

## 4. Marine Chemistry

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Figure 4.1. Wadden Sea areas.



Table 4.1. QSR coding and summarized areadescription of the Wadden Sea.

Code	Description
N1	Western Dutch Wadden Sea. The area receives fresh water directly from Lake IJsselmeer by the sluices of Den Oever and Kornwerderzand at an average rate of $16.3 \cdot 10^9 \text{ m}^3/\text{yr}$ . The water mass which originates from the river Rhine passes Lake IJsselmeer in about 50 days. The coastal North Sea water entering the Wadden Sea at the Marsdiep constitutes about 15% Rhine water.
N2	Eastern Dutch Wadden Sea. The area receives a minor freshwater source from Lake Lauwers and an industrial waste line. The area is considered to be dominated by coastal North Sea water.
N3	Ems-Dollard estuary. The freshwater sources to the area are the river Ems (90%) and Westerwoldsche Aa (10%) at a total average rate of about $3.4 \cdot 10^9 \text{ m}^3/\text{yr}$ . Industrial and harbour activities border the estuary at Emden, Delfzijl and Eemshaven.
NS1	Niedersachsen Wadden Sea. The area is slightly influenced by local fresh water sources. Only small harbours are present. The area is considered to be dominated by coastal North Sea water.
NS2	Jade Basin. The harbour of Wilhelmshaven is the main activity in the area. Virtually no fresh water enters the area. The area is considered to be dominated by coastal North Sea water, which becomes enriched by sediment efflux of components during high tide.
NS3	Weser estuary. The river Weser is the main freshwater source at an average rate of $11.3 \cdot 10^9 \text{ m}^3/\text{yr}$ . The river borders are densely populated. Harbour activities are present at the cities of Bremen and Bremerhaven.
SH1	Elbe estuary. The river Elbe is the main freshwater input into the area at an average rate of $24.5 \cdot 10^9 \text{ m}^3/\text{yr}$ , which is about 43% of the total freshwater input in the international Wadden Sea. The river is bordered by large cities (e.g. Hamburg), harbours and industrial activities.
SH2	Eider estuary. The river Eider constitutes a relatively small freshwater source of about $0.9 \cdot 10^9 \text{ m}^3/\text{yr}$ on average. The population density is moderate. Some small recreational and fisheries harbours are present.
SH3	Halligen. Virtually no freshwater input and a low population density. The area is considered to be dominated by coastal North Sea water.
D1	Sylt-Rømø basin. The area is physically bordered by the dams connecting Sylt and Rømø to the mainland. The area is considered to be dominated by coastal North Sea water. The freshwater input from southern Jutland was about $0.8 \cdot 10^9 \text{ m}^3/\text{yr}$ in 1990, which was about $1.3 \cdot 10^9 \text{ m}^3/\text{yr}$ to D1+D2 in the same year.
D2	Ribe and Konge Å estuary (Knudedyb), Rejsby and Brøns Å (Juvredyb). The rivers Ribe, Konge, Rejsby and Brøns Å are small rivers, thus constituting a small freshwater input. The input to D1 + D2 is about $1.2 \cdot 10^9 \text{ m}^3/\text{yr}$ on average. The area is considered to be dominated by coastal North Sea water. Part of Denmark.
D3	Varde and Sneum Å estuary (Grådyb). The last natural estuary of the Wadden Sea. The city of Esbjerg is the main center of population and harbour and industrial activity. The area is considered to be dominated by coastal North Sea water.

## 4.1 Introduction

The evaluation and assessment of chemical data includes both nutrients and contaminants. Only parameters, for which data were available for the entire Wadden Sea were assessed. The evaluation of polyaromatic hydrocarbons is an exception.

The assessment procedure follows a compound-(group) from its source to the accumulation in sediment and biota. The data were evaluated for temporal and spatial developments. The present, 1996 or 1995, concentrations were compared with background and ecotoxicological assessment criteria, recently accepted by OSPAR (OSPAR, 1997). The results of all assessments are tabulated in a single overview. Similar trends were, however, not

checked for (cor)relation, *e.g.* between input and concentration in sediments.

For the purpose of the assessment the Wadden Sea has been divided into 12 coherent areas consistent with the QSR of 1993. Some of the areas are of an estuarine nature due to the riverine freshwater input. The North Sea coastal water is the sole source of marine water for all areas (Figure 4.1).

Areas will be referred to by their QSR code, which is shown in table 4.1 including a short characterization.

## 4.2 Assessment of Nutrients

### 4.2.1 Methodology

Nutrient concentrations were standardized to 10 and 27 psu using the concentration-salinity plots, according to the method of the 1993 QSR (GESAMP, 1987; de Jong *et al.*, 1993). Standardized concentrations were evaluated with statistical methods.

In a number of areas, highly variable nutrient concentrations were found at equal salinity. These areas, like the Jadebusen (NS2), are presumably dominated by the efflux of remineralized nutrients from the sediment during high tide and not by a nutrient-rich fresh water source. The nutrient enrichment of North Sea coastal water during high tide can be dramatic, as can be illustrated with data from the Jadebusen. Nutrient concentrations close to the inner basin can be 2 – 5 fold the marine, diluted nutrient concentrations, pointing at the importance of sediment remineralization as a source of nutrients. In those sediment-dominated areas, the concentration-salinity procedure is not applicable. Averaged concentrations were used for the assessment.

The assessment was carried out for either a significant change between the years 1985 and 1996 or a significant trend throughout this period. A change, implying a significant difference between the data sets of two years (1985,1996), evaluated by non-overlapping 95% confidence limits, is shown in italics. A trend, indicating both a significant and an ongoing change throughout the evaluation period (1985-1996), is shown in bold. In Table 4.2, developments in salinity standardized nutrient concentrations and quantitative inputs are summarized.

### 4.2.2 Assessment of nitrogen compounds

In the Niedersachsen (NS1) Wadden Sea a significant 40 - 50% decrease of DIN (Dissolved Inorganic Nitrogen: ammonia + nitrate/nitrite) could be established, corresponding with the 70% ammonia reduction in the Ems-estuary (N3) (Table 4.2, Figure 4.2, Figure 4.3).

The 60% reduced ammonia load by the Ems river (Figure 4.4), and the Westerwoldsche Aa (Dollard), in addition to the estuarine nitrification of ammonia to nitrate (Helder and de Vries, 1983) can explain the observation of ammonia reduction in the Ems estuary and an ammonia/nitrate reduction in NS1. The initial (1986 - 1990) reduction of estuarine ammonia was succeeded by an increase of nitrate from 1990 - 1993. This may be related to the progressive implementation of purification plants in the watershed of both rivers (Dijkhuizen *et al.*, 1996; Riegman *et al.*, 1992). The decrease of nitrate and total-nitrogen (and total phosphorus) in the Ems estuary (N3) since 1993 is probably related to the closing of the waste water discharges of the potato-processing industry into the Westerwoldsche Aa and consequently the Dollard. The N3 trend in nitrate and

total-nitrogen at 10 psu is not significant over the entire evaluation period, due to the peak period of 1989 - 1992, but is significant between 1992 and 1996.

In the Weser and Elbe estuaries a significantly lower concentration in 1996 compared to 1985 was observed for nitrate, nitrite and total nitrogen. This reflects the strong ammonia input reduction by the river Elbe.

The 55% ammonia input reduction by Lake IJsselmeer is not reflected in the development of Wadden Sea ammonia concentrations.

No trends in total nitrogen and nitrate input were observed, partially because these inputs are mainly controlled by the, variable, river flow.

In the 10 psu area of the western Dutch Wadden Sea (N1) a significant 30% increase in nitrate was observed (35% nitrate plus nitrite).

Riverine input/ Area	Flow (km <sup>3</sup> /yr)		N <sub>tot</sub>		P <sub>tot</sub>		NH <sub>4</sub> <sup>+</sup>		NO <sub>3</sub> <sup>-</sup>		PO <sub>4</sub> <sup>3-</sup>		SiO <sub>4</sub> <sup>3-</sup>
	trend	average	trend	1996	trend	1996	trend	1996	trend	1996	trend	1996	trend1996
Lake IJsselmeer		15.8			<b>-50%</b>		<b>-55%</b>				<b>-80%</b>		
N1	10 psu			211 <sup>1)</sup>	<b>-30%</b>	3.2		13	<b>+30%</b>	145 <sup>1)</sup>	<b>-90%</b>	0.84	56 <sup>1)</sup>
	27 psu			59 <sup>1)</sup>	<b>-30%</b>	3.2		13		17 <sup>1)</sup>	<b>-60%</b>	0.84	14 <sup>1)</sup>
N2	27 psu			85	<b>-30%</b>	4.3		22		28	<b>-60%</b>	1.53	31
Ems		2.9					<b>-60%</b>						
N3	10 psu			232		9.9	<b>-70%</b>	24 <sup>1)</sup>		146	<b>-60%</b>	2.44	<b>-20%</b> 111 <sup>1)</sup>
	27 psu			54		4.0		3 <sup>1)</sup>		60	<b>-40%</b>	1.59	45 <sup>1)</sup>
NS1	27 psu			54**		5.9**	<b>-40%</b>	7	<b>-50%</b>	22	<b>-40%</b>	1.48	53
NS2	27 psu			48		4.5		2		31		1.56	89
Weser		10.9											
NS3	10 psu			-53%	n.d.	n.d.		n.d.	<b>-50%</b>	n.d.	<b>-65%</b>	n.d.	n.d.
	27 psu			139		6.5		2		107		2.5	180
Elbe		24.6			<b>-40%</b>		<b>-80%</b>				<b>-60%</b>		
SH1	10 psu			-23%	326	7		34	<b>-18%</b>	208		2.34	119
	27 psu			-49%	174	7		10	<b>-73%</b>	66		2.34	66
Eider		0.8											
SH2	10 psu			240		9.5		21		220	<b>-40%</b>	2.95	177
	27 psu			108		9.5		11		81		2.95	30
SH3	27 psu			52		2		9		27	<b>-60%</b>	1.57	19
D1	27 psu			109 <sup>1)</sup>		4.3 <sup>1)</sup>		12 <sup>1)</sup>		65 <sup>1)</sup>	<b>-60%</b>	1.11 <sup>1)</sup>	41
County Sønderjylland		0.5											
D2	27 psu			96 <sup>1)</sup>		3.3 <sup>1)</sup>		10 <sup>1)</sup>		56 <sup>1)</sup>		0.79 <sup>1)</sup>	n.d.
County Ribe		<b>+80%</b>	1.2	<b>+95%</b>									
D3	27 psu			130 <sup>1)</sup>		4.2 <sup>1)</sup>		8 <sup>1)</sup>		88 <sup>1)</sup>		0.95 <sup>1)</sup>	n.d.

Table 4.2. Temporal developments of riverine nutrient inputs (shaded rows) and salinity standardized winter nutrient concentrations in the Wadden Sea over the period 1985-1996 and 1996 average or standardized nutrient winter concentrations ( $\mu\text{mol/l}$ ).

Trends refer to a significant and ongoing increase or decrease during the period 1985-1996 and are expressed in bold.

Changes refer to a significant difference between the data sets of compared years and are expressed in italics.

The average riverine inputs (km<sup>3</sup>/year) relate to the period 1985-1996.

<sup>1)</sup>: data of 1995. \*\*: based on a single set of data at the same day.

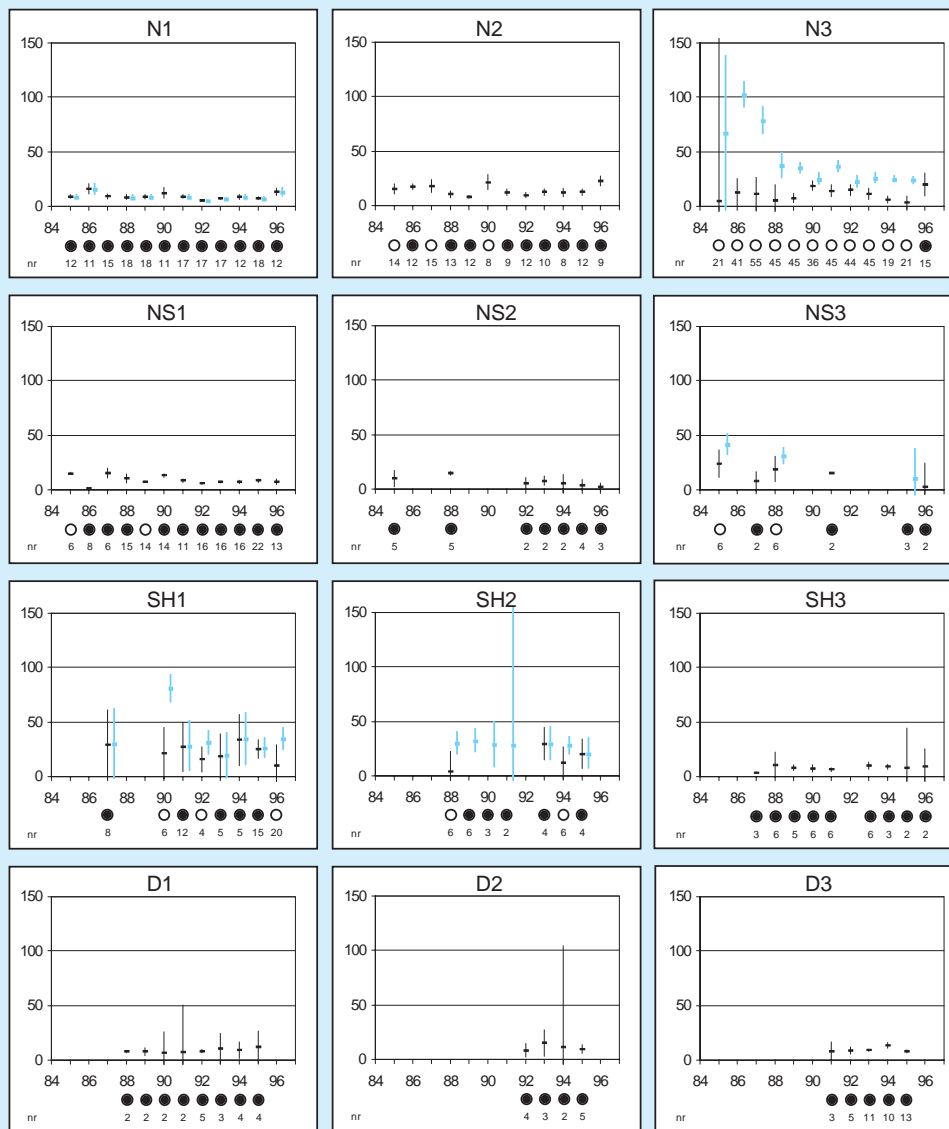


Figure 4.2. Ammonia ( $\text{NH}_4^+$ ) winter concentrations ( $\mu\text{mol/l}$ ) standardized at 10 psu (blue) and 27 psu (black).  $\nu$ : salinity gradient mean value (-) and 95% confidence limits (|).  $\bar{j}$ : salinity gradient interpolated value (-) and 95% confidence limits (|). (Winterperiod: December–January–February). nr: number of samples.

Total nitrogen concentrations in the marine Wadden Sea are in the order of  $55 \mu\text{mol/l}$  in the western part and Halligen, being two- to three-fold this level from the Weser estuary up to the Danish Wadden Sea (Table 4.2).

### 4.2.3 Assessment of phosphorus compounds

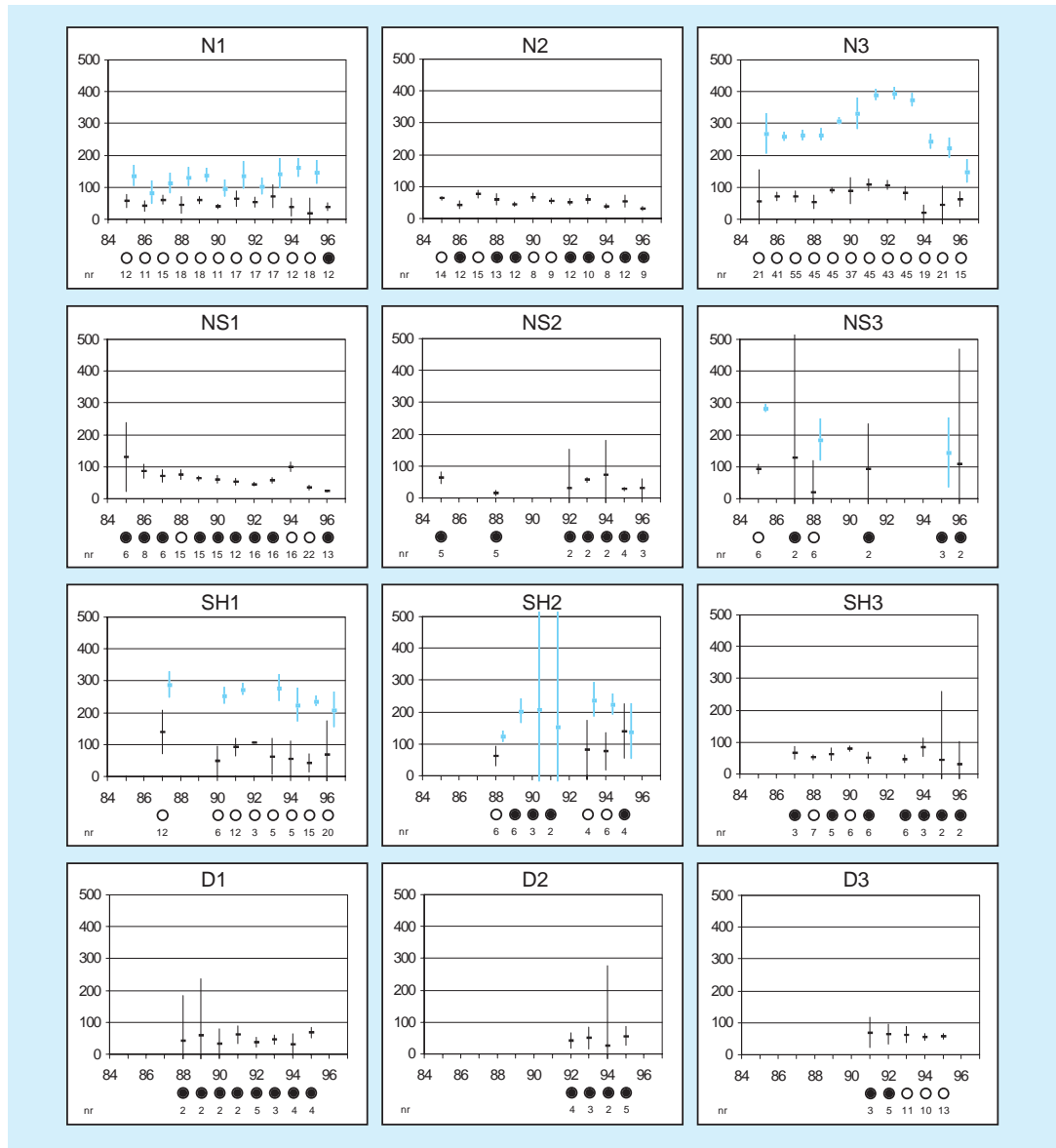
Between 1985 and 1996, phosphate concentrations decreased significantly in most areas of the Wadden Sea (Table 4.2; Figure 4.5). In the western Dutch Wadden Sea, the 90% reduction was significantly related to the 80% input reduction by the Lake IJsselmeer (Figure 4.4) which, in turn, is related to the reduction in Rhine loads. In the western (N1) and eastern (N2) Dutch Wadden Sea, a 30 - 60% reduction in respectively phosphate

and total phosphorus concentrations was significant.

The significant 60% reduction in phosphate load by the Elbe did not show up as a concentration reduction in the Elbe estuary. The observed 40 - 60% reduction north of the Elbe outflow, in areas SH2, SH3 and D1, probably does relate to the Elbe input reduction due to the residual current pattern of the German Bight.

Phosphate concentrations (1996) in the marine parts of the Wadden Sea were in the order of  $1 \mu\text{mol/l}$  in the western Dutch (N1) and Danish (D1-D3). Concentrations in the area in between are 2-3  $\mu\text{mol/l}$ .

Figure 4.3. Nitrate + nitrite ( $\text{NO}_3^- + \text{NO}_2^-$ ) winter concentrations ( $\mu\text{mol/l}$ ) standardized at 10 psu (blue) and 27 psu (black).  
 ▽ : salinity gradient mean value (-) and 95% confidence limits (|).  
 j : salinity gradient interpolated value (-) and 95% confidence limits (|).  
 (Winterperiod: December–January–February).  
 nr: number of samples.



#### 4.2.4 Assessment of silicate

Silicate, a usually not anthropogenically influenced nutrient used by *a.o.* diatoms, decreased significantly by 20% in the 10 psu range of the Ems-Dollard estuary (N3). This may be related to the decreased remineralization rates in the Dollard region, due to the sanitized inputs of the Westervoldsche Aa from the potato-processing industry.

The silicate concentrations in the marine Wadden Sea are in the order of 15 - 180  $\mu\text{mol/l}$ . Relatively low concentrations were present in the western Dutch Wadden Sea (N1) and Halligen (SH3). Silicate concentrations in the marine Wadden Sea are reaching a maximum in the Weser (NS3) area. Estuarine silicate concentrations are in the order of 60 (N1) to 180 (SH2)  $\mu\text{mol/l}$ .

#### 4.2.5 Eutrophication status

It is nearly impossible to indicate natural background levels of nutrients in mixing areas, like the Wadden Sea and its contributing estuaries, with the existing techniques (Laane, 1992). Historical winter data for the Southern North Sea and German Bight, within the 31 - 33 psu range reported by Laane (1992) and OSPAR (1996) and estimates by van Raaphorst *et al.* (1999) are shown in Table 4.3. Combining the available data, the 1996 winter nutrient concentrations would, merely indicative, be 2 - 10 times background levels.

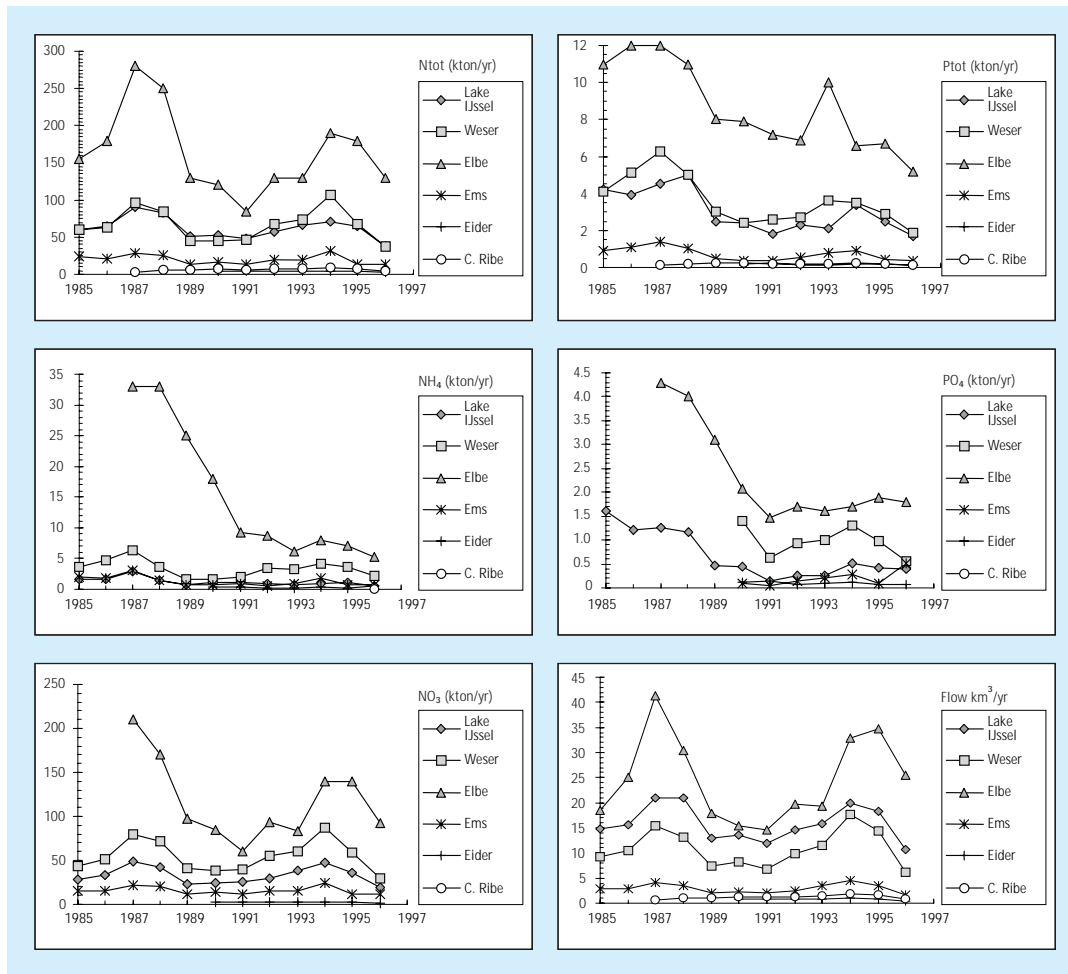


Figure 4.4 Riverine nutrient inputs to the Wadden Sea 1985–1996.

Area	No. of Samples	Salinity	PO <sub>4</sub> <sup>3-</sup>	SiO <sub>4</sub>	NO <sub>2</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	Tot-N	Tot-P
Southern North Sea (Laane)	9	31-33	0.48 - 0.65	9 - 15	0.2 - 0.7	-		
Southern North Sea (Laane)	11	31-33	0.67 - 0.90	12 - 21	0.05 - 0.7	19.5 - 32.2		
German Bight (OSPAR)	18	31-33	0.43 - 0.60	9 - 17	0.4 - 1.2	-		
Netherlands coast (OSPAR)		31-33	0.48 - 0.90	9 - 21	0.05 - 0.70	19.5 - 32.2		
western Dutch Wadden Sea (van Raaphorst <i>et al.</i> , 1999)		24-27					10 - 24	0.6 - 1.2

#### 4.2.6 Remarks with respect to nutrient monitoring

The salinity method is the best way to standardize estuarine nutrient winter data and thus determine and compare temporal and geographical trends. For optimal standardization, data should be evenly distributed along the salinity gradient, preferably at least 5 stations in the range of 1 to 30 psu. If the standardization procedure can be carried out properly, the variation of individual data can be smoothed out with a higher level of significance.

It appears from the data that build-up of nutrients continues throughout the winter period

(Figure 4.6). As mentioned earlier, this effect may be stronger in sediment-dominated areas where remineralization of organic matter causes an efflux of nutrients from the sediment. This phenomenon highly affects the present evaluation method where all data of the months December, January and February are combined. Monitoring strategy may have to be adapted in such a way that winter build up and the role of sediment efflux can be followed until the phytoplankton spring bloom starts. The peak nutrient value just before the bloom best represents the winter nutrient levels and should be used in trend analysis. This implies a monitoring frequency increase (weekly) during

Table 4.3. Range in the background winter concentration of dissolved phosphate, silicate, nitrite, nitrate, total N and total P ( $\mu\text{mol/l}$ ).

After: Laane, 1992; OSPAR, 1997 (OSPAR/ICES workshop in Hamburg, 22–25 October 1996, Annex 6); van Raaphorst *et al.*, 1999).

Figure 4.5 ortho-Phosphate ( $\text{o-PO}_4^{3-}$ ) winter concentrations ( $\mu\text{mol/l}$ ) standardized at 10 psu (blue) and 27 psu (black).  $\nabla$  : salinity gradient mean value (-) and 95% confidence limits (|).  $\dot{\jmath}$  : salinity gradient interpolated value (-) and 95% confidence limits (|). (Winterperiod: December-January-February). nr: number of samples.

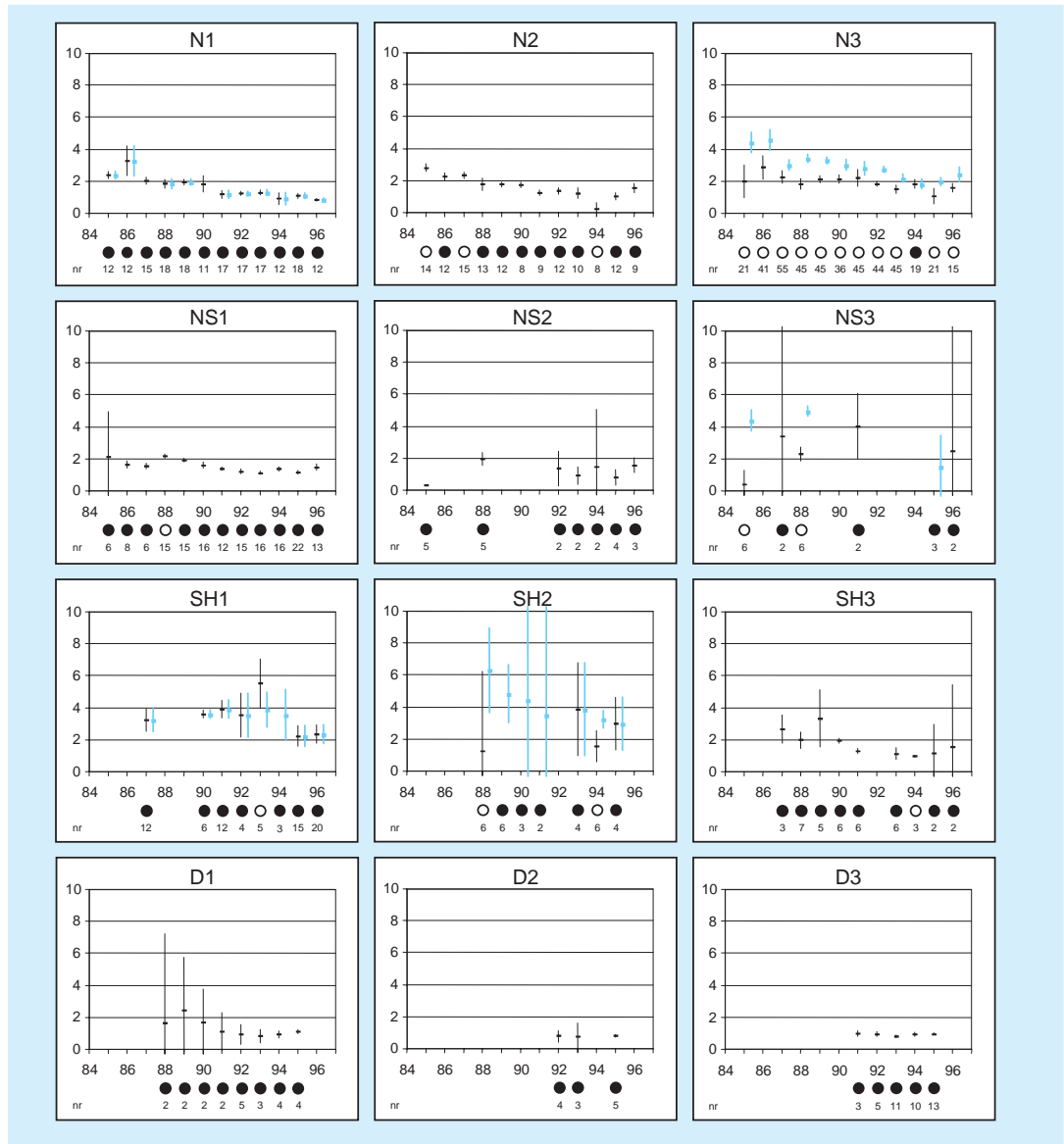
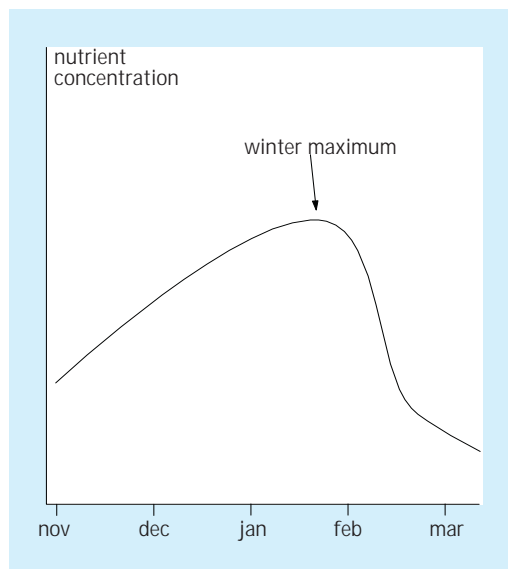


Figure 4.6. Schematic development of nutrient concentration during the winter period. The spring bloom starts directly after the winter maximum.



the period February- March and a good coverage of the entire salinity and/or geographical (inner to outer Wadden Sea) gradient.

For many areas, trend detection is severely hampered by the large variation in concentration within one winter-data set, often in combination with a limited number of data. Generally, the shortage of appropriate data gets more serious for recent years, apparently due to a further reduction of the national monitoring effort. The absence of a detectable reduction in some areas is also due to the limited amount of data. In some areas, there are only 3 or 4 years of data with a restricted amount of data for each year. There might be a reduction in concentration but it cannot be statistically confirmed.

Both aspects may be solved in the framework of the TMAP.

## 4.3 Assessment of Hazardous Substances

### 4.3.1 Introduction

Heavy metals, Poly Aromatic Hydrocarbons (PAHs), Poly Chlorinated Biphenyls (PCBs), HexaChloro-Benzene (HCB) and lindane ( $\gamma$ -HCH) data were assessed for sediments, blue mussel and bird eggs. Data are rather scattered and not consistently available for all matrices. In Table 4.6 developments in concentrations and inputs are summarized. The input, sediment and mussel data were tested for trend. The bird egg data were evaluated as significant change. More details can be found in sections 4.3.3-4.3.5 'Metal assessment'. Matrix concentrations were compared with agreed natural background (Table 4.4) and EAC levels (ecotoxicological assessment criteria) shown in Table 4.5.

Water, sediment and blue mussel data were obtained from national monitoring programs, stored in national databases (NL: DONAR, D: MUDAB, DK: NERI) and local databases.

Bird egg data were kindly supplied by P. Becker (Inst. f. Vogelforschung, Vogelwarte Helgoland, Wilhelmshaven), who has been running the bird egg research project and has been responsible for the TMAP bird egg analytical program since 1998.

### 4.3.2 Methodology

#### Sediments

Considerable methodological differences exist between the Wadden Sea countries. This applies both to analytical procedures (e.g. metal extraction) and analyzed matrix. In The Netherlands and Denmark, contaminants are analyzed in the wet sieved <math><63 \mu\text{m}</math> sediment fraction using partial metal extraction, whereas German data originate largely from the dry sieved <math><20 \mu\text{m}</math> fraction using total metal extraction. In the present evaluation, preferably data analyzed in the <math><63 \mu\text{m}</math> sediment fraction were used. The conversion method provided by Koopmann *et al.* (1993), was used to complement the metal data set where necessary with metal analyses in the <math><20 \mu\text{m}</math> fraction.

Extraction of organic contaminants was comparable between countries where differences in analyzed matrix were compensated for by standardization at 10% organic matter. Where necessary, organic matter data were derived from organic carbon data according to the formula provided by Bakker *et al.* (1996).

Comparing sediment data still faces the problem of methodological differences between the cooperating countries. The variation of yearly averaged within-area contaminant levels is large,

impeding proper evaluation of temporal and geographical trends. Reduction of variation may require data sets with a higher frequency. Alternatively, standardization has been shown to eliminate large variation due to differences in sediment composition (Smedes, 1997). Additionally extraction and destruction (total or partial) methods must be harmonized. This applies, especially, to the potential application of aluminum as a standardization parameter viz. an indicator of the <math><2 \mu\text{m}</math> fraction (OSPAR, 1997).

With respect to background concentration, an enrichment factor of metal concentration to the aluminum concentration in the same sample is used as a standardization procedure to define the background level of metals (Laane, 1992; OSPAR, 1997). As described by Smedes (1997) and Bakker *et al.* (1996) the destruction method of the sample has a profound effect on the aluminum concentration. Given this drawback, and the general absence of aluminum data, the metal/aluminum ratio could not be applied.

Generally, the top 5 cm of sediment is sampled for the sieving operation with the exception of Ribe county. Here, the top 5 mm was sampled. The top 5 cm provides a more time integrated picture of the contaminant levels, although depending on the turbation of the sediment. The top 5 mm shows a more recent, just settled, sediment. This fine layer, however, is highly variable. Suspended matter monitoring, collected by e.g. a flow-through centrifuge, is representative for this 5 mm layer and may serve as an alternative.

For future QSRs, it is important to reconsider and harmonize the monitoring strategy, sampling and fractionation procedures in the framework of both the Trilateral Monitoring & Assessment Program (TMAP) and the JAMP, as soon as possible.

#### Blue Mussel (*Mytilus edulis*)

Contaminants were analyzed in freeze dried soft body tissue of the blue mussel (*Mytilus edulis*) for most data. PAH and PCB data from Denmark and the German Federal Environmental Specimen Bank were analyzed in homogenized wet soft body tissue. All mussels were taken from *in situ* growing mussel beds. This type of monitoring is also referred to as PBM (passive biological monitoring), which is part of the Joint Monitoring and Assessment Program (JAMP) of OSPAR. Alternatively, the ABM (active biological monitoring of temporarily exposed mussels) is part of the Dutch monitoring program in the areas N1, N2 and N3. Those data were not included in the assessment.

All contaminants were expressed as dry weight (DW), which was chosen to exclude wet weight variance. Favorably PAHs and PCBs should have been expressed on a lipid basis but lipid data were not available for all data sources. It should be noted that Danish data on PAHs and PCBs could only be expressed on wet weight (WW) basis, which renders concentrations of about 5 - 6 times less than dry weight concentrations.

The comparison of mussel data depends very much on a proper standardization of contaminant levels. The dry weight was chosen now but, preferably, metals would have to be expressed as ash free dry weight, and organic contaminants on the basis of the lipid fraction. The ash-free dry weight represents the tissue really accumulating the metals. The lipid analysis has to be harmonized into a joint TMAP/JAMP standard method. Harmonization is essential to improve the quality of the trend analysis in future QSRs.

**Eggs of oystercatcher (*Haematopus ostralegus*) and common tern (*Sterna hirundo*)**

The egg, as sample unit, has several methodological advantages as matrix (Gilbertson *et al.*, 1987;

Becker, 1989; Becker *et al.*, 1991). In 1981 and from 1986 onwards, 10 fresh eggs per species per year per area were collected in areas N1 (Griend), N3 (Dollard), NS2 (Jadebusen), SH1 (Hullen, Elbe estuary), SH2 (Trischen), and SH3 (Norderoog). After completion of the clutch (May), one egg was taken for analysis. Organochlorine residues, since 1987 also 28 PCB congeners, and mercury have been analyzed (not yet in all samples from 1992-94). The residue levels are given in  $\mu\text{g}/\text{kg}$  fresh egg mass.

Sampling, storage and pre-treatment of seabird eggs was done in a standardized form (Becker *et al.*, 1998; JAMP Biota monitoring guidelines). The chemicals were analyzed by standard procedures (Tierärztliche Hochschule Hannover, 1981-1990, Becker *et al.*, 1991; Fachhochschule Wilhelms-haven, 1991-1996; Sommer *et al.*, 1997). Analytical quality assurance was achieved by intercalibration of the two laboratories as well as by participation in the European program QUASIMEME.

For monitoring of bird eggs in the framework of the TMAP program, it was decided to collect eggs by national effort but to do the sample preparation and analysis at a central institute, *i.e.* in

Metal	Laane (1992) Sediment	Laane (1992) Sediment $C_m/Al$	OSPAR (1997) Sediment $C_m/Al$	Pachur (1995) Sediment	OSPAR (1997) Mussel
Cd	0.5±0.01	0.11•10 <sup>-4</sup>	0.007-0.03•10 <sup>-4</sup>	0.28	0.07-0.11 [0.6]**
Cu	22±2.0	4.6•10 <sup>-4</sup>	2.2-5.7•10 <sup>-4</sup>	10.3	0.76-1.1 [6.2]**
Hg	0.067±0.009	1.4•10 <sup>-6</sup>	0.34-0.66•10 <sup>-6</sup>	0.02-0.04	0.005-0.01 [0.05]**
Pb	37±2.9	7.7•10 <sup>-4</sup>	1.8-4.0•10 <sup>-4</sup>	15.1±2.43	0.01-0.19 [0.7]**
Zn	103±5.2	21.4•10 <sup>-4</sup>	8.8-18•10 <sup>-4</sup>	102.1	11.6-30 [139]**
Σ <sup>6</sup> PAHs Borneff			1.480*		
Fluoranthene			0.341*		
Benz- <i>a</i> -Pyrene			0.179*		
Σ <sup>6</sup> PCBs					0.35-1.68 [6.8]**
PCB153					0.1-0.5 [2]**
HCB			0.00057*		

Table 4.4. Background concentrations of hazardous substances in sediment and blue mussel.

Metals: Estimated background levels of metals in pre-industrial sediments (fraction <63  $\mu\text{m}$ ; Metal content ( $C_m$ ) as mg/kg dry weight (Sediment and Mussel).  $C_m/Al$ : Metal/Aluminum ratios. The sediment core of Pachur *et al.* (1995) was not dated. Laane (1992): western Wadden Sea (Mokbay), OSPAR (1997): median values of world wide low polluted areas as  $C_m/Al$  ratios, Pachur *et al.* (1995): Ems estuary (Bocht van Watum), sediment slice depth: 310 - 320 cm.

Σ<sup>6</sup> PAHs Borneff: Sum of Benzo-*b*, *k*-Fluoranthene (Bb, kF), Fluoranthene (Flu), Benzo-*a*-Pyrene (BaP), Benzo-*ghi*-Perylene (BghiP), Indeno-123cd-Pyrene (InP).

Σ<sup>6</sup> PCBs: Sum of CB 28, 101, 118, 138, 135, 180, derived

from OSPAR (1997) Σ<sup>7</sup> PCBs, assuming a 1% contribution by CB52. The by OSPAR (1997) mentioned concentration in mussel is mg/kg wet weight. This is interpreted as a typing error and read into  $\mu\text{g}/\text{kg}$  wet weight (ref. Table 4.5: EAC values).

HCB: Value provided for the Skagerrak, a sedimentation area for the (southern) North Sea area.

\*: OSPAR (1997) sediment data converted to 10% organic matter containing sediments. OM% = 2.196-TOC%

Concentration as  $\text{mg}\cdot\text{kg}^{-1}$  10% OM sediment by Dry Weight. \*\*: Mussel: for estimation of average DW (dry weight) concentration from wet weight: 15% dry weight in wet tissue was assumed. Estimated DW background between [ ] in mg/kg DW.

the Fachhochschule in Wilhelmshaven (Prof. P. Becker). The potential advantages of this approach are high, ensuring, *e.g.*, identical analytical methods for the entire Wadden Sea area, and should be evaluated for the next QSR.

### 4.3.3 Assessment of metals: temporal trends

Although the incomplete data sets and methodological differences between years and areas impede a proper evaluation, some conclusions may carefully be drawn.

Temporal trends in sediments and blue mussel were analyzed for the period 1985 - 1996 and determined with the parameter-free Man-Kendall test on yearly averaged data, using  $p < 0.05$  for a significant trend. The trends were double-checked using Box-Whisker-plots on all data, indicating calculated median values and 25-75 percentile boxes.

The significance of temporal trends in bird eggs was tested using Spearman correlation coeffi-

icients. Percentual change of year X to year Y was defined as  $X-Y = (C_x * 100 / C_{(x-y)}) - 100$ .

In understanding the trends it is important to realize that the entire period 1985-1996 was assessed. If contaminant levels in 1985 and 1996 were of the same order of magnitude, this will be interpreted as "no trend", although an intermediate period of higher contaminant levels may have occurred. Many contaminants show such temporal fluctuations, especially when background levels are reached.

Trends are tabulated in Table 4.6. Actual (1996) Wadden Sea levels are shown in Table 4.7. Agreed background levels are shown in Table 4.4, ecotoxicological assessment criteria in Table 4.5 (OSPAR, 1997). Background levels are dependent on the mineralogical history of the area. To show the area specific situation, the data of a long sediment core, taken in the Bocht van Watum (Ems estuary, N3) were added to Table 4.4 for illustration (Pachur *et al.*, 1995).

Compound	Sediment (mg/kg DW) 1% TOC (= 2% OM)	Mussel (mg/kg DW)
Cd	0.1-1	
Cu	5-50	
Hg	0.05-0.5	
Pb	5-50	
Zn	50-500	
Fluoranthene	0.5-5 (2.5-25)*	1-10
Benzo-a-Pyrene	0.1-1 (0.5-5)*	5-50
Σ6 PCBs	0.001-0.01	0.005-0.049 (f)
TBT	0.000005-0.00005	0.001-0.01(f)

Table 4.5. Agreed ecotoxicological assessment criteria. OSPAR, 1997. All values are provisional, except for (f): firm. (\*)\*: value at 10% OM standardized sediment.

Riverine input/ Area	Cd	Cu	Hg	Pb	Zn	g-HCH	β-HCH	Σ <sup>6</sup> PCBs	Σ <sup>14</sup> PAHs
<b>IJsselmeer</b>	<b>-50%</b>	<b>-60%</b>	<b>-30%</b>	<b>-10%</b>	<b>=</b>	<b>-80%</b>			
<b>N1 sediment</b>	<b>-40%</b>	<b>=(1988)</b>	<b>=</b>	<b>=</b>	<b>-25%</b>			<b>-60%</b>	<b>-50%</b>
<i>Mussel</i>									
<i>Bird eggs</i>			<i>s.</i>			<b>-84%</b>		<b>-73%</b>	
<b>N2 sediment</b>	<b>-40%</b>	<b>=*</b>	<b>-35%</b>	<b>-25%</b>	<b>-30%</b>			<b>-70%</b>	<b>-50%</b>
<i>Mussel</i>									
<i>Bird eggs</i>									
<b>Ems</b>	<b>-75%</b>	<b>=</b>	<b>=</b>	<b>=</b>	<b>=</b>	<b>-50%</b>		<b>=</b>	
<b>N3 sediment</b>	<b>=</b>	<b>=</b>	<b>=</b>	<b>=</b>	<b>=</b>			<b>-60%</b>	<b>-50%</b>
<i>Mussel</i>	<b>=</b>	<b>-15%</b>	<b>=</b>	<b>-70%*</b>	<b>=</b>			<b>-50%</b>	<b>-60%</b>
<i>Bird eggs</i>			<b>=</b>			<b>=</b>		<b>-69%</b>	
<b>NS1 sediment</b>	<b>-50%</b>	<b>=</b>	<b>=</b>	<b>=</b>	<b>=</b>				
<i>Mussel</i>	<b>&lt;</b>	<b>&lt;</b>	<b>=</b>	<b>=</b>	<b>=</b>			<b>-40%</b>	
<i>Bird eggs</i>									
<b>NS2 sediment</b>	<b>-70%</b>	<b>=</b>	<b>=</b>	<b>=</b>	<b>=</b>				
<i>Mussel</i>	<b>&lt;</b>	<b>&lt;</b>	<b>=</b>	<b>=</b>	<b>&lt;</b>			<b>-55%</b>	
<i>Bird eggs</i>			<b>-18%(CT)</b>			<b>=</b>	<b>+185%(OC)</b>	<b>-76%</b>	
<b>Weser</b>	<b>=</b>	<b>=</b>	<b>=</b>	<b>+250%</b>	<b>&gt;</b>	<b>-70%</b>		<b>=</b>	
<b>NS3 sediment</b>	<b>-60%</b>	<b>=</b>	<b>=</b>	<b>=</b>	<b>=</b>				
<i>Mussel</i>									
<i>Bird eggs</i>									
<b>Elbe</b>	<b>-55%</b>	<b>-45%</b>	<b>-75%</b>	<b>-60%</b>	<b>-50%</b>	<b>-80%</b>		<b>-85%</b>	
<b>SH1 sediment</b>	<b>-60%*</b>	<b>&gt;*(1994)</b>	<b>=</b>	<b>&lt;</b>	<b>-50%</b>				
<i>Mussel</i>	<b>-45%</b>	<b>=</b>	<b>-60%</b>	<b>+200%</b>	<b>-70%*</b>			<b>=</b>	
<i>Bird eggs</i>			<b>-69%</b>			<b>-98%(CT)</b>	<b>-87%(CT)</b>	<b>-71%</b>	
<b>Eider</b>	<b>=</b>	<b>&lt;</b>	<b>=</b>	<b>&lt;</b>	<b>=</b>	<b>-50%</b>		<b>-50%</b>	
<b>SH2 sediment</b>	<b>=</b>	<b>&gt;*(1995)</b>	<b>&gt;*(1995)</b>	<b>=</b>	<b>&gt;*(1995)</b>				
<i>Mussel</i>									
<i>Bird eggs</i>			<b>-44%</b>			<b>+8%(CT)</b>	<b>-65%(OC)</b>	<b>-64%</b>	
<b>SH3 sediment</b>	<b>=</b>	<b>=</b>	<b>=</b>	<b>=</b>	<b>=</b>				
<i>Mussel</i>	<b>=</b>	<b>-40%</b>	<b>-55%</b>	<b>&gt;</b>	<b>-25%</b>			<b>-30%</b>	
<i>Bird eggs</i>			<b>=</b>			<b>=</b>	<b>-68%(OC)</b>	<b>-70%</b>	
<b>D1 sediment</b>	<b>(&lt;)</b>	<b>(&lt;)</b>	<b>(=)</b>	<b>(&lt;)</b>	<b>(&lt;)</b>				
<i>Mussel</i>	<i>s.</i>	<i>s.</i>	<i>s.</i>	<i>s.</i>	<i>s.</i>			<i>s.</i>	<i>s.</i>
<i>Bird eggs</i>									
<b>County Sønderjylland</b>									
<b>D2 sediment</b>	<b>()</b>	<b>(&lt;)</b>	<b>s.</b>	<b>s.</b>	<b>(&lt;)</b>				
<i>Mussel</i>	<i>s.</i>	<i>s.</i>	<i>s.</i>	<i>s.</i>	<i>s.</i>			<i>s.</i>	<i>s.</i>
<i>Bird eggs</i>									
<b>County Ribe</b>									
<b>D3 sediment</b>	<b>(&lt;)</b>	<b>(&lt;)</b>	<b>s.</b>	<b>=</b>	<b>(&gt;)</b>				
<i>Mussel</i>	<b>=</b>	<b>&gt;</b>	<b>=</b>	<b>=</b>	<b>=</b>			<i>s.</i>	<i>s.</i>
<i>Bird eggs</i>									

Table 4.6. Temporal developments of riverine hazardous substances inputs (shaded rows) and Wadden Sea concentrations over the period 1985–1996. Trends refer to a significant and ongoing increase or decrease during the period 1985–1996 and are expressed in bold. Changes refer to a significant difference between de data sets of compared years and are expressed in italics.

Trends according to yearly averaged values were analyzed with parameter-free Man-Kendall. The Man-Kendall p-value is on the right of each box. A p-value ≤ 0.05 was considered to indicate a significant trend.

\*: Significance boundary, implying the presence of a trend depends on Man-Kendall with averaged or median values. In some occasions a strong reduction is followed by a strong increase in recent years.

s.: single year.

(Year): last year for which data available.

Bird eggs: average of common tern (CT) and oystercatcher (OC) eggs, unless otherwise mentioned. blank : not investigated; s.: single year.

= No trend.

(=) No trend; not enough data.

< Decreasing; merely indicative, doubtful quality of data or otherwise uncertain.

(<) Decreasing; not enough data.

> Increasing; merely indicative, doubtful quality of data or otherwise uncertain.

(>) Increasing; not enough data.

() Not enough data.

Riverine input/ Area	Cd mg/kg (1% TOC)	Cu mg/kg (1% TOC)	Hg mg/kg (1% TOC)	Pb mg/kg (1% TOC)	Zn mg/kg (1% TOC)	g-HCH (µg/kg)	HCB (µg/kg)	Σ <sup>6</sup> PCBs (µg/kg)	Σ <sup>6</sup> PAHs (µg/kg)	Flu 1% TOC	BaP 1% TOC
<b>IJsselmeer</b>											
<b>N1 sediment</b>	0.7 (0.2)	20 (6)	0.3 (0.1)	58 (18)	147 (46)		1	15	780	47	21
Mussel	nd	nd	nd	nd	nd		nd	nd	nd		
Bird eggs	nd	nd	677-326*	nd	nd	7-7*	14-nd	500*-302*	nd		
<b>N2 sediment</b>	0.6 (0.2)	16 (6)	0.2 (0.1)	46 (18)	117 (47)		1.3	13	804	43	22
Mussel	nd	nd	nd	nd	nd		nd	nd	nd		
Bird eggs	nd	nd	355*-353*	nd	nd	5*-5*	13-4*	398*-403*	nd		
<b>Ems</b>											
<b>N3 sediment</b>	0.5 (0.2)	16 (7)	0.2 (0.1)	43 (19)	116 (52)		3.1	14	1009	55	28
Mussel	1.0*	6.6	0.2	0.5	94		0.7	100*	145		
Bird eggs	nd		nd-167	nd	nd	nd-6	nd-11	nd-531*	nd		
<b>NS1 sediment</b>	0.5* (0.2)	20* (6)	0.4* (0.1)	78* (17)	140* (51)		1.1*	11*			
Mussel	0.6*	6.5*	0.1*	0.7*	70*		0.4*	42*			
Bird eggs	nd	nd	nd	nd	nd	nd	nd	nd			
<b>NS2 sediment</b>	0.4* (0.4)	14* (8)	0.2* (0.1)	49* (24)	102* (72)		0.5*	11*			
Mussel	0.9*	7.5*	0.1*	0.9*	79*		0.4*	64*			
Bird eggs	nd	nd	342-260	nd	nd	6-13	21-8	338*-378*			
<b>Weser</b>											
<b>NS3 sediment</b>	0.5* (0.5)	13* (10)	0.2* (0.2)	51* (37)	115* (120)		0.5*	13*			
Mussel	nd	nd	nd	nd	nd		nd	nd			
Bird eggs	nd	nd	nd	nd	nd	nd	nd	nd			
<b>Elbe</b>											
<b>SH1 sediment</b>	0.4* (0.3)	82* (8)	0.3* (0.2)	30* (27)	108* (122)		nd				
Mussel	0.9	10.3	0.2	1.0	106		8.3	154			
Bird eggs	nd	nd	1826-227	nd	nd	13-14	372-43	1096*-401*			
<b>Eider</b>											
<b>SH2 sediment</b>	0.5* (0.3)	14* (11)	0.3* (0.2)	40* (26)	111* (79)		nd				
Mussel	nd	nd	nd	nd	nd		nd	nd			
Bird eggs	nd	nd	871-273	nd	nd	10-16	65-11	467*-349*			
<b>SH3 sediment</b>	0.6* (0.3)	11* (7)	0.2* (0.1)	34* (18)	99* (57)		nd				
Mussel	0.4	6.3	0.1	0.7	74		0.4	41			
Bird eggs	nd	nd	413-392	nd	nd	6-8	16-4	239*-238*			
<b>D1 sediment</b>	0.1* (0.4)	4* (7)	0.2* (0.1)	10* (17)	51* (57)		nd				
Mussel	0.8*	7.1*	0.2*	1.4*	77*			nd			
Bird eggs	nd	nd	nd	nd	nd	nd	nd				
<b>County Sønderjylland</b>											
<b>D2 sediment</b>	nd	nd	nd (0.2?)	nd	nd		nd				
Mussel	0.7*	8.7*	0.2*	1.8*	85*			nd			
Bird eggs	nd	nd	nd	nd	nd	nd	nd				
<b>County Ribe</b>											
<b>D3 sediment</b>	nd	nd	nd	nd	nd		nd				
Mussel	0.6	8.9	0.3	2.0	101			nd			
Bird eggs		nd	nd	nd	nd	nd	nd				

Table 4.7. Actual levels (1996, or as recent as available marked \*) of contaminants in Wadden Sea matrices. All data dry weight (DW), except bird eggs wet weight (WW).

Bird eggs: first number: Common tern, second number: Oystercatcher (data after Becker *et al.*, 1998).

nd: no data.

ΣHCH: g-a-b-g-HCH.

Σ<sup>6</sup>PCBs: sum CB 28,101,118,138,153,180.

Σ<sup>6</sup>PAHs: sum of Fluoranthene, Benzo-b/k-Fluoranthene, Benzo-a-Pyrene, Indene-123,cd-Pyrene, Benzo-ghi-Perylene (Borneff PAHs).

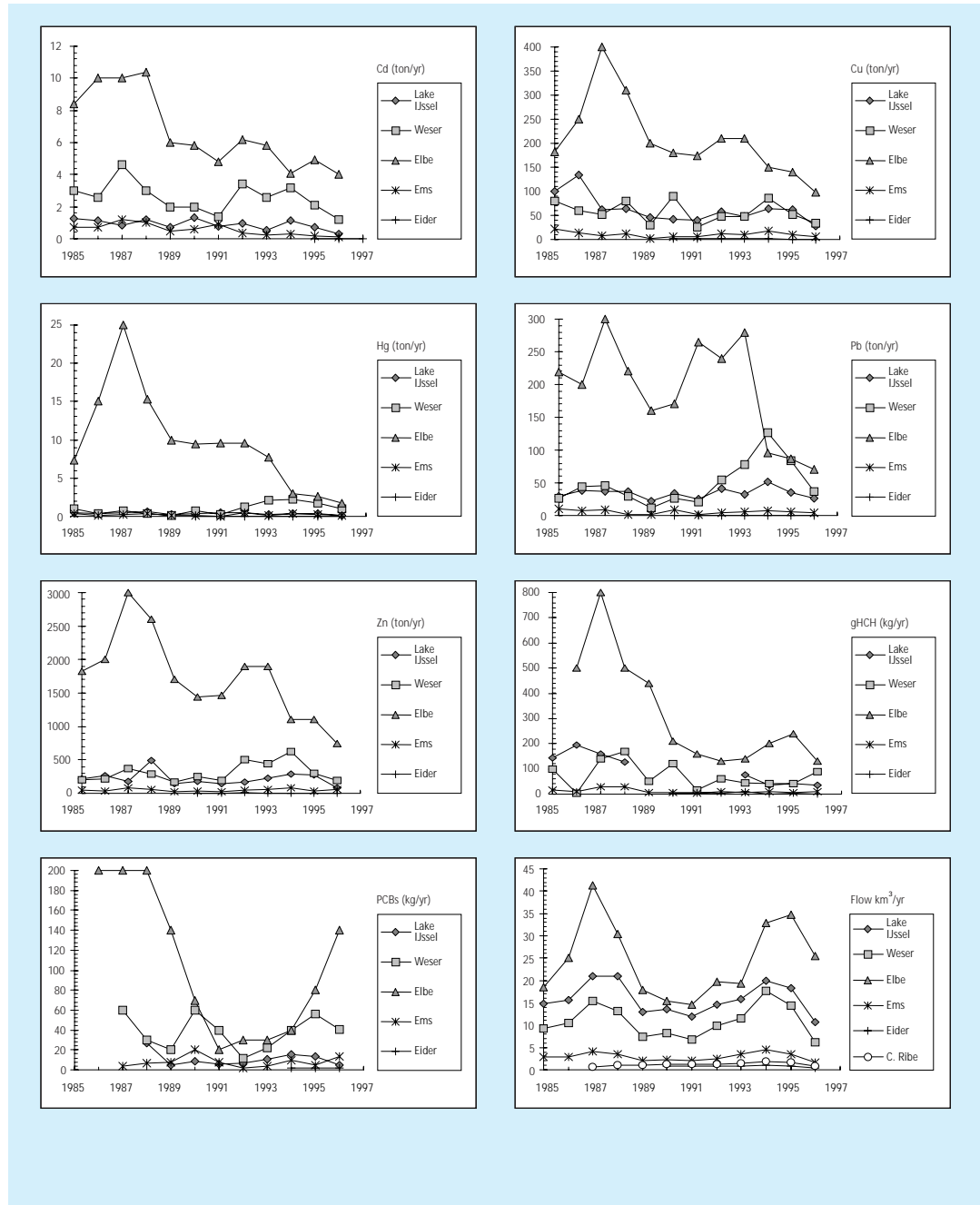
1% TOC: sediment data were standardized to sediment containing 1% (T)OC by the formula: Cm (1% TOC) = Cm \* (1/[TOC]).

To be used with EACs (Table 4.5).

Cm: metal content.

TOC: organic carbon content.

Figure 4.7. Riverine inputs of metals, lindane ( $\gamma$ -HCH) and PCBs ( $\Sigma^6$ PCBs) into the Wadden Sea.



**Cadmium**

A true (not dependent on low river flows) input reduction of cadmium by the Lake IJsselmeer and Elbe (Figure 4.7; Table 4.6) also shows up as reduction in the concentrations in sediments and mussels in the corresponding estuarine areas (Figure 4.8, Figure 4.9). In the case of Lake IJsselmeer, the decrease in concentration in mussel started in 1982 (data not shown), which was a peak year compared to preceding and following years. The decrease in sediment concentrations in the western Dutch Wadden Sea (N1) was quick between

1988 and 1990, gradually further decreasing with less incidence of peak concentrations.

The Elbe quantitative input of cadmium quickly decreased between 1988 and 1989, while the cadmium concentration steadily decreased since (before) 1985. While sediment cadmium contents have gradually decreased since 1983 (which was a relative peak year), mussel concentrations have been decreasing since 1989 (which was a peak year relative to the period 1986-1989). This may indicate a relation between cadmium input and concentration in mussel, whereas sediments re-

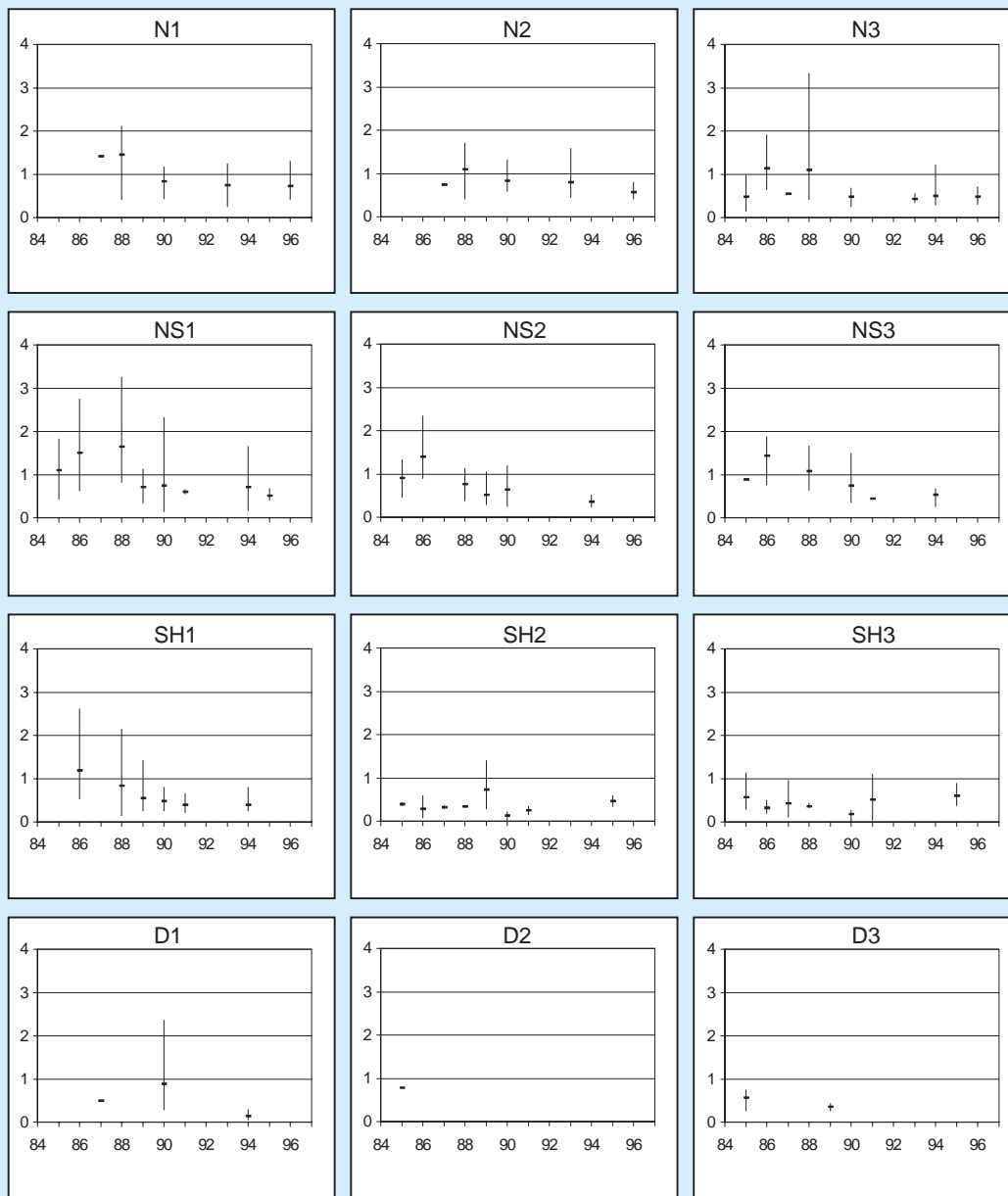


Figure 4.8. Cadmium (Cd) contents (mg/kg DW) of Wadden Sea sediments in the fraction <63 μm. Average (-) and minimum/maximum (|) values are shown (DW=dry weight).

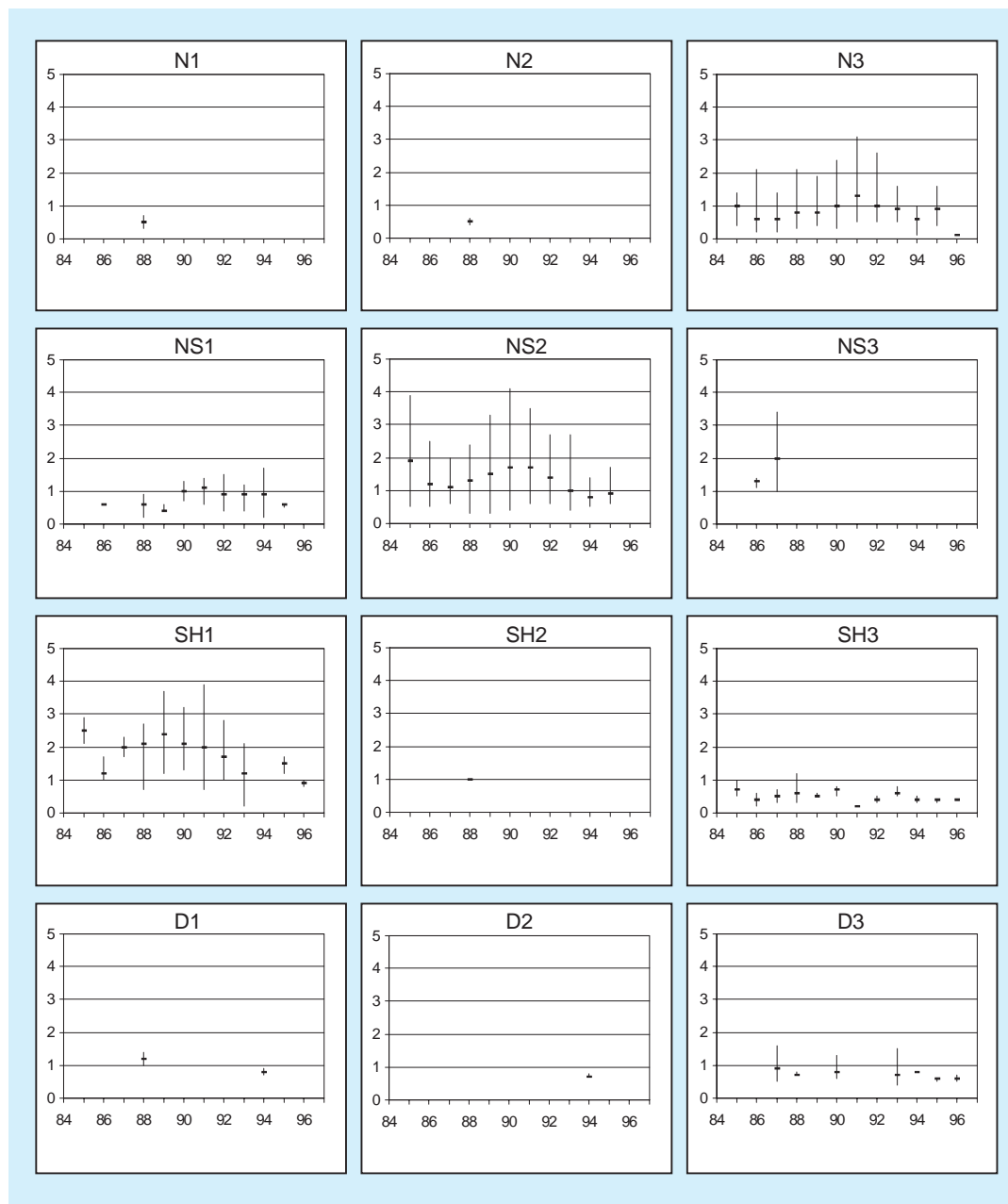
spond to cadmium concentration in river water. No significant trends could be found for sediments and mussels in the Ems estuary.

The Ems river shows a cadmium input reduction and river water concentration decrease since 1991 (Table 4.6). Mussel cadmium levels in the Ems estuary are decreasing since 1991 as well, apparently following the riverine reduction (Figure 4.7). Sediments in the eastern Dutch (N2) and Niedersachsen (NS1) Wadden Sea are showing a decrease, which may be related to the Ems reduction.

The river Weser does not show a significant reduction in cadmium input, mainly due to the period to period fluctuations. There is, however, a significant decrease in sediments of the Weser estuary (NS3), which is not discernible in mussel due to missing data.

The Eider river shows input fluctuations like the Weser. No trends could be found for mussel and sediment north of the SH2 area. Partly due to a lack of data, but mainly because cadmium concentrations here are at the lowest of the entire Wadden Sea and most close to the agreed background.

Figure 4.9. Cadmium (mg/kg DW) in mussel (soft body). Yearly average (-) and minimum/maximum (|) of all length classes per area (DW = dry weight).



Cadmium concentrations in sediment are within, but at the high end of the agreed background range in most areas (Table 4.4 and 4.7), whereas concentrations in mussel are slightly above background. The cadmium contents of Wadden Sea sediments (period 1994-1996) is within the range of provisional ecotoxicological assessment criteria (OSPAR, 1997; Table 4.5).

#### Copper

Only for the Elbe has a significant quantitative input reduction since 1987 (Figure 4.7; Table 4.6). This reduction has started to show up

as a (not significant) reduction of copper concentration in Elbe estuarine mussels since 1993. This may be related to the dramatic decrease in copper concentrations in river water since 1993. Thus the mussel copper content may not be determined by the quantitative load but by the riverine copper concentrations.

The Elbe (SH1) and Eider (SH2) estuary sediments have shown since about 1990, an unexplained increasing copper content, known as the "copper anomaly" (Stachel and Lüchow, 1996).

In both sediments and mussel, no significant reduction or downward trend was found in most

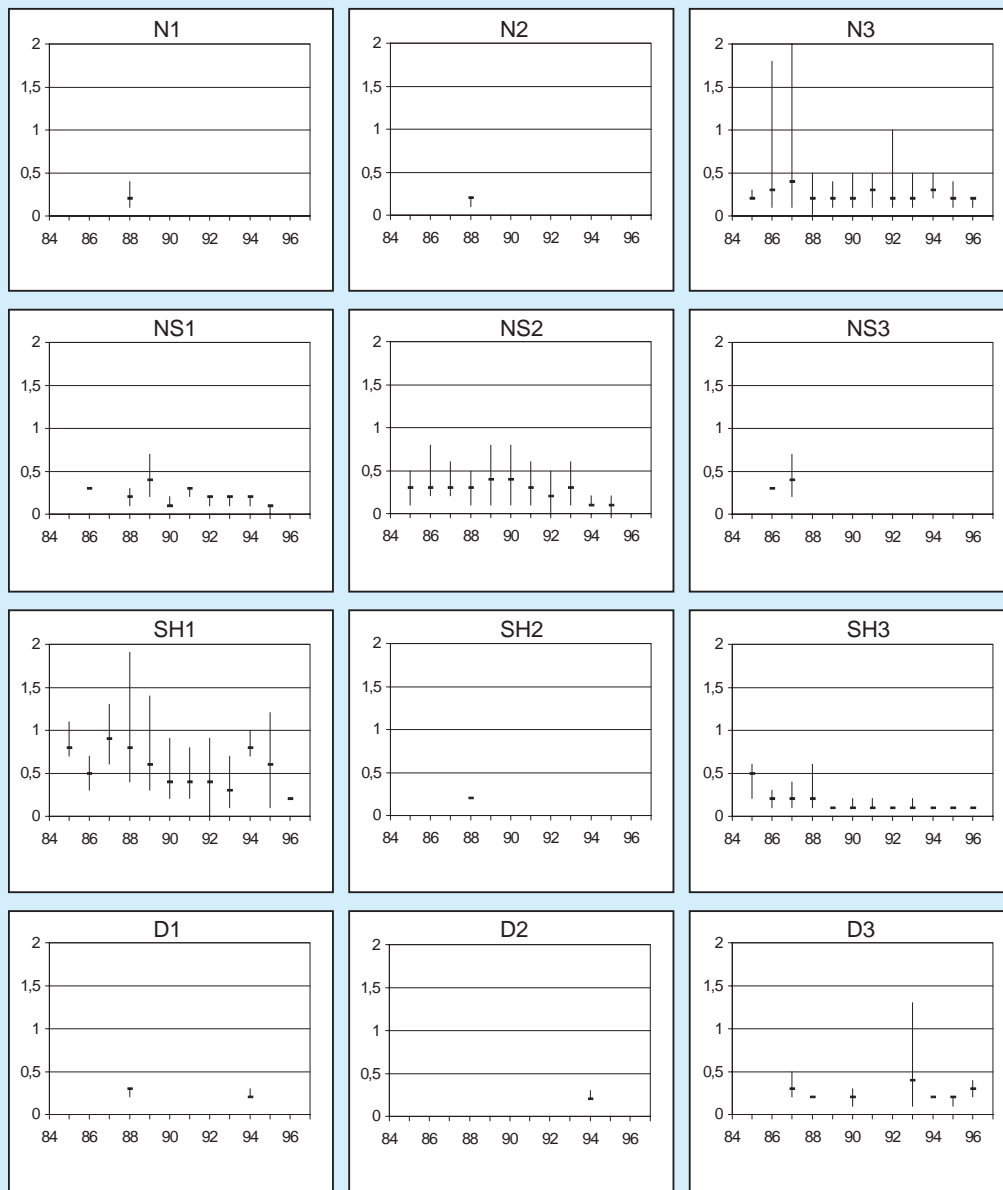


Figure 4.10. Mercury (mg/kg DW) in mussel (soft body). Yearly average (—) and minimum/maximum (|) of all length classes per area (DW = dry weight).

of the estuarine areas (Table 4.6). The sediment copper reduction in the 1985-1996 period was mainly caused by the 1985 peak.

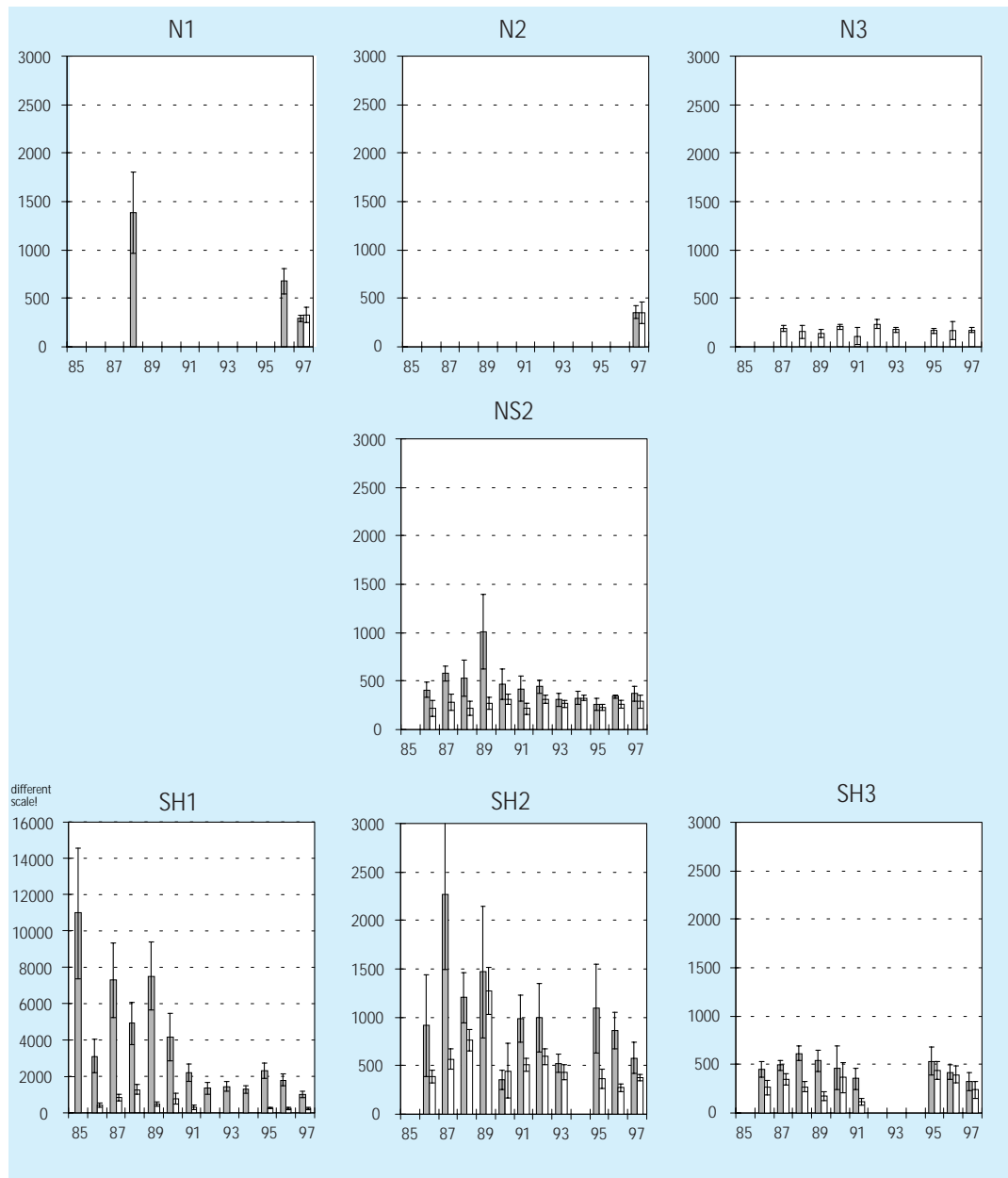
The absence of trends in concentrations in sediments of most marine areas may be explained by the fact that copper concentrations have reached the agreed background range (Table 4.4). Copper concentrations in mussel are slightly above background in the Elbe estuary.

Copper contents of Wadden Sea sediments (period 1994-1996) were within the range of provisional ecotoxicological assessment criteria (OSPAR, 1997; Table 4.5 and 4.7).

### Mercury

The mercury input by the Elbe shows a significant dramatic reduction (Figure 4.7; Table 4.6). Like copper, the strong reduction of the quantitative mercury input started in 1987. The reduction in riverine mercury concentration however, only began in 1991. Unlike copper, mercury in mussel is following the input reduction. Because mussel mercury levels increased again in recent years, no significant reduction trend was obtained (Figure 4.10). Mercury levels in bird eggs (common tern, *Sterna hirundo*, and oystercatcher, *Haematopus ostralegus*) are significantly decreasing, follow-

Figure 4.11. Mercury concentrations ( $\mu\text{g}/\text{kg}$  WW) in eggs of the oystercatcher (*Haematopus ostralegus*, open bars) and common tern (*Sterna hirundo*, hatched bars). average: bars, 95% confidence limits:|. WW= wet weight egg mass. Data from Becker, P. (Institut für Vogelforschung Wilhelmshaven) and Becker *et al*, 1998.



ing the mercury input reduction with some delay (Figure 4.11). No trend was found in Elbe estuary sediments (Figure 4.12).

In the Schleswig-Holstein area, sediment mercury content, like copper, has been rather increasing since 1990. Mercury in mussel and bird eggs tends to decrease, however. Considering the elevated mercury levels in SH1 mussels and SH2 sediments, both in 1995, suggests a water mediated transport of suspended matter from the Elbe estuary (accumulated by mussel) into the sediments of the Eider area (sedimentation).

The reduction in mercury concentrations in

sediment of the Dutch and Niedersachsen Wadden Sea is significant only in the eastern Dutch Wadden Sea (N2; Table 4.6). This is not reflected by concentrations in mussels or bird eggs, except for bird eggs in the Jadebusen (NS2), and, partly, due to the absence of data, in N2. Generally, mercury levels are either decreasing or remaining at the same, variable level. The Weser and SH1 and SH2 areas are suspect of increasing mercury levels.

In all areas, mercury levels in sediment are 3 - 10 times higher and mercury levels in mussel about 2 - 4 times higher than the agreed back-

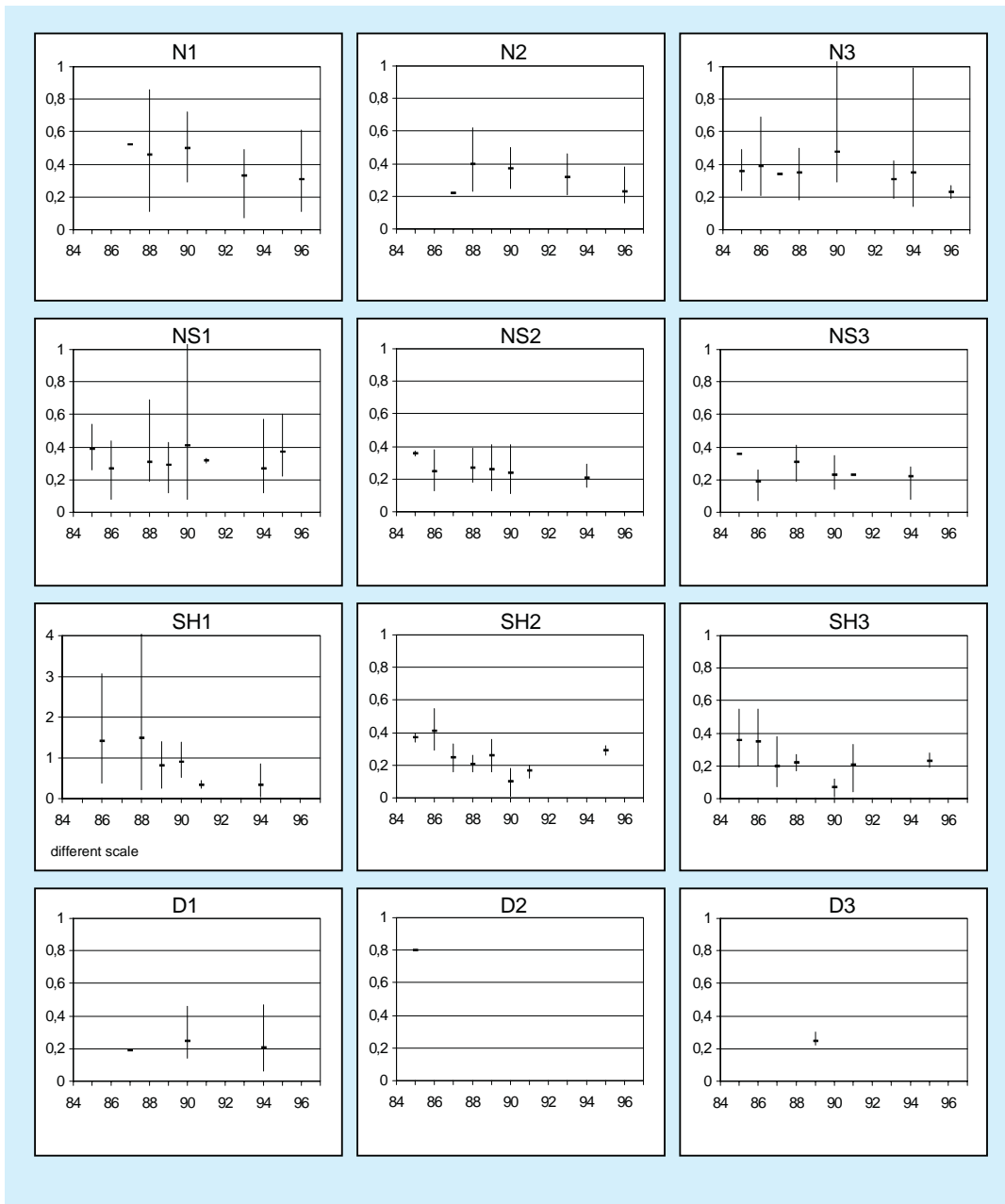


Figure 4.12 Mercury (Hg) contents (mg/kg DW) of Wadden Sea sediments in the fraction <math><63 \mu\text{m}</math>. Average (-) and minimum/maximum (|) values are shown (DW = dry weight).

ground range (Table 4.4). The mercury contents of Wadden Sea sediments (period 1994-1996) is within the range of provisional ecotoxicological assessment criteria (OSPAR, 1997; Table 4.5 and 4.7).

#### Lead

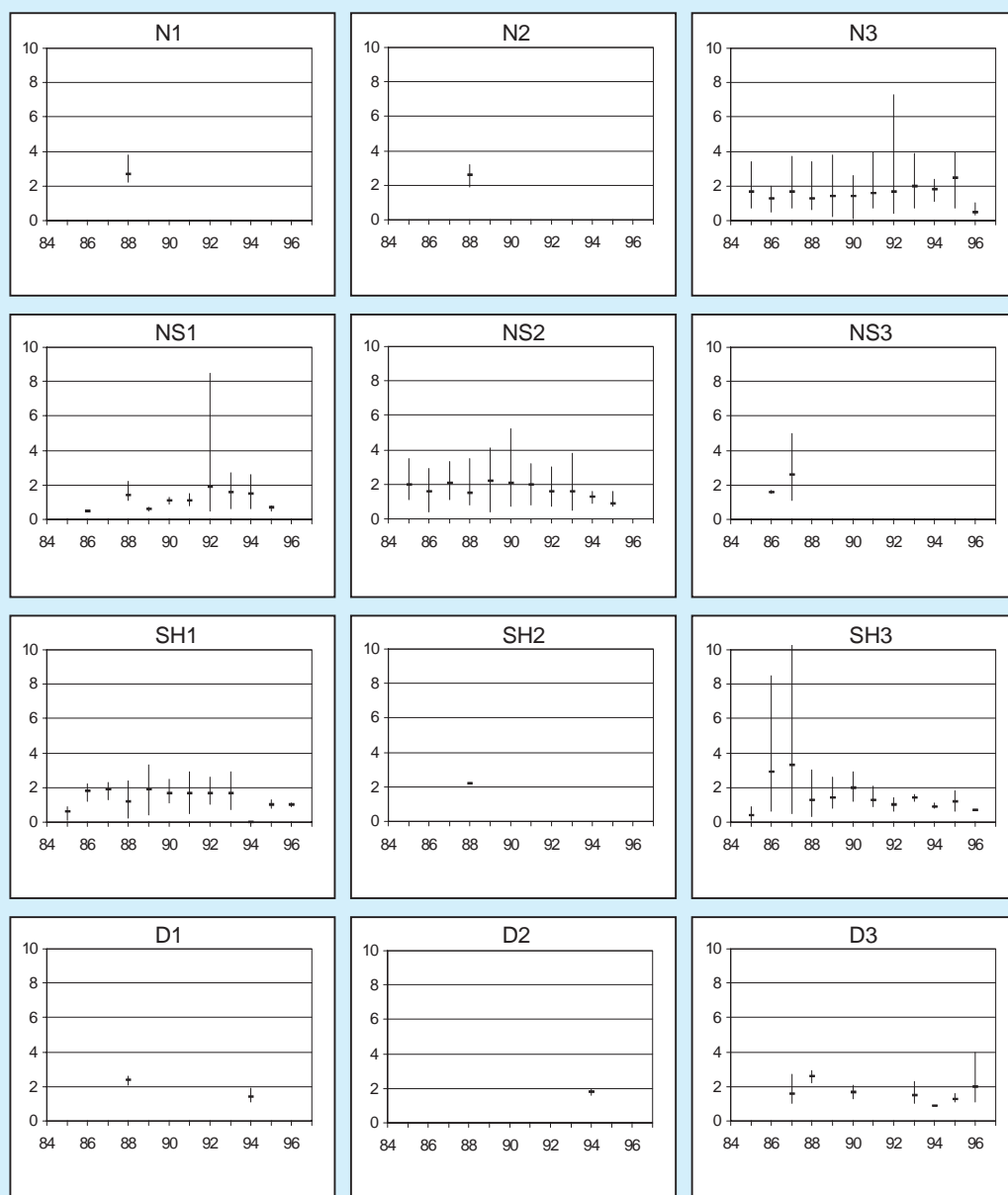
The strongest input reduction of lead can be attributed to the river Elbe, beginning in 1993 after a period of increasing levels (Figure 4.7; Table 4.6). The input reduction is reflected by a decreasing level in mussels (Figure 4.13), being less explicit in sediments due to the variability (Figure 4.14).

In the other Wadden Sea areas, lead inputs and levels in sediment and mussel do not show clear trends in the period 1985-1996.

The Weser input (Table 4.6) and riverine lead levels are suspected to have increased since 1991, which is, however, not reflected in the sediment data. Mussel data were not sufficient to draw conclusions.

Lead levels in sediments of the Dutch and Niedersachsen Wadden Sea are slightly higher compared to background levels (Table 4.4). The elevation factor of 1.5 - 2 can, however, easily be explained by the effect of differences in grain size

Figure 4.13. Lead (mg/kg DW) in mussel (soft body). Yearly average (-) and minimum/maximum (|) of all length classes per area.



distribution of the sediments. Lead levels in mussel are within the range of agreed background levels.

Lead contents of Wadden Sea sediments (period 1994-1996) are within the range of provisional ecotoxicological assessment criteria (OSPAR, 1997; Table 4.5 and 4.7).

#### Zinc

Again, the most dramatic drop in riverine zinc inputs and concentrations in water are achieved in the river Elbe (Figure 4.7; Table 4.6). This shows

up in the Elbe estuarine sediments (SH1) were zinc levels have dropped significantly since 1987.

Although zinc is regulated by the mussel, by accumulation in metallothioneines, a remarkable drop (a factor 4 reduction), can be observed in the Elbe estuary following 1991, reaching the lowest level in the entire Wadden Sea in 1994 (partially 1995). This occurred after a period (1989-1991) of elevated zinc levels in mussel. The concurrent reduction in mussel zinc levels in the Halligen area (SH3) suggests a relation to the Elbe input, too. Unfortunately, this cannot be checked

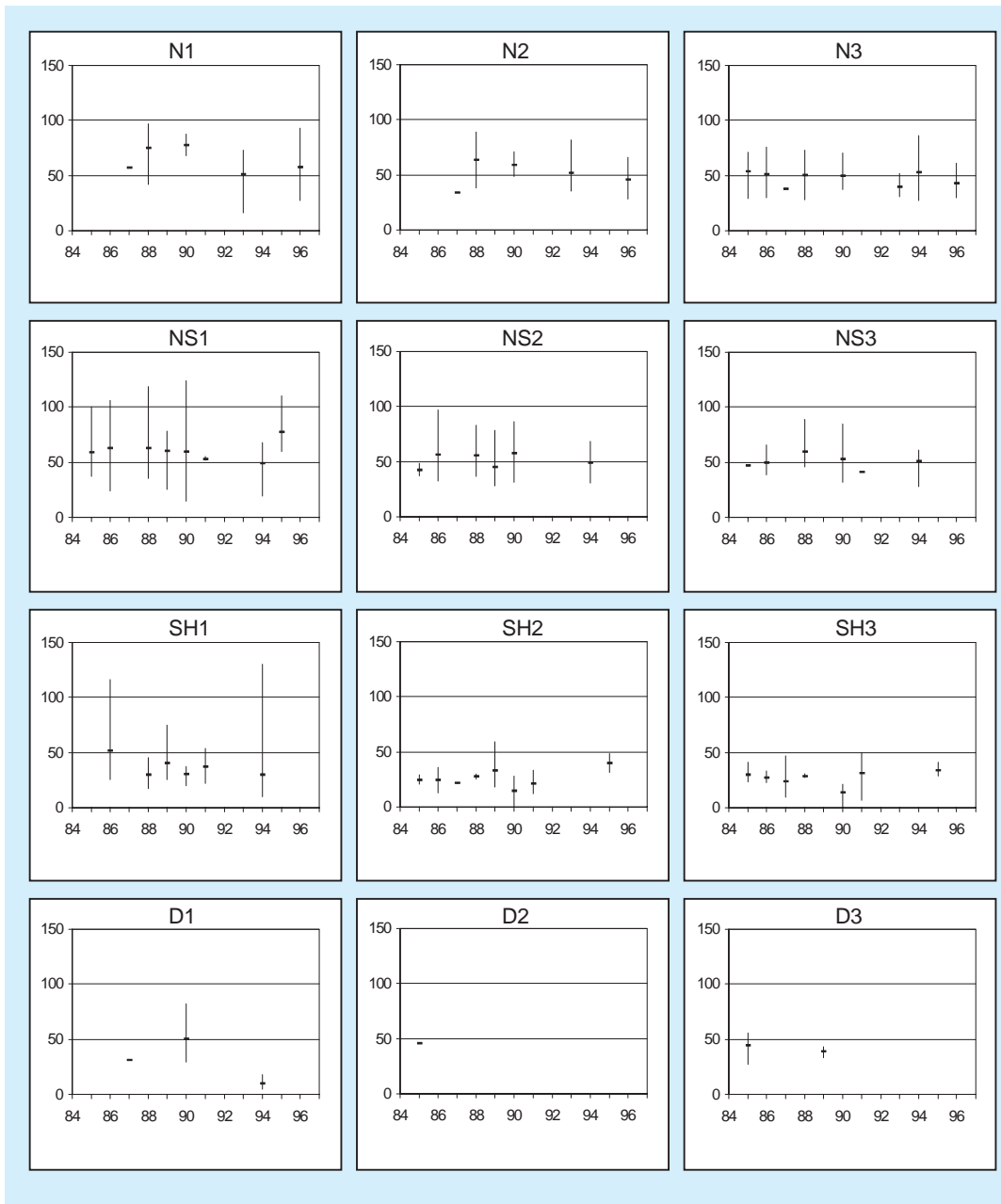


Figure 4.14. Lead (Pb) contents (mg/kg DW) of Wadden Sea sediments in the fraction  $< 63 \mu\text{m}$ . Average (—) and minimum/maximum (|) values are shown. (DW=dry weight).

for the Eider area (SH2) due to a lack of mussel data. The quantitative input reduction started from 1987 onwards but the riverine zinc levels decreased sharply after 1991. This suggests that riverine zinc levels, like copper, are important for concentrations in mussel, whereas riverine flux is important for sediment levels.

No significant zinc input reduction was found for the remaining rivers. Apart from the western (N1) and eastern (N2) Dutch Wadden Sea, where a significant reduction in sediment zinc levels was observed, no trends were found in other Wadden

Sea sediments. In the Ems estuary (N3), zinc levels appear to decrease (not significantly) after a period (1989-1991) of elevated levels, like in the Elbe estuary (SH1). Zinc in mussel of the Jadebusen (NS2) also seems to decrease again, after having reached a maximum in 1991.

In the period 1994-1996 zinc levels in Wadden Sea sediments and mussel have been near background levels. Grain size distribution differences may explain part of the observed variation in sediment concentrations (Table 4.4). Zinc contents of Wadden Sea sediments (period 1994-

1996) are within the range of provisional ecotoxicological assessment criteria (OSPAR, 1997; Table 4.5 and 4.7).

#### 4.3.4 Temporal trends in metals: conclusions

Trend evaluation covered the period 1985 - 1996. This implies that trends occurring after the strong reductions in the period 1980-1985 are not part of the evaluation anymore, although being a witness of successful environmental management. The large variation in metal concentrations in sediment, mussel and bird eggs (where applicable) is getting less extreme throughout the evaluated period. As a net result, this leads to an overall reduction of metal contamination in the Wadden Sea, converging to the natural background for most metals, except mercury. This also explains why trends are getting less explicit and significant. All investigated metals are within the range of provisional ecotoxicological criteria for sediment (OSPAR, 1997).

#### 4.3.5 Assessment of metals: geographical trends

Metal levels in sediments (Table 4.7) were generally higher in the western and southern Wadden Sea (N1-SH1). In the Schleswig-Holstein and Danish Wadden Sea, sediment metal levels were near background levels (Table 4.4) and roughly a factor 2 - 3 lower than in the other areas, although recent data for D2 and D3 were not available.

For contaminant contents of sediments, no internationally accepted management targets exist. In the framework of OSPAR, background values have been proposed by a NSTF workshop (Laane, 1992) and agreed on recently (OSPAR, 1997; Table 4.4). Additionally historical data were derived from a core taken in the Bocht van Watum in the Ems estuary (Pachur *et al.*, 1995). The metal content at 300 cm depth represents most likely background levels, although attempts to date the core failed.

The present range of metal levels in the Wadden Sea shows that the Danish and Schleswig-Holstein Wadden Sea is generally close to background levels (Table 4.7). The Dutch and Niedersachsen Wadden Sea show, locally, enrichment of metals, especially cadmium and mercury, and, to a lesser extent, lead.

#### 4.3.6 Assessment of Polyaromatic Hydrocarbons (PAHs)

Only for the Dutch Wadden Sea sufficient PAH data were available for trend evaluation in sediment and for mussel only in the Ems estuary (N3). The 14 EPA PAHs were evaluated for sediments of the Dutch Wadden Sea, while the 6 of Borneff PAHs were evaluated for Dutch Wadden Sea sediments and Ems estuary (N3). Compared to 1988 data, PAH concentrations in sediment have decreased in 1996, but no trend could be observed since 1990. Mussel concentrations in the Ems estuary show the same picture, lacking a significant trend. PAH levels are within the range of agreed background levels and well below the ecotoxicological assessment criteria (Tables 4.4, 4.5, 4.7).

#### 4.3.7 Assessment of Polychlorine Biphenyls (PCBs)

##### Temporal trend

The input of PCBs decreased dramatically for the Elbe river in the period 1989-1991. (Table 4.6, Figure 4.7). The inputs of IJssel, Ems and Weser fluctuated by a factor two at about the same level. Riverine concentration fluctuated strongly for Ems, Weser, Elbe and Eider. During the period 1987 - 1991 river flows were low due to a series of relatively dry years. At the onset of this river flow reduction, riverine PCB concentrations increased for about two years, followed again by a reduction. In 1996, for the Elbe 1995, an increase in riverine concentration and input appeared again for the Ems, Weser, Elbe and Eider. This cannot be ascribed to increased river flow but does coincide with the first relatively dry years after the wet period of 1994 and 1995. The mechanism, if any, is not understood.

For those areas for which sufficient data are available, it can be concluded that the reduction in PCB concentrations mainly occurred in the period 1985 till about 1990/1992, being about 65% in Dutch Wadden Sea sediments, about 50% in mussel of areas NS1 and NS2, and 75% in bird eggs of all relevant areas (Table 4.6, Figure 4.15, Figure 4.16, Figure 4.17). For the Elbe the reduction in concentrations in mussel and bird eggs is clearly correlated with the riverine input reduction in the period 1989 till 1993 (Figure 4.7). The input, which increased since 1994, seems to be reflected by the increasing concentration in mussels and, to a lesser extent, in bird eggs. This suggests a stronger relation of accumulation in mussel with riverine input

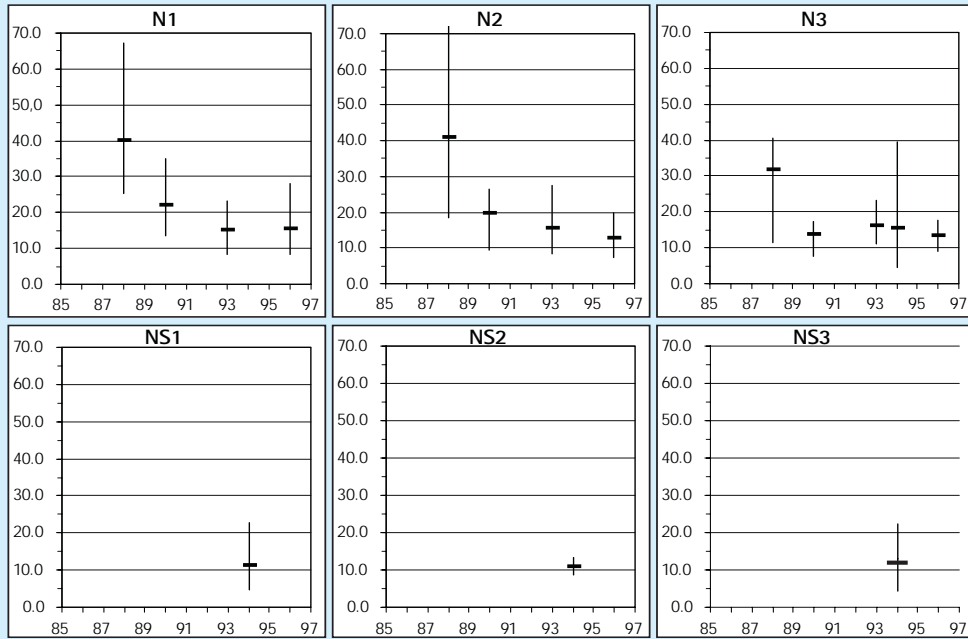


Figure 4.15. Sum of CBs 28,101,118, 138, 153, 180 ( $\Sigma^6$  PCB congeners of PolyChlorinated Biphenyls, PCBs) contents ( $\mu\text{g}/\text{kg}$  10% OM) of Wadden Sea sediments. Average (-) and minimum/maximum (|) values are shown. (DW=dry weight, 10%OM: sediment containing 10% organic matter, ca. 5% organic carbon, on DW).

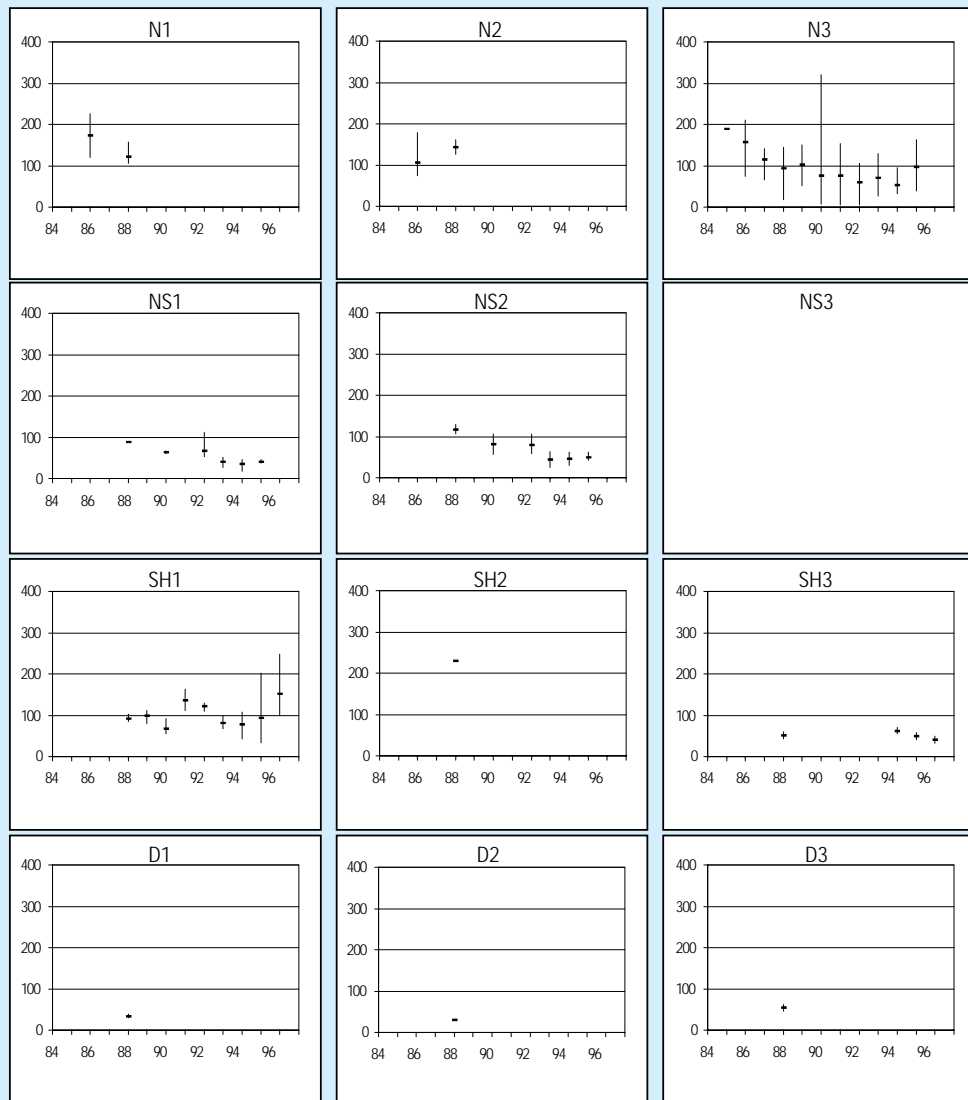
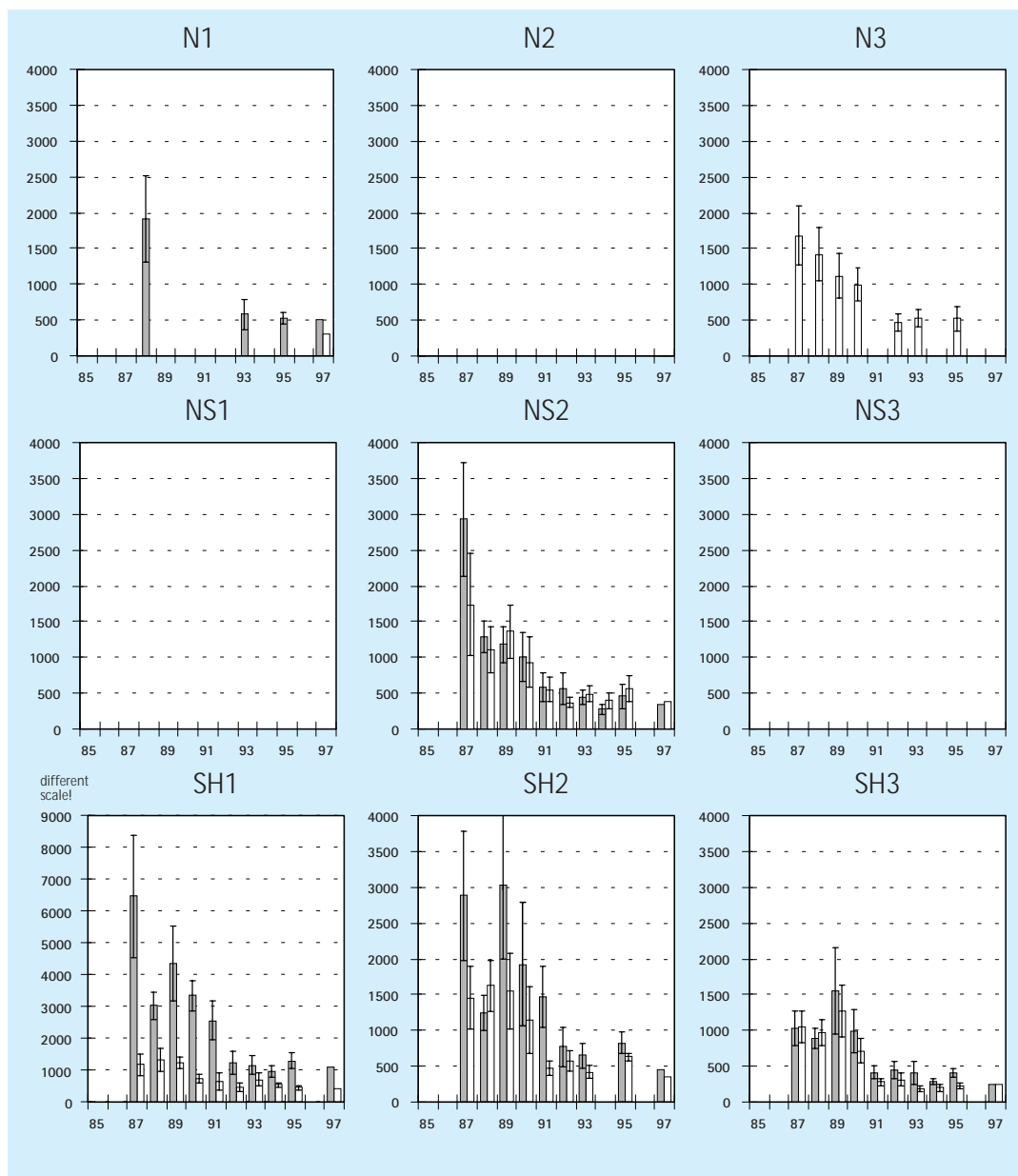


Figure 4.16. Sum of 6 PCBs ( $\mu\text{g}/\text{kg}$  DW) in mussel (soft body). Yearly average (-) and minimum/maximum (|) of all length classes per area.

Figure 4.17. Sum of 6 PCBs concentrations ( $\mu\text{g}/\text{kg}$  WW) in eggs of the Oystercatcher (*Haematopus ostralegus*, open bars) and Common Tern (*Sterna hirundo*, hatched bars). average: bars, 95% confidence limits:|. WW= wet weight egg mass. Data from Becker, P. (Institut für Vogelforschung Wilhelmshaven and Becker *et al.*, 1998).



than expected, since atmospheric input is assumed to be an important source for PCBs as well (de Jong *et al.*, 1993; Wulfraat *et al.*, 1993).

#### Geographical trend

The PCB and organochlorine residues in bird eggs are in general highest in the Elbe estuary (SH1), intermediate in the Eider estuary (SH2) and lowest in the remaining areas, irrespective of the year. This is consistent with the still relatively high inputs by the river Elbe.

Sediment contents of PCBs (CB138 and CB153), however, are relatively high in the Dutch and Niedersachsen Wadden Sea, about a factor 3 - 6 higher than in the Schleswig-Holstein and Danish areas (level 1994). This geographical pattern is confirmed

by mussel data (Bakker, 1994; Bakker *et al.*, 1994; Figure 4.16), and partially by bird egg data (Figure 4.17).

The 1995  $\Sigma$ PCBs concentration in mussel is a factor 6 (SH3) - 22 (SH1) higher than the agreed background level of OSPAR (Table 4.4, 4.7).

The ecotoxicological assessment criteria (Table 4.5) can be adapted to the 10% OM standardization according to (10% OM) = 5 \* (1% TOC). Comparing the provisional ecotoxicological criteria for sediment with the  $\Sigma$ PCBs sediment data (Table 4.7) shows that all Wadden Sea areas are within the criterion range. The maximum of the firm ecotoxicological criterion for mussel, however, is exceeded with a factor of 3 in the Elbe estuary (SH1).

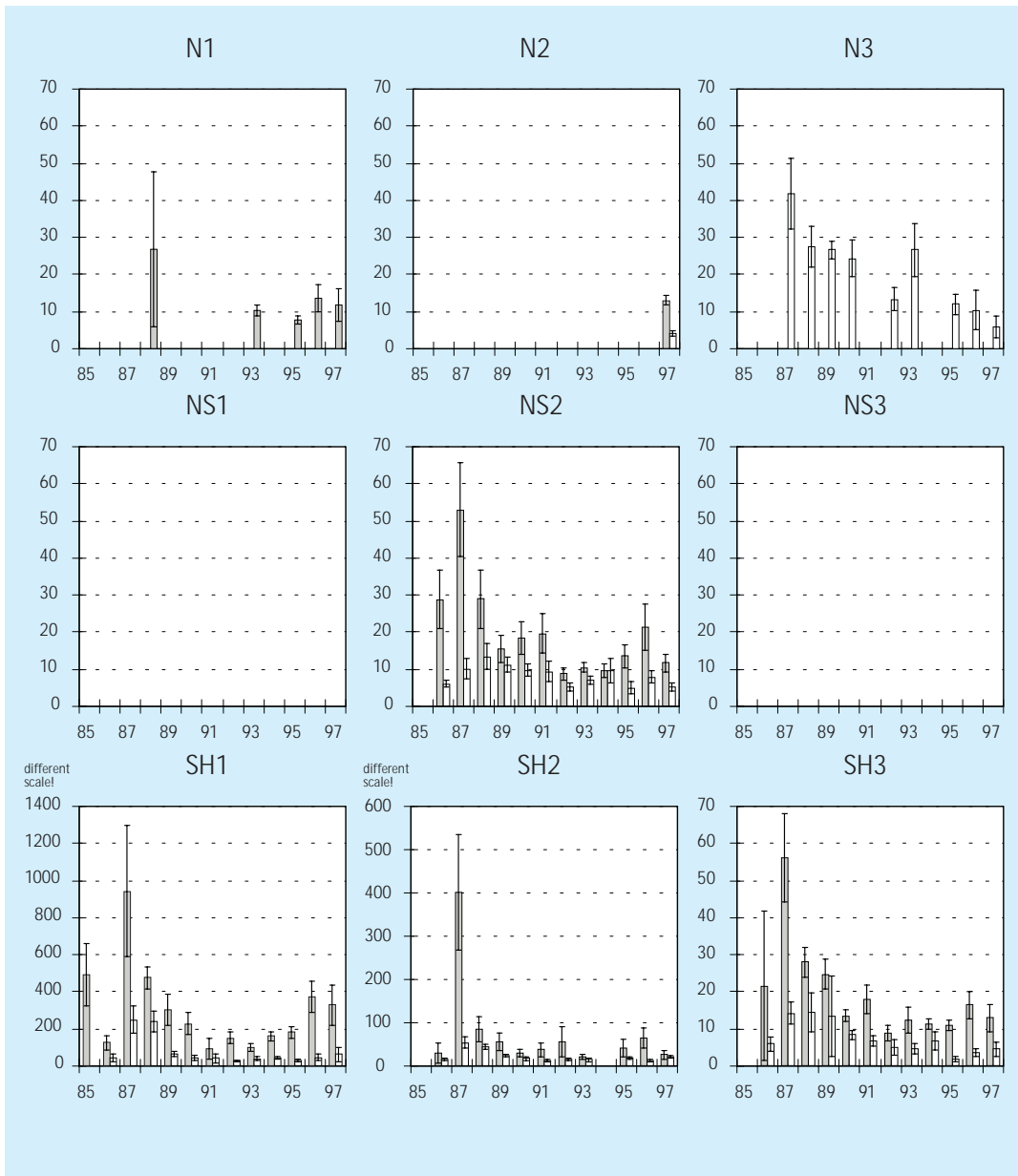


Figure 4.18. Hexachlorobenzene (HCB,  $\mu\text{g}/\text{kg}$  WW) in eggs of the Oystercatcher (*Haematopus ostralegus*, open bars) and Common Tern (*Sterna hirundo*, hatched bars). average: bars, 95% confidence limits:|. WW= wet weight egg mass. Data from Becker, P. (Vogelwarte Wilhelmshaven) and Becker *et al.*, 1998.

#### 4.3.8 Assessment of Hexachlorobenzene (HCB)

HCB is a widely used biocide in wood conservation and crop protection applications, as well as a byproduct of organochlorine solvents production. HCB is a suspect carcinogenic compound and has effects comparable to PCBs: a black-list compound.

HCB is extensively present in the biosphere but special attention is focused on the Elbe (SH1) and Ems-Dollard estuary (N3).

In the Elbe and Eider estuary, HCB levels in bird eggs (Figure 4.18) are substantially higher than in other Wadden Sea areas, probably due to the Elbe input. Both mussel (Figure 4.19) and bird eggs

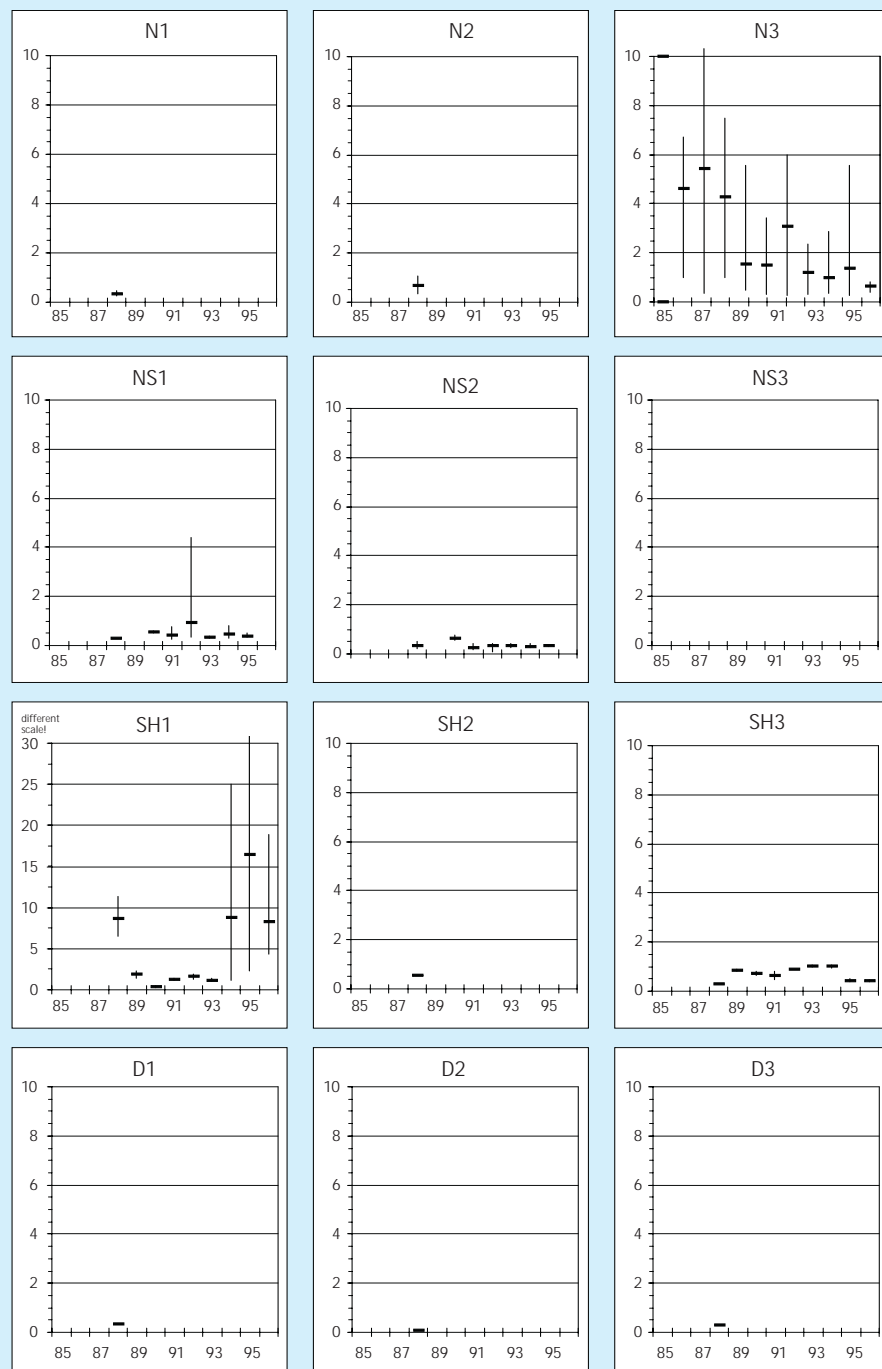
(Figure 4.18) show a HCB increase between 1994 and 1996.

In the Ems estuary, a long-term source has been cleaned-up in 1994. Results from mussel and bird-eggs monitoring (Becker 1989, Becker *et al.*, 1998, Eppinga, 1997) show a significant downward trend of 93% to 85% respectively between 1987 and 1996/1997.

In the Ems estuary sediment data do not show an explicit reduction, but show a period of more extreme peak values since 1993 (Figure 4.20).

Geographical trends can mainly be documented for the Elbe and Ems estuary versus the remaining Wadden Sea. Common tern eggs show a higher accumulation than oystercatcher eggs. This may

Figure 4.19. Hexachlorobenzene (HCB) ( $\mu\text{g}/\text{kg}$  DW) in mussel (soft body). Yearly average (-) and minimum/maximum (|) of all length classes per area (DW = dry weight).



be related to the prey choice of common terns, fish, which is a higher trophic level, and thus biomagnification step, than worms and mollusks which are the oystercatcher's prey. In the Elbe estuary, the 1997 median level in common tern eggs was  $325 \mu\text{g}/\text{kg}$  WW, whereas the median level in oystercatcher was  $60 \mu\text{g}/\text{kg}$  WW.

Sediment data do confirm the average HCB decrease, although levels in the Ems estuary are still reaching extremes, which are up to 10-fold those of the Dutch and Niedersachsen Wadden Sea (Fig-

ure 4.20). HCB contents in the Jadebusen and Weser estuary are at agreed background level (Table 4.4), while values in the Dutch Wadden Sea (N1, N2) and Ems estuary (N3) are 2 – 20 fold the agreed background (Table 4.7). Sediment HCB data for the Elbe estuary were not available, but are likely to reach rather high levels, considering the HCB levels in mussel and bird eggs.

No ecotoxicological assessment criteria have been defined for HCB.

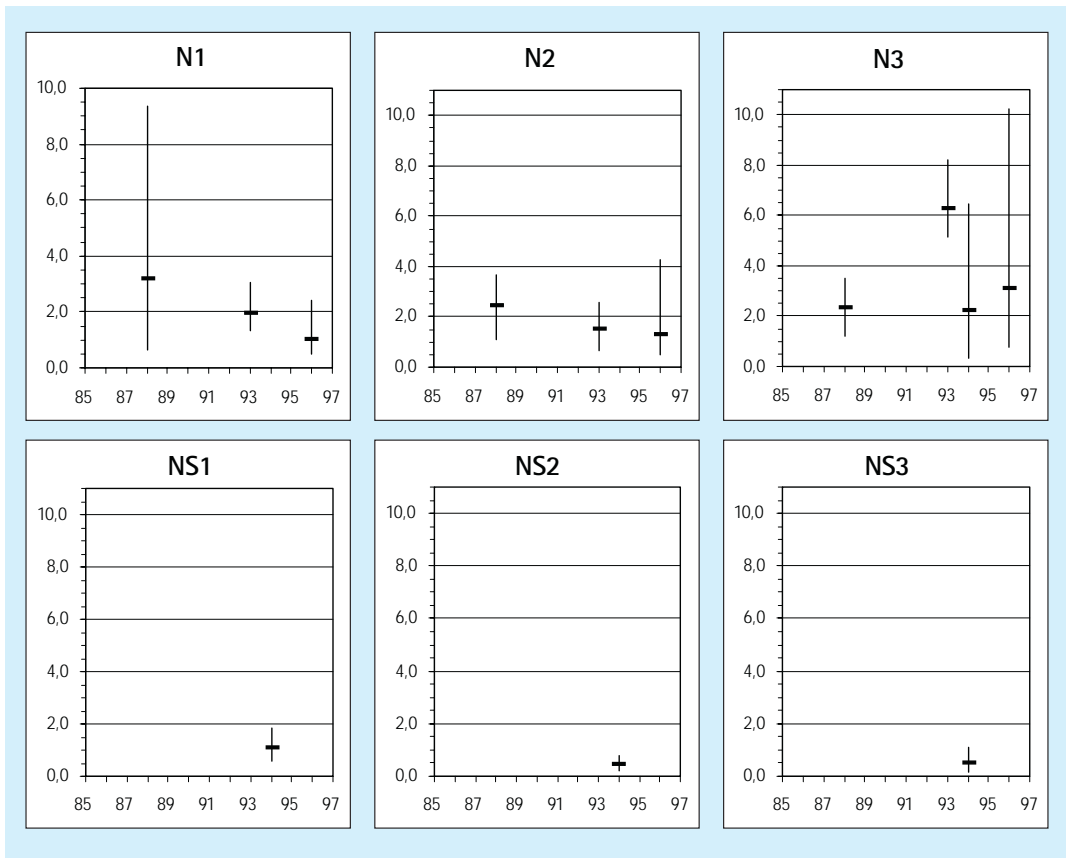


Figure 4.20 Hexachlorobenzene (HCB) contents ( $\mu\text{g}/\text{kg}$  10% OM) of Wadden Sea sediments. Average (—) and minimum/maximum (|) values are shown. (DW=dry weight, 10%OM: sediment containing 10% organic matter, ca. 5% organic carbon, on DW).

### 4.3.9 Assessment of TBT

Tributyltin-compounds (TBT), usually TBTO (TBT-oxide) and TBTCI (TBT-chloride), are extensively applied as an active compound in anti-fouling paints, catalyzer and stabilizer in plastics production, and as a biocide on roofing and as impregnation of cotton fabrics (Cameron *et al.*, 1998). The marine sources are mainly shipping and shipyard activities.

TBT accumulates largely in sediments where it is taken up by benthic organisms. It turned out that mainly mollusks (snails, oyster, mussel) are highly sensitive to TBT, affecting their hormonal control of reproductive organs eventually leading to sterility and extinction of the population (Cameron *et al.*, 1998; IVM, 1998). TBT sediment and water concentrations shown in Table 4.8 are derived from Cameron *et al.* (1998), Greenpeace Netherlands (IVM, 1998), Forschungsstelle Küste Norderney and Niedersächsisches Hafenamnt Norden.

The molar ratio of TBT and TBT determined as Sn (tin) was used to compare the various data (Table 4.8). The converted TBT levels found in total sediment of the German Wadden Sea are an order of magnitude higher than in the  $<63 \mu\text{m}$

sediment fraction of the western Dutch Wadden Sea. This is unexpected, because metal concentrations are usually higher in the fine fraction. Unless, fine TBT paint-particles in the fraction  $> 63 \mu\text{m}$  are corroborating both the higher levels and the heterogeneous analytical results of the total sediment. Such a situation was found for HCB contamination in harbor sludge of Delfzijl (Ems estuary) by Smedes *et al.* (1996).

Disregarding grain size correction, more recent data from the Niedersachsen Wadden Sea sediments (1997) indicate sediment concentrations which are in the same order of magnitude as in the western Dutch Wadden Sea.

#### Conclusions

Compared to the provisional ecotoxicological criteria for sediment, TBT is posing a huge problem to the Wadden Sea environment, because even in the open Wadden Sea TBT concentrations in sediment are exceeding the criteria over 1000-fold. The present data on TBT urge for a concerted investigation of all Wadden Sea areas, where agreement on and comparability of the analytical methods is, again, of primary importance. TBT is a TMAP monitoring parameter.

Location (Area) /Type	Year (source)	Sediment ( $\mu\text{g TBT/kg DW}$ )	Water (ng/l)	Mussel (mg/kg DW)
Mokbaai (N1) /R	1998(I)	73* (<63 $\mu\text{m}$ )		
Den Helder (harbour entrance, N1) /H	1998(I)	46* (<63 $\mu\text{m}$ )		
Griend (N1) /R	1998(I)	29* (<63 $\mu\text{m}$ )		
Dollart (N3)	1997(F)	7 - 25* (total sediment)		
Borkum (N3)	1997(F)	2 - 10* (total sediment)		
Leybucht (N3)	1997(F)	2 - 9* (total sediment)		
Norderney (NS1)	1997(F)	2 - 3* (total sediment)		
Spiekeroog (NS1)	1997(F)	2 - 6* (total sediment)		
Elisabeth-Groden (NS1)	1997(F)	1 - 4* (total sediment)		
Jadebusen (NS2)	1997(F)	7 - 36* (total sediment)		
Hoher Weg (NS1)	1997(F)	4 - 20* (total sediment)		
Tettens (NS3)	1997(F)	22 - 50* (total sediment)		
Cappel (NS3)	1997(F)	2 - 21* (total sediment)		
Dredge-spoil disposal sites (NS1-NS3)	1997(H)	2 - 452 (total sediment)		
Emden/Knock (N3) /R	1994(C)	300 - 750 (total sediment)		
Westermarsch (N3) /R	1994(C)	50 - 120 (total sediment)		
Norddeich (NS1) /M,H	1994(C)	610 - 1100 (total sediment)		
Dorumer/Accumersiel (NS1) /M	1994(C)	500 - 4100 (total sediment)		
Neuharlingersiel, Mole (NS1) /M,H	1994(C)	610 - 5400 (total sediment)		
Meldorf (SH2) /M	1994(C)	910 - 20000 (total sediment)		
Büsum (SH2) /M	1994(C)	750 - 3200 (total sediment)		
Husum (SH3) /H	1994(C)	600 - 5100 (total sediment)		
Südwesthörn (SH3) /R	1994(C)	93 - 170 (total sediment)		
WWF proposed limit level		0.005 - 0.05 (total sediment)		
Ecotoxicological assessment criterium (OSPAR)		0.005 - 0.05 (1% TOC)	0.1 - 1	0.001-0.01
Proposed Maximum Tolerable Risk (MTR) level Dutch environmental targets (1999)		0.7 $\mu\text{g/kg DW}$ (SRS)	1	

**Table 4.8.** TBT contents of sediments and water in ( / type): marinas (M), harbours (H) and reference areas (R). Modified after Cameron *et al.*, 1998 (C); IVM, 1998 (I); Forschungsstelle Küste 1999 (F); Niedersächsisches Hafenam Nordden (unpublished data) (H). The field data and ecotoxicological assessment criterion cannot be compared directly. Typically harbour sediments contain 3 - 5% TOC. Data measured as TBT-Sn have been transformed into TBT using the factor 290/118 ( $\text{C}_{12}\text{H}_{27}\text{Sn/Sn}$ ) on the original data. Transformed data are marked by \*. OSPAR EAC-level is from OSPAR, 1997. Dutch MTR target is from Beesen *et al.*, 1998. SRS: Standard Reference Sediment: sediment containing 10% organic matter (5% OC) and 25% clay (< 2  $\mu\text{m}$ ).

### 4.3.10 Assessment of pesticides and other xenobiotic substances

#### Introduction

Pesticides (insecticides, herbicides, fungicides) are widely used in the drainage area of the Wadden Sea for crop protection. Regular monitoring of those compounds in the marine and estuarine areas is absent, with the exception of lindane ( $\gamma$ -hexachlorocyclohexane, HCH). The expanding use of crop protection chemicals gave rise to the question whether these compounds are potentially harmful to the marine environment (de Voogt and Lourens, 1996). Although these compounds are supposed to biodegrade before reaching the marine environment, there is increasing evidence of the presence of such compounds and their metabolites in the North Sea and Wadden Sea. Pesticide concentrations in the water of the Wadden Sea have not been part of regular monitoring programs due to high changes in the respective water bodies, mainly caused by the strong seasonal and weather-dependent use of these chemicals, low detection limits, the high number of compounds and the high costs of analysis.

#### HCH

Inputs of lindane ( $\gamma$ -hexachlorocyclohexane) sharply decreased over the past decennium (Figure 4.7, Table 4.6), reflected by the lindane levels in bird eggs (Figure 4.21). Only in the Eider estuary (SH2)  $\gamma$ -HCH increased in the eggs of the common tern (*Sterna hirundo*), a fish predator, while  $\beta$ -HCH dramatically increased in oystercatcher eggs (*Haematopus ostralegus*) in the Jadebusen (NS2) (Figure 4.22). Since the oystercatcher is a predator of macrozoobenthos, the source is most likely local, but unknown.

The provisional ecotoxicological assessment criterion for lindane in water is between 5 - 50 ng/l (OSPAR, 1997), which is in the range of the present concentrations in the Wadden Sea estuaries (Table 4.5 and 4.7).

#### Dutch Wadden Sea survey

During the period 1990-1995, an extensive survey of the marine and brackish waters of the Dutch Wadden Sea showed that out of 88 different pesticides, 78 were detectable, of which 21 exceeded the current Dutch Maximum Permitted Risk level (Breukel *et al.*, 1996). To the top four frequently

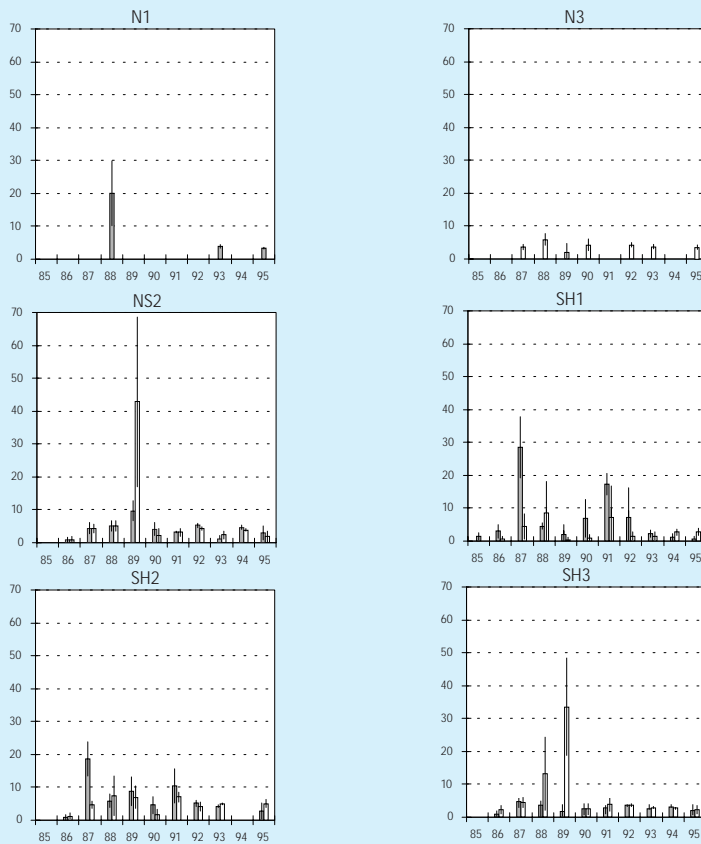


Figure 4.21. Lindane ( $\gamma$ -HCH) concentrations ( $\mu\text{g}/\text{kg}$  WW) in eggs of the oystercatcher (*Haematopus ostralegus*, open bars) and common tern (*Sterna hirundo*, hatched bars). average: bars, 95% confidence limits:|. WW= wet weight egg mass. Data from Becker, P. (Institut für Vogelforschung, Wilhelmshaven).

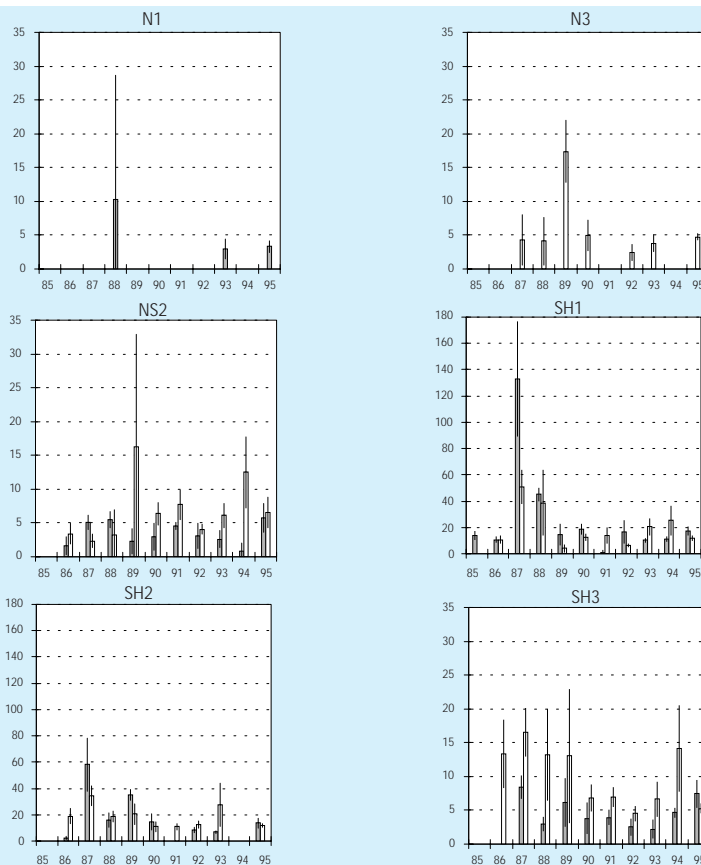


Figure 4.22.  $\beta$ -HCH concentrations ( $\mu\text{g}/\text{kg}$  WW) in eggs of the oystercatcher (*Haematopus ostralegus*, open bars) and common tern (*Sterna hirundo*, hatched bars). average: bars, 95% confidence limits:|. WW= wet weight egg mass. Data from Becker, P. (Institut für Vogelforschung, Wilhelmshaven).

detected compounds, belong organic phosphorus pesticides, triazines, phenylurea herbicides and TBTs. Moreover, triazine derivatives (IRGAROL), used to replace TBT as an anti-fouling agent, are a direct and increasing source of pesticide inputs into the Wadden Sea (Bester *et al.*, 1995). These herbicides are blocking the photosynthetic process and are a potential risk to algae. Bester and Hühnerfuss (1998) report concentrations of triazines between 100 and 1000 ng/l, which is within the effect range and, potentially one of the possible causes of eelgrass (*Zostera marina*) deterioration (Walsh *et al.*, 1982). Bester and Faller (1994) report triazine concentrations in German Wadden Sea sediments between 1 - 8 µg/kg wet weight.

Results from the Elbe (Bester and Hühnerfuss, 1993) and the Humber (Zhou *et al.*, 1996) show that within the estuaries modern pesticides are generally conservatively diluted with sea water. Thus, concentration data from the more limnic part of the estuaries can be used for an assessment. In Table 4.9, concentrations of pesticides, generally the highest detected concentration that were found in Elbe, Weser and Ems, are given. Only compounds with concentrations exceeding 100 ng/l are displayed. In general, there is a high

variety of compounds considering geographical distribution as well as on a year to year basis, which is challenging for monitoring programs.

#### The river Elbe and the German Bight

The river Elbe was found to be one of Europe's most polluted rivers with an extreme variety of xenobiotic compounds present (Franke *et al.*, 1995). A survey with the aim of identifying xenobiotic compounds was started in 1996 in the German Bight and Elbe estuary. Compounds identified included triazines (compare Bester and Hühnerfuss, 1993), trimethylthiophosphate (Gatermann *et al.*, 1996), benzothiazoles (Bester *et al.*, 1997), polycyclic musk compounds (Bester *et al.*, 1998a), chlorinated anilines (Bester *et al.*, 1998b), chlorinated nitroaromatic compounds (Gatermann *et al.*, 1995; Bester *et al.*, 1998c), chlorinated ethers and formaldehydes (Franke *et al.*, 1998) as well as nonylphenol (Theobald *et al.*, 1995), which has also been found in mussels (Thiele *et al.*, 1997). Table 4.10 shows a comparison of concentrations of diverse xenobiotics near the Eider peninsula. This station is part of the German monitoring program (BLMP).

The primary source of the respective compounds

Table 4.9. Concentrations of pesticides in Elbe, Weser, and Ems.

Generally, the highest detected concentration of all pesticides that were found with concentrations exceeding 100 ng/l are given, data extend from 1990 to 1996. n.a. = not analyzed; ? : unknown whether measured or not; Hemeln: another station in the respective sampling net.

Pesticide	Elbe [ng/l]	Weser, Farge (Steffen, 1996) [ng/l]	Ems, Herbrunn (Steffen, 1996) [ng/l]
Aldicarb-sulfone	n.a.	500	800
Ametryn	800, ARGE 1990	?	?
Amitrol	n.a.	700	<100
Atrazine	150, UBA 1996	200	<100
Atrazine-Desisopropyl	n.d. ARGE 1993	100	200
Carbofuran	n.a.	100	<100
Chlortoluron	n.a.	100 (Hemeln)	300
2,4-D	2000, ARGE 1990	?	?
2,6-Dichlorobenzamid	n.a.	<100	200
Dimethoate	4.500, UBA 1996	300 (Hemeln)	<100
Etrimpfos	<100 Knauth <i>et al.</i> 1993	100	<100
Furathiocarb	n.a.	200	200
Linuron	130, Knauth <i>et al.</i> 1993	?	?
Metalaxyl	230, Knauth <i>et al.</i> 1993	?	?
Metamitron	n.a.	300	100
Methabenzthiazuron	n.a.	<100	200
Parathion-Methyl	560, UBA 1996	?	?
Pentachlorophenol	370, Knauth <i>et al.</i> 1993	?	?
Simazine	2.400, UBA 1996	?	?
Terbutylazine	<100, UBA 1996	100	200
Terbutylazine-Desethyl	n.a.	100	<100
Trifluralin	n.a.	100 (Hemeln)	<100

Xanthen-9-on	2,5-DCA <sup>1</sup>	$\alpha$ -HCH <sup>2</sup>	4-CNB <sup>3)</sup>	MTB <sup>4</sup>	Polycyclic musk fragrances <sup>5</sup>	Atrazine <sup>6</sup>	Terbutylazine <sup>6</sup>	Chlorinated ethers <sup>7</sup>	Thiophosphates <sup>8</sup>
0.21- 0.37	0.4	0.5	0.3	0.4 -1.4	0.2 - 0.6	42	360	0.5 - 25	1 - 8

is diverse: Pesticide contamination in the river Elbe probably originates from intensive application as well as from bad manufacturing practices. Trimethylthiophosphate for example is a by-product of, e.g., malathion production. Benzothiazoles are used in rubber chemistry and reach the ecosystem via wear-off from rubber tires as well as from biocides used in leather and wood processing and from animal care. Chlorinated anilines, nitroaromatic compounds, chlorinated ethers and formaldehydes are most probably "involuntarily" released from industrial processes. On the other hand, polycyclic aromatic musk fragrances reach the environment from household washing powders via the sewage systems. Nonylphenol enters the environment from industrial textile production, paints, pesticide emulsifiers etc., whereas its application in domestic washing agents has most probably decreased (Thiele *et al.*, 1997).

#### Analysis of Wadden Sea sediments

Modern pesticides such as triazines and phenylurea herbicides do not readily absorb to sediment, as they are relatively hydrophilic. To assess the situation in the Wadden Sea more integrating parameters than the rapidly changing water are needed, thus some pesticide concentrations in the East Frisian sediments were measured (Table 4.11) (Bester and Hühnerfuss, 1996, 1997 and Bester, 1996). As these compounds do not accumulate to a high extent in the sediment, these low concentrations can reflect high concentrations in the water phase.

#### Conclusions

Modern pesticides are present in the water and sediment of the Wadden Sea. At least during some periods, concentrations of atrazine high enough

to affect phytoplankton have been measured and can be expected (Bester *et al.*, 1995).

The variety of xenobiotics that is introduced into the Wadden Sea represents all activities of mankind and the amount of different compounds is higher than found in previous studies.

#### 4.3.11 Effects of xenobiotic compounds

There is increasing evidence of the wide-spread, global distribution of sub-lethal concentrations of xenobiotic compounds and their metabolites.

The large amount of active compounds all add up to the total effect, although the concentrations of individual compounds are low (concentration addition). On the other hand, bioaccumulating and volatile compounds are transported towards the polar regions, where they (bio)-accumulate in mammals to very high concentrations e.g. DDE, Toxaphene, PCBs and poly-brominated biphenyls (PBBs), the extensively used compound group of flame retardants (de Boer *et al.*, 1999; Ballschmiter, 1999).

The observed sublethal effects are referred to the specific type of action. They comprise endocrine disruption, dioxine type of toxicity, inhibition of acetylcholinesterase, genotoxicity and general cell toxicity (narcosis).

For the assessment of unknown toxicity levels, the development of bioassays is now rapidly extending to the marine environment, where *a.o.* the dumping of harbor dredge spoil in the Netherlands is going to be subject to bioassay screening beginning about 2002 (MinVenW, 1998).

Pesticide	minimum concentration [ng/kg wet weight]	maximum concentration [ng/kg wet weight]
Atrazine	<5	50
Atrazine-Desethyl	< 5	1600
Linuron	<10	3300
Propazine	130	700
Simazine	11	400
Terbutylazine	<5	1800
Terbutylazine-Desethyl	<5	320

Table 4.10. Comparison of concentrations in ng/l of pollutants in the German Bight (area of station 30 within this study near the Eider peninsula).

Not all values originate from the same year.  
DCA = Dichloroaniline, MTB = Methylthiobenzothiazole, 4-CNB=4-Chloronitrobenzene  
1) Bester *et al.* 1998b,  
2) Theobald *et al.* 1996,  
3) Bester *et al.* 1998c,  
4) Bester *et al.* 1997,  
5) Bester *et al.* 1998a,  
6) Bester and Hühnerfuss, 1993,  
7) Franke *et al.* 1998,  
8) Gatermann *et al.* 1996

Table 4.11. Concentrations of pesticides in sediments of East Frisian Wadden Sea in 1993.

## 4.4 Inputs of dredge spoils

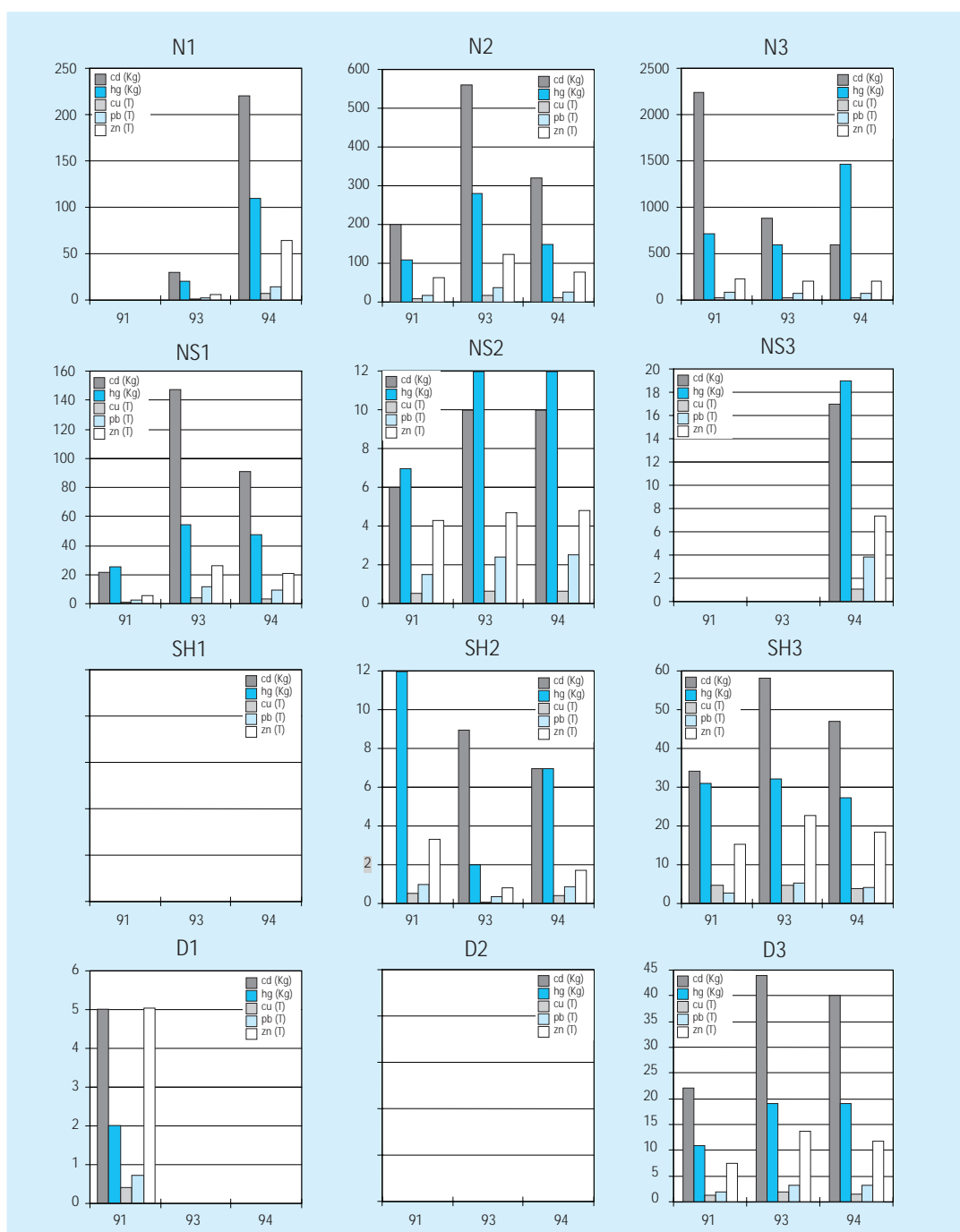
A number of busy harbors border the Wadden Sea and its estuaries. To keep the shipping lanes and harbors navigable, regular dredging is necessary. Most of the dredge spoils is allowed to be dumped back into the Wadden Sea area after having been assessed according to dredge spoil quality standards.

In Figure 4.23, the total amount of metals recurring to the Wadden Sea as a result of dumping of dredged material mainly originating from harbors, is shown. The figure shows a large difference in amounts (note the different scales),

which is due to the differences in the amounts of dredge spoil dumped (see also 2.11) and the fact that in many cases analysis of contaminant content is not required because the dredged material is not considered as excess input (difference of dredge spoil content and actual Wadden Sea sediment content).

A direct comparison with other inputs is tedious, because only the excess input should be considered. For the assessment of excess inputs, essential data are lacking.

Figure 4.23. Recurrence of metals to the Wadden Sea by dumping of dredge spoils (data from OSPAR).



## 4.5 Shipping and Oil

Shipping activities are a potential source of contamination with oil, garbage and hazardous substances. In the past years, several incidents have occurred with washed ashore chemicals and oil which originated from ships.

Oil spills have been reported in and along the traffic separation scheme north of the Wadden Sea Area in The Netherlands and Germany (see Figure 4.24 and Figure 4.25)(ZMK, 1996). The highest number of spills reported for the German North Sea since 1986 was 275 in 1987. After a decline in oil spill reports in the years of 1988/89 to 1990/91, the period in which reception facilities were free of charge in all German harbors, the reporting has shown a new increase since 1992. However, the "observed spills per flight hour", according to the results of the German aerial surveillance, do not show such differences.

It is unclear how much oil from operational discharges in the offshore area enters the Wadden Sea Area, however, birds are the most reliable biological indicator of oil pollution. The number of oiled birds washed ashore along the Wadden Sea coast remains high and, also, oil can regularly be found on the beaches in the Wadden Sea Area. Beached Bird Surveys (BBS) carried out according to standardized methods on a long-term basis, provide information on temporal changes and spatial differences in the oil pollution of the marine environment. The so-called oil rate, which is the number of oiled birds beached in a given region relative to the total number of dead birds washed ashore, provides a good index of the level of oil pollution in the adjacent waters. The concomitant collection of oil samples from oiled birds and their chemical analysis enables the identification of the source of oil pollution. The analysis of oil samples taken from the Danish, German and Dutch North Sea coasts in the period 1990 to 1992, indicates that bunker and lubrication oil residues are the main source of oil pollution in that region. In the Skagerrak area, crude oil from illegal tank cleaning is also involved.

The oil rates found in the Danish part of the Wadden Sea as well as in the Baltic Sea, a special area according to MARPOL Annex I, are decreasing. However, the continuing high oil rates found along the northwest coast of Jutland strongly indicate that no change in the behavior of offenders has occurred here since 1985 (Dahlman *et al.*, 1994; Danielsen *et al.*, 1990; Skov *et al.*, 1996).

After declines in oil rates on the German North Sea coast in the years 1988 to 1991 - the period in which reception facilities were free of charge in all German harbors - the data has shown an increase since 1991/92. The gradual implementa-

tion of charges for the disposal of oil residues since 1991 may have led to an increase in illegal dumping of such residues and to the increase in oil rates measured by the BBSs (Averbeck and Voigt, 1992; Dahlman *et al.*, 1994; Fleet *et al.*, 1995; Reineking, 1997).

In The Netherlands, the results of BBSs over

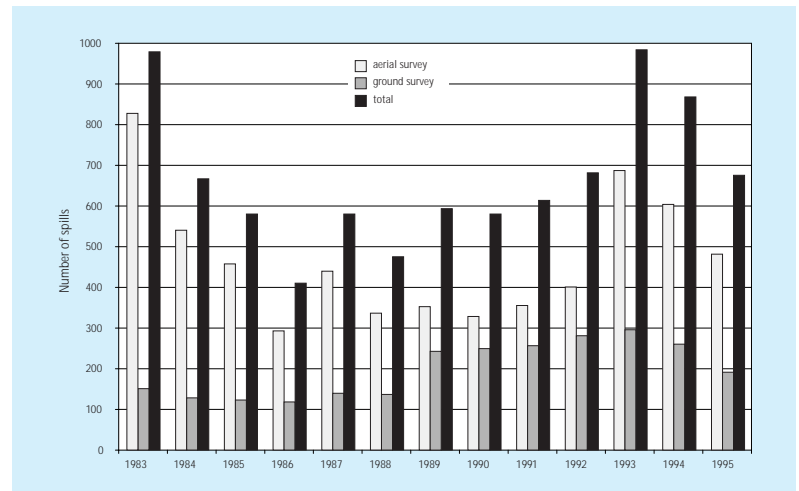


Figure 4.24. Reported oil spills in the Dutch Continental Shelf 1983 - 1995. (Data from Directoraat-Generaal Rijkswaterstaat, Directie Noordzee).

the past 30 years show consistent declines in oil rates in all areas - especially in the Dutch Wadden Sea - in all seasons and in virtually all species. The results of the Dutch investigations have not provided evidence for a sudden improvement since MARPOL Annex I came into effect in 1983, although the gradual implementation of MARPOL may have been a factor in the declining trend (Camphuysen, 1989, 1995, 1997, Camphuysen and van Franeker, 1991, 1992).

Figure 4.25. Reported oil spills in the German North Sea 1986 - 1997. (Data from the Wasser- und Schifffahrtsamt Cuxhaven).

