Ocean deoxygenation: Everyone's problem

Causes, impacts, consequences and solutions

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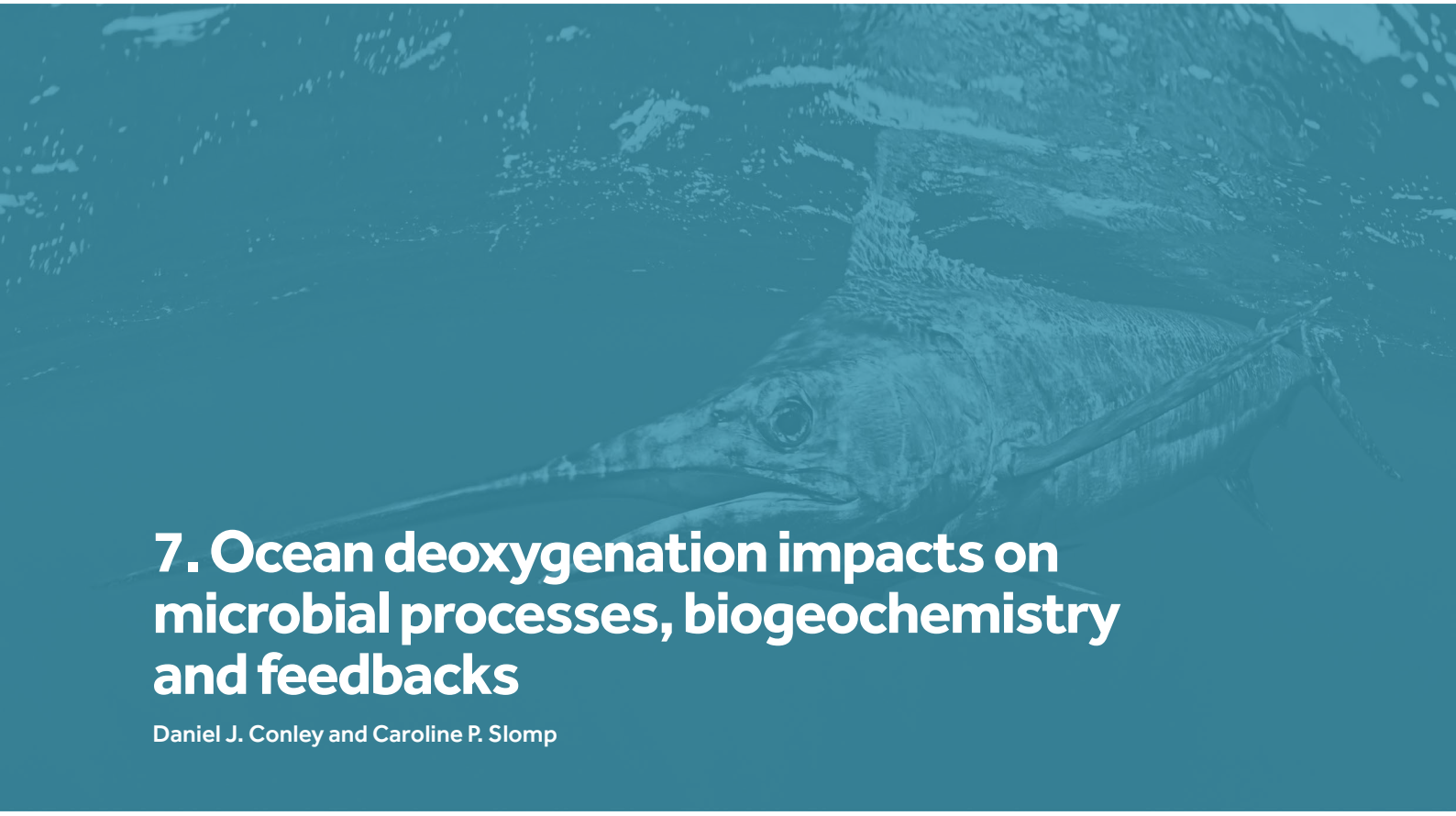
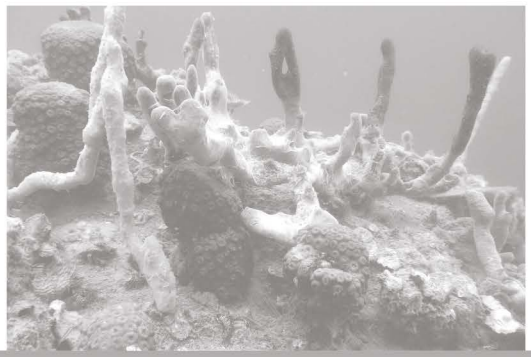


7. Ocean deoxygenation impacts on microbial processes, biogeochemistry and feedbacks

Daniel J. Conley and Caroline P. Slomp



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Ocean deoxygenation impacts on microbial processes, biogeochemistry and feedbacks

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Summary

- Ocean deoxygenation strongly impacts the rates and pathways of the breakdown of organic matter. The associated reactions dramatically change the sources, sinks and cycling of a range of important elements in the environment. This occurs especially for the biologically important elements such as nitrogen (N), phosphorus (P) and iron (Fe), but also for the production of carbon (C) and gases that contribute to Earth's warming by the greenhouse effect such as nitrous oxide (N_2O) and methane (CH_4).
- Increased oxygen loss in coastal waters is mostly caused by enhanced nutrient inputs from fertilizer and wastewater from land, which stimulate phytoplankton blooms. At the end of such blooms, phytoplankton sink to the sea floor where they degrade and thereby remove oxygen. The degradation of organic matter can increase the acidity of coastal waters and may enhance the release of methane from the sea floor. Global warming may exacerbate loss of oxygen from and methane release to coastal waters.
- Oxygen minimum zones (OMZs) in the ocean are well known for playing an essential role in the global nitrogen cycle, in which various chemical species such as ammonium, nitrite, nitrate, nitrous oxide, and nitrogen gas participate, and different bacterial processes are involved in transformations from one chemical species to another. Substantial nitrogen losses are observed in OMZs and they account for approximately 10% of global denitrification. OMZs also are responsible for a large fraction of the oceanic nitrous oxide emission to the atmosphere, which is a powerful greenhouse gas. With global warming, OMZs are projected to significantly expand, leading to alterations in the oceanic nitrogen balance and enhanced oceanic nitrous oxide emissions, further exacerbating warming of the Earth.
- The recycling of phosphorus (P) in marine systems is enhanced when oxygen in sea water is low. The resulting increased availability of phosphorous can further enhance productivity and, upon sinking of the organic matter, enhance the oxygen demand in deeper waters. This positive feedback-loop between productivity, oxygen loss and increased P availability can contribute to further deoxygenation.

- Sediments of continental margins can act as a source of the trace nutrient iron (Fe) to waters in adjacent open ocean areas. This sediment release of iron responds non-linearly to ocean deoxygenation and is at a maximum when oxygen concentrations near the sea floor are low and sulphide is not present. This implies that ocean deoxygenation may initially enhance iron availability for primary producers, followed by a decline in iron availability when waters become sulphidic.
- The Baltic Sea and Black Sea are the world's largest enclosed low oxygen marine ecosystems. While the deep basin of the Black Sea is naturally anoxic, the low oxygen conditions currently observed in the Baltic Sea have been caused by human activities and are the result of enhanced nutrient inputs from land, exacerbated by global warming.
- Understanding coupled element cycles and their links to oxygen can strengthen our ability to predict and manage the impacts of climate change.

Ocean hypoxia effect	Potential consequences
Decreasing oxygen concentrations will change biogeochemical cycles that alter the productivity of coastal and ocean ecosystems.	• Changes the cycling of different elements. • Enhanced P recycling. • Reduced N losses. • Enhanced Fe availability (initially).
Decreasing oxygen concentrations will increase greenhouse gas emission.	• Increased methane release. • Increased N_2O release.
Enhanced sequestration of organic matter under low oxygen conditions will leave a legacy of carbon and nutrients in the sediments.	• Organic matter degradation in sediments. continues to consume oxygen. • Nutrients (N, P) can be recycled. • Creates delays in recovery of ecosystems.

7.1 Introduction

Ocean deoxygenation not only impacts bottom-living organisms (Levin, 2017; Vaquer-Sunyer & Duarte, 2008) and fish communities but also alters the biogeochemical cycles of many elements. The concentrations of oxygen affect the rates and pathways of the breakdown of organic matter and the associated reactions dramatically change the sources, sinks and cycling of a range of important elements in the environment. This is true especially for the biologically important elements such as nitrogen (N), phosphorus (P) and iron (Fe), but also for the production of carbon (C) and N-bearing gases that contribute to Earth's warming by the greenhouse effect such as nitrous oxide (N_2O), and methane (CH_4). Here, we identify some of the most important biogeochemical changes in the cycling of elements with deoxygenation, how biogeochemical processes have changed through time, and the consequences for ecosystems and society. Finally, we evaluate how continued deoxygenation will influence internal ecosystem feedbacks that enhance the production of new organic matter contributing to further deoxygenation.

7.2 Definition of the issue

Biogeochemistry is the scientific discipline that involves the study of the chemical, physical, geological, and biological processes and reactions that govern the composition of the environment. Oxygen forms chemical bonds with almost all of the other elements to give corresponding oxides. These oxides, in turn, can bind elements through processes such as sorption. As a consequence, there is a wide range of elements that are affected by oxygen concentrations, including:

- *Carbon* forms a vast number of biologically relevant compounds more than any other element and is the basis for all known life on Earth. The carbon cycle involves both organic compounds such as cellulose and inorganic carbon compounds such as carbon dioxide, carbonate ions, and bicarbonate ions. The rate and extent of breakdown of organic compounds containing carbon varies tremendously depending on whether it occurs in an oxic or an anoxic environment. Aerobic remineralization of organic matter is generally greater than anaerobic remineralization in the absence of oxygen with the processes of decomposition producing different end products.

- *Methane* is produced in sediments during the breakdown of organic matter without oxygen and is a potent greenhouse gas. Eutrophication can accelerate the production of methane gas from the sea bed because enhanced organic matter deposition favours anaerobic remineralization.

- *Ocean acidification* is the decrease in the pH of the Earth's ocean that is primarily associated with the build up of carbon dioxide (CO_2) in the atmosphere from the burning of fossil fuels. When CO_2 is dissolved in ocean waters the pH decreases. In addition, the CO_2 produced during organic matter degradation increases acidity. Because deoxygenation occurs in poorly mixed waters, both hypoxia and decreases in pH can co-occur in many coastal and open ocean environments.

- *Nitrogen* gas (N_2) constitutes about 78% of the Earth's atmosphere, making it the most abundant uncombined element. Nitrogen occurs in all organisms, primarily in amino acids, proteins, nucleic acids (DNA and RNA) and in the energy transfer molecule adenosine triphosphate (ATP). Nitrogen can be limiting to growth in aquatic systems. Major perturbations have occurred in the global nitrogen cycle especially through the production of nitrogen as a fertilizer. Oxygen is a strong regulator of the remineralization of nitrogen compounds with end-products including nitrate, ammonium, dinitrogen gas from denitrification, and nitrous oxide.

- *Phosphorus* is essential for life. Phosphates (compounds containing phosphate (PO_4^{3-})) are a component of DNA, RNA, ATP, and the phospholipids. Phosphate can be limiting to growth in aquatic systems. Humans have caused major changes to the global phosphorus cycle through the use of phosphorus as fertilizer. Deoxygenation greatly influences the biogeochemical cycling of P and oxygen levels regulate the form of P buried in sediments.

- *Sulphur* chemically reacts with most elements and usually occurs as sulphide or sulphate. Hydrogen sulphide (H_2S) is produced in bottom sediments through anaerobic oxidation of methane and microbial breakdown of organic matter in the absence of oxygen, which is a globally important organic carbon oxidation pathway (Jørgensen & Kasten, 2006). It is a colourless gas with the characteristic odour of rotten eggs and is poisonous to most organisms.

- *Trace metals* are a subset of elements that are normally present in small but measurable amounts in sea water, animals and plants and are a necessary part of nutrition and physiology. Many trace metals are redox-sensitive. Key examples are manganese and iron, which undergo reduction upon the transition from oxic to anoxic conditions and are characterized by strong cycling at redox-interfaces in the water column and sediment. Reducing sediments are the ultimate repository for a large proportion of the trace metals in the oceanic dissolved pool (Little et al., 2015).

Historically, biogeochemical cycles have been studied individually, element by element. However, element cycles in the environment are intimately tied to one another, and a change in one cycle thus impacts multiple cycles. Ocean deoxygenation thus involves the alteration of a large number of interacting element cycles. In the biogeochemical nitrogen cycle, for example, low oxygen leads to changes in processes involving sulphur and carbon compounds besides oxygen and nitrogen. A mechanistic and quantitative understanding of all these processes and their rates is critical if we wish to predict and mitigate the impacts of continued ocean deoxygenation.

The *nitrogen cycle* has been profoundly affected by the activities of humans through the increased combustion of fossil fuels and the growing demand for nitrogen in agriculture (Galloway et al., 2008). As a consequence, concentrations of nitrogen compounds in aquatic ecosystems have increased greatly. Most loss of nitrogen compounds from aquatic ecosystems takes place through microbially facilitated processes, which ultimately transform dissolved inorganic nitrogen to nitrogen gas. Nitrogen gas is not chemically reactive and is not a form of nitrogen that is available to most organisms. Nitrifying microbes aerobically convert ammonium (NH_4^+) to nitrite (NO_2^-) and nitrate (NO_3^-). Denitrifying microbes convert nitrite to nitrogen gas and require a very low oxygen concentration as well as organic C for energy. Anammox bacteria convert nitrite and ammonium ions directly to nitrogen gas and water. Globally, this latter process may be responsible for 30-50% of the nitrogen gas produced in the ocean (Dalsgaard et al., 2003; Kuypers et al., 2003). Both denitrification and anammox are performed by

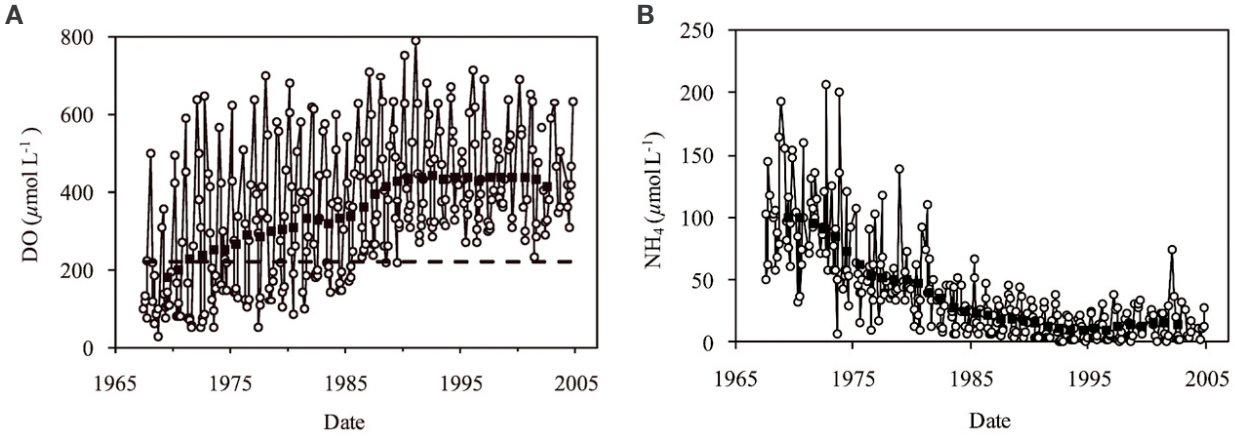

Figure 7.1 Examples of A) dissolved oxygen (DO) and B) ammonium (NH_4) in the Delaware River estuary, USA, in the urban river region (Sharp, 2009).

anaerobic microbes near oxic /anoxic interfaces. Some nitrogen gas can also be produced through reduction of nitrite coupled to methane oxidation (Z. He et al., 2015).

Nitrous oxide (N_2O) a potent greenhouse gas, is a by-product of both nitrification and denitrification (Bange et al., 2010). The amount of nitrous oxide produced is strongly dependent on prevailing oxygen conditions. Production of nitrous oxide is enhanced at the oxic / suboxic boundaries of low-oxygen waters such as found in OMZs, but nitrous oxide is further reduced to nitrogen gas in anoxic conditions, so small differences in oxygen concentration determine whether there is net production or consumption of this gas. Low-oxygen zones (including shelf and coastal areas) contribute a large fraction of the oceanic nitrous oxide emission to the atmosphere and expansion of low-oxygen zones with global warming may significantly enhance oceanic nitrous oxide emissions. Record air-sea nitrous oxide fluxes have recently been observed above the OMZ in the eastern tropical South Pacific (Arévalo-Martínez et al., 2015) suggesting that hotspots of nitrous oxide emissions occur in high-productivity upwelling ecosystems.

7.3 Trends and impacts

Over the past century, an increase in hypoxia has been observed around the world in hundreds of coastal areas and the open ocean oxygen minimum zones have

Figure 7.2 Thames estuary ©Terry Kent / Shutterstock.com.

expanded by several million km^2 (Breitburg et al., 2018). Hypoxia in coastal and shelf waters has increased largely because of increases in nutrient availability, but it also is affected by global warming. Warming reduces the amount of oxygen that can saturate in the water, increases rates of respiration and the degradation of organic matter, and strengthens the density difference between surface waters and bottom waters (stratification) decreasing the ventilation of near bottom waters. In turn, deoxygenation has a large influence on nutrient biogeochemical cycles especially elements that are redox sensitive. Below we examine trends of oxygen in a number of different marine environments where hypoxia occurs and its impact on biogeochemical cycles. This is not meant to be an exhaustive list but provide examples of marine systems that are impacted by low oxygen concentrations.

7.3.1 Upper reaches of estuaries

The upper reaches of estuaries are amongst the most heavily populated areas of the world and also suffer from degradation of water quality due to excessive nutrients from sewage, agriculture and animal wastes as well as pollutants including heavy metals, PCBs, oestrogens, etc. Deoxygenation occurs in the upper reaches of estuaries primarily due to inputs of oxygen demanding substances especially from poor wastewater treatment. There are a number of important examples of cities that have accomplished reductions in the organic pollution that consume oxygen during their degradation. This is termed biochemical oxygen demand (BOD) and is a measure of organic pollution. By instituting advanced sewage treatment this has resulted in remarkable improvements in water quality in recent decades (Figure 7.1). Reductions in nutrient loads from advanced wastewater treatment plants with both phosphorus and nitrogen removal have been clearly demonstrated to lead to increases in oxygen concentrations in diverse locations. Estuaries that have exhibited improved water quality from advanced wastewater treatment include Boston Harbour, MA, USA (Tucker et al., 2014), the Scheldt River estuary, The Netherlands/Belgian border (Soetaert et al., 2006), the urban region of the Delaware estuary, USA (Sharp, 2010), and the Mersey River Estuary (Jones, 2006) and Thames River Estuary in the UK (Figure 7.2) (Tinsley, 1998).

A global estimate by the United Nations Environment Programme (UNEP) and UN-HABITAT determined that 90% of all wastewater generated is released into

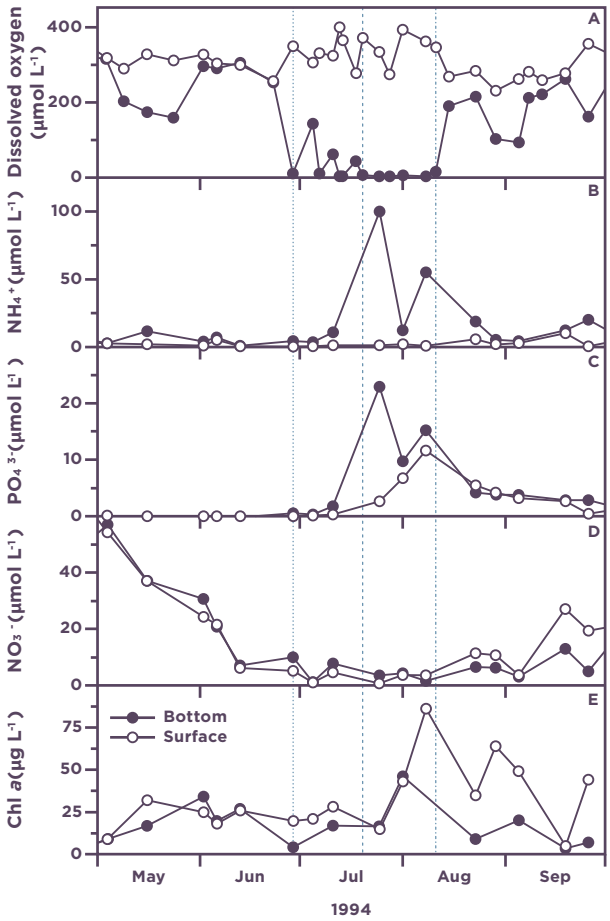

Figure 7.3 Time trend of the impact of deoxygenation on the biogeochemical cycles of nitrogen and phosphorus. Concentrations of (A) dissolved oxygen, (B) ammonia (NH_4), (C) phosphate (PO_4^{3-}), (D) nitrate (NO_3^-) plus nitrite (NO_2^-), and (E) chlorophyll a (Chl a) in bottom water and surface water in the central part of Skive Fjord, Denmark. Vertical lines indicate onset of hypoxia with intermittent re-oxygenation (dotted line), onset of the period with oxygen deficiency (dashed line), and the end of hypoxia (dashed and dotted line), respectively (Conley et al., 2007).

the environment untreated (Corcoran et al., 2010). The input of organic material not only depletes oxygen, but these hypoxic and anoxic environments lead to large concentrations of reduced species such as ammonium and the production of toxic hydrogen sulphide. In addition to aerobic respiration, processes such as nitrification substantially contribute to the consumption of oxygen, and may have a significant impact on carbonate equilibria and pH in coastal waters. For example, in the heavily impacted Pearl River Estuary (Dai et al., 2006; B. He et al., 2014), China, the oxygen depleted water is concentrated in the low salinity regions between 1 and ~5 and is accompanied by high pCO_2 (up to 7000 µatm) and nutrients (ammonium-N > 600 µM and nitrate N > 200 µM). Recent studies have confirmed that serious oxygen depletion occurred year-round throughout the water column in the upper reaches of the Pearl River Estuary primarily from sewage.

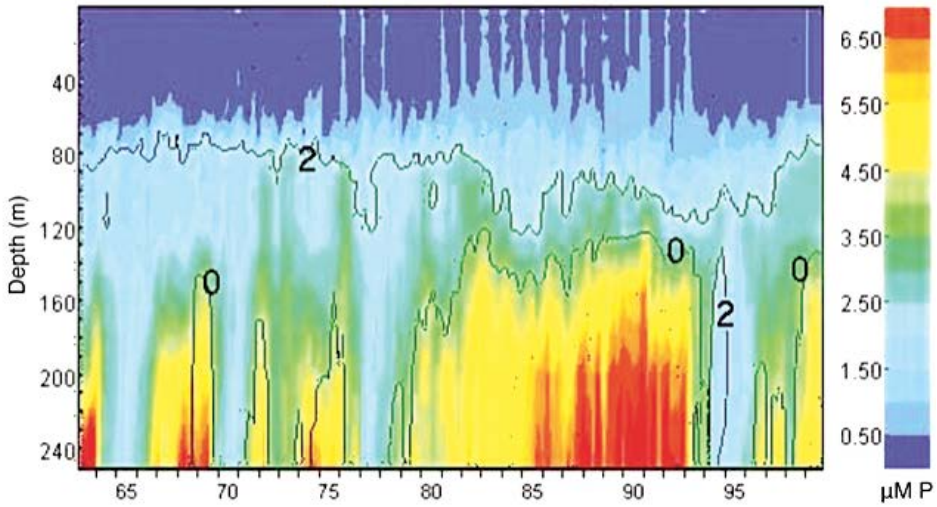

Figure 7.4 Time trends of dissolved inorganic phosphate (PO_4^{3-}) and dissolved oxygen (ml L^{-1}) isopleths from vertical profiles in the Gotland Deep, Baltic Sea from 1963-2000.

7.3.2 Estuarine systems

Estuaries form a transition zone between rivers and marine environments. The inflows of fresh water often provide high levels of nutrients making estuaries among the most productive natural habitats in the world. However, excessive nutrient inputs have increased the rate of deoxygenation with hundreds of estuaries experiencing hypoxia and anoxia (Breitburg et al., 2018). A classic example of time trends in nutrient biogeochemical cycles with deoxygenation is seen from Skive Fjord, Denmark (Figure 7.3). With decreasing bottom water oxygen concentrations, phosphate fluxes from sediments increase, less nitrogen is denitrified and more nitrogen is anaerobically reduced to ammonium (Conley et al., 2007). The accumulation of nutrients in the bottom water can accelerate the rate of growth of algae in surface waters as nutrients are mixed upwards during wind events. Many estuarine systems have high bottom water concentrations of nutrients during periods of hypoxia (Caballero-Alfonso et al., 2015; Kemp et al., 2009).

7.3.3 Enclosed large marine ecosystems

The Baltic Sea is the largest anthropogenically-induced zone of hypoxia in the world (Diaz & Rosenberg, 2008). Carstensen et al. (2014) reported a 10-fold increase of hypoxia in the Baltic Sea from the period 1898 to 2012 and showed that deoxygenation is primarily linked to increased inputs of nutrients from land, although increased respiration due to higher temperatures during the last two decades has contributed to worsening oxygen conditions. Conley et al. (2002) showed that annual changes in dissolved inorganic phosphate in the water column were positively correlated to the area of bottom covered by hypoxic water, but not to changes in total phosphorus load (Figure 7.4). The variations in phosphorus pools that have occurred during the past decades do not reflect any human activities to reduce nutrient inputs but are instead regulated by variations in vertical stratification of the water column and variations in phosphorous retention in the surface sediment. Denitrification is the dominant pathway for nitrogen loss in the water column and thus is of the same order of magnitude as sediment denitrification (Dalsgaard et al., 2013). The amount of dissolved inorganic nitrogen in the Baltic Proper is negatively correlated with the volume of hypoxic water suggesting that denitrification is enhanced when oxygen is low (Conley et al., 2009a). The expansion of hypoxia in the Baltic Sea has led to major changes in iron dynamics: while initially release of Fe from shelf sediments and the transfer to adjacent deep basins was enhanced, prolonged hypoxia has led to strong retention of Fe in shelf sediments, likely in the form of iron sulphides. This shelf iron, released in a “window of opportunity” when bottom waters were neither oxic nor sulphidic may have helped to initially buffer sulphide concentrations in the deep basins (Lenz et al., 2015). Changes in pathways of organic matter degradation associated with eutrophication and hypoxia can lead to an enhanced release of methane, ammonium and sulphide from sediments into the water column (Thang et al., 2013).

The Black Sea is the world’s largest naturally occurring anoxic basin and is characterized by a strong salinity stratification with well-mixed, oxic surface waters overlying nearly stagnant, anoxic and sulphide-rich

deeper water. Human-induced eutrophication and coastal hypoxia have been reported for the continental shelves surrounding the deep basin, especially in the vicinity of major rivers (Friedrich et al., 2014). The most prominent example is the coastal hypoxia observed on the north-western shelf where the fresh water and nutrient input from the Danube and other rivers contribute to thermohaline stratification and stimulate primary productivity in summer. The areal extent and intensity of the seasonal hypoxia on the north-western shelf increased from the 1960s to the 1990s, followed by a partial recovery, related to a strong reduction in nutrient input in the 1990s (Capet et al., 2013; Friedrich et al., 2014). Physical processes contribute strongly to the temporal and spatial variability of the coastal hypoxia on the shelf (Capet et al., 2013). The coastal hypoxia likely contributes to strong nutrient recycling from the sediments, which for phosphate and ammonium was equal in size to half of the yearly input from the Danube river in the late 1990s (Friedrich et al., 2002).

A major difference between the Black Sea and Baltic Sea is that in the latter system, the shallow, shelf areas surrounding the deep basin(s) are highly eutrophic (e.g. Jilbert et al., 2011), leading to one nearly uninterrupted area of anoxia in summer that extends from the deep basins into shallower waters (Carstensen et al., 2014). This clearly differs from the Black Sea where there is a distinct spatial separation between the coastal zone hypoxia and that of the deep basin (Friedrich et al., 2014).

7.3.4 Shelf ecosystems

Bottom-water hypoxia has occurred during summer in the northern Gulf of Mexico for more than three decades largely driven by nutrient inputs from the Mississippi River (Rabalais et al., 2014). Low oxygen concentrations on the Mississippi River shelf enhance denitrification and the sediment removal of nitrogen (McCarthy et al., 2015). Hu et al. (2017) reported that benthic (both aerobic and anaerobic) respiration-produced CO_2 flux could be responsible for acidifying hypoxic bottom water in addition to water column aerobic respiration.

The Changjiang (Yangtze River) is one of the largest rivers in the world and strongly influences its estuary and adjacent shelf forming stratified and turbid plumes, especially during summer (Zhang et al., 1999). Like many other rivers in the world, the Changjiang has been suffering from eutrophication and oxygen depletion for the past few decades (Figure 7.5) (Zhu et al., 2011). Coupled variation in particulate organic carbon (POC), dissolved inorganic phosphorus (DIP), dissolved inorganic nitrogen (DIN) and apparent oxygen utilization (AOU) occurs in near-bottom waters suggesting hypoxia is driven by the degradation of organic matter produced during intense phytoplankton blooms (Qian et al., 2017).

The Namibian shelf and Oregon shelf are examples of ecosystems where upwelling of nutrient-rich low oxygen waters is the main cause of shelf hypoxia. On the

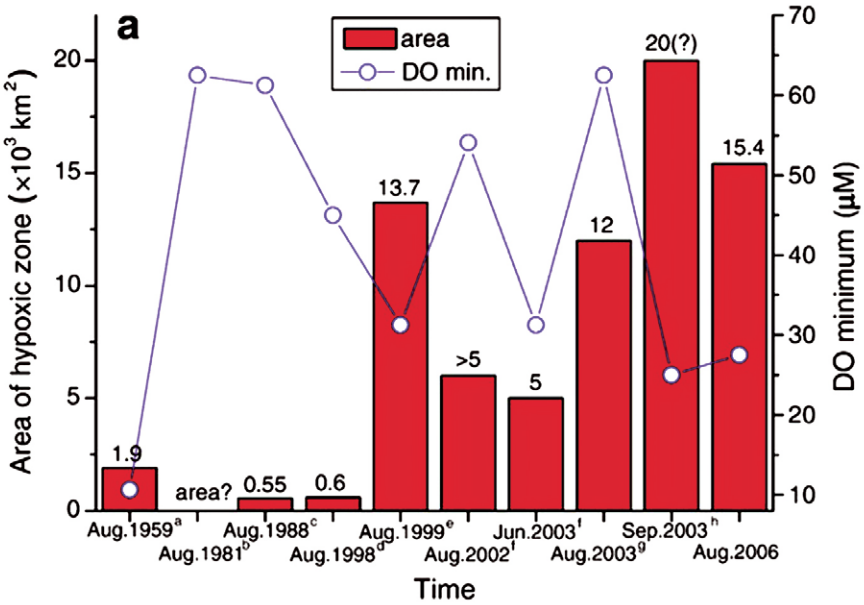

Figure 7.5 The long-term pattern of hypoxia off the Changjiang (Yangtze River) Estuary, China (Zhu et al., 2014).

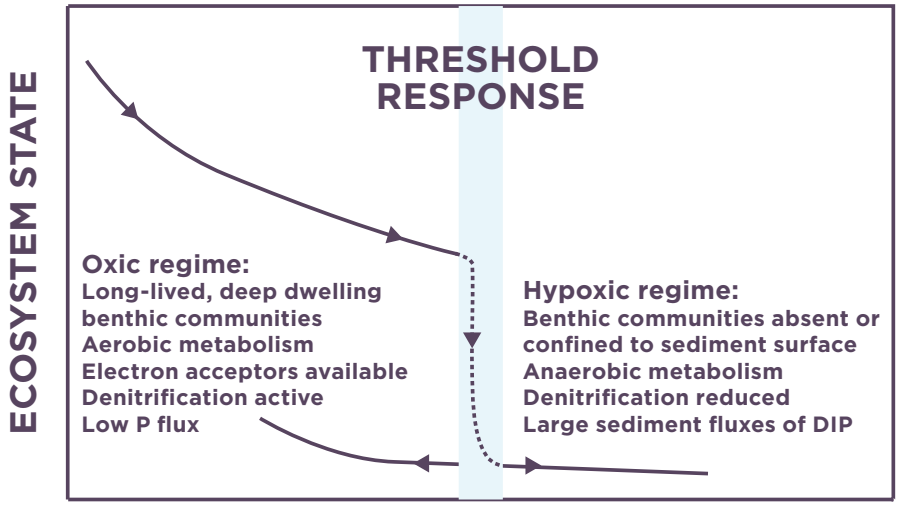

Figure 7.6 Hypothetical diagram showing change in ecosystem state as represented by bottom water oxygen concentrations versus nutrient concentrations. An ecosystem is believed to reach a threshold when bottom-living organisms are killed and the system switches to one dominated by anaerobic processes (Conley et al., 2009a).

Namibian shelf, seasonal and interannual variations in oxygen are primarily the result of variability in advective oxygen supply. On the Oregon shelf, advective flows are also key, but local respiration also accounts for a major proportion of the observed oxygen loss (Fennel & Testa, 2019; and references therein)

7.3.5 Oxygen minimum zones (OMZ) in the open ocean

Total loss of bioavailable nitrogen from the open ocean is currently estimated to be 65-80 Tg N y^{-1} from the water column and 130-270 Tg N y^{-1} from sediments (Somes et al., 2013). Analysis and modelling of global benthic data also indicate that denitrification in sediments underlying high nutrient-low oxygen areas such as OMZs remove around three times as much N per unit of carbon deposited as sediments underlying highly oxygenated water, and account for approximately 10% (i.e. 15 Tg N y^{-1}) of global benthic denitrification (Bohlen et al., 2012).

Deoxygenation of OMZ waters is expected to increase the volume of water where denitrification and anammox occur and may lead to increased marine nitrogen loss (Bristow et al., 2017). This could alter the ocean's nitrogen inventory and, eventually, biological production on millennial timescales if nitrogen losses are not compensated for by increases in nitrogen fixation (Gruber, 2016).

The direction and magnitude of change in the nitrous oxide budget and air-sea nitrous oxide flux are also unclear because increased stratification could reduce the amount of nitrous oxide that reaches the surface ocean and escapes to the atmosphere (Martinez-Rey et al., 2015).

Where OMZs impinge on continental margins, low oxygen in bottom waters may enhance the benthic release of dissolved iron (Scholz et al., 2014) and phosphate (e.g. Kraal et al., 2012). When these nutrients subsequently reach the surface water, they may increase productivity and contribute to a further expansion of OMZs. While for iron, the release occurs in a narrow redox window where neither oxygen nor sulphide is present (Scholz et al., 2014), for phosphate, the benthic release generally increases when conditions are more reducing (Algeo & Ingall, 2007). In some areas, phosphorite formation, which may be mediated by microbes, can partly counteract the enhanced benthic release of phosphorus (e.g. Schulz & Schulz, 2005).

Through a combination of molecular techniques and biogeochemical analyses, a hidden ("cryptic") cycle of sulphur was recently revealed to be active in the water column of the OMZ offshore Chile (Canfield et al., 2010). In such a cryptic cycle, sulphide produced through sulphate reduction can drive enhanced nitrate reduction thereby contributing to a coupling of the sulphur and nitrogen cycles in the water column. Other recent work points towards a link between the cycles of nitrogen and methane in OMZs, with methane from sediments potentially fuelling nitrite-dependent anaerobic oxidation of methane in the water column (Chronopoulou et al., 2017). Increased ocean deoxygenation is expected to

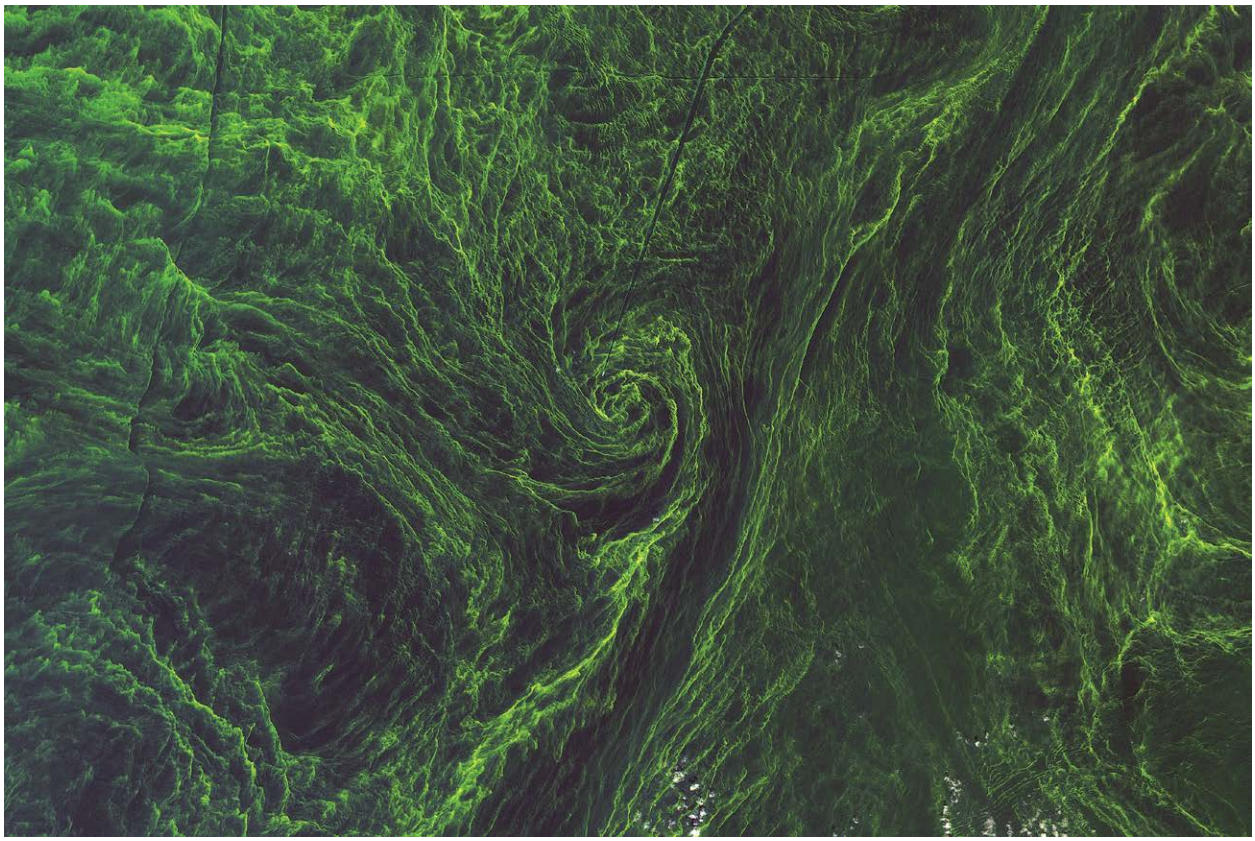

Figure 7.7 Cyanobacteria bloom in Baltic Sea © Iavizzara / Shutterstock.com.

increase the importance of these anaerobic pathways in the coupled S-C-N-O cycles.

7.4 Ecosystem consequences

7.4.1 Nutrients are not buried, but recycled

It is being increasingly recognized that there is a legacy of excess carbon and external nutrient loading from the last century in the sediments of many coastal and shelf ecosystems that contributes to continued eutrophication despite large-scale nutrient reductions. Labile organic carbon and associated nutrients buried in sediments can be remobilized during periods of low oxygen, especially phosphorus. Nitrogen cycling processes, especially denitrification is strongly regulated by oxygen concentrations with decreases in denitrification when oxygen becomes low, shifting nitrogen cycling towards the regeneration of nitrogen as a reduced compound such as ammonium instead of being lost from the system as nitrogen gas. The legacy of a higher sediment respiratory demand following eutrophication has been shown for a number of coastal systems (Kemp et al., 2009; Turner et al., 2008) whereby repeated hypoxic events lead to an increased susceptibility of further hypoxia and accelerated eutrophication (Figure 7.6) (Conley et al., 2009a).

Phosphorus previously buried in the sediments can be returned to the water column causing an increase in eutrophication. The supply of phosphorus released from the sediments is generally enhanced under anoxic conditions (Ingall & Jahnke, 1994; Scholz et al., 2014) and has the potential to further stimulate biological production if phosphorus and nitrogen reach well-lit surface waters, such as above the OMZs associated with coastal upwelling regions and the surface layer of coastal waters. Elevated dissolved inorganic phosphorus and chlorophyll are found in surface waters when anoxia occurs in fjords and estuaries (Conley et al., 2007) and in some systems, deep waters supply as much phosphorus to productive surface layers as do watershed discharges. Increased productivity will tend to increase oxygen consumption, may increase the sediment area in contact with low-oxygen waters, and may eventually lead to further release of phosphorus from the sediment. There is evidence for this positive feedback in enclosed seas like the Baltic Sea, where enhanced nitrogen fixation in response to deoxygenation has led to the recent proliferation of

undesirable cyanobacteria blooms (Figure 7.7) that can be toxic and have adverse impacts on ecosystems and society. Enhanced phosphate levels may generally favour nitrogen fixation by diazotrophs, especially in the presence of nitrogen loss when ordinary plankton are driven towards nitrogen limitation.

7.4.2 Changing nutrient limitation with deoxygenation

The availability of nutrients in the ocean frequently limits the activity and abundance of phytoplankton primary producers. Nitrogen availability tends to limit productivity throughout much of the surface low-latitude ocean, where the supply of nutrients from the subsurface is relatively slow. Iron often limits productivity where subsurface nutrient supply is enhanced, including within the main oceanic upwelling regions, and phosphorus and micronutrients may also (co-)limit marine phytoplankton (Moore et al., 2013). By contrast, coastal and shelf systems can be limited by both, or either, nitrogen and phosphorus and can vary both temporally and spatially (Conley et al., 2009b). The biogeochemical cycles of nitrogen and phosphorus are strongly governed by oxygen concentrations (Figure 7.8); thus, deoxygenation can have significant effects on primary productivity.

Marine nitrogen fixation occurs in close spatial association with the major regions of marine denitrification, such as the eastern tropical North and South Pacific (Gruber & Deutsch, 2015) and is related to the generation of nitrogen-deficient waters by denitrification in OMZs. The loss of fixed nitrogen through the microbial processes of denitrification and/or anammox thus creates a niche for cyanobacteria, through effectively generating an excess of phosphorus (Moore et al., 2013). Increases in phosphorus supply with enhanced biogeochemical cycling in OMZs lead to higher ocean productivity and oxygen demand in subsurface water (Watson et al., 2017) although sometimes nitrogen fixation is displaced downstream due to the availability of iron concentrations (Bonnet et al., 2017).

Low oxygen may affect the global distribution of trace metals, some of which serve as micronutrients for plankton growth, but the significance of such controls is yet to be fully evaluated. Nitrogen–iron co-limitation is pervasive in the ocean, with other micronutrients also approaching co-deficiency (Browning et al., 2017). Major questions remain regarding the long-term impact on primary productivity depending on changes in N-P-Fe cycling with continued ocean deoxygenation.

7.5 Societal consequences

As outlined by Rose et al. (Chapter 10) deoxygenation can kill fish, especially with the production of toxic hydrogen sulphide (Vaquer-Sunyer & Duarte, 2008). Trophic efficiency (landings per unit nitrogen loadings) are lower in systems with extensive hypoxia with reduced recruitment and population abundance. There are likely abiotic effects of hypoxia on egg survival and hatch success. All of these aspects reduce the quantity of fish available for fisheries. These aspects can affect food security making uncertain the availability of nutritionally and safe foods from marine environments and can affect the livelihood of fishermen.

Low oxygen enhances the biogeochemical cycling of phosphorus and can affect the cycling of nitrogen in different ways depending upon the times scales of hypoxia and circulation. These processes associated with deoxygenation leads to the rapid recycling of nutrients, reductions in the long-term sediment sink of nutrients, with excess nutrients cycling in the water column. For example, cyanobacteria blooms are closely linked with the appearance of hypoxia in the Baltic Sea (Funkey et al., 2014). Algal blooms create poor water quality conditions reducing the quality of life for those living near coastal areas. Algal blooms also reduce the opportunities for recreation by covering beaches with algae washed up on shore. In addition, some species of cyanobacteria are toxic.

It is being increasingly recognized that there is a legacy of excess external nutrient loading from the last century in the sediments of many coastal and shelf ecosystems that contributes to continued eutrophication despite large-scale nutrient reductions. The legacy of a higher sediment respiratory demand following eutrophication has been shown for other coastal systems (Turner et al., 2008) whereby repeated hypoxic events lead to an increased susceptibility of further hypoxia and accelerated eutrophication. Phosphorus previously buried in the sediments can be returned to the water column and the regeneration of nitrogen to ammonium can cause an increase in eutrophication (Conley et al., 2009a).

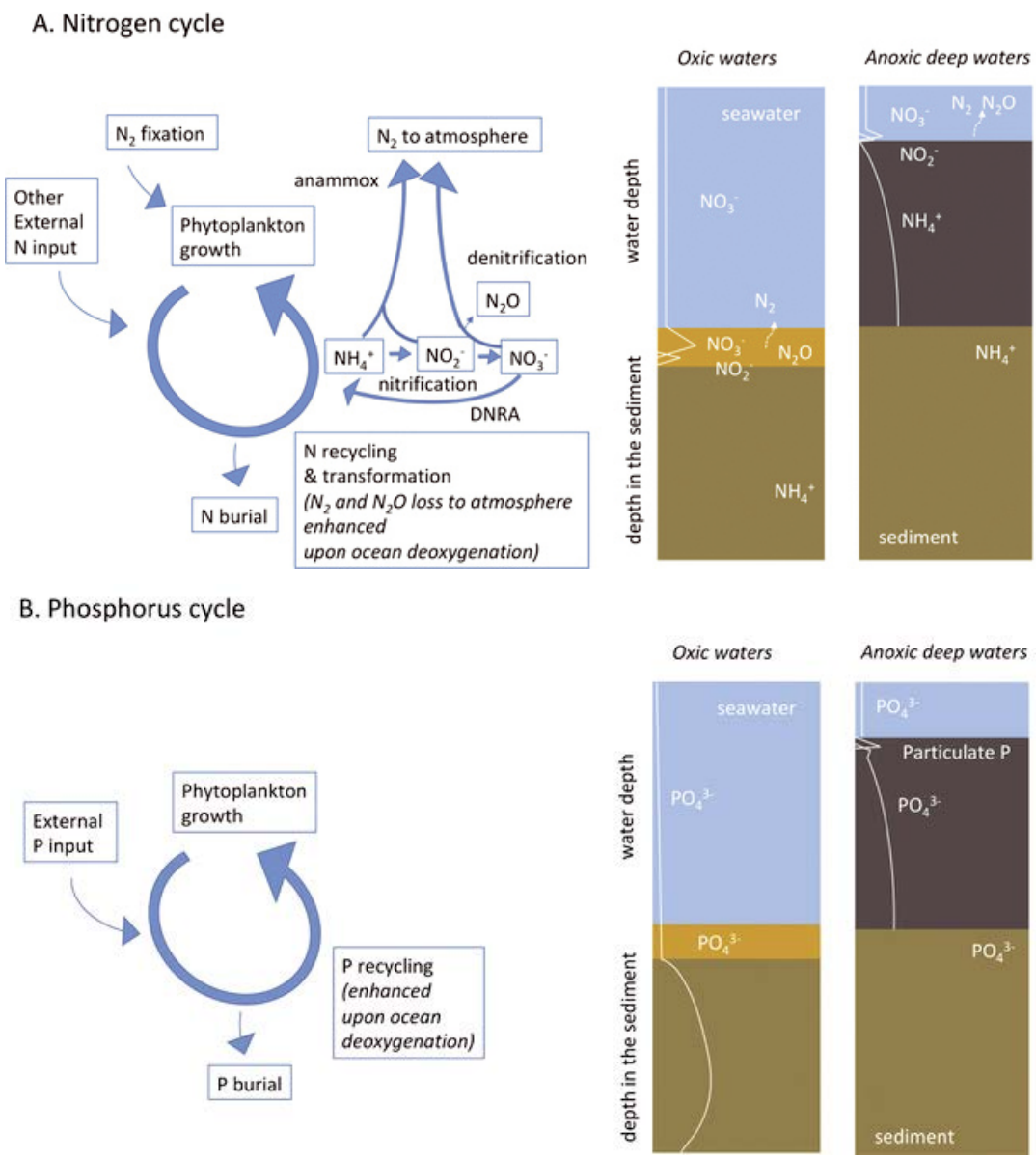

Figure 7.8 Conceptual figure of nutrient pathways for (A) the nitrogen cycle and (B) the phosphorous cycle. Differences in the cycles of nitrogen and phosphorous are depicted between oxic waters and in anoxic deep waters. For the nitrogen pathways N_2 and N_2O loss to the atmosphere are enhanced upon ocean deoxygenation. For phosphorous, enhanced recycling occurs upon ocean deoxygenation.

There are unequal capacities for adaptation throughout the world. Developing countries, who often have not significantly contributed to the amount of greenhouse gases in the atmosphere, will now be at an even greater disadvantage when it comes to dealing with the effects of ocean deoxygenation with climate change. In addition, many large cities in developing countries have limited capacity to reduce the input of sewage derived nutrients into adjacent waters fuelling eutrophication, and if the conditions are suitable, algal blooms with subsequent deoxygenation.

7.6 Implications of continuing ocean deoxygenation

Ocean deoxygenation is becoming an increasingly widespread phenomenon throughout the world (Breitburg et al., 2018). Despite nutrient reductions that have reduced the deleterious effects of eutrophication, it remains difficult to improve bottom water oxygen conditions (Anderson et al., 2017; Reimann et al., 2016). This does not mean that nutrient reductions are not important for improving oxygen concentrations;

deoxygenation would have been even worse if nutrient inputs had not been reduced. Failure to reduce nutrient inputs may lead to cascading effects of increasing hypoxia with the return to an ecosystem with less hypoxia becoming more and more unlikely. Nutrient reduction and efforts to reduce the effects of global warming are the only realistic management measures for improving oxygen conditions.

The time scales for improvement in oxygen conditions depend greatly on residence time and circulation. Changes in oceanic temperature with global warming leading to more deoxygenation in the OMZs are likely to lead to an expansion of OMZs with a decline in the extent of at least 10,000 years (Shaffer et al., 1989). In contrast the prospect of reducing the effects of deoxygenation on coastal areas and open shelf systems is much greater due to the shorter residence time allowing the ecosystems to more easily recover if nutrient reductions are implemented.

7.7 Conclusions / Recommendations

Ocean deoxygenation is leading to major changes in elemental cycling in the coastal zone and in oxygen minimum zones in the open ocean. Recycling of nutrients and burial of organic matter is enhanced (Figure 7.8). Deoxygenation increases the risk of enhanced release of the greenhouse gases nitrous oxide and methane to the atmosphere. While in the coastal zone anthropogenic nutrient inputs from land are the main driver of low oxygen, global warming plays an increasingly important role in modulating water column mixing and lowering oxygen solubility in both coastal and open ocean waters, thereby decreasing oxygen supply. Worldwide reductions in nutrient loss from land to the sea and measures to restrict global warming are essential to improve oxygen conditions in the ocean and avoid further harmful impacts on ecosystems.

7.8 References

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