In estuaries and coastal waters diatoms prominently dominated the phytoplankton (35–78%) since sampling was initiated in 1989 (Figure 2.19). The contributions from dinoflagellates have varied between 16% and 46% and the importance of other groups, mainly nanoflagellates, increased from 1989 to 1998.

Because diatoms dominate the spring bloom, of which a large fraction sediment to the bottom, they are important for the transfer of organic matter of pelagic origin to the benthic fauna. In addition, the input of organic matter to the water mass below the pycnocline will affect the subsequent development in bottom water oxygen conditions.

The biomass of diatoms has decreased significantly over the past 20 years in the open Kattegat and Belt Sea. During 1995–2000 the average biomass

of diatoms in these areas was 50% of the biomass in the early 1980s. In estuaries and coastal areas no long-term trend in diatom biomass was found (Figure 2.20).

Primary production in the open sea areas has shown an overall decline with major year-to-year variations from 1977 to 1997 (Figure 2.21). The subsequent increase in primary production during 1998–2001 may be due to a reduction in the number of monitoring stations and changes in the sampling strategy in 1998. During 1993-2001 primary production was significantly correlated with runoff, wind and temperature. The primary production index adjusted to changes in climatic conditions shows a lower production during the 1990s than during the 1980s. Despite the apparent decrease in primary production from the 1980s to the 1990s, the annual prima-
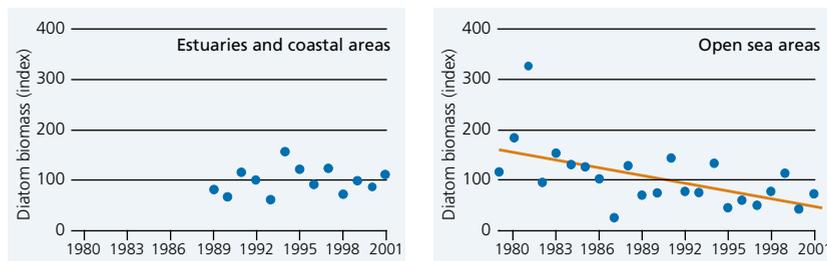


**Figure 2.20**
Annual averages of diatom biomass in Danish waters. Biomasses are given as indices (see box 5).

**Figure 2.21**
Indices for Secchi depth, chlorophyll concentrations and annual primary production in open sea areas. Indices are given for measured values (A, B and C) and adjusted for variations in climatic conditions (D, E and F). Adjustments for climatic variations are developed on data from time periods represented by hatched lines and up till 2001. Subsequently the adjustments were applied on data in all years.

ry production in the Kattegat area has increased 2- to 3-fold from the 1950s to 1984–1993, apparently as a result of eutrophication (Richardson & Heilmann 1995).

In estuaries and coastal areas primary production has decreased from 1980 to 1997 and subsequently increased during 1998-2001 (Figure 2.22). For the period 1993-2001 primary production was significantly correlated with runoff, irradiance and temperature. Index values adjusted for variations in climatic conditions showed a very consistent decline after 1993. This decline in primary production was presumably due to reduced phosphorus loading to the estuaries through the establishment of sewage treatment plants in the late 1980s and early 1990s and subsequent reduction in the nitrogen load both from point and diffuse sources.

Chlorophyll *a* concentrations have decreased in the open sea areas since the 1980s (Figure 2.21). However, mainly during the 1980s the year-to-year variations have been substantial and possibly related to the lack of standardised sampling strategies and methods for analyses prior to 1989. For the period 1990-2001 chlorophyll *a* concentrations correlated significantly with primarily irradiance during early spring and autumn. Chlorophyll *a* index values adjusted for variations in climatic conditions were very variable prior to 1990 and showed a general slight increase for the period 1990-2001. Since 1980 the concentrations of chlorophyll *a* in Danish open sea areas (Hansen et al. 2000) have been >50% above background concentrations (1.25 µg chl *a* l$^{-1}$) given by OSPAR (2001).

Chlorophyll *a* concentrations have decreased in estuaries and coastal waters since the mid 1980s (Figure 2.22). The concentrations of chlorophyll *a* correlated significantly with runoff during 1993–2001. When adjusted for variations in climatic conditions, chlorophyll *a* index values showed a very consistent decline from 1993 to 2001.

In open sea areas the Secchi depth, a measure of water transparency, has increased since the mid-1980s (Figure 2.21). The Secchi depth adjusted for variations in climatic conditions has increased despite a similar increase in chlorophyll concentration. In estuaries and coastal areas the decline in chlorophyll concentrations since the mid-1980s has been accompanied by increased Secchi depth (Figure 2.22).
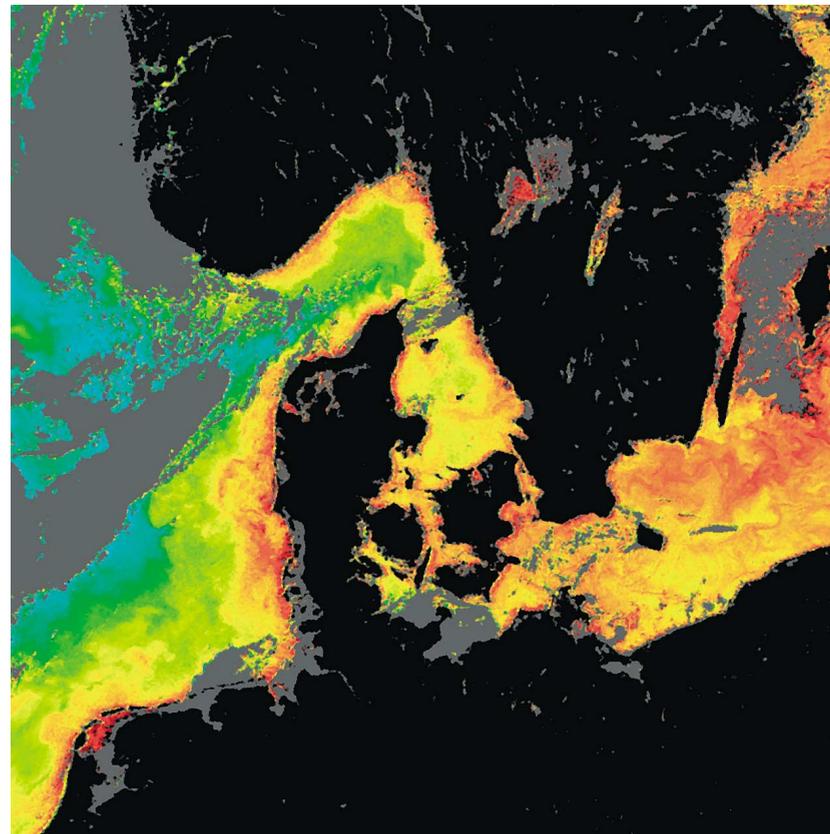


Satellite image of chlorophyll in Danish marine waters, the North Sea and the Baltic Sea 16 July 2002. Red colours indicate high concentrations of chlorophyll.

Image: SeaWiFS data from Orbimage processed by GRAS A/S, Denmark
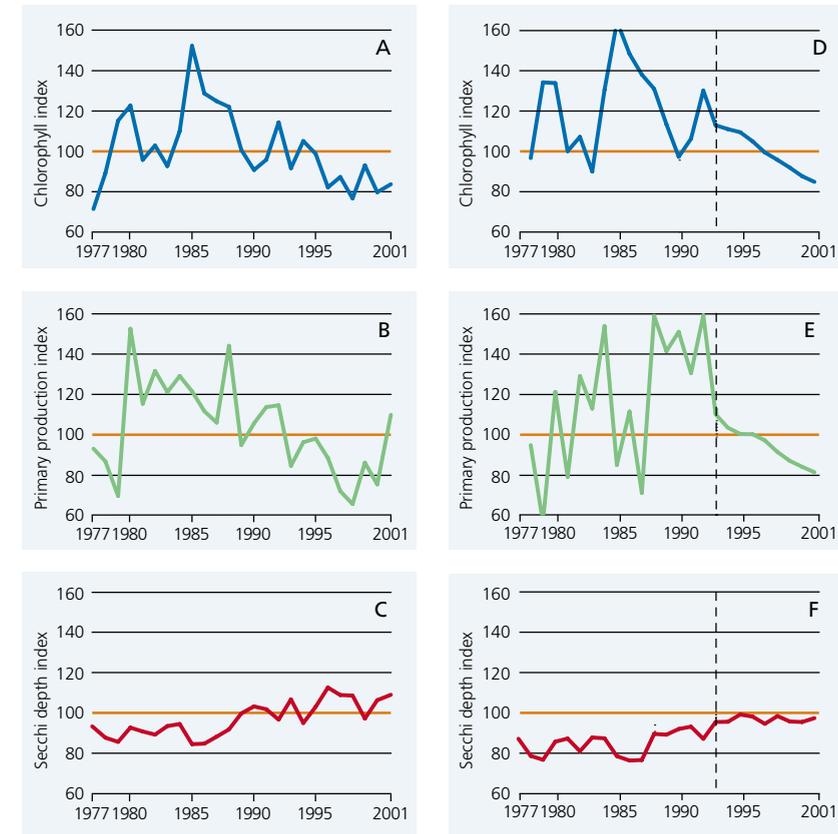


**Figure 2.22**
Indices for Secchi depth, chlorophyll concentrations and annual primary production in estuaries and coastal waters. Indices are given for measured values (A, B and C) and adjusted for variations in climatic conditions (D, E and F). Adjustments for climatic variations are developed on data from 1993–2001, but applied on data in all years.

## EXCEPTIONAL AND HARMFUL ALGAL BLOOMS

Several potentially toxic and harmful species of algae are common minor components of the phytoplankton communities in Danish waters. In some years, however, they form conspicuous blooms that may have severe effects on other organisms or on the tourist and fishing industries (Table 2.6). Blooms of some species, e.g. *Chrysochromulina polylepis*, have occurred only once, while blooms of other species are recurring, e.g. *Karenia mikimotoi* and *Chattonella* sp. The latter was found in high concentrations for the first time in 1998.

Potentially harmful species are registered and quantified in the national monitoring programme. In addition, the commercial bivalves fishermen and the mussel industry are undertaking monitoring of toxic phytoplankton and algal toxins in bivalve shellfish in all areas where shellfish are harvested. Areas may be closed for fishing of shellfish if toxic algae are found in concentrations above given limits (Bjergskov et al. 2001) or if algal toxins are detected in shellfish in concentrations above the limit for human consumption. Most registrations of shellfish containing algal toxins in concentrations above limits are from the 1980s and the early 1990s and from the eastern coast of Jutland (Figure 2.23) where the fished shellfish amounts to only one third of the catches in the Limfjorden in northern Jutland. ◼
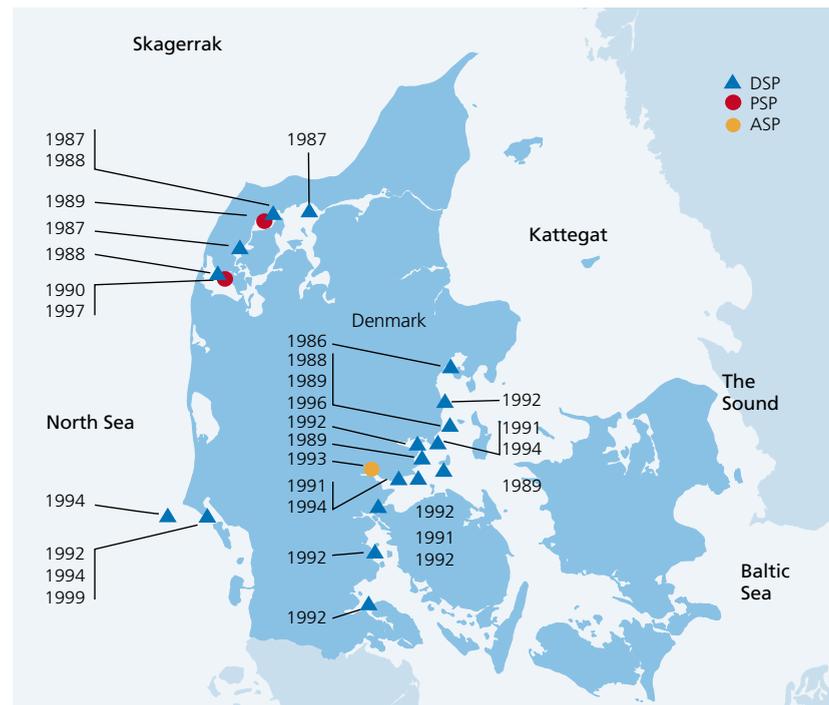
**Figure 2.23**
Registered accumulations in shellfish of algal toxins in concentrations above limits for human consumption. DSP, Diarrhetic Shellfish Poison; PSP, Paralytic Shellfish Poison and ASP, Amnesic Shellfish Poison. ASP detected in 1993 was analysed by a single laboratory and has not been confirmed by other laboratories. (From Bjergskov et al. 2001).



| Species | Year | Month(s) | Geographical area | Maximum abundance or biomass | Effects Fish kills |
|---|---|---|---|---|---|
| *Chattonella* spp. | **1998**, 2000, **2001** | Jan-May | Århus Bugt, Danish west coast, Skagerrak, Kattegat | 23 mill. l$^{-1}$ | Fish kills |
| *Chrysochromulina* spp. | **1988**, 1992 | May | Kattegat, Belt Sea | 100 mill. l$^{-1}$ | Fish kills, dead benthic invertebrates, macrophytes affected |
| *Dictyocha speculum* | **1983**, 1999 | May-Jun | Little Belt, Alssund | 25 mill. l$^{-1}$ | Fish kills in maricultures associated with bloom |
| *Gymnodinium chlorophorum* | 1999 | Aug-Dec | Nissum Bredning W Kattegat | 15 mill. l$^{-1}$ | None reported |
| *Karenia mikimotoi* [1] | **1968**, 1981, **1997** | Aug-Oct | Skagerrak Danish west coast, Kattegat, Belt Sea | 8.6 mill. l$^{-1}$ | Dead benthic invertebrates |
| *Nodularia spumigena* [2] | **1975**, 1976, 1992, **1994**, **1995**, 1997, 1999, **2001**, 2002 | Jul-Aug | Århus Bugt, W Kattegat, Belt Sea, W Baltic | 869 µg C l$^{-1}$ | Dogs dying after swimming in the water |
| *Phaeocystis* sp. | Yearly, **2000** | May-Jun | Danish west coast | | Foam on beaches |
| *Prorocentrum minimum* | **1983**, 1984, 1987, **1989**, **1992**, **1993**, **1994**, **1995**, **1996**, 1997, **1999** | Jul-Oct | Most Danish estuaries and coastal areas | 53 mill. l$^{-1}$ | None reported |
| *Pseudo-nitzschia* spp. | 1992, 1999, 2000 | May-Nov | Kattegat, Belt Sea SW Kattegat Danish west coast | 346 µg C l$^{-1}$ | None reported |

**Table 2.6**
Blooms of potentially toxic phytoplankton species or exceptional blooms in Danish waters. Years with major blooms are given, and the most significant ones marked in bold. Months indicate the most frequent time of year for blooms. Maximum abundance and effects refer to the most extreme episodes registered.

1 = *Gyrodinium aureolum*
2 = Maximum biomass given was total biomass of all cyanobacteria including *Aphanizomenon* sp. and *Anabaena* sp. registered in the national monitoring programme. Locally, much higher biomasses may have occured in accumulations along the shore.

## 2.6 ZOOPLANKTON

**Copepods have an increased importance towards the sea while the relative importance of protozooplankton and meroplankton is highest in the estuaries.**



Photo: Biofoto/N.T. Nicoll

The zooplankton are an important link between the phytoplankton and higher trophic levels such as fish. Zooplankton constitute a diverse group of organisms with respect to size, life cycle and behaviour. The smallest size class, nanozooplankton (2-20 μm), are single celled organisms. The larger size class, the microzooplankton (20-200 μm) are dominated by ciliates and heterotrophic dinoflagellates, small metazoans as rotiferans and the earliest developmental stages of copepods. The largest size class, mesozooplankton (> 200 μm), consist of copepods, cladocerans and larvae of benthic invertebrates. The more conspicuous jellyfish often dominates the gelatinous plankton.

Due to the doubtful usefulness of zooplankton as an indicator of eutro-

phication, zooplankton have been given relatively low priority in the Danish monitoring programme with respect to the number of sampling stations and sampling frequency. From 1998 zooplankton was given even lower priority in open waters, but is still included in the monitoring of many coastal waters.

In general the diversity of the zooplankton community decreases with salinity from the North Sea to the Baltic Sea and from the open sea to the low salinity estuaries. However, diversity is high in the Kattegat and the Belt Sea due to the influence of both brackish and Atlantic species as a result of the inflow of water from the Baltic Proper and the Skagerrak-North Sea, respectively. The relative importance

of protozooplankton, rotiferans, meroplankton and cladocerans is highest in the estuaries and decreases gradually towards the open sea. Conversely, the importance of copepods increases towards the sea.

During the period 1983-96 the winter biomass of mesozooplankton was generally low (2-5 mg C m$^{-3}$) in the open waters, increasing to a seasonal summer peak of about 30-40 mg C m$^{-3}$. Inter-regional differences were minor, also with respect to species composition. An analysis of copepod biomass data revealed a significant but only slight reduction in the mesozooplankton biomass from 1989 to 1997 at two out of three Kattegat stations (Ærtebjerg et al. 1998).

In the estuaries the composition and seasonal succession of the zooplankton community is much more variable than in the open sea. Both seasonal successions and time trends differ markedly among the estuaries monitored. In the Limfjord the mesozooplankton biomass has increased significantly since 1985, while the biomass of protozooplankton has decreased, though not significantly. In Ringkøbing Fjord the biomass of mesozooplankton has decreased significantly since 1989 while the protozooplankton biomass has increased, though not significantly. In Roskilde Fjord no time trend was observed in the biomass of either meso- or protozooplankton. The lack of general inter-fjord time trends is probably due to the effect of local conditions.

Eutrophication is believed to cause an increase in the relative importance of gelatinous zooplankton vs. crustacean zooplankton. Throughout the

monitoring period several estuaries like Roskilde Fjord, Kertinge Nor and Limfjorden have suffered from occasional blooms of gelatinous zooplankton such as the jellyfish *Aurelia aurita* (Frederiksborg Amt & Roskilde Amt 2002, Fyns Amt 2002). The jellyfish graze on the mesozooplankton, which in turn leads to lowered grazing on the phytoplankton. In Kertinge Nor it has been shown that high abundance of jellyfish reduces the importance of zooplankton as grazers on phytoplankton to almost negligible levels (Petersen et al. 1999). Moreover, jellyfish are suspected to affect the recruitment of fish negatively, both by grazing on fish eggs and larvae and by affecting the
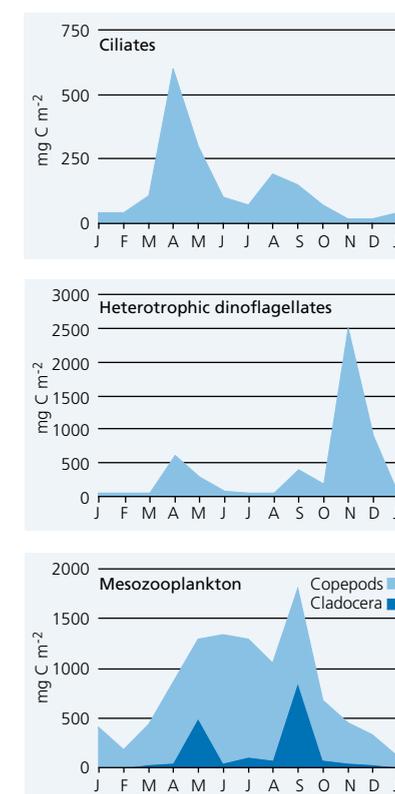


**Figure 2.24**
Seasonal variation in biomass (mg C m$^{-2}$) of ciliates, heterotrophic dinoflagellates and mesozooplankton in the southern part of Kattegat. (Modified from Nielsen & Hansen 1999).

feeding conditions for fish larvae and planktivorous fish by causing a decrease in the abundance of prey organisms such as copepods. Jellyfish themselves are in a sense a trophic dead end. Energy and organic matter that could otherwise be channelled into harvestable organisms is turned into non-utilisable jelly.

## THE CLADOCERAN *PENILIA AVIROSTRIS*: AN ADDITION TO THE DANISH FAUNA

Cladocerans have their main distribution in freshwater habitats and the number of species in Danish marine water is limited. Usually they constitute only a minor fraction of the meso-zooplankton biomass, but due to parthenogenesis they can increase rapidly in numbers when growth conditions are favourable and occasionally they become quantitatively important grazers. The two dominating genera *Evadne* and *Podon* are believed to graze mainly on large phytoplankton cells and on protozooplankton (Egloff et al. 1997).

In the autumn 2001 a new cladoceran species *Penilia avirostris* was observed in plankton samples from Århus Bight and Kattegat (Ærtebjerg et al. 2002). This species has its main distribution in tropical and subtropical seas, where it at times dominates the mesozooplankton biomass. It feeds mostly on nanoplankton (2-20 µm) (Turner et al. 1988) and thus plays a different role in the pelagic food web than the other marine cladoceran species. Due to this *P. avirostris* may be an important link between bacterioplankton and higher consumers because of its predation on bacterivorous flagellates. *P. avirostris* was reported in the North Sea as early as 1948 and since 1999 it has been a steady component of the zooplankton community in the southern and eastern parts of the North Sea, typically in September/October. Since the first record in the North Sea it has spread progressively northward. For example it was found around Helgoland (Germany) in the early 1990s and was recorded in Koster Fjorden (Sweden) in 1997. In 2001 *P. avirostris* was observed in relatively low abundances of about 100 individuals m$^{-3}$ in the Kattegat region, but in August-September 2002 it was among the dominating mesozooplankton species in the Sound with abundances up to 4000 individuals m$^{-3}$ (Per Juel Hansen, pers comm). *P. avirostris* has the capacity to quickly build dense populations and significantly influence the food web structure and the fate of the primary production. Therefore it is important to follow closely the occurrence and development of this new, invasive species which is probably well established in Danish waters.

The size of zooplankton varies from single cell microzooplankton to large organisms as jelly fish.
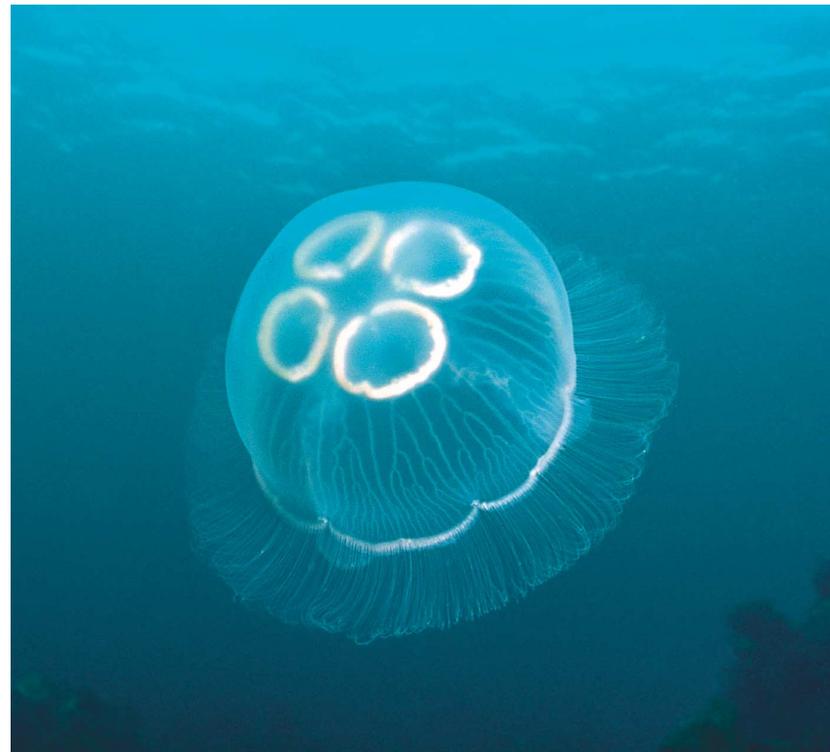
Photo: Ocean Photo, Norway/Erling Svensen
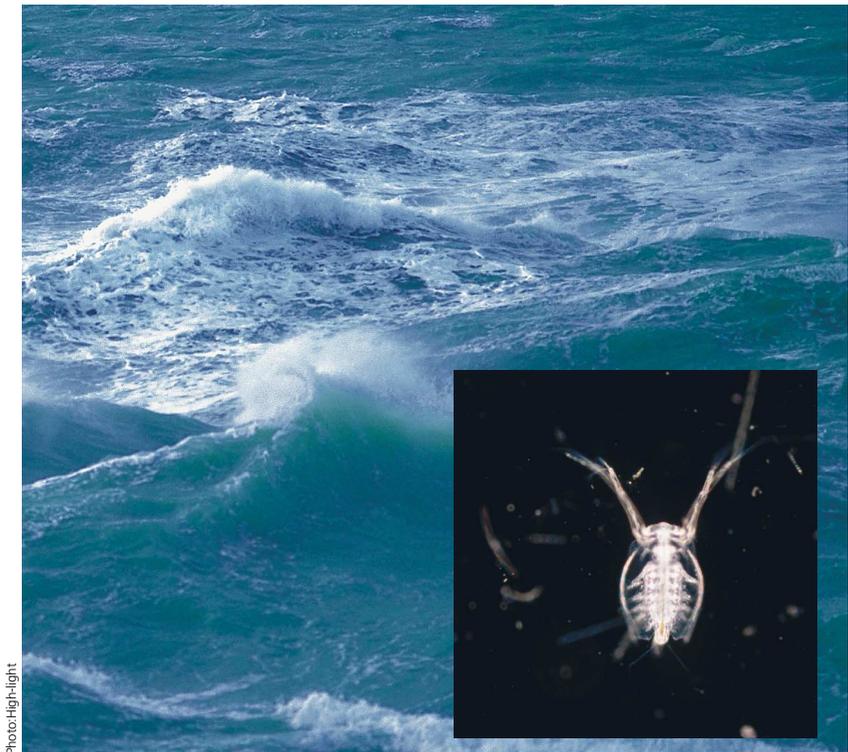
Photo:High-light

Photo (*Penilia avirostris*): MBL/Per Juel Hansen

**Figure 2.25**
The cladoceran *Penilia avirostris*, which is probably now established in Danish waters.

# 2.7 OXYGEN DEPLETION

**The "cloud" is sulphur in the water due to hydrogen sulphide released from sediments during a period of oxygen depletion.**



Photo: Fyn County/Nanna Rask

Nutrient enrichment/eutrophication may give rise to an increased rate of oxygen consumption, decreased oxygen concentrations and an increased frequency of oxygen depletion. In Denmark oxygen depletion is defined as oxygen concentrations below 4 mg l$^{-1}$ (2.8 ml l$^{-1}$), and severe (acute) oxygen depletion as below 2 mg l$^{-1}$ (1.4 ml l$^{-1}$). The observed oxygen concentrations in September 2001 and 2002 are shown in Figure 2.26.

Analyses of long term development in bottom water oxygen concentrations during late summer – autumn in the Kattegat-Belt Sea from the 1970s to late 1980s/1990s (Table 2.7) show significant decreases in all areas with a stratified water column, especially from the mid 1970s to the late 1980s.

In the period 1989–2001 no general development in the summer-autumn bottom water minimum oxygen concentration was observed. However, a tendency for a rise in minimum oxygen concentration in spring (April-June) has been found (Hansen et al. 2000, Ærtebjerg et al. 2002).

Oxygen depletion only occurs in stratified water columns where stratification prevents oxygen-rich surface waters to mix to the bottom. The oxygen concentration close to the sea bottom in stratified waters depends on two processes each varying in time and space: the consumption rate, which is mainly dependent on the supply of organic matter and the temperature, and the oxygen supply rate, which is mainly dependent on wind condi-

tions. Therefore, it is difficult to assess, if a particular oxygen depletion incident is due to increased consumption rate or decreased supply rate of oxygen, and thus to relate the oxygen concentrations to nutrient loads.

runoff and load as in 1996-1997 corresponded to higher oxygen levels than modelled (Figure 2.27). Hansen et al. (1995) made a scenario analysis of effects of reduced nitrogen input on oxygen conditions in the Kattegat and

| Area | Period | Annual change | Reference |
|---|---|---|---|
| Kattegat | 1971-82/90 | -0.05-0.1 ml l$^{-1}$ | Andersson & Rydberg 1988, 1993 |
| Kattegat NE | 1970-95 | -0.2% saturation | HELCOM 1996 |
| | 1975-88 | -1.16% saturation | Agger & Ærtebjerg 1996 |
| Kattegat S | 1975-88 | -1.17-1.41% saturation | Agger & Ærtebjerg 1996 |
| The Sound | 1970-95 | -0.5% saturation | HELCOM 1996 |
| | 1975-88 | -1.10% saturation | Agger & Ærtebjerg 1996 |
| Great Belt | 1974-95 | -0.7% saturation | HELCOM 1996 |
| Little Belt S | 1976-97 | Decrease | Ærtebjerg et al. 1998 |
| Fehmarn Belt | 1975-97 | Decrease | Ærtebjerg et al. 1998 |
| | 1979-93 | -0.5% saturation | HELCOM 1996 |
| | 1975-88 | -2.97% saturation | Agger & Ærtebjerg 1996 |
| Kiel Bight | 1957-86 | -0.10-0.11 ml l$^{-1}$ | Babenerd 1991 |
| | 1976-90 | -0.15 ml l$^{-1}$ | Weichart 1992 |

**Table 2.7**
Published statistical significant results of analyses of the development in bottom water oxygen concentrations late summer – autumn in the Kattegat-Belt Sea from the 1970s to late 1980s/1990s.

Therefore, oxygen level in the bottom layer (20–40 m) in the southern Kattegat and Belt Sea was modelled as a function of a temperature dependent gross oxygen consumption rate, water temperature and residence time. The later defined as the time since the bottom water advected below the pycnocline. The residuals between modelled and observed oxygen saturation was interpreted to arise from inter-annual variations in the availability of organic matter for respiration (Henriksen et al. 2001). In the period 1982–2000 the residuals (mean May–Sept.) correlated significantly to the runoff and N-load in the previous hydrological year (June–May). High runoff and load generally corresponded to lower oxygen levels than modelled, and low

Belt Sea. They concluded, that the nationally and internationally agreed nitrogen load reductions would significantly improve the oxygen situation, but to reach the oxygen level in the 1950s it would probably be necessary also to lower the atmospheric nitrogen deposition.

Most of the Danish estuaries-coastal waters are shallow, and the wind can easily mix the water column to the bottom. Stratification only occurs periodically during calm and warm periods building up a thermocline, or by inflow of saline bottom water creating a temporary halocline. In a detailed study of a shallow Danish estuary (Skive Fjord/Lovns Bredning) it was possible to separate the effect of meteorological forcing (wind, solar radiation) and
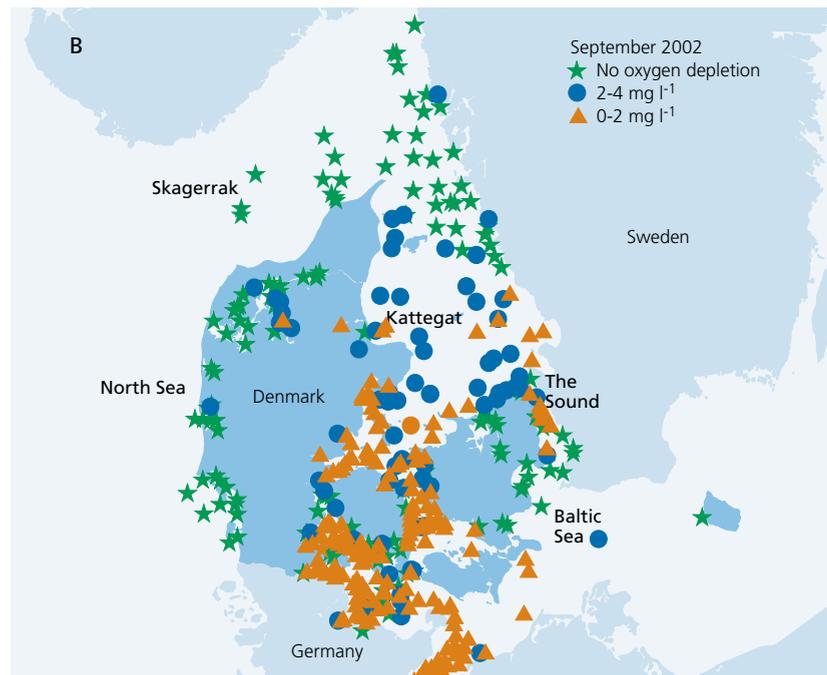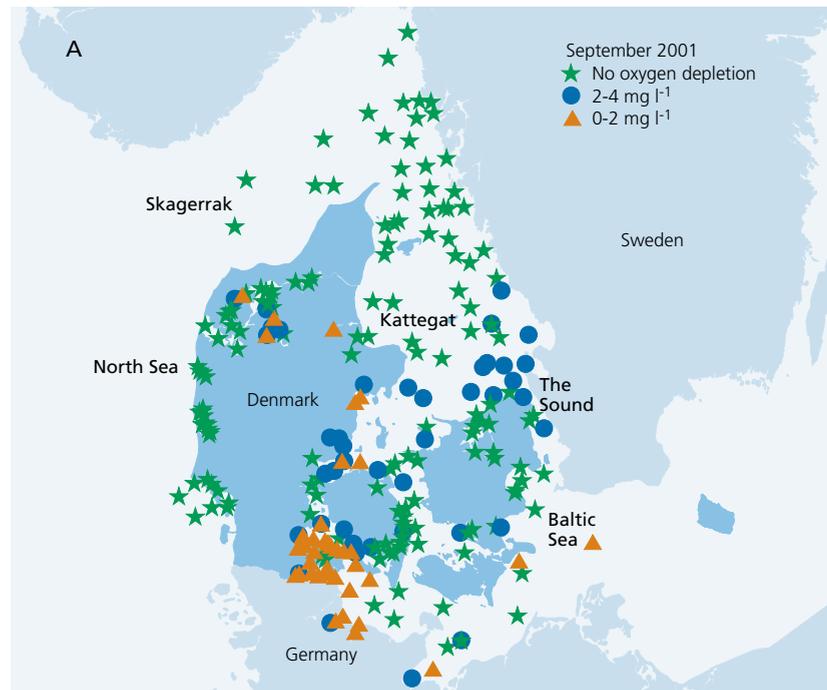
Figure 2.26
Oxygen depletion in Danish and neighbouring waters within September 2001 (A) and 2002 (B). Swedish and German monitoring data are included.

nutrient load on oxygen depletion in bottom water. During summer periods of stratification oxygen saturation could be attributed to the time elapsed after the onset of stratification and the accumulated nitrogen loading 10 months prior to measurement. Using 10 years meteorological data and an empirical model, it was calculated that a 25% reduction in nitrogen loading would reduce the number of days with severe oxygen depletion (<15% saturation) by more than 50% (Møhlenberg 1999).
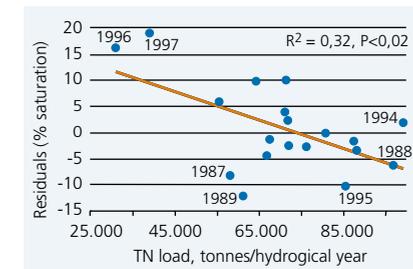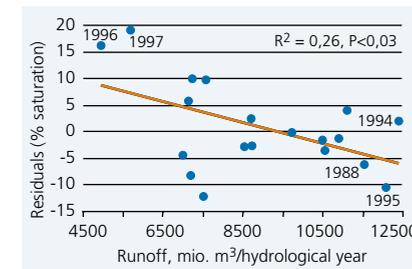


Figure 2.27
Residuals between modelled and observed oxygen saturation (mean May-September per year) as a function of (A) the runoff, and (B) the N-load during the previous hydrological year (June-May). The two hydrological years with lowest and the three hydrological years with highest runoff are indicated.

Sulphur formed by oxidation of hydrogen sulphide released from the sediment in Odense Fjord.



Photo: Fyn County/Søren Larsen

# 2.8 Degradation of organic matter in estuarine sediments



**Photosynthetic microalgae living in sunlit surface sediments can produce small oxygen bubbles.**

Photo: NERI/Peter Bondo Christensen
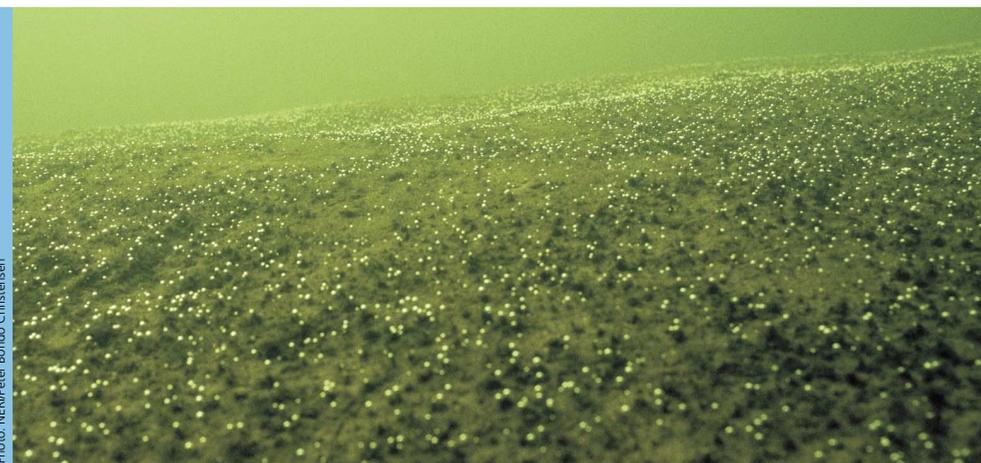
In marine sediments, organic matter is mainly degraded through bacterial processes, by which N and P bound in organic compounds as a result of primary production are released once again.

Up to half of the bacterial degradation taking place in the sediments proceeds through oxygen respiration (i.e. aerobically). The remaining degradation takes place anaerobically through respiration of nitrate, iron, manganese or sulphate (Jørgensen 1996).

Besides the release of $CO_2$, $NH_4^+$ and $PO_4^{3-}$, anaerobic degradation results in the formation of waste products (such as hydrogen sulphide from sulphate respiration) that are ultimately oxidised, thereby consuming

the exact amount of oxygen that would have been used if the entire degradation process had been aerobic. Therefore, a measurement of the amount of oxygen consumed within the sediment in darkness will correspond quite closely to the total metabolism of organic matter going on within the sediment, since this measurement is the sum of aerobic and anaerobic degradation.

## Oxygen

The sediment oxygen consumption describes a typical bell-shaped curve, the lowest values being found in the winter months and maximum values from May to September (Figure 2.28). This variation corresponds closely to the variation in water temperature. An analysis of the correlation between temperature and oxygen consumption shows that temperature explains 55% of oxygen consumption ($R^2=0.5467$, n=644, p<<0.0001). For the remaining part, the explanation probably lies in the amount of organic matter reaching the sea floor during spring and summer.

## Nitrogen

The flux of nitrogen (and of phosphorus, for that matter) between the marine sediment and the bottom water is governed by differences in concentrations between pore water (within the sediment) and water column. Thus, sediments will always take up $NH_4^+$ or $NO_3^-$ when water-column concentrations of the respective N compounds are greater than porewater concentrations, and accordingly release nitrogen to the bottom water when nitrogen porewater concentrations are higher.



**Fig 2.28**
Box-Whiskers plot of the seasonal variations in sediment oxygen consumption/respiration expressed as the numerical magnitude of the $O_2$ flux measured in darkness. The dataset is a compilation of observations from 6 estuaries each represented with 3 stations sampled 16 times over a two-year period. Median (line), 25% and 75% quantiles (boxes) and 10% and 90% quantiles (bars) are shown.
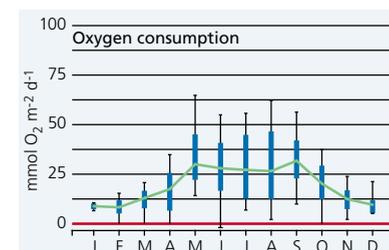
Sheets of white sulphur bacteria on a mussel bed.



Photo: Fyn County/Nanna Rask

**Figure 2.29**

Box-Whiskers plot of the seasonal variations in the sediment $NO_3^-$ flux (A), $NH_4^+$ flux (B) and $PO_4^{3-}$ flux (C). Positive values indicate net release, and negative values indicate consumption. The dataset is a compilation of observations from 6 estuaries each represented with 3 stations sampled 16 times over a two-year period. Median (line), 25% and 75% quantiles (boxes) and 10% and 90% quantiles (bars) are shown.



**Figure 2.30**

Internal nitrogen supply in 2000 at 17 stations representing 6 types of estuaries, Roskilde Fjord, Odense Fjord, Horsens Fjord, Ringkøbing Fjord, Limfjorden and Skive Fjord, shown for the entire year (annual flux) and for the months of June, July and August (summer flux). Positive values indicate net release, and negative values indicate consumption.
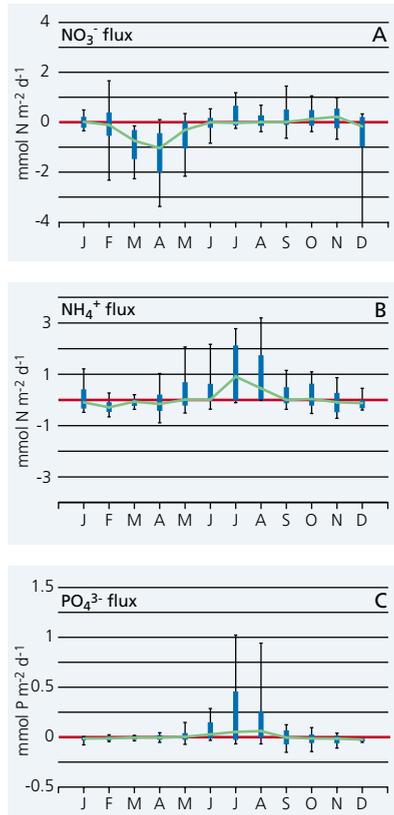


From January to May, estuarine sediments take up dissolved inorganic nitrogen ($DIN=NH_4^++NO_3^-$), primarily in the form of $NO_3^-$ (Figure 2.29). During this period, the water-column concentration of $NO_3^-$ is high. Therefore, the sediments $NO_3^-$ uptake may be a result of a lower pore-water concentration of $NO_3^-$, perhaps governed by denitrification activity and a high $NO_3^-$ assimilation by active benthic microalgae. Not until the summer months (June, July and August) does the estuarine sediment release nitrogen in the form of $NH_4^+$ (Figure 2.30). Low water-column $NO_3^-$ concentrations and a high sediment oxygen demand resulting in less favourable oxygen conditions cause both nitrification and denitrification to decline markedly or stop altogether. At the same time, $NO_3^-$ assimilation ceases. Thus, in the summer months, $NH_4^+$ constitutes the major part of the DIN flux from sediment to water column.

The flux of nitrogen from the sediment to the water column continues into autumn; but gradually $NO_3^-$ becomes dominating in the release of nitrogen (Figure 2.29 A and B). During autumn, the sediment oxygen demand decreases (Figure 2.28), and this causes the oxygen content of the sediment to increase. This means that nitrification gains more and more importance, and that more and more $NH_4^+$ is oxidised to $NO_3^-$ (nitrified) within the sediment. As benthic microalgae only assimilate insignificant amounts of $NO_3^-$ during autumn because of lowered activity (see Figure 2.29 A), $NO_3^-$ accumulates within the sediment, even though some denitrification is taking place, and eventually diffuses from the sediment, since water-column $NO_3^-$ concentrations, at least until November, are low.

## PHOSPHORUS

Through mineralisation, phosphorus is released as inorganic phosphate ($PO_4^{3-}$) (Eq. 1). Contrary to nitrogen compounds, a considerable amount of phosphate is bound more or less permanently within the sediment, while a smaller fraction is found dissolved in pore water.

Eq. 1:

$$106CO_2 + 16NH_4^+ + PO_4^{3-} + 106H_2O$$

Primary production ↓ ↑ Bacterial degradation

$$(CH_2O)_{106}(NH_4^+)_{16}(PO_4^{3-})+53O_2$$
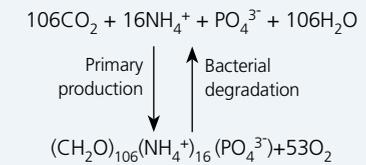
It is the pool of oxidised iron ($Fe_{ox}$) that binds part of the phosphate found in estuarine sediment (Jensen & Thamdrup 1993). Good oxygen conditions

**Figure 2.31**

Internal phosphorus supply in 2000 at 17 stations representing 6 types of estuaries, Roskilde Fjord, Odense Fjord, Horsens Fjord, Ringkøbing Fjord, Limfjorden and Skive Fjord, shown for the entire year (annual flux) and for the months of June, July and August (summer flux). Positive values indicate net release, and negative values indicate consumption.
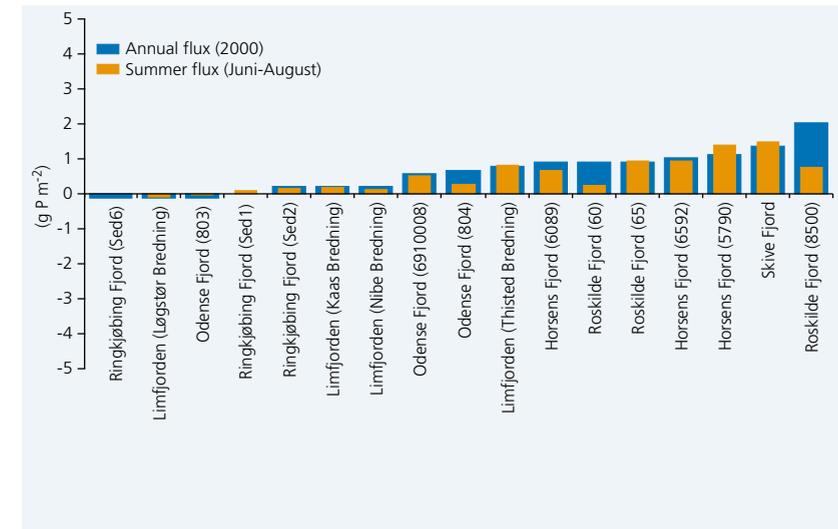
within the sediment increases the $Fe_{ox}$ pool, which is able to retain either phosphate or hydrogen sulphide (through a reaction forming ferrous sulphide; FeS – see Eq. 2). On the other hand, poor oxygen conditions cause the pool of oxidised iron to grow gradually smaller. As the $Fe_{ox}$ concentration decreases, phosphate is released from the sediment to the water column.

Eq. 2:

$$Fe_{ox} - PO_4^{3-} + H_2S \longrightarrow FeS + PO_4^{3-}$$

In the "typical" estuary the flux of $PO_4^{3-}$ is insignificant in spring, autumn and winter (Figure 2.31). Significant $PO_4^{3-}$ release from the sediment to the water column is seen only in June, July and August. This period coincides with

$NH_4^+$ release to the water column, and, as described above, the release of $PO_4^{3-}$ is caused by poor oxygen conditions within the sediment that stimulate hydrogen sulphide production, so to speak, leading to increased consumption of oxidised iron.

## INTERNAL NUTRIENT LOAD

Nation-wide observations of nutrient fluxes in Danish estuaries from Roskilde Fjord in the east to Ringkøbing Fjord in the west show that during the summer of 2000 (June-August) nitrogen was released from the sediment at 14 of 17 stations (Figure 2.29 C). At almost half of the stations an annual net release of nitrogen from the sediment to the water column was seen in 2000, and the flux of nitrogen during the summer months contributed most to the total net flux that year. Likewise,

a net release of phosphorus took place during the summer months at all stations except three (Figure 2.31), and, on average, more than 75% of the total annual $PO_4^{3-}$ release to the water column took place during this period.

It is in the summer months that water-column concentrations of nitrogen and phosphorus are low. Thus, growth of algae within the estuaries depends on a steady supply of nutrients to the water column from land (streams etc.), atmosphere, adjacent seas or through degradation of organic matter in the water column or the sediment. In June, July and August 2000, the total nutrient supply from land constituted 10% of the annual supply. Thus, a relatively low external nutrient supply during summer means that release of nitrogen and phosphorus through organic matter degrada-

tion in the sediment (the internal supply) may stimulate primary production in the estuaries at this time of year.

The internal and external supplies of nitrogen ($NO_3^- + NH_4^+$) and phosphorus ($PO_4^{3-}$) to four estuaries representing four different types of area, Roskilde Fjord, Odense Fjord, Horsens Fjord and Ringkøbing Fjord, in the period June-August 2000 are shown in Table 2.8, assessed as the total supply to the entire estuary. It is evident that fluxes from the sediment of both nitrogen and phosphorus contributed significantly to the nutrient supply reaching the estuaries in the summer of 2000. In this period, between 36 and 93% of the supply of phosphorus to the estuaries came from the sediment, and in the case of nitrogen, the internal supply was almost as large (10-78%). ■

**Table 2.8**
Internal vs. external supply of N and P to four types of estuary in the period June-August 2000

|  | Nitrogen | | | | Phosphorus | | | |
|---|---|---|---|---|---|---|---|---|
|  | Internal | External | Total | Internal | Internal | External | Total | Internal |
|  | tonnes | tonnes | tonnes | % | tonnes | tonnes | tonnes | % |
| Roskilde | 387,1 | 107,8 | 494,9 | 78% | 81,7 | 8,3 | 90,0 | 91% |
| Odense | 17,3 | 152,6 | 169,9 | 10% | 7,2 | 6,5 | 13,7 | 53% |
| Horsens | 39,7 | 108,0 | 147,7 | 27% | 43,1 | 3,2 | 46,3 | 93% |
| Ringkøbing | 263,8 | 884,8 | 1.148,7 | 23% | 10,3 | 18,4 | 28,7 | 36% |

Photo: NERI/Ole Schou Hansen