as cadmium, mercury, lead, copper, zinc, and nickel (Figure 2.2). All heavy metals occur naturally in the environment, and have been present since the formation of earth. Normalization to background levels is therefore necessary in order to assess anthropogenically enhanced contaminant levels. For sediments, normalization to aluminium and/or lithium content is often used, as these elements are seldom mobilized by human activity. Alternatively, normalization to the metal content of the silt fraction at suitable reference stations can be used.

Living organisms require trace amounts of some heavy metals as micronutrients to function, for example copper and zinc, the so-called essential metals. However, when excessive amounts are present in the organism, essential metals also may be detrimental to the organism (Figure 2.3). The other heavy metals have no known vital or beneficial biological functions for organisms and are therefore non-essential. In the Danish monitoring programme, six heavy metals are included: zinc (Zn), copper (Cu), nickel (Ni), mercury (Hg), cadmium (Cd), and lead (Pb).

2.2.1 SOURCES AND INPUTS

Heavy metals are introduced into the Danish marine environment from



Non-Metals

Atomic #
Symbol
Atomic Mass

1 **H** 1.0094																	2 **He** 4.00260
3 **Li** 6.941	4 **Be** 9.0122											5 **B** 10.81	6 **C** 12.011	7 **N** 14.007	8 **O** 15.999	9 **F** 18.998	10 **Ne** 20.179
11 **Na** 22.990	12 **Mg** 24.305											13 **Al** 26.982	14 **Si** 28.086	15 **P** 30.974	16 **S** 32.06	17 **Cl** 35.453	18 **Ar** 39.948
19 **K** 39.098	20 **Ca** 40.08	21 **Sc** 44.956	22 **Ti** 47.88	23 **V** 50.942	24 **Cr** 51.996	25 **Mn** 54.938	26 **Fe** 55.847	27 **Co** 58.933	28 **Ni** 58.69	29 **Cu** 63.546	30 **Zn** 65.39	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.922	34 **Se** 78.96	35 **Br** 79.904	36 **Kr** 83.80
37 **Rb** 85.468	38 **Sr** 87.62	39 **Y** 88.906	40 **Zr** 91.224	41 **Nb** 92.906	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.75	52 **Te** 127.60	53 **I** 126.91	54 **Xe** 131.29
55 **Cs** 132.91	56 **Ba** 137.33	57 to 71	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.85	75 **Re** 186.21	76 **Os** 190.2	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.97	80 **Hg** 200.59	81 **Ti** 204.38	82 **Pb** 207.2	83 **Bi** 208.98	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** 226.03	89 to 103	104 **Unq** (261)	105 **Unp** (262)	105 **Unh** (263)	107 **Uns** (262)	108 **Uno** (265)	109 **Une** (266)	110 **Uun** 6.941								

Metals

Rare Earth Elements

Lanthanide Series	57 **La** 138.91	58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** (145)	62 **Sm** 150.36	63 **Eu** 151.96	64 **Gd** 157.25	65 **Tb** 158.93	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.26	70 **Yb** 173.04	71 **Lu** 174.97
Actinide Series	89 **Ac** 227.03	90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** 237.05	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (260)

Figure 2.2
Periodic table of the elements. The heavy metals monitored in NOVA/NOVANA are highlighted in orange.

point sources, such as effluents from sewage treatment plants and industry, and from diffuse sources, including transport by watercourses (streams and rivers), runoff from land, and deposition from the atmosphere. The amount of heavy metals introduced into marine areas from the atmosphere is dependent on several factors, such as emission quantities, distance to the sources, wind direction, and the amount of precipitation. The most

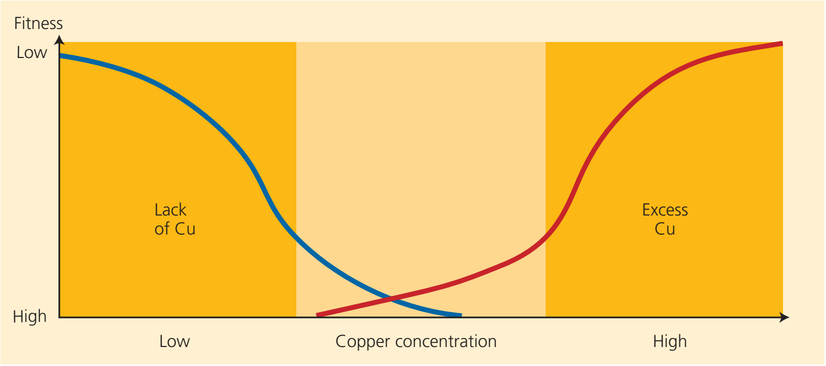


Figure 2.3
Effects of copper on algae. The blue curve shows the effects of copper on algal fitness when there is lack of copper as an essential metal. The red curve shows the toxic effects of copper at excess concentrations.

important sources for emissions of heavy metals into the atmosphere are the combustion of fossil fuels and the incineration of waste.

Precipitation from the atmosphere is responsible for the largest input of lead and zinc into Danish waters, compared to the contributions from regional streams and point sources. Lead enters the atmosphere locally from fireworks and on a global scale from smelters. Cadmium and mercury are mainly introduced into the environment from point sources, such as municipal waste/disposal and industrial activities. Mercury enters the marine environment by atmospheric deposition, which for the North Sea is estimated to be 10.5 tonnes per year, as well as by riverine and direct inputs which range between 6.8 tonnes and 8.5 tonnes per year (OSPAR, 1999). Other sources may also contribute to a large extent, for example, anti-fouling paints used on ship hulls introduce copper to the marine environment, with an estimated input in 1992 of 18–28 tonnes per year (Bach et al., 2001).

During the past 25 years, the use of heavy metals has been greatly reduced, which has resulted in a reduced discharge into the environment. This is especially true for the three most toxic heavy metals, mercury, cadmium, and lead (EEA, 2003). From 1990 to 1999, there was a pronounced decrease in emissions of heavy metals, ranging from 4% for copper to 94% for lead. The reduction is partly due to the increased cleaning of flue gases at power plants and district heating plants, whereas for lead the decline is due to the introduction of unleaded petrol.

2.2.2 TOXICOLOGY

Non-essential metals have no known biological function and their levels in tissues are generally not well regulated by biological functions in marine organisms. Most heavy metals are highly toxic to organisms and affect vital biological processes such as energy production, protein synthesis, and enzyme function.

Metals generally bioaccumulate in tissues other than fat owing to their affinity to sulphur compounds, which are mainly found in proteins, and thereby inhibit the normal functioning of enzymes and proteins.

Cadmium affects vital biological processes such as ion exchange, energy production, and protein synthesis, mainly through interaction with the metabolism of essential trace metals such as zinc and calcium. Cadmium combines with sulphur-containing groups in proteins, thereby affecting the functioning of enzymes. In vertebrates, cadmium accumulates in kidneys and liver, whereas lead accumulates in bone.

Mercury is considered to be one of the most dangerous heavy metals in the aquatic environment. It is found in both organic and inorganic forms; the organic form has a high toxicity and potential for bioaccumulation, and it may also biomagnify. Particularly under anoxic conditions, such as in sediments, the transformation of inorganic mercury to organic forms is favoured. Organomercury is lipophilic and fat-soluble, moving across membranes into fatty tissues; it tends to affect the nervous system, and to be accumulated and expressed in the brain. In marine ecosystems, organisms at the top of the food chain have been identified as the most sensitive species, owing to secondary poisoning and potential biomagnification. Inorganic mercury affects a range of cellular processes, in the same way as cadmium, based on its ability to combine with sulphur-containing groups in proteins.

Lead is rarely found in high concentrations in seawater owing to its high affinity for particles. Especially algae have been found to be very sensitive to lead, but lead can affect aquatic species at different levels in the food chains (EEA, 2003).

Detoxification in organisms may consist of "hiding", or sequestering, the active metal ions within certain proteins, called metallothioneins, or depositing them in insoluble form in intracellular granules for long-term storage or excretion through hair, feathers, or fur.

2.2.3 STATUS AND TRENDS

The concentrations of heavy metals in Danish mussels in 2003 are shown in Figure 2.4 A-D. The Norwegian classification system (SFT) has been used for assessing the environmental status of heavy metals in blue mussels, whereas EAC limits have been used for sediments.

COPPER

The concentrations of copper in mussels were highest in the Ringkøbing fjord where all stations were markedly contaminated (STF Class III). There were two areas, Århus Bugt and Little Belt, with only diffuse contamination by copper (SFT Class I), whereas all other areas were classified as moder-

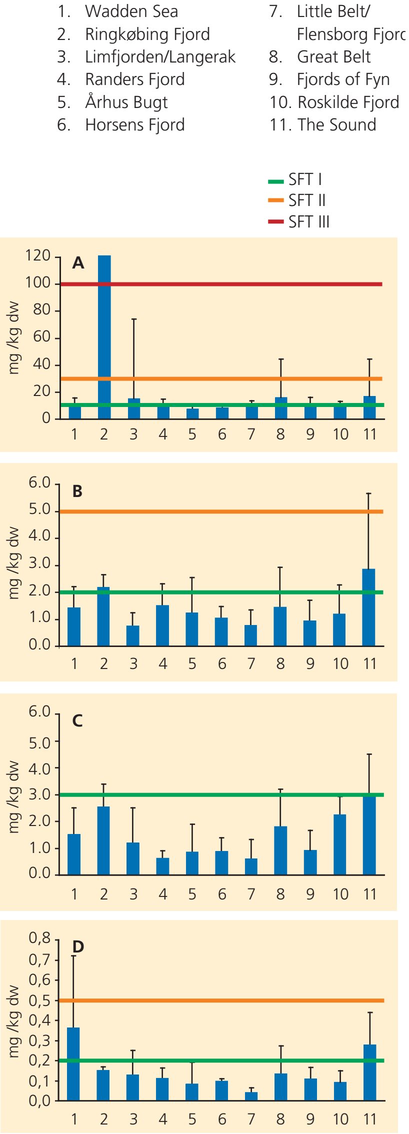


Figure 2.4
Concentrations of **A**) copper, **B**) cadmium, **C**) lead, and **D**) mercury in mussels from 11 coastal areas in Denmark, shown as average (bar) and maximum (line) concentrations. The Norwegian classification system is used for evaluation of the contaminant levels. For lead most areas are classified as SFT I.

ately contaminated. Copper concentrations in sediments exceeded the lower EAC limit in the inner Danish waters, and even at one station in the North Sea/Skagerrak.

CADMIUM

The concentration of cadmium in mussels was highest in the Sound and Ringkøbing Fjord that on average was moderately contaminated (STF Class II). Moderate contamination by cadmium was seen at one station each in the Wadden Sea, Randers Fjord and the Great Belt area. The lower EAC limit for sediments was exceeded for cadmium in all areas, and the higher EAC limit was exceeded in some of the stations in the Baltic, the Belt Sea, the North Sea, as well as some of the fjords, indicating that effects on the ecosystem are likely.

LEAD

The concentration of lead in mussels was highest in Ringkøbing Fjord and the Sound, but only at a few stations was the limit for moderate contamination exceeded. On the other hand, lead concentrations in sediments were above the lower EAC limit at all sites, and above the high EAC limit in the Sound, the Belt Sea, the Kattegat, and in some of the fjords.

MERCURY

The concentration of mercury in mussels was highest in the Wadden Sea, where one station was markedly polluted (SFT Class III). The Wadden Sea and the Sound have been classified as moderately contaminated (SFT Class II), as has one station in the Great Belt area. Mercury concentrations in sediments exceeded the lower EAC limit in the Wadden Sea, the Sound, the Baltic Sea, the Belt Sea, and Århus Bugt as well as in some of the fjords, implying that there is a risk of effects on the ecosystem. The Sound region has a history of high chemical loading over the past 100 years and particularly sediments from Copenhagen harbour contain large amounts of mercury. The high mercury levels in the Wadden Sea can be ascribed to large inputs from the rivers Elbe and Weser.

Another way to estimate the contamination of sediments by some of the heavy metals is to normalize the content of the metal in the <63µm (silt) fraction to that in the same fraction in

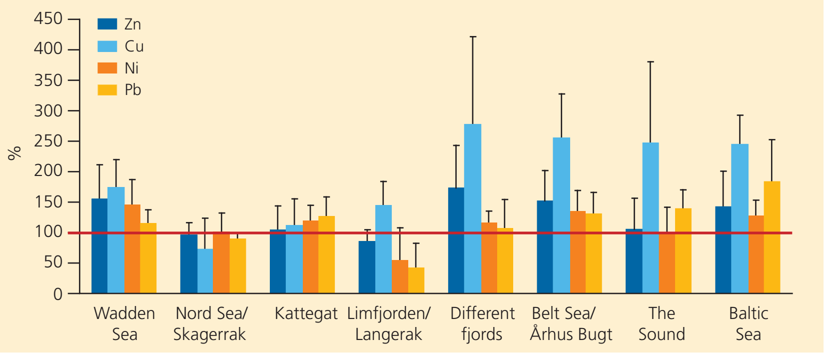
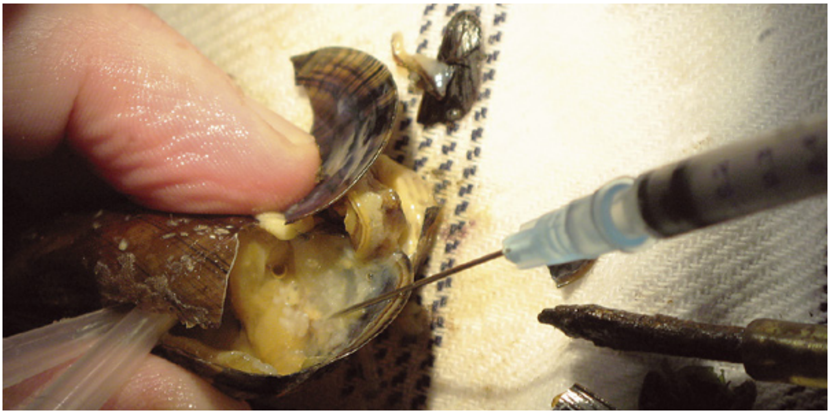


Figure 2.5
Metal concentrations in sediments as percent of the natural background concentration, which is set to 100% after normalization to silt content.



Sampling of mussel haemolymph for measurement of lysosomal activity.

Table 2.1 Metal concentrations in fish (flounder) (average ± S.D) in mg/kg dry weight in liver (except where otherwise noted).

Area	Zn	Cu	Cd	Hg	Hg muscle
The Sound					
– Nivå Bugt **	172 ± 8	44 ± 3	0.40 ± 0.08	0.20 ± 0.03	0.61 ± 0.07
– Vedbæk *	172 ± 16	53 ± 10	0.73 ± 0.21	0.34 ± 0.12	0.74 ± 0.21
– Copenhagen harbour*	188 ± 11	37 ± 10	0.38 ± 0.12	0.22 ± 0.03	0.62 ± 0.05
Great Belt **	183 ± 8	68 ± 6	1.26 ± 0.32	0.31 ± 0.06	0.53 ± 0.08
Wadden Sea*	135 ± 11	44 ± 5	0.18 ± 0.08	0.22 ± 0.01	0.36 ± 0.02
North Sea *	186 ± 17	78 ± 8	0.57 ± 0.07	0.35 ± 0.07	0.52 ± 0.06
– Plaice **	176 ± 11	17 ± 2	0.23 ± 0.03	0.31 ± 0.02	0.36 ± 0.03

**: n=25 *: n=10

sediments from reference stations. However, this is only valid for those metals that have a strong correlation with the silt fraction, which does not include cadmium or mercury owing to their affinity to organic matter. When using this approach for zinc, copper, nickel, and lead, the degree of contamination is compared to the natural background concentrations represented by 100% (Figure 2.5). Especially for copper, but also for the other heavy metals in some areas, background concentrations are clearly exceeded.

HEAVY METALS IN FISH

Heavy metal concentrations were measured in flounder from the Sound, the Wadden Sea, the Great Belt, and the North Sea (Table 2.1). Nickel and lead concentrations were below the detection limit in most samples. For heavy metals, there is a Danish limit for mercury in seafood of 0.5 mg/kg wet weight (~ 2.0 mg/kg dry weight), and this limit was not exceeded in any of the 114 fish or 95 mussel samples collected in 2003.

Temporal trends of metals in mussels only cover the past five years, which in most cases is too short a time period to provide adequate statistical power for the analyses. However, for concentrations of mercury, cadmium,

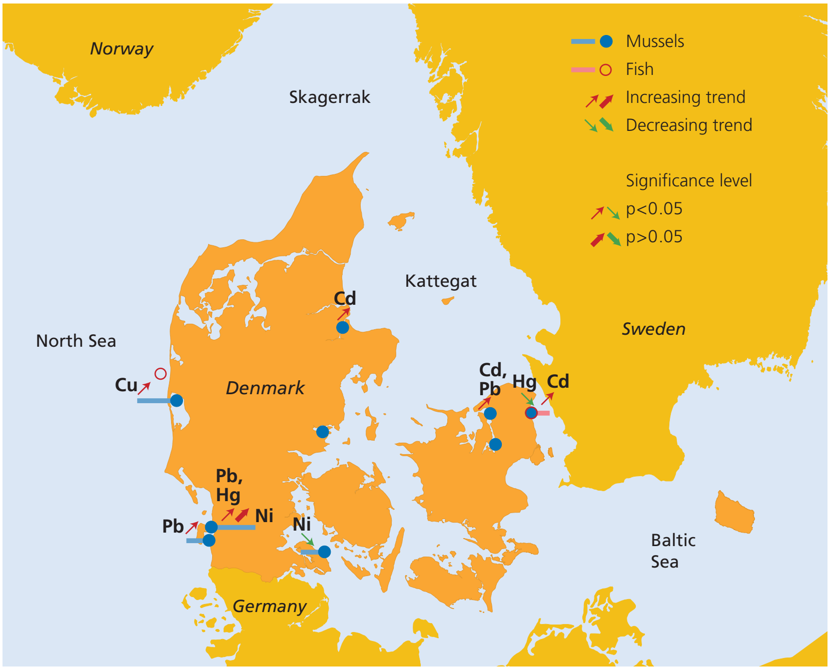


Figure 2.6
Temporal trends of metal concentrations in mussels: cadmium (Cd), copper (Cu), lead (Pb), nickel (Ni), and mercury (Hg).

copper, and lead in mussels, there were significant increases at some stations, while only the concentration of nickel decreased at a single station (Figure 2.6).

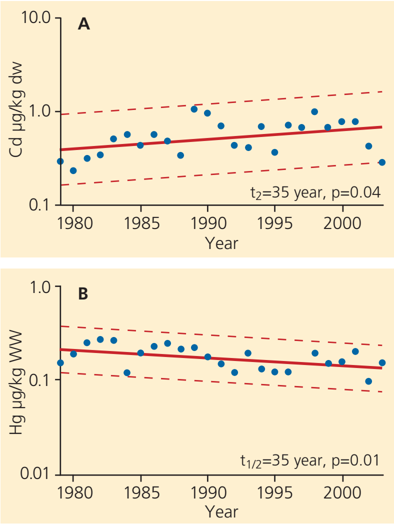


Figure 2.7
Temporal trends of metals in fish: **A**) cadmium, and **B**) mercury. t$_2$ is the time it will take for the concentration to double; t$_{1/2}$ is the time it will take for the concentration to be halved; p is the significance level of the trend. The stippled line indicate the 95% confidence level of the trend.

The temporal trends for concentrations of heavy metals in fish caught in the Sound and at the two stations in the Skagerrak are based on 20 years of measurements, thus providing greater statistical power. Out of the six metals investigated, only cadmium and mercury in fish from the Sound station showed a change over time (Figure 2.7 A-B). There was a significant decrease in the concentrations of mercury in flounder from 1980 to 2003, whereas a significant increase in cadmium was observed during the same period.

Temporal trends of heavy metals in sediments cannot be assessed based on the NOVA data set as there are only two time points, and the concentrations found in 2003–2004 were comparable to those found in 2000–2001

(Figure 2.8 A-D). However, when comparing these data with those collected in 1985/1986, there seems to be a decrease in the concentrations of copper in the North Sea and in Skagerrak during the period up to 2000–2004, whereas an increase in the mercury concentrations has occurred in the same areas and time period. The sediment cores from Århus Bugt and Mariager Fjord (Figure 2.9) show a two to three-fold increase in the concentrations of heavy metals from the first half of the 19th century until today.

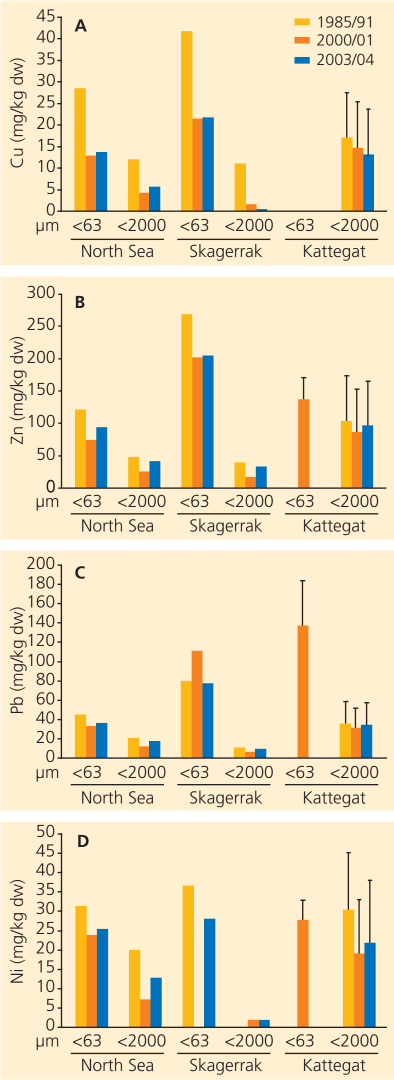
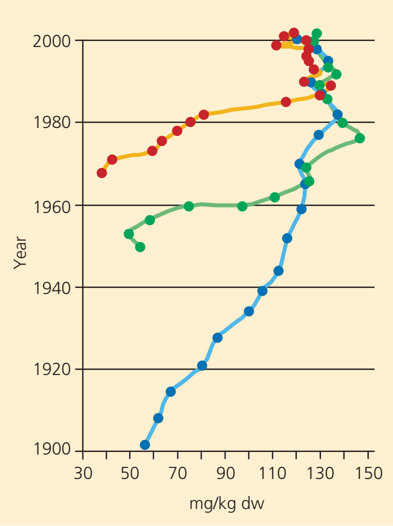


Figure 2.8
Distribution of metals in two size fractions (<63 µm (silt) and <2000 µm (whole sediment)) of sediments during three sampling periods: **A**) copper, **B**) zinc, **C**) lead, and **D**) nickel. Replicate cores were only sampled for in the Kattegat, where the error bars show the standard deviation between replicates.

Figure 2.9
Distribution of zinc in three sediment cores from Århus Bugt showing trends of zinc contamination time.



2.3 POLYAROMATIC HYDROCARBONS


Photo: DMU/Anders Mosbech

Polyaromatic hydrocarbons (PAHs) are a group of compounds consisting of molecules with three or more fused benzene rings. Naphthalene, which is the only 2-ringed aromatic hydrocarbon, is also included in the PAH data presented here. PAHs originate from tar substances present in oil (petrogenic PAHs), and from all types of incomplete combustion, whether it be fossil fuels such as coal, oil and gas, or wood and waste incineration (pyrogenic PAHs). Some PAHs can also be formed naturally due to forest fires and volcanic activity. It is possible to relate the source of PAHs at a site based on its composition of light and heavy molecular weight PAHs, where heavy molecular weight PAHs and PAHs with side chains are mainly produced by pyrogenic sources, while light molecular weight PAHs mainly originate from petrogenic sources.

2.3.1 SOURCES AND INPUTS

The majority of PAHs in Danish waters in terms of weight (approximately 75%) derive from oil spilled directly into the sea from ships or oil production (Faktuelt, 2000). The major sources of the remaining 25% of PAHs in the Danish marine environment are fossil fuels and incomplete combustion of organic materials. The latter consists of PAHs from energy production, small oil or straw burners, and the transport sector. PAHs from combustion processes are emitted to the air as volatile components or adsorbed onto particles and may travel long distances before they precipitate onto the ground or into the sea.

PAHs are transported to marine sediments mainly due to their strong binding to organic matter that settles on the seafloor. The typical environmental conditions of Danish marine sediments, such as low oxygen concentrations, low temperatures, and low levels of UV light, all slow down the degradation and thereby the PAHs become more persistent in these environments.

2.3.2 Toxicology

PAHs are generally considered to be toxic to aquatic organisms. They are highly soluble in organic tissues and the radical metabolites formed during metabolism can interfere with proteins and nucleic acids in the cell, causing a variety of effects depending on the specific target. PAHs constitute the largest group of carcinogenic substances because many of the metabolites are genotoxic in that they bind irreversibly to DNA molecules and thereby damage the genome. Concentrations in water down to 0.4 µg/L have been found to be mutagenic and harmful to reproduction in fish. Higher concentrations of PAHs can also cause damage to the structure of membranes, a so-called narcotic effect.

When PAHs are exposed to sunlight, the radicals formed can be extremely reactive and up to 50 000 times more toxic than their parent compound (Boese *et al.*, 1998; Lyons *et al.*, 2002). These radicals can, in turn, react with organic matter and produce other damaging radicals of non-PAH origin, as well as affect organisms that themselves do not metabolize PAHs to radicals. This mechanism is known as phototoxicity.

Oil fingerprinting

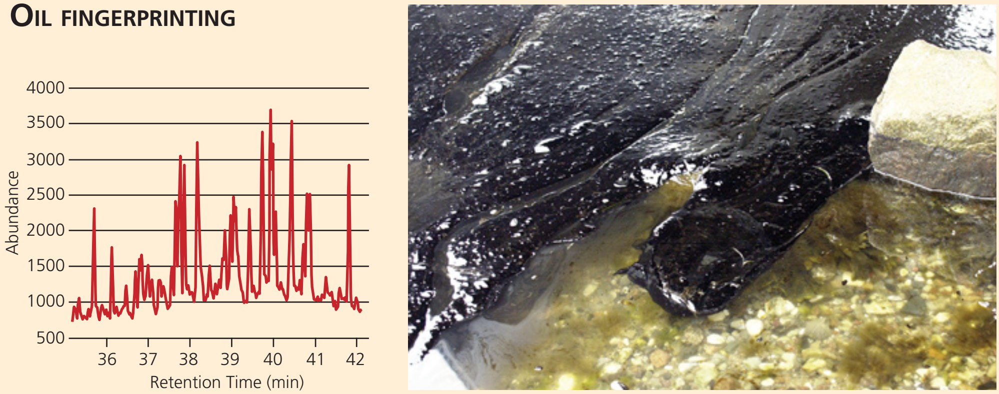


Photo: DMU/Anders Mosbech

Oil fingerprint from the Baltic Carrier that grounded in the south of Denmark in 2001. Each type of oil has its own individual chemical composition. If an oil spill is detected in Danish waters from an unknown source, a chemical fingerprint of the oil is constructed from analysis of its PAH composition. The fingerprint can then be compared to oil from ships or other sources, and with the use of multivariate data evaluation, the source can be determined with almost 100 % accuracy (CEN, 2006).

1. Wadden Sea
2. Ringkøbing Fjord
3. Limfjorden/ Langerak
4. Randers Fjord
5. Århus Bugt
6. Horsens Fjord/ Vejle Fjord
7. Little Belt/ Flensborg Fjord
8. Belt Sea area
9. Roskilde Fjord/ Isefjord

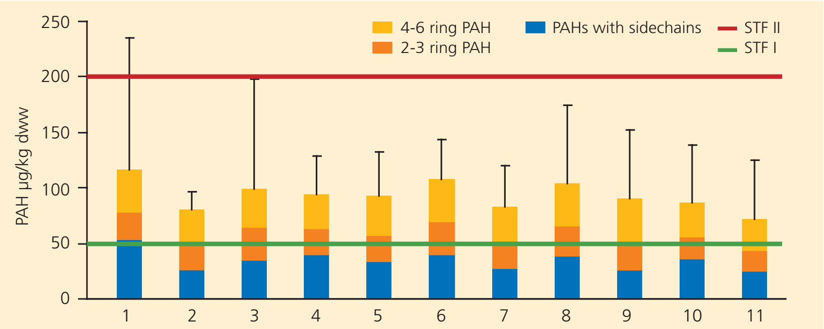


Figure 2.10

Concentrations of total PAHs in mussels from nine coastal areas, shown as average (bar) and maximum (line) concentrations. The Norwegian classification system (SFT I and II) is used for evaluation of the contaminant levels.

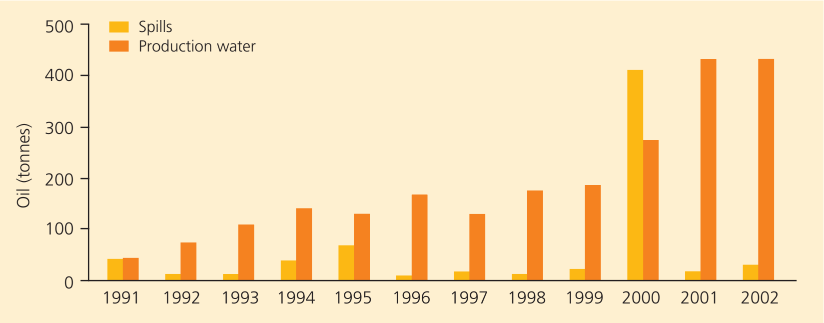


Figure 2.11

Oil discharges into the North Sea separated into oil in production water and oil spills during the period 1991 to 2002.

2.3.3 Status and trends

NOVA includes analyses of 26 PAHs in all, but with the main focus on the 16 PAHs defined in the United States Environmental Protection Agency standard. The PAHs are separated into groups based on number of rings in their structure (2, 3, 4, or 5 rings), and on the presence of side chains in their structure.

The concentrations of individual PAHs in mussels were generally below the lower EAC limit except for anthracene, where the lower EAC limit was exceeded at 44% of all sampling sites, with the highest levels in Horsens Fjord. In all but three areas the sum of the 16 PAHs exceeded the lower limit in the Norwegian classification system (Figure 2.10), where the Wadden Sea had the highest average concentration. Generally, it is the high molecular weight PAHs in mussels that may cause effects according to the assessment criteria.

The concentrations of PAHs in

sediments exceeded the lower EAC limit at most stations and in sediments the concentrations of all monitored PAH groups are causes of concern.

Temporal trends for PAHs have so far only been determined for two stations in Roskilde Fjord, as some data in the 1998–2002 period are under reevaluation. The only significant increase at one of these two stations was for fluoranthene, whereas the sum of PAHs was constant.

Data from Norwegian and Danish oil fields show that up to 95% of the total sum of PAHs in offshore production waters consists of low molecular weight PAHs such as naphthalenes. The amount of PAHs from oil spills from Danish oil rigs in the North Sea does not show any temporal trend, whereas oil discharges through production water have been increasing each year between 1991 and 2002 (Figure 2.11).

Reports of oil spills from ships have been fairly constant at around 400 per year, with a declining tendency during the past few years (Grønnegaard & Bruun, 2004). Oil spills that may not have been reported to authorities, but that have been documented as a consequence of spill incidents such as oil-covered seabirds, have declined between 1984 and 1995 in the Baltic Sea and the North Sea (Skov *et al.*, 1996).

Photo: DMU/Anders Mosbech

2.4 ORGANOHALOGEN COMPOUNDS

Photo: Mogens Hansen

Organohalogen compounds are organic chemicals containing one or more atoms of a halogen (fluorine, chlorine, bromine or iodine); many are polyhalogenated aromatic compounds, i.e., containing one or more benzene rings, in which one or more hydrogen atoms are substituted with a halogen. The substitution with halogens results in a variety of different versions of the compound, so-called congeners, and the environmental concentrations of these compounds are often given as the sum of some or all of the congeners. The use of polychlorinated biphenyls (PCBs) and organochlorine pesticides such as Lindane (hexachlorocyclohexane (HCH)), DDT, hexachlorobenzene (HCB), and Chlordane is banned in Denmark. However, due to their chemical stability, and in the case of PCBs, their presence in older products still in use, they are found throughout the Danish marine environment and are therefore included in the monitoring programme. Brominated flame retardants (BFRs) and dioxins and furans are considered as newer compounds of environmental concern and were screened once during the NOVA period.

2.4.1 SOURCES AND INPUTS

PCBs have been used extensively in many industrial applications, including hydraulic fluids, cooling liquids in transformers and dielectric liquids in capacitors, and as plasticizers and lubricants, as well as in inks and paints. Although they have been banned in Denmark since the 1970s, PCBs are still being introduced into the Danish environment via diffuse sources such as atmospheric deposition, water from rivers with sediment-bound PCBs, old dumping grounds, and from houses with material containing PCBs (Markager *et al.*, 1999). The ratio between the different congeners of PCBs is used to determine whether the PCBs found are of old or new origin. This ratio in the Baltic Sea has been decreasing since the 1980s; however, in the past 3–4 years the ratio has been increasing again, indicating new inputs from countries where PCBs are still in use (Tidlund & Brenner, 1999), for example, Russia.

DDT is mainly used to control insects in crops, but has been banned in Denmark since the 1970s. It is still produced and used in Asia and Central and South America, and possibly also in China and Russia (Markager *et al.*, 1999). The contamination of DDT in Denmark today is therefore the result of old contamination and long-range input.

Lindane (HCH), HCB and Chlordane are also insecticides used for soil and seed treatment, wood preservation, and for spraying fruits and vegetables. HCH and Chlordane have been banned in Denmark, but are still used in some European countries (Table 2.2).

Brominated flame retardants comprise a wide range of chemicals that are used in many products such as computers, textiles, televisions, and cars. They enter the marine environment by diffuse routes such as long-range transport in the atmosphere, discharges from washouts, and evaporation from and the destruction of products containing flame retardants imported into Denmark. Substances that are used in large volumes include polybrominated diphenylethers (PBDEs), hexabromocyclododecane (HBCDD) and tetrabromobisphenol-A (TBBP-A). The production of polybrominated biphenyls (PBBs) ceased worldwide in 2003.

Dioxins and furans are by-products from industrial processes such as paper bleaching and chemical manufacturing, and from the combustion of fossil fuels, as well as waste and wood incineration, where chloride often functions

Table 2.2
Input of Lindane to the North Sea (OSPAR, 2006).

	Lindane (kg) to the North Sea								
Country	**1990**	**1991**	**1992**	**1993**	**1994**	**1995**	**1996**	**1997**	**1998**
Belgium	102	100-102	77-88	62-98	52-97	54-57	n.i.	56-76	101-120
Denmark	0-30	0-30	0-30	0-30	0-30	0-30	n.i.	n.i.	n.i.
France	175	175	175	175	175	175	120	n.i.	n.i.
Germany	342	183	207-209	193-194	250-272	291	234-243	370	261
Netherlands	11	2,4	6,6	360	150-310	352-385	300	300	258-261
Norway	420	216	70	61	61	70	48	46	57
UK*	147-234	224-351	142-239	245-298	196-265	154-251	96-140	70-108	61-130
Total (kg)	**1197-1314**	**900-1060**	**678-818**	**1096-1216**	**884-1210**	**1096-1259**	**798-731**	**798-900**	**738-829**

n.i. No information

* There is further significiant discharge from the UK to the Irish Sea and the Atlantic.

as a catalyst in the formation of dioxins. The main sources to the atmosphere are combustion processes, which cause diffuse inputs into the marine environment, whereas industrial processes can lead to direct inputs. Dioxins and furans can also originate from forest fires and volcanic activity.

2.4.2 TOXICOLOGY

Polyhalogenated aromatic compounds have low water solubility, high lipophilicity, high stability, and high resistance to biodegradation, and these properties result in high bioavailability, uptake, and accumulation in the fatty tissues of living organisms. The biomagnification through the food chain of many such compounds has been reported, and the highest concentrations are found in top predators, such as seabirds and marine mammals. The compounds and their metabolites may disrupt the immune system, hormone production and transport, and thereby impair reproduction, increase susceptibility to disease, and damage the nervous system. PCBs and dioxins can bind irreversible to a variety of macromolecules such as DNA, as well as reversibly react with specific enzymes and reaction sites in the cell, where, for example, dioxins exhibit anti-oestrogenic effects by blocking the normal function of the oestrogen-receptor.

The metabolites of polyhalogenated aromatic compounds are also known to be toxic. For example, DDT and its breakdown product DDE were discovered to be responsible for eggshell thinning, causing decreased reproductive success in predatory birds; this resulted in a ban on the use of DDT in Denmark and other countries. DDE also affects the testosterone concentration in porpoises, for example, which may have consequences for reproduction, because testosterone plays a crucial role in normal male sexual differentiation and sexual behaviour. Other contaminants that affect the hormonal system include the metabolites of PCBs that bind to the protein responsible for transporting the thyroid hormone thyroxin. This hormone is important for growth and development, so the reduced transport of this hormone may damage early life stages of organisms.

The toxicity and mode of action of brominated flame retardants are not yet well understood. Some of the polybrominated biphenylethers screened for under NOVA have been classified as highly toxic to aquatic organisms, but the toxicity is dependent on the degree of bromination, whereby the less brominated compounds are more toxic. Other effects, such as endocrine disruption and neurotoxic effects, have also been reported, but generally the environmental effects are poorly studied.

Dioxins are highly toxic compounds that can cause cancer and alter reproductive, developmental, and immune functions. Their environmental impact is, however, poorly studied. The mode of action is through binding to a specific receptor that, in turn, binds to specific parts of the DNA, which changes the gene expression of the cell.

2.4.3 STATUS AND TRENDS

PCB

NOVA included analyses of 13 PCBs in all, but with the main focus on seven of the congeners (CB28, CB52, CB101, CB 118, CB138, CB153, CB180), also denoted as ΣPCB7.

Although a majority of countries in Western Europe have banned the use of PCBs, the sum of seven congeners was found at concentrations in mussels that exceeded the low EAC limit at all but one of the areas monitored (Figure 2.12). In 2004, the highest

Photo: DMU/Henny Rasmussen

concentrations were found in Roskilde Fjord, as was the case in 2003, and at some stations the concentrations also exceed the high EAC limit. The concentrations of PCBs in sediments were measured in 2003, and in general the lowest concentrations were found in the open marine areas, whereas high concentrations were found at some stations in the inner Danish waters, for example, Limfjorden and the Sound (Figure 2.13).

DDT, HCH AND BFR

NOVA included analyses of DDT and its breakdown products DDE and DDD, as well as HCH, reported here as the sum of α-, β-, and γ-HCH, the different congeners of HCH.

Concentrations of the degradation products of DDT, DDE and DDD, in mussels did not exceed the low EAC limit of 0.8 g/kg wet weight at any station. For HCH, the concentration was below 0.5 µg/kg wet weight for all stations, corresponding to insignificant and moderate pollution according to the Norwegian classification system.

The concentrations of ΣPCB7, DDT+DDE, and HCH in liver from flounder were all highest in the Sound area (Copenhagen); this was most marked for the PCB levels, which were 2–3 times higher there than in other areas. Since there was no significant difference in the amount of extractable fat from the fish at the different stations, the data accurately reflect differences in contamination level between the stations (Table 2.3).

The most frequently used BFRs were all found in sediment, mussels, and fish in Denmark (Christensen & Platz, 2001) (Figure 2.14). An initial screening in 2000 of the PBDEs at ten sediment stations and fifteen mussel stations showed that the highest contamination was found in sediments (21.5 ng/g dry weight) and mussels (0.811 ng/g wet weight) close to harbours and waste dumps (Christensen & Platz, 2001).

The temporal trends of concentrations of ΣPCB7, DDT, and HCH in mussels showed a significant decrease at some coastal stations in the period from 1998 to 2003 (Figure 2.15); however, no trends were observed at the majority of stations. Concentrations of ΣPCB7, DDT, and HCH were only available for fish from the Sound from 1998 to 2003, and here a significant decrease in HCH concentrations were recorded, while a significant increase in ΣPCB7 concentrations were evident.

Table 2.3
Organochlorine concentrations in flounder liver, given as average concentration ± standard error. ww = wet weight

	ΣPCB7	**ΣHCH**	**HCB**	**ΣDDT**	**Extractable lipid**
	(µg/kg ww)	**(µg/kg ww)**	**(µg/kg ww)**	**(µg/kg ww)**	**Content, %**
Copenhagen	118 ± 26.8	1.9 ± 0.3	1.1 ± 0.2	29.0 ± 8.0	10.2 ± 1.6
Vedbæk	52.5 ± 13.3	1.7 ± 0.3	0.9 ± 0.1	21.8 ± 5.3	9.5 ± 1.7
Great Belt	38.8 ± 7.0	1.8 ± 0.2	1.1 ± 0.2	19.9 ± 3.0	11.7 ± 1.3
Wadden Sea	19.0 ± 1.3	0.4 ± 0.0	0.7± 0.1	4.8 ± 0.3	9.6 ± 0.9
North Sea	32.3 ± 3.9	1.0 ± 0.1	1.8 ± 0.3	10.0 ± 1.1	12.0 ± 1.4

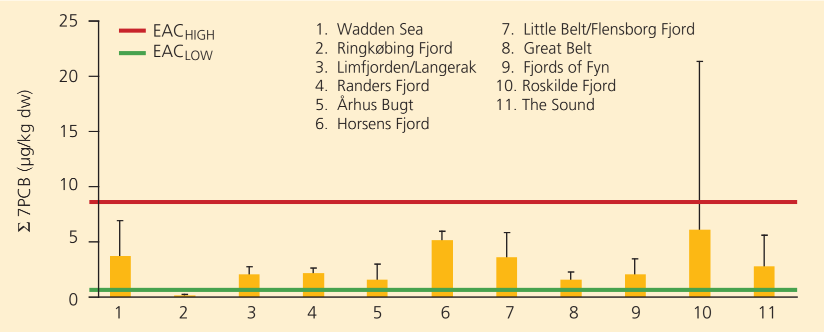


Figure 2.12

Concentrations of the sum of seven PCBs in mussels in the Danish marine environment, shown as average (bar) and maximum (line) concentrations. OSPAR EACs are used for evaluation of the contaminant levels.

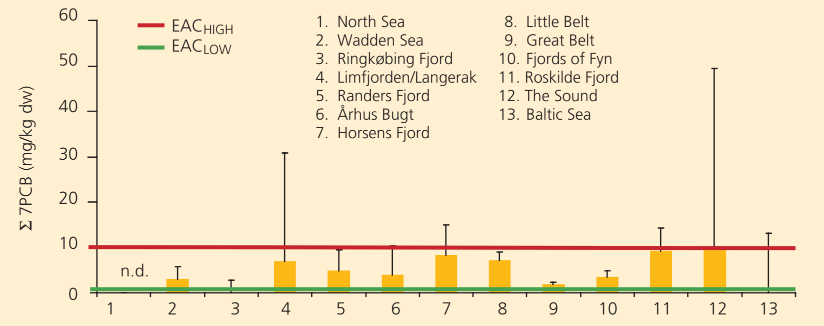


Figure 2.13

Concentrations of the sum of seven PCBs in sediments in the Danish marine environment, shown as average (bar) and maximum (line) concentrations. OSPAR EACs are used for evaluation of the contaminant levels. n.d. = not detected

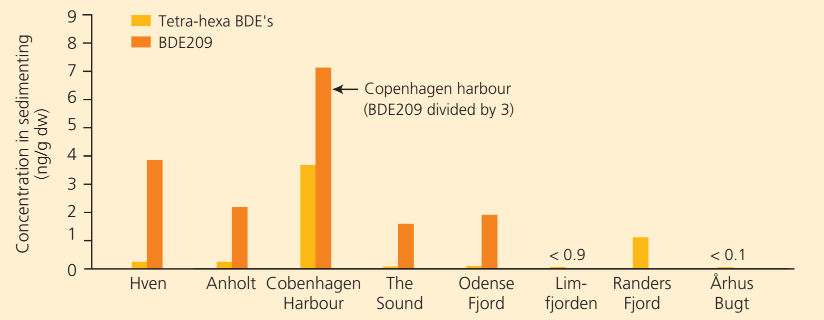


Figure 2.14

Concentrations of brominated flame retardants in Danish marine sediments.

2.5 OTHER ORGANIC SUBSTANCES

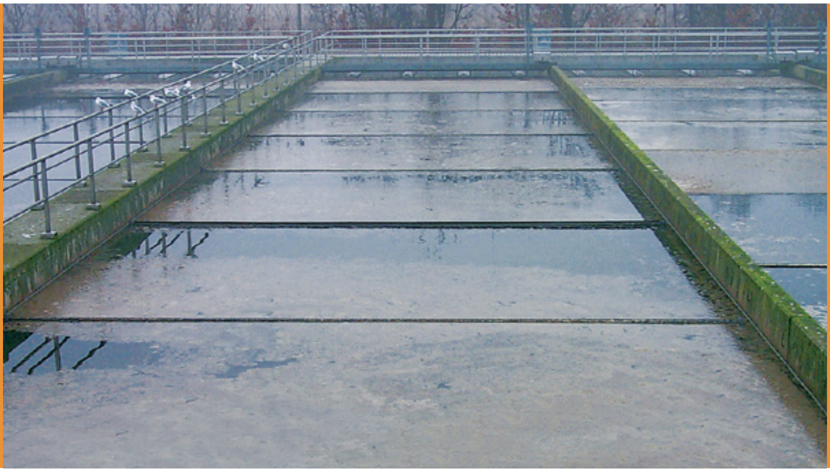


Photo: DMU/Patrik Fauser

Several compounds chosen from the OSPAR List of Chemicals for Priority Action and List of Substances of Possible Concern were screened for during NOVA in order to assess whether they should be included in the new monitoring programme NOVANA. These included additives in detergents (LAS), oestogenic-mimicking compounds such as phthalates and nonylphenolethoxylates found in plastics and industrial detergents, and musk compounds used as fragrances. There will be more focus on these groups in the future, as it has been shown that these compounds are toxic to aquatic species, bioaccumulate, and degrade slowly in natural environments.

2.5.1 LAS

Linear alkylbenzene sulphonates (LAS) are the most extensively used detergents in cleansing agents. LAS compounds consist of an alkyl chain (10–13 carbon atoms) and a sulfonate group attached to a benzene ring. They readily adsorb onto the surfaces of dissolved or solid particles owing to their high lipophilicity and low water solubility. Despite the high separation efficiency in sewage treatment plants, LAS water concentrations from the outlet are in the range of 0.02–0.9 mg/L (Danish EPA, 2002). LAS are only slowly degradable in anoxic environments and high concentrations may be found in the marine environment. In estuaries and near-shore marine waters, LAS have been found in concentrations that affect the normal growth and development of marine organisms. LAS inhibit oxygen uptake in fish, reduce growth, and affect flagella activity in ciliates and mussel larvae (Christensen *et al.*, 1998; Hansen *et al.*, 1997; Kimerle, 1989). Their mode of action is believed to involve interference with ion transport across cell membranes. LAS are now on the Danish Environmental Protection Agency's list of undesirable substances in the group of non-anaerobically degradable substances.

LAS concentrations in coastal marine sediments were up to 22 mg/kg dw (Glob, 1998). The highest concentration was found in a fjord in the vicinity of the discharge outlet for effluents from a municipal wastewater treatment plant.

2.5.2 Oestrogen-mimicking substances

The most severe effects ascribed to oestrogen-mimicking substances such as nonylphenols and phthalates are on human reproductive health, where they are suspected of reduceding sperm quality and inducing testicular cancer in men, and breast cancer in men and women, as well as causing other forms of cancer (Toppari *et al.*, 1995). Although the oestrogen-mimicking effects of nonylphenols and phthalates are weak compared to those of many other substances and to oestrogen itself, the concentrations of these compounds in wastewater are comparatively high. Hence, nonylphenols and phthalates presumably play a significant role in the total oestrogen-mimicking effect of sludge and wastewater, which in turn

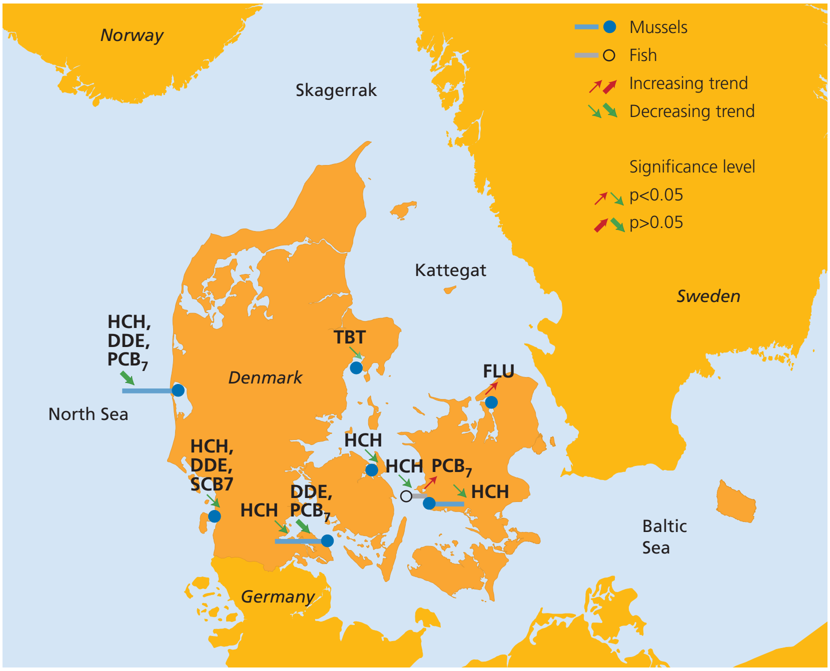


Figure 2.15
Temporal trends of hazardous organic substances in mussels: Fluoranthene (FLU), Lindane (HCH), DDE, ΣPCBs (PCB_7), and TBT.

are the main sources of inputs of these compounds to the marine environment.

PHTHALATES

Phthalates are high-volume synthetic compounds used as plasticizers. The total use of phthalates in Denmark amounted to 9,000–14,000 tonnes per year in 1996. Phthalates enter the marine environment through a variety of routes including effluents from wastewater treatment, industrial effluents, waste disposal, and atmospheric precipitation.

Two phthalate compounds are considered to be the most toxic, namely DEHP (di(2-ethylhexyl)phthalate) and DBP (di-n-butyl phthalate). They are both damaging to reproduction, and DEHP is also carcinogenic. Generally, phthalates have a moderate to high toxicity to aquatic organisms.

DEHP was found in sediments in all areas screened for in 2003 (Figure 2.16). The highest concentrations occurred in coastal waters, but DEHP can also be found in the Skagerrak and the North Sea.

The occurrence, sources, transport, and fate of phthalates in the aquatic environment of a fjord were investigated in a study in Roskilde Fjord (Vikelsøe *et al.*, 2001). DEHP was the most abundant in water samples, with concentrations of 25–211 ng/L. There was no significant spatial variation, but a seasonal pattern was observed, with a maximum in June and a minimum in December. The seasonal variation can mainly be attributed to the higher solubility of phthalates at higher temperatures, and also a larger dissociation from the sediment in the fjord during summer.

High concentrations were found in sediments from the innermost part of the fjord in a decreasing gradient away from a wastewater treatment plant. DEHP and Di-n-DBP were the most abundant phthalates in the fjord sediment. The mean sediment concentration of DEHP in Roskilde Vig was 724 µg/kg dw, but individual concentrations ranged up to nearly 2,000 µg/kg dw.

NONYLPHENOL AND NONYLPHENOLETHOXYLATES (NPEs)

NPEs are high-volume chemicals that have been used for more than 40 years as detergents, emulsifiers, and wetting

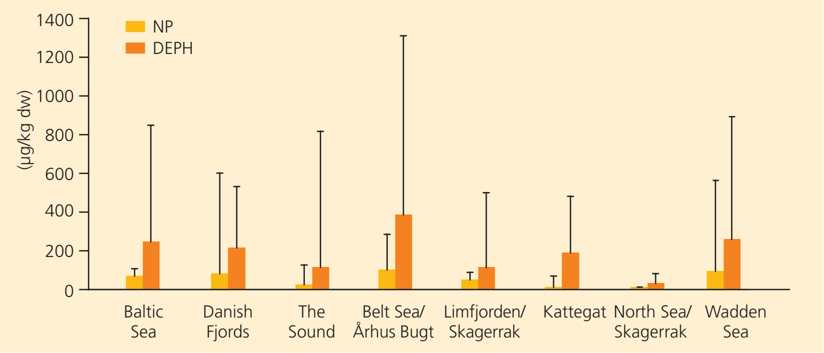


Figure 2.16
Concentrations of the phthalate DEHP and nonylphenol (NP) in Danish marine sediments, shown as median (bar) and maximum (line) concentrations.

and dispersing agents. Nonylphenol and polyethoxylate-containing products are used in textile processing, pulp and paper processing, paints, resins and protective coatings, oil and gas recovery, steel manufacturing, pest control products, and power generation. NPEs are also used in a wide range of consumer products, including cosmetics, cleaning agents, and paints, and in a variety of applications. The annual consumption is approximately 675–1. 200 tonnes/year (Pallesen *et al.*, 1996). The main pathways to the marine environment are through industrial effluents and municipal wastewater treatment plants.

Nonylphenolethoxylates are degraded to nonylphenols, which are severely toxic to aquatic organisms and have hormone-like effects on humans. They induce oedema and abnormal mucus production in fish gills, and osmoregulation, respiration, and ion transport in mussels are affected. Nonylphenols stimulate the synthesis of vitellogenin (Vtg), which is a precursor to yolk protein and is synthesised in the liver of all egg-laying vertebrates. Females primarily produce the protein, but males produce it if they are exposed to oestrogen-mimicking substances. The presence of, for example, vitellogenin in the plasma of male fish, and the development of oocytes in male testes, serve as sensitive biomarkers of effects from oestrogen-mimicking substances.

Nonylphenol was detected in sediments in all samples screened in 2003 (Figure 2.16), with the same geographical distribution as that of DEHP.

Photo: DMU/Britta Munter

Photo: DMU/Britta Munter

In 1998, nonylphenols were found in sediment samples from 66 stations in the Great Belt and the Little Belt at concentrations of 150–33,000 µg/kg dw, with a mean of 1,877 µg/kg dw (Glob, 1998). The highest concentrations were found in the fjords of Vejle, Kolding, Haderslev, and Odense (>3-500 µg/kg dw).

2.5.3 MUSK COMPOUNDS

Musk compounds are widely used as fragrance ingredients in washing and cleaning agents, fabric softeners, air fresheners, shampoos, perfumes and other cosmetic products, and as food additives in fish baits and in cigarettes. Musk compounds are only partly degraded in sewage treatment plants and thus they are introduced into the environment via effluents from sewage plants and sewage sludge. The compounds are stable in the environment and may also biomagnify in the food chain.

According to the Danish Product

Register, the consumption in Denmark is: Galaxolide 333 kg/year, mainly used in cosmetics and cleaning agents; Tonalide 33 kg/year and Traseolide 14 kg/year, both mainly occurring in cleaning agents; Cashmeran and Celestolide about 1 kg/year and Phantolide less than 1 kg/year. Musk xylene, 134 kg/year, and muskketone, 20 kg/year, are mainly used in cosmetics.

Phantolide (AHDI) and Tonalide (AHTN) were detected in the tissues of blue mussels sampled in Denmark in a Nordic screening study (Mogensen *et al.*, 2004). The environmental significance of this finding is difficult to assess, as there is a lack of data for synthetic musk compounds.

2.5.4 PHOSPHATE TRIESTERS

Phosphate triesters are used as plasticizers and additives in a wide range of products such as resins, paint, and metal working oils. They are highly toxic to aquatic organisms; they degrade in aerobic environments, but not under anaerobic conditions. Tributylphosphate has been found in sediments from twelve stations in the Great and Little Belt area, with the highest concentration 220 µg/kg dw in Haderslev Fjord. The mean concentration of the twelve sampling stations was 65 µg/kg dw (Glob, 1998).

2.5.5 PFAS

Perfluorinated alkylated substances (PFAS) are carbon chains covalently bonded with fluorine atoms. PFAS chemicals are used for the surface treatment of textile and leather products, in detergents, in car and floor waxes, in the hydraulic liquids of aeroplanes, and in the electronics industry. They are released into the environment through wastewater, sludge, and landfills.

Originally PFAS were thought to be biologically inert, and in the last 50 years the production and use of PFAS have been increasing. However, during the past ten years it has been discovered that PFAS-related residues are highly toxic and very persistent in the environment. They are believed to interfere with fatty acid metabolism and have been found to have an adverse impact on mammalian liver tissues. The half-life of PFAS compounds in human tissues is estimated to be several years.

A Nordic survey of PFAS compounds was carried out during the year 2003 in Finland, Sweden, Norway, Denmark, Iceland, and the Faroe Islands (Kalleborn *et al.*, 2004). Various types of environmental samples were taken: water samples, sediment samples from lakes and coastal waters, sewage sludge samples, and tissue samples from fish, seals, and whales. Perfluorinated alkylated substances were found in almost all the environmental samples. The most commonly found substances were perfluorooctane sulphonate (PFOS) and perfluorooctanoic acid (PFOA). These compounds are known to have adverse effects on the environment. Concentrations in surface water and coastal water samples were low. In biota, the highest concentrations were found in liver samples from Danish harbour seals (551 µg/kg ww). A larger screening survey of PFOS from both freshwater and coastal marine areas was initiated in 2004 within the NOVANA programme. ■

2.6 ANTI-FOULING COMPOUNDS

Photo: DMU/Britta Munter

Photo: DMU/Ingela Dahllöf

Figure 2.17
Biological fouling on the hull of a boat.

Fouling on ship hulls reduces speed during sailing, thus raising fuel consumption, hampers manoeuvring, and causes corrosion, all with economic and safety consequences (Figure 2.17). To protect the hulls, anti-fouling compounds are added to ship paints such as copper (cuprous oxide), which inhibits the settling of hard fouling organisms, such as barnacles and mussels, along with a booster biocide, which inhibits the settling of soft fouling organisms, e.g., bacteria and algae.

The most toxic and effective booster biocide is tributyltin (TBT). However, in the beginning of the 1980's, after approximately 20 years of use, it was discovered that TBT had a number of unexpected side effects on non-target organisms. In 1991, the use of TBT-containing paints for boats smaller than 25 m was banned in Denmark and other European countries. The use of certain other anti-fouling compounds (Irgarol 1051, Diuron) on ships of less than 25 metres in length has also been banned in Denmark, but TBT is still used in paints for ships larger than 25 metres such as ferries, tankers, and large trawlers (Figure 2.18). However, a convention banning the use of TBT in anti-fouling paints has been signed (see Chapter 4.3.1). Other booster biocides have been introduced to replace TBT; they include Sea-nine 211® and Zinc Omadine®.

2.6.1 SOURCES AND INPUTS

Organotins such as TBT and triphenyltin (TPhT) compounds have been registered as anti-fouling substances, wood preservatives, disinfectants, and as general biocides with a wide range of applications, for example, in cooling systems (Mikkelsen, 1999). Ships, however, have been a major source of input of TBT to inner Danish waters (Figure 2.19). Another source of TBT, which is increasing in importance as the use of TBT is being phased out for ships, is TBT-contaminated harbour sediments that are dredged and then dumped into the sea.

There are restrictions on the concentrations of PAHs and PCBs that such sediments can contain before dumping is allowed, and recently limits have also been introduced for TBT. However, it is difficult to estimate the impact of contaminants in dumped dredged sediments because the sedi-

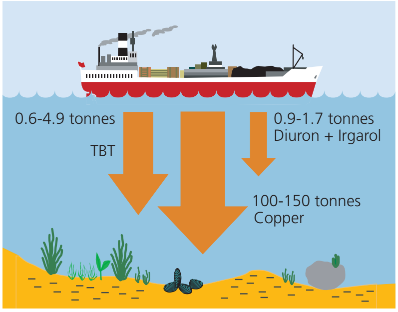


Figure 2.18
Estimated release of anti-fouling substances from commercial shipping in Danish marine waters (Foverskov *et al*, 1999).

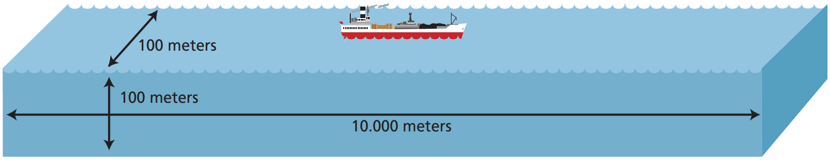


Figure 2.19
Estimate of the volume of water in which the TBT released from one ship during one day's sailing results in a concentration of 1 ng/L, a concentration that can induce imposex in marine snails (Foverskov *et al*, 1999).

ments are dumped in erosion areas and the final sedimentation area is often not known.

2.6.2 TOXICOLOGY

TBT is considered to be the most hazardous of the organotin compounds currently monitored. The first negative effects of TBT were detected in the marine environment as shell deformation and poor recruitment in oysters (Alzieu *et al.*, 1981). It is also known to reduce resistance to infection in flounder, as well as to affect the human immune system. TBT also acts as an endocrine disrupter, leading to disorders such as imposex and intersex in prosobranch gastropods (see Chapter 2.7.1). In addition, it disrupts proton gradients in cells, leading to effects on energy metabolism and thereby effects on growth in algae and bacteria.

Irgarol 1051 is a triazine compound related to the herbicide Atrazine, which inhibits photosynthesis and is therefore especially toxic to algae. It is persistent in the aquatic environment, with low abiotic and biotic degradation. Diuron is a herbicide that also inhibits photosynthesis as well as causes damage to membranes.

2.6.3 STATUS AND TRENDS

In NOVA, TBT and its degradation products dibutyltin (DBT) and monobutyltin (MBT) were monitored annually in mussels, whereas Diuron and Irgarol were screened for in water samples twice during the monitoring period. The occurrence of imposex and intersex as biomarkers for TBT contamination was also investigated on an annual basis (see Chapter 2.7.1).

TBT and its breakdown products DBT and MBT were present in mussels at all monitoring stations in Danish waters, and the concentrations were above the high EAC limit at all stations. The highest concentrations in 2004 were found in Randers Fjord, the fjords of Fyn, in the Sound and the Great Belt area, which are areas with heavy ship traffic and shipyard activities (Figure 2.20). TBT and its breakdown products have also been found throughout the marine foodweb in Denmark, with relatively high concentrations in fish, bivalves, and mammals (Strand & Jacobsen, 2005).

TPhT is rarely found in mussels or sediment, except in some harbours. However, TPhT has been found in some invertebrates, fish, and birds from the Belt Sea area (Strand *et al.*, 2005).

TBT concentrations in sediments were measured in 2003, and high values were generally found in Limfjorden, the Danish fjords, and the Sound (Figure 2.21). Concentrations of TBT in sediments exceeded the EAC limit in all areas. TPhT was detected in Odense and Horsens fjords in 1998, but otherwise was below the detection limit.

A temporal trend analysis for TBT in mussels showed that only in Århus Bugt, out of 14 stations, could a significant decrease in TBT concentration be established.

In 2000, the anti-fouling compounds Diuron and Irgarol 1051 were measured in water samples; the levels were generally low, often with a decreasing gradient from the harbours. However, in close proximity to the source, the concentration of Irgarol 1051 was higher than the recommended water quality criteria suggested by the Danish EPA, which is 0.001 µg/L (Madsen *et al.*, 1998). In 2001, Diuron and Irgarol 1051 were found in all harbour sediments sampled; the highest concentrations of Diuron were found in Marselisborg marina, Vejle harbour, Odense harbour, and Åbenrå harbour. Irgarol 1051 was found in high concentrations in Marselisborg marina, Sønderborg marina, Kolding harbour, and Vejle harbour (Jensen & Gustavson, 2001).

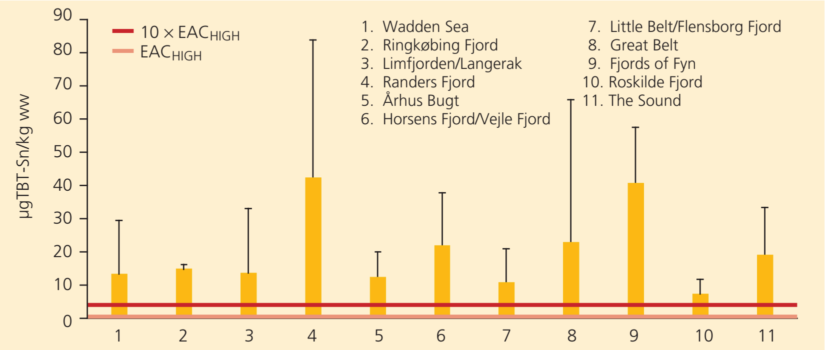


Figure 2.20

Concentrations of TBT in mussels in the Danish marine environment, shown as average (bar) and maximum (line) concentrations. OSPAR EACs are used for evaluation of the contaminant levels.

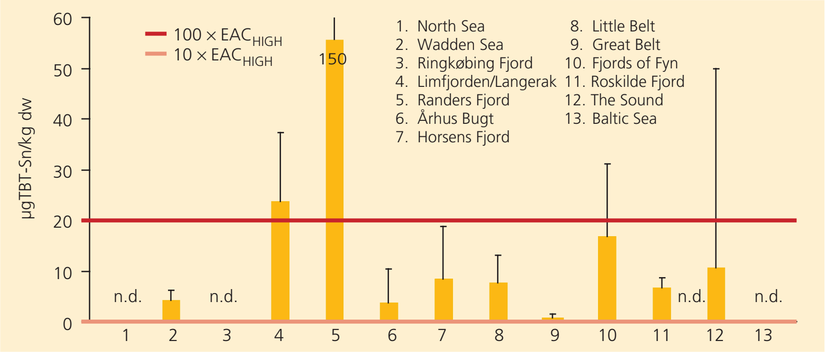


Figure 2.21

Concentrations of TBT in sediments in the Danish marine environment, shown as average (bar) and maximum (line) concentrations. OSPAR EACs are used for evaluation of the contaminant levels. n.d. = not detected.

2.7 BIOLOGICAL EFFECTS OF HAZARDOUS SUBSTANCES


Photo: DMU/Britta Munter

The only assessment of biological effects during NOVA concerned imposex and intersex as biomarkers for contamination by TBT.

2.7.1 IMPOSEX AND INTERSEX

The determination of imposex and intersex in certain marine snails, so-called prosobranch gastropods, was used in NOVA as a specific biomarker for TBT contamination (OSPAR, 2003b; Oehlmann, 2004). Imposex and intersex are terms for morphological changes in females. Imposex refers to the development of male sexual characteristics in addition to the female characteristics, and has been found to occur in more than one hundred species worldwide. Intersex refers to a change of female sexual charactistics to male characteristics and is specific to the periwinkle (*Littorina littorea*). The different stages of imposex are classified using a vas deferens sequence index (VDSI) (Figure 2.22), while intersex is classified according to the intersex stage index (ISI).

Imposex has been observed in nine different species in Danish waters, together with intersex in periwinkles. Generally, the level of imposex is high in the coastal waters, but imposex is also found in open waters in the most sensitive species. Intersex occurs especially near harbours with high concentrations of TBT, where a large number of periwinkles were also found to be sterile owing to advanced intersex (Figure 2.23). A significantly reduced number of penial glands have also

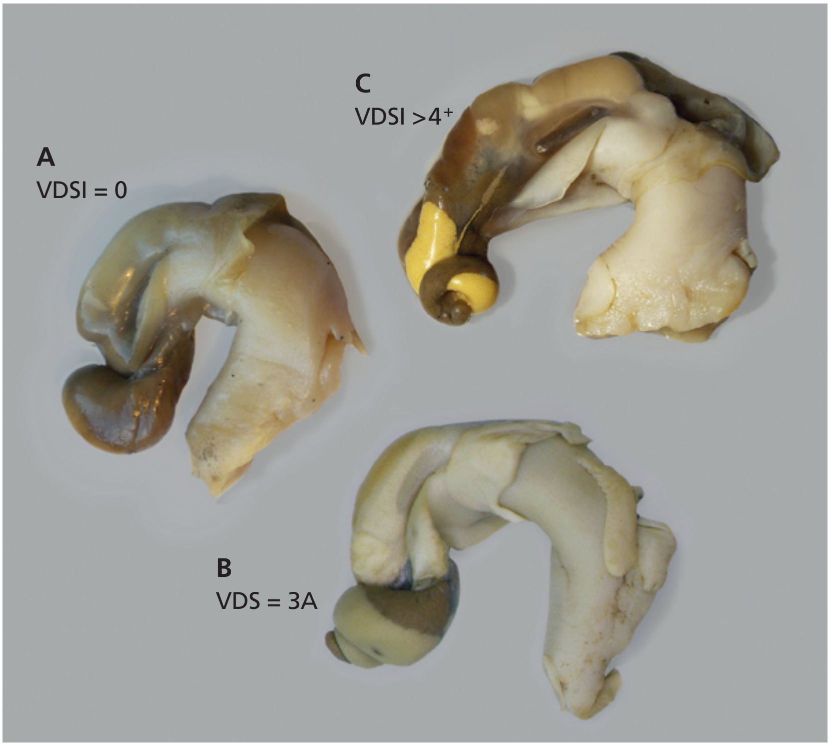


Photo: DMU/Jakob Strand

Figure 2.22
Imposex development in marine snails (*Buccinidae*) from open Danish waters:
A) Normal female without imposex.
B) Female with an enlarged penis and a sequence of a vas deferens.
C) Sterile female, which in addition to a penis and a vas deferens, also has a curled oviduct blocking the passage of oocytes from the ovary to the palliale oviduct.

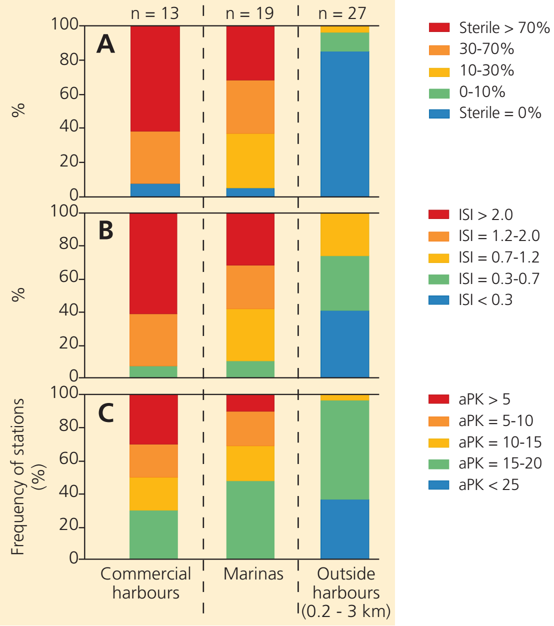


Figure 2.23
The distribution of intersex severity in periwinkles (*Littorina littorea*) measured as:
A) % sterile females.
B) ISI.
C) Average penial glands (aPK) in 13 Danish harbours and 19 marinas compared to 27 stations outside harbours.

been found on male periwinkles in harbour areas.

Other snail species have been used as TBT indicators in NOVA, as these species differ in geographical distribution, as well as in sensitivity towards TBT (Figure 2.24). Imposex was found in 90–100% of individuals of dogwhelk (*Nucella lapillus*) (VDSI = 2.2–4.0) at the West Coast of Denmark. In the open North Sea and in the Skagerrak, 11–79% of red whelk (*Neptunea antiqua*) (VDSI = 0.1–1.4) and 15–31% of common whelk (*Buccinum undatum*) (VDSI = 0.2–0.3) developed imposex. In the inner Danish areas, 99% of red whelk (VDSI = 2.5–4.0) and 2–52% of common whelk (VDSI = 0.02–0.6) developed imposex, with the highest levels found in the Great Belt and the Sound. The netted whelk (*Hinia reticulata*) (VDSI = 0.05–3.9) is the preferred indicator for coastal waters and fjords, where the highest levels of imposex are found close to harbours and in narrow shipping lanes.

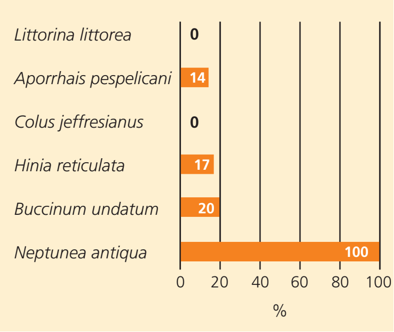
No temporal trends for imposex or intersex could be observed in 22 out of 25 stations between 1998 and 2003. In the Sound, the degree of imposex has decreased significantly at two stations, whereas an increase in the degree of imposex was observed at one station.

2.7.2 NEW BIOMARKERS FOR MONITORING EFFECTS OF HAZARDOUS SUBSTANCES

Two new general biomarkers have been introduced in NOVANA: reproductive success in eelpout (*Zoarces viviparus*) and lysosomal stability of mussel haemolymph (blood). Both biomarkers have been recommended by the International Council for the exploration of the Seas (ICES) and are used in other European monitoring programmes (Neuman *et al.*, 1999; Moore *et al.*, 2004). They were chosen because they do not demand sophisticated instrumentation and can be applied in most areas around Denmark.

The eelpout is a stationary fish, which carries its brood of larvae in the ovary cavity. The eggs begin to mature in late summer, one year before ovulation; after fertilization, the larvae develop in the ovary over a period of 5 to 6 months before their release in winter. Owing to the strong maternallarval relationship, the larvae will reflect the

Figure 2.24
The frequencies of females with imposex or intersex in six species of prosobranch gastropods, all sampled in the same area in the southeastern part of the Kattegat between Kullen and Gilleleje. The differences in imposex frequency indicate the different sensitivities of the species towards TBT.



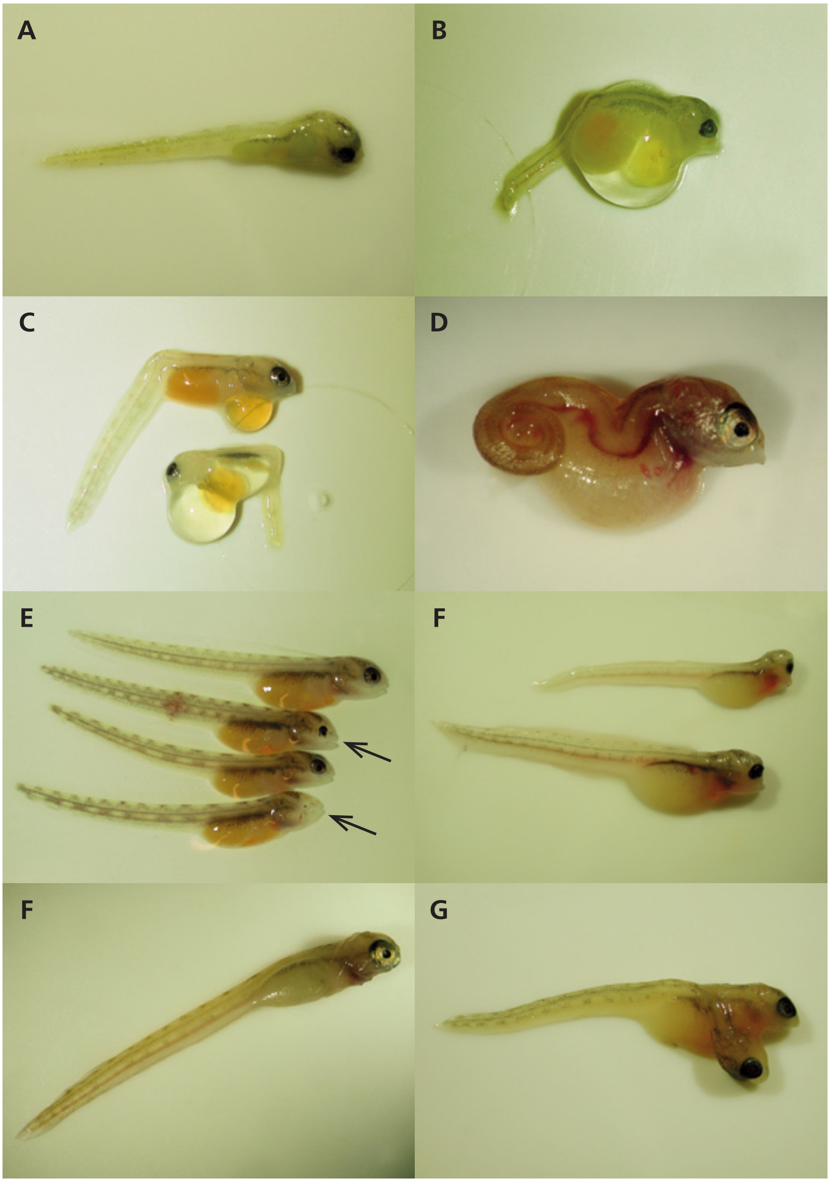


Photo: DMU/Jakob Strand

Figure 2.25
Classification of gross abnormalities observed in eelpout broods: **A**) early dead larvae without characteristic malformations; **B**) yolk sac or intestine defects; **C**) bent shape axial deformations; **D**) spinal axial deformations; **E**) eye defects including rudimentary or missing eye(s); **F**) cranio-facial defects; **G**) Siamese twins, more or less separated; and **H**) others, including calcified larvae from previous year's brood (not shown). Reproduced with kind permission of Springer Science and Business Media.

nutritional and exposure history of the female, thereby also reflecting the state of the environment for the area of habitation. The development of deformities in the larvae is mainly attributed to the impact of contaminants, although early dead larvae and small-sized larvae may be the consequences of other environmental factors, such as oxygen depletion or poor nutritional status (Strand *et al.*, 2004). In areas regarded as reference areas, levels of deformities generally fall between 0–2% of the females having more than 5% deformed larvae. In NOVANA, eight different classes for the classification of deformities are used (Figure 2.25).

A large number of other biomarkers have been developed for the eelpout, and in NOVANA, fecundity, condition index, and liver somatic index of the female are used. As a supplement, it is recommended to measure the activity of detoxification enzymes (EROD activity) (Stagg & McIntosh, 1998), which provides a measure of the possible impact of aromatic organic hazardous substances such as PAHs and PCBs. A

Figure 2.26
EROD activity in male and female (measured as pmol/min*mg protein) eelpout. Fakse Bugt represents a less contaminated area.

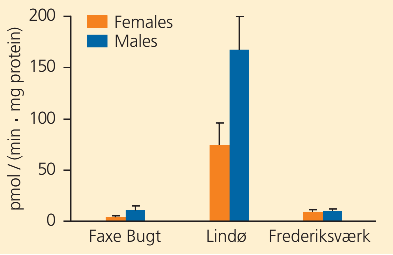


Figure 2.27
Sampling stations for eelpout in the preliminary study in 2001–2002.

pilot study performed in 2002 showed that EROD activity in eelpout was elevated close to Lindø shipyard in Odense fjord, compared to that at other sites (Figure 2.26). Sex differentiation of the larvae can also be used as an indication of hormone-disrupting hazardous substances (Larsson & Förlin, 2002).

Preliminary studies were performed on eelpout from ten sites in Denmark in 2001 and 2002 (Figure 2.27, map). Three of these areas could be classified as less contaminated or reference areas (areas 1, 2 and 9), while in the seven other areas, more than 5% and up to 53% of the females had broods with more than 5% deformed larvae (Figure 2.28). The types of deformities also varied between sites, reflecting the different effects of contaminants (Figure 2.29).

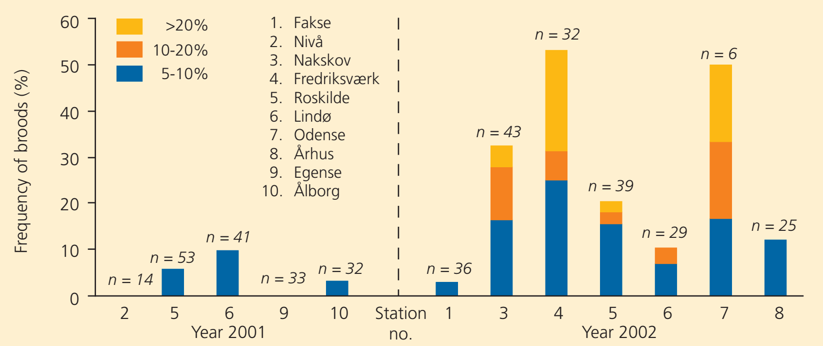


Figure 2.28

Proportion of the broods examined with elevated levels of deformed larvae (types B-G from Figure 2.25) in the ten sampling areas in 2001 and 2002. *n* = number of broods examined at each station (Strand *et al*., 2005).

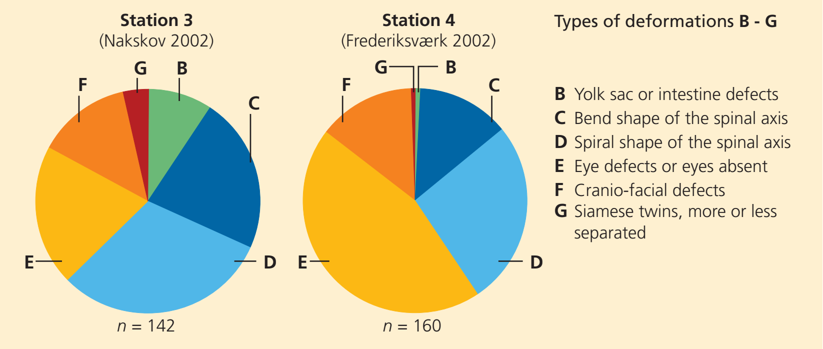


Figure 2.29

Distribution pattern of deformed larvae (types B–G) in broods from two highly affected areas, Stations 3 and 4 in Figure 2.28. *n* = number of broods examined (Strand *et al*., 2004).

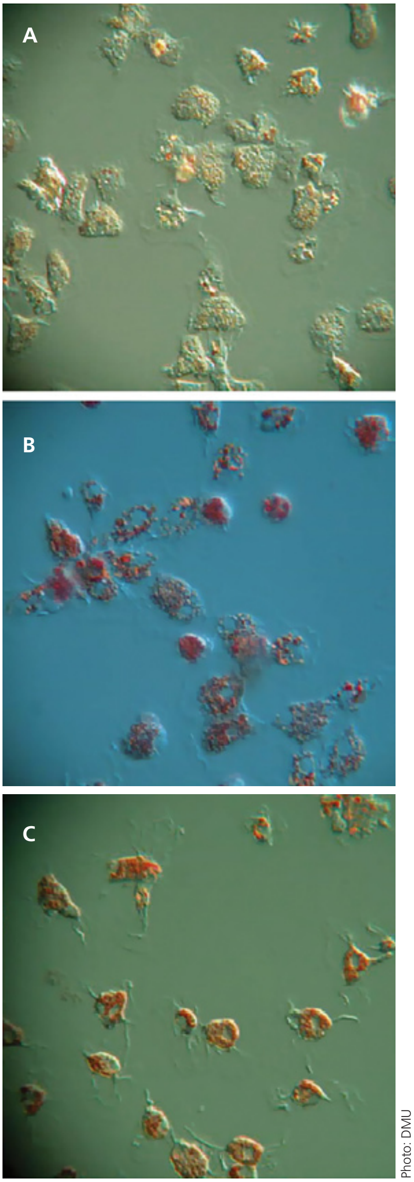


Figure 2.30
Cell death due to lysosomal instability: **A**) normal blood cells, **B**) 50% dead blood cells, and **C**) 100% dead blood cells. Normal blood cells are irregularly shaped and weakly dyed compared to dead blood cells that are more round and strongly dyed.

Photo: DMU/Jens E.N. Larsen

The other general biomarker used in NOVANA is lysosomal stability of mussel haemolymph. Lysosomes are organelles in the cell where organic hazardous substances such as PAHs are metabolized. The metabolized product can interfere with the membrane of the lysosomes, as can other hazardous substances such as heavy metals. If the membranes are compromised, the lysosomes will burst and cause cell death. This phenomenon is used in an assay where haemolymph cells are sampled, the lysosomes dyed, and the time to cell death is measured (Figure 2.30). For healthy mussels, the time to cell death is around 120 minutes, but for affected mussels from contaminated areas it is shorter (Figure 2.31).

Delayed sexual maturation and skewed sex ratios in mussel populations can also be used as biomarkers for hazardous substances, which was shown in a pilot study of these biomarkers in a contaminated area and a reference area in Odense fjord (Ærtebjerg *et al.*, 2005).

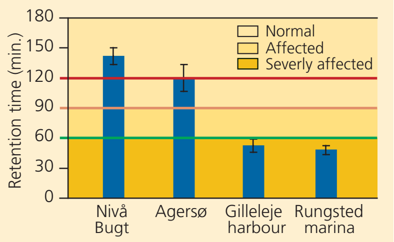


Figure 2.31

Lysosomal stability in the haemolymph of mussels from the Danish marine environment. The green line indicates the lower limit of reference areas and the red line indicates significant differences compared to reference areas.

Photo: DMU/Ingela Dahllöf

Radioactive Substances: Status and Temporal Trends

3

Radioactive substances occur naturally in the environment and originate mainly from the matter of which the solar system and the earth are formed and partly from the interaction of the earth's atmosphere with high-energy cosmic radiation, mainly from the sun. Examples of the first type of naturally occurring radionuclides are isotopes of uranium, thorium, and potassium, with half-lives of the same order of magnitude as the age of the earth, i.e., billions of years. Examples of the second kind of naturally occurring radionuclides are tritium (^{3}H, super-heavy hydrogen) and carbon-14 (^{14}C), with half-lives of 12 years and 5.700 years, respectively.

The long-lived isotopes uranium-235 (^{235}U), uranium-238 (^{238}U), and thorium-232 (^{232}Th) are transformed into series of decay products, which are radioactive and therefore contribute additional radioactive substances to the environment, i.e., radium-226 (^{226}Ra) and polonium-210 (^{210}Po), with half-lives of 1600 years and 140 days, respectively.

Therefore, Danish marine waters contain naturally occurring radioactive substances like all other marine areas in the world. One cubic metre of seawater typically contains 1 Bq ^{3}H, 4 Bq ^{14}C, 40 Bq ^{238}U, 4 Bq ^{226}Ra, 4 Bq ^{210}Po, and 12000 Bq ^{40}K (National Academy of Sciences, 1971).

The development and use of nuclear energy for military and peaceful purposes have resulted in the production of a range of man-made radioactive substances. Atmospheric nuclear explosions distribute all radioactive substances produced to the environment, whereas nuclear explosions underground give rise to small or no releases of radioactivity to the environment. Routine operations of nuclear power plants cause small, controlled releases of radioactivity, while accidents at nuclear power plants may cause considerable releases of radioactivity to the environment. Man-made radionuclides of particular importance for man and the environment are strontium-90 (^{90}Sr) and caesium-137 (^{137}Cs), which are formed by nuclear fission.

Both of these radionuclides have half-lives of about 30 years, which means that once released to the environment, they remain there for many years. Furthermore, ^{90}Sr and ^{137}Cs are incorporated into and transported through food webs because strontium and caesium are chemically similar to calcium and potassium, which are important constituents of all biological systems. Thus, these two radioisotopes may pollute foodstuffs and cause radiation doses to humans. Other man-made radionuclides of importance are plutonium-239 (^{239}Pu) and technetium-99 (^{99}Tc), with half-lives of 24.000 years and 210.000 years, respectively.

There are three main causes for the occurrence of man-made radioactive substances in Danish waters. First, during 1950–1980, the United States and the Soviet Union carried out atmospheric nuclear weapons tests, which peaked in the 1960s and caused radioactive contamination of the entire Northern Hemisphere. This contamination is still significant in both marine and terrestrial environments (UNSCEAR, 2000). Second, the accident at the Chernobyl nuclear power plant in 1986 caused heavy radioactive pollution in the environment close to the power plant and significant fallout over the Baltic Sea. Denmark did not receive serious amounts of radioactive fallout from the Chernobyl accident partly owing to a lack of rainfall when the first radioactive cloud passed over Danish territory. Third, the operation of the two European facilities for reprocessing of spent nuclear fuel, Sellafield in the UK and La Hague in France, have caused releases to the sea of radioactive substances, which have been transported to the North Sea and to some extent further to the Baltic Sea.

Since the 1960s, Risø National Laboratory has carried out studies on environmental radioactivity in Denmark focusing on ^{90}Sr and ^{137}Cs. These studies have considered national obligations according to the Euratom Treaty, by which member states are required to carry out monitoring of radioactivity in air, water, and soil, and to the Helsinki Convention (HELCOM), which covers protection of the environment of the Baltic Sea including from radioactive substances. ■

Photo: DMU/Britta Munter

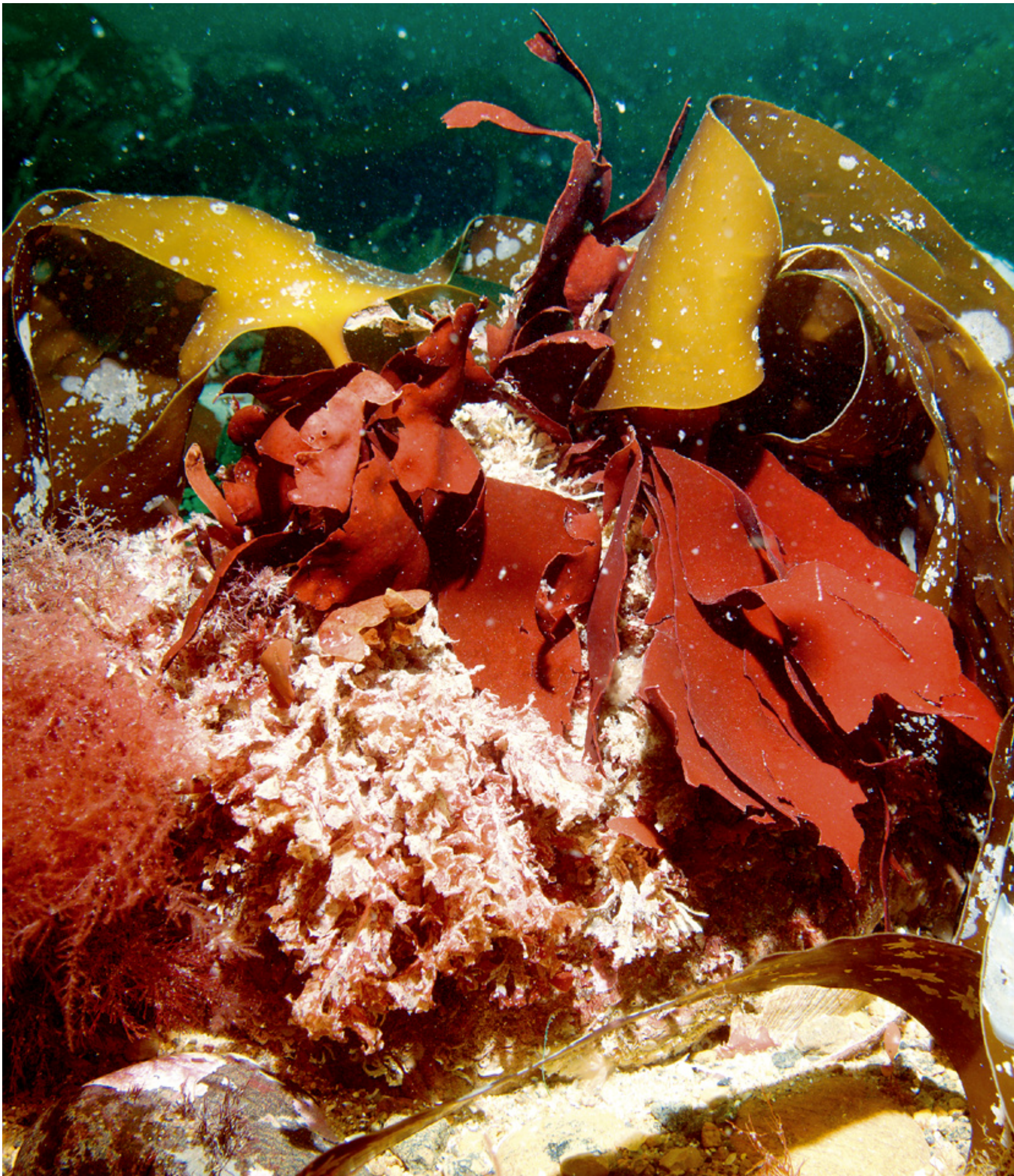


Photo: DMU/Karsten Dahl

3.1

MONITORING OF RADIOACTIVE SUBSTANCES


Photo: DMU/Ingela Dahllöf

Risø's current monitoring programme for the inner Danish waters covers samples of seawater, sediments, and biota (macroalgae and fish). Seawater samples of 50–100 litres are collected twice a year with assistance from the Royal Danish Administration of Navigation and Hydrography. Samples of surface and bottom water are collected from twelve locations around Sjælland, and sediment samples of 1–3 kg are collected from four locations around Sjælland by the National Environmental Research Institute. Samples of macroalgae of 2–4 kg are collected quarterly from Klint near Nykøbing Sjælland and fish samples are collected annually from Bornholm, Hundested, and Hirtshals. The positions for the sampling of seawater are shown in Figure 3.1, which also shows one of the positions for the sampling of sediment.

All the sample types mentioned are pre-treated and processed chemically in order to isolate the radionuclides in question. Different techniques are applied for seawater samples for the initial pre-concentration of the radionuclides. Special chemicals are used to adsorb caesium from the seawater samples. For strontium, chemical procedures are applied in order to isolate strontium from other, in particular naturally occurring, radionuclides in the sample. Sediment and biota samples are freeze-dried, followed by ashing to remove the organic material.

The content of ^{137}Cs in the samples is determined by gamma spectrometry, where the characteristic gamma radiation from this radionuclide is identified and quantified using germanium detectors. Strontium-90 in the samples is determined indirectly by analysing yttrium-90 (^{90}Y), which is a short-lived decay product of ^{90}Sr. The beta radiation from ^{90}Y is measured in Geiger-Müller counters. Corresponding measurement techniques are used for other radionuclides.

Good quality of the analytical results is ensured primarily by careful work through all sample procedures, including sampling, pre-treatment, chemical analysis, radiometric analysis, and calculation of the results. In addition, the analytical procedures used include the use of yield tracers, which makes it possible to determine the chemical yields for each sample and correct the final results correspondingly. Participation in international intercomparisons of laboratory analyses is important to ensure that the analytical quality is acceptable, and therefore Risø frequently takes part in such exercises. Risø's analytical results generally are very satisfactory in these intercomparisons of laboratory analyses, e.g., as described by HELCOM (2003).

STRONTIUM-90

The concentrations of ^{90}Sr in seawater collected around Sjælland since the 1960s vary from about 40 Bq/m^3 in 1965 to 2–10 Bq/m^3 in 2004 (Figure 3.2). The dominant source of ^{90}Sr contamination in Danish waters is fallout from the atmospheric nuclear weapons tests carried out by the United

Figure 3.1
Sampling stations for measurements of radioactivity around Sjælland. The sediment station is denoted Kattegat.

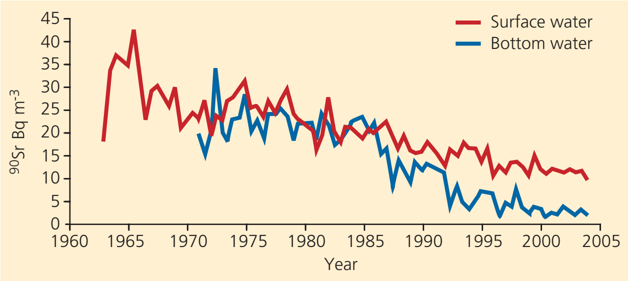


Figure 3.2

Concentrations of Strontium-90 in seawater around Sjælland.

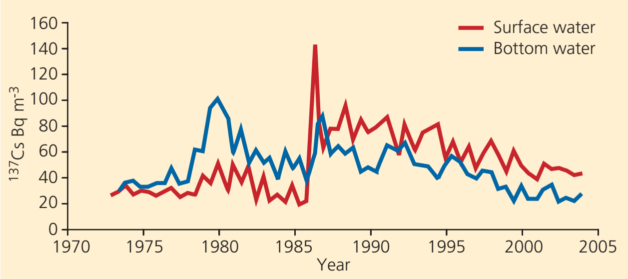


Figure 3.3

Concentrations of Caesium-137 in seawater around Sjælland.

Photo: Simon Ledingham

Sellafield nuclear fuel reprocessing plant, England.

States and the Soviet Union, which peaked in the beginning of the 1960s. This explains the declining trend in the concentrations since 1965. After 1985, the decline of the concentration of ^{90}Sr in surface water is slower than that in bottom water. The bottom water is dominated by saline water from the North Sea, which enters the Baltic Sea, while the surface water is dominated by brackish water flowing from the Baltic Sea to the North Sea. The higher concentrations in surface water are due to runoff of ^{90}Sr from the large catchment areas of the Baltic Sea combined with the slow exchange of water between the Baltic Sea and the North Sea.

Caesium-137

The concentrations of ^{137}Cs in seawater collected around Sjælland since the 1970s show a time course quite different from that of ^{90}Sr (Figure 3.3). In the 1970s, the concentrations of ^{137}Cs were about 30 Bq/m^3 and, as for ^{90}Sr, they were dominated by fallout from the atmospheric nuclear weapons tests. However, in 1979 the concentrations increased to about 100 Bq/m^3 in bottom water and 50 Bq/m^3 in surface water owing to discharges from the reprocessing facility Sellafield in England. These discharges were at their maximum in 1975 and caused a comprehensive pollution of European coastal seas including the inner Danish waters, where the concentrations peaked four years later. After 1975, Sellafield succeeded in reducing the discharges of ^{137}Cs considerably, which was also reflected in the concentrations in Danish waters. In 1986, the Chernobyl accident occurred in a Russian nuclear power plant near Kiev, from which large amounts of radioactive pollution were distributed over Europe, causing considerable pollution of the Baltic Sea, particularly in the Bothnian Sea and the Gulf of Finland. This pollution resulted in an increase in ^{137}Cs concentrations in surface water to about 140 Bq/m^3 and about 90 Bq/m^3 in bottom water. Since 1986, the 137Cs concentrations have decreased, with relatively higher concentrations remaining in surface water than in bottom water because the pollution results mainly from the Baltic Sea.

Following the Chernobyl accident in 1986, Risø started collecting seawater samples from Bornholm; Figure 3.4 shows results from analyses of these samples. In addition to ^{137}Cs, this graph shows results for another radioactive caesium isotope, ^{134}Cs, which also originates from the Chernobyl accident. This isotope has a half-life of 2 years, which is why its concentrations in seawater since 2000 have been reduced to levels below the limit of detection.

The concentrations of ^{137}Cs in cod, herring, and flatfish from Sjælland and Bornholm (Figure 3.5 a-c) reflect the levels of the Chernobyl fall-out, with higher concentrations in fish from Bornholm than in those from Sjælland.

TECHNETIUM-99

The reprocessing facilities Sellafield and La Hague have discharged radionuclides other than ^{137}Cs to the sea. One of these is ^{99}Tc, which like ^{137}Cs remains dissolved in seawater and therefore is transported over large distances. Figure 3.6 shows concentrations of ^{99}Tc in Danish waters during

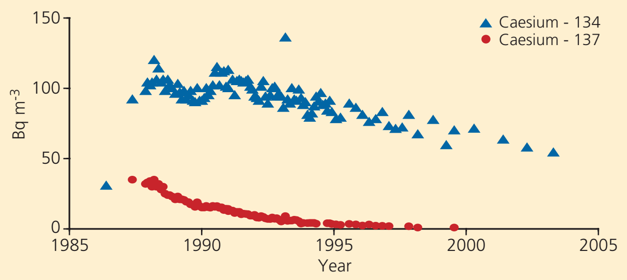


Figure 3.4

Concentrations of Caesium-134 and Caesium-137 in surface seawater collected at Svenskehavn on Bornholm.

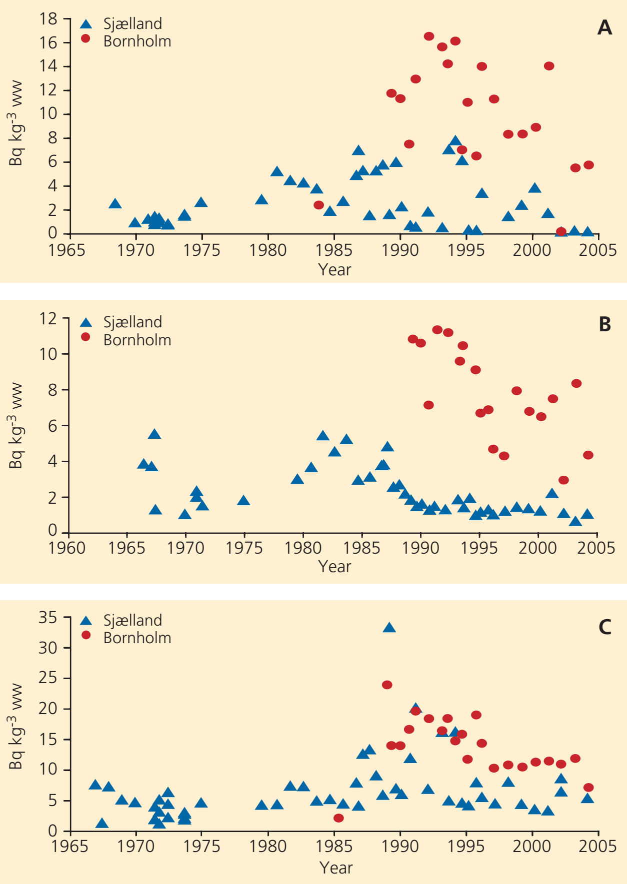


Figure 3.5

Concentrations of Caesium-137 in **A**) cod, **B**) herring, and **C**) flatfish collected at Bornholm and Sjælland.

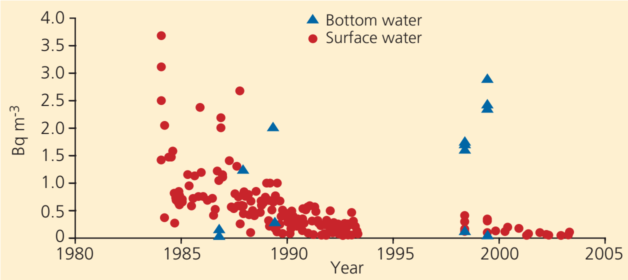


Figure 3.6

Concentrations of Technetium-99 in inner Danish waters.

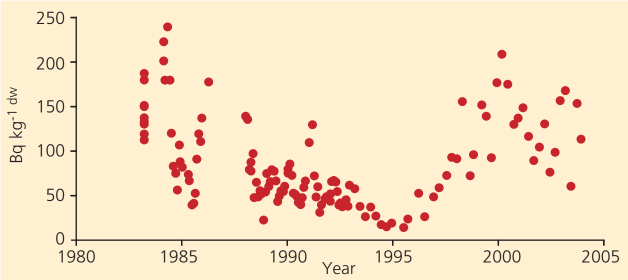


Figure 3.7

Concentrations of Technetium-99 in bladderwrack collected at Klint, North Sjælland.

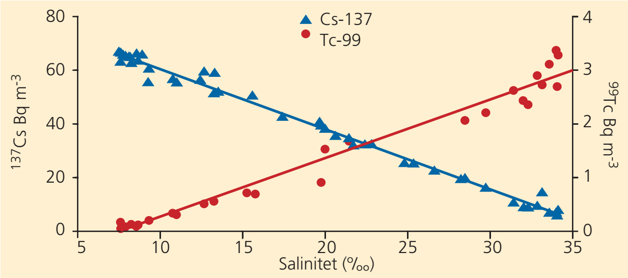


Figure 3.8

Concentrations of Caesium-137 and Technetium-99 in Danish waters in 1999 shown as a function of salinity.

1984–1993 and 1998–2004. During 1981–1990, discharges of ^{99}Tc from La Hague dominated over those from Sellafield and gave rise to concentrations in Danish waters of 2–4 Bq/m^3. From 1994, the discharges of ^{99}Tc from Sellafield increased considerably, which was reflected in Danish waters four years later, when the concentrations increased to 2–3 Bq/m^3. Bladderwrack (*Fucus vesiculosus*) has a preferential uptake of ^{99}Tc, with a concentration factor of 100.000 Bq/kg dry weight per Bq/kg seawater. This is reflected in Figure 3.7, which shows the levels in the macroalgea bladderwrack collected at Klint since 1983. The concentrations of ^{99}Tc vary up to 200–250 Bq/kg dry weight and reflect the discharges from La Hague and Sellafield.

The salinity in Danish marine waters is characterised by geographical location between the North Sea and the Baltic Sea; the salinity varies from 30–35 psu, corresponding to Kattegat bottom water, to 7–10 psu corresponding to surface water at Møn and Gedser. The concentrations of ^{137}Cs and ^{99}Tc collected around Sjælland in 1999 are shown in Figure 3.8 as a function of salinity. It appears that the ^{99}Tc concentrations are positively correlated with salinity, while the ^{137}Cs concentrations are negatively correlated with salinity. The data illustrate that ^{137}Cs originates from Chernobyl fallout over the Baltic Sea and flows with the less saline surface water through the inner Danish waters to the North Sea, while ^{99}Tc originates from Sellafield and follows the saline bottom water inflow from the North Sea into the Baltic Sea.

Photo: DMU/Ingela Dahllöf

3.2 Risk Assessment

Photo: DMU/Britta Munter

Radiation doses to man from man-made radioactivity in Danish waters have been studied in connection with the MARINA-BALT project (EC, 2000). This project included the calculation of radiation doses to individuals having high consumption rates of fish, crustaceans, and shellfish, and their residence in coastal areas. Figure 3.9 shows the annual radiation doses to individuals living near the Kattegat during 1950–2000 according to the source of pollution. The sources are: fallout from the Chernobyl accident, dumping of radioactive waste into the Baltic Sea, routine liquid discharges from nuclear power plants into the Baltic Sea, liquid discharges from the reprocessing facilities Sellafield and La Hague, liquid discharges from nuclear research establishments into the Baltic Sea, and fallout from the atmospheric nuclear weapons tests. The radiation doses arise mainly from the two radionuclides ^{134}Cs and ^{137}Cs. The graph illustrates the time course of the

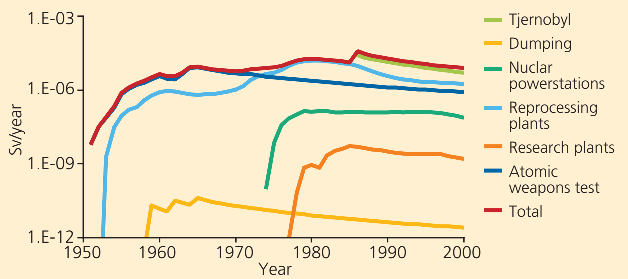


Figure 3.9

Radiation doses during 1950–2000 to individuals near the Kattegat from different sources owing to radioactive contamination of marine waters.

dose rate and the relative significance of the releases from the different sources. The calculated annual dose from 1950 to 2000 varied from 1 µSv to 40 µSv. The largest contribution is from the Chernobyl accident in 1986. The contribution from the Chernobyl accident was 70% of the total radiation dose from man-made radioactivity in the Kattegat in 1986, while in 2000 the contribution dropped to 65%. For comparison, the naturally occurring radionuclides in Danish waters cause annual radiation doses of 700 µSv, mainly from ^{210}Po in marine organisms with a high up-take of this radionuclide (crustaceans and shellfish).

The radiation doses from man-made radioactivity are considerably lower than the annual dose limit of 1.000 µSv for members of the general public, as recommended by the EU (Council Directive 96/29, 1996). ■

Photo: DMU/Karsten Dahl

Photo: DMU/Peter Henriksen

Perspectives on Current Status and the Future of Management

4

The data collected during the NOVA and NOVANA programme from 1998 to 2005 and related activities have provided the basis for the first comprehensive assessment of contaminant levels in the Danish marine environment.

4.1 STATUS AND TRENDS

Photo: DMU/Britta Munter

The status of the Danish marine environment with respect to hazardous substances gives rise to concern. Most of the hazardous substances included in the monitoring programme have been detected in the Danish marine environment (Annex I). However, it should be emphasized that for many hazardous substances the monitoring programme has been limited to a one-time screening, and that adequate sampling for statistical evaluation of temporal trends only exists for a limited number of hazardous substances. It is questionable whether there are areas that can be considered as truly uncontaminated as most substances can be detected over the entire area, although in the open waters in the Kattegat, the Skagerrak, and the North Sea contaminant levels are relatively low. The most impacted areas are fjords and coastal regions close to major point sources and with heavy shipping traffic.

Increased regulation of the use of hazardous substances has resulted in a reduction in the consumption of substances such as polyhalogenated aromatic compounds (PCBs and DDT), mercury, lead, and TBT, but so far only a few declining trends can be detected in the marine environment based on the NOVA data (Table 4.1). However, other studies have shown that the concentrations of PCBs and DDT have declined by about one order of magnitude since the 1980s. Of the 142 possible temporal trends that could be calculated for hazardous substances in mus-

Table 4.1. Number of temporal trends for hazardous substances in mussels calculated from NOVA data that show no significant trend (0), an increasing trend (+), or a decreasing trend (–). The power calculation is based on an average for all stations included.

Substance	0	+	–	Power %	Number of years to achieve 80% power
Cd	12	2	0	15	11
Cu	12	2	0	23	11
Ni	13	0	1	7	14
Pb	11	3	0	15	12
Zn	14	0	0	38	10
Hg	13	1	0	10	13
ΣPCB7	12	0	2	25	10
DDE	12	0	2	7	16
γ-HCH	9	0	5	13	12
TBT	13	0	1	8	13
Fluoranthene	1	1	0	7	15

sels using NOVA data, the majority (122) showed no significant trend over time. Eleven declining trends could be established, all of which were for compounds that have been phased out or are heavily regulated such as HCH, for which five statistically significant declining trends could be established. Nine temporal trends showed significant increases, and this group also included regulated hazardous substances such as the heavy metals cadmium, copper, and mercury. The average statistical power for detecting a 10% change is low, and it is estimated to take between 10 and 16 years to reach sufficient statistical power for all stations included, provided that the trends from now on are monotonic (i.e., all in the same direction, whether up or down), and that sampling is continued on an annual basis. To establish temporal trends using sediments will take even longer, because the sampling frequency has been reduced in the present monitoring programme to once every fifth year. After the conclusion of the new monitoring programme NOVANA in 2009, better statistical power should have been achieved for hazardous substances in mussels.

Our knowledge of the spatial distribution and temporal trends for newer hazardous substances such as brominated flame retardants is poor, and will be for many years ahead, as there is a time lag between the identification of hazardous substances and their inclusion in a screening or monitoring programme. The introduction of general biological effects biomarkers into the new monitoring programme is one way to attempt to include an assessment of environmental risks of substances that have not been subject to chemical analysis, as well as to provide a measure of the integrated contamination level. However, these general biomarkers do not provide information concerning which particular hazardous substance or combination of substances that are responsible for the response detected.

4.2 THE ECOSYSTEM APPROACH TO MANAGEMENT

Photo: DMU/Britta Munter

The European Commission has in 2005, due to increasing concerns for the environmental state of European oceans and seas, issued its Thematic Strategy for the protection and conservation of the marine environment, in an attempt to create an overall, integrated policy. The EU Marine Strategy Framework Directive was adopted in 2008, which is intended to be the legal instrument aimed at implementing the Thematic Strategy proposed. The Marine Strategy has the following aim:

"The Marine Strategy is aimed at protecting Europe's seas and oceans and ensuring that human activities in these seas and oceans are carried out in a sustainable manner so that we and future generations can enjoy and benefit from biologically diverse and dynamic oceans and seas that are safe, clean, healthy and productive."

A central theme in the Marine Strategy is to develop and apply an "Ecosystem Approach" (EC 2005), defined as: "the comprehensive integrated management of human activities based on best available scientific knowledge about the ecosystem and its dynamics, in order to identify and take action on influences which are critical to the health of the marine ecosystems, thereby achieving sustainable use of ecosystem goods and services and maintenance of ecosystem integrity."

With respect to hazardous substances, the following goals are included in the Marine Strategy Directive:

- To phase out pollution in the marine environment so as to ensure that there are no significant impacts or risks to human and/or ecosystem health and/or on uses of the sea.
- To progressively reduce discharges, emissions, and losses of substances hazardous to the marine environment with the ultimate aim to reach concentrations of such substances in the marine environment near background values for naturally occurring substances and close to zero for manmade synthetic substances.
- To prevent pollution from ionizing radiation through progressive and substantial reductions of discharges, emissions, and losses of radioactive substances, with the ultimate aim to reach concentrations in the marine environment near background values for naturally occurring radioactive substances and close to zero for artificial radioactive substances. ■

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4.3 THE FUTURE

Photo: DMU/Ingela Dahllöf

The near future will bring into force current EU and Danish policies with regard to hazardous substances and other stressors on the marine environment, under which the implementation of the Water Framework Directive, the Natura 2000 Directives and the Marine Strategy is central. The WFD operates with threshold concentrations for hazardous substances, so-called Environmental Quality Standards (EQS). EU adopted EQS-values for 41 hazardous substances in 2006 (EU 2006), which all relate to concentrations in water as EQS for sediment and biota are still tentative due to lack of sufficient background data. However, concentration levels in biota are included if it is judged that the contaminants present a risk to top predators or humans owing to secondary poisoning from the intake of food from aquatic sources.

These threshold levels are based on extrapolations of Predicted No-Effect Concentrations (PNEC), according to the Technical Guidance Document that supports the Commission Directive on risk assessment (EU 1996). This is a similar approach to the derivation of OSPAR EAC limits (OSPAR, 1998; Lepper, 2002) (see Chapter 1.3.1), or by using Species Sensitivity Distributions (SSD). The EQS includes an application or an uncertainty factor between 10 and 1,000 as a precaution when using the NOEC values determined in the hazard identification. The size of the application factor used depends on the confidence with which the PNEC can be derived from the data available, that is, it depends on the quantity and quality of the data and on the number of trophic levels, taxonomic groups, and life styles representing various feeding strategies for which data are available. The uncertainty in the extrapolation from laboratory toxicity tests on a limited number of species to the "real" environment is thereby considered to have been addressed, by which the most sensitive species should also be protected, which implies that below the EQS, adverse effects are unlikely to occur in the marine environment.

As the EQS for a substance is expressed as an annual average, a so-called Maximum Admissible Concentration Quality Standard (MAC-QS) is also used in the WFD. MAC-QS relates to "short-term transient exposure", with the intention that it should not be exceeded at any time. A MAC-QS is derived on the basis of the lowest acute toxicity test available. Below the MAC-QS, adverse effects due to short-term exposure are predicted to be unlikely to occur in the marine ecosystem.

Furthermore, the Water Framework Directive includes measures for many hazardous substances in order to bring about a cessation of emissions, discharges, and losses within 20 years after the substances are included in the directive.

In the quality objectives within the WFD, both the chemical and biological status of the environment should be assessed using both physico-chemical and biological quality elements. The definitions of the physico-chemical and biological quality elements in the

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High status	Good Status	Moderate status
Concentrations close to zero and at least below the limits of detection of the most advanced analytical techniques in general use.	Concentrations not in axcess of the standards set in accordance with the procedure in the Technical Guidance Document (TGD) for WFD, e.g. concentrations below EQS.	Conditions consistent with the achievement of the values specified for the biological quality elements

Table 4.2

Physico-chemical quality elements for specific synthetic pollutants. Definitions from WFD annex V to the directive 2000/60/EC.

High status	Good status	Moderate status	Poor status	Bad status
The level of diversity and abundance of invertebrate taxa is within the range normally associated with undisturbed conditions. All the disturbance-sensitive taxa associated with undisturbed conditions are present.	The level of diversity and abundance of invertebrate taxa is slightly outside the range associated with the type-specific conditions. Most of the sensitive taxa of the type-specific communities are present.	The level of diversity and abundance of invertebrate taxa is moderately outside the range associated with type-specific conditions. Taxa indicative of pollution are present. Many of the sensitive taxa of the type-specific communities are absent.	The relevant biological communities deviate substantially from those normally associated with undisturbed conditions.	Large portions of the relevant biological communities normally associated with undisturbed conditions are absent.

Table 4.3

Biological quality elements for benthic invertebrate fauna as an example of a relevant biological community. Definitions from WFD annex V to the directive 2000/60/EC.

WFD are provided in Table 4.2 and Table 4.3, respectively. The assessment shall identify whether the chemical and biological status is high, good, moderate, poor, or bad as the worst case. The WFD physico-chemical and biological quality standards are intended to protect the structure and function of ecosystems in transitional, coastal, and territorial marine waters (and freshwaters) from any significant alterations by the impact of hazardous substances. According to current scientific knowledge, the objective of maintaining ecosystem function can best be achieved by protecting the community structure, for example, species diversity, abundance, and seasonal dynamics. Thus, not only toxic or adverse effects on growth or reproduction should be considered when assessing possible impacts on community structure by a hazardous substance, but also all relevant effects on the population dynamics and abundance of species. For example, effects on behaviour or avoidance of the habitat should also be accounted for. It is generally accepted that community structure is preserved by protecting the most sensitive species known and by accounting for additional uncertainties due to limitations in the data available (Lepper, 2002).

Using EQS in the ecotoxicological risk assessment of priority substances means that significant alterations owing to the impact of hazardous substances are not tolerated on a population level, as the whole ecosystem should be protected; the underlying reason for this is probably that the nature of this problem is considered to be less reversible. If persistent contaminants appear in the environment, they will often remain there for decades and thereby pose a continuous threat. Therefore, the acceptance of "a slight impact on diversity and abundance", as defined in the biological quality elements to achieve "good status", will not be suitable for use in assessing the impact of hazardous substances, because by the time hazardous substances have caused effects on populations, the changes can be considered to be almost irreversible. The definition of "good status" in the following assessment will therefore be based on the ecotoxicologically derived chemical quality criteria (Table 4.4) and considered to be achieved if the concentration in the environment does not exceed the EQS derived in the WFD (Lepper, 2002).

As described earlier (Chapter 1.3.1), both the Swedish and the Norwegian national five-class schemes of environmental assessment criteria for hazardous substances are based on the amount of deviation from background levels, with the focus on concentration levels in sediment and biota. The same applies for the OSPAR Ecotoxicological Assessment Criteria (EACs) that are derived from ecotoxicological threshold levels, which have been extrapolated from exposure levels in seawater to corresponding levels in sediment and biota. The intention was that the contaminant data for biota could additionally be used to assess the exposure level in situations where organisms at the lower trophic levels in the pelagic or benthic communities may be at risk. This was a first step to attempt to include the environmental risks of contaminant-induced effects on the marine ecosystem in the assessments of measured contaminant levels.

It was suggested at a recent OSPAR workshop that the quality standards EQS and MAC-QS in the WFD should also be converted to corresponding accumulation levels in biota (OSPAR, 2004), as is the case for the EACs. One major argument for this conversion is that most contaminant data from the marine monitoring programmes in the Baltic Sea and the North Atlantic consist of chemical analyses of concentration levels in sediment and biota samples. An extrapolation from assessment criteria for seawater to assessment criteria for sediment and biota is therefore necessary if this general strategy for the monitoring of contaminants is to be comparable for example between OSPAR and the Water Framework Directive. If this is not done, it could result in the cessation of existing time series of measurements, which first in recent years have reached a length, and thereby a statistical power, for temporal trends to be assessed. An additional practical consideration is that it takes a much larger sampling regime to evaluate contaminant levels using water samples, with short-term variations in concentrations, compared to the sampling of biota and sediments, which integrate concentrations over longer periods. Another important consideration is that lipophilic contaminants, comprising most of the organohalogens, do not associate with water, so their concentrations in water are very low, thus presenting serious analytical problems and often requiring more expensive equipment for their determination in water.

Based on the discussion above, the following basic principles (see Table 4.4) are suggested for deriving a five-class scheme for environmental assessment criteria for synthetic priority substances, which takes into account the objectives for both the chemical and the biological quality elements within the WFD and within OSPAR. The status Classes I and II refer to the high and good chemical quality standards defined in the WFD, that is, near-zero concentration and below the EQS, respectively. In this approach, as an exercise, three additional status classes, Classes III, IV, and V, have also been integrated, so that the assessment criteria derived can be compared with the five-class scheme of assessment criteria that has been used in Sweden and Norway. These status classes correspond to concentration levels lower than and above the LC_{50}-value from which the MAC-QS-value was derived. However, it must be emphasized that all thresholds in this scheme refer to mean concentrations, which may cause acute effects in short-term episodic events, and not to exposure level. Addressing acute effects by mean concentrations, as in status Classes III and IV, may therefore not be completely consistent, but the definition of the status classes should rather be seen as a potential tool that may be useful in the interpretation of monitoring data and the development of monitoring strategies. Full definitions of the five status classes are given in Table 4.4.

This five-class approach has been applied in a study of TBT contamination in the Skagerrak and Kattegat (Strand *et al*., 2006). In this study, an extensive set of Nordic data on TBT concentrations in seawater, mussels, and sediment, together with data on the effects of TBT (i.e. imposex and intersex) in five species of marine snails, were combined into an integrated assessment of the environmental conditions. The analyses showed that the open waters of the Skagerrak can generally be classified as Class II or III, while coastal waters are generally classified as Class III or IV and har-

Status Class I:	**High status.** Concentration of priority substance is close to zero and at least below the limits of detection of the most advanced analytical techniques in general use. An assessment of the achievement of the objective also requires that no biological effects can be detected at the individual nor at the population level that can be related specifically to exposure to the priority substance. For example, the response must not be significantly different from the natural background level.
Status Class II:	**Good status.** Concentration of priority substance is not in excess of the chemical quality standards, e.g., it is below the ecological quality standard ($< EQS = < PNEC$). Adverse effects in the most sensitive species caused by long-term exposure to the priority substance are predicted to be unlikely to occur.
Status Class III:	**Moderate status.** Concentration of priority substance is not in excess of the so-called maximum admissible concentration quality standard ($< MAC\text{-}QS = < 1/10 * LC_{50}$). Risk of adverse effects in the most sensitive species caused by long-term exposure to the priority substance. However, adverse effects in the most sensitive species caused by short-term exposure are predicted to be unlikely to occur in the marine ecosystem.
Status Class IV:	**Poor status.** Concentration of priority substance is not in excess of the LC_{50}-value derived for the most sensitive species ($< LC_{50}$). Substantial deviations of relevant biological communities can occur due to adverse effects caused by long-term exposure to the priority substance in both the more and the less sensitive species. In addition, there is a risk of adverse effects caused by short-term exposure in the most sensitive species.
Status Class V:	**Bad status.** Concentration of priority substance is in excess of LC_{50}-value derived for the most sensitive species ($> LC_{50}$). Severe alterations of relevant biological communities occur due to adverse effects in the more and the less sensitive species caused by long-term exposure to the priority substance. Risk of adverse effects caused by short-term exposure in both the more and the less sensitive species.

Table 4.4

Suggested basic principles for the derivation a five-class scheme of environmental assessment criteria for synthetic priority substances.

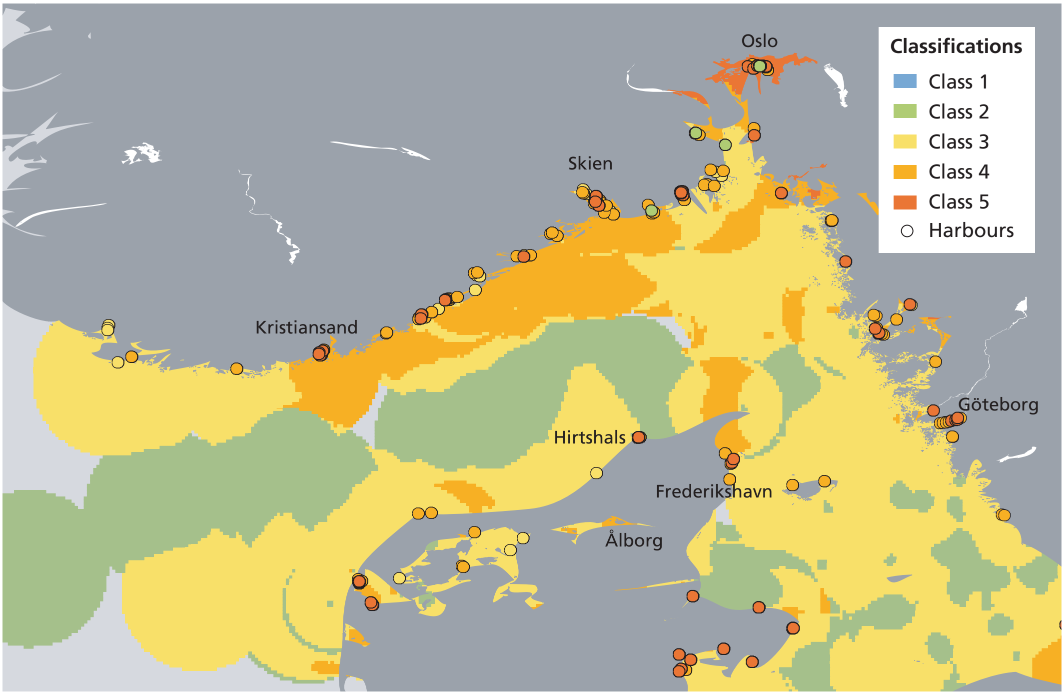

Figure 4.1
Classification of TBT contamination in the Skagerrak and the Kattegat based on nordic data for TBT in sediment and molluscs as well as imposex/intersex levels in marine gastropods. The small coloured circles indicate harbour areas, which are not included in the GIS-based classification of the general TBT levels in the coastal and open waters.

bours as Class IV or V (Figure 4.1) Consequently, TBT seems to pose a significant risk to marine organisms in this region. There is a risk of chronic effects in most coastal waters, and there is even a risk for more severe effects in shallow fjords and in the proximity of harbours. The TBT level does not seem to pose a risk in most parts of the open waters of the Skagerrak; however, in the open waters of the Kattegat, there may still be a risk of chronic effects.

A further complication is the need for synchronization with the Habitats Directive that aims to protect biodiversity. The Habitats Directive provides for the creation of a network of special areas of conservation called Natura 2000, to "maintain and restore, at favourable conservation status, natural habitats and species of wild fauna and flora of Community interest". One of the indicators suggested for ensuring that marine areas are at a favourable conservation status is the presence of hazardous substances (Dahl et al., 2004), where both their concentrations in sediments and biota, as well as biomarkers, can be integrated into the assessment.

Finally, it should be pointed out that the criteria in the Water Framework Directive have been set for individual hazardous substances. This implies that one area can be deemed as having a wide range of different environmental statuses based on the assessments of individual substances; as yet, no recommendations have been agreed concerning how to weigh and/or aggregate the various assessments of individual hazardous substances.

■

Photo: DMU/Ingela Dahllöf

CONCLUSIONS

5

Many activities aimed at reducing contamination of the seas have been initiated and implemented since the 1970s. They have led to a drastic reduction of deliberate contamination, such as a ban on the dumping of chemical waste into the sea and reductions in contaminant discharges from point sources. Past and present initiatives, including monitoring activities, have also raised awareness of marine pollution by hazardous substances, in manifestations and policies such as the recent EU Marine Strategy Framework Directive.

It has so far been difficult to detect the impact of these reductions directly in the marine environment, although there have been positive reductions in some of the older hazardous substances. Many hazardous and radioactive substances can be found in the Danish Marine environment today. The most impacted areas are fjords and coastal areas, close to point sources, whereas the more open waters are less contaminated. Using the Norwegian and OSPAR classification systems for assessing the status of the environment, and the temporal trend analysis the following conclusions can be drawn.

HEAVY METALS

- For mercury and cadmium there are areas, based on concentrations in mussels, that are classified as moderately contaminated (SFT class II), whereas for lead all areas belong in SFT class I. For copper no area can be classified as SFT class I, and many areas can also be classified as moderate (SFT class II) to markedly contaminated (SFT class III).
- Heavy metals in sediments show that for cadmium, lead and copper there are no areas that are under the lowest EAC limits and in some cases like The Sound, the Belt Sea and some of the fjords also the higher EAC limits are exceeded indicating that effects on the ecosystem are likely. For mercury the lower EAC limit is exceeded in some areas like The Sound, The Wadden Sea and the Belt Sea, whereas there are no areas where the higher EAC limit is exceeded.
- The temporal trends show that in most cases, changes in heavy metal concentrations cannot be established. There are increasing trends at some stations for cadmium, copper, lead and mercury, whereas it is only for nickel at one station where there is a significant decrease.

POLYAROMATIC HYDROCARBONS

- Concentrations in mussels show that most areas are under the lower EAC-level for individual PAHs, but as the sum of 16 PAHs most areas can be classified as moderately contaminated (SFT Class II). The data for temporal trends of PAHs is so far very limited.
- For sediments the lower EAC limit is also exceeded at most stations, and in some cases the higher EAC limit.

ORGANOHALOGEN COMPOUNDS

- The sum of seven PCBs in mussels exceed the lower EAC limit in most areas, and in some cases also the higher EAC limit. For DDT and it breakdown products DDE and DDE, all areas are below the lower EAC limit. The HCH-congeners are still found at some station at levels which can be classed as moderately polluted (SFT class II), but the majority of areas belong to SFT class I.
- The largest number of significantly decreasing temporal trends is found for organohalogen compounds, with no increasing trends detected.

TRIBUTYLTIN (TBT)

- All areas in the Danish marine environment are heavily affected by TBT, in many cases at levels ten times above the highest EAC limit for mussels and sediments, and even above 100 times the level of the high EAC limit for sediments.
- Decreasing temporal trends for TBT has been found at one station, but mainly no trends can be established.

BIOLOGICAL EFFECTS

- The high concentrations of TBT have induced imposex and intersex in marine snails throughout the Danish waters.
- New biomarkers show that other effects than imposex and intersex

on the marine environment are present, although the link between which substance, or which combination of substances, that cause these effects is difficult to establish.

Furthermore, contamination by newer substances is difficult to assess, as is the overall contribution of hazardous substances to the present state of the environment. The introduction of hazardous substances into the monitoring programme NOVA in Denmark constituted the beginning of the assessment of the status and trends in Danish waters. However, it should be kept in mind that monitoring and the assessment of status and trends comprise an on-going, iterative process closely linked to research. Better understanding of causality between exposure and effects on populations, communities and ecosystems, risk assessments of new substances, and new analytical methods will continuously necessitate making changes in assessment criteria and the priorities for monitoring.

The new monitoring programme NOVANA will, in the years to come, further strengthen the assessment ability. However, based on the data available today, it will be post-NOVANA before clear conclusions can be made regarding the impacts of past and present initiatives to reduce contaminant levels in the sea.

Photo: DMU/Britta Munter

Foto: DMU/Britta Munter

GLOSSARY AND ABBREVIATIONS

The glossary and list of abbreviations is based on (1) the NERI glossary, (2) the EEA multilingual environmental glossary available at http://glossary.eea.eu.int/EEAGlossary.

Accumulation bottoms – A sub–surface area where settling particles are accumulated. Usually biologically very active sites.
Acute toxic effects – Effects that occur within a short period of exposure in relation to the organism's life span. See also chronic toxic effects.
Al – Aluminium, an element.
BAT – Best Available Technology.
Benthic – Living on the bottom under a body of water. See also pelagic.
BEP – Best Environmental Practice.
Biodegradation – The natural process whereby microbes degrade (consume) a substance, e.g., oil.
Biological effects monitoring – Specific monitoring of biological effects likely to be caused by hazardous substances.
Biota – All living organisms of an area; the flora and fauna considered as a unit.
Bq – Becquerel, a unit used for radioactivity.
BRC – Background reference concentration.
Bunker oil – Heavy oil, used as boat and tanker fuel.
By-product – A product or service deriving from a manufacturing process that is not the primary product or service being produced.
Carbon (C) – An element.
CAS – Chemical Abstract Services, provides an identification system for chemical substances, where each substance is given a CAS number.
Cd – Cadmium, an element classified as a heavy metal.
Chronic toxic effects – Effects that occur during a relatively long period, usually over more than 10 % of the life span of the organism. See also acute toxic effects.
Congener – A chemical term for many variants or configurations of a common chemical structure.
Crude oil – The primary state of oil. Crude oil has not yet been refined into different petroleum products.
Cu – Copper, an element classified as a heavy metal.
Density – The mass (weight) of a unit volume of a substance. Water, for instance, has a density of (approximately) 1 kg/L.

Dispersion – Fine droplets of oil are transferred into the water. Usually occurs when the surface oil slick is disrupted by breaking waves. The opposite of emulsification.

Distillation fractions – The different (usually commercially interesting) petroleum fractions in a heavy oil. At atmospheric pressure, gasoline is distillable at around 10°C, jet fuel at 200°C, and diesel at 300°C.

DSD – Dangerous Substance Directive.

EAC – Environmental Assessment Criteria

EcoQO – Ecological Quality Objective.

Emulsification – The process of water becoming mixed with oil, in severe cases creating a very viscous "mousse". The opposite of dispersion.

EQS – Ecological Quality Standard.

Hazardous substances – Substances or groups of substances that are toxic, persistent, and liable to bioaccumulate, and other substances or groups of substances which give rise to an equivalent level of concern.

HCH – Hexachlorocyclohexane (Lindane).

HELCOM – See Helsinki Convention.

Helsinki Convention – The Convention on the Protection of the Marine Environment of the Baltic Sea Area, 1992 (entered into force on 17 January 2000), also called the Helsinki Convention, which is administered by the Helsinki Commission (HELCOM).

Hg – Mercury, an element classed as a heavy metal.

ICES – The International Council for the Exploration of the Sea (ICES) is the oldest intergovernmental organisation in the world concerned with marine and fisheries science. The council was first established in Copenhagen in 1902, but now operates under the terms of the 1964 Convention for the International Council for the Exploration of the Sea. Since its establishment in 1902, ICES has been a leading scientific forum for the exchange of information and ideas on the sea and its living resources, and for the promotion and coordination of marine research by scientists within its member countries. The area of competence of the council is, broadly speaking, the Atlantic Ocean and its adjacent seas, with an emphasis on the North Atlantic. There is no precise delimitation of this area.

IMO – International Maritime Organisation, a UN organisation concerned with shipping and pollution from shipping.

Imposex – A pseudo–hermaphroditic condition in female gastropods (snails) caused by TBT and manifested by the development of a false penis.

Inorganic – Substances or elements not containing carbon.

Interfacial tension – An intermolecular force between two surfaces. For example, the interfacial tension governs the shape of a liquid droplet (how spherical it is).

Intersex – Change of female sexual characteristics to those of the male, specific to the periwinkle (Littorina littorea).

ISI – Intersex Stage Index.

Isomers – A chemical species with the same number and types of atoms as another chemical species, but possessing different properties.

Li – Lithium, an element.

Littoral zone – The marine ecological realm situated roughly between the high–tide level and the limit of the continental shelf. It is characterised by intricate inter–relationships between floral and faunal populations, high wave energies and, in the intertidal subzone, by alternating submergence and exposure.

Metabolites – Breakdown products of substances that are the result of chemical and biological tranformation processes.

Microsievert – A unit for exposure to radioactivity.

Ni – Nickel, an element classified as a heavy metal.

Normalisation – adjusting a measured concentration to a common factor, for example, adjusting the concentration of a heavy metal to background values.

Organic – A substance containing carbon

Organotin – A substance in which the tin atom is bound to a carbon–containing substance.

OSPAR – See OSPAR Convention.

OSPAR Convention – Convention for the Protection of the Marine Environment of the Northeast Atlantic. It was opened for signature at the Ministerial Meeting of the Oslo and Paris Commissions in Paris on 22 September 1992. The convention entered into force on 25 March 1998, and is administered by the OSPAR Commission.

PAH – Polyaromatic hydrocarbon.

Pb – Lead, an element classified as a heavy metal.

PCB – Polychlorinated biphenyls.

Pelagic – Living in or frequenting the water column. Applied especially to organisms that live in the upper water layers of the sea, away from the coast. See also benthic.

Photo-oxidation – A chemical process whereby the energy of sunlight (or artificial light) causes chemical reactions.

POP – Persistent organic pollutant.

psu – Practical salinity unit.

Radioactive contamination – The contamination of any material, surface, environment or person by radioactive substances. In the specific case of the human body, this radioactive contamination includes both external skin contamination and internal contamination irrespective of method of intake.

Radioactive substances – See radionuclide.

Radioactivity – Spontaneous emission of radiation, normally alpha or beta particles, often accompanied by gamma rays, from the nucleus of an (unstable) isotope.

Radionuclide – A nuclide that exhibits radioactivity.

Sediment – Solid particles of organic and inorganic material at the sea floor.

Sedimentation – Deposition of material of varying size, both mineral and organic, away from its site of origin by the action of water, wind, gravity or ice.

Sievert – See microsievert.

Solubility – A measurement of the mass of a solute (solid, liquid or gas) that will dissolve in a given volume or mass of solvent. When dissolving one liquid in another, it is also called miscibility.

Specific gravity – See density.

TBT – Tributyltin, a very toxic organic compound containing tin. It is used in anti–fouling paints on vessels and fixed marine structures.

Toxicity – The degree of danger posed by a substance to animal or plant life.

Trophic level – The feeding position of an organism in the food web.

Vapour pressure – Vapour pressure is a measure of the tendency of a material to change into the gaseous or vapour state, and it increases with temperature.

VDSI – Vas Deferens Sequence Index.

Weathering – A number of physical, biological, and chemical processes that, for example, degrade oil.

WFD – Water Framework Directive.

Zn – Zinc, an element classified as a heavy metal.

WHERE CAN I READ MORE?

BOOKS

Basic Environmental Toxicology, 1993: Cockerham, LG., Shane, BS. (Eds), Taylor & Francis, CRC Press, 368 pp.

Handbook of Ecotoxicology, 2002; Hoffman DJ., Rattner, BA. (Eds), Taylor & Francis, CRC Press, 1312 pp.

Coastal and Esturarine Risk Assessment, 2001: Newman, MC., Roberts MH, jr., Hale RC. (Eds), Environmental and Ecologial Risk Assessment, Taylor & Francis, CRC Press, 368 pp.

Ærtebjerg, G., Andersen, J.H. & Schou Hansen, O. (eds.) 2003: Nutrients and Eutrophication in Danish Marine Waters. A Challenge for Science and Management. National Environmental Research Institute. 125 pp.

REPORTS

Vandmiljø og Natur 2004. 2005. Andersen, J.M., Boutrup, S., van der Bijl, L., Svendsen, L.M., Bøgestrand, J., Grant, R., Lauridsen, T.L., Ellermann, T., Ærtebjerg, G., Nielsen, K.E., Søgaard, B., Jørgensen, L.F. & Dahlgren, K. c: 132 s. (In Danish).

Marine områder 2004 - Tilstand og udvikling i miljø- og naturkvaliteten. Ærtebjerg, G., Bendtsen, J., Carstensen, J., Christiansen, T., Dahl, K., Dahllöf, I., Ellermann, T., Gustafsson, K., Hansen, J.L.S., Henriksen, P., Josefson, A.B., Krause-Jensen, D., Larsen, M.M., Markager, S.S., Ovesen, N.B., Skjøth, C.A., Strand, J., Söderkvist, J., Mouritsen, L.T., Bråten, S., Hoffmann, E. & Richardson, K. 2005. NERI Technical report No 551. 94 s. (In Danish).

NOVANA. Nationwide Monitoring and Assessment Programme for the Aquatic and Terrestrial Environments. Programme Description – Part 1. 2005. NERI Technical re-port No 532. Svendsen, L.M. & Norup, B. 54 pp.

Analysis, fate and toxicity of zinc- and copper pyrithione in the marine environment. 2005: Dahllöf, I., Grunnet, K., Haller, R., Hjorth, M., Maraldo, K. & Petersen, D.G. – Nordic Council of Ministers, Tema-Nord, 550:33.

Environmental Status of the European Seas. 2003: Federal Ministry for the Environment, Nature Conservation and Nu-clear Safety. ICES, 75 pp.

Modeller i miljøkemien – hvad kan de bruges til? 2001: Fauser, P; Sørensen, P. B., Carlsen, L., NERI Thematic report No. 36. 40 pp.

Towards a Cleaner Marine Environment. 2000: Brochure from the Danish Environmental Protection Agency. Danish EPA.

Predicting Impacts of Oil Spills – Can Ecological Science Cope? A Case study concerning birds in Environmental Impact Assessments. 2000. Mosbech, A. NERI Report, 126 pp.

Bundmaling til skibe – et miljøproblem. 1999: Foverskov, S., Strand, J., Jacobsen, J. A., Rieman, B., Pritzl, G., Nielsen, P. Ø. & Aagaard, A. NERI Thematic report No. 36. 48 pp. (In Danish).

LINKS

- Danish EPA: http://www.mst.dk/homepage
- NERI: http://www.dmu.dk
- EEA: http://www.eea.eu.int
- HELCOM: http://www.helcom.fi
- ICES: http://www.ices.dk
- OSPAR: http://www.ospar.org
- USEPA: http://www.usepa.gov
- IMO: http://www.imo.org

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REFERENCES

Alzieu, C., Héral, M., Thibaud, Y., Dardignac, M.J. & Feuille, M. 1981-1982: Influence des peintures antisallisures à base d´organostanniques sur la calcification de la coquille de l´huitre. Crassostrea gigas. Rec. Trav. Int. Pêches Marit., 45: 101-116.

Angersen T.V., Danish EPA. 2004. Offshore chemicals in Denmark. EOSCA meeting September 2004 in Stavanger.

Bach, H., Christensen N. & Kristensen P. (Eds.) 2001: The State of the Environment in Denmark. National Environmental Research Institute. NERI Technical Report No. 409. 368 pp.

Bekendtgørelse nr. 753. 2001: Bekendtgørelse af lov om miljøbeskyttelse. BEK nr. 753 af 25/08/2001.

Bekendtgørelse nr. 1042. 1997: Bekendtgørelse om begrænsning af salg og anvendelse af visse farlige kemiske stoffer og produkter til specielt angivne formål.

Bekendtgørelse nr. 784. 1999: Bekendtgørelse af lov om arbejdsmiljø. 11/10/1999.

Bekendtgørelse nr. 975. 1986: Bekendtgørelse om dumpning af optaget havbundsmateriale (klapning). 19/12/1986.

Bekendtgørelse nr. 1003. 2002: Bekendtgørelse om modtagefaciliteter for affald fra skibe, om skibes aflevering af affald og havnes affaldsplaner. 10/12/2002.

Bekendtgørelse om udtømning af olie fra skibe. BEK nr. 485 af 15/06/1999.

Boese, B.L., Lamberson, J.O., Svartz, R.C., Ozretich, R, & Cole, F. 1998: Photoinduced toxicity of PAHs and alkylated PAHs to a marine infaunal amphipod (Rhepoxynius abronius). Archives of Environmental Toxicology. 34: 235-240.

CEN, 2006: European Committee for Standardization, Oil spill Identification – waterborne Petroleum and Petroleum Products. Part 2: Analytical Methodology and interpretation of Results, TC/BT TF 120 WI CSS27003.

Christensen, J.H. & Platz, J. 2001: Screening for polybromated diphenyl ether in blue mussels, marine and freshwater sediments in Denmark. J. Environmental Monitoring, 2001, 3: 543-547.

Christensen, P.D., Brozek, M. & Hansen, B.W. 1998: Energetics and behavioral responses by the common goby, Pomatoschistus microps (Krøyer) exposed to linear alkylbenzene sulfonate. Environmental Toxicology and Chemistry. 17: 2051-2057.

Council Directive. 1976: Council Directive on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community. 76/464/EEC.

Council Directive. 1979: Council Directive on the quality required of shellfish waters. 79/923/EEC.

Council Directive. 1991: Council Directive concerning the placing of plant protection products on the market. 91/414/EEC.

Council Directive. 1996: Council Directive laying down basic safety standards for the protection of the health of workers and the general public against the dangers arising from ionizing radiation. 96/29/EURATOM.

Council Directive. 1998: Council Directive of the European Parliament and of the Council on the placing of biocidal products on the market No 98/8/EC.

Council Directive. 2000: Council Directive of the European Parliament and of the Council. Establishing a framework for Community action in the field of water policy. 2000/60/EC.

Dahl, K., Larsen, M.M., Andersen, J.H., Rasmussen, M.B., Petersen, J.K., Josefson, A. B., Lundsteen, S., Dahllöf, I., Christiansen, T., Krause-Jensen, D., Hansen, J.L.S., Ærtebjerg, G., Henriksen, P., Helmig, S.A. & Reker, J. 2004: Tools to assess the conservation status of marine Annex 1 habitats in Special Areas of Conservation. Phase 1: Identification of potential indicators and available data. National Environmental Research Institute. NERI Technical Report 488: 94 pp.

Danish EPA. 1995: Esbjerg Declaration. 4th International Conference on the Protection of the North Sea, Esbjerg, Denmark, 8-9 June 1995. pp. 144.

Danish EPA. 1996. Consolidated Act no. 21 of January 16, 1996 from the Ministry of Environment and Energy on Chemical Substances and Products.

Danish EPA. 1997. Status of the Minister for the Environment's Action Plan for Reducing the Consumption of Pesticides.

Danish EPA. 2000. Faktuelt, no. 35 (in Danish).

Danish EPA. 2002. Udfasning af Lineære Alkylbenzen Sulfonater (LAS) i rengøringsmidler. Working Report. Danish Environmental Protection Agency; no. 29. 32 pp. (In Danish).

Danish EPA. 2004. Principles on setting water quality standards for substances in surface waters. Guidance Document no. 4 (in Danish).

Danmarks Miljøundersøgelser. 2004. NOVANA. Det nationale program for overvågning af vandmiljøet og naturen. Programbeskrivelse – del 1. Danmarks Miljøundersøgelser. 48 s. Faglig rapport nr. 495 (In Danish).

EC. 1994. Technical Guidance document in support of commission directive 93/67/EEC on risk assessment for new notified substances and commission regulation (EC) N° 1488/94 on risk assessment for existing substances.

EC. 2000. The radiological exposure of the population of the European Community to radioactivity in the Baltic Sea, Marina-Balt project. Radiation Protection 110. EUR-19200 (EN). European Commission, Luxembourg.

EC. 2005. Annex to the Communication from the Commission to the Council and the European Parliament: Thematic strategy on the protection and conservation of the marine environment. SEC(2005) 1290: p. 26.

EEA. 2003. Hazardous substances in the European marine environment: Trends in metals and persistent organic pollutants. EEA Topic report No 2/2003: 75 pp.

EU Commission. 2002. Communication from the Commission to the Council and the European Parliament. Towards a strategy to protect and conserve the marine environment. COM (2002) 539 final.

EU Commission proposal. 2003. Proposal for a regulation of the European parliament and of the council concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH). Proposal No. 644.

EU Commission. 1996. Technical guidance documents in support of the Commission Directive 93/67/EEC on risk assessment for new substances and the Commission Regulation EC 1488/94 on risk assessment for existing substances. Brussels, Belgium.

EU Commission directive. 2006. Directive on environmental quality standards in the field of water policy and amending Directive 2000/60/EC, COM398 final, SEC(2006) 947.

Foverskov, S, Strand, J., Jacobsen J.A., Riemann, B., Pritzl, G., Nielsen, P.Ø. & Aagaard, A. 1999. Bundmaling til skibe – et miljøproblem. Miljø- og Energiministeriet. Danmarks Miljøundersøgelser. 48 pp. (In Danish).

Glob, E. (Ed.). 1998. Miljøfremmede stoffer i havbunden. Lillebæltsamarbejdet 1998. Fyns Amt, Sønderjyllands Amt & Vejle Amt.

Grønnegaard, H. & Bruun, H.P. (Eds.). 2004. Natur of Miljø 2003. Vores Vand. Miljøministeriet. (In Danish)

Hansen, B., Fotel, F. L., Jensen, N. J. & Wittrup, L. 1997: Physiological effects of the detergent linear alkylbenzene sulphonate on blue mussel larvae (Mytilus edulis) in laboratory and mesocosm experiments. Marine Biology 128: 627-637.

HELCOM. 1992. Convention on the Protection of the Marine Environment of the Baltic Sea Area, Annex II: Criteria for the use of Best Environmental Practice and Best Available Technology

HELCOM. 2002. 4th Periodic Assessment. Baltic Sea Environmental Procedings No. 87. Helsinki Commission. 48 pp.

HELCOM. 2003. Radioactivity in the Baltic Sea 1992-1998. Baltic Sea Environment Proceedings No. 85. Helsinki Commission, Baltic Sea Environment Protection Commission, Helsinki.

HELCOM. 2004. Clean Seas Guide 2004 (www.helcom.fi)

Henriksen, P., Andersen, J., Carstensen, J. Christiansen, T., Conley, D.J., Dahl, K., Dahllöf, I., Hansen, J.L.S., Josefson, A.B., Larsen, M. M., Lundsgaard, C., Markager, S., Nielsen, T.G., Pedersen, B., Rasmussen, B., Strand, J., Ærtebjerg, G., Fossing, H., Krause-Jensen, D., Middelboe, A.-L., Risgaard-Petersen, N., Ellermann, T., Hertel, O., Ambelas Skjøth, C., Ovesen, N.B., Glasius, M., Pritzl, G. & Gustafson, B.G. 2001. Marine områder 2000 – Miljøtilstand og udvikling. NOVA 2003. Danmarks Miljøundersøgelser. Faglig rapport fra DMU 375: 110 s. (in Danish with English summary).

ICES. 2004. Report of the ICES Advisory Committee on the Marine Environment. ICES Advice, 1(1): 12–28.

IMO. 2001. International Convention on the Control of Harmful Anti-fouling Systems on Ships.

Jensen, A. & Gustavson, K. 2001. Havnesedimenters indhold af miljøfremmede organiske forbindelser. Environmental Project. Danish Environmental Protection Agency. No. 627: 56 pp.

Højenvang, J. 2003. Redegørelse om miljørigtig fjernelse og slibning af bundmaling retningslinier for afrensning og vedligeholdelse af bundmaling på lystbåde. Dansk Sejlunion maj 2003.

Kalleborn, R., Berger U. & Järnberg U., 2004. Perfluorinated alkylated substances (PFAS) in the Nordic environment. TEMA Nord 552

Kimerle, R. A. 1989. Aquatic and terrestrial ecotoxicology of linear alkylbenzene sulphonate. Tenside Surfact Deter. 26(6): 169-176

Larsen, M.M., Strand, J. & Stedmon, C., 2004. Analyse og udvikling i koncentration af miljøfarlige stoffer. In: Ærtebjerg et al., 2004. Marine områder 2003. Faglig rapport fra Danmarks Miljøundersøgelser, nr. 513. 97 pp. (In Danish with English Summary).

Larsson D.G.J. & Förlin L. 2002. Male-biased sex ratios of fish embryos near a pulp mill: Temporary recovery after a short-term shutdown. Environmental Health Perspectives. 110: 739-742.

Lepper P. 2002. Development of Methods for the Derivation of Quality Standards in the Context of the Water Framework Directive. Final report of the study: Identification of quality standards for priority substances in the field of water policy. 04 September 2001. Frauenhofer-Institute Molecular Biology and Applied Ecology, 124 pp.

Lov nr. 476. 1993. Lov om beskyttelse af havmiljøet.

Lov nr. 279. 2001. Lov om ændring af fødevareloven m.fl. (offentliggørelse af kontrolresultater, oprettelse af råd til administration af kvalitetsmærkningsordningen, udvidet klageadgang for forbrugerorganisationer mv.

Lyons, B.P., Pascoe, C.K., McFadzen, I.R.B. 2002. Phototoxicity of pyrene and benzo[a]pyrene to embryo-larval stages of the pacific oyster Crassostrea gigas Marine Environmental Research 54 (3-5): 627-631 Sp. Iss. 2002.

Maag, J. & Lassen, C. 2000. PCB i apparater i Danmark. Arbejdsrapport fra Miljøstyrelsen nr. 15, 2000 udført af COWI Rådgivende Ingeniører for Miljøstyrelsen.

Madsen, T., Gustavson K., Samsøe-Petersen, L., Simonsen, F., Jacobsen, J., Foverskov, S. & Larsen, M.M. 1998. Kortlægning og vurdering af antibegroningsmidler til lystbåde i Danmark. Environmental Project, Danish Environmental Protection Agency. No. 384. 108 pp.

Markager, S., Nielsen, T.G., Carstensen, J., Conley, D.J., Dahl, K., Hansen, J., Henriksen, P., Josefson, A.B., Larsen, M.M., Pedersen, B., Rasmussen, B., Strand, J., Ærtebjerg, G., Fossing, H., Lauersen, J.S., Hertel, O., Skov, H., Svendsen, L.M., Cleemann, M. & Pritzl, G. 1999: Marine områder. Status over miljøtilstanden i 1998. NOVA 2003. Danmarks Miljøundersøgelser. Faglig rapport fra DMU nr. 290. pp. 164.

Mikkelsen, S.H. 1999. Tributyltin. Environmental Project. Danish Environmental Protection Agency. no. 451. 33 pp.

Miljø- og energiministeriet og Ministeriet for fødevarer, landbrug og fiskeri. 2000. Pesticidhandlingsplan II.

Miljøministeriet. 1996. Bekendtgørelse nr. 921 af 08/10/1996 om kvalitetskrav for vandområder og krav til udledning af visse farlige stoffer til vandløb, søer eller havet.

Miljøministeriet og Fødevareministeriet. 2003. Evaluering af Pesticidhandlingsplan II og Aftalen om afvikling af pesticidanvendelsen på offentlige arealer.

Miljøstyrelsen. 1983. Vejledning i recipientkvalitetsplanlægning. Del 2, kystvande.

Miljøstyrelsen. 1999. Strategi for en styrket indsats på kemikalieområdet i Danmark, i EU og globalt.

Miljøstyrelsen. 2000. NOVA. Nationalt program for overvågning af vandmiljøet 1998-2003. Redegørelse fra Miljøstyrelsen nr. 1/2000. 397 s.

Miljøstyrelsen. 2002. Vejledning Nr. 11. Tilslutning af industrispildevand til offentlige spildevandsanlæg.

Miljøstyrelsen. 2004. Listen over uønskede stoffer 2004. Orientering fra Miljøstyrelsen nr. 8.

Ministry for the Environment. 2003. Act no. 1150 of 17 December 2003. (In Danish: Lov om miljømål m.v. for vandforekomster og internationale naturbeskyttelsesområder (miljømålsloven).

Ministry of the Interior Finland. 1977. Man and the Baltic Sea. 34 pp.

Mogensen, B.B., Pritzl, G., Rastogi, S., Glesne, O., Hedlund, B., Hirvi, J-P., Lundgren, A. & Sigurdsson A. 2004. Musk compounds in the nordic environment. TemaNord: 503. Nordic Council of Ministers. 69 pp.

Moore, M.N., Lowe D. & Köhler A. 2004. Biological effects of hazardous substances: Measurement of lysosomal membrane stability. ICES Techniques in Marine Environmental Sciences No. 36. http://ices.dk/pubs/times36/TIMES36.pdf.

National Academy of Sciences. 1971. Radioactivity in the marine environment (RIME). Report. National Academy of Sciences, Washington DC, USA.

National Institute for Minamata Disease, Hama Minamata City Kumamoto, JAPAN. http://nimd.go.jp

Naturvårdsverket. 1999. Kust och hav. Bedömningsgrunder för miljøkvalitet. Rapport 4914. Naturvårdsverket Förlag. 134 pp.

Neuman, E., Sandström, O., Thoresson, G. 1999: Guidelines for coastal fish monitoring. National Board of Fisheries, Institute of Coastal Research, Ôregrund, Sweden. 44 pp.

Oehlmann, J. 2004. Biological effects of hazardous substances: Use of intersex in the periwinkle (Littorina littorea) as a biomarker of tributyltin pollution. 22pp. ICES Techniques in Marine Environmental Sciences No. 37.

Oslo and Paris Commissions. 1984. The First Decade. 377 pp.

OSPAR. 1992. Convention on the Protection of the Marine Environment of the North East Atlantic Appendix 1.

OSPAR. 1998. Report of the Third OSPAR Workshop on Ecotoxicological Assessment Criteria (EAC). The Hague, 25-29 November 1996, Oslo and Paris Commissions.

OSPAR. 2000a. Harmonised Mandatory Control System for the Use and Discharge of Offshore Chemicals OSPAR Decision 2000/2

OSPAR, 2000b. Quality Status Report 2000. Region II – Greater North Sea. OSPAR Commission. 136 pp.

OSPAR Recommendation 2001/1 for the Management of Produced Water from Offshore Installations.

OSPAR. 2003. Strategy for a Joint Assessment and Monitoring Programme (JAMP), Reference number 2003-22.

OSPAR. 2003b. Harmonisation of Criteria for the Assessment of TBT–specific Biological Effects, Agenda item MON 03/3/1-E, Presented by the Netherlands at the Meeting of the Working Group of Monitoring, Copenhagen 16-18 December 2003.

OSPAR. 2003c. Proposed amendments to the current OSPAR Guidelines on TBT-specific effect monitoring. ASMO meeting 28 April – 2 May 2003 in Svolvær, Norway, document 03/4/2E.

OSPAR. 2004. Bignert, A., Cossa, D., Emmerson, R., Fryer, R., Füll, C., Fumega, J., Laane, R., Calls, H.M., McHugh, B., Miller, B., Millward, G., Moffat, C. (ed.), Pijnenburg, J. (ed.), Roose, P., Ruus, A., Schmolke, S., Smedes, F., Strand, J., Stronkhorst, J., Thain, J., Tissier, C., Traas, T. (ed.) & Tronczynski, J. OSPAR/ICES workshop on the evaluation and update of background reference concentrations (B/RCs) and ecotoxicological assessment criteria (EACs) and how these assessment tools should be used in assessing contaminants in water, sediment, and biota. Workshop The Hague, 9-13 February 2004. Final Report. OSPAR Commission. 116 pp.

Peakall, D.B. 1996. A Practical Basis for Using Physiological Indicators In Environmental Assessment. AMBIO, vol. 21:6, pp. 437-438

Pallesen, K., Stengaard, V. & Kaysen, O. 1996. Kortlægning af anvendelsen af alkylphenolethoxylater og alkylphenoler. Working Report. Danish Environmental Protection Agency, no. 1, 29 pp.(In Danish).

SFT. 1997. Klassifisering av miljøkvalitet i fjorder og kystfarvann. Virkning av miljøgifter. SFT-veiledning nr. 97:03. Statens Forurenningstilsyn. 34 pp. (In Norwegian)

Skov H, Christensen K.D. & Duinck J. 1996. Trends in marine oil pollution in Denmark 1984-1995: An analysis of beached bird surveys. Arbejdsrapport fra Miljøstyrelsen nr. 75.

Stagg, R., & McIntosh, A. 1998. Biological effects of hazardous substances: Determination of CYP1A-dependent mono-oxygenase activity in dab by fluorimetric measurement of EROD activity. ICES Techniques in Marine Environmental Sciences no. 23, 16 pp.

Stockholm Convention on Persistent Organic Pollutants, 22 May 2001.

Strand J. & Jacobsen, J.A. 2002. Imposex in two sublittoral neogastropods from the Kattegat and Skagerrak: the common whelk Bucci-num undatum and the red whelk (Neptu-nea antiqua). Marine Ecology Progress Series, 244: 171-177.

Strand, J. 2003. Coupling marine monitoring and risk assessment by integrating exposure, bioaccumulation and effect studies. A case study using the contamination of organotin compounds in the Danish marine environment. National Environmental Research Institute & Roskilde University. 94 pp.

Strand, J., Andersen, L., Dahllöf, I. & Korsgaard, B. 2004. Impaired larval development in broods of the viviparous blenny (Zoarces viviparus) in Danish coastal waters. Fish Physiology and Biochemistry 30: 37–46.

Strand, J. & Jacobsen, J.A. 2005. Trophic transfer of organotin through the marine food web in the inner Danish waters. The Science of the Total Environment, in press.

Strand, J., Larsen, M.M., Næs, K., Cato, I. & Dahllöf, I., 2006. Tributyltin (TBT). Forekomst og effekter i Skagerrak. Uddevalla, Sweden: Forum Skagerrak II. 39 s.

Swarzenbach, R.P., Gschwend, P.M. & Imboden, D.M. 1993. Environmental organic chemistry. p. 4. Wiley Interscience.

Tidlund, A. & Brenner, U. (Eds). 1999. Östersjö '99. Stockholms Marina Forskningscentrum. (In Swedish with English Summary)

Tidlund, A., Brenner, U. (Eds). 1998. Östersjö '98. Stockholms Marina Forskningscentrum. (In Swedish with English Summary)

Toppari, J., Larsen, J.C., Christiansen, P., Giwercman, A., Grandjean, P., Guilette Jr, L.J., Jégou, B., Jensen, T.K., Jouannet, P., Keiding, N., Leffers, H., McLachlan, J.A., Meyer, O., Müller, J., Meyts, E.R.-D., Scheike, T., Sharpe, R., Sumpter, J., & Skakkebæk, N.E. 1995. Male reproductive health and environmental chemicals with estrogenic effects. Miljøstyrelsen, Miljøprojekt nr. 292.

UNEP. 1995. Global Programme of Action for the Protection of the Marine Environment from Land-based Activities and adoption of the Washington Declaration

UNSCEAR. 2000. Sources and effects of ionizing radiation, United Nations Scientific Committee on the Effects of Atomic Radiation, UNSCEAR 2000 Report to the General Assembly, United Nations, New York.

Vighi, M., Gramatica, P., Consolaro, F. & Todeschini, R. 2001. QSAR and Chemometric Approaches for Setting Water Quality Objectives for Dangerous Chemicals, Ecotoxicology and Envrionmental Saftey 49, 206-220

Vikelsøe, J., Fauser, P., Sørensen, P.B. & Carlsen, L. 2001. Phthalates and Nonylphenols in Roskilde Fjord. A Field Study and Mathematical Modelling of Transport and Fate in Water and Sediment. The Aquatic Environment. National Environmental Research Institute, Roskilde. NERI Technical Report. No. 339. 106 pp

Ærtebjerg, G., Andersen, J.H & Hansen, O.S. (Eds). 2003. Nutrients and Eutrophication in Danish Marine Waters. A Challenge for Science and Management. National Environmental Research Institute. 126 pp.

Ærtebjerg, G., Bendtsen, J., Carstensen, J., Christiansen, T., Dahl, K., Dahllöf, I., Ellermann, T., Gustafsson, K., Hansen, J.L.S., Henriksen, P., Josefson, A.B., Krause-Jensen, D., Larsen, M.M., Markager, S.S., Ovesen, N.B., Ambelas Skjøth, C., Strand, J., Söderkvist, J., Mouritsen, L.T., Bråten, S., Hoffmann, E. & Richardson, K. 2005. Marine områder 2004 – Tilstand og udvikling i miljø- og naturkvaliteten. NOVANA. Danmarks Miljøundersøgelser. Faglig rapport fra DMU 551: 94 s (in Danish).

Background documents on hazardous substances:

HELCOM. 2001. The pesticides selected for immediate priority action.

HELCOM. 2001. Guidance Document on Polychlorinated Biphenyls (PCBs).

HELCOM. 2002. Guidance Document on Cadmium and its Compounds.

HELCOM. 2002. Guidance Document on Mercury and Mercury Compounds.

HELCOM. 2002. Guidance Document on Dioxins.

HELCOM. 2002. Guidance Document on Nonylphenol/Nonylphenolethoxylates (NP/NPEs).

OSPAR. 2000. OSPAR Background Document on Mercury and Organic Mercury Compounds. Hazardous Substances Series, No. 100.

OSPAR. 2000. OSPAR Background Document on Organic Tin Compounds. Hazardous Substances Series, No. 103.

OSPAR. 2001. OSPAR Background Document on Polychlorinated Biphenyls (PCBs). Hazardous Substances Series, No. 134.

OSPAR. 2001. OSPAR Background Document on Certain Brominated Flame Retardants – Polybrominated Diphenylethers, Polybrominated Biphenyls, Hexabromo Cyclododecane. Hazardous Substances Series, No. 135.

OSPAR. 2001. OSPAR Background Document on Nonylphenol/Nonylphenolethoxylates. Hazardous Substances Series, No. 136.

OSPAR. 2001. OSPAR Background Document on Polycyclic Aromatic Hydrocarbons (PAHs). Hazardous Substances Series, No. 137.

OSPAR. 2002. OSPAR Background Document on Lead. Hazardous Substances Series, No. 148.

OSPAR. 2002. OSPAR Background Document on Cadmium. Hazardous Substances Series, No. 151.

OSPAR. 2002. OSPAR Background Document on Lindane. Hazardous Substances Series, No. 153.

OSPAR. 2003. OSPAR Background document on trichlorobenzenes. Hazardous Substances Series, No. 170.

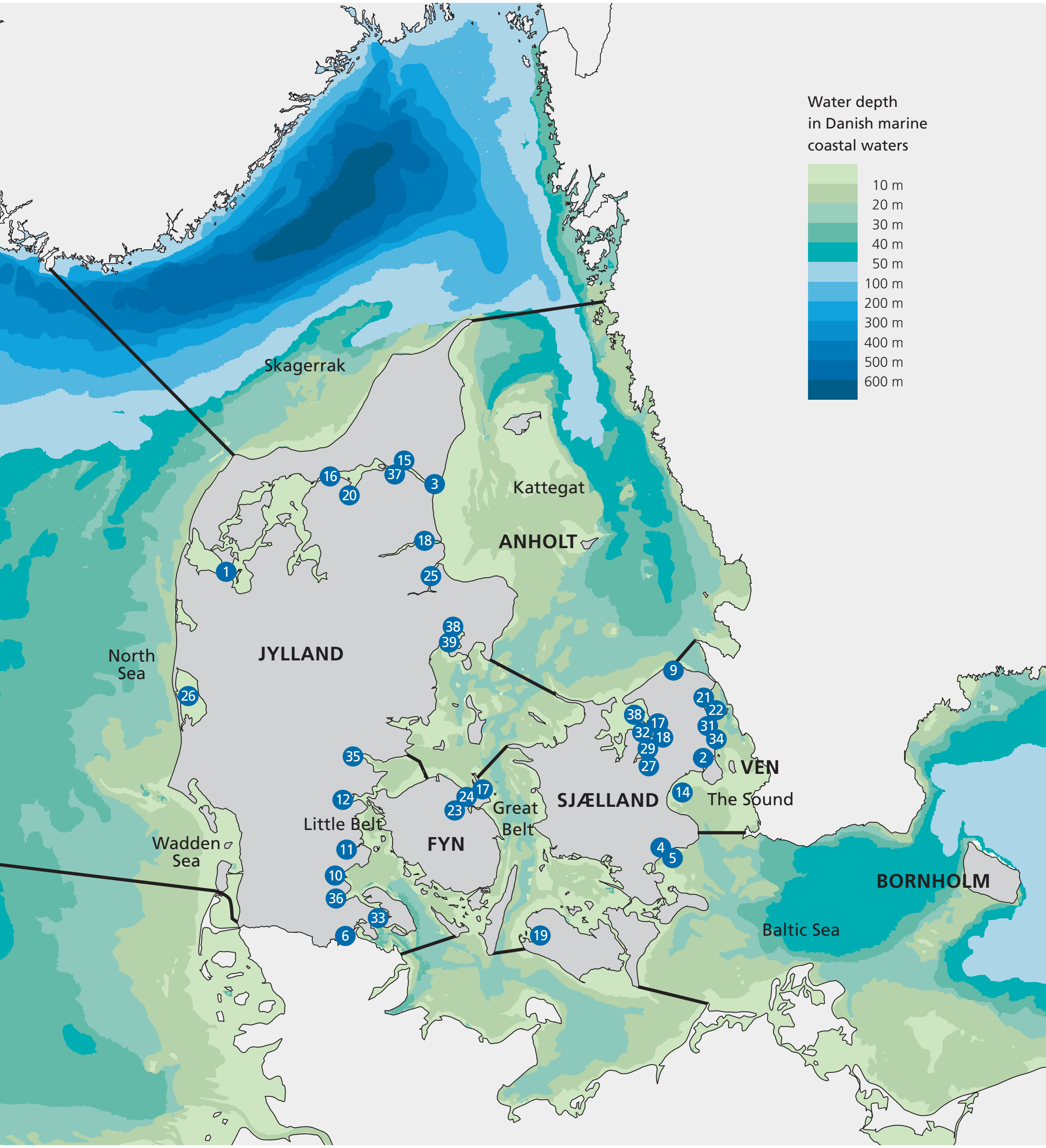
OSPAR. 2004. Background document on musk xylene and other musks. Hazardous Substances Series, No. 200.

OSPAR. 2004. Background document on tetrabromobisphenol-A (TBBPA). Hazardous Substances Series, No. 202.

OSPAR. 2005. OSPAR Background Document on Dioxins. Hazardous Substances Series, No. 152.

OSPAR. 2005. OSPAR Background Document on Phthalates. Hazardous Substances Series, No. 226.

OSPAR. 2005. OSPAR Background Document on PFOS. Hazardous Substances Series, No. 227.


Water depth
in Danish marine
coastal waters
10 m
20 m
30 m
40 m
50 m
100 m
200 m
300 m
400 m
500 m
600 m
Skagerrak
Kattegat
ANHOLT
North
Sea
JYLLAND
Wadden
Sea
Little Belt
FYN
Great
Belt
SJÆLLAND
VEN
The Sound
BORNHOLM
Baltic Sea
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ANNEXES

MAP OF THE DANISH MARINE WATERS

The estuaries, coastal waters and open marine waters mentioned in the report are indicated on the map on the opposite page. Names referring to the numbers on the map are listed below. The translation of the Danish names to English are: “Bredning“ – a broad; “Bugt“ – a bay; “Bælt“ – a belt; “Bælthav“– a belt sea; “Fjord“ – an inlet, but often used as a general term for estuaries and should not be confused with the definition of a classical fjord with a sill; “Nor“ – a cove; “Sund“– a strait or sound; “Vig“ – a cove; “Øhav“ – archipelago; “Farvand“ – waters.

Danish marine sub areas

1 Agerø
2 Copenhagen
3 Egense
4 Fakse
5 Fakse Bugt
6 Flensborg Fjord
7 Frederiksværk
8 Frederikssund
9 Gilleleje
10 Haderslev Fjord
11 Horsens Fjord
12 Kolding Fjord
13 Kulhuse
14 Køge Bugt
15 Langerak
16 Limfjorden
17 Lindø
18 Mariager Fjord
19 Nakskov
20 Nibe Bredning
21 Nivå
22 Nivå Bugt
23 Odense
24 Odense Fjord
25 Randers Fjord
26 Ringkøbing Fjord
27 Roskilde
28 Roskilde Bredning
29 Roskilde Fjord
30 Roskilde Vig
31 Rungsted
32 Skuldelev
33 Sønderborg
34 Vedbæk
35 Vejle Fjord
36 Åbenrå
37 Ålborg
38 Århus
39 Århus Bugt

Appendix I.

Summary table of hazardous substances that were included in the NOVA monitoring programme and screening activities.

Substance	**Average concentration and range 1998-2004**				**Criteria by which the substances were selected**
Sediment		**Biota**		**Water**	
		Mussel*	**Fish****		
Heavy metals	mg/kg dw	mg/kg dw	mg/kg dw	mg/l	
Lead (Pb)	29	1.2	0.3/0.5	n.m	OSPAR (A), CEMP,
	[4.8-108]	[0.1-5.6]	[<0.2-8.0]		HELCOM, NSC, Nat I, EU
Cadmium (Cd)	0.41	1.25	0.70/0.80	n.m	OSPAR (A), CEMP, HEL
	[0.01-1.9]	[0.28-7.2]	[<0.02-20]		COM, NSC, EU
Copper (Cu)	17	11.6	53/21		HELCOM, NSC, EU
	[0.7-42]	[2.3-120]	[2.4-232]	n.m	
Mercury (Hg)	0.13	0.149	0.51/0.4		OSPAR (A), CEMP,
	[0.001-0.67]	[0.005-0.892]	[0.01-2.5]	n.m	HELCOM, NSC, EU
Nickel (Ni)	19	2.8	0.3/0.6	n.m	
	[1.5-54]	[0.3-51]	[<0.2-6.7]		HELCOM, Na II
Zinc (Zn)	91	127	159/158		HELCOM, NSC, Na II
	[6.2-260]	[57-313]	[8-384]	n.m	
Pesticides	mg/kg dw	µg/kg ww	µg/kg ww	µg/l	
Aldrin	n.m	n.m	n.m	n.m	OSPAR (B), NSC, EU
Atrazine	n.m	n.m	n.m	0.007	NSC
				[0.007-0.009]	
DDT	0.44	0.20	1.3/1.6	n.m	OSPAR (B), HELCOM,
[0.04-17]	[<0.1-6.0]	[<0.1-9.8]		NSC, EU	
DDE	0.57	0.5	10.9/9.3	n.m	OSPAR (B), HELCOM,
[0.04-15]	[0.1-2.9]	[0.4-70]		NSC, EU	
Dieldrin	n.m	n.m	n.m	n.m	OSPAR (B), NSC, EU
Diuron	n.m	n.m	n.m	0.039	PP
				[0.01 - 0.17]	
Endrin	n.m	n.m	n.m	n.m	OSPAR (B), OSPAR (B)
					NSC, EU
Irgarol 1051	n.m	n.m	n.m	0.008	PP
				[0.004-0.054]	
Isodrin	n.m	n.m	n.m	n.m	OSPAR (A), NSC, EU
gamma-Lindane	0.50	0.2	1.0/2.0	n.m	OSPAR (A), HELCOM,
	(HCH)	[0.04-3.7]	[0.1-0.5]	[0.3-6.5]	NSC, EU
Simazine	n.m	n.m	n.m	0.0125	
				[0.008-0.091]	
Polyaromatic hydrocarbons (PAHs), including Naphthalene					
	µg/kg dw	µg/kg ww			
Naphthalene	49	5.9	n.m	n.m	Nat I, PP
	[4-180]	[1.6-164]			
Σ 16 PAHs	1391	59	NOVA	n.m	OSAR (A), CEMP, Nat I
	[70-8070]	[4-960]			

Substance	Average concentration and range 1998-2004				Criteria by which the substances were selected
Sediment		Biota		Water	
		Mussel*	Fish**		
Phenols	µg/kg dw				
Nonylphenol	85 [<0.5 - 610]	n.m	n.m	n.m	OSPAR (A), NSC, PP
Halogenated aliphatic hydrocarbons					
	µg/kg dw	µg/kg ww	µg/kg ww		
1,2-dichlorethane	n.m	n.m	n.m	N.D	EU, NCS
Trichlorethylene	n.m	n.m	n.m	N.D	EU, NCS
Trichlormethane	n.m	n.m	n.m	N.D	EU, NCS
Hexachlorbenzene (HCB)	0.10 [0.03-0.6]	0.1 [<0.1-0.8]	1.2/1.3 [<0.1-6.7]	n.m	OSPAR (B), HELCOM, NSC, EU
Polychlorinated biphenyls (PCBs)					
	µg/kg dw	µg/kg ww	µg/kg ww		
Σ 7 PCBs	4.1 [0.4-49]	53 [0.3-23]	3.4 [17-157]	n.m	OSPAR (A), CEMP, HELCOM, NSC, EU
Organotin compounds					
	µg Sn/kg dw	µg Sn/kg ww			
Tributyltin (TBT)	12	10.7	n.m	n.m	OSPAR (A), HELCOM, Na
[0.1-150]	[0.4-136]			I, NSC	
Dibutyltin (DBT)	3.6 [0.4-51]	5.9 [0.3-83]	n.m	n.m	OSPAR (A), Na I, NSC
Monobutyltin	3.2 [0.5-20]	2.8 [<0.1-31]	n.m	n.m	OSPAR (A), Na I, NSC

OSPAR (A):	OSPAR List of Chemicals for Priority Action
OSPAR (B):	OSPAR Substances of Possible Concern
CEMP:	OSPAR Co-ordinated Environmental Monitoring Programme
NSC:	North Sea Conferences
EU:	EU priority substances, List I
Nat I:	Candidate substances for the Danish list of priority substances
PP:	Precautionary Principle
*	Mussel: Average value of *Mytilus edulis* and *Mya arenaria*, range for *M. edilus* (preferred species)
**	Fish: Flounder/Plaice average, range flounder (preferred species)

Σ 7 PCBs = CB28 + CB52 + CB101 + CB118 + CB138 + CB153 + CB180
Σ 16 PAHs = Naphthalene + Acenaphthylene + Acenaphthene + Fluorene + Phenanthrene + Anthracene + Fluoranthene + Pyrene + Benz[*a*]anthracene + Chrysene/triphenylene + Benzo[*b*,*j*,*k*]fluoranthene +Benzo[*a*]pyrene + Dibenzo[*a*,*h*]anthracene + Benzo[*g*,*h*,*i*]perylene + Indeno[1,2,3-*c*,*d*]pyrene

N.D. =	Not detected
n.m. =	Not measured
dw =	Dry weight
ww =	Wet weight

DATA SHEET

Title: Hazardous and Radioactive Substances in Danish Marine Waters
Subtitle: Status and Temporal Trends

Editors: Ingela Dahllöf and Jesper H. Andersen

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Summary: This book fulfils the Danish reporting obligations in relation to the OSPAR Trend Assessment on Dangerous Substances, and describes the degree of contamination from hazardous and radioactive substances and their temporal trends, as well as the effects of some of these hazardous substances, in the Danish marine environment. The assessment is based on existing information, primarily data collected via national and regional Danish monitoring activities until 2004.

Keywords: Hazardous substances, heavy metals, organic pollutants, anti-fouling, biological effects, imposex, radioactive substances, environmental protection, management of aquatic resources

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This assessment report has been written in order to fulfil Danish reporting obligations in relation to the OSPAR Trend Assessment on Dangerous Substances. The assessment is based on existing information, primarily data collected via national and regional Danish monitoring activities until 2005.

The report consists of a general introduction to hazardous substances and their fate and potential effect in the marine environment, followed by the present contamination status and trends in Danish waters together with effects monitored through the use og biomarkers. Finally a discussion on future management and assessment is included.

The assessment shows that hazardous substances can be found in Danish waters with the highest - concentrations in fjords and coastal areas close to point-sources, where also responses in biomarkers are seen. Concentrations are declining for older, now banned, organohalogen substances like DDT, whereas for some heavy metals the concentrations are increasing. For most substances no trends can be established as yet.

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