

chapter

4

Chemistry

4.1 Introduction

This chapter summarises available data on the inputs, concentrations, spatial distribution and temporal trends of trace metals, persistent organic substances, nutrients, radionuclides and oil in the OSPAR Convention area. It is based on the information presented in the five regional Quality Status Reports produced by OSPAR, only references to additional sources of information are included. The first section deals, in general terms, with inputs to the sea through rivers, direct discharges (i.e. industrial and municipal outlets) and deposition from the atmosphere. Subsequent parts discuss concentrations of substances in water, sediments and marine biota. Where appropriate, the concentrations are compared to existing guidelines or standards. The data used in the current assessment were extracted from relevant OSPAR documents, the ICES database, national monitoring programmes and the scientific literature.

Substances are either natural or anthropogenic (i.e. man-made). Many substances (such as nutrients and metals) occur naturally in soils, plants and animals and it is therefore important to distinguish between the natural concentrations and fluxes of these substances and the extent to which these are augmented by human activities. Such distinctions, although often difficult to make, are essential if informed decisions are to be made regarding the management of contaminants.



The substances discussed in this report can be divided into trace metals, organic contaminants (in particular persistent organic pollutants (POPs)), oil, radionuclides and nutrients. Some examples of the main anthropogenic sources are summarised in **Table 4.1**.

Table 4.1 Examples of anthropogenic sources of contaminants.	
	Main sources
Heavy metals	
cadmium	metallurgical processes, fossil fuel, fertiliser
mercury	fossil fuel, incineration, metallurgical industry
lead	mining, petrol
copper	mining, antifoulants
Persistent organic pollutants	
PCBs	industrial products, oils
TBT	antifoulants
PAHs	oil production, fossil fuel
DDT, HCH, toxaphene, dieldrin, chlordane	pesticides
HCB	industrial processes
dioxins and furans	incineration
Nutrients	
nitrate, ammonia, phosphate	agriculture, mariculture, sewage
Radionuclides	
caesium, polonium, technetium	reprocessing plants, phosphate production

The effects of substances on biota are dependent on a number of factors. These include bioavailability (see **Box 4.1**), bioaccumulation, biomagnification, toxicity and the capability of the organism to metabolise the substance. The bioavailability of the substance is

Box 4.1

Bioavailability: The extent to which a substance can be absorbed into the tissues of organisms and so influence their physiology. Bioavailability is possibly the most important factor in determining the extent to which a contaminant in water or sediment will enter the food chain and accumulate in biological tissues. It depends on a) the properties of the substance, especially its solubility in water, and b) the habitats and feeding mechanisms of the organisms concerned. The bioavailability of contaminants that are tightly bound to clay sediments is relatively low. On the other hand those substances that are more soluble in lipid (i.e. fats) than in water, and that are loosely bound to fine suspended sediments easily scavenged by filter feeders (e.g. mussels), tend to be readily available and accumulated in fatty tissues.

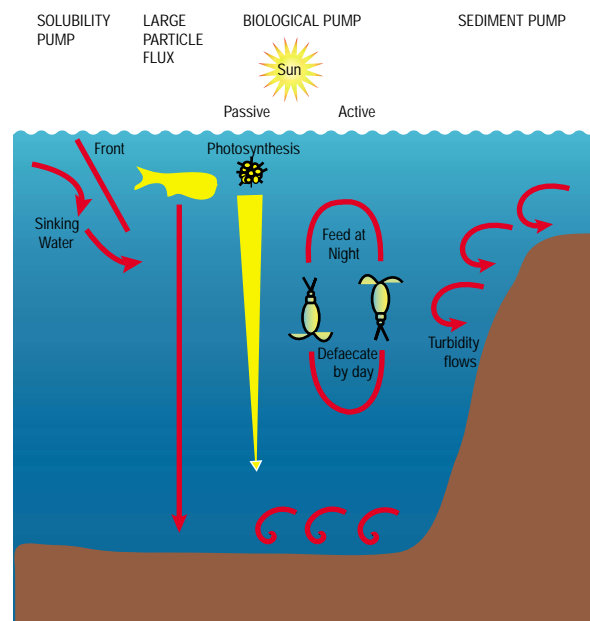
dependent on the matrix (sediment, water, biota) and the chemical form (speciation) in which it occurs.

Contaminants may occur in the water column either in solution or attached to particles. Many of the contaminants of concern in the marine environment have low water solubility and a high affinity for particles. There are several ways that contaminants can reach the seafloor (**Figure 4.1**) and once there they may become incorporated in seabed sediments. Contaminants can be taken up by organisms either directly, by absorption from sea water, or by ingestion of particles and can be relayed to successively higher levels in the food chain via grazing and predation.

In marine animals, individual contaminants tend to concentrate in specific organs. Persistent organic substances (e.g. POPs) which are highly lipophilic, accumulate mainly in fatty tissues; the highest levels are thus often found in liver tissue and in blubber. Amongst the heavy metals, cadmium tends to concentrate in the kidneys, mercury in the liver and lead in bone tissue. The ability to accumulate a particular contaminant varies between species but is also dependent on the form of the contaminant and the route of uptake. For example, methyl mercury is absorbed through the intestine of fish six times more effectively than inorganic mercury. Excretion rates also vary. The tendency for cadmium and mercury to be excreted slowly partly explains the high levels of these metals in long-lived species.

Many of the persistent organic contaminants that have

Figure 4.1 Schematic diagram of the various 'pumps' whereby material is exported to the ocean.



traditionally been monitored in the marine environment are no longer produced and the use of others is severely restricted. However, because of the scale of historical usage, large reservoirs of some POPs still exist in soils and sediments as well as in landfills and abandoned equipment. Continuing releases from such sources means that environmental concentrations are slow to decline. However, for most contaminants, the extent to which they are remobilised from marine sediments, particularly those in the deep ocean, is unclear. Some contaminants are also transported into the OSPAR area through the atmosphere and by ocean currents.

It has not always been possible to make confident comparisons between regions.

4.2 Input of contaminants (in general)

Input of contaminants to the maritime area is via three main routes; direct, riverine and atmospheric inputs. The relative importance of individual input routes differs between and within regions, and also for individual contaminants. For large parts of the maritime area, especially the oceanic parts, the atmospheric transport source is dominant. **Table 4.2** shows the contribution of different routes for cadmium and lead.

Direct input of contaminants arises as a consequence of municipal and industrial outfalls in coastal waters and from offshore activities and dumping. The major impacts of direct inputs are therefore likely to occur in coastal waters and especially in semi-enclosed areas and/or

where water exchanges are low. The extent to which sewage is treated prior to discharge varies but in most locations improvement schemes are under way and indications are that in impacted areas the concentrations of some associated contaminants are decreasing. As a consequence of national legislation and improvements to industrial manufacturing processes, the direct input of contaminants to the Convention area has in general decreased.

In the offshore oil and gas industry, discharges of oil via cuttings have been strongly reduced and produced water constitutes the main source of oil input. The quantity of produced water is increasing and it is anticipated that the quantity of chemicals associated with this source will follow the same trend.

Dredging activity is often regarded as relocation of material. Old dumpsites are potential ongoing sources of contaminants.

Riverine input is made up of the run-off from land and discharges into the rivers and their tributaries. Estimates of the flux of substances from riverine inputs are heavily dependent on river flow. Estuarine processes can also significantly modify the level of inputs to the marine environment. This makes it difficult to interpret trends and to make regional comparisons.

When considering riverine inputs it is important to be aware that the catchment area of individual rivers can include areas in more than one country, some of which may be outside the OSPAR Convention area. It is not appropriate therefore to ascribe the total load to the most downstream country.

Table 4.2 Aquatic and atmospheric contributions to the total inputs (t/yr) of cadmium and lead to the maritime area.

	Aquatic input (direct + riverine)		Atmospheric deposition*	Total (aquatic + atmospheric)		Proportion of atmospheric deposition to total (%)	
	min	max		min	max	min	max
Cadmium							
Region I	2	10.7	2.6	4.6	13.3	20	57
Region II	36	64	14.6	50.6	78.6	19	29
Region III	36	51	1.8	37.8	52.8	3	5
Region IV	9	9	4.5	13.5	13.5	33	33
Region V	0	0	3.5	3.5	3.5	100	100
TOTAL	83	134.7	27	110	161.7	17	25
Lead							
Region I	19.8	65.9	235	254.8	300.9	78	92
Region II	999	1095	1531	2530	2626	58	61
Region III	389	492	199	588	691	29	34
Region IV	680	680	501	1181	1181	42	42
Region V	0	0	345	345	345	100	100
TOTAL	2087.8	2332.9	2811	4898.8	5143.9	55	57

* the atmospheric deposition values are derived from modelling based on estimations of European emissions in 1990. Region I and Region V are not fully covered by the receptor grid used in the modelling exercise, particularly to the west, therefore the deposition estimates for these regions are likely to be underestimates.

Atmospheric input is the dominant source to the marine environment for several substances including mercury, lead, POPs and some nitrogen compounds. Its quantification, especially for POPs, is affected by large uncertainties. The sources of atmospheric inputs may be located within or outside the OSPAR area. Some substances have a relatively short residence time in the atmosphere and are consequently deposited close to their sources, while others (mercury, POPs) can be transported on a global scale through the atmosphere. Atmospheric contributions from non-OSPAR countries are likely to be proportionately smaller in coastal waters near industrialised areas, such as in the southern North Sea, but more significant elsewhere in the OSPAR maritime area.

Ocean currents are important in the transport and distribution of contaminants. The transport is both to and within the Convention area. Although contaminant concentrations in sea water are low the high volumes transported mean that fluxes are large and that ocean currents represent a major contributor of soluble contaminants and nutrients to the Convention area.

Many contaminants are adsorbed onto particulate matter and may become trapped in the sediment. The sediment however is subject to resuspension and bioturbation, leading to the potential re-mobilisation of contaminants or their burial in deeper layers.

4.3. Assessment criteria

OSPAR has developed and adopted 'Background/Reference Concentrations' (BRCs) and 'Ecotoxicological Assessment Criteria' (EAC) values as assessment criteria.

In general man-made substances would be expected to have a background concentration of zero. However, due to their persistence and long-range transport many substances are now detected all over the world. Therefore typical concentrations in remote and selected parts of the OSPAR area are used as background/reference concentrations. For naturally occurring substances the BRC is the range of concentrations that would be anticipated to be present in the environment in the absence of any human activity. **Tables 4.3, 4.4, 4.5 and 4.6** summarise available BRCs for trace metals in sea water, sediments and biota (mussel tissue) and for some persistent organic contaminants in sediments and sea water.

EACs are defined as concentration levels of a substance above which concern is indicated. Criteria for the specific contaminants were derived using all the available ecotoxicological data that passed predefined selection and quality criteria. In a number of cases EACs are provisional due to insufficient information and in these cases higher safety factors are included. These assessment criteria can be used to identify possible areas of concern and to indicate which substances might be a

Table 4.3 Ranges in background/reference concentrations of cadmium, mercury, lead and copper for fine-grained marine sediments, sea water and blue mussel within the OSPAR area.

	Sediment (metal/Al (x 10 ⁻⁴) ratio)	Sea water (ng/l)	Blue mussel (mg/kg ww)
Cadmium	0.007 – 0.04	5 – 25	0.07 – 0.11
Mercury	0.0034 – 0.0066	0.1 – 0.5	0.005 – 0.01
Lead	1.8 – 4	5 – 20	0.01 – 0.19
Copper	2.2 – 5.7	50 – 360	0.76 – 1.1

Table 4.4 Ranges in background/reference concentrations of PAHs in surface sediments (µg/kg dw) for application in selected regions of the OSPAR area.

	northern North Sea/Skagerrak	southern North Sea	Arctic Ocean/ Iceland Sea
Benzo[<i>a</i>]pyrene	8.8 – 112	< 0.2 – 51	1.0 – 3.8
Fluoranthene	14 – 160	0.72 – 97	1.5 – 7.5
Benzo[<i>b+k</i>] fluoranthene	46 – 434	1.1 – 142	7.4 – 30
Pyrene	11 – 128	0.6 – 78	1.7 – 6.4

Table 4.5 Ranges in background/reference concentrations of PAHs in surface water (ng/l) for application in selected regions of the OSPAR area.

	northern North Sea	central and southern North Sea	North-east Atlantic
Benzo[<i>a</i>]pyrene	0.002 – 0.005	0.002 – 0.004	0.001
Fluoranthene	0.073 – 0.285	0.104 – 0.264	0.036 – 0.054
Benzo[<i>b</i>] fluoranthene	0.004 – 0.017	0.003 – 0.009	0.001 – 0.004
Pyrene	0.014 – 0.053	0.011 – 0.024	0.02 – 0.033

Table 4.6 Ranges in background/reference concentrations of HCB, DDE and selected PCBs in surface sediments (ng/kg dw) for application in selected regions of the OSPAR area.

	southern Norway/ Skagerrak	Iceland Sea/ Norwegian Sea
HCB	70	40
CB28	31	< 10
CB52	32	< 10
CB101	62	16
CB138	116	26
CB153	90	20
CB180	60	< 10
DDE	66	40

goal for priority action. **Table 4.7** provides EACs for some important contaminants.

Caution should be exercised in using the assessment tools in specific situations. (See Chapter 5 for the use and limitations of EACs.) Use of the tools should not preclude the use of common sense and expert judgement with regard to the natural concentrations.

4.4 Trace metals

4.4.1 Introduction

The presence of detectable concentrations of metals in the environment does not necessarily indicate the existence of pollution. With the exception of man-made radionuclides, the ubiquitous presence of metals in water, sediments and biota is an inevitable consequence of their natural occurrence in the Earth's crust. Human activities have effectively increased the rate of natural weathering and consequently the rate at which metals are introduced into the environment. At their natural concentrations many metals play an essential role in biochemical processes;

organisms are also able to adapt themselves, at least partly, to changing metal levels.

4.4.2 Inputs

The relative importance of input sources for individual metals varies between regions. For offshore areas remote from riverine and direct discharges, atmospheric inputs are likely to dominate. Conversely, in near shore and coastal areas the situation is likely to be reversed. Riverine and direct discharge data for the OSPAR Regions are shown in **Figure 4.2**. The atmospheric input of metals has been less well studied, consequently information is scarcer. Estimates based on models have been made however and these are summarised in **Table 4.2**. For some regions, such as the North Sea, time-series estimates of atmospheric inputs based on observations are available (**Figure 4.3**).

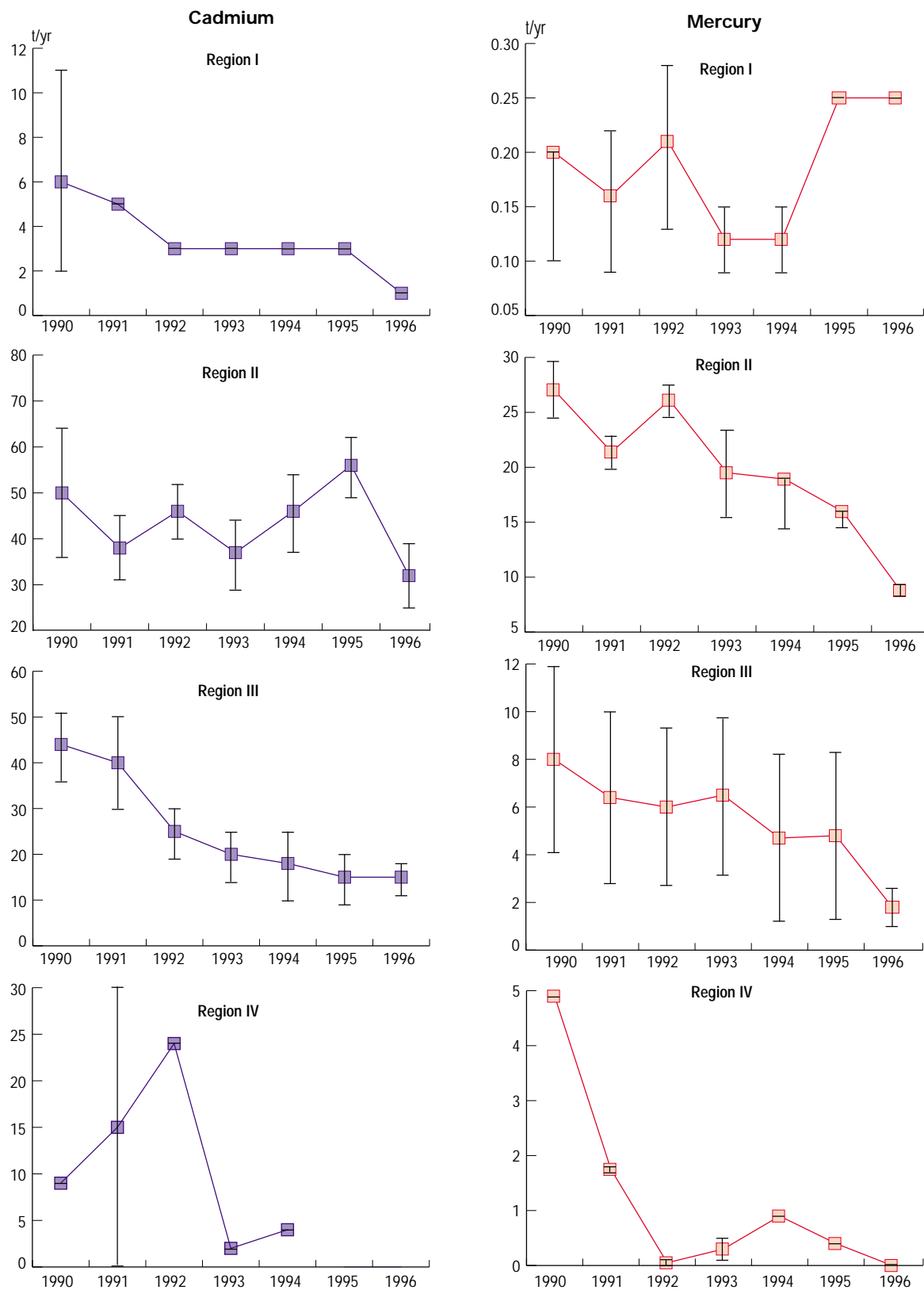
There was a general reduction in direct and riverine inputs between 1990 and 1996 as can be seen in **Figure 4.2**. The reduction in point source discharges, which are the most amenable to control, were mainly responsible for this trend. Specific examples include mercury inputs

Table 4.7 Overview of ecotoxicological assessment criteria for trace metals, PCBs, PAHs, TBT and some organochlorine pesticides.

	Water ($\mu\text{g/l}$)	Sediment (mg/kg dw)	Fish (mg/kg fw)	Mussel (mg/kg dw)
Cd	0.01 – 0.1*	0.1 – 1 [†]	fc	fc
Cu	0.005 – 0.05* [‡]	5 – 50 [†]	fc	fc
Hg	0.005 – 0.05*	0.05 – 0.5 [†]	fc	fc
Pb	0.5 – 5*	5 – 50 [†]	fc	fc
Zn	0.5 – 5*	50 – 500 [†]	nr	nr
DDE	nr	0.0005 – 0.005 [†]	0.005 – 0.05*	0.005 – 0.05*
Dieldrin	nr	0.0005 – 0.005 [†]	0.005 – 0.05*	0.005 – 0.05*
Lindane	0.0005 – 0.005	nr	0.0005 – 0.005*	nr
Naphthalene	5 – 50*	0.05 – 0.5*	nr	0.5 – 5 [†]
Phenanthrene	0.5 – 5 [†]	0.1 – 1*	nr	5 – 50 [†]
Anthracene	0.001 – 0.01 [†]	0.05 – 0.5*	nr	0.005 – 0.05 [†]
Fluoranthene	0.01 – 0.1 [†]	0.5 – 5 [†]	nr	1 – 10 [†]
Pyrene	0.05 – 0.5 [†]	0.05 – 0.5 [†]	nr	1 – 10 [†]
Benz[<i>a</i>]anthracene	nd	0.1 – 1 [†]	nr	nd
Chrysene	nd	0.1 – 1 [†]	nr	nd
Benzo[<i>a</i>]pyrene	0.01 – 0.1 [†]	0.1 – 1 [†]	nr	5 – 50 [†]
ΣPCB_7	nr	0.001 – 0.01 [†]	0.001 – 0.01*	0.005 – 0.058
TBT	0.00001 – 0.0001*	0.000005 – 0.00005 [†]	nr	0.001 – 0.01*

Sediment data are for a reference content of 1% organic carbon. * firm; [†] provisional; [‡] this range is within the range of background values for natural waters. This value should be compared with the bioavailable fraction of copper in sea water; fc for future consideration; nr not relevant to the current monitoring programme; nd no data available or insufficient data available; ΣPCB_7 represents the sum of CB28, CB52, CB101, CB118, CB138, CB153 and CB180.

Figure 4.2 Trends in direct and riverine inputs of cadmium, mercury, lead and copper. Data for Region I cover the Norwegian and Barents Sea sub-regions only.



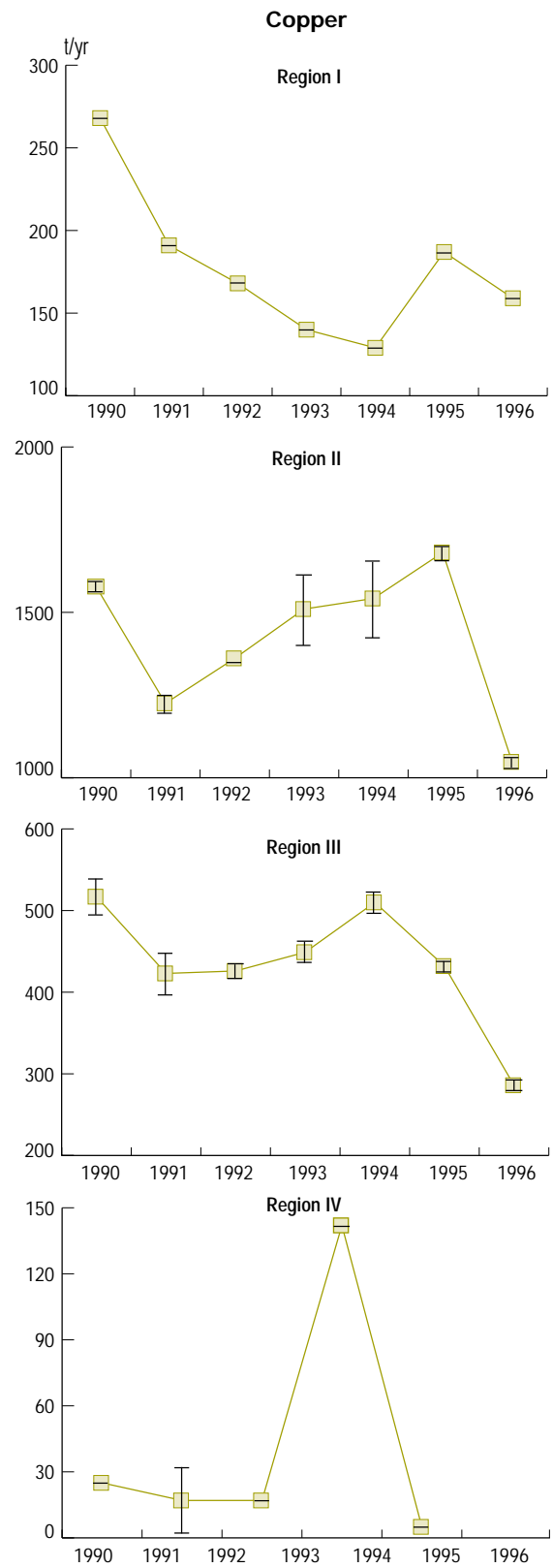
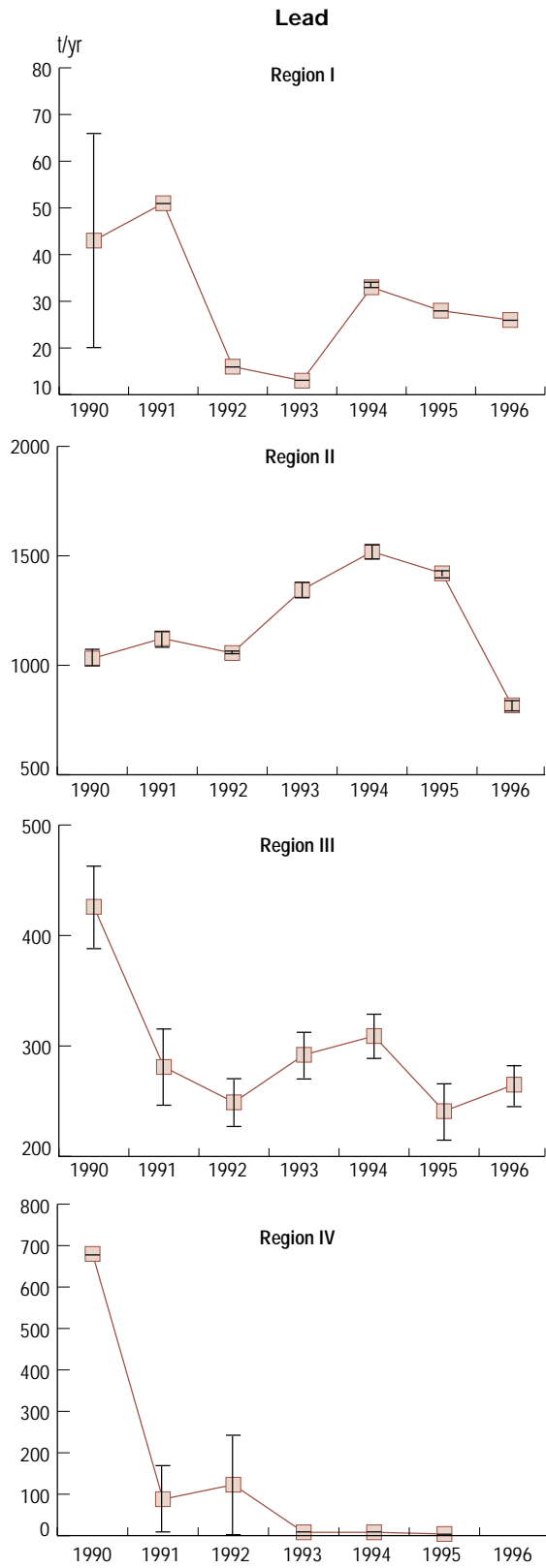
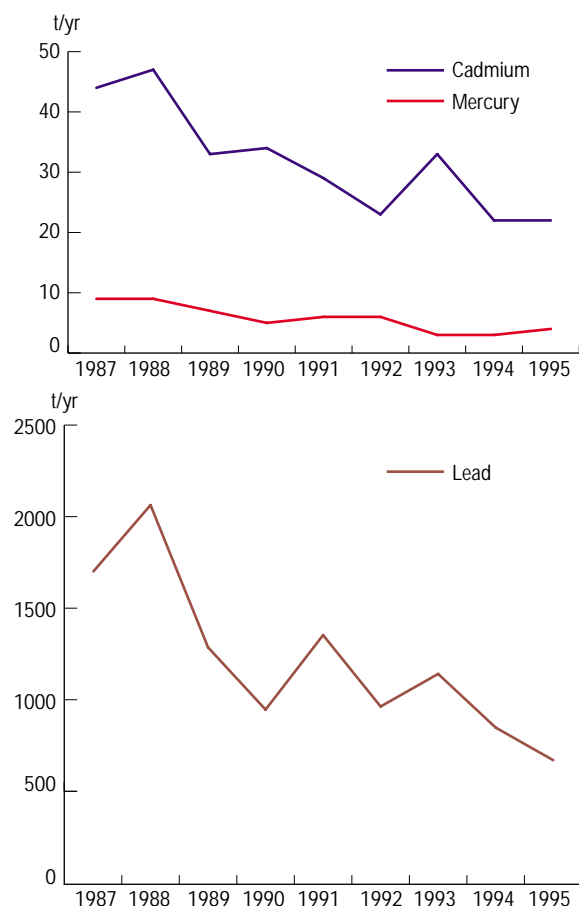


Figure 4.3 Atmospheric inputs of cadmium, mercury and lead to the North Sea (~ 525 000 km²) based on measurements.



from two chlor-alkali plants in Portugal where, between 1991 and 1996, inputs decreased from 284 to 45 kg/yr. The pattern of input reduction varies however, for example between 1990 and 1996 there was a strong decrease in lead in the river Elbe while an increase was reported for the Weser. Even where particular activities have ceased (e.g. within the mining and chlor-alkali sectors), their historical activity is likely to provide a legacy of contamination to specific areas (e.g. lead inputs from historic mining activities in Region III).

The reductions in inputs associated with the control of point sources, lead to an increase in the relative importance of diffuse sources. The inherent variability associated with river flows and rainfall means that considerable uncertainty remains regarding the magnitude of inputs relating to diffuse sources.

Atmospheric inputs of metals to the North Sea have generally decreased (*Figure 4.3*). In the North Sea, atmospheric inputs of lead decreased by 50 – 65% between 1987 and 1995 such that the dominant source is now taken to be rivers. Decreasing atmospheric lead inputs are reported

from several Regions and these have been attributed to the reduction in use of alkyl lead derivatives in petroleum.

Changes in the pattern of use of chemicals are also evident in other industries. An example arises as a consequence of the banning of TBT-based antifoulants in mariculture and on small boats. The consequent shift to copper-based formulations has resulted in increased inputs of copper and this is of particular relevance to semi-enclosed areas and bays, for example those on the French Atlantic coast.

Since the introduction of PARCOM Decision 90/3, emissions of mercury to air from chlor-alkali plants in the Convention area have fallen significantly and now meet the key emission limit value of 2 g Hg/t chlorine capacity, due to better emission controls and conversion to less polluting technology. Total mercury losses through 'product, water and air' from the 48 'mercury cell' chlor-alkali plants operating in Western Europe (34 within the Convention area) decreased from 56.7 t in 1982 to 8.5 t in 1997.

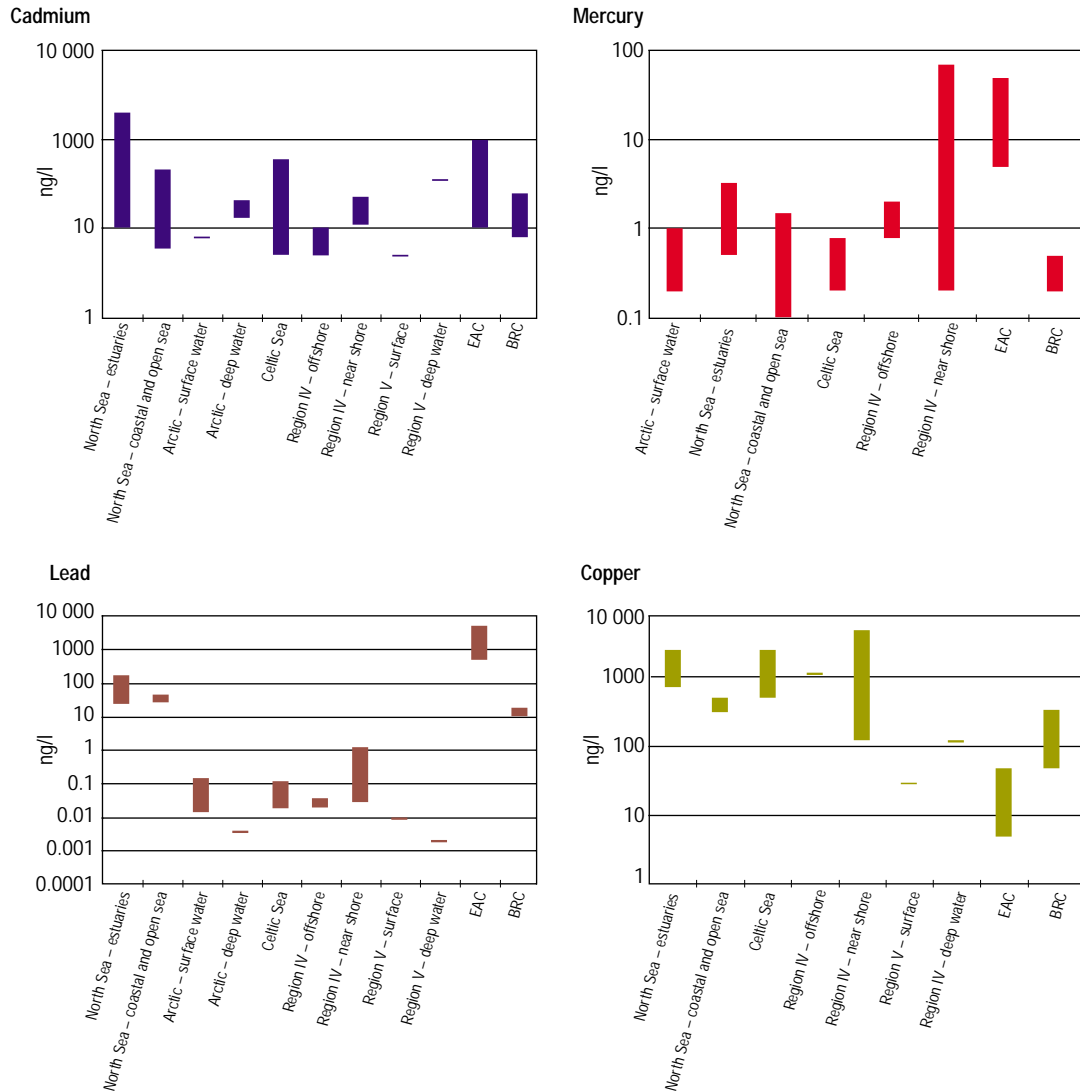
4.4.3 Concentrations in sea water

Figure 4.4 provides a selection of representative data on metal concentrations in sea water from the different Regions of the maritime area. In oceanic areas, cadmium, and to a lesser extent copper, behave similarly to nutrients. Biological activity in surface waters incorporates the elements into particulate material, depleting concentrations in the dissolved phase. The decomposition of the particulate material as it sinks leads to a regeneration of the incorporated elements, and a consequent increase in dissolved phase concentrations with depth. By contrast the depth profile for lead (with a dominant atmospheric source) exhibits a surface maximum in concentration, followed by a decrease with depth associated with dilution and scavenging by particles.

In coastal and estuarine waters the observed pattern of dissolved trace metal distributions reflects the increased importance of riverine inputs, and also the extent to which the elements interact with suspended particulate material. Cadmium and copper tend to exhibit inverse relationships with salinity, this relationship is less apparent for lead and mercury that are termed 'particle reactive' and rapidly become associated with particulate material.

For oceanic and offshore areas the reported concentrations are comparable to the BRCs, indicating that widespread contamination is not a general problem. Close to known point sources however the BRCs are sometimes exceeded, indicating localised contamination (*Figure 4.4*). The practical difficulties in applying BRCs have been recognised. For example, given that riverine concentrations of metals generally exceed those in sea water, it is almost inevitable that BRCs based on offshore concentrations will be exceeded in estuaries. Additionally,

Figure 4.4 Concentrations of cadmium, mercury, lead and copper in sea water.



the estuarine geochemistry of metals must also be taken into account. For example the solubilisation of particulate cadmium during estuarine mixing leads to a general mid-estuarine maximum in concentration for this element.

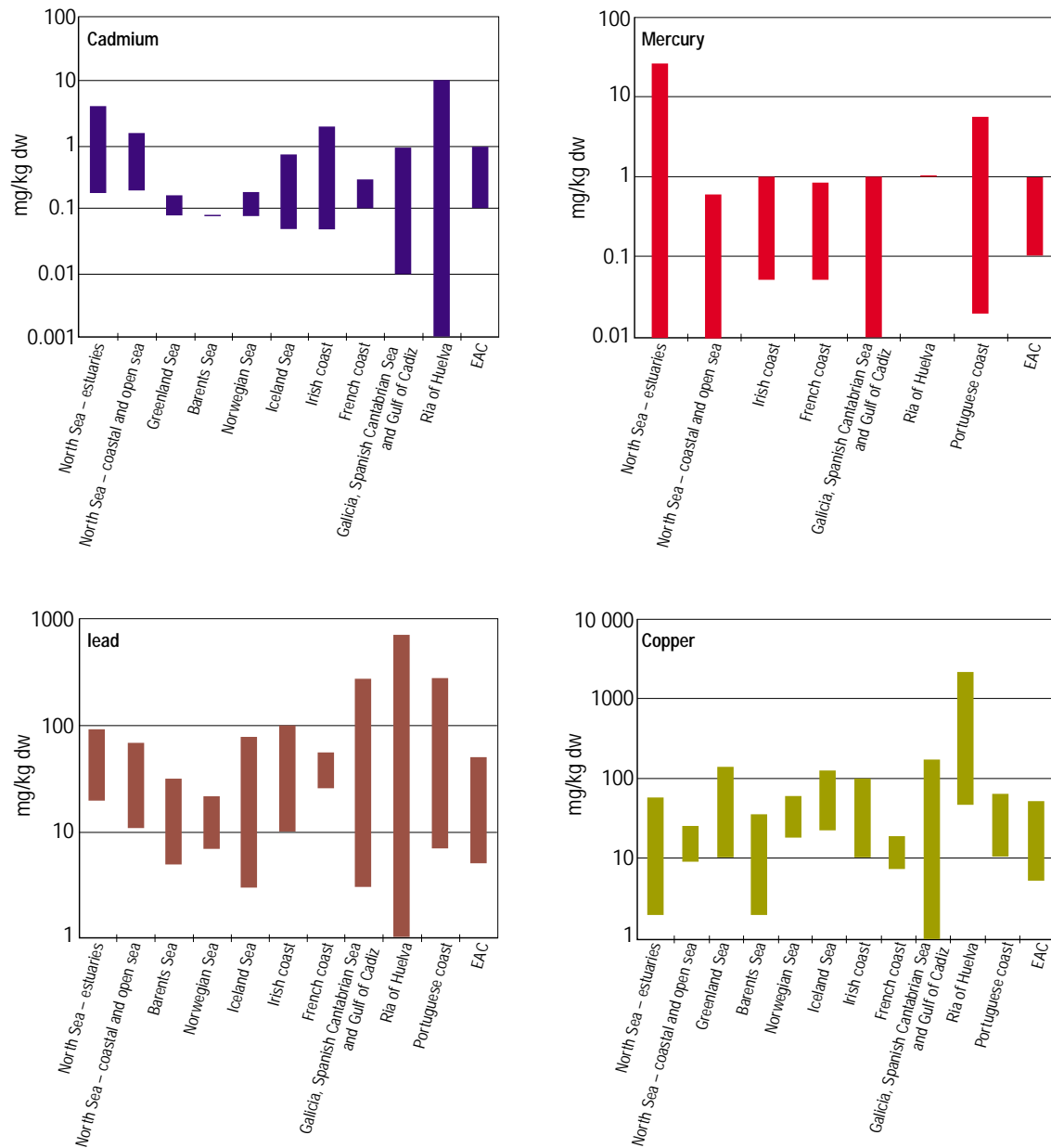
Examples of situations where metal (except copper) concentrations exceed the upper EAC limits are unusual. Such instances are limited to cadmium (upper EAC 0.1 µg/l) in estuaries of the North Sea and mercury (upper EAC 0.05 µg/l) in near shore areas of Region IV. In those areas where monitoring has taken place for copper, the upper EAC limit of 0.05 µg/l is routinely exceeded almost everywhere. The EAC for copper is less useful as a criterion because the toxicological value is only slightly higher than the value needed to avoid biological deficiency.

In some areas decreases in concentration over time have been reported for some metals, for example a 50% decrease in dissolved cadmium for the southern Bight of the North Sea. Decreases in particulate mercury concentrations have been observed in the river Elbe, comparable to those in the Seine and the Scheldt estuaries. Because there have been major improvements in analytical methods for metals in recent years, it is not always possible to compare recent and historical (pre-1980s) data.

4.4.4 Concentrations in sediments

Figure 4.5 provides a selection of representative data on metal concentrations in sediments from the different

Figure 4.5 Concentrations of cadmium, mercury, lead and copper in sediment.



Regions of the maritime area.

When interpreting trace metal in sediment data the difficulty is to establish the extent to which the concentrations observed are determined by geological sources and/or anthropogenic inputs. The geological sources can be non-negligible; for example, in Region I differences in copper concentration between areas dominated by tertiary volcanic rock (9 – 140 mg/kg dw) and those with non-volcanic rock (10 – 40 mg/kg dw) are explained by variations in local geological influences. Trace metals associate preferentially with fine-grained material in the sediment. Natural variability is taken into account by

normalising the measurements in order to compare sediments from different regions. OSPAR has adopted metal/aluminium ratios as the basis for its background/reference concentrations for fine-grained sediments. In Region I, mercury in Arctic sediments showed a general pattern of increase in the upper layers of sediment cores.

Results reveal a general tendency for metal concentrations to be higher close to coastal inputs of anthropogenic or riverine origin. The upper EACs for cadmium, lead, mercury and copper (respectively 1, 50, 0.5 and 50 mg/kg dw) are exceeded at some locations (*Figure 4.5*). The elevated metal concentrations at these

locations are associated with their proximity to particular activities or industries, both contemporary and historical. Examples include dredged spoil disposal areas (e.g. for lead in the Rotterdam Harbour area), mercury from the chlor-alkali industry (Spain: Pontevedra ria; Portugal: Aveiro and Lisbon; UK: Mersey Estuary) and cadmium from earlier phosphoric acid manufacture (north-eastern Irish Sea).

In general, metal concentrations in sediments from estuaries tend to be higher than in those from coastal areas. Mercury concentrations have been reported to decrease over time in the vicinity of disused disposal sites, for example in the German Bight and off the Belgian coast. In Region II, cadmium levels in sediments from the Dutch coastal zone have significantly decreased in those areas where concentrations had previously been the highest. In the Scheldt estuary the maximum concentrations decreased by a factor of three between 1990 and 1995. Copper concentrations decreased between 1981 and 1996 in the areas north and south of the Rhine/Meuse mouth, and in the area offshore. Decreases were also observed along the Belgian coast and in the Wadden Sea.

4.4.5 Concentrations in biota

Table 4.8 (for mercury) and **Figure 4.6** (for cadmium, lead and copper) provide a selection of representative data on trace metal concentrations in a range of biota from the different Regions of the maritime area.

Mussels

The highest concentrations tend to occur in the vicinity of specific industrial sources or are associated with diverse inputs from densely populated areas. Ratios of observed cadmium and lead concentrations to BRCs are high in Norwegian fjords with smelting activity (Sørfjord). Despite introduction of cleaner technologies, the chlor-alkali industry continues to represent a source of mercury con-

amination in several places.

Some of the reported decreases in contaminant concentrations in biota can be linked to reductions in specific discharges. Examples include a 50% reduction in cadmium concentrations in mussels from the Seine Estuary following the prohibiting of phospho-gypsum discharges in 1992, and a decline in copper concentrations in mussels from the Elbe, associated with the decline of the former GDR chemical industries.

For the period up to 1996, trend analysis of metal concentrations in mussel has revealed:

- significant decreases in cadmium concentrations in mussels from the Netherlands (Westerschelde and Ems-Dollard), Norway (Sørfjord and Hardangerfjord) and along the French coast;
- significant decreases in lead concentrations in mussels from Germany (Borkum), the Dogger Bank, Norway (Sørfjord) and Spain (Pontevedra, A Coruña and Bilbao);
- significant decreases in copper concentrations in mussels from Denmark (Hvide Sande), Germany (Jadebusen, Borkum), the Netherlands (Terschelling), Norway (Oslofjord, Sande and Sørfjord) and Spain (Bilbao);
- significant decreasing trends in lead concentrations in mussels from the vicinity of the Loire, Germany, along the Belgian coast, the Dogger Bank and Norway;
- significant decreasing trends in mercury concentrations in mussels from Spain (A Coruña and Bilbao); and
- no significant temporal trends in cadmium concentrations in mussels from the Spanish coast.

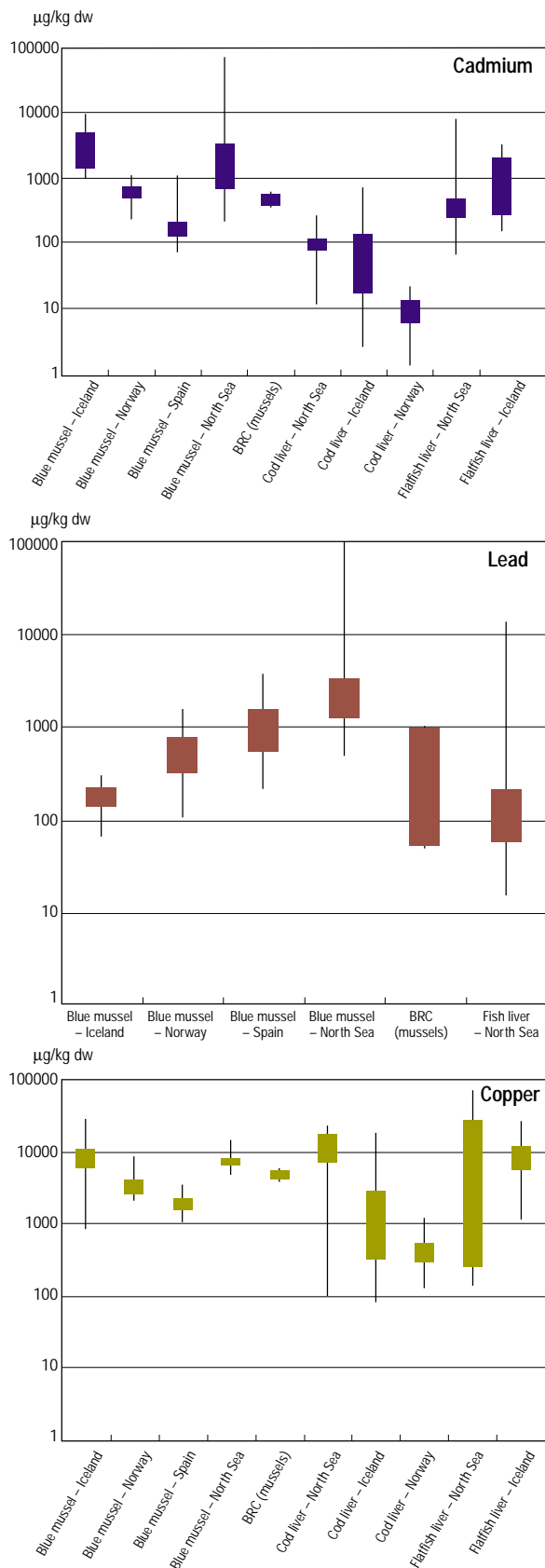
Time trend analysis of copper in mussel and/or fish tissue revealed linear downward trends in Denmark, Germany, the Netherlands, Norway and Spain. By contrast, increasing concentrations of copper have been reported in oysters from the Bay of Arcachon. Concentrations have approximately doubled over the past

Table 4.8 Mercury in biota (mg/kg ww).

	Mussel	Roundfish liver	Roundfish muscle	Flatfish	Deepwater species – liver	Deepwater species – muscle
Region I						
Arctic	0.01 – 0.02		0.01 – 0.1			up to 0.21
Region II						
whole Region	0.01 – 0.03		0.05 – 0.1			
Region III						
Ireland	0.02 ± 0.01		0.11 ± 0.07			
Region IV						
Bay of Biscay	0.11 – 0.26*					
Spanish coast	0.05 – 0.66*			0.15 – 0.4*		
Region V						
Atlantic					0.015 – 0.288	0.02 – 0.88

* mg/kg dry weight (all the other data are expressed as wet weight).

Figure 4.6 Concentrations of cadmium, lead and copper in biota.



ten years, and this has been attributed to copper-based antifoulants which, since 1982, have been used as a replacement for the TBT-based paints that were banned in that year.

Fish

As for mussels the geographical patterns of metal concentrations in fish continue to reflect historical and current sources of contamination. For example, past discharges of mercury from chlor-alkali plants close to the Mersey and Wyre estuaries in north-west England are well documented and result in higher concentrations of mercury in fish muscle from that area. Data for mercury in fish flesh from this area, obtained for the application of an environmental quality standard (EQS), suggest declining concentrations. In Region III, mercury is the only metal for which the observed concentrations in biota gave rise to concern. Provided that measures to control the input of mercury continue to be applied, it is unlikely that concentrations will present a threat to marine organisms or human consumers of seafood.

The time trend analysis of metals in fish data indicates significant downward trends in cadmium concentrations for flounder (*Platichthys flesus*) livers in Westerschelde and the inner Sørfjord and for cod livers at the Swedish site Fladen. Significant downward trends for mercury in flounder are observed along the Belgian coast, in the Ems-Dollard, Wadden Sea and Elbe, and also in plaice from the Southern Bight of the North Sea.

Mammals

Information on metal concentrations in marine mammals is largely limited to Regions I and III. Cadmium concentrations tend to be higher in kidney than liver and muscle and blubber levels are low. By contrast mercury concentrations tend to be highest in the liver. The differences in lead concentration between tissues are not as distinct as for cadmium and mercury, the highest concentrations tending to be in liver and kidney. An increase in cadmium and mercury concentrations with age has been noted for seals, whales and polar bear.

Copper concentrations are believed to be homeostatically controlled within marine mammals and are therefore generally not of concern. In Region III, samples of various tissues taken from stranded and by-caught marine mammals over a number of years have been analysed. Most of the animals were taken around the Irish Sea and off the Scottish coast. With the exception of cadmium, where the highest concentrations are found in the kidney, the highest concentrations of metals are generally found in the liver. High concentrations of lead and mercury were found in animals from the Liverpool Bay area, probably due to past industrial discharges: highest concentrations, 7 and 430 mg/kg respectively, were encountered in grey seals (*Halichoerus grypus*). Marine mammals appear to

have a mechanism for detoxifying the mercury as mercury selenide. The highest concentrations of cadmium (up to 11 mg/kg) were found in the livers of striped dolphins (*Stenella coeruleoalba*). This is attributed to the dominance of squid, which accumulate cadmium naturally, in their diet rather than to direct anthropogenic sources. There are few data for samples from the Irish coast, but mercury concentrations in samples from Strangford Lough in Northern Ireland were among the higher values encountered in the Region. Off the Scottish coast, samples taken from a variety of stranded marine mammal species (over a period stretching back almost twenty-five years) have been analysed. In all cases, the concentrations found were at the lower end of the ranges for the species concerned.

4.5 Organic pollutants

4.5.1 Introduction

Many organic substances are released to the marine environment. Many of them are degraded rather effectively, while more persistent compounds may be distributed over large areas and accumulate in organisms. Within OSPAR, attention is given not only to POPs but also to a range of hazardous substances based on a range of criteria such as bioaccumulation and toxicity (see Glossary).

Most of the contaminants dealt with in this section are not single substances, in some cases they are made up of several hundreds or even thousands of individual compounds. This complicates the presentation of analytical results since these can represent the whole mixture or one or several individual compounds. Furthermore these results can be related to different matrices, for example wet weight, dry weight or lipid weight. Additionally variations in the composition of the matrix can influence the result, for example the number of particles in the air or water, the organic carbon content of the sediment and the lipid content of the tissue. The absence of information on these factors limits the extent to which data from different sources can be compared.

4.5.2 Organotin compounds

Inputs

Organotin compounds have had a widespread use as antifouling agents in paint formulations for ships. Despite the ban (introduced in 1990) on the use of TBT on vessels under 25 m in length, many areas still show the legacy of historical inputs. However, its continued use on larger vessels is now the major source for the marine environment. In addition to direct leaching from hulls, dry docks

(where the hulls of ships are cleaned by sandblasting) and wastewater treatment plants (where a proportion of the organotin compounds may be discharged in the effluent) also represent potentially important sources. In the past, finfish aquaculture sites were a significant local source of TBT. This industry now uses modern antifoulants that contain copper and booster biocides as the active ingredients. Recent studies in Denmark indicate that both copper and booster biocides, which are now replacing TBT-based antifoulants, are likely to be present in certain areas of the marine environment at concentrations which might impact on the biota. Sewage treatment plants can be a significant source of dibutyltin in coastal areas and estuaries.

Sea water

The toxicological effects of TBT on molluscs occur at very low concentrations in sea water, below the levels that can be routinely measured by most laboratories. Consequently, the existence of TBT contamination is frequently inferred from biological indicators (i.e. imposex measurements).

The general picture of TBT levels in sea water indicates that concentrations offshore are generally less than the detection limit, whereas much higher values are found in frequently used waterways. This creates great difficulties for sea water monitoring. TBT released to the water will degrade to dibutyltin and monobutyltin. Usually only TBT and total organotin values are reported, which makes it difficult to construct budgets for the fate and distribution of organotin compounds.

Toxicological effects due to TBT have been observed at very low concentrations and therefore the EACs are very low, even below detection limits.

Sediments

Sediments are sinks for TBT. However, resuspension can sustain higher concentrations in overlying waters. TBT is highly persistent in anaerobic sediments. The concentrations in sediment vary over a wide range. The highest concentrations of organotins are observed in harbours, marinas and along major shipping routes (e.g. as high as 10 mg/kg). In offshore areas it can be difficult to detect these compounds.

The EAC is 5 – 50 ng/kg dw; in all places that were monitored the concentrations were above the EAC and in some places the concentrations exceeded the EAC by six orders of magnitude.

Biota

In blue mussels and some other species, a geographical distribution similar to that in sediments is observed. A wide range of concentrations has been reported. TBT has now also been identified in higher organisms including whales, although the levels in mammals are at the lower end of the range.

4.5.3 Polychlorinated biphenyls

Inputs

Polychlorinated biphenyls are synthetic compounds that were used extensively in a variety of industrial products, including transformer and capacitor oils, hydraulic and heat exchange fluids, and as plasticisers in paints, plastics and sealants. There are 209 different forms of PCB (congeners) of which about 150 are used in technical products. However, the same properties that led to their extensive use in industry (resistance to degradation, low volatility etc.) also make them persistent environmental contaminants.

Total accumulated world production of PCBs has been estimated at 2 million t and much is still contained in sealed systems. Releases occur for example as leaks from sealed systems, accidental losses and spills, and emissions from PCB-containing materials and soils. OSPAR countries have banned the major PCB uses for some years. OSPAR and EU regulations aim at a complete phase out of PCBs in the period between 1995 and 2010. However, not all PCBs in smaller applications, in particular in electrical equipment, may be removed within that period.

PCBs emitted and deposited during the years of intensive production and use are still a diffuse source to the global environment. Evaporation of PCBs from polluted soils and waters has been shown to be a significant source to the atmosphere. Once in the atmosphere, PCBs enter the global circulation and can be transported to remote places. The atmospheric input through precipitation in the OSPAR Convention area is estimated to be 3 – 7 t/yr for the period 1992 to 1994. Riverine and direct inputs of PCBs are low in absolute terms. Although it is not possible to derive reliable estimates of inputs because most concentrations are below the limit of detection, estimates derived for the Greater North Sea were in the range 0.13 – 2.4 t/yr for the period 1990 to 1995.

Individual PCB congeners have a range of toxicity and physical properties, such as their solubility and vapour pressure. Thirteen of them, which have a flat (planar) structure, cause effects similar to those of the chlorinated dioxins, but they are not as potent as the most toxic dioxins. PCB concentrations are often reported as the sum of seven congeners (ΣPCB_7) or as 'total PCB'.

Sea water

PCBs are hydrophobic compounds; i.e. they have extremely low water solubilities. Concentrations in ocean water are generally very low and this makes reliable quantification difficult. PCB concentrations in filtered ocean water are usually reported to be in the low pg/l range.

Sediments

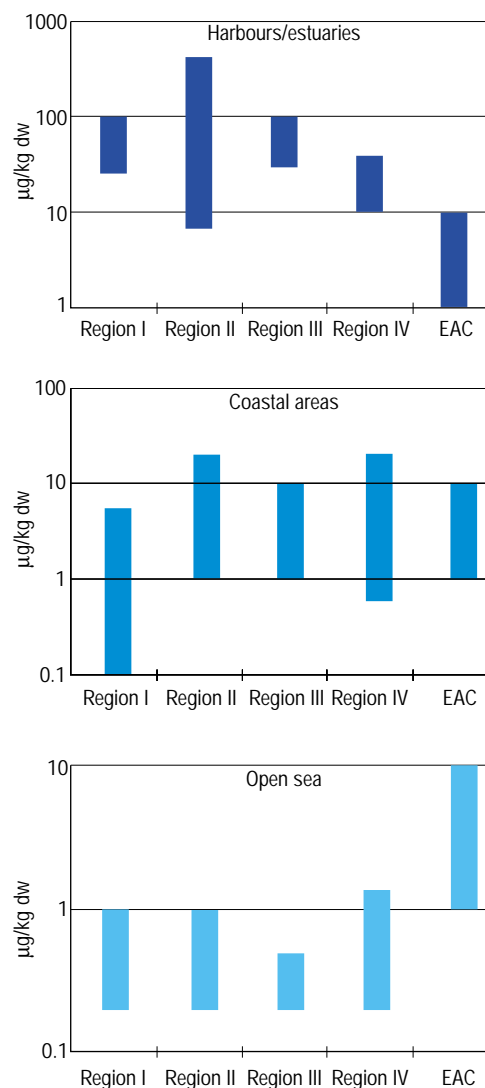
The ΣPCB_7 concentrations found in sediments depend

not only on the distance from point sources, but also on the organic carbon content of the sediment. Therefore, in more contaminated estuarine areas, concentrations of several hundred $\mu\text{g}/\text{kg dw}$ have been measured, and in areas distant to the coasts levels are relatively low (Figure 4.7). These sediment-bound PCBs may re-enter overlying waters as a result of resuspension of the sediment. The provisional EAC for ΣPCB_7 in sediment is 1 – 10 $\mu\text{g}/\text{kg dw}$, indicating that there may be cause for concern in the more contaminated areas.

Biota

As a consequence of their hydrophobic and persistent character PCBs are bioaccumulated and high concentrations are found in biota. Mussels are used to monitor the

Figure 4.7 ΣPCB_7 in sediment.



levels in several places and in all Regions except Region V levels higher than the EAC have been reported.

Elevated PCB concentrations have been measured in many of the Regions. PCBs are accumulated by marine organisms, especially within the fatty tissues of piscivorous birds and marine mammals. Anomalously high concentrations of PCBs were found during the early 1990s in cetaceans from Cardigan Bay in the southern Irish Sea and in otters from south-west Ireland.

Most of the reported concentrations of ΣPCB_7 in fish exceed the EAC (1 – 10 $\mu\text{g}/\text{kg}$ fw), sometimes by several orders of magnitude. In the livers of whiting from Liverpool Bay and Morecambe Bay the levels of ΣPCB_7 recorded in 1996 were 1900 $\mu\text{g}/\text{kg}$ and 1700 $\mu\text{g}/\text{kg}$ ww respectively. The range in cod liver from Region I is 28 to 615 $\mu\text{g}/\text{kg}$ ww (Figure 4.8). Seabirds (in Region I) and marine mammals, at the top of the food chain, contain still higher ΣPCB_7 concentrations (Figure 4.9).

The declining use and progressive elimination of PCBs have been reflected in the decreasing concentrations observed in ten of the long-term monitoring programmes evaluated. An example is gannet eggs from Ailsa Craig and Scar Rocks (Region III) where PCB concentrations decreased by more than 90% between the 1970s and the mid-1980s. In recent years, a decline in PCBs has been observed in cod liver from Iceland and in seabirds from northern Norway and Svalbard. The same trend has been observed elsewhere, but the rate of reduction decreased in the 1990s and concentrations appear to have levelled out.

There is weak evidence that PCB concentrations in biota have generally decreased. A small number of significant downward trends were observed along the south-west coast of Norway and in the southern North Sea (the Oyster Ground and along the west coast of Belgium).

4.5.4 Dioxins and furans

Inputs

The term dioxin is used to describe two groups of substances: polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs). There are 210 congeners of dioxins and furans, but only seventeen are regarded as very toxic. The World Health Organisation (WHO) has adopted a human Tolerable Daily Intake (TDI) for dioxins (including the PCBs) of 1 – 4 pg/kg body weight per day. In several European countries the human intake of dioxins is within or above this range and this provides an extra reason to reduce emissions of these hazardous substances to the environment.

Dioxins are not produced intentionally, but arise as by-products in some chemical processes. They are formed during a number of thermal processes, such as waste incineration and metallurgical processes, through

Figure 4.8 ΣPCB_7 in cod liver in Region I.

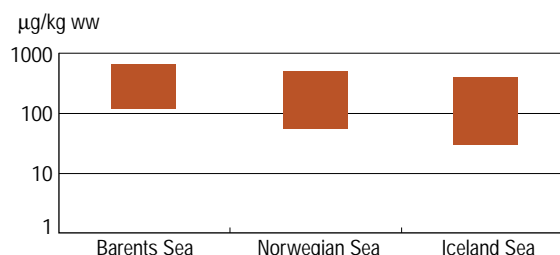
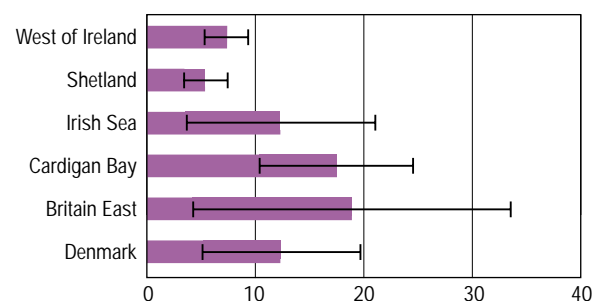


Figure 4.9 Mean concentrations (± 1 standard deviation) of ΣPCB_7 in the blubber of male harbour porpoises (mg/kg lipid) from areas of Region II and Region III.



the use of active chlorine, for example in the bleaching of pulp, and during the production of certain chlorinated chemicals.

Sediments and biota

Information on dioxin levels in the Convention area is scarce, but a few point source emissions have been well studied, such as in Frierfjorden in Region II. Comparison of measurements for surface sediments shows that dioxin concentrations seem ten to twenty times lower in samples from the Barents Sea than in samples from the northern North Sea. The proportion of more volatile congeners is relatively high in the Barents Sea indicating a fractionation process. In general, concentrations of PCDD/Fs in Arctic seals are lower than in animals from the Baltic Sea and the North Sea, but higher than those found in Antarctic seals.

High levels of dioxins in sediments and biota were found near a magnesium production plant on the south coast of Norway. Concentrations in sediments were five to a hundred times higher than the background levels, even 20 km from the source. The presence of high dioxin levels in the tissue of several seafood species from locations close to the factory reflects the high values in sediments at those sites. Despite the 1990 reduction target, concentrations of these compounds in edible species have not decreased enough to lift the restrictions on consumption.

In the Dutch coastal zone, the highest concentrations

of dioxins have been measured in the estuaries of the rivers Scheldt and Rhine. In these areas there was no significant change in the concentrations of dioxins between 1985 and 1994.

4.5.5 Hexachlorobenzene

Inputs

Hexachlorobenzene was previously used as a fungicide, but today the major sources are associated with incomplete combustion, limited use as a pesticide and disposal at dumpsites.

Sea water

As HCB is hydrophobic concentrations in the relatively few sea water samples analysed are in the ng/l range or below the detection limit. High HCB concentrations are reported in sediments from the Forth Estuary (two orders of magnitude higher than elsewhere in Scotland) reflecting known historic inputs. Concentrations in the Scheldt Estuary were comparable. In Irish Sea sediments HCB is present at low, almost background levels.

Biota

Concentrations of HCB in the livers of flatfish sampled at sites in the Irish Sea were low, while slightly higher levels occurred in the livers of dab (*Limanda limanda*) from Liverpool Bay. The levels of HCB in the blubber of harbour porpoises stranded on the coasts of the Irish Sea and to the west of Ireland are in the range 300 – 600 µg/kg lw. No EAC or BRC has been adopted for HCB. The International Programme on Chemical Safety (IPCS) has identified a TDI of 160 ng/kg body weight per day, indicating that the levels observed in fish do not pose a problem for human consumption.

There is evidence that HCB concentrations in biota have generally decreased. A number of significant downward trends were observed in some southern Norwegian fjords, in the Kattegat, in the southern North Sea (including the German Bight) and along the north coast of Wales.

4.5.6 Pesticides

Lindane is the name for the early technical formulations of hexachlorocyclohexane (HCH) products (α -, β -, γ -HCH). Today, however, pure γ -HCH is used. Lindane is relatively volatile and consequently effectively transported over long distances via the atmosphere. Lindane is also more water-soluble than most of the other chlorinated hydrocarbons discussed in this report, and a major input is via rivers from the application areas. There are indications of a slight decrease in the riverine input of lindane to the Irish Sea.

In water, lindane concentrations are higher in the

southern North Sea and the German Bight than in the north-western North Sea. The highest concentrations exceed the EAC (0.5 – 5 ng/l).

Concentrations of lindane in fish liver and mussel tissue generally decreased during the period 1990 to 1995, especially in relatively polluted regions of estuaries, fjords and near coastal zones. In contrast, a significant upward trend was observed in dab muscle from Lista (southern Norway) for the same period. Concentrations of lindane in mussels around the Irish Sea, Bristol Channel, Celtic Sea and Atlantic coasts are in the µg/kg ww range and, in the livers of flatfish from the Irish Sea, are approximately ten times higher. In a UK study, the highest levels of lindane in fish liver occurred in Liverpool Bay. Concentrations of α - and γ -HCH in the blubber of stranded male harbour porpoises from the Irish Sea and west of Scotland during the past ten years have been approximately 2000 – 4000 µg/kg lipid.

There is evidence that lindane concentrations (α -, γ -HCH) in biota have generally decreased. A number of significant downward trends were observed in southern and south-western Norwegian fjords, in the Kattegat, and in the southern North Sea (along the west coast of Belgium, the Oyster Ground, the German Bight).

DDT is metabolised in the environment to produce DDE and DDD; the major compound found in biota is often DDE. The analytical results are, however, often expressed as total DDT, which is the sum of the parent compound and its metabolites. DDT has been used in large amounts, but is today banned in many countries, including those in Western Europe and North America. It is still used in other parts of the world, especially in tropical climates, areas from which it is subject to long-range transport.

In sediments DDD is the major component of the DDT derivatives; but data are usually reported as total DDT. Comparison with EACs is difficult because only an EAC for DDE is available. The available data, however, have not revealed any locations with significantly elevated concentrations.

All concentrations of DDT in commercial species from the Irish Sea, for the ten years prior to 1996, were below EACs for DDE. Some DDE data for mussel and fish exceed the EACs (i.e. mussel: 5 – 50 µg/kg dw, fish: 5 – 50 µg/kg ww) which indicates that some concern is still necessary.

Up to the mid-1980s, the eggs of seabirds from colonies in the Malin Sea and Celtic Sea, as well as on the Atlantic coast of Ireland, had concentrations of DDE in excess of 1000 µg/kg ww. However, records from the 1990s indicate that there has been a marked decrease in concentrations of DDE at most of these sites and in the eggs of seabirds levels are now generally below 400 µg/kg ww. Levels of DDE in the blubber of male harbour porpoises stranded in the Irish Sea and to the west of

Scotland and Ireland during the past ten years have been in the range 2000 – 6000 µg/kg lipid (**Figure 4.10**).

For DDT there is evidence that concentrations in biota have generally decreased, whereas for related compounds (e.g. DDE, TDE) no such conclusions can be drawn. Four of seven DDT time series revealed significant downward trends, for example in the Kattegat and in the southern North Sea. A number of DDE time series from several sites, for example on the north coast of Wales, the west coast of Belgium, the western Dogger Bank, the Kattegat, and in some southern Norwegian fjords, showed significant decreasing trends.

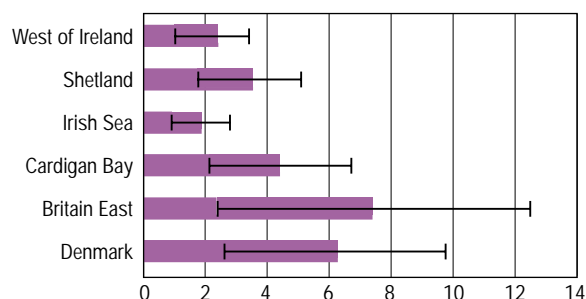
Toxaphene is a trade name for a pesticide of very complex composition. Until recently the analytical results were reported as total toxaphene, but today reference compounds have been synthesised and major emphasis is given to three individual congeners that seem more stable than the others. Toxaphene has not been used in the OSPAR region. However, the pesticide has been used extensively in cotton-producing countries, and is another example of a pollutant that is subject to long-range transport. This pesticide, because of its high toxicity to fish, was also used as a piscicide in some non-OSPAR countries.

The large volumes that were produced (no known production today) and the use pattern have resulted in high toxaphene concentrations in the environment and these concentrations are often the highest of all the organochlorine contaminants. Analyses of white fish and mackerel sampled around Ireland and the UK indicate higher levels to the west of Ireland than in the Channel. Some years ago Germany introduced a tolerance level (10 µg/kg ww) for toxaphene in fish to be marketed. This level was exceeded in many fish samples, including species from the marine environment. This tolerance level was reconsidered and adjusted to 100 µg/kg ww for the sum of three congeners. Areas remain where toxaphene concentrations can be expected to cause effects on the ecosystem.

Dieldrin has no known use today but previous usage may still affect the environment. The concentrations reported in fish (except for some liver oil samples) are below the EAC of 5 – 50 µg/kg fw. Data from Regions I and II indicate low and decreasing concentrations in the marine environment.

Triazines, such as atrazine and simazine, are still being used in some applications and are still detected in sea water, the highest levels are observed along the coast. Concentrations of atrazine and simazine measured in a survey of the eastern Irish Sea ranged from 42 and 37 ng/l respectively in samples from the Mersey Estuary down to less than 2 ng/l in the open sea. Atrazine and simazine were detected in the waters of the Wear (27 ng atrazine/l), Humber, Tees and Tyne (up to 6 ng simazine/l) and in the German Bight.

Figure 4.10 Mean concentrations (± 1 standard deviation) of DDE in the blubber of male harbour porpoises (mg/kg lipid) from areas of Region II and Region III.



Dichlorvos was used at salmon farms to control external parasites. This use has been virtually phased out in response to concerns and the North Sea Conference reduction targets.

4.5.7 Polycyclic aromatic hydrocarbons

Some polycyclic aromatic hydrocarbons are persistent and toxic to aquatic organisms and also bioaccumulate. They can influence the development of liver tumours in several fish species and may adversely affect the reproductive process in fish and other aquatic organisms. PAHs include aromatic molecules containing fused aromatic rings. In general the two main contributors to PAHs in the environment are fossil fuels, mainly crude oil, and the incomplete combustion of organic materials such as wood, coal and oil. Both the atmospheric and aquatic pathways to the maritime area are important. Information on riverine inputs is very limited. Emissions of PAHs from North Sea riparian states have been estimated at 7000 t in 1990. In addition to the many domestic and industrial combustion processes, coal tar containing coating systems are important sources of PAHs. Offshore activities, oil spills, offshore installations and shipping exhausts are important sources. Under anaerobic conditions some naturally synthesised compounds can be reduced to PAHs. Among the PAHs formed by natural processes are perylene, retene, and phenanthrene homologues. PAHs are also formed naturally in forest fires and volcanic eruptions. As a consequence of their hydrophobic nature, PAHs in aquatic environments rapidly tend to become associated with particulates. Sediments therefore represent the most important reservoir of PAHs in the marine environment. The background levels of PAHs in the marine environment are also present as a result of biosynthesis and natural oil seeps. Anthropogenic activities are generally accepted as the most important source of PAH release to the environment.

High variability is typical for total and individual PAH concentrations in sea water. PAH concentrations in

Atlantic sea water range from 0.3 ng/l for individual, more water-soluble, lower molecular weight PAHs (two and three ring compounds) to less than 0.001 ng/l for the high molecular weight PAHs (five or more ring compounds). Higher concentrations were generally found in coastal and estuarine samples with total PAH concentrations ranging from not detectable to 8500 ng/l.

On a worldwide basis, background values for PAHs in sediments appear to be within the range 0.01 to approximately 1 mg/kg dw. Several areas of the Arctic have elevated levels of PAHs relative to global background concentrations, and sediments from near Svalbard contained up to 8.1 mg/kg dw. The highest levels of oil in bottom sediments typically occur in river mouths, estuaries, and bays, as well as in areas of regular shipping, oil production and transportation.

From a sediment survey, which described the presence of PAHs in twenty-two estuaries in Western Europe, it appeared that fluoranthene was the most prominent PAH. Total PAH concentrations in the twenty-two estuaries were between 200 µg/kg dw (Wadden Sea) and over 6000 µg/kg dw (Scheldt Estuary).

PAHs are less prone to bioaccumulation or biomagnification than the organochlorine compounds. Fish and organisms higher in the food chain tend to metabolise and excrete PAHs relatively rapidly. Little is known about the degradation products of PAHs in the sea, such as their sulphone, hydroxy and nitro analogues, which are often appreciably more toxic than their parent compounds. Some of these can be expected to have a greater persistence than their precursors. In marine invertebrates, like blue mussel, the processes of PAH metabolism are usually slower. Consequently these organisms are considered more suitable for monitoring purposes.

The EACs for the majority of individual PAHs in sea water are not usually exceeded at most locations. PAH concentrations in sediments often exceed the EAC, especially in the estuaries of the Seine, Humber and Scheldt.

4.5.8 Other substances of concern

Use of several of the classic persistent organic compounds has been banned or severely restricted. There are, however, still other chemicals in use that are sufficiently persistent to show up as global environmental contaminants. These are not yet included in the ongoing monitoring programmes and knowledge of their occurrence is consequently more sporadic. For many of these substances, there are no agreed assessment criteria. However, much information on the sources and pathways of these substances is being gathered in connection with risk assessments being carried out under the EC Existing Substances Regulation (Commission Regulation (EC) No 1488/94).

Brominated flame retardants are a diverse group of various brominated substances, some of which are used as additives to polymers and textiles. The polybrominated diphenyl ethers (PBDEs), especially those with four to six bromine atoms, are found in biota and sediments in the marine environment far from known sources.

The input of PBDEs via rivers to the Convention area has been investigated, sediments from river mouths were analysed and large differences in concentration were observed. Sediment and fish samples from Region II also reveal a wide variation in the PBDE levels, indicating the dominance of localised point sources. The concentration of DeBDE in sediment in the North Sea varies from < 0.001 to 1.7 mg/kg dw. The occurrence of these compounds in sperm whales (*Physeter macrocephalus*), normally staying in offshore waters, indicate that PBDEs are widespread contaminants.

Chlorinated paraffins are an extremely complex group of compounds that are used as plasticisers, flame retardants and additives in metalworking fluids and the leather industry. These mixtures are difficult to analyse and it is not possible to determine individual compounds. To some extent however it is possible to distinguish between six groups: short- medium- and long-chain lengths, all with a low or high degree of chlorination. The highly chlorinated short-chained chlorinated paraffins have been the most extensively studied.

There are only a few data available on chlorinated paraffin concentrations in the Convention area. Sediment from river mouths was found to contain up to 10 µg/kg dw, fish samples from the North Sea have been shown to contain up to 100 µg/kg ww. A recent EU risk assessment for short-chained chlorinated paraffins with a high degree of chlorination identified a need to limit the exposure of aquatic organisms to local emissions associated with metalworking applications. PARCOM Decision 95/1 provides for the phase-out of the use in a range of applications of short-chained chlorinated paraffins.

Synthetic musks are used as fragrances in products such as cosmetics, soaps and detergents. There are two main groups in use today: nitro musks and polycyclic musks. Both groups contain compounds that are relatively persistent and can be found at high concentrations in water, sediment and biota, especially in freshwater systems.

The database for musks in marine environments is very limited. For individual nitro musks levels in marine waters are between < 0.02 and 0.17 ng/l and in mussels are between < 1 and 8 µg/kg ww. Among the polycyclic musks, HHCB (trade name: Galaxolide®) and AHTN (trade name: Tonalid®) have been detected in mussels from the North Sea at levels of around 1 µg/kg ww.

Octyl- and nonylphenol ethoxylates (OPE and NPE) have a wide range of applications in industry and public uses. The main environmental burden results from their

use in industrial cleaning and public institutional cleaning as well as from textile and leather processing. Only very few data are available with regard to the marine environment. However, high levels of OPE and NPE were found in sediments in the river Scheldt (20 µg/kg and 300 µg/kg respectively) and in the Elbe (5.6 µg/kg and 107 µg/kg respectively). In the UK, the OPE levels varied between < 0.1 µg/kg and 15 µg/kg and the NPE levels between 23 and 44 µg/kg. In line with PARCOM Recommendation 92/8, the use of NPEs as cleaning agents for domestic uses was phased out by 1995.

4.6 Inputs from mariculture

Both finfish and mollusc culture operations generate significant amounts of organic wastes that, in sheltered locations, accumulate on the adjacent seabed. Fish farms release dissolved nutrients to the surrounding water, which may have the potential to contribute to eutrophication effects. In general, the flux of nutrients from fish farms to coastal waters is small compared to natural fluxes, such as from rivers and through the advection of coastal waters. Over recent years, there have been considerable improvements in the formulation and utilisation of feeds, and current rates of nitrogen excretion from salmon farms per tonne of fish produced are probably about 30 to 40% of those in the 1980s.

A number and variety of chemicals are used in the sea-cage culture of salmon, the dominant form of intensive mariculture in the OSPAR region. In terms of quantity, the main contaminating materials from these operations are antibiotics, parasiticides and antifoulants. Most antibiotics used to control disease are administered as feed additives and enter the sea via waste feed and faeces. Due to the use of vaccines, there has been a marked reduction in recent years in the use of antimicrobial agents in Norway, Ireland and Scotland, even though the production of fish has increased considerably.

A major problem in salmon farming is parasitic sea lice. Traditionally, control has been achieved through the use of a range of compounds (such as dichlorvos, organophosphate compounds, pyrethroids, benzoylphenylureas, avermectins and hydrogen peroxide) to kill the lice although in some areas cleaner fish (wrasse) have been used effectively to graze the lice off the salmon. The compounds used are mostly released to the environment after use, where they can present some hazard to non-target marine organisms.

TBT was commonly used as an antifoulant on mariculture cages prior to 1987. Copper has replaced TBT as the active ingredient in some antifouling agents so that – assuming a 20% leaching rate – cage aquaculture today represents a significant copper source. However, the loss rate from various formulations is likely to vary significantly,

therefore it is very difficult to estimate the quantity of copper released.

4.7 Offshore chemicals

Sources of contaminants arising from the offshore oil and gas industry are drilling muds and cuttings, produced water and spills. Produced water contains considerable amounts of dissolved substances, including monocyclic aromatic hydrocarbons (i.e. BTEX), PAHs and phenols. There may also be (as yet) unidentified organic compounds. **Table 4.9** gives a partial overview of the amounts of some of the priority contaminants in produced water discharged to the North Sea. As the amount of produced water has increased it might be expected that the amount of chemicals associated with this source has followed the same trend. Due to lack of harmonised reporting formats, it is not yet possible to present an overview of the total amount of offshore chemicals discharged on either a Convention-wide basis or even on a Region-wide basis. As oilfields mature, it is anticipated that the discharges of produced water and associated oil will increase. In the case of the relatively small discharges of produced water from gas platforms, the discharge of aromatic compounds may exceed the discharge of dispersed oil (ICES, 1999).

Table 4.9 Estimated amounts of PAHs, organohalogens and substances other than oil in aqueous discharges to the North Sea from offshore installations in 1996.

	Quantity discharged (t)	Average Concentration* (mg/l)
Cadmium	0.6	0.01
Mercury	0.3	0.0003
Lead	6.9	0.09
Nickel	18.6	0.3
Total aromatics	2130	28
phenol/benzoic acids*	1345	14
benzene	454	
PAHs (95% naphthalene)	28	0.36
Organohalogens	< 0.003	

Data show estimated discharges for Denmark, the Netherlands and Norway, except * (Norway only). Information for the UK is not available.

4.8 Oil

Crude oil is a complex mixture of tens of thousands of compounds. Most of the compounds (> 75%) are types of hydrocarbons in the classes n-alkanes, branched alkanes, cycloalkanes, triterpanes, aromatics, naphthoaromatics and PAHs with up to ten condensed

aromatic rings. In addition, organosulphur compounds, acids, phenols, pyridine and pyrroles are present, as are highly complex asphaltenes.

Petrogenic hydrocarbons arise from natural oil seeps, emissions, spillages or effluents during the production and transportation of crude oil, from the refining and petrochemical industries, from general shipping activities and from the dumping of oil-contaminated dredged materials. Riverine inputs of oil constitute a significant part of the overall load of oil entering the maritime area. 'Oil' occurs naturally in the marine environment but not necessarily everywhere and, consequently, when it is present it is more likely to be there due to human activity than to natural causes.

The quantity of oil discharged by refineries decreased by more than 90% between 1981 and 1997; from > 9000 t/yr to < 800 t/yr. Concentrations of oil in water discharged have to comply with the 5 mg/l standard of PARCOM Recommendation 89/5.

Oil exploration and production activities continue to expand into previously unexploited areas (Rockall, west of the Shetland Islands etc). This has raised concerns about localised impacts, however experience in the North Sea suggests that with careful and sensitive environmental management the impacts can be minimised.

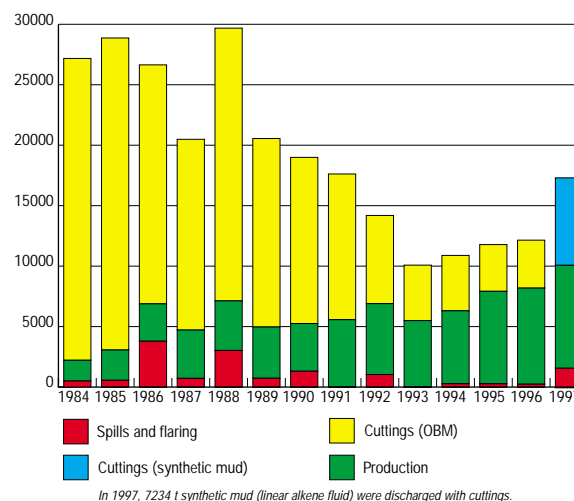
Produced water is the main source of oil from the offshore oil and gas sector; quantities discharged have progressively increased even though the concentration of oil has fallen in line with the OSPAR target standard of 40 mg/l. Oil discharged via cuttings has, however, been drastically reduced as a result of alternative technologies and increased use of synthetic-mud based drilling fluids and water-based drilling fluids. Discharges of oil-based mud ceased at the end of 1996. Leaching from old drill cuttings is a possible source of oil, but quantities released will be small if the cuttings are not disturbed. The contributions from the different sources for oil discharged to the North Sea from offshore installations are shown in **Figure 4.11**.

The majority of accidental spills involve < 1 t of oil, but larger spills resulting from tanker accidents have occurred, often in shallow waters. In the spill from the oil tanker Aegean Sea in 1992, 80 000 t of oil were released in shallow waters at the rias of northern Spain and following the grounding of the MV Braer on the southern tip of the Shetland Islands in January 1993 some 85 000 t of crude oil were lost from the ship.

The Sea Empress spill resulted in a release of 72 000 t of oil at the entrance to Milford Haven in February 1996. For the purpose of judging return to normality following the Sea Empress oil spill, background concentrations of total petroleum hydrocarbons for the region were judged to be 200 to 900 ng/l in water, up to 10 000 µg/kg in dry sediments and 2000 to 10 000 µg/kg in biota.

The oil spill from the timber carrier Pallas off the northern German Wadden Sea in 1998 released only a

Figure 4.11 Contributions from the different sources of oil input (tonnes) to the North Sea from offshore installations.



small amount of oil (250 m³). However, due to unfavourable conditions the impact on the environment was considerable (see Section 5.3.11).

On 12 December 1999, the wrecking of the tanker Erika off the French Atlantic coast resulted in a spill of 12 000 t of bunker C oil. By the following weeks, 400 km of coast were polluted. At the end of March 2000, 130 000 t of waste were collected and beaches cleaned. Forty per cent of marine cultures on the Atlantic French coast stopped their exploitation during this period because the total concentration of the sixteen PAHs easily identified in shellfish exceeded 500 µg/kg dw, a health safety limit decided by the national health authorities.

Illegal discharges from ships continue to be a matter of concern. Oil slicks are still detected along the main shipping corridor of the North Sea, although their frequency and volume seems to have generally decreased.

4.9 Radioactivity

4.9.1 Sources and input

Radioactivity has both natural and anthropogenic sources. Natural radiation stems from decay of radionuclides in the Earth's crust and cosmic radiation. The anthropogenic input can be divided into three main categories: historic (weapons testing), accidents (Chernobyl) and industrial processes (e.g. nuclear reprocessing facilities and phosphate fertiliser production). There is also some concern about leakage from old dumpsites and sunken submarines within and outside the Convention area.

All authorised releases of radioactivity, including those

unrelated to reprocessing, are subject to regular monitoring. Environmental levels due to authorised releases unrelated to reprocessing are relatively low and difficult to distinguish from radiation discharged from European reprocessing plants and fallout from nuclear weapons testing. In all cases, individual radiation exposures are generally also very low and well within international dose limits.

Anthropogenic inputs contain both naturally occurring and artificial radionuclides. Phosphate fertiliser production is the main anthropogenic source of naturally occurring uranium which results in substances such as radium-226, polonium-210 and uranium-238, but mining and ore processing, and the burning of coal, oil or natural gas in

thermal power plants also contributes. Amongst others, the artificial radionuclides caesium-137, technetium-99 and iodine-129 originate from reprocessing facilities (e.g. Sellafield and Cap de La Hague). Soluble radionuclides like caesium-137 are transported from the Sellafield reprocessing facilities by the Norwegian Coastal Current to the Arctic via the North Sea (**Figure 4.12**). The input from La Hague follows the currents through the Channel to the North Sea and subsequently the Arctic (Region I). The contaminants reach the Barents Sea after four to five years and the Iceland and Greenland Seas after seven to nine years.

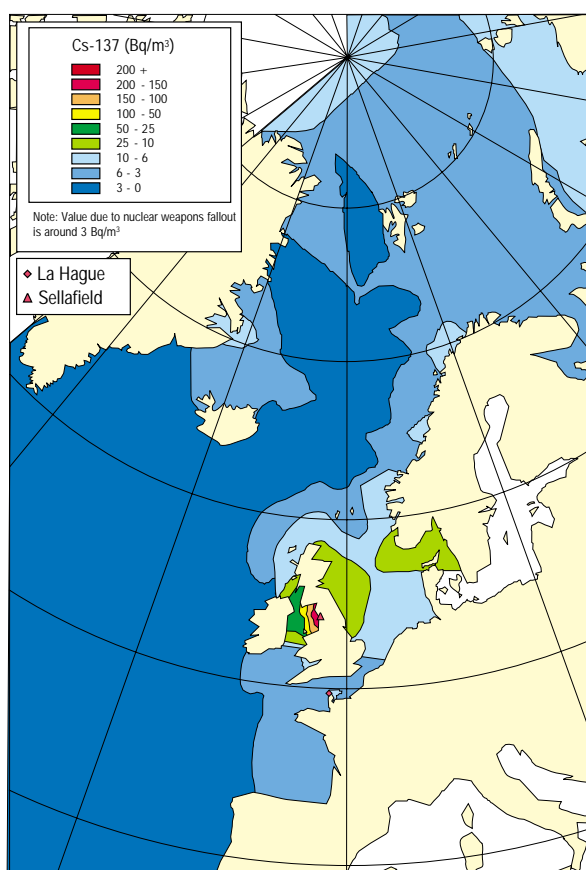
4.9.2 Sea water

Traces of man-made radionuclides are found with a decreasing gradient with increasing distance from the reprocessing facility. The level of caesium-137 ranges from approximately 500 Bq/m³ in the vicinity of the outlets of reprocessing plants down to 2 Bq/m³ in the open ocean. The trend has been steadily downward in the Irish Sea since 1988, however the signal is still present in the Irish Sea and as far afield as the Norwegian west coast and in the Arctic. At Sellafield, releases of the actinides and ruthenium have decreased, but there were consequential increases of the less radiologically significant technetium-99 in 1994 and 1995 and the level of technetium-99 in the Irish Sea close to Sellafield outfalls were approximately 350 Bq/m³. This has resulted in the rapid spread and detection of technetium-99 in the North Sea and along the Norwegian west coast at very low concentrations. Discharges of technetium-99 from Sellafield have decreased since 1997.

4.9.3 Sediment

Concentrations of artificial and natural radionuclides in sediments are in general low except near outlets from the reprocessing industry and from phosphate fertiliser production. The specific activity of caesium-134 and caesium-137, a major fraction of the Chernobyl fallout in 1986, decreased between 1990 and 1996 confirming a decline in the Chernobyl contribution. The accumulation of sediments in both sub-tidal and inter-tidal areas of the Irish Sea act as a long-term sink for plutonium and other long-lived particle reactive elements. These sediments contain substantial amounts of artificial radionuclides, particularly caesium, plutonium and americium, the redistribution of which is now being observed in the Irish Sea. Sub-tidal sediments contain the highest proportion of the estimated inventory of plutonium in the Irish Sea (c. 200 kg in the total sediment of the area). It is however the inter-tidal sediment that is more critical in terms of human contact.

Figure 4.12 Activity concentrations of caesium-137 in sea water in the North-east Atlantic (based on measurements made 1992 to 1996). Source of data: Bailly du Bois and Guéguéniat (1999); Dahlgard *et al.* (1995); Josefsson *et al.* (1998a,b); Kershaw *et al.* (1997); Nies *et al.* (1998); MAFF/SEPA (1997).



This map was produced using a computer contouring package and is based on available published data for 1992 to 1996. Consequently, it provides a general picture of the spread of activity from Sellafield and La Hague but may not reflect actual current activity levels. Because of the sparsity of sampling data in some areas, some localised slight elevations in activity may be an effect of the contouring package used.

4.9.4 Biota

Seaweeds are good indicators of soluble radionuclides such as caesium and technetium in the surrounding environment. Concentrations of caesium-137 in seaweed diminish with increasing distance from Sellafield and have fallen in response to reductions in the discharge. For example the concentration decreased by approximately 20% per annum during the period 1983 to 1986 on the east coast of Ireland, and although the downward trend continues it is now less pronounced. Parallel decreases have been measured in fish and shellfish from the same area during the same period.

Concentrations of technetium-99 in seaweeds and the edible tissues of lobsters rose rapidly in the Irish Sea in response to increased discharges after 1994. As with caesium, the concentrations decrease with increasing distance from Sellafield. Monitoring on the UK coast close to the discharge shows levels declining in response to decreased inputs.

In general, the concentrations of plutonium and americium are higher in shellfish than in fish. The most recent monitoring indicates that their concentrations in fish and shellfish from routinely monitored sites in the Irish Sea are relatively stable. In the North Sea and Arctic Waters concentrations of caesium-137 of 0.4 – 1.4 and 0.2 – 0.5 Bq/kg ww respectively, were reported.

4.9.5 Exposure

Radiation exposures from unenhanced sources of natural radioactivity are in most cases higher than those from anthropogenically derived sources. An estimate of the maximum likely individual dose to man from natural radionuclides amounts to about 2 mSv/yr. Most of the dose that humans obtain by consuming marine food is due to polonium-210, which was found to be more strongly incorporated into several marine organisms than the other radionuclides.

With regard to individual exposure from artificial radionuclides, generally caesium-137 has by far the greatest significance. However, the dose to man is at least two orders of magnitude less than the dose from natural radionuclides indicated above. For areas in the proximity of discharges, other radionuclides such as technetium-99, plutonium-239, plutonium-240 and americium-241 may be a more significant contribution to the doses to the local critical group.

4.10 Nutrients and oxygen

4.10.1 Introduction

Nutrients are necessary for the growth of marine algae, including phytoplankton. For most of the maritime area

natural processes (light, temperature, hydrography etc.) regulate nutrient availability and plankton growth. There are a number of natural and anthropogenic sources contributing to the nutrient inputs to the marine environment. These sources include wastewater inputs, agriculture, and emissions from fuel combustion and traffic. Information on inputs, concentrations, and trends and effects of nutrients is currently being used within OSPAR to classify the maritime area with regard to its eutrophication status (see *Figure 5.4*).

4.10.2 Inputs of nutrients

Information regarding the input of nutrients from direct, riverine and atmospheric sources is far from complete. In the North Sea area, more comprehensive data are available on waterborne nutrients. These show that since the mid-1980s there has been a reduction of the order of 50% in the riverine inputs of phosphorus but, due to variability of flow, no consistent reduction in the riverine inputs of nitrogen. Direct inputs of nitrogen and phosphorus have reduced by 30% and 20% respectively since 1990. However, inputs may vary on a local scale. Consideration of losses and discharges of nitrogen at source indicates that some improvement (up to 25% reduction) has been achieved in the North Sea catchment area. The atmospheric deposition of nitrogen to the North Sea has remained static at about 350 000 t/yr. The relative proportions of nitrogen input for riverine, atmospheric and direct inputs are 10:3:1.

In general, rivers are the dominant source of nutrients in near shore areas. Although the pattern of nutrient input to estuaries closely follows that of river water flow, which varies widely within and between years, the net seaward flux of nutrients through estuaries to coastal waters may be strongly influenced by estuarine processes. Although nutrient fluxes associated with the import of oceanic water masses are substantially higher than anthropogenic inputs, only a proportion of these fluxes is available for primary production. Nevertheless, on parts of the Atlantic seaboard upwelling of nutrient-rich oceanic water plays a significant role in seasonal phytoplankton production.

4.10.3 Concentrations and trends of nutrients

Only a few time trend data sets exist for areas other than the North Sea area. Although there is no clear trend in the area as a whole, this is not the case in local areas that are directly influenced by anthropogenic inputs. For example, a significant decreasing trend in phosphorus concentration was detected in Danish waters (between 1989 and 1997) and the German Bight. The decrease in the phosphorus concentrations in nearly all Danish areas is due to a significant decrease in the load from sewage, industry and detergents (80% reduction in the phosphorus

load). The same trend was also seen for phosphorus concentrations in the Wadden Sea. Data sets from a site in the central Irish Sea, near the Isle of Man, suggest that there has been an increase in winter nitrate and phosphate concentrations since sampling started at the site in 1954. This trend may be partially climate-related.

Monitoring programmes and modelling studies have shown that water rich in nutrients and organic content, and originating in the southern North Sea, reaches the Norwegian Skagerrak periodically. This flux leads to reduced environmental quality especially in threshold fjords and coastal basins.

4.10.4 Oxygen

The production and subsequent degradation of excess plant biomass and large input of organic matter may lead to oxygen depletion in the marine environment. This is a major problem in areas with restricted water exchange and stratified water bodies.

Oxygen depletion in marine waters, not permanently stratified, generally occurs in summer–autumn periods when a thermocline develops that reduces the vertical water exchange. Nitrogen is generally regarded as the limiting nutrient for algal growth in marine waters. Danish data have shown that in stratified water in the Kattegat, where oxygen depletion problems are pronounced, nitrogen loading has the most significant influence in relation to oxygen depletion. Model calculations by the Danish Environmental Protection Agency showed that a 50% reduction in the actual nitrogen load would result in an almost equal reduction in the duration of anoxia in these environments.

Low oxygen concentrations in the water are periodically observed in many estuaries, bays, fjords, and in the Wadden Sea, Kattegat and the eastern Skagerrak. In the outer Clyde Estuary and Liverpool Bay oxygen depletion is occasionally detected at times of stratification. In both cases this was attributable to sewage sludge dumping, and the situation is anticipated to improve following the cessation of sludge dumping.

