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Nitrate in Coastal Waters

CONTRIBUTED BY CANDACE A. OVIATT AND
ARTHUR J. GOLD, UNIVERSITY OF RHODE ISLAND

Much of the nitrogen that gets into streams and rivers ends up in the sea, where it remains a potent source of controversy, particularly in the estuaries and bays in which rivers meet the ocean. Chapter 1 detailed the enormous increase in the use of nitrogen fertilizer since 1900. This has been accompanied by large increases in the deposition of nitrogen oxides generated by traffic and industry and, as a result of this human activity, the quantity of nitrogen circulating in the global nitrogen cycle has doubled since pre-industrial times. Rivers now contribute twice as much nitrogen to marine waters as they did 100 years ago (Vitousek *et al.*, 1997). Eutrophication is therefore a problem in marine as well as in fresh waters. It has caused startling changes in the growth of aquatic plants and algae in coastal waters (Nixon, 1995). The excessive algal growth in particular has destroyed critical aquatic habitats and lowered the concentration of dissolved oxygen, thereby killing fish and shifting the balance between marine organisms (Howarth *et al.*, 2000). This eutrophication threatens the long-term sustainability of fisheries and the use of coastal waters for recreation.

This chapter introduces the environmental consequences of the enrichment of marine waters by plant nutrients, particularly nitrogen (Table 8.1), together with the principal concepts needed to understand it and the methods used to study it. It reviews the evidence implicating nitrogen in the fouling of marine waters and presents several case studies of large marine ecosystems. These studies, of the Baltic Sea, the Gulf of Mexico and the open waters of the Pacific, provide a warning against assuming that any single factor can explain all the complexities and intricacies of marine waters.

Table 8.1. Responses of aquatic ecosystems to eutrophication.

Increased biomass of phytoplankton and suspended and attached algae.
Decreased transparency of water column.
Shift in phytoplankton composition to bloom-forming species, some of which may be toxic.
Accumulation of carbon within the system.
Changes in vascular plant production and species composition.
Decrease in living aquatic habitats, including seagrasses and coral reefs.
Depletion in deep-water oxygen concentration, resulting in hypoxia.
Changes in species and production of fish.
Decline in aesthetic values.

Consequences of Eutrophication of Coastal Waters

Stratification and oxygen depletion

Two levels of oxygen depletion are defined for marine studies. Either can arise from enrichment of coastal waters with plant nutrients:

- Hypoxia, defined as when the supply of oxygen is low.
- Anoxia, which implies there is no oxygen supply at all.

Hypoxia resulting from eutrophication has caused widespread damage to fisheries ranging from Chesapeake Bay and the Gulf of Mexico in North America to the Baltic and Black Seas in Europe (Howarth *et al.*, 2000). Oxygen depletion occurs, as it does in fresh water, as an after-effect of the stimulation of algal growth by a supply of nutrients in the water. Large algal blooms fix carbon dioxide from the atmosphere and increase the organic biomass in the water. (Biomass is simply the mass of living material.) These algae increase the oxygen concentration in the water while they are photosynthesizing during active growth, but the microorganisms that decompose them when they die consume oxygen. The resulting oxygen demand can be a problem for the whole ecosystem.

This is a particular problem in stratified aquatic systems that are isolated from the oxygen in the atmosphere. Summer stratification occurs in freshwater lakes deeper than 3–5 m when the upper water layers absorb heat from the sun and become warmer and therefore less dense than the water at the bottom of the lake. When this stratification occurs, a layer with a steep temperature gradient known as the *thermocline* effectively isolates the water at the bottom and prevents oxygen from diffusing from the atmosphere to the water beneath the thermocline (Wetzel, 2001). Estuarine systems have a related problem. When fresh water from the river meets salt water coming in from the ocean, a layer of low-salinity water floats above a layer of denser saline water. This, combined with the temperature gradient, gives rise to a steep density gradient known as the *pycnocline*, which also prevents oxygen from diffusing from the atmosphere to the water at the bottom. The combination of the pycnocline and decomposing algal biomass settling to the bottom can cause severe oxygen depletion in the water at the bottom.

Changes in species composition

Enrichment with plant nutrients may favour the metabolic processes of one set of organisms at the expense of another, allowing the favoured organisms to grow more rapidly and dominate the ecosystem. It can therefore alter the species composition and the biodiversity, ultimately affecting the structure and food web of the whole ecosystem. In estuaries and bays, eutrophication has been linked to harmful algal blooms described as 'red tides' that can kill many fish and other marine organisms (Vitousek *et al.*, 1997; Howarth *et al.*, 2000).

Seagrass destruction

Patches of seagrass form important spawning and nursery habitats for fish and other marine organisms in shallow estuaries. The rates of seagrass destruction rival those of tropical forests and its loss causes serious problems in the Baltic Sea, the Gulf of Mexico and in estuaries along the east coast of the USA. The survival and growth of seagrass depend on the amount of light that can penetrate through to it (Howarth *et al.*, 2000). Increasing the supply of nitrogen in the water decreases the penetration of light to the surface of the seagrass leaf by stimulating the growth of two undesirable types of species: phytoplankton (floating algae) in the water above the seagrass and epiphytes (attached algae) growing directly on seagrass leaves (Fig. 8.1).

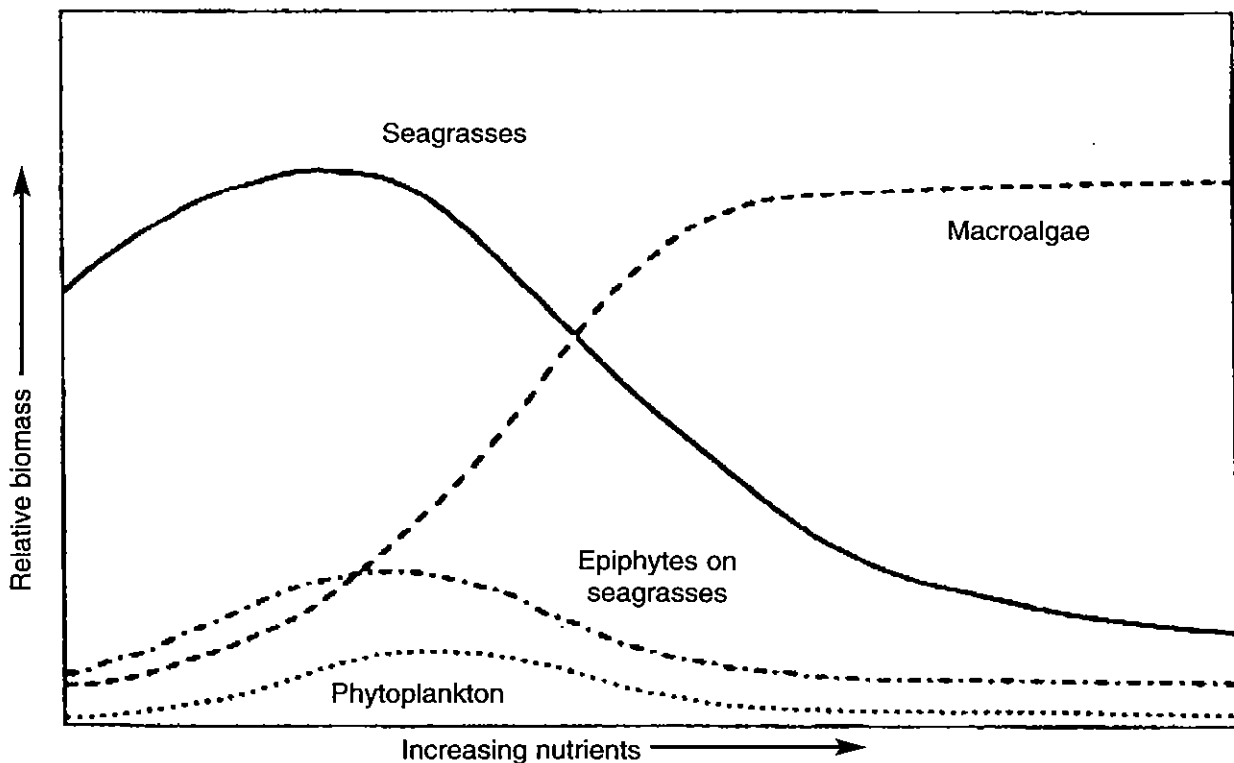


Fig. 8.1. Effect of nitrate with other nutrients in shallow marine systems. Decline in seagrass beds with increase in other species. (Redrawn from Harlin, 1995.)

Seagrass is important not just as a spawning habitat, but also because it stabilizes sediments on the bottom. Its loss therefore increases suspended sediment in the water, further decreasing water clarity and hastening the loss of submerged aquatic vegetation. To restore the habitat of the seagrass, we need to control the supply of nitrogen in the water.

Eutrophication can also stimulate troublesome blooms of *benthic macroalgae*, or 'green seaweeds' that require less light than seagrass (Fig. 8.1). The macroalgae form thick extensive mats over seagrass beds and the sediment surface, thereby decreasing spawning habitats, especially for fish that need mineral substrates to spawn. The macroalgae die off periodically, and their decay depletes oxygen and kills some fish. They also leave an unpleasant accumulation of rotting remains along the shoreline.

Degradation of corals

Coral reefs are among the most productive ecosystems on the planet, but they thrive best in sea water that is entirely clear and has very small concentrations of plant nutrients. Nutrient enrichment is therefore a threat to them, and both nitrogen and phosphate are involved. Only slight enrichment of coral reefs is needed to stimulate the growth of macroalgae, which attach themselves to the reef and inhibit the propagation of the coral. Periodic blooms of the macroalgae also cause hypoxia in the reef environment. Degradation of coral reefs by plant nutrients is a global problem, and examples are reported from the Great Barrier Reef, the Caribbean and Hawaii.

Principles of Nutrient Enrichment in Coastal Waters

The effects of nutrient enrichment in fresh water were discussed in Chapter 7. The work of the early researchers Liebig, Brandt and Redfield on plant nutrients in fresh water is also relevant to coastal and marine waters (e.g. Smith, 1998).

Which nutrient limits the growth of unwanted biomass in coastal waters?

The concept of the limiting nutrient – that is, that one nutrient limits the growth of biomass in an ecosystem – suggests that we should be able to manage aquatic systems by controlling a single limiting nutrient (Smith, 1998). We saw in Chapter 7 that there is plenty of evidence that in fresh water this nutrient is phosphate, but in many coastal marine systems the limiting nutrient is usually nitrogen (Howarth *et al.*, 2000). We need to consider carbon too, but this is rarely limiting, being readily available from the atmosphere. Aquatic ecosystems, particularly estuarine systems, are notoriously complex, and these insights came only after extensive

experimentation and vigorous debate. The literature shows that some issues remain unresolved. To understand this important difference between freshwater and marine systems, we need to understand the cycles of the two nutrients.

Differences between the phosphorus and nitrogen cycles

Nitrogen and phosphorus are both brought into aquatic systems in both soluble and particulate forms, but the two nutrients subsequently undergo markedly different processes. Biological processes have a large effect on the supply of nitrogen available for biomass production in aquatic systems. Blue-green algae (cyanobacteria) fix nitrogen from the atmosphere, so adding it to the water. Nitrogen as nitrate is lost from the water when denitrifying bacteria reduce the nitrate to gaseous nitrous oxide and dinitrogen. Nitrogen can accumulate in bottom sediments, but remains vulnerable to loss in gaseous form, which reduces the potential for mineral nitrogen (ammonium and nitrate) to be released from the sediments.

The behaviour of phosphorus contrasts with that of nitrogen in that biological processes neither introduce phosphorus nor remove it from an aquatic ecosystem. The quantity of phosphorus in a water body is controlled solely by chemical and physical factors. Rivers are the primary source of phosphorus for marine ecosystems, and the amount of phosphorus in a river depends on its geochemistry and oxygen concentration and on physical factors such as residence time and dilution.

Influence of nutrient cycles on eutrophication in fresh and marine waters

We saw in Chapter 7 that a principal factor determining whether nitrogen or phosphorus is the limiting nutrient in an aquatic ecosystem is the ratio of nitrogen to phosphorus. Redfield suggested that if the N:P atomic ratio was smaller than 16:1 nitrogen might be the limiting nutrient, and if it was greater phosphorus might be. Why does the ratio tend to be more than 16:1 in lakes and less than 16:1 in coastal waters? One reason is simply that the sources of water for lakes and coastal systems differ. Both receive inputs of water from the land and from the atmosphere, but coastal systems also receive inputs from the ocean, and the water from the ocean tends to have low N:P ratios because of denitrification on the continental shelf. Another reason is that blue-green algae seem to fix less nitrogen in estuarine waters than they do in lakes (where the blooms they form are often a considerable problem).

The final reason lies in differences in geochemistry between the two water systems. In freshwater systems, phosphate tends to react with iron and settle into sediments in which it becomes unavailable to plants or microorganisms. In sea water, anions such as hydroxyl, sulphate and borate

compete for sites on particles, and their concentrations are orders of magnitude greater than that of phosphate. As a result, particles carried in water from land tend to release the phosphate they are holding when the water transporting them mixes with water in a marine system (Froelich, 1988). Sulphate concentrations in particular are very large in marine waters and iron seems to sorb sulphate in preference to phosphate. Fresh water usually contains small concentrations of sulphate, so that iron sorbs more phosphate in fresh than in sea water.

The conclusion that phosphorus is the limiting nutrient in fresh water but nitrogen in sea water seems generally applicable but should not be regarded as invariant.

Experimental Methods for Marine Systems

Assessing the limiting nutrient – another scale problem

The problem of scale, which we encountered on land in Chapter 5, emerges again when we take to the sea (or at least to its fringes). Nutrient enrichment and the responses to it involve processes and responses occurring within individual components of the ecosystem. We can study these individual processes and responses, often perhaps in a relatively small volume. We might, for example, use laboratory assays to study the responses of specific algae to particular nutrients. But many of the processes interact with each other, and serious errors will result from simply aggregating the individual processes. As in the soil, so in the marine ecosystem, the whole is much more than the sum of the parts.

For example, those laboratory bioassays for the response of specific algae to particular nutrients give useful information on which nutrients limit growth, but simple experiments such as these may fail to take account of important processes such as the regeneration of nutrients from sediments or factors such as locations and substrates for nitrogen fixation. To address the complexity of the marine ecosystem, we need to use a 'whole system' approach in our experiments. In practice, however, questions of logistics, cost, replicability and time usually restrict the scope of the experiment to the simplest 'whole system' capable of answering the question posed.

Whole system studies are not necessarily on a large scale. What is essential is to have an experimental unit that incorporates all the critical processes and factors that characterize the natural system under study. According to the nature of this system, the study may be made in a *microcosm* (commonly a test tube), a *mesocosm* (a large tank or bag) or a homogeneous patch of open ocean. Given the complexity of the ecosystem and the concern about interactions between processes, would it be better to study entire bays and estuaries? The problem with this idea is that experiments of this nature tend to run into problems with uncontrolled boundaries and unknown interactions. Also, data may have to be collected in rough seas and high winds or with a recalcitrant crew – problems unfamiliar to scientists working on land.

Whole system experiments in aquatic ecosystems

Soil scientists will be interested to learn that aquatic scientists trace the origin of their whole system studies back to the long-term experiments begun by Lawes and Gilbert at Rothamsted that were described in Chapter 1. These whole system studies aim to make experiments on bodies of water that can be isolated from dilution and contamination during the course of the study, but are subjected to the critical environmental conditions of the ecosystem under study.

Some of the earliest aquatic studies were concerned with phytoplankton metabolism and were made in bottles. In an experiment in Massachusetts in the 1920s, water from a reservoir was placed in either dark or clear bottles and incubated in the water so that respiration and photosynthesis could be measured simultaneously. This study established the basis for methods still in use today and which are described in detail below. Working from the Plymouth Laboratory in the UK in 1922, Aikens hung water bottles in the English Channel and measured the decrease in phosphate concentrations, from which he estimated the amount of biomass produced in the water. He also employed a new colorimetric technique for measuring phosphate that allowed important new insights into nutrient depletion during short periods of time (Mills, 1989).

Large floating bags and spheres became available in the 1960s and 1970s. These enabled large volumes of water, 10 m³ or more, to be isolated and subjected to the natural variations of climate and temperature, thereby giving further insights into nutrient and population dynamics. Kiel towers, which were widely used in the western part of the Baltic Sea, modified the floating bag concept by attaching the bag to undisturbed natural sediment, enabling interactions between plankton and sediment to be studied.

There is no magic formula for designing whole system experiments, nor can any design, scale or statistical test be said to be optimal. But successful whole system experiments all meet three conditions:

- The experiment is not dominated by any artefact.
- There is enough replication to detect change.
- All the natural components and processes that control the system have been incorporated.

These conditions are not easily satisfied, and failure to meet them has compromised many studies.

Microcosms: Trade-offs between Size and Replicability

Where there is a need for replication, perhaps due to variability in a natural process, experimental volumes often have to be small and they are accommodated in microcosms. Bottles provide small microcosms that often work well, better perhaps than their reputation suggests. They have been used to determine which nutrient limits plankton metabolism by measuring oxygen

use in dark and clear (or light) bottles and tracing the fate of ^{14}C -labelled carbon dioxide. The oxygen measurement in the dark bottle estimates respiration from the decrease in oxygen, while that in the light bottle estimates the net production of phytoplankton from the increase in oxygen. The sum of the two is the gross production.

The experimental procedure is essentially to add each nutrient to its set of replicated microcosms, and find which one gives the largest changes in oxygen. Until recently, the method was restricted to fairly productive systems because oxygen could not be measured sufficiently precisely to detect the small changes in its concentration that were found in systems with low productivity such as pristine lakes and the open ocean. The carbon-14 technique has frequently been used in these low-productivity systems because of its sensitivity, but it does not measure respiration and, according to the length of the incubation, it gives a measurement that lies between net and gross production of phytoplankton.

Bottles have been popular but they have attracted a cautionary large literature about their use. The concerns raised include:

- Artefacts from bacterial growth on their walls during longer incubations.
- Leaching of nutrients or toxic material from the glass or the plastic of which the bottle is made.
- Exclusion of ultraviolet radiation.
- Size effects.
- Grazing effects.

Perhaps the most important concern is that the size of the bottle may exclude processes that are important to the system (Hecky and Kilham, 1988). But bottles have played an important part in research because they are cheap, readily replicated and have simple logistics.

Mesocosms: Optimizing Size and Replicability

Mesocosms may comprise large tanks or bags or even exclusion towers extending from the sea floor to the surface. They provide a more comprehensive description of the complexity of the system at the expense of increased cost and some loss of replicability, but they do not avoid all problems. Artefacts, particularly the wall effects noted with bottles, can confound the experimenter's intentions more than lack of replicability. Growth on walls out-competes growth in the water unless it is controlled.

Sediments have to be considered for some nutrients but the way they are included can introduce artefacts. For the Kiel towers, for example, the bags were attached to the otherwise undisturbed sediment. But this apparently reasonable approach failed because differences in pressure between the inside and the outside of the bags forced water through the sediments and into bags, thereby altering the waterborne concentrations of nutrients and other ions (Smetacek *et al.*, 1982). Researchers sometimes seem to be so concerned about artefacts that they pay more attention to the

artefact than to the ecological problem that was the reason for the research facility.

Another serious problem is that the financial resources and engineering skills used to establish large structures in coastal areas can occasionally be wasted because the structures have a short lifetime in the stormy conditions that prevail in such areas. Despite all these difficulties, research facilities at Loch Ewe, Kiel and CEPEX, and in Maryland, Rhode Island, Florida, New Hampshire, Norway, The Netherlands and other centres, have improved the understanding of nutrient dynamics in coastal waters.

The MERL Facility

The Marine Ecosystems Research Laboratory (MERL) at Narragansett, Rhode Island, has mesocosms that were designed to sustain natural processes at a size at which repeated sampling would not have a detrimental impact. There is a set of 14 tanks, each more than 5 m deep, and each tank is filled with 13 m³ of natural sea water and a 37 cm depth of undisturbed sediment (Fig. 8.2). The tanks have precise controls that enable them to mimic many of the natural processes that control primary production in an estuary. These processes include light penetration, the residence time of the water, temperature, tidal mixing and inputs and exports of water. The mesocosms have proved very useful for investigating the following:

- The dynamics of nutrients in estuaries and the rates of their uptake by phytoplankton.
- Grazing.
- Sedimentation and sediment diagenesis.
- Nitrogen fixation, denitrification and nitrogen cycling under different regimes.

The mesocosms enable processes in both the water and in the sediment to be studied, and dozens of characteristics of both can be sampled repeatedly for more than a year. Seasonal cycles can thus be investigated thoroughly without compromising the integrity of the mesocosm as an ecosystem.

The MERL experimenters expended considerable effort to make sure that artefacts such as growth on the walls were minimized and natural processes dominated the system. Walls were cleaned on a regular schedule to avoid excessive growth. Not all problems could be eliminated. For example, rates of vertical mixing exceeded those in natural systems. But the tanks provided simplified replicated systems that could be sampled on a seasonal or annual basis.

A simple whole system experiment with added nutrients in the mesocosms at MERL established that nitrogen could be the nutrient that limited productivity in estuaries (Oviatt *et al.*, 1995). The treatments were:

- Control – no nutrients added.
- Nitrogen.

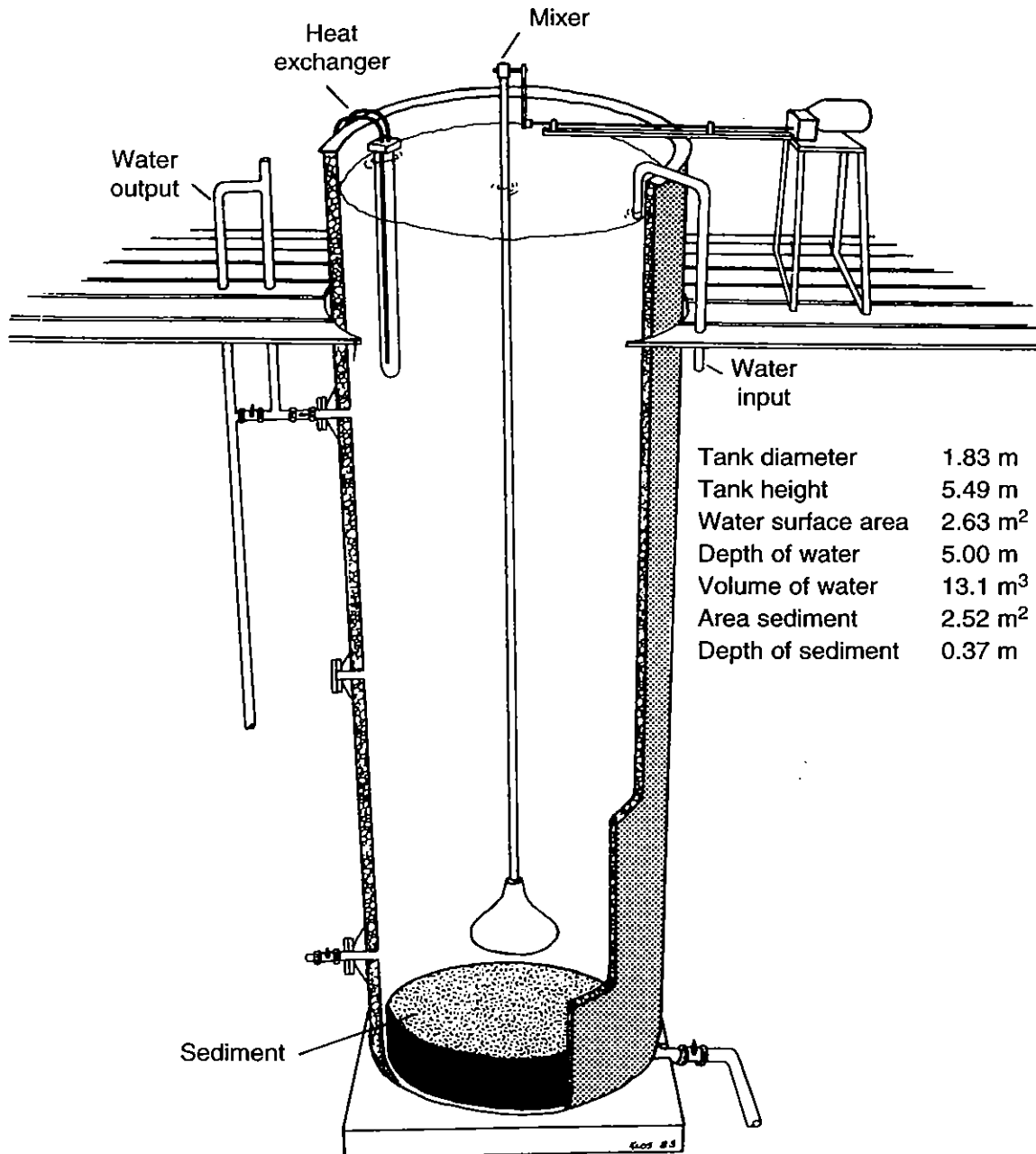


Fig. 8.2. A Marine Ecosystems Research Laboratory (MERL) mesocosm and its input and output pipes, mixer, sediment container and heat exchanger. The mesocosm is made of fibreglass-reinforced resin, and the walls are white to maximize the reflection of sunlight. Sea water is fed in a pulsed flow of 10 l/min for 12 min every 6 h and its temperature is controlled by the heat exchangers. It is mixed by the plunger, 50 cm in diameter, which moves up and down over 60 cm at 5 cycles/min for 2 in every 6 h. (Courtesy of the University of Rhode Island.)

- Phosphorus.
- Nitrogen+phosphorus.

Phytoplankton biomass and metabolism were about five times greater in the nitrogen and nitrogen+phosphorus treatments than in the control and

phosphorus treatments. The phosphorus treatment differed little from the control. Furthermore, rates of denitrification exceeded those of nitrogen fixation in the control and phosphorus treatments, emphasizing the nitrogen limitation in those treatments (Oviatt *et al.*, 1995).

A more elaborate experiment at MERL examined nutrient limitation and the processes controlling it along a gradient in salinity extending from fresh water (0 g/l of dissolved ions) to saline water (25 g/l of dissolved ions) (Doering *et al.*, 1995). Bioassays, nutrient concentrations and N:P ratios all showed that phosphorus was the limiting nutrient when the salinity was low but that nitrogen was limiting at 25 g/l. Examining nutrient effects over the whole range of salinity suggested that solubility of phosphorus dictated the switch in limiting nutrient.

Whole ecosystem studies and long-term field monitoring

Why not test hypotheses about limiting nutrients at the ecosystem scale – on whole lakes, bays or harbours? This would provide the ultimate whole system study, with all the processes, interactions and feedbacks of natural ecosystems. But, even if society and particularly environmental pressure groups were to accept the risk to such ecosystems, there remains the problem that studies of this kind cannot be subjected to the normal scientific regime of controls and replication. There would be no way of separating treatment effects from those of variation. It is probably worth accepting this limitation if the effect found is large enough to leave little doubt, as was the case with the lake studied by Schindler (1974). This study, discussed in the previous chapter, had a decisive effect in persuading decision makers that phosphate was the nutrient that limited algal blooms in fresh water (Smith, 1998).

Whether such a study is needed in a coastal water ecosystem is questionable, given the evidence already discussed and the case studies discussed below.

Case Studies: Eutrophication of Large Coastal Estuarine and Marine Systems

Intensive studies on a number of large coastal ecosystems have inevitably highlighted both similarities and differences in the responses of the systems to enrichment with nutrients. In this section we summarize the results – and key questions – that have emerged from the dedicated, long-term efforts of the many scientific teams who have worked in the Gulf of Mexico, Chesapeake Bay, San Francisco Bay and the Baltic Sea. Each of these ecosystems has unique attributes that illustrate the dynamic and complex nature of such systems. Each also shows how we need to assess the current condition of the system and the options for managing it in the light of its natural patterns and historic behaviour.

Gulf of Mexico

The detection of a large and expanding hypoxic zone at the outlet of the Mississippi River to the Gulf of Mexico has stimulated great interest in the effect on marine ecosystems of nitrogen lost from the land. The hypoxia has been linked to nutrients carried in the Mississippi from farms in the mid-western states of the USA all the way to the Gulf.

The zone of hypoxia, in which the concentration of oxygen in the water is 2 mg/l or less, covers more than 20,000 km² of water at the bottom of the Gulf. The seasonal development of the zone, its size and duration, and its causes and impacts, have been studied by Rabelais and her co-workers since 1985 (Rabelais and Turner, 2001). The worsening hypoxia has been attributed to increases in farming activity in the Mississippi catchment, and this has led to considerable ecological and economic debate, because that catchment covers 41% of the main part of the USA (excluding Alaska and Hawaii).

The hypoxia in the water develops in late spring and persists until late summer (Rabelais and Turner, 2001). First the water stratifies as described above, isolating the water at the bottom. This happens because the surface water warms in spring and the wind and its mixing effect decline. This stratification is enhanced by the greater flow of less dense water from the Mississippi in spring. The flow peaks between March and May and is low during summer and autumn. The spring flow in particular carries nutrients that stimulate blooms of phytoplankton. The organic matter from these blooms sinks, either directly or as faecal pellets from grazers, to the water beneath the pycnocline where it adds considerably to the oxygen demand.

Hypoxia in the Gulf of Mexico is not a new phenomenon. It has been increasing since about 1900, but the concern has arisen because of the rapid expansion of the problem in recent decades. Palaeo-oceanographers have found that organisms characteristic of well-oxygenated water were common between 1700 and 1900 but disappeared completely from the sediment record in the early 1900s (Sen Gupta *et al.*, 1996). The area in which the bottom water was hypoxic in midsummer was around 8000–9000 km² between 1986 and 1992. By the period 1992–2000, the extent of the hypoxia had increased to 16,000–20,000 km² (Rabelais and Turner, 2001). Hypoxic water is found typically between 5 and 30 m beneath the surface along near-shore to along deep-shelf locations, west of where the Mississippi flows into the Gulf. During early investigations the hypoxia seemed to develop in spots associated with the deltas, but it is now more uniformly distributed to the west of the deltas.

The extent of the hypoxic zone increases in years when the river is in flood and carries a large load of nutrients and decreases when the water flow and nutrient flux are lessened by drought. Indicators of annual phytoplankton production show that it is of the order of 300 g/m², and during the past 50 years this production has been correlated with the amount of dissolved inorganic nitrogen in the river.

During recent years, the Mississippi has discharged 1.6 Mt of nitrogen

into the Gulf of Mexico each year, of which about two-thirds was nitrate and one-third organic nitrogen (Goolsby *et al.*, 1999). The mean annual concentration of nitrate was relatively constant between 1905 and 1950 but had doubled by the 1990s (Rabelais and Turner, 2001). There was an equally dramatic change in the silicate concentration, which halved between the 1950s and the 1990s. This could be a significant change because silicate is a key nutrient for diatoms, a common type of algae in the Gulf. If the supply of silicate limits the growth of diatoms, non-siliceous algae could become more plentiful. This could alter the foundations of the food chain and have a serious impact on the ecosystem of the Gulf. There does not seem to be a problem yet. In the 1990s, the atomic ratios for N:Si, N:P and Si:P were 1.1:1, 15:1 and 14:1, close to the values established by Redfield (Justic *et al.*, 1995). The ratios for silicon remain appropriate for the production of diatoms at present, while the N:P ratio shows a tendency towards nitrogen limitation.

The impacts of the nutrient enrichment and the hypoxia on fish and crustaceans in the Gulf have not yet been well quantified, but there are signs of some negative impacts. Analyses of trawl data suggest that bottom-dwelling species avoid not only specifically hypoxic bottom water but also areas in which the concentration of dissolved oxygen is between 2 and 5 mg/l (Craig *et al.*, 2001). Brown shrimp also seem to avoid hypoxic water. Zimmerman and Nance (2001) found that the catch of brown shrimp was significantly and negatively related to the area of hypoxia during July and August. There is little indication that mobile species are killed by the hypoxia – they just change their distribution to avoid it.

These changes from the traditional distribution of fish stocks can affect commercial fisheries. Poor catches of menhaden in 1995, for example, may have resulted from hypoxia in near-shore waters off Louisiana during late July and August (Smith, 2001). Species such as clams that cannot move fare less well and have declined in numbers in response to the hypoxia. The recovery in the communities of such organisms may take up to 2 years following a hypoxic event (Rabelais *et al.*, 2001; Rosenberg *et al.*, 2002).

Chesapeake Bay

Chesapeake Bay, the largest and most productive estuary on the east coast of the USA, has also suffered increased hypoxia in bottom waters during recent decades. Several states have cooperated in efforts to curtail the input to the bay of nitrogen in waste water, and oyster reefs have been promoted as a means of cleansing the overlying water by natural filtration.

The pattern of development of the hypoxia is similar to that in the Gulf of Mexico. Spring runoff in the Susquehanna River creates a pycnocline and stratifies the main stem of the bay, isolating the water at the bottom (Cerco, 2000). A phytoplankton bloom usually begins in February and ends in May. Its size depends on the quantity and nutrient concentration of the water in the river. Much of this bloom sinks beneath the pycnocline, increasing oxygen demand in the bottom water and leading to anoxia.

Hypoxia in the bottom water begins in late May, with large rates of respiration in the organic matter under the pycnocline. Later, the autumn winds break the stratification down and mix the hypoxic with aerobic surface water. Flemer *et al.* (1983) concluded that the volume of anoxic water in Chesapeake Bay had increased by an order of magnitude between 1959 and 1980, but this conclusion proved controversial and there were doubts as to whether the evidence available was sufficient to support it (Cerco, 2000). Further studies, including stratigraphy of the sediments and long-term monitoring, have led to the general conclusion that the volume of hypoxic water depends on the amounts of water and nutrients flowing into the bay each year.

The nutrient that limits the phytoplankton bloom may switch between seasons, from phosphorus in early spring, when the river flow is high, to nitrogen in summer, when the river flow is much smaller (D'Elia *et al.*, 1986). All studies, however much they may disagree otherwise, suggest that the river is the main source of nutrients, both nitrogen and phosphorus, into the bay.

During the 1960s and 1970s, the extent of seagrass meadows in Chesapeake Bay decreased dramatically, stimulating investigations (Orth and Moore, 1983) into possible causes such as turbidity, nutrients and herbicides in the flow from the river. The eventual consensus was that increases in nutrients of agricultural origin in the river had stimulated phytoplankton blooms which shaded out the eelgrass. But the issue is not as simple as this, because of other changes. A few decades ago, the number of oysters in the bay was sufficient to filter the entire bay every few days, but by the 1990s the oysters had become so scarce that they could barely filter the bay in a year (Newell, 1988). The absence of the oysters would also have allowed the blooms to proliferate and prevent light from reaching the seagrass meadows.

San Francisco Bay

The studies in San Francisco Bay illustrate further the importance of filter feeders in controlling eutrophication (Officer *et al.*, 1982). Benthic bivalves, such as mussels and cockles, restrict phytoplankton to small amounts during summer and autumn by filtering them out of the water as fast as they grow despite large nutrient concentrations in the water and abundant light. But during spring, stratification isolates the surface water from the bottom-dwelling bivalves allowing a bloom to develop. Over shoals the phytoplankton biomass may peak in June giving concentrations of chlorophyll of more than 35 $\mu\text{g}/\text{l}$, but during late summer and autumn, these concentrations fall to less than 10 $\mu\text{g}/\text{l}$. Averaging nutrient concentrations over several years shows a low N:P ratio, suggesting that nitrogen is the limiting nutrient in the bay (Hammond *et al.*, 1985).

Large nutrient concentrations are supported in the bay by inputs of sewage effluent, and these should support a high level of primary produc-

tivity, but rates of net production measured in the South Bay are relatively small (Cloern, 1999). This is because the potentially large production of phytoplankton is controlled by a large population of benthic filter feeders. The size of this population is a result of the inadvertent introduction to the South Bay of several large, exotic and fecund species, including the Japanese cockle (*Japes japonica*) and the Japanese mussel (*Muscular senhonsia*) (Nichols, 1979).

The Baltic Sea

The Baltic Sea has since the 1960s experienced increasing inputs of sewage and nutrients from agriculture that have led to worsening hypoxia or even anoxia in the bottom waters (Elmgren, 2001). Concentrations of nutrients during winter increased from the 1960s to the 1980s, since when they have more or less levelled off. A fourfold increase in the concentration of nitrogen and an eightfold increase in that of phosphorus have been correlated with increasing oxygen depletion of the deep Baltic. But the oxygen depletion has also corresponded with changes in the period of stagnation of the bottom waters, and the involvement of stagnation suggests that episodes of oxygen depletion could on a historic scale have been related to natural climate variability. As in other eutrophic areas, increased organic matter production in surface waters has led to an increase in oxygen demand in bottom waters.

The Baltic is not very saline compared with other large seas, with 6–8 g/l salinity in surface waters, depending on ice-melt and rainfall. There is a strong density discontinuity between the surface water and the deep water in which the salinity ranges from 13 to 20 g/l. The bottom water derives from irregular inflows coming from the Kattegat through the Danish Straights. These erratic inflows can result in periods of stagnation lasting from 2 to 4 years and occasionally up to 16 years (Elmgren, 2001). During the longer periods the deep waters may become hypoxic.

The management of nutrient inputs to the Baltic Sea has led to the question of whether nitrogen or phosphorus is the more important nutrient to remove from sewage effluent. Experience with lakes and a Redfield N:P ratio of 44:1 initially suggested phosphorus was the limiting nutrient (Elmgren and Larsson, 2001) but growth experiments in the 1970s suggested that nitrogen limited phytoplankton production. The latter experiments were not entirely conclusive (Graneli *et al.*, 1990). The spring bloom appeared to be limited by nitrogen, but the brackish Baltic waters experience summer blooms of nitrogen-fixing cyanobacteria. These summer blooms may be limited by phosphorus or even iron. The current management solution is to remove both nitrogen and phosphorus.

The Open Ocean

Until recently, nobody knew which nutrients limited production in the deep oceans, but nitrogen and phosphorus were assumed to do so. Two recent experiments have, however, revealed a more complex situation. In the first, Chisholm and Morel (1991) showed that iron was the nutrient that limited production in large areas of the Pacific Ocean. And the second set, the US Joint Global Ocean Flux Study (Buesseler, 2001), comprised a decade-long time series of measurements in the north subtropical gyres (large-scale counter-clockwise current circulation patterns) of the Atlantic and Pacific Oceans. These showed that iron played a critical role in production in the Pacific but that production was limited mainly by phosphate in the Atlantic.

Ocean patch studies

The study of nutrient dynamics in the open ocean has been accelerated recently by the use of ocean patches for experiments with added nutrients. An ocean patch comprises a large area of homogeneous water that is defined by the addition of conservative tracers. The patches are often as large as 8 km² in area but mix minimally with the surrounding water for weeks at a time, even while moving distances of up to 1000 km. A research vessel distributes tonnes of nutrients on to the patch and then follows it and measures the growth of phytoplankton. Such studies require great skill and dedication, particularly when made in the rigours of the Southern Ocean surrounding Antarctica. But the experimenters nevertheless relate the concept of whole system studies like these back to Broadbalk and the other experiments begun by Lawes and Gilbert in the peace of the English countryside.

Ocean patch studies – conclusive results

Some regions of the Pacific and Southern Oceans are characterized by large nutrient concentrations but small concentrations of chlorophyll (from phytoplankton, etc.). Experiments in replicated bottles suggested that iron was the limiting nutrient in these regions, but the bottles were suspected of having excluded critical processes, and the diatoms they contained were thought to be an artefact because they were so rare in nature. The bottles could have excluded grazing organisms that maintain small populations of diatoms in nature.

Martin and Fitzwater (1988) were the first to develop clean techniques that enabled trace metals to be determined accurately in sea water. The concentrations of iron they found where nutrients were plentiful but chlorophyll scarce were of the order of a picomole (10^{-12} M), leading them to suspect that iron was the limiting factor for primary production. Martin and

his co-workers made incubations in bottles in the Pacific sub-Arctic, the tropical Pacific and the Southern Ocean which showed in all three regions that adding iron in nanomolar concentrations stimulated diatom blooms. Then, faced with continuing scepticism about bottle experiments, they made iron fertilization experiments in patches of open ocean which showed that the diatoms grew as long as the iron was present. Grazing and similar processes did not control the growth of phytoplankton. It is worth noting that the simple bottle experiments had correctly predicted the results of the patch experiments, and seemed therefore to have incorporated all the essential natural processes that controlled the diatoms.

The first two fertilized patch experiments were made in the tropical Pacific and a third was made by other workers in the Southern Ocean (Martin *et al.*, 1994; Coale *et al.*, 1996; Boyd *et al.*, 2000). All showed iron to stimulate primary production, causing originally scarce diatoms to bloom. The first experimental patch was dragged beneath the surface by currents after 4 days and the iron disappeared rapidly, resulting in only a minor bloom. During the second experiment, iron infusions were added for several days and resulted in a major bloom (Frost, 1996). The experiment in the Southern Ocean also led to a major bloom, but an attempt to measure sinking organic matter was not successful because of the mixing processes occurring at the time (Boyd *et al.*, 2000).

The ocean patch experiments were a turning point in the debate about the limiting nutrient for primary production in the open ocean. Their decisive impact in establishing the critical role of iron in the Pacific and Southern Oceans compares with the impact of the whole-lake nutrient addition experiments in establishing that phosphorus was the limiting nutrient for eutrophication in fresh water.

Differences between the Atlantic and Pacific Oceans

The ocean patch experiments provided insights into crucial differences between the Atlantic and Pacific Oceans in the role of phosphorus in primary productivity. Wu *et al.* (2000) recently showed in a time-series experiment that phosphorus concentrations were 100 to 200 times greater at a Pacific station near Hawaii than they were at an Atlantic station near Bermuda. Iron is probably the key to this difference. The Atlantic receives a generous supply of iron-containing dust in winds blowing from the Sahara but the Pacific receives very little. If iron limited diatom blooms in the Pacific, it probably also limited bacterial growth and processes, including nitrogen fixation, so phosphorus concentrations were greater in the Pacific than in the Atlantic. Rates of nitrogen fixation in the iron-rich Atlantic Ocean (~ 72 mmol N/m² per year) are about double those in the Pacific (31–51 mmol N/m² per year) and it is phosphorus that becomes the limiting nutrient.

Iron limitation in the ocean and global warming

Iron limitation of primary production in a major part of the world's ocean has implications for the regulation of carbon dioxide in the atmosphere (Martin and Fitzwalter, 1988). These authors suggested that, during the dry windy climate of the last glaciation, dust containing iron was deposited in the ocean, where it stimulated production of phytoplankton. This decreased the concentration of carbon dioxide in the atmosphere, a process summarized as the 'biological pump'. The quantities of dust and iron in ice cores from the Antarctic support this hypothesis, as do proxy concentrations for silicate from diatoms in sediment from the Southern Ocean (Falkowski *et al.*, 1998). But the ocean patch experiments have not yet been able to quantify the efficiency of the 'biological pump' in sequestering carbon from the atmosphere into primary production which, when it dies, falls to the bottom of the ocean.

The conclusion from this chapter has to be that, as with so many natural systems, it is unwise to generalize about the waters of the sea without adequate information. In the context of the book we need to note that nitrogen is the nutrient that limits primary production in coastal and estuarine waters off the Atlantic and Pacific coasts of the USA. But there seems to be no evidence that nitrogen limits production in the open waters of the Pacific Ocean, which are probably iron-limited, or the subtropical waters of the Atlantic, which may be limited by phosphorus. The Baltic Sea is the most enclosed of the systems discussed and suffers severe eutrophication for which nitrogen and phosphorus seem to share the responsibility.