

# Nitrogen processes in coastal and marine ecosystems

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## Executive summary

### Nature of the problem

- Nitrogen (N) inputs from human activities have led to ecological deteriorations in large parts of the coastal oceans along European coastlines, including harmful algae blooms and anoxia.
- Riverine N-loads are the most pronounced nitrogen sources to coasts and estuaries. Other significant sources are nitrogen in atmospheric deposition and fixation.

### Approaches

- This chapter describes all major N-turnover processes which are important for the understanding of the complexity of marine nitrogen cycling, including information on biodiversity.
- Linkages to other major elemental cycles like carbon, oxygen, phosphorus and silica are briefly described in this chapter.
- A tentative budget of all major sources and sinks of nitrogen integrated for global coasts is presented, indicating uncertainties where present, especially the N-loss capacity of ocean shelf sediments.
- Finally, specific nitrogen problems in the European Regional Seas, including the Baltic Sea, Black Sea, North Sea, and Mediterranean Sea are described.

### Key findings/state of knowledge

- Today, human activity delivers several times more nitrogen to the coasts compared to the natural background of nitrogen delivery. The source of this is the land drained by the rivers. Therefore, the major European estuaries (e.g. Rhine, Scheldt, Danube and the coastlines receiving the outflow), North Sea, Baltic Sea, and Black Sea as well as some parts of the Mediterranean coastlines are affected by excess nutrient inputs.
- Biodiversity is reduced under high nutrient loadings and oxygen deficiency. This process has led to changes in the nutrient recycling in sediments, because mature communities of benthic animals are lacking in disturbed coastal sediments. The recovery of communities may not be possible if high productivity and anoxia persist for longer time periods.

### Major uncertainties/challenges

- The magnitude of nitrogen sources are not yet well constrained. Likewise the role of nutrient ratios (N:P:Si ratios) may be a critical variable in the understanding of the development of harmful algae blooms.
- Whether only inorganic forms of nitrogen are important for productivity, or whether organic nitrogen is also important is not well understood and needs future attention.

### Recommendations

- For the future it will be necessary to develop an adaptive transboundary management strategy for nitrogen reduction. The starting point for such regulation is located in the catchments of rivers and along their way to the coastal seas.
- An overall reduction of nitrogen inputs into the environment is urgently necessary, especially in the case of diffuse nitrogen inputs from agricultural activities.

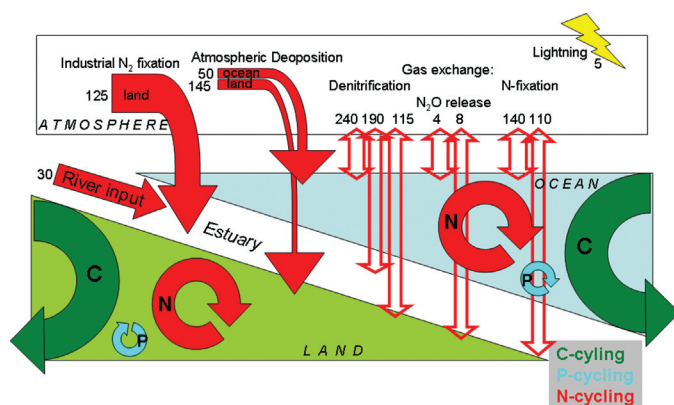
## 8.1 Introduction

The marine and terrestrial nitrogen cycles are closely linked, although intellectual boundaries in disciplines often lead to separate treatment of both cycles (Gruber, 2004). Since humans have perturbed the nitrogen cycle considerably via the production of artificial fertilizers, fossil fuel combustion or animal husbandry, the man-made sources of reactive nitrogen (fixed nitrogen,  $N_r$ ) are now larger than the amount produced by natural nitrogen fixation (Gruber and Galloway, 2008). Furthermore the transport of anthropogenically produced nitrogen to the ocean is accelerated relative to the previous century and close links between watersheds, airsheds and the marine system result in excess nutrient supply not only to the coastal zones (Rabalais, 2002) but also to the open ocean (Duce *et al.*, 2008; Figure 8.1). Moreover Duce *et al.* (2008) argue that the coastal area is a sink not a source of nitrogen for the open ocean. Nitrogen may also strongly perturb natural fluxes and processes responsible for the production and release of trace gases which are relevant to climate such as nitrous oxide ( $N_2O$ ).

The global  $N_r$  budget has changed from one that was almost balanced in preindustrial times to one in present times with much higher inputs than losses (Vitousek *et al.*, 1997) which impacts coastal systems significantly. Here, we summarize the current knowledge on N-pathways in marine waters, the anthropogenic impact and how the cycling, mass transfer and effects of this nitrogen have changed the European coastal waters (e.g. estuarine systems and enclosed seas).

## 8.2 Nitrogen-cycle processes in the open ocean and coastal systems

The marine environment has unique characteristics that distinguish it from other aquatic systems. First of all the salinity varies from almost zero in inner estuaries to almost 40 in the Mediterranean (earlier salinity was given in grams of salts per litre, since 1978 no units are used because it refers to a



**Figure 8.1** Schematic of the coupling of the marine and the terrestrial nitrogen cycles. The numbers are estimates of the natural plus anthropogenic N transports in  $Tg\ N\ yr^{-1}$  as taken from Gruber and Galloway (2008). The circles visualize the cycling of carbon (green), phosphorus (blue), and nitrogen (red). The industrial fixation is purely anthropogenic, and the atmospheric deposition on land (145) is dominated by 70% anthropogenic N. The graph is inspired by the same paper.

conductivity ratio of a seawater sample to a standard KCl solution). The salinity increases the density of the water and therefore strongly shapes the stratification of a water body so that a change of only  $1\ g\ l^{-1}$  equals a  $5\ ^\circ C$  difference in density. Salinity and temperature differences are responsible for the structure of a water body and a stable stratification is sustained by lighter waters on top of heavier ones. Only winds, tides and currents are able to break up the interfaces.

Stratification prevents the exchange of dissolved substances between layers of water, so that nutrients may accumulate at a certain depth. Particulate material like phytoplankton aggregates, faecal pellets from zooplankton etc. sink through this interface and are degraded. The microbial degradation of this organic matter leads to the accumulation of nutrients and the depletion of oxygen below the interface. If the oxygen consumption is higher than the oxygen renewal of the deep waters, anoxia can develop with large scale die-offs of benthic animals. The abundance of such 'dead zones' is increasing in many coastal areas worldwide (Diaz and Rosenberg, 2008).

Primary production in the oceans is to a large extent driven by the availability of inorganic and organic nitrogen compounds; mostly nitrate, ammonium, and dissolved organic nitrogen (DON). Coastal systems receive their nutrients from recycling of organic matter, river input, atmospheric deposition, onshore transport of nutrients from the open sea, and to a small extent from  $N_2$ -fixation. For a long time, research on riverine N-inputs into coastal areas was mainly focused on inorganic N-species, especially nitrate and ammonium. In the last decade the importance of DON as a nutrient has received attention, especially after several studies showing that it can comprise up to 90% of the total nitrogen input (Seitzinger and Sanders, 1997), and that its bioavailability for phytoplankton and algae may be significant (Twomey *et al.*, 2005; Bronk *et al.*, 2007). In the past N was considered the major limiting nutrient of marine systems. However, since the delivery of P from watersheds has decreased (with improvement of P treatment in wastewater treatment plants), waters have become P limited in several locations (Cugier *et al.*, 2005; Lancelot *et al.*, 2007). However, the magnitude of delivery of both N and P has remained in excess relative to silica, which has often led to diatoms being replaced by harmful non-diatomaceous species (Billen and Garnier, 2007).

In the open ocean regeneration of organic matter, plus convection (in temperate latitudes down to the seasonal thermocline), atmospheric deposition, and diazotroph  $N_2$ -fixation provide most of the nutrients to the productive, sunlit surface waters. However, in the shallow coastal areas there is a tight coupling between the processes in the water-column and the sediments (Herbert, 1999). Groundwater efflux from sediments may also introduce nutrients to the water column (Slomp and Van Cappellen, 2004) in certain circumstances. Strong links exist between the N-, P- and C- cycles (Gruber and Galloway, 2008) as well as between trace metals and oxygen concentrations.

The degradation and turnover processes of the various nitrogen compounds are mostly mediated by bacteria. A key process in the N-cycle is **ammonification**, carried out not only

by bacteria but also by actinomycetes and fungi, which converts organic N (as found in proteins, amino-sugars, nucleic acids etc.) to inorganic ammonium (Herbert, 1999). Ammonium is taken up by phytoplankton and by bacteria, with bacterial uptake as high as 49% of total  $\text{NH}_4^+$  uptake in the surface water and up to 72% at the bottom of the water column (Bradley *et al.*, 2010). Some  $\text{NH}_4^+$  is oxidized during bacterial or archaeal **nitrification** via nitrite to nitrate. **Nitrification** is an obligatory aerobic two-step process; the first step is the oxidation of ammonia to nitrite by ammonia oxidizing bacteria and in the second step nitrite is oxidized to nitrate by nitrite oxidizers. The rate of nitrification is controlled by temperature unless there is an insufficient supply of oxygen and ammonium. Therefore numerous studies report seasonal cycles with increasing rates at higher temperatures (Tuominen *et al.*, 1998). At oxygen concentrations below  $10 \mu\text{mol l}^{-1}$  the process additionally produces  $\text{N}_2\text{O}$  as a by-product (Hynes and Knowles, 1984; Jorgensen *et al.*, 1984). Nitrification occurs in the water column as well as in oxygenated sediment layers, and the generated nitrate is either assimilated by phytoplankton and algae or is reduced to  $\text{N}_2$  and  $\text{N}_2\text{O}$  during bacterial denitrification.

It was accepted for a long time, that **denitrification** is the only process that permanently removes reactive nitrogen from the aquatic and terrestrial environment. Under hypoxic conditions ( $<10 \mu\text{mol l}^{-1}$ ), the heterotrophic denitrifiers can use nitrate as a final electron acceptor during respiration and produce  $\text{N}_2$  gas as final end product and  $\text{N}_2\text{O}$  as an intermediate. The extent of this process is strongly controlled by temperature, nitrate concentrations and the availability of organic carbon (Hulth *et al.*, 2004), which makes the process seasonally variable (Tuominen *et al.*, 1998). Autotrophic denitrification with  $\text{CO}_2$  as a carbon source may temporarily occur as the dominant process, at anoxic-oxic interfaces such as found in the Baltic Sea (Hannig *et al.*, 2007). In sediments below oxic water-columns there is often a tight coupling between nitrification and denitrification, and the nitrate generated during nitrification in the oxic sediment layer diffuses downwards in sub-oxic sediment regions where it is rapidly denitrified (Herbert, 1999).

Mulder *et al.* (1995) was the first paper to describe an alternative pathway which generates  $\text{N}_2$  from reactive N. Although originally described from sewage-treatment plants **anaerobic ammonia oxidation (anammox)** is considered as important as denitrification in some upwelling regions (Kuypers *et al.*, 2006) but not in all (Ward *et al.*, 2009). During anammox, the strictly anaerobic chemoautotrophic bacteria of the group Planctomyces fix  $\text{CO}_2$  and use  $\text{NH}_4^+$  to reduce  $\text{NO}_2^-$ , which results in the production of  $\text{N}_2$  (Schmidt *et al.*, 2002). In sediments the process only occurs at oxygen concentrations below  $1.1 \mu\text{mol l}^{-1}$  and can account for up to 80% of the total  $\text{N}_2$  production. Its importance seems to decrease with decreasing water depths (Thamdrup and Dalsgaard, 2002).

There are several other N-transformation processes which most likely occur in the marine environment, but are not well understood: (i) sedimentary **chemodenitrification**, where manganese species react with nitrate or ammonium to produce  $\text{N}_2$  (Brandes *et al.*, 2007); (ii) **dissimilatory nitrate reduction**

**to ammonia (DNRA)**, which is carried out by strictly anaerobic, fermentative bacteria (Herbert, 1999). High rates of DNRA are measured under highly reducing conditions in sediments (Christensen *et al.*, 2000) and the water column (Lam *et al.*, 2009); (iii) **oxygen-limited autotrophic nitrification-denitrification (OLAND)**, which has been detected in sediments (Brandes *et al.*, 2007).

Many N-transformation processes are strongly affected by humans (Figure 8.1). Together with increasing emissions of nitrogen and phosphorus (P) into the marine, terrestrial and atmospheric environment, these may lead to dramatic changes which can be summarized under the term of eutrophication (see Section 8.5). Coastal areas and estuaries suffer particularly from excess nutrient inputs, since they form the transition zone between the terrestrial and the marine environment. Anoxic coastal waters have been reported in many coastal areas worldwide such as the Gulf of Mexico, the Baltic Sea, or the Black Sea (Diaz, 2001). The increased input of nitrogen which is often accompanied by oxygen limitation has a strong negative effect on benthic metabolism and nitrogen mineralization (Karlson *et al.*, 2007) (see Section 8.8). Therefore processes which remove reactive N and thus counteract eutrophication become of considerable interest. In this case denitrification is key, since anammox is usually not as important as denitrification in shallow waters (Thamdrup and Dalsgaard, 2002).

### 8.3 Dissolved gaseous nitrogen compounds ( $\text{NO}$ , $\text{N}_2\text{O}$ , $\text{N}_2$ , $\text{NH}_3$ )

Nitric oxide ( $\text{NO}$ ), nitrous oxide ( $\text{N}_2\text{O}$ ), dinitrogen ( $\text{N}_2$ ) and ammonia ( $\text{NH}_3$ ) are constituents of the Earth's atmosphere and play important roles in the chemistry and climate of the present-day Earth. Moreover, they are intermediates or by-products of the marine nitrogen cycle (see above). An overview on current knowledge of the distribution and pathways of  $\text{NO}$ ,  $\text{N}_2\text{O}$ ,  $\text{N}_2$  and  $\text{NH}_3$  in European marine ecosystems is given here. If not cited otherwise, further details and references can be found in Bange (2006, 2008).

#### 8.3.1 Nitric oxide ( $\text{NO}$ )

$\text{NO}$  is chemically very reactive and thus it is a short-lived compound in aquatic systems. In nitrite-rich surface waters,  $\text{NO}$  is photochemically produced via the reduction of nitrite. The photochemically induced build-up of  $\text{NO}$  during the day is balanced by degradation during the night. Depth profiles of  $\text{NO}$  in the Pacific Ocean indicate that subsurface  $\text{NO}$  might be produced and consumed as an intermediate of nitrification and denitrification, respectively (Bange, 2008). Unfortunately, there are only a few measurements of oceanic  $\text{NO}$  available. In European marine ecosystems these are limited to one study of the  $\text{NO}$  flux from Wadden Sea sediments in northern Germany (Bodenbender and Papen, 1996). Because global oceanic  $\text{NO}$  emissions are only of marginal importance in comparison to emissions of  $\text{N}_2\text{O}$  (see below),  $\text{NO}$  emissions from European coastal and marine ecosystems are most probably negligible as well.

### 8.3.2 Nitrous oxide (N<sub>2</sub>O)

The world's oceans (including their coastal zones) are sources of atmospheric N<sub>2</sub>O (a powerful greenhouse gas) and play a major role in the global budget of atmospheric N<sub>2</sub>O. N<sub>2</sub>O in oceanic environments is mainly formed as a by-product during nitrification (NH<sub>4</sub><sup>+</sup> → NO<sub>3</sub><sup>-</sup>) and as an intermediate during denitrification (NO<sub>3</sub><sup>-</sup> → N<sub>2</sub>).

Based on the comprehensive compilation of N<sub>2</sub>O measurements from European coastal waters (Bange, 2006), three main conclusions can be drawn. (i) The highest concentrations of N<sub>2</sub>O occur in estuaries and fjords, whereas in open coastal waters (i.e. shelf waters not influenced by river plumes) N<sub>2</sub>O concentrations are close to the expected equilibrium with the atmosphere. This indicates that N<sub>2</sub>O is mainly formed in estuarine systems. (ii) It seems that sedimentary denitrification and water column nitrification are the major N<sub>2</sub>O formation processes. However, the yield of N<sub>2</sub>O from both processes strongly depends on the local O<sub>2</sub> concentrations, thus O<sub>2</sub> is the key factor in the regulation of N<sub>2</sub>O production (and its subsequent emissions to the atmosphere). Any pronounced changes of the O<sub>2</sub> regimes in coastal waters (see Section 8.5.4 this chapter) may lead to conditions which are favourable for temporarily enhanced N<sub>2</sub>O production. In shallow waters this 'excess' N<sub>2</sub>O can be easily ventilated to the atmosphere, whereas in non-ventilated anoxic deep waters, e.g. in the central basin of the Baltic Sea, N<sub>2</sub>O can be consumed by water column denitrification. (iii) European coastal waters are a net source of N<sub>2</sub>O to the atmosphere. The major contribution comes from the estuarine/river systems rather than the open shelf areas. The mean overall N<sub>2</sub>O emissions calculated for the European coastal water area of 3.2 × 10<sup>12</sup> m<sup>2</sup> (Bange, 2006) are 0.5 Tg N yr<sup>-1</sup> with a methodologically caused uncertainty of 0.3–0.7 Tg N yr<sup>-1</sup>. Therefore European coastal waters contribute significantly (about 9%) to the present global oceanic N<sub>2</sub>O emissions of 5.5 Tg N yr<sup>-1</sup> (IPCC, 2007). Future N<sub>2</sub>O emissions from European coastal areas will be strongly influenced by nitrogen inputs to coastal waters and will most likely increase in the future.

There might be two further, however, largely unknown N<sub>2</sub>O sources in European coastal areas. First, small coastal upwelling sites along the European coasts from subsurface layers may be an additional, physically driven, sources of N<sub>2</sub>O to the atmosphere. In addition, a large coastal upwelling site is situated off the Atlantic coast of Portugal, but N<sub>2</sub>O emissions during upwelling events are not yet quantified. Second, organic matter release from fish farming activities could increase the dissimilatory nitrate reduction to ammonium (DNRA) in sediments (Christensen *et al.*, 2000). An additional source of N<sub>2</sub>O may be sedimentary DNRA and third, submarine groundwater discharge (Crusius *et al.*, 2008).

### 8.3.3 Dinitrogen (N<sub>2</sub>)

Despite the inert nature of N<sub>2</sub>, the atmospheric N<sub>2</sub> pool is available for biological productivity via N<sub>2</sub> fixation (N<sub>2</sub> → NH<sub>4</sub><sup>+</sup>). An example of which is the Baltic Sea, where fixation takes place in the surface layer during the summer. Estimates for N<sub>2</sub> fixation in the Baltic Sea range from 0.03 to 0.9 Tg N yr<sup>-1</sup> (Rahm *et al.*,

2000; Schneider *et al.*, 2003). The release of dinitrogen (N<sub>2</sub>) from the fixed inorganic nitrogen pool (i.e. NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>) is mediated by denitrification (NO<sub>3</sub><sup>-</sup> → N<sub>2</sub>) and anaerobic ammonium oxidation (anammox, NO<sub>2</sub><sup>-</sup> + NH<sub>4</sub><sup>+</sup> → N<sub>2</sub>). This N<sub>2</sub> production has not yet been extrapolated to the European scale. Denitrification in sediments and in the water column of the Baltic Sea has been estimated to range from 0.5 to 0.6 Tg N yr<sup>-1</sup> (Shaffer and Rönner, 1984; Eilola and Stigebrandt, 1999). In the Black Sea the annual water column production of N<sub>2</sub> via anammox has been estimated to be about 0.4 Tg N/yr<sup>-1</sup> (Kuyppers *et al.*, 2003). Thus, we might roughly estimate a total N<sub>2</sub> production in the Baltic and Black Seas of about 1 Tg N yr<sup>-1</sup>. This estimate should be regarded as conservative, because it does not include N<sub>2</sub> production in the sediments of the Black Sea.

### 8.3.4 Ammonium/ammonia (NH<sub>4</sub><sup>+</sup>/NH<sub>3</sub>)

The distribution of dissolved NH<sub>3</sub> is tightly coupled to the distribution of dissolved NH<sub>4</sub><sup>+</sup> via the NH<sub>3</sub>/NH<sub>4</sub><sup>+</sup> equilibrium. Because the mean pH of today's ocean surface layer is about 8.1, dissolved NH<sub>3</sub> can exist in the seawater as a dissolved, non-protonated gas and thus it is available for gas exchange across the ocean/atmosphere interface. At a pH of 8.1, a water temperature of 25 °C, and a salinity of 35, only about 6% of the sum of (NH<sub>3</sub>) and (NH<sub>4</sub><sup>+</sup>) is available as dissolved NH<sub>3</sub>. NH<sub>4</sub><sup>+</sup> is the substrate or final product of major biological transformation processes of the oceanic nitrogen cycle such as bacterial and archaeal nitrification (NH<sub>4</sub><sup>+</sup> → NO<sub>3</sub><sup>-</sup>), assimilation by phytoplankton (NH<sub>4</sub><sup>+</sup> → organic matter) and excretion by zooplankton. Moreover, NH<sub>4</sub><sup>+</sup> can be formed by photochemical decomposition of dissolved organic nitrogen. As the biological uptake of NH<sub>4</sub><sup>+</sup> is very rapid, concentrations of dissolved NH<sub>4</sub><sup>+</sup> and NH<sub>3</sub> are generally low.

In coastal areas which are heavily influenced by anthropogenic activity, such as the North and Baltic Seas, high atmospheric NH<sub>3</sub> concentrations lead (despite high biological production and associated ammonia production) to a net flux of NH<sub>3</sub> from the atmosphere to the ocean. Moreover, it was recently demonstrated that even at low atmospheric NH<sub>3</sub> concentrations, the coastal North Sea is a sink for atmospheric NH<sub>3</sub>. Based on the limited amount of oceanic and atmospheric NH<sub>3</sub> measurements available from European coastal areas, the NH<sub>3</sub> exchange across the ocean/atmosphere interface is poorly known.

### 8.3.5 Outlook

Despite the fact that our knowledge on the distribution of gaseous nitrogen compounds in European coastal waters is still associated with a high degree of uncertainty, a rough impact assessment of various parameters which might influence today's emissions is given in Table 8.1. It is obvious that the ocean is a source of N<sub>2</sub>O and other gases under eutrophying conditions. Owing to the unknowns (Table 8.1) and in view of the ongoing environmental changes, we need integrated long-term measurement programmes in European coastal and marine ecosystems.

**Table 8.1** Impact assessment of various parameters which might influence today's emissions of gaseous nitrogen compounds from European coastal waters

	NO	N <sub>2</sub> O	N <sub>2</sub>	NH <sub>3</sub>
Eutrophication/hypoxic events	?	++	++	++
Coastal upwelling	?	+	–	–
Fish farming	?	–	?	+
Ecosystem shifts due to climate change	?	?	?	?

Classification scheme: – = minor; + = moderate; ++ = high; ? = unknown. In essence, today's N<sub>2</sub>O emissions are highly sensitive to eutrophication/hypoxic events whereas the effect of fish farming activities on the present N<sub>2</sub>O emissions will be negligible.

## 8.4 Atmospheric inputs

### 8.4.1 Atmospheric N emissions and transport to the oceans

Atmospheric nitrogen emissions are predominantly in the form of oxidized (NO and NO<sub>2</sub>) and reduced nitrogen (NH<sub>3</sub>). Emissions of oxidized nitrogen are dominated by combustion processes and those of reduced nitrogen by agricultural activity. Although the emission estimates in Table 8.2 are rather uncertain, they do indicate that emissions of both forms of N are of broadly similar magnitude and that emissions are now several times greater than natural emissions. A recent global compilation not broken down by emission sector quoted total emissions in 2000 of between 3.7 and 4.6 × 10<sup>12</sup> mol N yr<sup>-1</sup> with 75% of this being anthropogenic (Duce *et al.*, 2008). Here we briefly summarize atmospheric N sources and transformations and their impacts, first on the open ocean and then on coastal areas.

There is an active inorganic N atmospheric chemistry and only the relevant parts are summarized here, based on Jickells (2006). A more detailed discussion can be found in Seinfeld and Pandis (1998). Upon emission to the atmosphere, NH<sub>3</sub> gas will react with available acids and some of these reactions are reversible (e.g. the formation of ammonium nitrate) and some are essentially irreversible (e.g. the formation of ammonium sulphate). Hence both ammonia gas and aerosol ammonium species are often present in the atmosphere, with ammonium predominantly as fine mode aerosol (particles with diameters in the range 0.1–1 μm), which is the characteristic size distribution for aerosols formed by gas to particle reactions (Raes *et al.*, 2000). NO and NO<sub>2</sub> are usually referred to as NO<sub>x</sub> because these forms can interchange rapidly. They are oxidized on a timescale of hours to days to nitric acid which can react with bases such as ammonia in the atmosphere. In the marine boundary layer nitric acid will also react with sea salt by the reaction:



The efficiency of this reaction means that there is little free nitric acid in the marine atmosphere and also that the

**Table 8.2** Atmospheric emissions of fixed nitrogen in 1993 (10<sup>12</sup> mol N yr<sup>-1</sup>) (based on Galloway *et al.*, 2004)

Anthropogenic activity	NO <sub>x</sub>	NH <sub>3</sub>
Biomass burning <sup>a</sup>	0.5	0.6
Agricultural activity	0.2	2.8
Fossil fuel combustion	1.5	0.01
Industry	0.5	0.2
<b>Natural</b>		
Soils, vegetation and animals	0.2	0.3
Lightning	0.4	—
Natural fires <sup>b</sup>	0.06	0.06
Stratosphere exchange	0.04	0.04
Ocean exchange	—	0.4
<b>Total</b>	<b>3.4</b>	<b>4.5</b>

<sup>a</sup>Some of the tropical biomass burning included here could be natural.

<sup>b</sup>Under 'natural fires' only high-latitude forest fires are included.

aerosol nitrate is primarily associated with the coarse mode (>1 μm) sea spray aerosol, which is mechanically generated (Raes *et al.*, 2000). Desert dust is also associated with this larger coarse mode and is alkaline, therefore in regions where dust supply is important such as in the tropical Atlantic, Indian and North West Pacific Oceans, reactions between dust aerosol and nitric acid can also be important (Usher *et al.*, 2003).

In addition to these inorganic N forms, organic N is found in the atmosphere, particularly as aerosol, where soluble organic N represents a variable but significant fraction (often ~20%–30%) of total N (Cornell *et al.*, 2003). An insoluble organic N component may also exist (Russell *et al.*, 2003). The sources of this organic nitrogen are uncertain and likely to be many and varied, but recent evidence suggests it includes a significant anthropogenic component (Zhang *et al.*, 2008). The bioavailability of this organic nitrogen is also uncertain, although Seitzinger and Sanders (1999) suggest that at least a part of it is readily bioavailable.

Deposition of nitrogen to the oceans occurs by wet and dry deposition, and the rates of both processes depend in part on the aerosol size distribution, with large aerosols depositing more rapidly. Deposition rates for coarse mode aerosol are an order of magnitude or more greater than those of the fine mode (Duce *et al.*, 1991), so the transformation of nitrate size distribution by the reaction with sea salt has a significant influence on the global flux distribution. Ammonia exchange at the ocean surface is a two way gaseous process. Increasing ammonia concentrations (as a result of human activity) have been suggested to have altered the direction of the flow of ammonia exchange in many regions (see Jickells, 2006, for a review). However, Johnson *et al.* (2008) emphasized the sensitivity of ammonia air–sea exchange to temperature and suggested that the flux will be predominantly into the oceans at low water temperatures and potentially out of the oceans at higher temperatures, although this is modulated by atmospheric ammonia concentrations.

## 8.4.2 Effects of atmospheric N deposition on the oceans

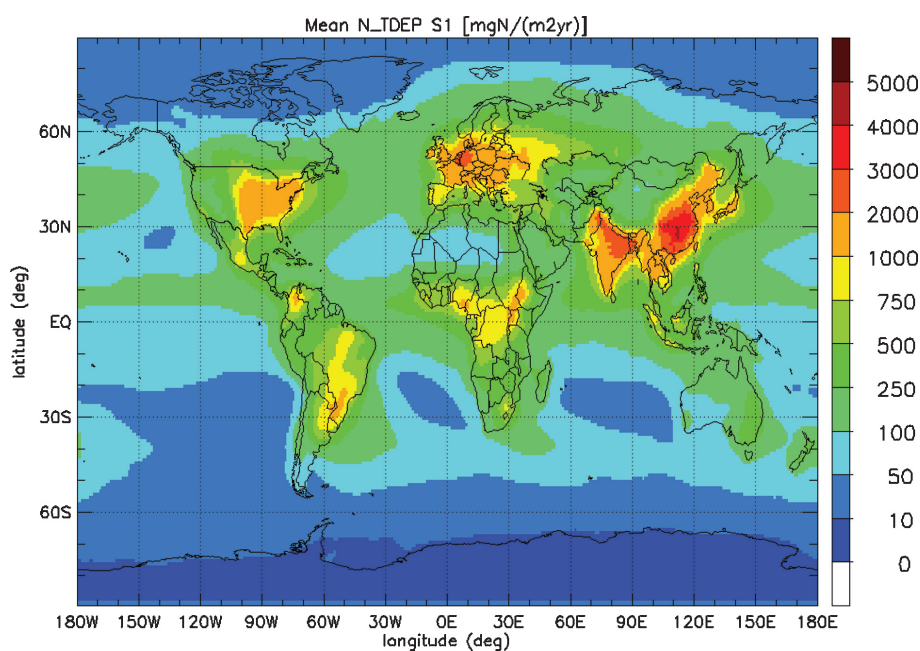
Estimates of atmospheric nitrogen inputs (including organic N) to the global ocean ( $4.8 \times 10^{12}$  mol N yr<sup>-1</sup>, ~80% of which is anthropogenic) now rival riverine ( $3.6\text{--}5.7 \times 10^{12}$  mol N yr<sup>-1</sup>) and natural biological N<sub>2</sub> fixation ( $4.3\text{--}14.3 \times 10^{12}$  mol N yr<sup>-1</sup>) rates (Duce *et al.*, 2008). The distribution of these inputs is of course very different with fluvial inputs dominating in coastal waters and N<sub>2</sub> fixation in tropical waters (Westberry and Siegel, 2006). There is considerable variability in N deposition fluxes to the oceans (Figure 8.2), reflecting global emission patterns and atmospheric transport pathways with most inputs falling into the North Pacific, Northern Indian and Atlantic Oceans.

Duce *et al.* (2008) consider the impact of this increasing atmospheric input of fixed nitrogen on the open ocean. The dispersal of this flux over the vast areas of the ocean means that deposition at any one point is small and hence unlikely to trigger significant ecological impacts such as algal blooms or suppression of nitrogen fixation. However, large areas of the open oceans are believed to be nitrogen limited (Duce *et al.*, 2008) and hence the deposition of nitrogen will allow somewhat higher total and 'new' primary production (in the terminology of Dugdale and Goering (1967)). The latter should on a long enough timescale be equivalent to the export of nitrogen to the deep sea within sinking organic matter – the 'oceanic organic pump' – which can draw atmospheric CO<sub>2</sub> into the oceans. Duce *et al.* (2008) estimate this enhanced drawdown due to 'fertilization' with atmospheric fixed N to be about 0.3 Pg C yr<sup>-1</sup>, which can be compared to a total oceanic uptake rate of CO<sub>2</sub> equivalent to  $2.2 \pm 0.5$  Pg C yr<sup>-1</sup>, emphasising the potential importance of this process. An alternative analysis by Krishnamurthy *et al.* (2007) estimated a lower ( $0.16$  Pg C yr<sup>-1</sup>),

but still significant, fertilization effect. Such an increase in productivity and carbon export to deep waters acts within a series of important feedbacks within the ocean atmosphere climate system. For instance, Duce *et al.* (2008) note the potential for changes in oceanic N<sub>2</sub>O emissions, which could offset the CO<sub>2</sub> storage benefits (in terms of greenhouse gas forcing) since N<sub>2</sub>O is a much stronger greenhouse gas than CO<sub>2</sub>.

There are of course a wide variety of complex feedbacks between the ocean and atmosphere components of the Earth System and global change pressures such as nitrogen fluxes to the oceans do not exist in isolation. Changes in nitrogen inputs in coming decades will likely be accompanied by changes in temperature and ocean stratification which may act to enhance nutrient limitation.

Atmospheric inputs of nitrogen also do not operate in isolation. A variety of nutrients and contaminants are transported together through the atmosphere and the full range of synergistic and antagonistic interactions between these is unknown. However, in terms of nutrients, we do know the transport and deposition of iron to the oceans reasonably well, although there are still many unknowns (Jickells *et al.*, 2005; Mahowald *et al.*, 2005). Areas of high nitrogen deposition in the tropical North Atlantic, North Indian and Northwest Pacific Oceans are also regions of high dust and iron deposition. High dust/iron inputs can sustain nitrogen fixation in tropical waters (Mills *et al.*, 2004) and in some high latitude HNLC (high nutrient low chlorophyll) waters, allow more efficient phytoplankton growth and water column nitrogen and phosphorus uptake (Boyd *et al.*, 2007). It is also clear that the atmospheric supply of phosphorus in comparison to both nitrogen and iron is small when compared to the biological requirements and hence atmospheric supply of nutrients will tend to push the system toward P limitation (Baker *et al.*, 2003, 2007; Mahowald *et al.*, 2008).



**Figure 8.2** Nitrogen deposition flux ( $\text{mg N m}^{-2} \text{ yr}^{-1}$ ) to the Earth's surface in 2000 for the S1 baseline scenario (after Dentener *et al.*, 2006).

**Table 8.3** Atmospheric vs. riverine N deposition for some European Coastal Seas ( $10^3$  tonnes  $\text{yr}^{-1}$ )

	Atmospheric	Riverine	Reference
Mediterranean	1084	1000	Guerzoni <i>et al.</i> (1999)
Baltic	185	830	Voss <i>et al.</i> (2005)
North Sea	412	1073	Rendell <i>et al.</i> (1993)

### 8.4.3 Effects of atmospheric N deposition on coastal waters

The atmosphere makes a significant contribution to the total nitrogen input to many European coastal waters, as illustrated in Table 8.3. The exact fluxes will vary with time due to varying management regimes and the fluxes listed in Table 8.3 are for different years. They are also sensitive to slightly different assumptions about deposition processes and the role of different forms of nitrogen in both rivers and the atmosphere, but the table clearly illustrates that the atmospheric input is significant.

Atmospheric inputs to coastal waters close to anthropogenic N sources may be substantially higher than to open ocean waters, while they may be very similar in coastal waters remote from anthropogenic sources. Meteorological conditions can also act to deliver atmospheric inputs in short intense bursts under certain conditions (Spokes and Jickells, 2005). Coastal areas receiving higher atmospheric inputs often also receive increased nutrient inputs from fluvial and groundwater sources. However, even in areas such as the North Sea (into which major river systems enriched in nutrients discharge), the atmosphere can still contribute a substantial part of the total land derived nutrient input (Spokes and Jickells, 2005). The consequences of these inputs vary greatly since the biogeochemistry of any particular coastal region is profoundly and closely linked to the physical environment, particularly the rates of exchange with open ocean waters (e.g. Jickells, 1998). This process can both remove land-derived nutrients and supply nutrients from deep ocean waters. Paerl and Withall (1999) considered the link between algal blooms and atmospheric deposition. However, Spokes and Jickells (2005) concluded that although atmospheric deposition may contribute significantly to overall terrestrially derived nutrient loadings, comparisons of nutrient supply to overall productivity in coastal waters, fuelled by terrestrial, offshore and internal recycling supplies of nutrients suggest the overall impact on productivity is modest. Hence atmospheric inputs are unlikely to directly trigger blooms. However, atmospheric inputs do contribute to overall nutrient loadings and hence to eutrophication pressure and under certain conditions may act to sustain blooms as they develop.

## 8.5 Linkages to other elemental cycles

### 8.5.1 C-cycling and ocean acidification

The cycling of nitrogen is closely linked to other biogeochemical cycles, in particular to C and P. The tight coupling of these cycles was highlighted by the famous work of Alfred C. Redfield

(1890–1983). The ‘Redfield ratio’ describes the molar stoichiometric relationship between C, N and P in marine organic matter, which is 106:16:1 and is a cornerstone of marine biogeochemistry. However, the general applicability of the Redfield ratio is under debate and there are numerous examples which show its systematic deviation on the organism and species level, with the trophic status of the system, or over time and space (Banse, 1973; Geider and La Roche, 2002). Nevertheless, deviations of the C:N ratio in particulate organic matter from the Redfield ratio generally are within the range of 20%–30% (Sterner *et al.*, 2008), which is very narrow compared to terrestrial systems. A somewhat greater decoupling of C and N is observed for processes involving inorganic compounds (Banse, 1994).

The uptake of more DIC (dissolved inorganic carbon) than that inferred from nitrate supply and Redfield stoichiometry is referred to as ‘carbon overconsumption’ (Toggweiler, 1993). Estimates of carbon overconsumption in the field vary between 17% and 300% (Sambrotto *et al.*, 1993; Michaels *et al.*, 1994; Marchal *et al.*, 1996). Hypotheses that seek to explain carbon overconsumption are the preferential remineralization of organic nitrogen compounds (Thomas and Schneider, 1999), and the enhanced release of dissolved organic carbon (Engel *et al.*, 2002; Schartau *et al.*, 2007).

The close coupling between N and C is of special relevance, because it constrains the biological draw down of  $\text{CO}_2$  in the ocean. In many oceanic domains as well as in coastal systems, the uptake of  $\text{CO}_2$  by primary production is limited through the bioavailability of nitrogenous nutrients. Biological nitrogen fixation is the major process to transform dinitrogen,  $\text{N}_2$ , into combined forms, such as  $\text{NH}_4^+$  and ultimately support the marine food web. Over long time scales the coupling between biological  $\text{CO}_2$  uptake and  $\text{N}_2$ -fixation has therefore been proposed to affect natural climate cycles through indirect feedbacks to atmospheric  $\text{CO}_2$  (McElroy, 1983). However, primary production based on  $\text{N}_2$ -fixation ultimately becomes limited by the availability of phosphorus (Tyrrell, 1999; Sanudo-Wilhelmy *et al.*, 2001) and in some regions by iron (Mills *et al.*, 2004). As a consequence, the role of the ‘biological pump’ in the uptake of anthropogenic  $\text{CO}_2$  is limited as long as nutrient concentrations in the world’s ocean or  $\text{N}_2$  fixation rates do not increase accordingly.

There is still little known about the direct effects of anthropogenic perturbations, in particular the increase of  $\text{CO}_2$  concentrations and the associated acidification of seawater, on the coupling between N and C in marine systems. Recent studies have shown that rising  $\text{CO}_2$  concentration (to levels expected for the next century), stimulates growth and  $\text{N}_2$ -fixation in *Trichodesmium* spp. (Barcelos e Ramos *et al.*, 2007; Hutchins *et al.*, 2007; Levitan *et al.*, 2007), a tropical and subtropical

cyanobacteria, which is responsible for over 50% of biological  $N_2$ -fixation in the ocean (Capone *et al.*, 1997). Hutchins *et al.* (2007) estimated that  $N_2$ -fixation by *Trichodesmium* will increase by 35%–100% until the year 2100, which would substantially raise the total amount of pelagic  $CO_2$ -fixation in the ocean. Determining the response of other diazotroph species (including unicellular cyanobacteria), to ocean acidification and the combined effects of nutrients and rising temperature, is a priority task for building an understanding of the future of the marine N-cycle.

Another mechanism, which could potentially lead to a decoupling of C and N cycles in the future ocean, is the release and subsequent gel particle formation of non-utilized photosynthesis products by the cell. It has been demonstrated that increasing  $CO_2$  concentration can enhance photosynthesis in various phytoplankton species (Riebesell, 2004). In comparison to multicellular autotrophs, the spatial capabilities for storage of assimilates are limited in a phytoplankton cell. Excess carbohydrates are disposed to the surrounding seawater and often accumulate during vernal seasons. A fraction of these exudates comprises acidic polysaccharide, which aggregate into transparent exopolymer particles (TEP) and increase the C:N ratio of particulate matter (Engel, 2002). TEP production has been shown to increase with  $CO_2$  concentration in experimental studies (Engel, 2002; Engel *et al.*, 2004; Mari, 2008). Since TEP enhance particle aggregation and export, they may be of special relevance for the sustained or even enhanced decoupling of carbon from nitrogen in export fluxes in the future ocean (Schneider *et al.*, 2004; Arrigo, 2007).

## 8.5.2 P-cycling and eutrophication effects

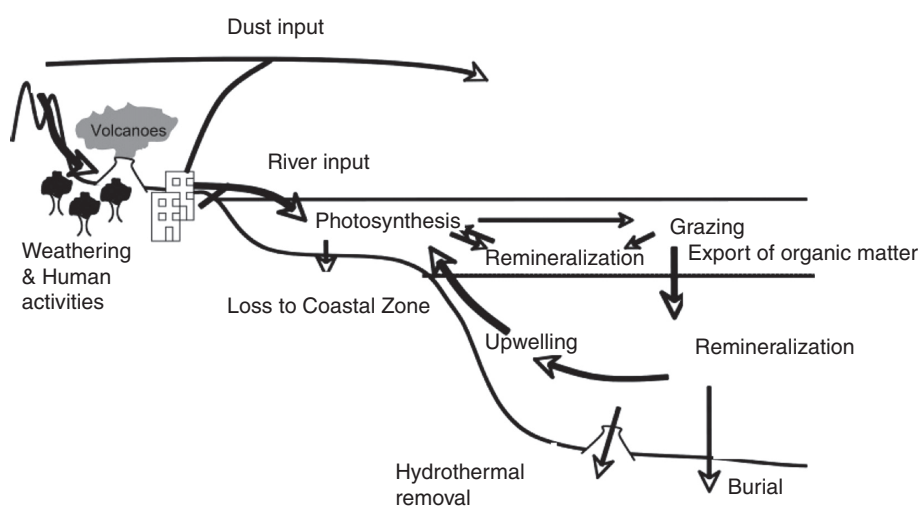
### Phosphorus as a limiting nutrient and its availability in marine systems

Along with N and iron (Fe), P is one of the key nutrient elements that can limit phytoplankton growth in marine environments. Phosphorus is assumed to be the ultimate limiting nutrient on geological time scales, based on the fact that at these time scales (> 1000 years), N requirements of phytoplankton

can always be met through  $N_2$  fixation from the atmosphere (Tyrrell, 1999). On shorter time scales, N availability typically controls phytoplankton growth in most coastal and marine systems (Howarth and Marino, 2006), with P being (co-) limiting in specific regions, such as the coastal zone of China (Harrison *et al.*, 1990), the Mediterranean Sea (Krom *et al.*, 1991b) and open ocean oligotrophic sites in the Atlantic and Pacific Ocean (Benitez-Nelson, 2000; Arrigo, 2005 and references therein).

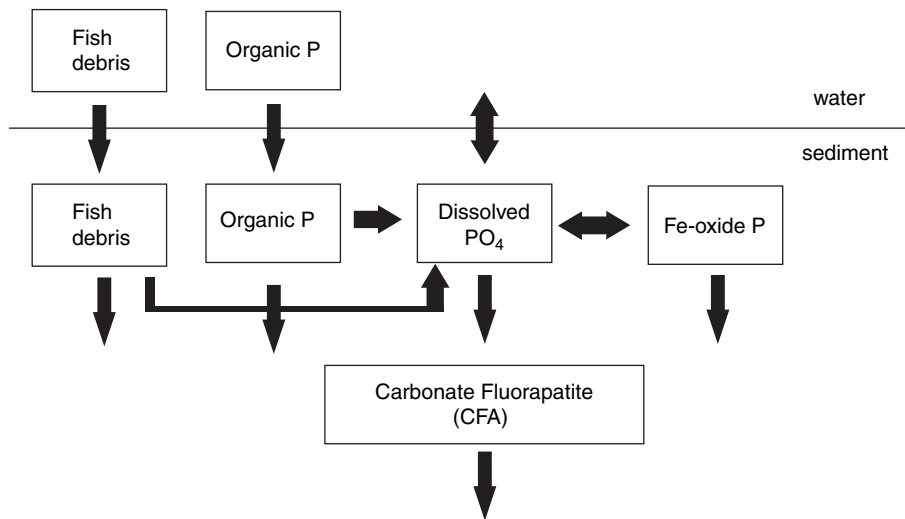
The availability of P in the oceans depends on the balance between the input of reactive P (i.e. biologically available P) from rivers, burial in sediments and the recycling in the marine system (Figure 8.3). In contrast to the N cycle, atmospheric inputs are generally unimportant, with the exception of the highly oligotrophic open ocean environments where dust inputs may alleviate both P and Fe co-limitation of  $N_2$  fixers (Mills *et al.*, 2004). Burial of P in sediments mostly takes place in the form of organic P, authigenically formed calcium-phosphate phases, such as carbonate fluor apatite (CFA), and as P bound to Fe (hydr)oxides. Fish debris (biogenic Ca-P) can be an important sink in low-oxygen settings (Schenau and de Lange, 2000). Although the major proportion of the total burial of P likely takes place in continental margin sediments (50%–90%; Follmi, 1996; Ruttenger, 2003), the overall removal of reactive P to marine sediments is not well-quantified. As a consequence, current estimates of the oceanic residence time of P vary significantly, with estimated values ranging from 8000 to 40 000 years (Benitez-Nelson, 2000; Ruttenger, 2003). This is considerably higher than the oceanic residence time for N (< 3000 years; Gruber, 2004).

Given this relatively long oceanic residence time of P, distributions of dissolved inorganic phosphorus (DIP) in the water column of the open ocean are mainly determined by oceanic circulation patterns, temporal and spatial variability in biological activity and the rate of recycling (Louanchi and Najjar, 2000). In surface waters, the DIP has a rapid turnover time (< days to weeks) suggesting that low DIP levels can support a high primary production (Benitez-Nelson, 2000). Turnover times for Dissolved Organic Phosphorus (DOP) are typically longer (> months). The DOP must first be hydrolyzed to DIP prior to uptake by phytoplankton but the rate of this regeneration from DOP is not well quantified (Ruttenger, 2003; Paytan and McLaughlin, 2007).



**Figure 8.3** The marine phosphorus cycle (modified from Paytan and McLaughlin, 2007).





**Figure 8.4** The sedimentary P cycle (modified from Slomp *et al.*, 1996). Fish debris refers to the bones and scales of fish; these consist of hydroxyl apatite.

In coastal environments, sediments play a critical role in the recycling and net removal of DIP. Fe-oxide bound P is most important as a temporary sink for P (Slomp *et al.*, 1998; Figure 8.4), with seasonal or more long-term variations in organic matter remineralization and sediment redox conditions playing a role in regulating sediment-water exchange fluxes of DIP. In the Baltic Sea, for example, water column DIP concentrations are correlated with the extent of the area of hypoxia, suggesting large scale periodic release of P from Fe-(hydr) oxide pools in the sediment (Conley *et al.*, 2002). Authigenic Ca-P and organic P are the major burial sinks for P, both in near shore (Ruttenberg and Berner, 1993) and offshore (Slomp *et al.*, 1996) marine settings.

#### Increased P inputs to the coastal zone by humans

Increased terrestrial inputs of N and P to the marine environment since 1950 are greatly modifying coastal nutrient cycling and are leading to problems with eutrophication and hypoxia worldwide. Given the enhanced release of P from sediments under low oxygen conditions, these changes are increasing the availability of P for primary producers in many coastal systems. The changes in the P cycle can be directly linked to human activities and are the result of the increased use of P fertilizers in agriculture and the discharge of P-containing wastewater to rivers and coastal waters (Mackenzie *et al.*, 2002).

The results of a recent spatially explicit modelling study (Seitzinger *et al.*, 2005 and references therein) suggest that anthropogenic activities account for 65% of the DIP exported to the coastal zone at the global scale, while the remainder is derived from natural weathering. Point sources (mainly human sewage) are by far the dominant source of anthropogenic DIP. Humans account for only 19% of total DOP export, with diffuse sources being dominant. Although both DIP and DOP export to the coastal zone is significant (at 1.09 and 0.67 Tg yr<sup>-1</sup>, respectively), total riverine P inputs to the coastal zone are dominated by particulate P (PP; 9.03 Tg yr<sup>-1</sup>). However, only a small part of this PP is likely to be bioavailable. In general, PP:DIP ratios are predicted to be lower in systems with more human activity (Seitzinger *et al.*, 2005).

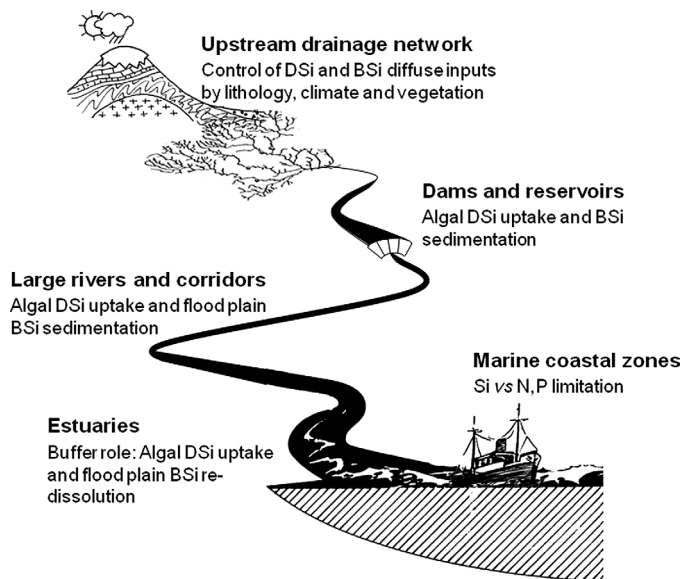
Increased nitrogen loading is driving many large rivers to higher DIN/DIP ratios, affecting the phytoplankton community structure and the occurrence of harmful algal blooms. Increased submarine groundwater discharge of nutrients may further modulate nutrient ratios in coastal waters since DIN/DIP ratios in fresh groundwater are typically far above the Redfield ratio (N:P = 16:1; Slomp and Van Cappellen, 2004). Apart from restricted basins, nutrient dynamics in more off-shore areas are dominated by ocean inputs and are, as yet, not affected by anthropogenic P-inputs (Jickells, 1998).

#### 8.5.3 Si-linkage and eutrophication

In contrast to N and P riverine fluxes (which have been strongly modified in the past 50 years), silica fluxes (which originate essentially from the weathering of rocks) has remained rather constant or even decreased, due to eutrophication and/or trapping in reservoirs (Figure 8.5). Therefore silica has become a limiting factor for river diatoms in the main branch of the large rivers resulting in lower DSi/DIN and DSi/P ratios in estuaries and coastal regions. Whereas increased N, P deliveries to the coastal zone are recognized as a major threat to the ecological functioning of near shore coastal ecosystems, less attention has been paid to their imbalance in regard to silica (see Officer and Ryther, 1980; Conley *et al.*, 1993; Turner and Rabalais, 1994; Justic *et al.*, 1995a; Justic *et al.*, 1995b; Billen and Garnier, 1997; Turner *et al.*, 1998; Conley, 1999; Humborg *et al.*, 2000; Cugier *et al.*, 2005; Billen and Garnier, 2007; Humborg *et al.*, 2008). However, water column P/Si and N/Si ratios determine the phytoplankton community structure, especially the shift from diatoms to non-diatoms and these changes may have major impacts on water quality in the proximal, i.e. near-shore part of the coastal zone (Turner *et al.*, 2003; Cugier *et al.*, 2005; Howarth and Marino, 2006).

#### 8.5.4 Oxygen consumption and hypoxia

Hypoxia in bottom waters, e.g. oxygen concentrations <2 ml l<sup>-1</sup>, is a growing problem worldwide (Diaz, 2001) and occurs when



**Figure 8.5** ‘Anthropocene’ silica transfers from land to sea. Routing of riverine silica, silica cycling, and retention along the aquatic continuum. Strahler ordination of the head water and diffuse Si sources; reservoir Si transformation and retention; large wetland Si retention; large city input of DSi and BSi; estuarine Si transformation and accumulation of BSi in the turbidity maximum; DSi limitation at the coastal zone and BSi recycling at sediment interface and redistribution within the water column (from Garnier *et al.*, 2006).

oxygen supply through physical processes does not meet the demand for the biological processes that consume it. Hypoxia is one of the common effects of eutrophication in coastal marine ecosystems and is not only harmful for organisms (see Section 8.8) (Diaz and Rosenberg, 1995, 2008), but also disrupts biogeochemical processes (Vahtera *et al.*, 2007). Essentially all of the nitrogen transforming processes are regulated by oxygen concentrations, thus making hypoxia a significant process for the evaluation of nitrogen turnover in coastal and marine ecosystems (Figure 8.6). As nitrogen removal (denitrification and anammox) is dependent on  $\text{NO}_2^-$  and  $\text{NO}_3^-$  produced in oxic conditions by nitrification, these processes are of key importance in enabling nitrogen removal from coastal and marine ecosystems.

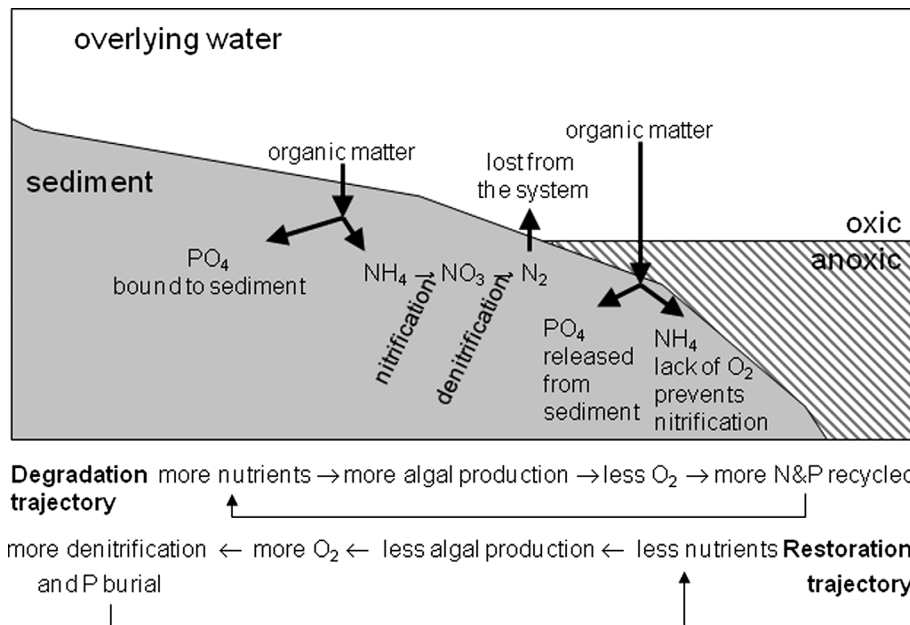
Two important factors allow for hypoxia to occur in marine environments. First, the bottom water must not be able to be mixed with the surface water so that the bottom layer is isolated from the surface layer. This happens when there is a large difference in salt content between the surface and the bottom water or a difference in temperature during the warm summer months. This causes the bottom water to be cut off from the normal resupply of oxygen from the surface. Second, there is organic matter that can be decomposed by bacteria utilizing the oxygen in the bottom waters. The source of the organic matter that decomposes and uses the oxygen in bottom water is mostly from the growth of phytoplankton. The growth is stimulated by nutrients, both N and P, delivered to the marine environment by rivers and from run-off from land. The increase in nutrient concentration in coastal waters has caused the amount of algae to increase and thus the amount of hypoxia to increase.

Significant alterations in nitrogen turnover processes occur with hypoxia and have been extensively studied in shallow coastal marine ecosystems. One of the most significant responses observed are large releases of  $\text{NH}_4^+$  from sediments during hypoxia (Koop *et al.*, 1990) due to decreases in the sediment demand for  $\text{NH}_4^+$ , i.e. for nitrification and assimilation. The loss of nitrification is due to a number of different processes including the lack of oxygen, which is required for nitrification to occur, the lack of available  $\text{NO}_3^-$  substrate (Kemp *et al.*, 1992), and or the inhibition of nitrification by sulphide poisoning of the process (Joye and Hollibaugh, 1995). After re-oxygenation of bottom water, nitrification can be rapidly re-established if the period of hypoxia has been short (Hietanen and Lukkari, 2007), however, it may not occur immediately with time needed for a nitrifying population to be re-established if sulphide poisoning occurs (Dalsgaard, 2003).

Another important sink for remineralized  $\text{NH}_4^+$  is the assimilation by the benthic microalgae community during primary production in shallow sediments where light can reach the bottom. Benthic primary production creates a demand for  $\text{NH}_4^+$  at the sediment surface and benthic microalgae may act as a barrier for the release of  $\text{NH}_4^+$  from the sediment to the water column (Sundbäck and McGlathery, 2005). The benthic primary producers die with extended hypoxia, thus removing this important sink. Furthermore, the pelagic primary production can increase during hypoxia. Significant increases in both pore water and bottom water  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  concentrations are found during hypoxia (Souchu *et al.*, 1998). These nutrients can be mixed into surface waters creating algal blooms (Conley *et al.*, 2007), and through sedimentation adding new organic matter to bottom waters that can keep the system hypoxic.

The lack of oxygen during hypoxia can have significant effects on nitrogen removal and eutrophication in coastal and marine ecosystems (Smith and Hollibaugh, 1989). Denitrification and anammox are key processes removing  $\text{NO}_2^-$  and  $\text{NO}_3^-$ , yet the starting products, e.g. both nitrite and nitrate, are produced in oxic conditions. Nutrient enrichment from N and P input from watersheds increase the productivity of aquatic systems and potentially increase the occurrence of hypoxia, thus limiting the ability of the system to remove nitrogen and increasing the effects of eutrophication.

In deep coastal and marine ecosystems and the enclosed seas of Europe it is rare that hypoxia occurs throughout the bottom waters and is often confined to the deepest waters. In these waters, it is possible to have denitrification occurring in the water and not only at the sediment-water interface. Recently, a significant negative correlation was found between the amount of dissolved inorganic nitrogen and the volume of hypoxic water in the Baltic Sea (Vahtera *et al.*, 2007), suggesting enhanced nitrogen removal during large-scale hypoxia. Water column denitrification has been found to occur at the interface between anoxic, stagnant deep water and overlying oxic water in the central Baltic Proper using acetylene blockage (Rönnner and Sørensen, 1985; Brettar and Rheinheimer, 1992). However, a recent study using state-of-the-art stable isotope techniques failed to detect any denitrification potential in Baltic sub-oxic, sulphide-free water (Hannig *et al.*, 2007),



**Figure 8.6** Schematic showing the interaction of N- and P-cycling depending on oxygen concentrations (modified from Boesch *et al.*, 2001).

however, bacteria capable of anammox were observed in the water column (Hannig *et al.*, 2007). In addition, potential for N<sub>2</sub> production was found in the sulphide-containing, deeper layer, making it very likely a chemolithotrophic rather than heterotrophic process (Hannig *et al.*, 2007). Chemolithotrophic N<sub>2</sub> production occurs in the water column redox transition zone of the Cariaco Trench (Taylor *et al.*, 2001). The rates of water column denitrification can be substantial in sub-oxic deep waters (Deutsch *et al.*, 2007). Thus, in deep coastal and marine ecosystems the overall rates of denitrification and the loss of N may in fact be the same order of magnitude or even greater with hypoxia, although more research is needed to clarify and estimate the rates.

## 8.6 Physical and biogeochemical processes in estuarine systems

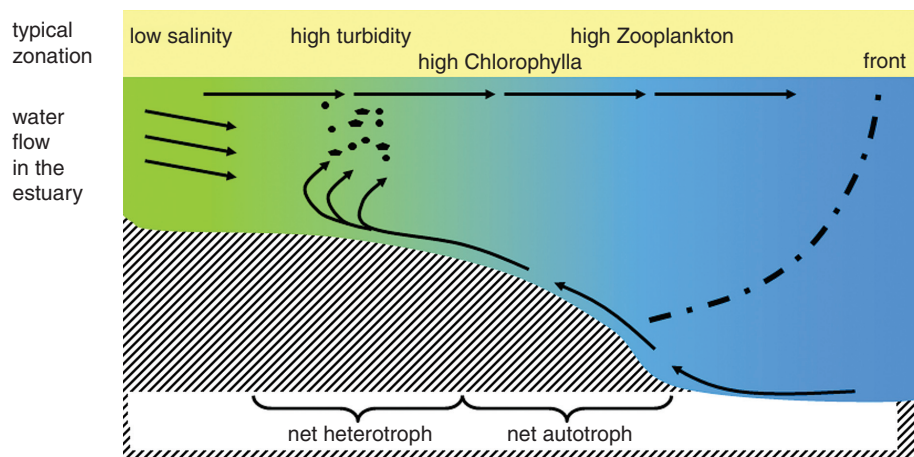
Estuaries are presented here briefly but most aspects on riverine loads and links to coastal eutrophication can be found in Billen *et al.* 2011 (Chapter 13 this volume). They mediate and transform land to ocean fluxes of nitrogen. An estuary is defined as part of the river confluence that experiences reversing landward flow due to tides. Estuaries come in all sizes and shapes ranging from large drowned river valleys, deep glacial excavated silled-fjords, tectonic depressions and much smaller and shallower longshore bar-built coastal lagoons. Whatever their size the estuaries are characterized by large salinity gradients resulting from the mixing of riverine freshwater from land with tidal inflow from the seawater. Apart from the plethora of sizes and shapes, the challenge in studying nitrogen transformation processes in estuaries stems from the large temporal and spatial variability inherent to these systems requiring a unique understanding of each estuarine system.

Estuarine circulation patterns are highly variable and are influenced by their size and shape, tidal mixing and fresh water flux. The basic premise, however, is a downslope seaward flow

of lower-density fresher water at the surface and an inflow of saline water at depth (Figure 8.7). Entrainment of salt water into the outflowing upper layer is replaced by the underlying inflow from the sea. The distinct landward bottom flow of salt water that develops in some estuaries is called a salt wedge.

Although only some estuaries develop a salt wedge all are characterized by a two-layer circulation which plays a pivotal role in N transformation in estuaries by trapping particles and nutrients. With the exception of very fine-grained material, sedimentary particles that are carried downstream to the estuary settle as the flow velocity decreases when the confined river flow discharges into the relatively open coastal zone. The landward-moving net bottom flow acts to carry particles up-estuary, so that particles settling from the surface outflow can literally be carried back up the estuary at depths. In addition, when the particles are introduced to saltier water, a high ionic strength medium, they tend to aggregate to form larger and thus faster-settling particles. This process, termed flocculation, promotes sedimentation of riverine particulate organic matter in estuaries. Further, the salinity gradient has been shown to contribute to phosphorus desorption (Némery and Garnier, 2007) whereas silica dissolution could be ten times higher in the saline waters compared to the freshwater ones (Roubeix and Lancelot, 2008; Garnier *et al.*, 2006). All these estuarine processes may affect the nutrient fluxes delivered to the marine waters. Finally, wetland systems bordering estuaries (tidal flats, reed beds, salt marshes, etc.) retards flow and retains particles particularly when the estuaries overflow into adjoining wetlands due to high tides and flood conditions. The net result is that estuaries effectively trap particulate organic matter delivered from rivers and produced within the estuary preventing it from reaching the open sea.

One noteworthy feature of estuarine sedimentation is the turbidity maximum. This feature is maintained by the residual circulation, and is intrinsic to the idea that estuaries trap particles. The turbidity maximum consists of sediments settling



**Figure 8.7** Idealized schematic of the zonation of an estuarine system showing major processes and currents along the gradient from fresh water (green) to full marine waters (blue).

from the river input plus resuspended bottom sediments brought up estuary by the saline bottom flow mixed with estuarine algal material and other anthropogenic discharges. The high concentrations of particles promote flocculation within the turbidity maximum. Some of the particles (characteristically those that are relatively fine-grained) are mixed upward into the outward-flowing surface layer, only to settle back later into the bottom inflow. Thus, a turbidity maximum should be viewed as a dynamic feature. In extreme cases, the turbidity maximum may stretch many kilometres and maybe so concentrated that it becomes a fluid mud lens. An example of this is seen in the Gironde Estuary in Southern France.

Estuaries along European coasts are mostly net heterotrophic systems, where bacterial-mediated degradation of organic matter (heterotrophy) exceeds primary production by estuarine phytoplankton (autotrophy). The surplus organic matter for heterotrophy is brought mostly from the land but also from the sea in salt wedge and partially-mixed estuaries. The turbidity maximum can host intense bacterial activity in the upper estuary due to high concentrations of particulate organic matter where fresh planktonic remains are mixed with old organic matter derived from land and resuspended from sediments. Thus the turbidity maximum can be viewed analogous to a bio-reactor, turning estuaries into hotspots for nitrogen processing through regeneration, nitrification and denitrification. In general, the high turbidity in the upper estuary inhibits phytoplankton growth by limiting light penetration. The net result is that many estuaries are net autotrophic only in the outer part towards the open ocean aided by nutrients carried from upper estuary (Figure 8.7).

Anthropogenically and terrestrially-derived N enters estuaries through riverine transport or via atmospheric deposition, including both direct deposition to the surface of estuaries and indirect watershed runoff (Castro and Driscoll, 2002). In addition estuaries are historical population centres and today's urban settlements release N-compounds also through direct discharge. Excess N input can lead to eutrophication, whereby overall increases in primary production are accompanied by major shifts in the dominant flora (Duarte, 1995) and fauna (Heip, 1995) if light penetration of the water column is adequate. The fact that estuaries trap particulate and dissolved

nitrogen makes them prone to severe oxygen depletion and in some extreme cases they can become anoxic. Such changes also alter N transformation processes and the capacity of estuaries to retain N (see Section 8.5.4) (Horrigan *et al.*, 1990). The extent to which DIN is processed in estuaries appears to be influenced by the size and fresh water residence time in European estuaries. For instance in large continental estuaries nitrate and ammonia showed removal during estuarine mixing (Middelburg and Nieuwenhuize, 2001). In contrast, in the smaller UK estuaries of the Tyne and Tweed rivers very little removal of nitrate and ammonia occurred which is attributed to their low fresh water residence time (Ahad *et al.*, 2006). Therefore alteration of estuarine circulation due to human activities can profoundly influence the estuarine capacity to process N. Intertidal and subtidal mud flats are areas of enhanced capacity to retain N through sedimentation resulting from retarding water flow and denitrification. For instance in the Humber estuary (UK), organic N burial is estimated to be 216 tonnes annually of the 57 400 tonnes of the annual total N load. The intertidal area of the Humber also enhances N processing by denitrification of about 997 tonnes of N. Increasing these intertidal areas by management for coastal defences could significantly increase this N retention within the estuary (Andrews *et al.*, 2006; Jickells, 2006).

The extent of processing of  $N_r$  within estuaries therefore depends on a variety of factors such as oxygen status (particularly for processes involving redox change such as cycling of ammonia/ammonium and production of  $N_2O$  and  $N_2$ ) and light climate for both benthic and water column photosynthesis. The other key issue is residence time which depends on estuarine volume and exchange rates controlled by river inflow and tidal exchanges with coastal waters. The residence times of waters in estuarine systems can vary from hours to months depending on the hydrographic setting.

While the input of organic N and nitrate has declined in many urban estuaries due to sewage treatment, ammonia inputs through untreated sewage still occur. Elevated  $NH_4^+$  inputs may lead to enhanced generation of  $N_2O$  via nitrification in estuarine and coastal zones (Hashimoto *et al.*, 1999; de Wilde and de Bie, 2000). A comparative study of an urban and a rural estuary in UK showed evidence for intense nitrification in the urban estuary in the adjoining coastal zone (Ahad *et al.*,

2006). Therefore, increases in the atmospheric concentration of  $N_2O$  related to human activity could have wide-reaching implications for global climate change (Galloway *et al.*, 1995) by further enhancing already significant coastal emissions (Bange *et al.*, 1996; see Section 8.4). Currently global N inputs into the coastal zone are based on riverine fluxes and do not account for estuarine modification of these fluxes. Reliable global/European estimates of N processing in estuaries are currently lacking due to the large variability between individual estuaries in processing N.

## 8.7 N-budgets in coastal systems – linking inputs to transformations and losses

The coastal ocean is a highly dynamic and spatially heterogeneous compartment at the land–ocean interface. It includes estuaries, salt marshes, seagrasses, mangroves, coral reefs and open continental shelf systems. Coastal systems receive relatively large amounts of nutrients and particles from land via rivers and groundwater and exchanges matter with the open ocean and the atmosphere. Coastal ecosystems are relatively shallow implying that sediment processes (including benthic primary production, nitrification, denitrification and anammox) play a major role. Moreover, most of the global (marine) carbon and nitrogen burial occurs in coastal sediments (Duarte *et al.*, 2005).

### 8.7.1 Input terms

The delivery of land-derived nitrogen to the coastal ocean has been studied extensively and total riverine nitrogen input is about  $66 \text{ Tg N yr}^{-1}$ . However, there is substantial spatial variability around the world in the magnitude and form of the N delivery (Seitzinger *et al.*, 2005). Moreover, present-day riverine N delivery to the ocean has already doubled relative to pre-industrial delivery and it will probably further increase due to increased anthropogenic activity. Globally, about 40% of the total nitrogen is delivered as DIN, another 40% as PN and the remaining 20% as DON. We assume here that 50% of this N is natural and 50% anthropogenic, consistent with a doubling of total N delivery relative to pre-industrial inputs.

Submarine groundwater discharge is increasingly recognized as a potential source of nutrients to coastal systems. The magnitude of groundwater nitrogen input is highly uncertain because of our limited knowledge of submarine groundwater input, the difficulty in separating net from gross water fluxes and few data on the nitrogen distribution and processing in aquifers. Present-day estimates of submarine groundwater discharge are on the order of 5%–10% of surface water inputs and if one assumes similar dissolved nitrogen concentrations as surface waters this relates to less than  $4 \text{ Tg N yr}^{-1}$ . This input may be particularly important in certain regions, for instance limestone areas with few rivers, or certain regions of glacial sands.

At the global scale, atmospheric N deposition to continental shelves is on the order of  $8.4 \text{ Tg N yr}^{-1}$  as of the mid 1990s compared to pre-industrial deposition of  $1.4 \text{ Tg N yr}^{-1}$

(Galloway *et al.*, 2004). Therefore, we assume  $7 \text{ Tg N yr}^{-1}$  are anthropogenic. Atmospheric N deposition rates are highly variable spatially, temporally, and in terms of composition. Deposition rates vary with distance from source and one would expect higher deposition rates in coastal systems than in the open ocean systems, but the relative importance of atmospheric versus other external N sources is likely lower in coastal systems.

Biological  $N_2$  fixation represents a net addition of new nitrogen to oceanic systems and has been recognized as one of the key processes governing the marine nitrogen budget. During the last decade we have significantly advanced our knowledge on the identity and distribution of organisms involved in open ocean nitrogen fixation and we have seen a steady increase in published estimates of oceanic nitrogen fixation. However, few studies and consequently little progress have been made on nitrogen fixation in the coastal ocean. Capone (1988) summarized nitrogen fixation rates in the coastal zone and reported a total of about  $15 \text{ Tg N yr}^{-1}$ , mainly due to the benthic compartment in shallow systems ( $12 \text{ Tg N yr}^{-1}$ ). Nitrogen fixation estimates for the continental shelf and upwelling systems are scarce. Galloway *et al.* (2004) reported a global shelf biological nitrogen fixation rate of  $1.5 \text{ Tg N yr}^{-1}$ . Given the other terms in mass balance, in particular denitrification and exchange between shelf and open ocean waters, we will not further discuss biological nitrogen fixation although we do admit that this estimate may be highly conservative and may need upward revision.

### 8.7.2 Output terms

Nitrogen loss terms include burial in coastal sediments, fish landings, and gaseous emission in the form of dinitrogen gas, nitrous oxide and other nitrogen containing gases. Nitrogen burial represents a small loss term and can be estimated from intensively studied carbon burial estimates for the coastal ocean assuming a C:N ratio of 10 for buried organic matter. We estimate coastal ocean (except bays and lagoons) burial to be about  $4 \text{ Tg N yr}^{-1}$ . Global nitrous oxide emission from coastal systems is about  $0.5\text{--}2.9 \text{ Tg N yr}^{-1}$ . Fish landings have been estimated at  $3.7 \text{ Tg N yr}^{-1}$  (Maranger *et al.*, 2008) and we attribute all of this to coastal systems.

The conversion of fixed nitrogen into gaseous dinitrogen represents the major loss terms of nitrogen from the Earth system, the ocean and as well from the coastal systems. Most nitrogen gas production can be attributed to denitrification, the microbial conversion of nitrate via nitrite and nitrous oxide to dinitrogen, but some nitrogen gas is produced by the recently discovered process Anammox, the bacterially mediated process of anaerobic oxidation of ammonia with nitrite. For reconstruction of the coastal ocean nitrogen mass balance, it is not of first priority to partition nitrogen gas production to denitrification or Anammox or between the distal and proximal coastal ocean.

Denitrification in estuaries amounts to about  $8 \text{ Tg N yr}^{-1}$  (Seitzinger *et al.*, 2006). Nitrogen gas production in continental shelf systems is primarily limited to sediments and governed

**Table 8.4** Summary of global sources and sinks for the coastal seas in Tg N yr<sup>-1</sup>. Details in the text

Source	Tg N yr <sup>-1</sup>	Loss	Tg N yr <sup>-1</sup>
River input (Seitzinger <i>et al.</i> , 2005)	66	Burial (Middelburg <i>et al.</i> , 1996)	4
Ground water	4	N <sub>2</sub> O emissions (Bange, 2006)	0.5–2.5
Atmospheric deposition (Galloway <i>et al.</i> , 2004)	8.4	Fish landing (Maranger <i>et al.</i> , 2008)	3.7
N-fixation (Capone, 1988)	15	Denitrification estuaries (Seitzinger <i>et al.</i> , 2006)	8
		Denitrification shelf (Middelburg <i>et al.</i> , 1996; Seitzinger <i>et al.</i> , 2006)	107–250
<b>Sum</b>	<b>93.4</b>	<b>Sum</b>	<b>123.2–268.6</b>

primarily by organic nitrogen and carbon delivery to the sediments and only secondarily by nitrate concentration in the bottom water because most of the nitrate and or nitrite converted to dinitrogen are formed in the sediments (coupled nitrification-denitrification). Recent estimates of denitrification in continental shelf sediments vary from about 107 Tg N yr<sup>-1</sup> (Middelburg *et al.*, 1996, for continental shelf) to about 250 Tg N yr<sup>-1</sup> (Seitzinger *et al.*, 2006). Although these authors have used different approaches, i.e. a more mechanistic model by Middelburg *et al.* and a more empirical model by Seitzinger *et al.*, both these estimates depend on the delivery of particulate organic carbon and nitrogen to shelf sediments. This flux of particulate organic matter to shelf sediments depends in turn on two main factors: (1) the primary production of shelf ecosystems and (2) the water depth, because more organic matter is degraded in the water column with increasing depth so that less is available for degradation in the sediments (Middelburg and Soetaert, 2004).

### 8.7.3 Balance

If we balance nitrogen inputs to the coastal systems with nitrogen losses (Table 8.4) due to burial and nitrous oxide emission (together 28.5 Tg N yr<sup>-1</sup>) and fish landings (3.7 Tg N yr<sup>-1</sup>), we can derive a minimum denitrification in the coastal zone of 61 Tg N yr<sup>-1</sup>, including 8 Tg N yr<sup>-1</sup> denitrification in estuaries. This mass balance based number of 61 Tg N yr<sup>-1</sup> is smaller than the sum of independent estimates for estuaries (8 Tg N yr<sup>-1</sup>) and global shelf sediment denitrification (107 and 250 Tg N yr<sup>-1</sup>). This implies that coastal systems import between 123 and 270 Tg N yr<sup>-1</sup> from the open ocean, making coastal-open exchange a major input term. Although this nitrogen balance is not very accurate and will certainly be revisited in the coming years, it is clear that nitrogen losses due to sediment denitrification are primarily compensated by net import of nitrogen from the open ocean, consistent with previous nitrogen budget studies. We assume that all N input from the open ocean is natural.

Walsh (1991) in his seminal paper on the importance of continental margins in marine biogeochemical cycling of carbon and nitrogen reported a transfer from the open ocean onto shelves of 560 Tg nitrate-N yr<sup>-1</sup>. This indicates that the net transfer of nitrogen onto continental shelves from the open ocean represents 9%–35% of total nitrogen flow. These calculations of the coastal zone as a net sink for oceanic N rather than

a source are all based on model estimates, in part because estimating exchange rates between coastal waters and offshore are very difficult. Exchange rates between the continental shelves and open ocean are very variable temporally and spatially and difficult to quantify given the multiple processes involved. In a very thorough review Huthnance (1995) estimated that about 1 Sv (10<sup>6</sup> m<sup>3</sup> s<sup>-1</sup>) is exchanged for each 1000 km of shelf edge. For a total shelf break length of 314 400 km, we then obtain a water exchange rate of 9915 × 10<sup>12</sup> m<sup>3</sup> yr<sup>-1</sup>. This then implies very small difference between inflowing and outflowing water (about 1 mmol N m<sup>-3</sup>) to balance the nitrogen budget. Such a very small difference in nitrogen concentration is difficult if not impossible to accurately constrain given the dynamic nature of cross-shelf edge exchange processes and natural spatial heterogeneity of nitrogen stock and cycling processes. In addition, at least during parts of the year, there are likely to be steep gradients in N concentrations with depth over the upper few hundred metres of the water column, and hence the depth from which offshore water is brought into coastal areas as well as the amount of such exchange is important.

### 8.8 Effects on coastal and marine biodiversity resulting from eutrophication

Coastal and marine waters around Europe have to face a variety of anthropogenic impacts. Among those, nutrient enrichment has been seen as one major source for changes in pelagic and benthic communities and thus biodiversity. Similar changes and impacts have also been observed in other non-marine aquatic (Grizetti *et al.*, 2011, Chapter 17, this volume) or terrestrial (Dise *et al.*, 2011, Chapter 20, this volume) ecosystems. The biological responses to this nutrient enrichment are often grouped together under the term eutrophication. Generally, in coastal and marine waters, eutrophication can have both positive and negative effects on species' occurrence and abundance. Biotic responses to organic enrichment and threshold levels show great variations in coastal and marine ecosystems, partly because eutrophication varies from region to region. How and to what extent the structure and functioning of marine ecosystems is affected by eutrophication also depends on other factors such as prevailing hydrographical conditions, climatic forcing, the amount and duration of exposure to increased nitrogen loads or other anthropogenic impacts, e.g. contaminants and habitat destruction. This may lead to synergistic effects which

makes it more difficult to distinguish cause and effects and relate changes to a single environmental stressor. Nevertheless, there are some common features concerning the succession of reactions to increased organic matter and subsequent changes in diversity and ecosystem functioning.

### 8.8.1 Increase in biomass and change in species composition

Increasing nutrient loads stimulate primary production as long as enough light is available, resulting in higher biomass and increased sedimentation of pelagic production. With an excess to N and P compared to Si phytoplankton biomass may increase, but spring diatoms may be replaced by unpalatable algae (e.g. *Phaeocystis* in the North Sea (Lancelot *et al.*, 1987)) or toxic algae (e.g. *Dinophysis* in the Seine Bight (Cugier *et al.*, 2005)). Such shifts at the first trophic level can deeply modify the complex interactions within the food web (Pace *et al.*, 1999).

Active suspension feeders (e.g. bivalves) can regulate pelagic primary production when the water is shallow, the residence time is long, and the suspension feeder biomass is high (Cloern, 1996). Filter-feeding and deposit-feeding macrobenthic species benefit from high production, but the relative dominance of major trophic groups changes as was shown for polychaetes. With increasing organic input, non-selective deposit feeders were favoured over suspension feeders and selected deposit feeders (Grall and Chauvaud, 2002).

Furthermore, zoobenthos plays a major role in benthic nutrient regeneration, affecting primary production by supplying nutrients directly to the water and enhancing recycling rates. Experimental studies have shown that the impact of benthic fauna on benthic–pelagic coupling and nutrient release is considerable (Grall and Chauvaud, 2002). In the presence of macrofauna, degradation was faster and more efficient. Moreover, it became obvious that species' function also play a role for particle degradation, transport and recycling. For instance,  $\text{NH}_4^+$  and  $\text{NO}_3^-$  release were three times higher in sediments where the polychaete *Nereis diversicolor* – a suspension feeder – was present, and were only 1.5 times higher in sediments where *Nereis virens* – a deposit feeder – was present. Moreover, the presence of both *Nereis* species increased both  $\text{NO}_3^-$  and silicate fluxes by two orders of magnitude (Grall and Chauvaud, 2002). Forster and Zettler (2004) demonstrate that the presence/absence of the bivalve *Mya arenaria* in the southern Baltic Sea impacts pore water-exchange and thus benthic–pelagic matter transport and fluxes.

### 8.8.2 Hypoxia

Under 'normal' conditions the amount of primary production is in equilibrium with grazing and remineralization processes (Graneli *et al.*, 1990). However, in case sedimentation rate exceeds the grazing capacity or food requirements of benthic organisms it will generate layers of biodeposits (Grall and Chauvaud, 2002), which leads to increased oxygen consumption in the near-bottom water and surface sediments causing hypoxia with severe consequences for certain biogeochemical

processes as discussed in Section 8.5.4. Moreover, it could have a strong impact on the local fauna and its diversity. The occurrence of hydrogen sulphide causes an additional stress factor for many benthic organisms (Diaz and Rosenberg, 1995; Gray *et al.*, 2002; Diaz and Rosenberg, 2008). Benthic species differ in their tolerance to hypoxia (Gray *et al.*, 2002), nevertheless, mass mortality of benthos and fish over large areas have been reported for many marine coastal areas, and sensitive species have been permanently or periodically removed (Wu, 2002). Prolonged presence of hypoxia affects the important role of benthic organisms for organic matter degradation, nutrient remineralization and particle fluxes. Hypoxia reduces growth and feeding of benthic organisms and eventually their general fitness. Prolonged hypoxia might eliminate sensitive species, and thereby cause major changes in species composition. Hypoxia decreases species diversity and species richness and changes abundances of functional groups (Wu, 2002). During hypoxia there is a general tendency for suspension feeders to be replaced by deposit feeders, demersal fish are replaced by pelagic fish and macrofauna by meiofauna (Wu, 2002).

As mentioned before, tolerance of and sensitivity to low oxygen levels differ among species. However, the critical oxygen level for many benthic species is around  $2.8 \text{ mg O}_2 \text{ l}^{-1}$  while certain species can tolerate  $0.5\text{--}1 \text{ mg O}_2 \text{ l}^{-1}$  for several days or weeks (Wu, 2002; Vaquer, 2008). Polychaetes belong to a taxon most tolerant to stress due to organic loading and hypoxia. Therefore, frequent hypoxia may favour this taxonomic group. Moreover, seasonal hypoxic events often result in an increase in opportunistic species. For many Scandinavian and Baltic marine waters changes in dominant benthic species, their abundance and biomass have been documented in relation to oxygen deficiency caused by eutrophication (Karlson *et al.*, 2002; Berezina and Golubkov, 2008). Severe changes in species' composition and trophic structure have also been observed in the Black Sea with dramatic consequences for the ecosystem. In the Mediterranean, the analysis of long term time series from the lagoon of Venice documents how increased nutrients loads interact with changes in biotic compartments. Among others, a clear change in diversity is obvious as well as in species' composition, turning a system with mixed feeders to one where detritus feeders predominate with a short life time (Pranovi *et al.*, 2008).

### 8.8.3 The role of macrophytes

Dense assemblages of macrophytes covering sediments are also of great importance for nutrient cycling and they are likely to intercept nutrients from both the water column and the sediments. It has been argued that the water quality in macrophytes-dominated shallow-water systems is much better than in phytoplankton-dominated systems with similar nutrient loadings (Grall and Chauvaud, 2002). Presently, it has been observed that benthic eutrophication in estuaries and coastal lagoons can induce a shift from rooted plant communities, dominated by slow-growing species, like the eelgrass *Zostera*, towards free-floating (or partially free-floating), faster-growing macroalgae, such as *Enteromorpha* or *Ulva* (Patricio *et al.*,

2004). A large scale comparison of empirical relationships between distribution and abundance of marine vegetation documents that seagrasses and macroalgae generally respond to changes in eutrophication pressure by growing deeper, being more abundant and more widely distributed in clear waters with low nutrient concentrations as compared to more turbid and nutrient-rich environments (Krause-Jensen *et al.*, 2008).

Eutrophication profoundly changes rocky shore communities. The abundance of perennial macroalgae and their associated communities have severely declined in the western Baltic and the Adriatic Seas where they have been replaced by few bloom-forming annual species (Vogt and Schramm, 1991; Munda, 1993). Similar shifts in rocky shore diversity have also been reported for the coasts of the North Sea (Thompson *et al.*, 2002) or the Baltic Proper (Kautsky, 1991; Berger *et al.*, 2003). These examples indicate that changes in species composition due to eutrophication do occur in different ecological compartments; phytoplankton being the first functional group where changes impact zooplankton and benthic communities but also fish. Based on studies performed in Danish waters a conceptual model has been developed (Figure 8.8) indicating the different interactions between trophic levels in response to increased nutrient loads (Ærtebjerg *et al.*, 2003).

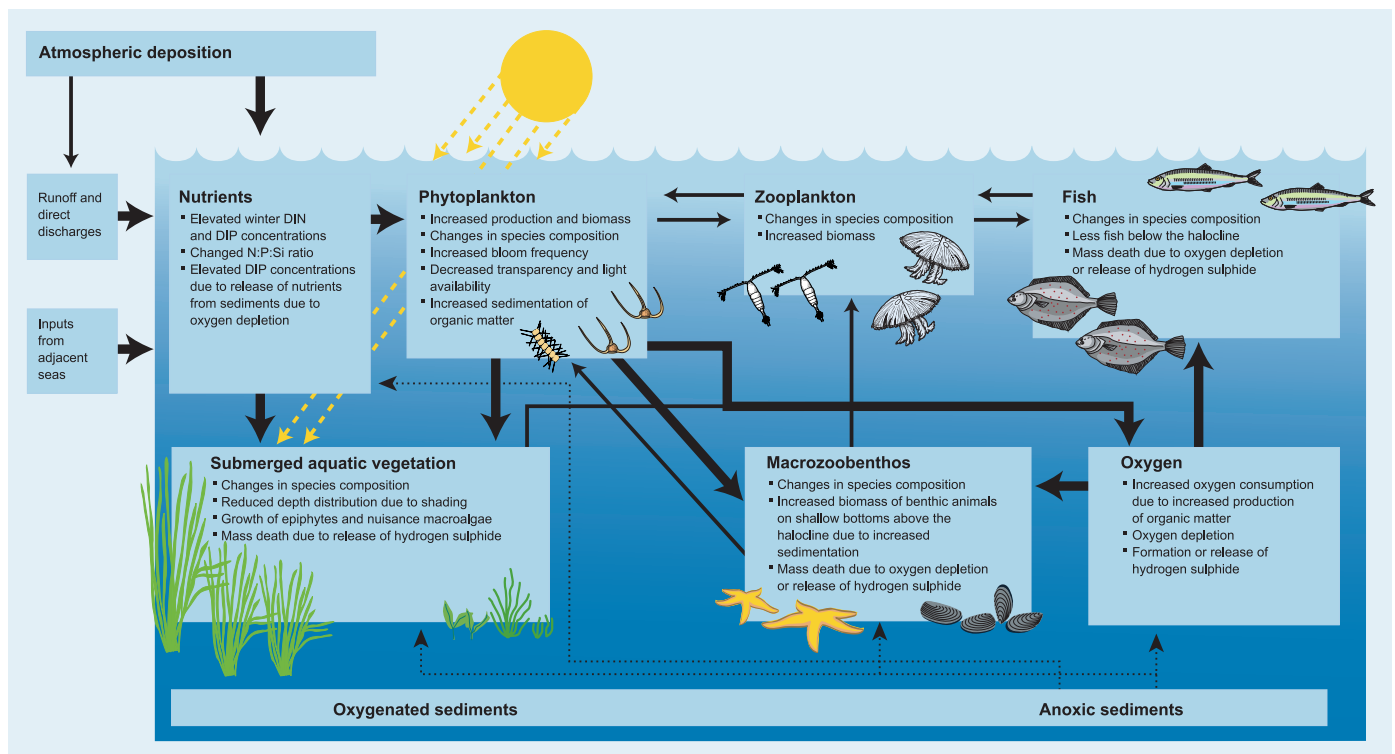
#### 8.8.4 Link to ecosystem functions and functioning

Changes in species' composition as described above are linked to losses of various functional types such as feeding guilds or plant growth forms or other functionally similar taxa. It is widely accepted that ecosystem functioning is dictated to a large degree by biodiversity and the community structure defined by

species richness and evenness and diversity. In turn community diversity characterizes an ecosystem (Gray, 1997). Changes in the diversity and therefore structure of the community may result in loss of specific functions with consequences for the functioning of the ecosystem (i.e. production, consumption, respiration, energy flow and cycling). As benthic communities are changed, biologically mediated geochemical cycles will be altered.

The presence or absence of benthic fauna drastically alters the rates and pathways of organic matter mineralization, as well as overall sediment features. Species richness also affect production of ammonium in surface sediments and benthic oxygen and nutrient fluxes (Emmerson *et al.*, 2001; Raffaelli *et al.*, 2003; Waldbusser and Marinelli, 2006). In the Baltic proper, the deposition of organic matter has increased 1.7 times from the 1920s to the 1980s. During the same period the biomass of benthic fauna has increased although the number of benthic species has decreased (Karlson *et al.*, 2002). Bottom areas with laminated sediments, indicating lack of macrobenthic bioturbation have increased rapidly since 1960. While in the 1940s and 1950s less than 20 000 km<sup>2</sup> of Baltic Sea sediments were laminated sediments – most of them naturally occurring, they covered about 70 000 km<sup>2</sup> in 1990 (Jonsson *et al.*, 1990). Most of these areas correspond to the occurrence of severe hypoxia in bottom water. Hypoxia may also affect the functional diversity of microbial communities (Olenin, 1997; Mermillod-Blondin *et al.*, 2004).

In contrast to fully marine ecosystems, the inner parts of Baltic Sea bays and fjords are often populated by one single species representing a functional guild (Olenin, 1997; Bonsdorff



**Figure 8.8** Conceptual model illustrating the effects and consequences of nutrient enrichment and eutrophication in the marine environment (Ærtebjerg *et al.*, 2003).



and Pearson, 1999). This makes the systems even more sensitive to changes on bottom oxygen concentrations. Disappearance of such a key species would result in the loss of the functional group which, in turn, may change the biogeochemical cycling of the system essentially. A rough estimate has been made of the extent of bioturbation by a key-species, the polychaete *Scoloplos armiger*, and its role in biogeochemical cycling in one part of the Baltic Sea. Based on the particle reworking rate of *Scoloplos* spp. and the area occupied by this species it was calculated that it reworks  $1.9 \times 10^9$  tons of sediments annually (Dippner *et al.*, 2008).

High diversity seems to be important for maintaining ecosystem processes under changing conditions providing a 'buffer' against environmental fluctuations (Loreau *et al.*, 2001). Ecosystems with a higher degree of biodiversity and thus functional redundancy are assumed to be able to cope better with increased nutrient loads. On the other hand species which have successfully established in an ecosystem with strong natural gradients (e.g. Baltic Sea) might have higher tolerance levels to additional stress.

Eutrophication processes do not occur in isolation but rather in parallel with other global change pressures including changing coastal management (Andrews *et al.*, 2006) and climate change, a process that has been shown for example to have caused major changes in plankton throughout the North Sea and Europe (Beaugrand *et al.*, 2002). When assessing the impact of eutrophication on organisms and species, climate change related changes and impacts on ecosystems have to be taken into account. Presently, we have only started to understand how an increase in temperature might affect primary production and its timing, and its likely consequences for other trophic levels and nutrient cycling. The adaptation capacity of organisms to higher temperature has to be considered and that the distribution range of certain species is likely to change due to climate change.

## 8.9 Examples from regional seas

### 8.9.1 The Mediterranean Sea example

The Mediterranean is a large enclosed sea, connected through narrow sills to the Atlantic Ocean by the Strait of Gibraltar and to the Black Sea by the Strait of Dardanelles (Çanakkale). Its average depth is around 1500 m, with considerable spatial variability: the Eastern Basin has several trenches exceeding 4000 m in depth, while the northern Adriatic, the shallowest part of the Mediterranean Sea, is less than 200 m deep.

Unlike the other regional examples, the Mediterranean is oligotrophic (nitrate concentration in surface waters typically  $<0.2 \mu\text{M}$ ) (EEA, 1999). There is a west-to-east nutrient gradient, with average concentrations in the waters of the Aegean about a factor of 12 less than in the Atlantic and eight times lower than in the Alboran Sea between Spain and Morocco (EEA, 1999). There is a limited supply of nutrients to the surface waters from the deep and from external sources (Cruzado, 1988), and the physical dynamics of the Mediterranean – an outflow of high-salinity, high-nutrient deep waters, and inflow of nutrient-poor

surface Atlantic water – and the rapid recycling of nutrients by the ecosystem (Krom *et al.*, 2005b; Lucea *et al.*, 2005) result in a tendency not to accumulate nutrients (Bryden and Stommel, 1984; Souvermezoglou, 1988; Caddy, 1993). Coste (1987) reports nitrate concentrations in the intermediate/deep waters of the Western Basin of  $8.5 \mu\text{M}$ , while in the Eastern Basin, concentrations are around  $6.0 \mu\text{M N}$  (Souvermezoglou *et al.*, 1992; Yilmaz and Tugrul, 1998). Unusually, primary production in the Mediterranean is phosphorus limited, most strongly in the Eastern Basin (Krom *et al.*, 2005a), while nitrogen and phosphorus co-limitation is evident elsewhere in the Mediterranean (Montserrat Sala *et al.*, 2002).

### Nitrogen inputs and trends

Although the main body of the Mediterranean is a low-nutrient system and assessments are that eutrophication is not a serious threat overall (EEA, 1999; Danovaro, 2003), nutrient enrichment is a concern in the near-coastal environment (Figure 8.1), where local and temporary occurrences of high biomass and productivity are seen especially in areas of restricted flow such as lagoon systems (Tett *et al.*, 2003). Winter mixing is a significant factor (Krom *et al.*, 1991a; Allen *et al.*, 2002), but the most concerns relate to nutrient enrichment in river plume areas, particularly in the shallow Adriatic (Degobbis and Gilmartin, 1990; Druon *et al.*, 2004).

River inputs to the Mediterranean Sea are dominated by discharges from its northern side, so this is primarily a European concern. Although the Nile's discharge is the greatest, at  $89 \text{ km}^3 \text{ yr}^{-1}$  at the level of the Aswan dam, its discharge is reduced to less than  $5 \text{ km}^3 \text{ yr}^{-1}$  as it reaches the Mediterranean (Skliris and Lascaratos, 2004), making the European inputs the major sources of nutrients and particulate matter (Bethoux, 1980; UNEP/FAO/WHO, 1996; UNEP-MAP, 2003). About a third of the annual water inflow comes from just two rivers: the Rhone ( $54 \text{ km}^3 \text{ yr}^{-1}$ ) flowing into the Gulf of Lions, and the Po ( $46 \text{ km}^3 \text{ yr}^{-1}$ ) flowing into the northern Adriatic (UNEP-MAP, 2003). Most of the Mediterranean rivers are affected by nitrate enrichment, albeit to a lesser degree than northern European rivers (UNEP-MAP (2003) reports average concentrations of  $1.24 \text{ mg N l}^{-1}$  for the 30 highest-output rivers flowing into the Mediterranean). However, nutrient enrichment is aggravated by the strong seasonality of river flows in this hot, dry region, which leads to episodic high concentrations in the river waters.

The trends and the relative importance of riverine nitrogen input to the Mediterranean remain somewhat unclear. The EEA (1999) flags the 'scarcity or unavailability of comparable and, in some cases, reliable data' as a major concern, and more recently EEA (2005) reports that there is as yet no source apportionment for nutrient inputs into the Mediterranean (see also Kronvang *et al.*, 2004, 2005). Nevertheless, 'in all documented cases' (EEA, 1999), the overall riverine nitrogen input to the Mediterranean has increased (EEA, 1999; UNEP-MAP, 2003). Inputs almost doubled from  $\sim 330 \text{ kt N yr}^{-1}$  prior to 1975 to  $\sim 600 \text{ kt N yr}^{-1}$  in 1995, although in recent years, the increase is apparently slowing (UNEP-MAP, 2003). (Phosphate loads have dropped to about 1975 values as a result of the widely applied ban of phosphorus detergents and the general improvement

of wastewater treatment facilities.) McGill (1969) determined that river run-off supplied 30% of the total input of nitrogen and phosphorus. Bethoux and Copin-Montegut (1986) used 1984 UNEP data to estimate terrestrial nitrogen discharges as 50%–70% of total input to the sea.

Atmospheric deposition of nitrogen species is also significant (Bashkin *et al.*, 1997; Guerzoni *et al.*, 1999; Sandroni *et al.*, 2007), and has been associated with episodic phytoplankton blooms (Guerzoni *et al.*, 1999). Loÿe-Pilot *et al.* (2004) reassessed the nitrogen budget for the Mediterranean Sea using 1974 UNEP regional data, and concluded that atmospheric inputs of dissolved inorganic nitrogen are of the same order as fluvial inputs in the western and northwestern zones of the Mediterranean (to the south of the more industrialised nations). The already high intensity of shipping in the Mediterranean is projected to increase (REMPEC, 2008), with implications for this component of the nitrogen budget.

The Po and Rhone rivers, which dominate river inputs to the Mediterranean, also have the greatest potential impacts. They are both in catchments with major industrial and urban centres and agricultural activity, and both flow into shallower regions of the Mediterranean: the Po River flows into the northern Adriatic, and the Rhone into the Gulf of Lions (the continental shelf break is typically <10 km along the Western basin, but east of the Golfe de Fos it widens to over 50 km). The coastal and lagoon ecosystems influenced by these rivers and those in other intensely cultivated river basins of Italy, Spain (particularly the Ebro river) and Greece (the Axios, which also flows into the Adriatic) have been comparatively well-studied, for example in two recent EU integrated coastal/river catchment projects:

- OAERRE (OAERRE 2010) and
- EuroCat (EuroCat 2010) and
- the Italian research network LaguNET (LaguNET 2010).

Agriculture is a major source activity, with diffuse sources contributing ~55% of the nitrogen in the Po river (Crouzet *et al.*, 1999; Behrendt, 2004) and >80% in the Axios (Behrendt, 2004; Milovanovic, 2006). Sewage, waste-water and other point sources are regionally variable, accounting for 43% of total nitrogen in the Po (Crouzet *et al.*, 1999), a somewhat higher proportion than for the other main rivers (Table 8.5).

### Ecological status of the Mediterranean Sea

Among all the European seas briefly presented here, the Mediterranean seems to be the most unaffected by human nutrient input. However, coastal areas especially along the northern shore are affected by enhanced productivity and algae blooms. The dam building activities e.g. in the Nile change the river flow and sediment transport considerably and seem to influence the fishery. The role of atmospheric deposition may therefore be more important than in other coastal areas with high riverine nutrient loads.

### Future of the Mediterranean Sea

Across most of the Mediterranean, there is still limited nitrogen abatement (primarily waste-water treatment), including on the high-flow Po river. A recent UNEP-MAP Global Environment Facility (GEF) activity (UNEP-MAP/RAC/CP, 2004) prepared

**Table 8.5** Relative importance of the different nitrogen species in the Po, Rhone and Ebro rivers (NH<sub>3</sub> contributes ~5% of DIN in all rivers)

	TN	DIN	DON	PN
	mg l <sup>-1</sup>	%	%	%
Po <sup>1</sup>	3.1	71.0	17.0	12.0
Rhone <sup>2</sup>	1.7	84.8	8.4	6.9
Ebro <sup>3</sup>	2.6	80.8	11.5	7.7

Sources: (1) Tartari *et al.* (1991), (2) Pont (1996), (3) Munoz and Prat (1989). Cited in UNEP-MAP (UNEP-MAP, 2003).

regional guidelines on good nutrient management practices that will be implemented more widely in coming years to ensure compliance with European legislation. Nevertheless, with the continuing intensification of agriculture, urbanization and shipping, particularly in the eastern end of the Mediterranean, and in a context where a comparatively small proportion of the coastline is protected under legislation and monitored, threats to ecosystems from anthropogenic nitrogen remain.

## 8.9.2 The Baltic Sea example

The Baltic Sea is a shallow brackish water sea average depth 52.3m with limited water exchange through the Danish sounds, resulting in an average residence time of the water of 30 years. Surrounded by heavily industrialized countries and a population of c. 85 million people the Baltic Sea is strongly impacted by nutrient loading, consequently eutrophication is the major problem of the Baltic Sea (HELCOM, 2004). The impacts of eutrophication are manifested as various symptoms such as increased nutrient concentrations and phytoplankton biomass, and oxygen deficiency and elimination of benthic fauna (review by Lundberg, 2005).

### Nutrient input and trends

The early signs of eutrophication were already present in early 1900 close to the larger municipalities that discharged their waste waters directly with minimal treatment to the coastal waters (Laakkonen and Laurila, 2007). Since then the nutrient loading from rivers has increased approximately seven times for nitrogen and four times for phosphorus (HELCOM, 2004) and the pools of nutrients have also increased considerably in the whole Baltic Sea (Larsson *et al.*, 1985; Nehring and Matthäus, 1991). Recently decreasing trends of nutrient levels have been reported in different parts of the Baltic (Fleming-Lehtinen *et al.*, 2008). However, many regions, particularly the Gulf of Finland, Baltic Proper, and the Southern Baltic, show clear signs of eutrophication (HELCOM, 2002; Rönnberg and Bonsdorff, 2004; Fleming-Lehtinen *et al.*, 2008).

The total riverine nitrogen load to the Baltic Sea varies between 600–800 ktons per year being closely related to the river run-off. About half of the total riverine nitrogen load is discharged via three large rivers: Vistula, Oder and Nemunas to the Southern Baltic Sea (HELCOM, 2002). Diffuse loading from agriculture and forestry is the major source of nitrogen (70%–95%) to the Baltic catchments (HELCOM, 2004). Other major nitrogen sources of the Baltic Sea are atmospheric deposition, estimated to be 185 ktons N in 1997 (HELCOM,

1997), and nitrogen fixation, estimated to vary between 370 ktons N (Wasmund *et al.*, 2001) and 926 ktons N per year (Schneider *et al.*, 2003). The effects of riverine nitrogen loading are more pronounced in the coastal areas than in the open Baltic Proper, and the coastal sediments appear to be very efficient in removing nitrogen by denitrification (Voss *et al.*, 2005; Vahtera *et al.*, 2007).

### Ecological status of the Baltic Sea

The anoxic conditions in the Baltic are promoting release of inorganic phosphorus from the sediments (Pitkänen *et al.*, 2001; Conley *et al.*, 2002) and may increase denitrification as the area covered by oxic and anoxic interfaces increase (Vahtera *et al.*, 2007). The supply of phosphorus favours the blooms of cyanobacteria that fix their nitrogen from the dissolved  $N_2$ . This has been described as a vicious circle resembling the situation in many lakes where internal sources of nutrients maintain eutrophication (Tamminen and Andersen, 2007; Vahtera *et al.*, 2007). The internal processes and feedbacks that maintain and enforce the eutrophied status of the Baltic Sea, suggest that there has been a regime shift from an earlier more oligotrophic to more eutrophic status that may be difficult to reverse (Österblom *et al.*, 2007).

### The future of the Baltic Sea

The EU Water Framework Directive calls for restoration of the 'good ecological status' of coastal waters by 2015. This is a key piece of legislation for the protection of the Baltic Sea as it requires holistic management of pressures and impacts on the catchment scale including the coastal zone. The Baltic Sea Action Plan (HELCOM, 2007) sets the ecological objectives and country allocations for nutrient reductions based on best scientific knowledge and information available. The Baltic Sea Action Plan is a pilot for implementing the new EU Marine Strategy Directive that calls for good marine environmental status to be reached in 2020, and adds to the requirements of the EU Water Framework Directive in the coastal zone.

Nutrient loading reductions that are required to reach the 'good status' of the Baltic are anticipated to be costly. Therefore more drastic management actions have been suggested to improve the status of the open Baltic Sea. Large scale engineering with artificial ventilation of the Baltic Proper deep waters with concurrent fertilization with nitrogen has been suggested to halt the 'vicious circle' of internal phosphorus loading and cyanobacterial blooms in the Baltic Proper (Stigebrandt and Gustaffson, 2007). Artificial ventilation could keep the patient alive, but not necessarily cure the cause of the disease. Halting the biological pump producing organic material that is suffocating the 'patient' would require tuning down the supply of both nitrogen and phosphorus at the source (Tamminen and Andersen, 2007; Vahtera *et al.*, 2007). Treating the central regions of the Baltic Sea separately would not necessarily improve the coastal areas where the majority of people meet the sea, and which provide a number of ecosystem services to humans.

The future climate change scenarios include a potential increase in the temperatures and precipitation in Northern Europe. Concurrent potential intensification of agricultural

practices, and increased precipitation and transport of nutrients to the warmer Baltic Sea is a scary scenario that calls for urgent planning to counteract the risk of magnified eutrophication.

## 8.9.3 The Black Sea example

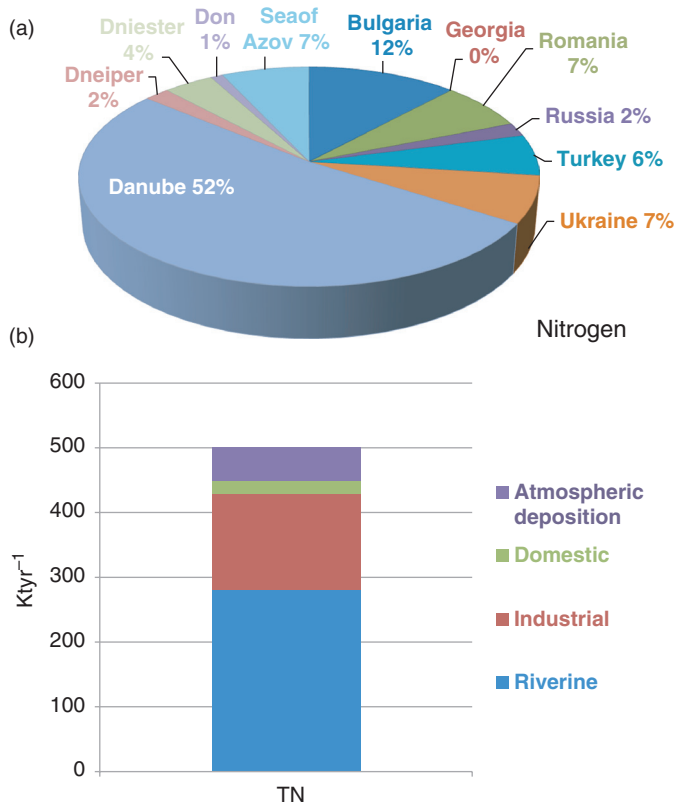
The Black Sea is almost cut off from the rest of the world's oceans and is up to 2200 m deep. The only connection to the open sea is through the Bosphorus Strait which has a depth of only 40 m. The Black Sea drains an extensive catchment consisting of 23 countries, covering a land area of 2 400 000 km<sup>2</sup>, and receiving waste water from more than 190 million people (daNUbs, 2005). The freshwater input to the Black Sea amounts to 350 km<sup>3</sup>, and comes from the largest European Rivers the Danube, Dnieper and Dniester. The Black Sea is naturally stratified below approximately 70 m, and is the world's largest permanently anoxic water body. The mean residence time of the water is approximately 1000 years. Because it receives considerable riverine input, the Black Sea in general and the shallow northwestern shelf in particular are susceptible to the effects of nutrient loading.

During the 1960s the Soviet agricultural revolution resulted in intensive fertilizer use and livestock production in the Black Sea catchment (Mee *et al.*, 2005). This led to severe eutrophication of the Black Sea's northwestern shelf during the 1970s and 1980s. During these years, the shelf experienced an increase in the magnitude, extent and frequency of algal blooms (Bodeanu, 1993) as well as the occurrence of a number of harmful algal bloom (or red tide) events (Moncheva *et al.*, 2001). The phytoplankton composition changed drastically between 1960 and 1990 (Bodeanu, 2002), much of the shelf area was hypoxic (Zaitsev and Mamaev, 1997), and the decline and in some cases loss of benthic floral and faunal communities was observed (Zaitsev and Mamaev, 1997). Alterations to the phytoplankton community precipitated changes in the zooplankton, including a decrease in non-gelatinous zooplankton species and an increase in gelatinous species such as *Noctiluca scintillans* and *Mnemiopsis leidyi*, an invasive ctenophore (Shiganova and Bulgakova, 2000). Species diversity and abundance of several valuable fish species (bonito, *Sarda sarda*; bluefish, *Pomatomus saltatrix*; flounder, *Platichthys flesus*; turbot, *Psetta maxima*; sole, *Solea lascaris*) decreased (Shiganova and Bulgakova, 2000). These disruptions to the food web, along with unregulated fishing efforts, damaged area fisheries (Daskalov, 2002).

### Nutrient input and trends

From the 1950s to the early 1980s, the annual discharge of nitrates to the Black Sea increased from 155 000 to 340 000 tons (Zaitsev and Mamaev, 1997). Overall, shelf waters of the Black Sea are phosphorus-limited and open waters are nitrogen-limited (Cociasu *et al.*, 1998; daNUbs, 2005).

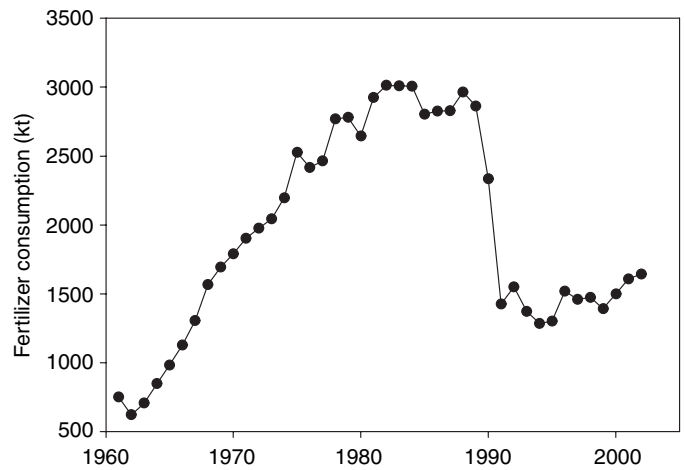
Riverine input is the primary source of land-based nitrogen to the Black Sea, contributing approximately 63% of the Black Sea's anthropogenic nitrogen load, 52% of which comes from the Danube River alone (Figure 8.9a, b) (Black Sea Environmental, 1996; Commission, 2002). Although the amount of fertilizer



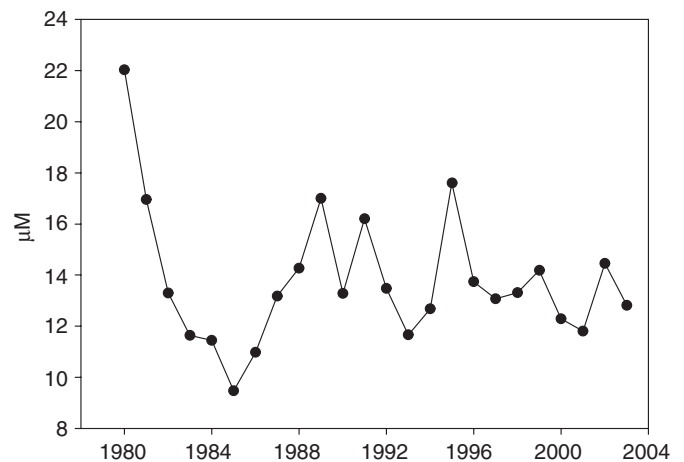
**Figure 8.9** Nitrogen inputs to the Black Sea (a) by source (Black Sea Environmental, 1996) and (b) by anthropogenic sector. Atmospheric contribution applies to northwestern shelf exclusively (data from Commission, 2002; Langmead *et al.*, 2007).

consumed in the Danube catchment has decreased significantly (Mee, 2006) (Figure 8.10), the amount of nitrogen in Danube waters has decreased only slightly due to retention of the nutrient in catchment soils and groundwater (daNUbs, 2005); this is reflected in the lack of clear trend in nitrogen concentrations in shelf waters (Figure 8.10). The decreased nitrogen load since 1990 (Figure 8.11) may be attributed to implementation of the Nitrates Directive in EU countries (Union, 1991; Commission, 2002), reduced fertilizer usage after the collapse of the communist bloc (Commission, 2002), and greater waste water treatment (Commission, 2002). As a result of decreasing nitrogen loads in the Danube, the concentration of nitrogen in the Black Sea shelf has recently begun to decline (Figure 8.12) (Cociasu and Popa, 2004).

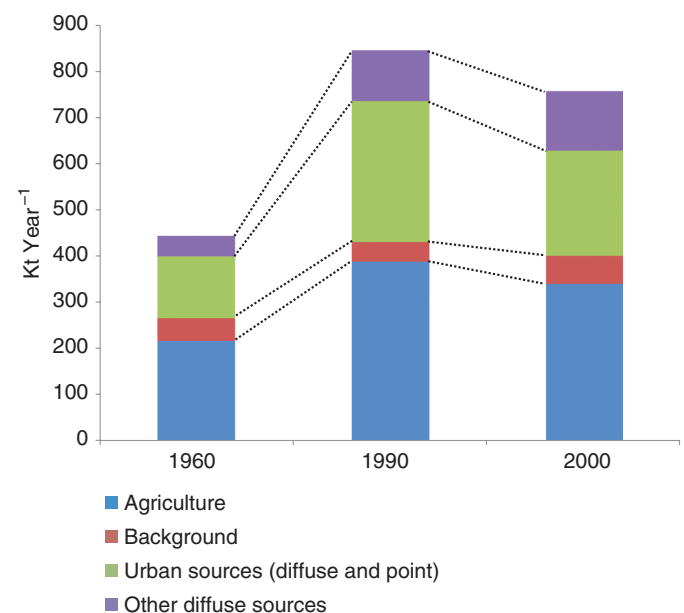
Industry is the second greatest contributor of land-based nitrogen (30%) directly to the Black Sea (Commission, 2002). Most industrial nitrogen entering the Black Sea comes from Ukraine (49%), Russia (30%) and Bulgaria (18%) (Figure 8.13a) (Black Sea Environmental, 1996). Domestic waste water is a minor contributor of nitrogen (<5%) to the Black Sea, as is atmospheric deposition (10%) (Figures 8.9b, 8.13b). The majority of industries in all Black Sea coastal states are connected to municipal wastewater treatment systems. Therefore, with implementation of the Urban Waste Water Treatment Directive in the accession states and recovering economies in other Black Sea nations enabling more efficient sewage treatment, the amount of untreated domestic and industrial



**Figure 8.10** Consumption of fertilizer in the Danube catchment (after Mee, 2006).

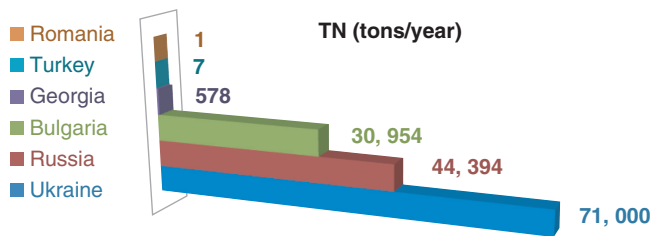


**Figure 8.11** Time-series of total nitrogen concentrations measured at Constanta, Romania (from Cociasu and Popa, 2004).



**Figure 8.12** Sources of nitrogen to the Danube (data from daNUbs, 2005; Mee *et al.*, 2005).

(a) Industrial sources



(b) Domestic sources

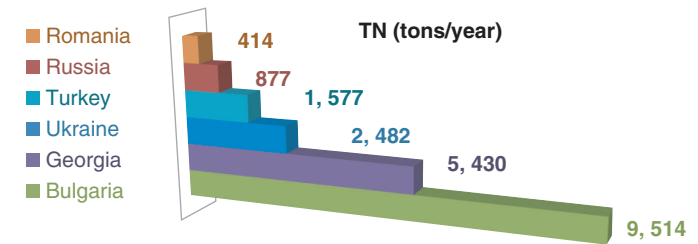


Figure 8.13 (a) Industrial and (b) domestic sources of nitrogen to the Black Sea (from Black Sea Environmental, 1996).

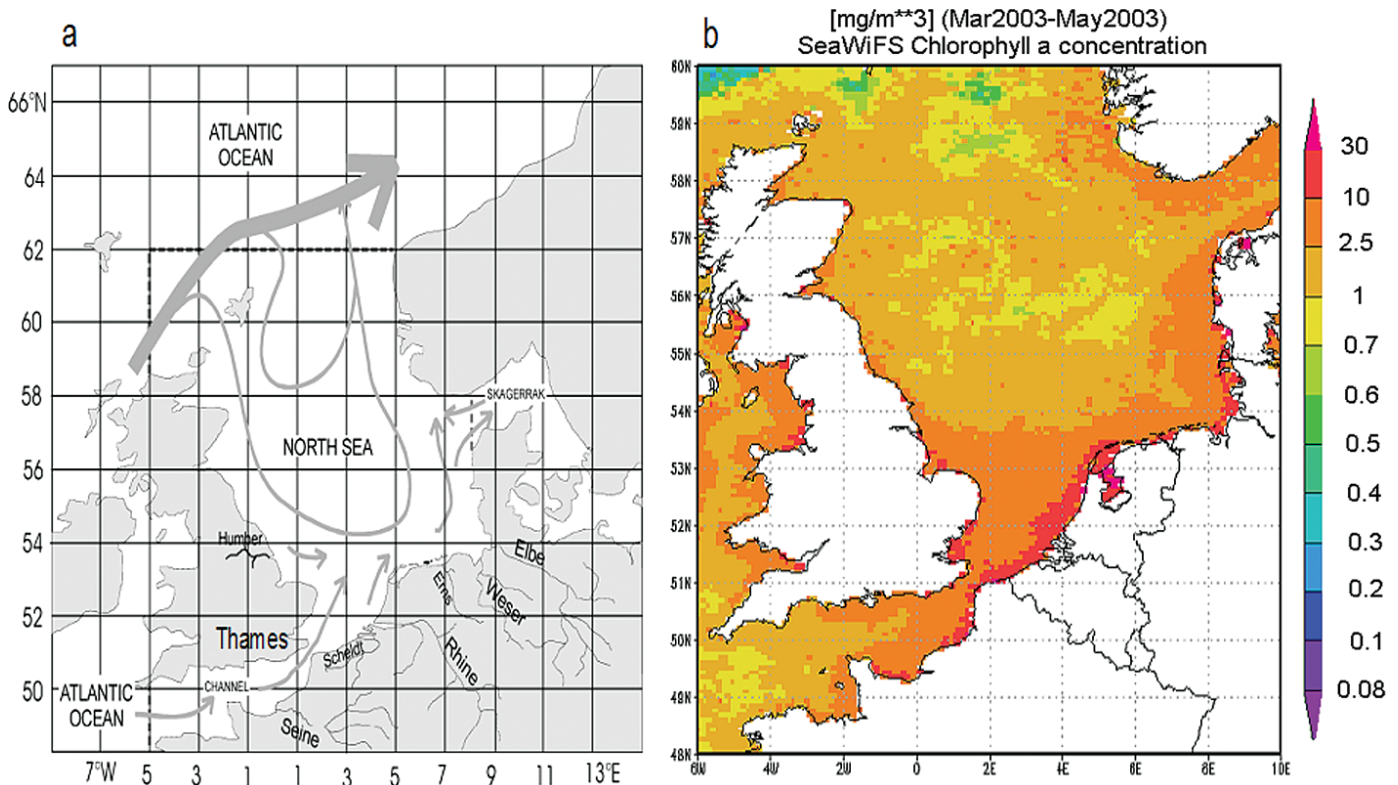


Figure 8.14 (a) The Greater North Sea and its major contributors; (b) SeaWiFS-derived chlorophyll *a* in the Greater North Sea for March–May 2003. Generated by NASA's Giovanni (Giovanni.gfsc.nasa.gov)

waste entering the Black Sea directly is expected to decrease (Commission, 2002).

### Ecological status

Although a recovery of the Black Sea ecosystem was observed in the past decades the system still seems to be fragile and needs attention and further nutrient reduction to become a stable oceanic environment. Nutrients are partly stored in sediments and deeper waters and can easily be mobilized (see below). The same may happen when nutrient loads from the rivers increase (Langmead *et al.*, 2007) e.g. through land use changes in the drainage basins.

### The future of the Black Sea

Due to economic decline in the 1990s of all Black Sea coastal countries except Turkey, and the consequent lack of support for centrally administered agriculture, the marine ecosystem has recently shown signs of recovery (Mee *et al.*, 2005). The

late 1990s saw fewer phytoplankton blooms than previous decades and the community structure has returned to a diatom-dominated state (Bodeanu, 2002). No hypoxic events were recorded on the shelf between 1993 and 2000 (Mee, 2006). However, although possible, recovery of the Black Sea is far from certain. During the exceptionally warm years of 2001 and 2002, 15 monospecific blooms occurred in Romanian waters and the phytoplankton community was again dominated by non-diatoms (Bodeanu *et al.*, 2004). Additionally, the climatic conditions of 2001 triggered a large scale hypoxic event which resulted in fish mortalities in shelf waters (Mee *et al.*, 2005). These signs indicate that nutrient concentrations in shelf waters remain sufficiently elevated to support eutrophic events, particularly in combination with anomalous climatic conditions. Additionally, overfishing continues, with further depletion of remaining stocks likely (Langmead *et al.*, 2007).

Despite recent ecosystem improvements, the Black Sea's future remains uncertain. Because of expected growth of farming in

Eastern Europe and additional pressures from shipping, poorly regulated fisheries, sewage treatment without nutrient removal, and changes in climate, the Black Sea may potentially revert back to its eutrophic state (Langmead *et al.*, 2007). Alternatively, this period of newfound regional prosperity, particularly with the expansion of the EU to include Bulgaria, Romania, and possibly Turkey, may be used as an opportunity for remediation of the Black Sea ecosystem. Even if eutrophication and overfishing are mitigated, there is no guarantee that the ecosystem will return to its pre-eutrophic state (Mee *et al.*, 2005).

#### 8.9.4 The North Sea example

The Greater North Sea is a semi-enclosed, epi-continental large marine ecosystem off North-Western Europe (Figure 8.14a). For the purpose of nutrient loading, the English Channel, the Kattegat and margins such as the Wadden Sea are considered as an integral part of the larger North Sea ecosystem (NSTF *et al.*, 1994). Depths greater than 100m prevail in the seasonally-stratified Northern North Sea, a rather oceanic system dominated by the influence of Atlantic water.

##### Nutrient input and trends

The southern part is a shallow (<50 m deep and <20 m near the coast) and continuously mixed region that receives the majority of the riverine nutrient loads to the North Sea (Seine, Thames, Scheldt, Rhine, Ems, Weser, Elbe; Figure 8.14a). Owing to the general water mass circulation, nutrient loads cumulate along a SW–NE gradient in the region (Lancelot *et al.*, 1987). In the plume area of these large rivers draining watersheds among the most industrialized, cultivated and densely populated (ca 185 million inhabitants) over the world, the increased nutrient loading has resulted in severe eutrophication problems visible as increased winter nutrient concentrations (Lancelot *et al.*, 1987; Anonymous, 1993; Radach and Pätsch, 1997) and spring phytoplankton biomass (Figure 8.14b; Radach and Pätsch, 1997), foam accumulation (Lancelot, 1995), oxygen deficiency (Radach, 1992) and toxin release (Maestrini and Graneli, 1991).

##### Ecological status of the North Sea

Eutrophication in the North Sea manifests itself as undesirable blooms of essentially two Haptophytes: *Phaeocystis globosa* forming colony blooms every spring (April–May) in coastal waters off France, Belgium, the Netherlands and Germany. There are associated ‘foam events’ (Lancelot, 1995) and, the toxin-producer *Chrysochromulina* spp. blooming between April and August in the Kattegat and Skagerrak off the coasts of Denmark, Sweden and Norway (Dahl *et al.*, 2005). The toxicity of *Chrysochromulina* varies however between species and within the same species, under control of environmental conditions (Johansson and Graneli, 1999). Extensive blooms of harmful *C. polylepis* were up to now only recorded in May–June 1988 when they decimated farmed fish (Dahl *et al.*, 2005).

In contrast, foam deposits on the beaches along the French, Belgian, Dutch and German beaches are well-known recurrent spring phenomena that correspond to the explosive development of large mucilaginous colonies of *Phaeocystis*. These

colonies enlarge when growing and reach sizes unmanageable for the current copepods (Weisse *et al.*, 1994). These blooms are not recent, having been reported already at the end of the nineteenth century (Cadée and Hegeman, 1991). However a model reconstruction of pristine time for the Seine and Scheldt watersheds (Lancelot *et al.*, 2009) suggest that grazable forms of *Phaeocystis* colonies were blooming under natural conditions in the Southern North Sea and efficiently transferred their production to higher trophic levels.

Eco-physiological studies show that both these Haptophytes follow an early-spring diatom bloom (Rousseau *et al.*, 2002; Dahl *et al.*, 2005) and their growth is sustained by excess nitrate under low phosphate conditions (Lancelot *et al.*, 1998; Dahl *et al.*, 2005; Breton *et al.*, 2006). Both species have indeed shown their ability to use organic forms of phosphorus (Veldhuis and Admiraal, 1987; Estep and MacIntyre, 1989; Veldhuis *et al.*, 1991; Nygaard and Tobiesen, 1993). Resistance to grazers was found as essential for forming exceptional blooms, *Phaeocystis* colonies by enlarging their size, *Chrysochromulina* by releasing toxins under phosphate depletion (Edvardsen *et al.*, 1990; Johansson and Graneli, 1999).

##### Linking harmful algal blooms with land-based nutrients

It is accepted that coastal eutrophication problems over the world are caused not only by increased nutrient loads but rather by the unbalance in the delivery of nitrogen and phosphorus in excess with respect to silica (Officer and Ryther, 1980; Billen *et al.*, 1991; Conley *et al.*, 1993; Turner *et al.*, 1998). Hence undesirable coastal eutrophication results with the development of non-siliceous algae responding to new sources of N and P. Land-based nutrients are discharged in the Greater North Sea through three pathways: direct tributaries, river inputs and atmospheric deposition. Annual nitrogen and phosphorus inputs to the North Sea (Table 8.6.) estimated for the 1989–1990 period show the large contribution of rivers (60% N, 77% P) some 70% of which is brought by rivers Seine, Rhine and Elbe, and point to an excess of N with respect to P delivery (molar N:P > 16; Table 8.5). This N excess with respect to P propagates in the coastal area, possibly explaining the successful development of both *Phaeocystis* and *Chrysochromulina* (Lancelot *et al.*, 1987; Dahl *et al.*, 2005). Supporting this, a positive relationship has been found between *Phaeocystis* abundance and nitrates (Lancelot *et al.*, 1998; Breton *et al.*, 2006; Lancelot *et al.*, 2007) in the Southern Bight of the North Sea while *Chrysochromulina* abundance has been shown to be positively correlated with spring and summer N:P (Dahl *et al.*, 2005).

##### The future of the North Sea

Historical trends of river nutrient inputs into the North Sea and the related coastal eutrophication problems have been appraised based on compilation of available data of nutrients and phytoplankton biomass (Radach and Patsch, 1997), and model simulations constrained by reconstructed river nutrient loads based on either available data (Radach and Pätsch, 1997) or river simulations (Billen and Garnier, 2007; Lancelot *et al.*, 2007). All results point towards an accelerated increase

**Table 8.6** Land-based sources of N and P (1989–1990) to the North Sea

	N kt yr <sup>-1</sup>	P kt yr <sup>-1</sup>	Molar N:P
Rivers	720	46	34
Direct	88	14	14
Atmosphere	412	—	>>>
Total	1,220	60	45

Sources: Rendell *et al.*, 1993; OSPAR *et al.*, 2005.

of N and P river inputs by a factor of ~5 between 1950 and 1985 while Si loads were unchanged. This N and P increase was linked to the combination of three factors: (i) the generalization of modern intensive agriculture and the use of synthetic fertilizers, (ii) the presence of polyphosphates in washing powders and (iii) the increased urban waste water collection and lack of efficient nutrient reduction treatment (Billen and Garnier, 2007). As a result spring phytoplankton biomass increased by a factor of ~3 in the river plume areas. This nutrient enrichment was beneficial to diatoms up to 1965 after which non-siliceous algae became highly dominant as for instances reported for the Helgoland time series (Radach and Pätsch, 1997) due to the imbalanced N:P:Si nutrient enrichment. Model simulations (Radach and Pätsch, 2007) suggest that the penetration of land-based nutrients extends to the area bordered by the line from the English coast south of 54 °N to northern Denmark, sustaining the high phytoplankton biomass recorded in that region by satellite-derived Chl *a* maps (Figure 8.14b). North of this area, the impacts of land based nutrient supply is much less evident with an increasing importance for offshore nutrient sources and little evidence of changes in plankton communities resulting from terrestrially sourced nutrients but important climatically driven changes (Beaugrand *et al.*, 2002).

In the late 1980s, however, the perception of coastal eutrophication problems was reaching a maximum in countries bordering the greater North Sea and recommendations for reducing nutrient inputs to the North Sea were made (North Sea conference, 1987). Instruments and procedures were implemented such as the OSPAR Strategy to combat eutrophication (OSPAR *et al.*, 2005) and the Water Framework Directive of the European Union (2000/60/EC). As a result of improved wastewater treatment P loads decreased considerably for all rivers (~ 65% in 2004) while the decrease of N loads was less efficient (~30% in 2004) due to the weak implementation of agro-environmental measures (Billen and Garnier, 2007). As a consequence, present-day measured and modelled river loads show severe imbalanced molar N:P ratios >> 16 (range: 22–60 for the different rivers) which propagate directly in the continental coastal strip (winter N:P > 25; Rousseau *et al.*, 2004) and favour the development of harmful *Phaeocystis* and *Chrysochromulina* blooms in the North Sea. In agreement, model reconstruction of diatom and *Phaeocystis* blooms in the Southern Bight of the North show a positive feedback of decreased nutrient loads after 1990 to both diatoms and *Phaeocystis* with however a larger impact on diatoms (Lancelot *et al.*, 2007).

We conclude that future management of nutrient emission reduction aiming at decreasing harmful algal blooms in the southern North Sea without impacting diatom blooms need

to target a decrease of N loads through the implementation of specific agro-environmental measures.

## References

- Ærtebjerg, G., Andersen, J. H. and Hansen, O. S. (2003). *Nutrients and Eutrophication in Danish Marine Waters: A Challenge for Science and Management*. National Environmental Research Institute.
- Ahad, J. M. E., Ganeshram, R. S., Spencer, R. G. M. *et al.* (2006). Evaluating the sources and fate of anthropogenic dissolved inorganic nitrogen (DIN) in two contrasting North Sea estuaries. *Science of the Total Environment*, **372**, 317–333.
- Allen, J. I., Somerfield, P. J. and Siddorn, J. (2002). Primary and bacterial production in the Mediterranean Sea: a modelling study. *Journal of Marine Systems*, **33**, 473–495.
- Andrews, J. E., Burgess, D., Cave, R. R. *et al.* (2006). Biogeochemical value of managed realignment, Humber estuary, UK. *Science of the Total Environment*, **371**, 19–30.
- Anonymous (1993). *North Sea Quality Status Report 1993*, North Sea Task Force. ICES/OSPAR Commissions, London.
- Arrigo, K. R. (2005). Marine microorganisms and global nutrient cycles. *Nature*, **437**, 349–355.
- Arrigo, K. R. (2007). Marine manipulations. *Nature*, **450**, 491–492.
- Baker, A. R. *et al.* (2007). Dry and wet deposition of nutrients from the tropical Atlantic atmosphere: links to primary productivity and nitrogen fixation. *Deep-Sea Research*, **54**, 1704–1720.
- Baker, A. R., Kelly, S. D., Biswas, K. F., Witt, M. and Jickells, T. D. (2003). Atmospheric deposition of nutrients to the Atlantic Ocean. *Geophysical Research Letters*, pp. 30.
- Bange, H. W. (2006). Nitrous oxide and methane in European coastal waters. *Estuarine, Coastal and Shelf Science*, **70**, 361–374.
- Bange, H. W. (2008). Gaseous nitrogen compounds (NO, N<sub>2</sub>O, N<sub>2</sub>, NH<sub>3</sub>) in the ocean. In: *Nitrogen in the Marine Environment*, ed. D. G. Capone *et al.* Elsevier, Amsterdam, pp. 51–94.
- Bange, H. W., Rapsomanikis, S. and Andreae, M. O. (1996). Nitrous oxide in coastal waters. *Global Biogeochem Cycles*, **10**, 197–207.
- Banase, K. (1973). On the interpretation of data for the carbon-to-nitrogen ratio of phytoplankton. *Limnology Oceanography*, **695**–699.
- Banase, K. (1994). Uptake of inorganic carbon and nitrate by marine plankton and the Redfield ratio. *Global Biogeochem Cycles*, **8**, 81–84.
- Barcelos e Ramos, J., Biswas, H., Schulz, K. G., LaRoche, J. and Riebesell, U. (2007). Effect of rising atmospheric carbon dioxide on the marine nitrogen fixer *Trichodesmium*. *Global Biogeochemical Cycles*, **21**.
- Bashkin, V. N., Erdman, L. K., Abramychev, A. Y. *et al.* (1997). *The Input of Anthropogenic Airborne Nitrogen to the Mediterranean Sea through its Watershed*, MAP Technical Reports Series. UNEP-MAP/MedPol/WMO, Athens.
- Beaugrand, G., Reid, P. C., Ibañez, F., Lindley, J. A. and Edwards, M. (2002). Reorganization of North Atlantic marine copepod biodiversity and climate. *Science of the Total Environment*, **296**, 1692–1694.
- Behrendt, H. (2004). *Past, Present and Future Changes in Catchment Fluxes*. European Commission.
- Benitez-Nelson, C. R. (2000). The biogeochemical cycling of phosphorus in marine systems. *Earth Science Reviews*, **51**, 109–135.
- Berezina, N. and Golubkov, S. M. (2008). Effect of drifting macroalgae *Cladophora glomerata* on benthic community dynamics in the easternmost Baltic Sea. *Journal of Marine Systems*, **74**, 80–85.
- Berger, R., Henriksson, E., Kautsky, L. and Malm, T. (2003). Effects of filamentous algae and deposited matter on the survival of

- Fucus vesiculosus* L. germings in the Baltic Sea. *Aquatic Ecology*, **37**, 1–11.
- Bethoux, J. P. (1980). Mean water fluxes across sections in the Mediterranean Sea evaluated on the basis of water and salt budgets and of observed salinities. *Oceanologica Acta*, **3**, 79–88.
- Bethoux, J. P. and Copin-Montegut, G. (1986). Biological fixation of atmospheric nitrogen in the Mediterranean Sea. *Limnology and Oceanography*, **31**, 1353–1358.
- Billen, G. and Garnier, J. (1997). The Phison River Plume: coastal eutrophication in response to changes in land use and water management in the watershed. *Aquatic Microbial Ecology*, **13**, 3–17.
- Billen, G. and Garnier, J. (2007). River basin nutrient delivery to the coastal sea: assessing its potential to sustain new production of non-siliceous algae. *Marine Chemistry*, **106**, 148–160.
- Billen, G., Lancelot, C. and Meybeck, M. (1991). N, P and Si retention along the Aquatic Continuum from Land to Ocean. In: *Ocean Margin Processes in Global Change*, ed. R. F. C. Mantoura, J.-M. Martin, and R. Wollast. John Wiley & Sons, New York, pp. 19–44.
- Billen, G., Silvestre, M., Grizzetti, B. *et al.* (2011). Nitrogen flows from European watersheds to coastal marine waters. In: *The European Nitrogen Assessment*, ed. M. A. Sutton, C. M. Howard, J. W. Erisman *et al.* Cambridge University Press.
- Black Sea Environmental (1996). *Black Sea Transboundary Diagnostic Analysis*. Global Environmental Facility.
- Bodeanu, N. (1993). Microalgal blooms in the Romanian area of the Black Sea and contemporary eutrophication conditions. In: *Toxic Phytoplankton Blooms in the Sea*, ed. T. J. Smayda and Y. Shimizu. Elsevier, Amsterdam, pp. 203–209.
- Bodeanu, N. (2002). Algal blooms in Romanian Black Sea waters in the last two decades of the 20th century. *Cercatari Marine*, **34**, 7–22.
- Bodeanu, N., Andrei, C., Boicenco, L., Popa, L. and Sburlea, A. (2004). A new trend of the phytoplankton structure and dynamics in Romanian marine waters. *Cercatari Marine*, **35**, 77–86.
- Bodenbender, J. and Papen, H. (1996). Bedeutung gasförmiger Komponenten an den Grenzflächen Sediment/Atmosphäre und Wasser/Atmosphäre. Sylter 20 Wattenmeer Austauschprozesse (SWAP), Projektsynthese, pp. 252–278.
- Boesch, D. F., Brinsfield, R. B. and Magnien, R. E. (2001). Chesapeake Bay eutrophication: scientific understanding, ecosystem restoration, and challenges for agriculture. *Journal of Environmental Quality*, **30**, 303–320.
- Bonsdorff, E. and Pearson, T. H. (1999). Variation in the sublittoral macrozoobenthos of the Baltic Sea along environmental gradients: a functional-group approach. *Australian Journal of Ecology*, **312**–326.
- Boyd, P. W. *et al.* (2007). Mesoscale iron enrichment experiments 1993–2005: synthesis and future directions. *Science*, **315**, 612–617.
- Bradley, P. B., Sanderson, M. P., Frischer, M. E. *et al.* (2010). Inorganic and organic nitrogen uptake by phytoplankton and heterotrophic bacteria in the stratified Mid-Atlantic Bight. *Estuarine, Coastal and Shelf Science*, **88**, 429–441.
- Brandes, J. A., Devol, A. H. and Deutsch, C. (2007). New developments in the marine nitrogen cycle. *Chemical Reviews*, **107**, 577–589.
- Breton, E., Rousseau, V., Parent, J. Y., Ozer, J. and Lancelot, C. (2006). Hydroclimatic modulation of diatom/*Phaeocystis* blooms in the nutrient-enriched Belgian coastal waters (North Sea). *Limnology and Oceanography*, **51**, 1–14.
- Brettar, I. and Rheinheimer, G. (1992). Influence of carbon availability on denitrification in the central Baltic Sea. *Limnology and Oceanography*, **37**, 1146–1163.
- Bronk, D. A., See, J. H., Bradley, P. and Killberg, L. (2007). DON as a source of bioavailable nitrogen for phytoplankton. *Biogeosciences*, **283**–296.
- Bryden, H. L. and Stommel, H. M. (1984). Limiting processes that determine basic features of the circulation in the Mediterranean Sea. *Oceanologica Acta*, **7**, 289–296.
- Caddy, J. F. (1993). Contrast between recent fishery trends and evidence from nutrient enrichment in two large marine ecosystems: the Mediterranean and the Black Seas. In: *Large Marine Ecosystems: Stress, Mitigation, and Sustainability*, ed. K. Sherman *et al.* American Association for the Advancement of Science, Washington DC, pp. 137–147.
- Cadée, G. C. and Hegeman, J. (1991). Historical phytoplankton data of the Marsdiep. *Hydrobiological Bulletin*, **24**, 111–118.
- Capone, D. G. (1988). Benthic nitrogen fixation. In: *Nitrogen Cycling in Coastal Marine Environments*, ed. T. H. Blackburn, John Wiley & Sons, New York, pp. 85–123.
- Capone, D. G., Zehr, J. P., Paerl, H. W., Bergman, B. and Carpenter, E. J. (1997). *Trichodesmium*, a globally significant marine cyanobacterium. *Science*, **276**, 1221–1229.
- Castro, M. S. and Driscoll, C. T. (2002). Atmospheric nitrogen deposition to estuaries in the mid-Atlantic and northeastern United States. *Environmental Science and Technology*, **36**, 3242–3249.
- Christensen, P. B., Rysgaard, S., Sloth, N. P., Dalsgaard, T. and Schwaerter, S. (2000). Sediment mineralization, nutrient fluxes, denitrification and dissimilatory nitrate reduction to ammonium in an estuarine fjord with sea cage trout farms. *Aquatic Microbial Ecology*, **27**, 73–81.
- Cloern, J. E. (1996). Phytoplankton blooms dynamics in coastal ecosystems: a review with some general lessons from sustained investigation of San Francisco Bay, California. *Review of Geophysics*, **34**, 127–168.
- Cociasu, A. and Popa, L. (2004). Significant changes in Danube nutrient loads and their impact on the Romanian Black Sea coastal waters. *Cercatari Marine*, **35**, 25–37.
- Cociasu, A., Popa, L. and Buga, L. (1998). Long-term evolution of the nutrient concentrations on the north-western shelf of the Black Sea. *Cercatari Marine*, **13**, 29.
- Commission, Black Sea (2002). *State of the Environment of the Black Sea: Pressures and Trends: 1996–2000*. Black Sea Commission.
- Conley, D. J. (1999). Biogeochemical nutrient cycles and nutrient management strategies. *Hydrobiologia*, **410**, 87–96.
- Conley, D. J., Carstensen, J., Ærtebjerg, G. *et al.* (2007). Long-term changes and impacts of hypoxia in Danish coastal waters. *Ecological Applications*, **17**, 165–184.
- Conley, D. J., Humborg, C., Rahm, L., Savchuk, O. P. and Wulff, F. (2002). Hypoxia in the Baltic Sea and basin scale changes in phosphorus biogeochemistry. *Environmental Science and Technology*, **36**, 5315–5320.
- Conley, D. J., Schelske, C. I. and Stoermer, E. F. (1993). Modification of the biogeochemical cycle of silica with eutrophication. *Marine Ecology Progress Series*, **81**, 121–128.
- Cornell, S. E., Jickells, T. D., Cape, J. N. *et al.* (2003). Organic nitrogen deposition on land and coastal environments: a review of methods and data. *Atmospheric Environment*, **37**, 2173–2191.
- Coste, B. (1987). Les sels nutritifs dans le bassin occidental de la Méditerranée. *Rapport Commission Internationale Mer Méditerranée*, **30**, 399–410.
- Crouzet, P., Leonard, J., Nixon, S. *et al.* (1999). *Nutrients in European Ecosystems*. EEA Environmental Assessment Report, Copenhagen.



- Crusius, J., Kroeger, K., Bratton, J. *et al.* (2008). N<sub>2</sub>O fluxes from coastal waters due to submarine groundwater discharge. *Geochimica et Cosmochimica Acta*, **72**, A191–A191, Suppl. 191.
- Cruzado, A. (1988). Eutrophication in the pelagic environment and its assessment. In: *Eutrophication in the Mediterranean Sea: Receiving Capacity and Monitoring of Long-term Effects*, UNESCO Reports in Marine Science, Paris, France, pp. 57–66.
- Cugier, P., Billen, G., Guillaud, J. F., Garnier, J. and Ménesguen, A. (2005). Modelling the eutrophication of the Seine Bight (France) under historical, present and future riverine nutrient loading. *Journal of Hydrology*, **304**, 381–396.
- Dahl, E., Bagoien, E., Edvardsen, B. and Stenseth, N. C. (2005). The dynamics of *Chrysochromulina* species in the Skagerrak in relation to environmental conditions. *Journal of Sea Research*, **54**, 15–24.
- Dalsgaard, T. (2003). Benthic primary production and nutrient cycling in sediments with benthic microalgae and transient accumulation of macroalgae. *Limnology and Oceanography*, **48**, 2138–2150.
- Danovaro, R. (2003). Pollution threats in the Mediterranean Sea: an overview. *Chemistry and Ecology*, **19**, 15–32.
- daNUbs (2005). *DaNUbs: Nutrient Management of the Danube Basin and its Impact on the Black Sea*. DaNUbs.
- Daskalov, G. M. (2002). Overfishing drives a trophic cascade in the Black Sea. *Marine Ecology Progress Series*, **225**, 53–63.
- de Wilde, H. P. J. and de Bie, M. J. M. (2000). Nitrous oxide in the Schelde estuary: production by nitrification and emission to the atmosphere. *Marine Chemistry*, **69**, 203–216.
- Degobbis, D. and Gilmartin, M. (1990). Nitrogen, phosphorus and biogenic silicon budgets for the Northern Adriatic Sea. *Oceanologica Acta*, **13**, 31–45.
- Dentener, F. *et al.* (2006). Nitrogen and sulfur deposition on regional and global scales: a multimodel evaluation. *Global Biogeochem. Cycles*, **20**.
- Dentsch, C., Sarmiento, J. L., Sigman, D. M., Gruber, N. and Dunne, J. P. (2007). Spatial coupling of nitrogen inputs and losses in the ocean. *Nature*, **445**, 163–167.
- Diaz, J. D. (2001). Overview of hypoxia around the world. *Journal of Environmental Quality*, **30**, 275–281.
- Diaz, R. J. and Rosenberg, R. (1995). Marine benthic hypoxia: a review of its ecological effects and the behavioural responses of benthic macrofauna. *Oceanography and Marine Biology*, **33**, 245–303.
- Diaz, R. J. and Rosenberg, R. (2008). Spreading dead zones and consequences for marine ecosystems. *Science*, **321**, 926–929.
- Dippner, J. W., Vuorinen, I., Daunys, D. *et al.* (2008). Climate-related marine ecosystem change. In: *Assessment of Climate Change for the Baltic Sea Basin*, ed. T. B. A. Team, Springer, New York, pp. 309–377.
- Dise, N. B., Ashmore, M., Belyazid, S. *et al.* (2011). Nitrogen as a threat to European terrestrial biodiversity. In: *The European Nitrogen Assessment*, ed. M. A. Sutton, C. M. Howard, J. W. Erisman *et al.* Cambridge University Press.
- Druon, J.-N., Schrimpf, W., Dobricic, S. and Stips, A. (2004). Comparative assessment of large-scale marine eutrophication: North Sea area and Adriatic Sea as case studies. *Marine Ecology Progress Series*, **272**, 1–23.
- Duarte, C. (1995). Submerged aquatic vegetation in relation to different nutrient regimes. *Ophelia*, **41**, 87–112.
- Duarte, C. M., Middelburg, J. and Caraco, N. (2005). Major role of marine vegetation on the oceanic carbon cycle. *Biogeosciences*, **2**, 1–8.
- Duce, R. A. *et al.* (1991). The atmospheric input of trace species to the world ocean. *Global Biogeochemical Cycles*, **5**, 193–259.
- Duce, R. A. *et al.* (2008). Impacts of atmospheric anthropogenic nitrogen on the open ocean. *Science*, **320**, 893–897.
- Dugdale, R. C. and Goering, J. J. (1967). Uptake of new and regenerated forms of nitrogen in primary productivity. *Limnology and Oceanography*, **12**, 196–206.
- Edvardsen, B., Moy, F. and Paasche, E. (1990). Hemolytic activity in extracts of *Chrysochromulina polylepis* grown at different levels of selenite and phosphate. In: *Physiological Ecology of Harmful Algal Blooms*, ed. E. Graneli, B. Sundstrom and L. Edler, Springer, Berlin, pp. 190–208.
- EEA (1999). *State and Pressures of the Marine and Coastal Mediterranean Environment*. Office for Official Publications of the European Communities, Luxembourg, Downloadable from reports.eea.europa.eu/medsea/en/medsea\_en.pdf
- EEA (2005). *Source Apportionment of Nitrogen and Phosphorus Inputs into the Aquatic Environment*. European Environment Agency, Copenhagen.
- Eilola, K. and Stigebrandt, A. (1999). On the seasonal nitrogen dynamics of Baltic proper biogeochemical reactor. *Journal of Marine Research*, **57**, 693–713.
- Emmerson, M. C., Solan, M., Paterson, D. M. and Raffaelli, D. (2001). Consistent patterns and the idiosyncratic effects of biodiversity in marine ecosystems. *Nature*, **411**, 73–77.
- Engel, A. (2002). Direct relationship between CO<sub>2</sub> uptake and transparent exopolymer particles production in natural phytoplankton. *Journal of Plankton Research*, **24**, 49–53.
- Engel, A., Goldthwait, S., Passow, U. and Alldredge, A. (2002). Temporal decoupling of carbon and nitrogen dynamics in a mesocosm diatom bloom. *Limnology and Oceanography*, **47**, 753–761.
- Engel, A., Delille, B., Jacquet, S. *et al.* (2004). Transparent exopolymer particles and dissolved organic carbon production by *Emiliania huxleyi* exposed to different CO<sub>2</sub> concentrations: a mesocosm experiment. *Aquatic Microbial Ecology*, **34**, 93–104.
- Estep, K. and MacIntyre, F. (1989). Taxonomy, life cycle, distribution and dasmotrophy of *Chrysochromulina*: a theory accounting for scales, haptonema, muciferous bodies and toxicity. *Marine Ecology Progress Series*, **57**, 11–21.
- EuroCat (2010). [www.cs.iaa.cnr.it/EUROCAT/project.htm](http://www.cs.iaa.cnr.it/EUROCAT/project.htm)
- Fleming-Lehtinen, V., Laamanen, M., Kuosa, H., Haahti, H. and Olsonen, R. (2008). Long-term development of inorganic nutrients and chlorophyll a in the open northern Baltic Sea. *Ambio*, **37**, 86–92.
- Follmi, K. B. (1996). The phosphorus cycle, phosphogenesis and marine phosphate-rich deposits. *Earth Sciences Reviews*, **40**, 55–124.
- Forster, S. and Zettler, M. L. (2004). The capacity of the filter-feeding bivalve *Mya arenaria* L. to affect water transport in sandy beds. *Marine Biology*, **144**, 1183–1189.
- Galloway, J. N. *et al.* (2004). Nitrogen cycles: past, present, and future. *Biogeochemistry*, **70**, 153–226.
- Galloway, J. N., Schlesinger, W. H., Levy, H., Michaels, A. and Schnoor, J. L. (1995). Nitrogen-fixation – anthropogenic enhancement – environmental response. *Global Biogeochemical Cycles*, **9**, 235–252.
- Garnier, J., Sfratore, A., Meybeck, M., Billen, G. and Dürr, H. (2006). Modelling silica transfer processes in river catchments. In: *The Silicon Cycle: Human Perturbations and Impacts on Aquatic Systems*, ed. V. Ittekkot *et al.*, Island Press, Washington DC, p. 296.
- Geider, R. J. and La Roche, J. (2002). Redfield revisited: variability of C:N:P in marine microalgae and its biochemical basis. *European Journal of Phycology*, **37**, 1–17.

- Grall, J. and Chauvaud, L. (2002). Marine eutrophication and benthos: the need for new approaches and concepts. *Global Change Biology*, **8**, 813–830.
- Graneli, E., Wallström, K., Arsson, U., Graneli, W. and Elmgren, R. (1990). Nutrient limitation of primary production in the Baltic Sea area. *Ambio*, **19**, 142–151.
- Gray, J. (1997). Marine Biodiversity: patterns, threats and conservation needs. *Biodiversity and Conservation*, **6**, 153–175.
- Gray, J., Shiu-sun Wu, R. and Or, Y. Y. (2002). Effects of hypoxia and organic enrichment on the coastal environment. *Marine Ecology Progress Series*, **238**, 249–279.
- Grizzetti, B., Bouraoui, F., Billen, G. *et al.* (2011). Nitrogen as a threat to European water quality. In: *The European Nitrogen Assessment*, ed. M. A. Sutton, C. M. Howard, J. W. Erisman *et al.* Cambridge University Press.
- Gruber, N. (2004). The dynamics of the marine nitrogen cycle and its influence on atmospheric CO<sub>2</sub> variations in carbon–climate interactions. In: *Carbon–Climate Interactions*, ed. M. Follows and T. Oguz, John Wiley & Sons, New York, pp. 1–47.
- Gruber, N. and Galloway, J. N. (2008). An Earth-system perspective of the global nitrogen cycle. *Nature*, **451**, 293–296.
- Guerzoni, S. *et al.* (1999). The role of atmospheric deposition in the biogeochemistry of the Mediterranean Sea. *Progress in Oceanography*, **44**, 147–190.
- Hannig, M., Lavik, G., Kuypers, M. M. M. *et al.* (2007). Shift from denitrification to anammox after inflow events in the central Baltic. *Limnology and Oceanography*, **53**, 1336–1345.
- Harrison, P. J., Hu, M. J., Yang, Y. P. and Lu, X. (1990). Phosphate limitation in estuarine and coastal waters of China. *Journal of Experimental Marine Biology and Ecology*, **140**, 79–87.
- Hashimoto, S., Gojo, K., Hikota, S., Sendai, N. and Otsuki, A. (1999). Nitrous oxide emissions from coastal waters in Tokyo Bay. *Marine Environmental Research*, **47**, 213–223.
- Heip, C. (1995). Eutrophication and zoobenthos dynamics. *Ophelia*, **41**, 113–136.
- HELCOM (1997). *Airborne Pollution Load to the Baltic Sea 1991–1995*.
- HELCOM (2002). Baltic Sea Environment Proceedings, Helsinki Commission. *Environment of the Baltic Sea area 1994–1998*. Baltic Sea Environment Proceedings, Helsinki Commission.
- HELCOM (2004). *The 4th Baltic Sea Pollution Load Compilation*. Baltic Sea Environment Proceedings, Helsinki Commission.
- HELCOM (2007). *Helcom Baltic Sea Action Plan*. [http://www.helcom.fi/BSAP/en\\_GB/intro/](http://www.helcom.fi/BSAP/en_GB/intro/).
- Herbert, R. A. (1999). Nitrogen cycling in coastal marine ecosystems. *Microbiology Reviews*, **23**, 563–590.
- Hietanen, S. and Lukkari, K. (2007). Effects of short-term anoxia on benthic denitrification, nutrient fluxes and phosphorus forms in coastal Baltic sediment. *Aquatic Microbial Ecology*, **49**, 293–302.
- Horrigan, S. G., Montoya, J. P., Nevins, J. L. and McCarthy, J. J. (1990). Natural isotopic composition of dissolved inorganic nitrogen in the Chesapeake Bay. *Estuarine, Coastal and Shelf Science*, **30**, 393–410.
- Howarth, R. W. and Marino, R. (2006). Nitrogen as the limiting nutrient for eutrophication in coastal marine ecosystems: evolving views over three decades. *Limnology and Oceanography*, **51**, 364–376.
- Hulth, S., Aller, R. C., Canfield, D. E. *et al.* (2004). Nitrogen removal in marine environments: recent findings and future research challenges. *Marine Chemistry*, **94**, 125–145.
- Humborg, C., Conley, D. J., Rahm, L. *et al.* (2000). Silicon retention in river basins: far-reaching effects on biogeochemistry and aquatic food webs in coastal marine environments. *Ambio*, **29**, 45–51.
- Humborg, C., Smedberg, E., RodriguezMedina, M. and Mörtz, C.-M. (2008). Changes in dissolved silicate loads to the Baltic Sea – The effects of lakes and reservoirs. *Journal of Marine Systems*, **73**, 223–235.
- Hutchins, D. A., Fu, F.-X., Zhang, Y. *et al.* (2007). CO<sub>2</sub> control of *Trichodesmium* N<sub>2</sub> fixation, photosynthesis, growth rates, and elemental ratios: implications for past, present and future ocean biogeochemistry. *Limnology and Oceanography*, **52**, 1293–1304.
- Huthnance, J. M. (1995). Circulation and water masses at the ocean margin: the role of physical processes at the shelf edge. *Progress in Oceanography*, **35**, 353.
- Hynes, R. K. and Knowles, R. (1984). Production of nitrous oxide by *Nitrosomonas europaea*: effects of acetylene, pH and oxygen. *Canadian Journal of Microbiology*, **30**, 1397–1404.
- IPCC (2007). *Climate Change 2007: The Physical Science Basis*. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel 25 on Climate Change. Cambridge University Press.
- Jickells, T. D. (1998). Nutrient biogeochemistry of the coastal zone. *Science*, **281**, 217–222.
- Jickells, T. D. (2006). The role of air–sea exchange in the marine nitrogen cycle. *Biogeosciences*, **3**, 271–280.
- Jickells, T. D. *et al.* (2005). Global iron connections between desert dust, ocean biogeochemistry and climate. *Science*, **308**, 67–71.
- Johansson, N. and Graneli, E. (1999). Cell density, chemical composition and toxicity of *Chrysochromulina polylepis* (Haptophyta) in relation to different N:P supply ratios. *Marine Biology*, **135**, 209–217.
- Johnson, M. T. *et al.* (2008). Field observations of the ocean–atmosphere exchange of ammonia: fundamental importance of temperature as revealed by a comparison of high and low latitudes. *Global Biogeochemical Cycles*, **22**.
- Jonsson, P., Carman, R. and Wulff, F. (1990). Laminated sediments in the Baltic: a tool for evaluating nutrient mass balances. *Ambio*, **19**, 152–158.
- Jorgensen, S. K., Jensen, H. B. and Sorensen, J. (1984). Nitrous oxide production from nitrification and denitrification in marine sediments at low oxygen concentrations. *Canadian Journal of Microbiology*, **30**, 1073–1078.
- Joye, S. B. and Hollibaugh, J. T. (1995). Influence of sulfide inhibition of nitrification on nitrogen regeneration in sediments. *Science*, **270**, 623–625.
- Justic, D., Rabalais, N. N., Turner, R. E. and Dortch, Q. (1995a). Changes in nutrient structure of river-dominated coastal waters: stoichiometric nutrient balance and its consequences. *Estuarine, Coastal and Shelf Science*, **40**, 339–356.
- Justic, D., Rabalais, N. N. and Turner, R. E. (1995b). Stoichiometric nutrient balance and origin of coastal eutrophication. *Marine Pollution Bulletin*, **30**, 41–46.
- Karlson, K., Bonsdorff, E. and Rosenberg, R. (2007). The impact of benthic macrofauna for nutrient fluxes from Baltic Sea sediments. *Ambio*, **36**, 161–167.
- Karlson, K., Rosenberg, R. and Bonsdorff, E. (2002). Temporal and spatial large-scale effects of eutrophication and oxygen deficiency on benthic fauna in Scandinavian and Baltic waters: a review. *Oceanography and Marine Biology*, **40**, 427–489.
- Kautsky, H. (1991). Influence of Eutrophication on the distribution of phyto-benthic plant and animal communities. *Internationale Revue der gesamten Hydrobiologie*, **76**, 423–432.
- Kemp, W. M., Sampou, P. A., Garber, J., Tuttle, J. and Boynton, W. R. (1992). Seasonal depletion of oxygen from bottom waters

- of Chesapeake Bay: roles of benthic and planktonic respiration and physical exchange processes. *Marine Ecology Progress Series*, **85**, 137–152.
- Koop, K., Boynton, W. R., Wulff, F. and Carman, R. (1990). Sediment-water oxygen and nutrient exchanges along a depth gradient in the Baltic Sea. *Marine Ecology Progress Series*, **63**, 65–77.
- Krause-Jensen, D., Sagert, S. and Schubert, H. C. B. (2008). Empirical relationships linking distribution and abundance of marine vegetation to eutrophication. *Ecological Indicators*, **8**, 515–529.
- Krishnamurthy, A., Moore, J. K., Zender, C. S. and Luo, C. (2007). Effects of atmospheric inorganic nitrogen deposition on ocean biogeochemistry. *Journal of Geophysical Research*, **112**.
- Krom, M. D., Brenner, S., Israilov, L. and Krumgalz, B. (1991a). Dissolved nutrients, preformed nutrients and calculated elemental ratios in the south-east Mediterranean Sea. *Oceanologica Acta*, **14**, 189–194.
- Krom, M. D., Kress, N., Brenner, S. and Gordon, L. (1991b). Phosphorus limitation of primary production in the eastern Mediterranean. *Limnology and Oceanography*, **36**, 424–432.
- Krom, M. D., Thingstad, T. F., Brenner, S. *et al.* (2005a). Summary and overview of the CYCLOPS P addition Lagrangian experiment in the Eastern Mediterranean. *Deep-Sea Research – Part II*, **52**, 3090–3108.
- Krom, M. D., Woodward, E. M. S., Herut, B. *et al.* (2005b). Nutrient cycling in the south east Levantine basin of the eastern Mediterranean: Results from a phosphorus starved system. *Deep-sea Research – Part II*, **52**, 2879–2896.
- Kronvang, B., Larsen, S. E., Jensen, J. P., Andersen, H. E. and Lo Porto, A. (2004). *Catchment Report: Enza, Italy – Trend Analysis, Retention and Source Apportionment*, EUROHARP report 4–2004, NIVA report SNO 4787–2004. Oslo, Norway.
- Kronvang, B., Larsen, S. E., Jensen, J. P., Andersen, H. E. and Reisser, H. (2005). *Catchment Report: Vilaine, France. Trend Analysis, Retention and Source Apportionment*. EUROHARP report 15–2005, NIVA report SNO 5081–2005. Oslo, Norway.
- Kuypers, M. M. M. *et al.* (2003). Anaerobic ammonium oxidation by anammox bacteria in the Black Sea. *Nature*, **422**, 608–611.
- Kuypers, M. M. M., Lavik, G. and Thamdrup, B. (2006). Anaerobic ammonium oxidation in the marine environment. In: *Past and Present Water Column Anoxia*, ed. L. N. Neretin, Springer, New York, pp. 311–335.
- Laakkonen, S. and Laurila, S. (2007). Changing environments or shifting paradigms? Strategic decision making toward water protection in Helsinki 1850–2000. *Ambio*, **36**, 212–219.
- LaguNET (2010). [www.dsa.unipr.it/lagunet/english/index.htm](http://www.dsa.unipr.it/lagunet/english/index.htm)
- Lam, P., Lavik, G., Jensen, M. M. *et al.* (2009). Revising the nitrogen cycle in the Peruvian oxygen minimum zone. *Proceedings of the National Academy of Sciences of the USA*, **106**, 4752–4757.
- Lancelot, C. (1995). The mucilage phenomenon in the continental coastal waters of the North Sea. *Science of the Total Environment*, **165**, 83–112.
- Lancelot, C., Billen, G., Sournia, A. *et al.* (1987). *Phaeocystis* blooms and nutrient enrichment in the continental coastal zones of the North Sea. *Ambio*, **16**, 38–46.
- Lancelot, C., Keller, M., Rousseau, V., Smith Jr, W. O. and Mathot, S. (1998). Autoecology of the Marine Haptophyte *Phaeocystis* sp. In: *Series G. Ecological Science – NATO Advanced Workshop on the Physiological Ecology of Harmful Algal Blooms*, ed. D. A. Anderson, A. M. Cembella and G. Hallegraeff, John Wiley & Sons, New York, pp. 209–224.
- Lancelot, C., Gypens, N., Billen, G., Garnier, J. and Roubeix, V. (2007). Testing an integrated river-ocean mathematical tool for linking marine eutrophication to land use: the *Phaeocystis*-dominated Belgian coastal zone (Southern North Sea) over the past 50 years. *Journal of Marine Systems*, **64**, 216–228.
- Lancelot, C., Rousseau, V. and Gypens, N. (2009). Ecologically based indicators for *Phaeocystis* disturbance in eutrophied Belgian coastal waters (Southern North Sea) based on field observations and ecological modeling. *Journal of Sea Research*, **61**, 44–49.
- Langmead, O., McQuatters-Gollop, A. and Mee, L. D. (2007). *European Lifestyles and Marine Ecosystems: Exploring Challenges for Managing Europe's Seas*. University of Plymouth Marine Institute, Plymouth, UK.
- Larsson, U., Elmgren, R. and Wulff, F. (1985). Eutrophication and the Baltic Sea. *Ambio*, **14**, 9–14.
- Levitan, O., Rosenberg, G., Setlik, I. *et al.* (2007). Elevated CO<sub>2</sub> enhances nitrogen fixation and growth in the marine cyanobacterium *Trichodesmium*. *Global Change Biology*, **13**, 531–538.
- Loÿe-Pilot, M. D., Martin, J. M. and Morelli, J. (2004). Atmospheric input of inorganic nitrogen to the Western Mediterranean. *Biogeochemistry*, **9**, 117–134.
- Loreau, M., Naem, S., Inchausti, P. *et al.* (2001). Biodiversity and ecosystem functioning: current knowledge and future challenge. *Science*, **294**, 804–808.
- Louanchi, F. and Najjar, R. G. (2000). A global monthly climatology of phosphate, nitrate, and silicate in the upper ocean: spring–summer export production and shallow remineralization. *Global Biogeochemical Cycles*, **14**, 957–977.
- Lucea, A., Duarte, C. M., Agusti, S. and Kennedy, H. (2005). Nutrient dynamics and ecosystem metabolism in the Bay of Blanes (NW Mediterranean). *Biogeochemistry*, **73**, 303–323.
- Lundberg, C. (2005). Conceptualizing the Baltic Sea ecosystem: an interdisciplinary tool for environmental decision making. *Ambio*, **34**, 433–439.
- Mackenzie, F. T., Ver, L. M. and Lerman, A. (2002). Century-scale nitrogen and phosphorus controls of the carbon cycle. *Chemical Geology*, **190**, 13–32.
- Maestrini, S. and Graneli, E. (1991). Environmental conditions and ecophysiological mechanisms which lead to the *Chrysochromulina* bloom: a hypothesis. *Oceanologica Acta*, **14**, 397–413.
- Mahowald, N. *et al.* (2008). The global distribution of atmospheric phosphorus deposition and anthropogenic impacts. *Global Biogeochemical Cycles*, **19**.
- Mahowald, N. M. *et al.* (2005). The atmospheric global dust cycle and iron inputs to the ocean. *Global Biogeochemical Cycles*, **19**.
- Maranger, R., Caraco, N., Duhamel, J. and Amyot, M. (2008). Nitrogen transfer from sea to land via commercial fisheries. *Nature Geoscience*, **2**, 111–113.
- Marchal, O., Monfray, P. and Bates, N. R. (1996). Spring–summer imbalance of dissolved inorganic carbon in the mixed layer of the northwestern Sargasso Sea. *Tellus*, **48B**, 115–134.
- Mari, X. (2008). Does ocean acidification induce an upward flux of marine aggregates? *Biogeosciences Discussion*, **5**, 1631–1654.
- McElroy, M. B. (1983). Marine biological controls on atmospheric CO<sub>2</sub> and climate. *Nature*, **302**, 328–329.
- McGill, D. A. (1969). A budget for dissolved nutrient salts in the Mediterranean Sea. *Cahiers Océanographiques*, **21**, 543–554.
- Mee, L. D. (2006). Reviving dead zones. *Scientific American*, **295**, 54–61.
- Mee, L. D., Friedrich, J. and Gomoiu, M.-T. (2005). Restoring the Black Sea in times of uncertainty. *Oceanography*, **18**, 32–43.
- Mermillod-Blondin, F., Rosenberg, R., Francois-Caraillet, F., Norling, K. and Mauclaire, L. (2004). Influence of bioturbation by three benthic infaunal species on microbial communities and

- biogeochemical processes in marine sediments. *Aquatic Microbial Ecology*, **36**, 271–284.
- Michaels, A. F., Bates, N. R., Buesseler, K. O., Carlson, C. A. and Knap, A. H. (1994). Carbon-cycle imbalance in the Sargasso Sea. *Nature*, **372**, 537–540.
- Middelburg, J. J. and Nieuwenhuize, J. (2001). Nitrogen isotope tracing of dissolved inorganic nitrogen behaviour in tidal estuaries. *Estuarine, Coastal and Shelf Science*, **53**, 385–391.
- Middelburg, J. J. and Soetaert, K. (2004). The role of sediments in shelf ecosystem dynamics. In: *The Sea*, ed. A. R. Robinson and K. H. Brink, Harvard University Press, Cambridge, MA, pp. 353–374.
- Middelburg, J. J., Soetaert, K., Herman, P. M. J. and Heip, C. H. R. (1996). Marine sedimentary denitrification: a model study. *Global Biogeochemical Cycles*, **10**, 661–673.
- Mills, M. M., Ridame, C., Davey, M., La Roche, J. and Geider, R. J. (2004). Iron and phosphorus co-limit nitrogen fixation in the eastern tropical North Atlantic. *Nature*, **429**, 292–294.
- Milovanovic, M. (2006). Water quality assessment and determination of pollution sources along the Axios/Vardar River, Southeastern Europe. *Desalination*, **213**, 159–173.
- Moncheva, S., Doncheva, V. and Kamburska, L. (2001). On the long-term response of harmful algal blooms to the evolution of eutrophication off the Bulgarian Black Sea coast: are the recent changes a sign of recovery of the ecosystem – the uncertainties. In: *Harmful Algal Blooms 2000*, ed. G. M. Hallegraeff, S. I. Blackburn, C. J. Bolch and R. J. Lewis, UNESCO, Paris, pp. 177–181.
- Montserrat Sala, M., Peters, F., Gasol, J. M. *et al.* (2002). Seasonal and spatial variations in the nutrient limitation of bacterioplankton growth in the northwestern Mediterranean. *Aquatic Microbial Ecology*, **27**, 47–56.
- Mulder, A., Van de Graaf, A. A., Robertson, L. A. and Kuenen, J. G. (1995). Anaerobic ammonium oxidation discovered in a denitrifying fluidized bed reactor. *FEMS Microbiology Ecology*, **16**, 177–184.
- Munda, I. A. (1993). Changes and degradation of seaweed stands in the Northern Adriatic. *Hydrobiologia*, **260/261**, 239–253.
- Munoz, I. and Prat, N. (1989). Effects of river regulation on the lower Ebro River, Northeast Spain. *Regulated Rivers: Research and Management*, **3**, 345–354.
- Nehring, D. and Matthäus, W. (1991). Current trends in hydrographic and chemical parameters and eutrophication in the Baltic Sea. *Internationale Revue der gesamten Hydrobiologie*, **76**, 297–316.
- Némery, J. and Garnier, J. (2007). Dynamics of Particulate Phosphorus in the Seine estuary (France). *Hydrobiologia*, **588**, 271–290.
- NSTF, Ducrot, J. P., Pawlak, J. and Wilson, S. (1994). *The 1993 Quality Status Report of the North Sea*. International Council for the Exploration of the Sea, Oslo and Paris.
- Nygaard, K. and Tobiesen, A. (1993). Bactivity in algae: a survival strategy during nutrient limitation. *Limnology and Oceanography*, **38**, 273–279.
- OAERRE (2010). [www.lifesciences.napier.ac.uk/OAERRE/index.htm](http://www.lifesciences.napier.ac.uk/OAERRE/index.htm)
- Officer, C. B. and Ryther, J. H. (1980). The possible importance of silicon in marine eutrophication. *Marine Ecology Progress Series*, **3**, 383–391.
- Olenin, S. (1997). Benthic zonation of the Eastern Gotland Basin. *Netherlands Journal of Aquatic Ecology*, **30**, 265–282.
- OSPAR, Pastch, J. and Radach, G. (2005). Long-term simulation of the eutrophication of the North Sea: temporal development of nutrients, chlorophyll and primary production in comparison to observations. *Journal of Sea Research*, **38**, 275–310.
- Österblom, H. O., Hansson, S., Larsson, U. *et al.* (2007). Human-induced trophic cascades and ecological regime shifts in the Baltic Sea. *Ecosystems*, **10**, 877–889.
- Pace, M. L., Cole, J. J., Carpenter, S. R. and Kitchell, J. F. (1999). Trophic cascades revealed in diverse ecosystems. *Trends in Ecology and Evolution*, **14**, 483–488.
- Paerl, H. W. and Whittall, D. R. (1999). Anthropogenically-derived atmospheric nitrogen deposition, marine eutrophication and harmful algal bloom expansion: is there a link? *Ambio*, **28**, 307–311.
- Patricio, J., Ulanowicz, R., Pardal, M. A. and Marques, J. C. (2004). Ascendency as an ecological indicator: a case study of estuarine pulse eutrophication. *Estuarine, Coastal and Shelf Science*, **60**, 23–35.
- Paytan, A. and McLaughlin, K. (2007). The oceanic phosphorus cycle. *Chemical Reviews*, **107**, 563–576.
- Pitkänen, H., Lehtoranta, J. and Räike, A. (2001). Internal nutrient fluxes counteract decreases in external load: the case of the estuarial eastern Gulf of Finland, Baltic Sea. *Ambio*, **30**, 195–201.
- Pont, D. (1996). *Evaluation des charges polluantes du Rhône à la Méditerranée: Synthèse et Recommandations*. Agence de l'Eau Rhône-Méditerranée-Corse, Lyon, France.
- Pranovi, F., Da Ponte, F. and Torricelli, P. (2008). Historical changes in the structure and functioning of the benthic community in the lagoon of Venice. *Estuarine, Coastal and Shelf Science*, **76**, 753–764.
- Rabalais, N. (2002). Nitrogen in aquatic ecosystems. *Ambio*, **31**, 102–112.
- Radach, G. (1992). Ecosystem functioning in the German Bight under continental nutrient inputs by rivers. *Estuaries*, **15**, 477–496.
- Radach, G. and Pätsch, J. (1997). Climatological annual cycles of nutrients and chlorophyll in the North Sea. *Journal of Sea Research*, **38**, 231–248.
- Radach, G. and Pätsch, J. (2007). Variability of continental riverine freshwater and nutrient inputs into the North Sea for the years 1977–2000 and its consequences for the assessment of eutrophication. *Estuaries and Coasts*, **30**, 66–81, 10.1007/BF02782968.
- Raes, F. *et al.* (2000). Formation and cycling of aerosols in the global troposphere. *Atmospheric Environment*, **34**, 4215–4240.
- Raffaelli, D. G., Emmerson, M., Solan, M., Biles, C. and Paterson, D. (2003). Biodiversity and ecosystem processes in shallow coastal waters: an experimental approach. *Journal of Sea Research*, **49**, 133–141.
- Rahm, L. *et al.* (2000). Nitrogen fixation in the Baltic proper: an empirical study. *Journal of Marine Systems*, **25**, 239–248.
- REMPEC (2008). Study of maritime traffic flows in the Mediterranean Sea.
- Rendell, A. R., Ottley, C. J., Jickells, T. D. and Harrison, R. M. (1993). The atmospheric input of nitrogen species to the North Sea. *Tellus*, **45B**, 53–63.
- Riebesell, U. (2004). Effects of CO<sub>2</sub> enrichment on marine phytoplanktons. *Journal of Oceanography*, **60**, 719–729.
- Rönner, U. and Sörensen, F. (1985). Nitrogen transformation in the Baltic proper: denitrification counteracts eutrophication. *Ambio*, **14**, 134–138.
- Roubeix, V. and Lancelot, C. (2008). Effect of salinity on growth, cell size and silicification of an euryhaline freshwater diatom, *Cyclotella meneghiniana*, Kütz. *Transitional Water Bulletin*, **1**, 31–38.
- Rousseau, V., Leynaert, A., Daoud, N. and Lancelot, C. (2002). Diatom succession, silicification and silicic acid availability in Belgian

- coastal waters (Southern North Sea). *Marine Ecology Progress Series*, **236**, 61–73.
- Rousseau, V., Breton, E., De Wachter, B. *et al.* (2004). Identification of Belgian maritime zones affected by eutrophication (IZEUT). Towards the establishment of ecological criteria for the implementation of the OSPAR Common Procedure to combat eutrophication. *Belgian Science Policy Publications*, 77.
- Russell, K. M., Keene, W. C., Maben, J. R., Galloway, J. N. and Moody, J. L. (2003). Phase partitioning and dry deposition of atmospheric nitrogen at the mid-Atlantic U.S. coast. *Journal of Geophysical Research*, **108**, 1–1–1–16, doi:10.1029/2003JD003736.
- Ruttenberg, K. C. (2003). *The Global Phosphorus Cycle*. Elsevier, New York.
- Ruttenberg, K. C. and Berner, R. A. (1993). Authigenic apatite formation and burial in sediments from non-upwelling continental margins. *Geochimica et Cosmochimica Acta*, **57**, 991–1007.
- Sambrotto, R. N., Savidge, G., Robinson, C. *et al.* (1993). Elevated consumption of carbon relative to nitrogen in the surface ocean. *Nature*, **363**, 248–250.
- Sandroni, V., Raimbault, P., Migon, C. and Garcia, N. E. G. (2007). Dry atmospheric deposition and diazotrophy as sources of new nitrogen to northwestern Mediterranean oligotrophic surface waters. *Deep-Sea Research – Part I*, **54**, 1859–1870.
- Sanudo-Wilhelmy, S. A., Kusta, A. B., Gobler, C. J. *et al.* (2001). Phosphorus limitation of nitrogen fixation by *Trichodesmium* in the central Atlantic ocean. *Nature*, **411**, 55–59.
- Schartau, M., Engel, A., Schröder, J. *et al.* (2007). Modelling carbon overconsumption and the formation of extracellular particulate organic carbon. *Biogeosciences*, **4**, 433–454.
- Schenau, S. J. and de Lange, G. J. (2000). A novel chemical method to quantify fish debris in marine sediments. *Limnology and Oceanography*, **45**, 963–971.
- Schmidt, I., Sliemers, A. O., Schmid, M. *et al.* (2002). Aerobic and anaerobic ammonia oxidizing bacteria: competitors or natural partners? *FEMS Microbiology Ecology*, **39**, 175–181.
- Schneider, B., Engel, A. and Schlitzer, R. (2004). Effects of depth- and CO<sub>2</sub>-dependent C:N ratios of particulate organic matter (POM) on the marine carbon cycle. *Global Biogeochemical Cycles*, **18**, 1–13.
- Schneider, B. *et al.* (2003). The surface water CO<sub>2</sub> budget for the Baltic Proper: a new way to determine nitrogen fixation. *Journal of Marine Systems*, **42**, 53–64.
- Seinfeld, J. H. and Pandis, S. N. (1998). *Atmospheric Chemistry and Physics: from Air Pollution to Climate Change*. Wiley-Interscience, New York.
- Seitzinger, S. P. and Sanders, R. W. (1997). Contribution of dissolved organic nitrogen from rivers to estuarine eutrophication. *Marine Ecology Progress Series*, **159**, 1–12.
- Seitzinger, S. P. and Sanders, R. W. (1999). Atmospheric inputs of dissolved organic nitrogen stimulate estuarine bacteria and phytoplankton. *Limnology and Oceanography*, **44**, 721–730.
- Seitzinger, S. P., Harrison, J. A., Dumont, E., Beusen, A. H. W. and Bouwman, A. F. (2005). Sources and delivery of carbon, nitrogen, and phosphorus to the coastal zone: an overview of Global Nutrient Export from Watersheds (NEWS) models and their application. *Global Biogeochemical Cycles*, **19**, 1–11.
- Seitzinger, S., Harrison, J. A., Böhlke, J. K. *et al.* (2006). Denitrification across landscapes and waterscapes: a synthesis. *Ecological Applications*, **16**, 2064–2090.
- Shaffer, G. and Rönner, U. (1984). Denitrification in the Baltic Proper deep water. *Deep-Sea Research – Part I*, **31**, 197–220.
- Shiganova, T. A. and Bulgakova, Y. V. (2000). Effects of gelatinous plankton on Black Sea and Sea of Azov fish and their food resources. *ICES Journal of Marine Science*, **57**, 641–648.
- Skliris, N. and Lascaratos, A. (2004). Impacts of the Nile River damming on the thermohaline circulation and water mass characteristics of the Mediterranean Sea. *Journal of Marine Systems*, **52**, 121–143.
- Slopp, C. P., Epping, E. H. G., Helder, W. and van Raaphorst, W. (1996). A key role for iron-bound phosphorus in authigenic apatite formation in North Atlantic continental platform sediments. *Journal of Marine Research*, **54**, 1179–1205.
- Slopp, C. P., Malschaert, J. F. P. and van Raaphorst, W. (1998). The role of sorption in sediment-water exchange of phosphate in North Sea continental margin sediments. *Limnology and Oceanography*, **43**, 832–846.
- Slopp, C. P. and Van Cappellen, P. (2004). Nutrient inputs to the coastal ocean through submarine groundwater discharge: controls and potential impact. *Journal of Hydrology*, **295**, 64–86.
- Smith, S. V. and Hollibaugh, J. T. (1989). Carbon controlled nitrogen cycling in a marine “macrocosm”: an ecosystem scale model for managing coastal eutrophication. *Marine Ecology Progress Series*, **52**, 103–109.
- Souchu, P., Gasc, A., Collos, Y. *et al.* (1998). Biogeochemical aspects of bottom anoxia in a Mediterranean lagoon (Thau, France). *Marine Ecology Progress Series*, **164**, 135–146.
- Souvermezoglou, E. (1988). Comparaison de la distribution et du bilan d'échanges des sels nutritifs et du carbone inorganique en Méditerranée et en Mer Rouge. *Oceanologica Acta*, **SI9** 103–109.
- Souvermezoglou, E., Hatzigeorgiou, E., Pampidis, I. and Siapsali, K. (1992). Distribution and seasonal variability of nutrients and dissolved oxygen in the northeastern Ionian Sea. *Oceanologica Acta*, **15**, 585–594.
- Spokes, L. J. and Jickells, T. D. (2005). Is the atmosphere really an important source of reactive nitrogen to coastal waters? *Continental Shelf Research*, **25**, 2022–2035.
- Sterner, R. W., Andersen, T., Elser, J. J. *et al.* (2008). Scale-dependent carbon : nitrogen : phosphorus seston stoichiometry in marine and freshwaters. *Limnology and Oceanography*, **53**, 1169–1180.
- Stigebrandt, A. and Gustaffson, B. G. (2007). Improvement of Baltic Proper water quality using large-scale ecological engineering. *Ambio*, **36**, 280–286.
- Sundbäck, K. and McGlathery, K. (2005). Interactions between benthic macroalgal and microalgal mats. In: *Interactions between Macro- and Microorganisms in Marine Sediments*, ed. E. Kristensen, R. R. Haese and J. E. Kostka, American Geophysical Union, Washington DC, pp. 7–29.
- Tamminen, T. and Andersen, T. (2007). Seasonal phytoplankton nutrient limitation patterns as revealed by bioassays over Baltic Sea gradients of salinity and eutrophication. *Marine Ecology Progress Series*, **340**, 121–138.
- Tartari, G., Milan, C. and Felli, M. (1991). *Idrochimica dei nutrienti. Quaderni Istituto di Ricerca Sulle Acque*, **92**, 1–29.
- Taylor, G. T., Iabichella, M., Ho, T. -Y. *et al.* (2001). Chemoautotrophy in the redox transition zone of the Cariaco Basin: a significant mid-water source of organic carbon production. *Limnology and Oceanography*, **46**, 148–163.
- Tett, P., Gilpin, L., Svendsen, H. *et al.* (2003). Eutrophication and some European waters of restricted exchange. *Continental Shelf Research*, **23**, 1635–1671.
- Thamdrup, B. and Dalsgaard, T. (2002). Production of N<sub>2</sub> through anaerobic ammonium oxidation coupled to nitrate reduction

- in marine sediments. *Applied and Environmental Microbiology*, **68**, 1312–1318.
- Thomas, H. and Schneider, B. (1999). The seasonal cycle of carbon dioxide in Baltic Sea surface waters. *Journal of Marine Systems*, **22**, 53–67.
- Thompson, R. C., Crowe, T. P. and Hawkins, S. (2002). Rocky intertidal communities: past environmental changes, present status and predictions for the next 25 years. *Environmental Conservation*, **29**, 168–191.
- Toggweiler, J. R. (1993). Carbon overconsumption. *Nature*, **363**, 210–211.
- Tuominen, L., Heinänen, A., Kuparinen, J. and Nielsen, L. P. (1998). Spatial and temporal variability of denitrification in the sediments of the northern Baltic Proper. *Marine Ecology Progress Series*, **172**, 13–24.
- Turner, R. E., Qureshi, N. A., Rabalais, N. N. *et al.* (1998). Fluctuating silicate:nitrate ratios and coastal plankton food webs. *Proceedings of the National Academy of Sciences of the USA*, **95**, 13048–13050.
- Turner, R. E. and Rabalais, N. N. (1994). Evidence for coastal eutrophication near the Mississippi River Delta. *Nature*, **368**, 619–621.
- Turner, R. E., Rabalais, N. N., Justic, D. and Dortch, Q. (2003). Global patterns of dissolved N, P and Si in large rivers. *Biogeochemistry*, **64**, 297–317.
- Twomey, L. J., Piehler, M. F. and Paerl, H. W. (2005). Phytoplankton uptake of ammonium, nitrate and urea in the Neuse River estuary, NC, USA. *Hydrobiologia*, **533**, 123–134.
- Tyrrell, T. (1999). The relative influences of nitrogen and phosphorus on oceanic primary production. *Nature*, **400**, 525–531.
- UNEP-MAP (2003). *Riverine Transport of Water, Sediments and Pollutants to the Mediterranean Sea*, MAP Technical Series no. 141.
- UNEP-MAP/RAC/CP (2004). *Guidelines for the Application of Best Environmental Practices (BEPs) for the Rational Use of Fertilizers and the Reduction of Nutrient Loss from Agriculture for the Mediterranean Region*, MAP Technical Series no. 143.
- UNEP/FAO/WHO (1996). *Assessment of the state of eutrophication in the Mediterranean Sea*, MAP Technical Series no. 106.
- European Union (1991). *Nitrates Directive*. Directive 91/676/EEC.
- Usher, C. R., Michel, A. E. and Grassian, V. H. (2003). Reactions on mineral dust. *Chemical Reviews*, **103**, 4883–4939.
- Vahtera, E., Conley, D. J., Gustafsson, B. G. *et al.* (2007). Internal ecosystem feedbacks enhance nitrogen-fixing cyanobacteria blooms and complicate management in the Baltic Sea. *Ambio*, **36**, 186–194.
- Vaquer, R. C. D. (2008). Thresholds of hypoxia for marine biodiversity. *Proceedings of the National Academy of Sciences of the USA*, **105**, 15452–15457.
- Veldhuis, M. J. W. and Admiraal, W. (1987). Influence of phosphate depletion on the growth and colony formation of *Phaeocystis pouchetii*. *Marine Biology*, **95**, 47–54.
- Veldhuis, M. J. W., Colijn, F. and Admiraal, W. (1991). Phosphate utilization in *Phaeocystis pouchetii* (Haptophyceae). *Marine Ecology Progress Series*, **12**, 53–62.
- Vitousek, P. M., Mooney, H. A., Lubchenko, J. and Melillo, J. M. (1997). Human domination of Earth's ecosystems. *Science*, **277**, 494–499.
- Vogt, H. and Schramm, W. (1991). Conspicuous decline of fucus in Kiel Bay (Western Baltic): what are the causes? *Marine Ecology Progress Series*, **69**, 1105–1118.
- Voss, M., Emeis, K. C., Hille, S., Neumann, T. and Dippner, J. W. (2005). Nitrogen cycle of the Baltic Sea from an isotopic perspective. *Global Biogeochemical Cycles*, **19**, 1–16.
- Waldbusser, G. G. and Marinelli, R. L. (2006). Macrofaunal modification of porewater advection: role of species function, species interaction, and kinetics. *Marine Ecology Progress Series*, **311**, 217–231.
- Walsh, J. J. (1991). Importance of continental margins in the marine biogeochemical cycling of carbon and nitrogen. *Nature*, **350**, 53–55.
- Ward, B. B., Devol, A. H., Rich, J. J. *et al.* (2009). Denitrification as the dominant nitrogen loss process in the Arabian Sea. *Nature*, **461**, 78–82.
- Wasmund, N., Voss, M. and Lochte, K. (2001). Evidence of nitrogen fixation by non-heterocystous cyanobacteria in the Baltic Sea and re-calculation of a budget of nitrogen fixation. *Marine Ecology Progress Series*, **214**, 1–14.
- Weisse, T., Tande, K., Verity, P., Hansen, F. and Gieskes, W. W. C. (1994). The trophic significance of *Phaeocystis* blooms. *Journal of Marine Systems*, **5**, 67–79.
- Westberry, T. K. and Siegel, D. A. (2006). Spatial and temporal distribution of *Trichodesmium* blooms in the world's oceans. *Global Biogeochemical Cycles*, **20**.
- Wu, R. S. S. (2002). Hypoxia: from molecular responses to ecosystem responses. *Marine Pollution Bulletin*, **45**, 35–45.
- Yilmaz, A. and Tugrul, S. (1998). The effect of cold- and warm-core eddies on the distribution and stoichiometry of dissolved nutrients in the northeastern Mediterranean. *Journal of Marine Systems*, **16**, 253–268.
- Zaitsev, Y. and Mamaev, V. O. (1997). Biological diversity in the Black Sea: a study of change and decline. *Black Sea Environmental Series*, **3**, 208.
- Zhang, Y., Zheng, L., Liu, X. *et al.* (2008). Evidence for organic N deposition and its anthropogenic sources in China. *Atmospheric Environment*, **42**, 1035–1041.