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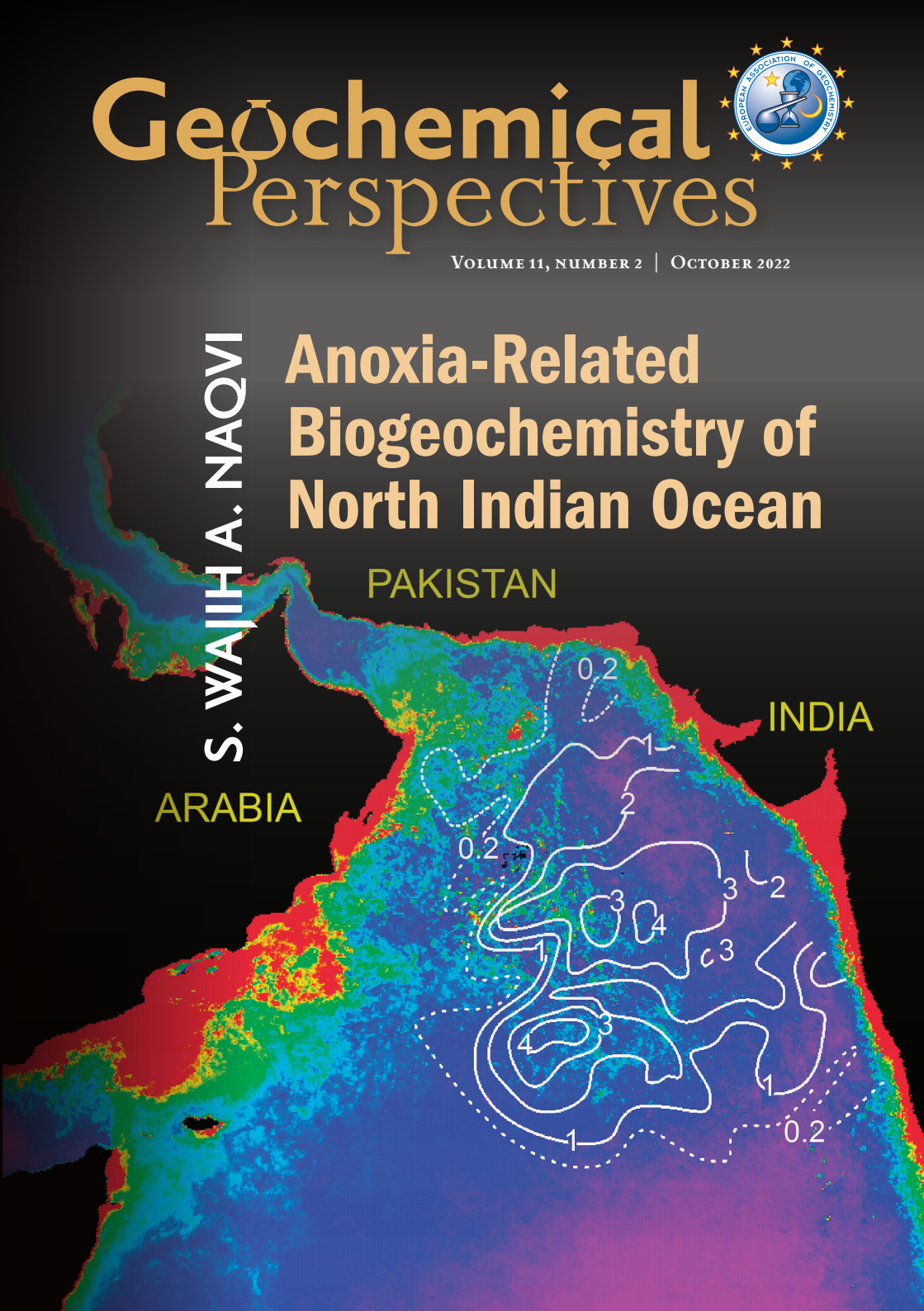
S. Wajih A. Naqvi

# Anoxia-Related Biogeochemistry of North Indian Ocean



# Geochemical Perspectives

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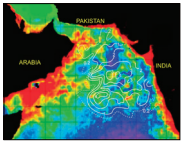


About the cover

Composite image of remotely sensed ocean colour for August showing phytoplankton blooms formed due to upwelling in the western Arabian Sea (red – high chlorophyll; magenta/blue – low chlorophyll), and location of oxygen deficient zone demarcated by the presence of secondary nitrite maximum.

Image courtesy: Amit Sarkar



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# ANOXIA-RELATED BIOGEOCHEMISTRY OF NORTH INDIAN OCEAN


## ABSTRACT

This article provides a brief account of my early life and career, and a more detailed description of the contributions of the groups with which I have been associated to the biogeochemistry of the North Indian Ocean, especially nitrogen cycling in oxygen deficient waters.

Some of the most intense oxygen depletion in the water column in the open ocean occurs at mid-depths in the two northern basins of the Indian Ocean – the Arabian Sea and the Bay of Bengal. This pattern, arising from the presence of land masses that restrict the northern expanse of the Indian Ocean, contrasts with the oxygen distribution in the Atlantic Ocean and the Pacific Ocean, where the oxygen minima are the most intense along their eastern boundaries. Moreover, the two open ocean oxygen-depleted systems in in the north Indian Ocean are quite different: while the oxygen minimum layer in the Arabian Sea is functionally anoxic and contains a prominent nitrite maximum (called the secondary nitrite maximum or SNM), oxygen in traces (sub-micromolar levels) is almost always present within its minimum layer in the Bay of Bengal, where the SNM is conspicuously absent. Nitrate concentration within the nitrite-bearing oxygen deficient zone (ODZ) of the Arabian Sea is about half of the corresponding

value in the Bay of Bengal, indicating its loss to molecular nitrogen ($N_2$) through denitrification and/or anaerobic ammonium oxidation (anammox). Estimates of $N_2$ production rates in the Arabian Sea range between ~12 and 41 Tg N $yr^{-1}$, comparable to the published estimates for each of the two Pacific Ocean's ODZs. Other characteristic features of the Arabian Sea ODZ, not observed in the Bay of Bengal, are as follows. (1) Low (minimum) concentrations of nitrous oxide ($N_2O$) sandwiched between two maxima located at the boundaries of the ODZ. (2) Large enrichment of $^{15}N$ relative $^{14}N$ in nitrate and $N_2O$, resulting from preferential reduction of $^{14}NO_3^-$ and $^{14}N^{14}NO$, respectively. (3) Elevated $N_2$/Ar ratio relative to the region outside the ODZ. (4) Maxima in respiration rates, as inferred from the activity of the respiratory electron transport system (ETS), in particulate protein, in total bacterial counts and in suspended particles, as determined by light transmission. In addition to nitrogen, oxidised forms of some other polyvalent elements (such as iodine, manganese and iron) are also reduced within the ODZ, as evident from elevated concentrations of their reduced species ($I^-$, Fe(II) and Mn(II)). Lateral advection from the highly reducing continental margin sediments is another potential source of these species. As in the case of the ODZs in the eastern tropical Pacific, the intermediate particle maximum/nepheloid layer, is overlain by a relative sterile (low bacterial counts) and remarkably clear (low suspended particles) zone that defines the transition from oxic to anoxic conditions in the upper water column.

Unlike the ODZs of the eastern Pacific, the Arabian Sea ODZ is geographically separated from centres of upwelling in the western Arabian Sea, in part because the relatively more oxygenated waters advecting from the south and from the Persian Gulf in the northwestern region prevent the development of anoxic conditions. Because they are slightly oxygenated, waters upwelling in the western Arabian Sea have a high nitrate to iron ratio, such that toward the end of the upwelling season primary productivity becomes iron limited. Under iron stress, diatoms consume more silicate when normalised to nitrate, leading to a community shift to smaller taxa offshore. The consequent offshore shoaling of the depth of organic matter re-mineralisation is the other possible reason for the offshore location of the ODZ.

Over the past few decades the oceans have been steadily losing oxygen globally due to ocean warming and increased anthropogenic nutrient loading. The available data from the North Indian Ocean, however, show much smaller decreasing trends than those reported for other regions, particularly the Pacific Ocean, with the exception of data from the western Arabian Sea. However, results of modelling studies reveal the likelihood for large changes occurring in the near future.

The issue of why the oxygen minimum layer in the Bay of Bengal retains traces of oxygen and does not support vigorous combined nitrogen loss is examined in detail utilising both published and unpublished information. It is concluded that anoxic conditions do not develop in the Bay of Bengal mainly due to a low rate of upwelling, which is most likely linked to a greatly subdued

exchange at intermediate depth with the rest of the Indian Ocean. A strong stratification of the upper water column may also contribute to a lower diffusive flux of nitrate into the surface layer. The persistent presence of oxygen in traces probably results in low organic matter degradation rates (a kinetic control) with the ballast-driven faster sedimentation of the particulate organic matter being another potentially important factor. Finally, the presence of oxygen, albeit in traces, prevents large scale nitrate reduction (a thermodynamic control), which provides nitrite for denitrification and anammox.

The intense oxygen minimum layer in the Arabian Sea is the only one in the world that receives freshly formed and relatively oxygenated waters from the two Mediterranean-type marginal seas (the Red Sea and the Persian Gulf). Both of these seas, especially the Persian Gulf, are currently being subjected to significant human induced changes (warming, increase in salinity and anthropogenic loading of nutrients) that are projected to bring about significant modifications of the Arabian Sea ODZ. The increased nutrient supply appears to have led to a large increase in primary production in the Gulf, although zooplankton grazing does not allow the build-up of phytoplankton biomass. The increased availability of organic matter has led to development of large scale hypoxia in bottom waters of the Persian Gulf in summer–autumn. The resultant decrease in the pre-formed oxygen content and increase in the pre-formed total organic carbon content of the Persian Gulf Water (which advects directly into the core of the ODZ in the Arabian Sea) may cause significant expansion and intensification of the ODZ. Model simulations show that the intensity and volume of the ODZ are also highly sensitive to physico-chemical characteristics of the outflows from the marginal sea, especially the temperature of the Persian Gulf Water. The ongoing warming within the Persian Gulf, which will reduce the density of the Persian Gulf Water, is expected to make the greatest contribution to the ongoing/future expansion and intensification of the Arabian Sea ODZ.

Anoxic conditions also develop seasonally along the Indian west coast, over a shelf area that is the largest in the world, during the Southwest Monsoon when this region behaves like a mini-eastern boundary upwelling system. The upwelled water is generally capped by a warm, low salinity lens formed by the enormous precipitation in the coastal zone, which results in strong thermohaline stratification very close to the surface and a strong oxygen depletion, culminating in sulfidic conditions in near bottom waters. One distinguishing feature of this system is huge accumulation of $N_2O$ (to several hundreds of nM), mostly due to incomplete denitrification. Such conditions do not develop along the shores of the Bay of Bengal because the Bay of Bengal experiences much weaker upwelling than the Arabian Sea. On the other hand, an enormous amount of reactive nitrogen is released to the environment in South Asia due to human activities. However, the quantity of combined nitrogen transported to the ocean by the South Asian rivers is much lower than model predictions, indicating loss in/retention by the terrestrial systems of a large fraction of the reactive nitrogen being anthropogenically released. Recent work has demonstrated two pathways of such losses – methanotrophy – denitrification coupling in the

hypolimnia of freshwater reservoirs that turn anoxic in summer, and heterotrophic denitrification in groundwaters of the Indo-Gangetic Plain. Such processes probably also operate in other aquatic ecosystems such as lakes, ponds, rice paddies and soils/sediments of river beds and wetlands. The consequently lower inputs of nutrients (especially nitrogen) to coastal waters by rivers may explain the absence of human-induced formation of large coastal hypoxic zones in the northeastern Indian Ocean unlike other coastal areas (*e.g.*, the Gulf of Mexico and the Black Sea) that also receive large land runoff.

# 1. INTRODUCTION

## 1.1 My Early Life

I was born on August 10, 1954, in Amroha, an ancient little town located some 130 km east of Delhi within the heart of the Indo-Gangetic Plain. The community my family is a part of is called Sadat-e-Amroha (*Syeds* of Amroha). Traditionally, this community has been quite conservative as it claims lineage to Prophet Muhammad through his daughter Fatima, *a.k.a.* Syeda (from which 'Syed', the first part of my name, is derived). One of our forefathers, Ali Buzurg, along with his family migrated to India from Al-Wasit (Iraq) and settled at Amroha in 1290, during the early days of Delhi's Khalji dynasty. His son, Husain Sharafuddin, became a Sufi saint, whose shrine (Fig. 1.1) is one of Amroha's main attractions because, even though it is infested with menacing scorpions, they are not known to have ever stung a human being within the boundaries of the shrine. Popularly known as *Bichchu wali dargah* (the shrine with scorpions), this place has served as the final resting place for many of the saint's descendants, including one of my brothers, and this is where I may eventually end up, in the company of snakes and scorpions!

**Figure 1.1** The shrine of Husain Sharfuddin Shah Wilayat, my ancestor and a Sufi saint who came to India from Iraq in 1290 AD. It is popularly known as *Bichchu Wali Dargah* (the shrine with scorpions) because scorpions are believed not to sting humans here.

***The Syed Family Lineage***

The Syeds of Amroha constitute an exclusive group, seldom marrying outside their clan, which has severely limited their genetic diversity. One notable exception was Syed Abdul Aziz, the younger son of Husain Sharafuddin, who while serving in Delhi Court got married to Zubaida Khatoon, a princess from the Tughlaq dynasty. My family belongs to this branch, and so any inconsistency in my behaviour can be attributed to Taghlaq genes: after all Sultan Muhammad bin Tughlaq is infamous for taking numerous apparently sound, but badly timed as well as poorly implemented, decisions including shifting the capital from Delhi to Daulatabad (Devagiri) in the Deccan and then back to Delhi. As a result of this, he is often referred to as the intelligent fool in Indian history.

Education has always been strongly encouraged among the Syeds. For example, Jabir bin Hayyan, the father of modern day Chemistry, was a student of Imam Jafar as-Sadiq, the 6$^{th}$ Shia Imam, of whom I am the 31$^{st}$ descendant. However, until about a century ago education was mostly restricted to learning Arabic, Persian and Urdu, with a strong focus on Shia theology. Financially, Syeds of Amroha had been quite well off due to vast stretches of land (*jagirs*, which included hundreds of villages) awarded to them from time to time for the administrative and military services rendered to Delhi sultans and emperors. Ibn Batuta, the famous Moroccan who visited Amroha in 1341, describes in his travelogue how he was hosted by the then Qazi of Amroha, Syed Amir Ali, the elder son of Husain Sharfuddin. However, the relative affluence came to an abrupt end following the abolition of the *zamindari* system as a part of the post-independence land reforms implemented by the Government of India in 1952, two years before I was born. This inevitably brought financial hardships to the entire community including our family that was quite large – we were seven siblings. With the compensation received from the Government, my father (Syed Sibte Mehmood) started a construction business and also established a furniture workshop in Bareilly, another city close to Amroha. However, due to insufficient experience and his simple nature, he suffered heavy monetary losses.

The economic condition in India was quite grim in the 1960s and early 1970s, especially after the country had fought two wars with Pakistan and one with China. There was widespread shortage of food. I remember queuing up for several hours on one occasion in 1966 to collect a few kilograms of poor quality rationed wheat that was supplied by the US under the PL 480 scheme. As there was not enough time to get it cleaned, I took it straight to the flour mill for grinding. The flour had lots of sand and we had trouble eating the bread. Thus, we went through some really hard times. But being brought up in a semi-urban area with a rich culture had its advantages too. I developed strong interest in Urdu literature at a very early age, remembering hundreds of couplets by famous poets such as Mirza Ghalib and Muhammad Iqbal. I also indulged in the family passion of growing mangoes. I am told this tradition goes back to the time of Akbar the Great in the 16$^{th}$ Century, and that my ancestors who started it were pioneers in grafting and developing new varieties of mangoes. I have inherited this passion from my grandfather, who was a real authority on mangoes.

It is something I still enjoy, more than any other hobby. Even in Goa, where we lived on the campus of National Institute of Oceanography (NIO), we had several mango trees including a few in the Director's Bungalow. To the horror of security guards and my family members (wife Zarreen, son Asad, and daughter Sumbul), I used to climb the trees and pluck the fruits myself. Also, participation in activities such as *mushairas* (recitations of Urdu poems), swimming in the local pond (*Kushak*) and playing field hockey made my childhood quite enjoyable, the financial hardships notwithstanding.

Educational facilities in Amroha were quite rudimentary in the 1950s, 1960s and even 1970s. However, I and my two elder siblings, Maya and Masood, were fortunate to be tutored at home by one Munshi Majan, who was my first teacher. I was very young (not more than two and a half years old) at that time. My formal education began a year later when I was admitted to a primary school run by the Municipal Board where the medium of instruction was Urdu. I started learning Hindi in Class III and English only in class VI after we moved briefly to Bareilly. The Fazlur Rahman Islamia College in Bareilly, where I studied for one year (1963–1964), had better facilities, but we were forced to move back to Amroha in 1964, where I was admitted to Imamul Madaris (I.M.) Intermediate College (Fig. 1.2). I performed quite well in the school largely because I was gifted with an extraordinary memory; if I read a text twice I could reproduce it *verbatim*. Because of this I had a good reputation in the school; in hindsight I was over-rated. This became apparent when I answered my High School (Class X) examination (in 1968) which is conducted on the provincial level by the Uttar Pradesh Board of High School and Intermediate Education. I could only secure a second division, which surprised my classmates, teachers and family members. They all expected me to do much better. Unfortunately, the newly introduced syllabus (such as trigonometry) was not fully covered in the class. It may sound incredible, but the students were then not aware of the full syllabus. Moreover, for some unknown reason I did not do too well in languages (Hindi and English), although I still think I learnt most of the English grammar before I completed high school.

I must mention that even though 'I.M. College' was not highly rated and the teachers it then employed were poorly and irregularly paid, I was very fortunate to have been taught by some really outstanding people. I wish to mention two of them: Mirza Sajid Husain, a top-notch Urdu poet, who taught me basic sciences, including the chemical symbols of elements, and Hubbe Hasnain, from whom I learnt English grammar. Those were different days. Today, my 3 year old grandson, Sahil, communicates well in English, but at that time we had no opportunity to speak this language. Sahil is also fortunate that he does not face violence in school. In our days, poor performance was rewarded by "punishment" that could be quite severe. In fact, my father, who had also studied in the same school (I.M. College) three decades before me, was once assaulted so badly by one of his teachers that he dropped out of the school. The same gentleman also taught me social sciences, but he was quite kind to me. Perhaps

it was because he was reaching the end of his teaching career; but I suspect that a more important reason was that his son (Baqar Abbas) was my classmate. He still continues to be one of my best friends; the other (Fazil) passed away recently.

**Figure 1.2** The Imamul Madaris (IM) Inter College, Amroha, where I had most of my early education.

After the Bareilly debacle, my father sat at home for a couple of years. Those were by far our worst times financially. But my father was not the type to give up easily. He moved to Lucknow in 1965 to run a mess in Shia College Hostel, which generated some income. Lucknow, the capital city of the Uttar Pradesh state, had a far better educational infrastructure than Amroha. However, Shia College, to which I was admitted (it was then headed by Afzal Ahmad, a very kind person and my future father-in-law), was not much better than I.M. College. Our lives were fairly unsettled due to financial constraints, which also affected my academic performance that was not too good even though I managed to remain close to the top of the class. My grades in the Intermediate (Class XII) Board examination were below my expectation. The degree section of the college had a much more qualified faculty, especially in the Physics and Mathematics departments, which were headed by Dr. Iftikhar Ahmad and Mr. Raghunath Saran, respectively. Both of them mentored me and helped me realise my full potential. By then, our family had also gradually settled down. As a result of these, my academic performance greatly improved, despite another change in medium of instruction from Hindi to English at the graduate level. I did very well in the B.Sc. examination in 1972 and got admitted to the Master's course in Chemistry in Lucknow University. The Chemistry department of the University was highly rated, and I had some wonderful teachers. I finished the M.Sc. in 1974, and was at the top of the Class in my discipline (Physical Chemistry). My elder brother, Masood, also did his M.Sc. from the same department in the same year, but in Organic Chemistry.

I had already decided to pursue research, mainly because my paternal uncle, Syed Mahmood Naqvi, was a well known geochemist, working at the National Geophysical Research Institute, Hyderabad, one of the 40 plus national laboratories run by the Council of Scientific & Industrial Research (CSIR), New Delhi. CSIR was the first scientific body in India established by the British India government way back in 1942. My uncle was my role model.

There were four CSIR institutions in Lucknow, one of which was the Industrial Toxicology Research Centre (ITRC, later renamed as the Indian Institute for Toxicology Research - IITR). The founder director of ITRC was Sibte Hasan Zaidi, with whom I had an opportunity to meet just after I had completed my M.Sc. For some reason Dr. Zaidi was impressed by me and offered me a studentship in ITRC. I was delighted, but I was required to secure financial support from CSIR in the form of a Junior Research Fellowship (JRF). At that time, CSIR JRFs were selected 'on merit' rather than through a competitive examination, as is the case today. I had to fill a form, get the director's endorsement and send it to CSIR. I did that, but soon after I had sent this application to CSIR, I happened to see an advertisement for a similar research opportunity in NIO, Goa. I was very tempted to get into Oceanography, and sent another form to NIO, which was then headed by Syed Zahoor Qasim. Dr. Qasim also agreed to support my candidature for a CSIR fellowship. Thus, I had two placements, and somebody in CSIR, for reasons not known to me, chose to award me a fellowship to work at NIO. My mother, who wanted me to remain in Lucknow, was very disappointed. Thus, my entry into Oceanography was more due to an accident than by design.

## 1.2 Historical Background and Birth of Indian Ocean Oceanography

The 21st of December is a very special day for oceanography because it was on this day in 1872 that H.M.S. *Challenger* sailed from Portsmouth on her famous four year long voyage that laid the foundation of this interdisciplinary science. The fact that the scientific complement and crew decided to be out at sea rather than spend Christmas and New Year with their loved ones reflects on their dedication to work. This is something I always cited to my colleagues if and when they showed reluctance to go on a research cruise during a festival, and it always worked!

Unfortunately, the *Challenger* Expedition had bypassed the Indian Ocean; instead, it studied the Indian sector of the Southern Ocean. Following the grand success of this expedition, however, the colonial British government decided to initiate oceanographic observations in Indian waters (Qasim, 1979). In 1881, a 580 ton vessel, R.I.M.S. *Investigator, was* commissioned by the Marine Survey of India, and was fitted with some gear from the *Challenger.* Her complement included a "Surgeon Naturalist" who was tasked with marine biological collections. The *Investigator (I)* was replaced by a bigger vessel (the 1078 ton R.I.M.S.

*Investigator II*) in 1908. In 1910, Dr. R.B.S. Sewell was appointed as Surgeon Naturalist. Dr. Sewell is credited for initiating the first systematic observations of core oceanographic variables in the seas around India. Sewell, who retired as a Lt. Col. from the British government service in India, was a polymath. Trained as a medical practitioner, he had diverse scientific interests including human anatomy, anthropology and archaeology, oceanography and marine biology (Roonwal, 1962).

Before the Second World War (WWII), Sir John Murray decided to sponsor an expedition to the Red Sea and the Arabian Sea. Sir John Murray was a resourceful person. Regarded by many as the father of modern oceanography, he had been a leading participant of the *Challenger* Expedition and instrumental in the publication of its results. Dr. Sewell was tasked to lead the John Murray Expedition that was carried out in 1933 using an Egyptian ship *Mabahiss* (Aleem and Morcos, 1984). Being the first systematic multi-disciplinary study of the northwestern Indian Ocean, the John Murray Expedition was potentially very significant. However, its results were underutilised, not adequately interpreted, nor did they attract the worldwide attention they deserved (Deacon and Rice, 1984).

The WWII caused severe disruption of oceanographic research worldwide, and while there was redoubled interest in oceanography after the war due to technological advances that had been made in the meantime, especially in the US, the same was not true for the Indian Ocean region. With the British departing South Asia in 1947, the nascent Indian nation, and most other Indian Ocean Rim countries, did not have the resources to indulge in this rather expensive science. Therefore, for several years after independence, marine scientific research in India was largely shore based and confined to marine biology, especially taxonomy. With the researchers from the West largely concentrating on the Pacific and Atlantic Oceans in the two decades after the War, the Indian Ocean continued to be the least studied of the major oceans. The situation changed in the early 1960s, however, when the international scientific community decided to launch a major international collaborative project to study the Indian Ocean.

The 3 year long International Indian Ocean Expedition (IIOE) started in 1962. Nearly 40 ships from 20 countries took part in this expedition. Jointly sponsored by the newly formed Scientific Committee on Ocean Research (SCOR) and the Intergovernmental Oceanographic Commission (IOC) of UNESCO, the IIOE was one of the most successful collaborative scientific projects ever. One major scientific product of the IIOE was the *Oceanographic Atlas of the International Indian Ocean Expedition* (Wyrtki, 1971). Arguably the most important outcome of the expedition was the establishment in January 1966 of a major oceanographic research centre in the region (NIO as a national laboratory under CSIR, India) making excellent use of human resources developed during the IIOE. The Institute's headquarters were temporarily located in Delhi, but were shifted to Goa in 1969. When I joined NIO as a research student in 1974, almost the entire staff of NIO comprised of IIOE veterans.

# 2. ANOXIA IN THE OPEN OCEAN AND ANOMALOUS LOCATION OF OXYGEN DEFICIENT ZONES IN THE INDIAN OCEAN

## 2.1 Historical Background

One of the main goals of the *Challenger* Expedition was "to investigate the distribution of organic life at different depths and on the deep seafloor". This was because, well into the 19th century, many people – prominent among whom was the British naturalist Edward Forbes (1815–1854) – had believed that the deep sea was anoxic and, consequently, azoic (Anderson and Rice, 2006). The *Challenger* expedition would settle this controversy once and for all. Three years before this expedition began, however, first measurements of dissolved oxygen in the deep sea had already been made (although not yet published): Carpenter (1874), as cited by Richards (1957), had determined oxygen content of seawater up to a depth of 2090 fathoms (3822 m) during an expedition of the H.M.S. *Porcupine*, a precursor of the *Challenger* Expedition, which was organised by the Royal Society off the west coast of Ireland. Oxygen measurements by William Dittmar during the *Challenger* Expedition led him to conclude, *"Amongst the many deep sea waters that were analysed for their gas contents, we found none that were quite free from absorbed oxygen, which confirms our conviction that absolute stagnation nowhere exists in the ocean, not even at its greatest depths"* (Dittmar, 1984, as cited by Richards, 1957). Dittmar was not entirely correct though. We now know that there are some parts of the ocean where water contains no measurable oxygen (Paulmier and Ruiz-Pino, 2009) even though these waters are not absolutely stagnated; but then *Challenger* Expedition could only cover a limited area of the ocean and measuring oxygen at low concentration continues to be a challenge even today.

The general pattern of oxygen distribution in the oceans became known as a result of several oceanographic expeditions undertaken in the early part of the last century, mostly in the Atlantic and, to a smaller extent, the Pacific (see Richards, 1957, and references therein). However, a satisfactory interpretation of the observed patterns (relative importance of supply through circulation and consumption largely by organisms for their respiration, which determines the oxygen content of subsurface waters) had to wait till the 1960s (Wyrtki, 1962). Some of these early studies deserve special mention. An expedition of the Danish motor schooner *Dana* to the Pacific led to the discovery of the oxygen deficient zone (ODZ)[1] of the eastern tropical North Pacific (ETNP): it was first noticed in the Gulf of Panama in January 1922 (Schmidt, 1925), and was later found to extend westward during the voyage of *Dana II* from Panama towards

1. The term "oxygen deficient zones (ODZs)" rather than the more commonly used "oxygen minimum zones (OMZs)" (*e.g.,* Paulmier and Ruiz-Pino, 2009) is used here to emphasise complete exhaustion of dissolved oxygen from water.

New Caledonia in September–November 1928 (Thomsen, 1931). In between these voyages, an expedition was planned by the Germans using the Survey Vessel *Meteor* from 1925 to 1927 to test the feasibility of Fritz Haber's secret project to extract gold from seawater to enable Germany to pay off the huge reparations to the Allies after the First World War (Taylor, 2018). As it turned out, the gold concentration in seawater was too low for Haber's project to succeed, but the ostensible oceanographic goals of the expedition were more than achieved. In addition to mapping the seafloor and delineating the mid-oceanic ridge in the South Atlantic, the *Meteor* Expedition generated priceless data on several key ocean variables including oxygen concentration that demonstrated intensification of the mid-depth oxygen minimum along the eastern boundary of the Atlantic (Wattenberg, 1938). Subsequent work showed that the eastern boundary intensification of the oxygen minimum comparable to that observed in the ETNP (Thomsen, 1931) also occurs in the tropical and subtropical South Pacific Ocean (Richards, 1957).

Results of the John Murray Expedition had revealed that an acute oxygen deficiency at intermediate depths, comparable to that reported from the ETNP (Schmidt, 1925; Thomsen, 1931) also occurs in the Arabian Sea (Sewell, 1934; Fig. 3, p. 670). It is most surprising that Richards' (1957) exhaustive review of oxygen in the ocean does not mention this work, even though it was published in *Nature*! The connection between this layer impinging upon the seafloor and apparently "azoic" conditions in the benthic realm was not made (Deacon and Rice, 1984).

## 2.2 Anomalous Location of the Indian Ocean's Oxygen Deficient Zones

Even before the IIOE, the pattern of oxygen distribution in the Indian Ocean (general northward decreases at all depths and widespread mid-depth oxygen deficiency in the Arabian Sea and the Bay of Bengal) had become broadly known due to occasional cruises of ships from outside the region, especially the erstwhile Soviet Union (*e.g.*, Ivanenkov and Rozanov, 1961; Nejman, 1961; Ivanenkov *et al.*, 1964). The IIOE data further confirmed this trend (Wyrtki, 1971). More information was gathered by subsequent workers including our group at NIO, a synthesis of which is made in this section.

The pattern of oxygen distribution in the Indian Ocean contrasts with that observed in the Atlantic and Pacific oceans. In the latter two oceans the most intense oxygen deficiency occurs along their eastern boundaries for two reasons. First, the regions where the oxygen minimum is the most intense fall under the shadows of subtropical gyres (systems where waters circulate around the basins, clockwise in the Northern Hemisphere and anti-clockwise in the Southern Hemisphere); as a result of this, subsurface water renewal is sluggish and the associated oxygen supply is limited. Second, surface winds are

favourable for upwelling of nutrient-rich deep water, resulting in high biological productivity, making more organic matter available for decomposition and consequently raising oxygen demand at depth (Paulmier and Ruiz-Pino, 2009). Subsurface water circulation in the Indian Ocean is quite different owing to two unique features of its geography.

(1) The Indian Ocean is bounded in the north at rather low latitudes (~25 $^{o}$N) by the Eurasian landmass (Fig. 2.1). This has two effects:

(a) Formation of subsurface waters in the region is severely limited, except to a small extent in the two marginal seas (Red Sea and Persian Gulf), and, to an even smaller extent, in the northern Arabian Sea (areas marked as A, B and C in Fig. 2.1). This is because subsurface waters are formed mainly due to cooling of surface waters that makes them denser. Because of its relatively high temperature, the Arabian Sea high salinity water is not dense enough to ventilate the ODZ. The cooler and more saline outflows from Persian Gulf and Red Sea do sink to the depths of the ODZ, but the volumes of these water masses are not large enough to greatly impact oxygen balance at intermediate depths (Swallow, 1984). It is estimated that 90 % of the oxygen supply to the ODZ is by waters that advect into the region from the south (Naqvi *et al*., 2010a). These waters have elevated oxygen content to begin with, but they get trapped in the equatorial circulation and lose oxygen (Swallow, 1984). When a parcel of water moves from one hemisphere to another, the direction in which it is rotating due to Earth's spin around its axis reverses. Because of this 'vorticity' constraint, intermediate waters flowing into the Arabian Sea from the south can cross the equator only along the western boundary. This mainly happens during the summer (Sharma, 1976; Quadfasel and Schott, 1982; Swallow, 1984). These waters can be identified by an oxygen maximum, which rapidly attenuates northward and completely disappears around 10 $^{o}$N latitude in the Arabian Sea (Naqvi *et al*., 1993). Thus, oxygen supply to subsurface waters diminishes northward and is particularly limited north of the equator (Sen Gupta and Naqvi, 1984).

(b) The proximity of landmasses profoundly affects atmospheric circulation due to differential heating and cooling of land and water, giving rise to the monsoonal cycle involving complete reversals of the atmospheric and upper oceanic flows twice in a year (Fig. 2.1). During the winter and spring seasons (November–March; Northeast Monsoon (NEM)), trade winds blow from the northeast, causing cooling of surface waters in the northernmost parts of the Indian Ocean that triggers weak convection in the northern Arabian Sea. By contrast, strong winds blow from southwest during the summer and early autumn (May–September; Southwest Monsoon (SWM)). The winds are particularly strong in the western Arabian Sea, driving intense upwelling off Somalia, Yemen and Oman (Fig. 2.1). The upwelled water spreads about 1,000 km offshore, supporting extensive phytoplankton blooms (Naqvi *et al*., 2003). This is, in fact, the only major western boundary upwelling system in the world.

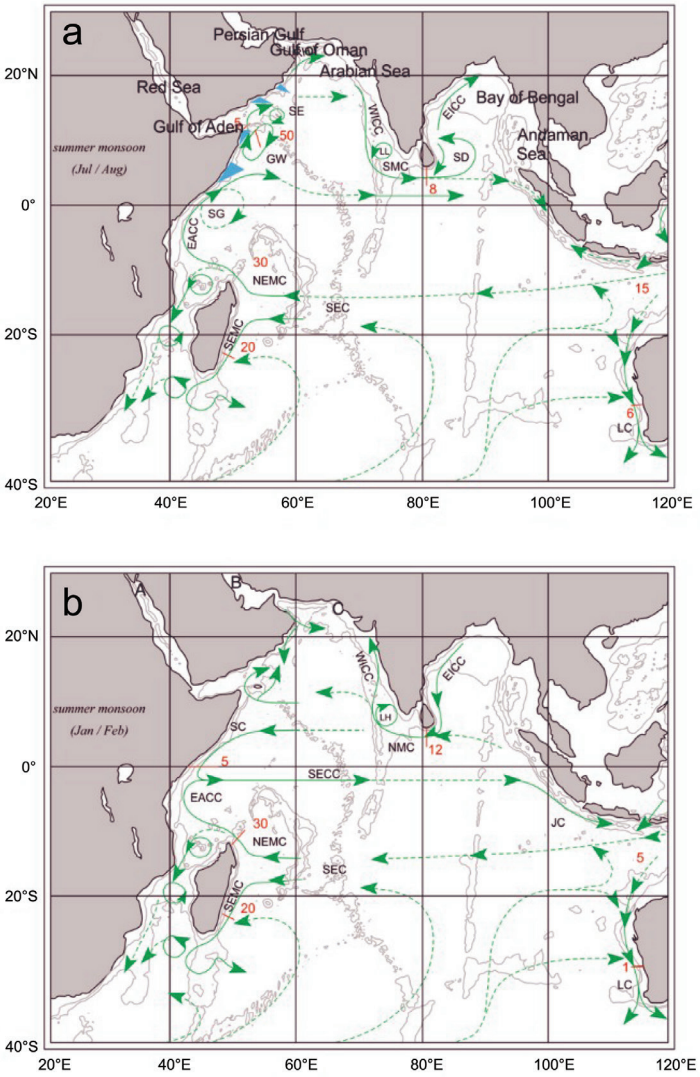



**Figure 2.1** A schematic representation of surface currents in the Indian Ocean during **(a)** Summer/Southwest Monsoon (SWM), and **(b)** Winter/Northeast Monsoon (NEM). Numbers in red are estimated volume transports (million cubic metres per second). The currents/features shown are: South Equatorial Current (SEC), South Equatorial Countercurrent (SECC), Northeast and Southeast Madagascar Current (NEMC and SEMC), East African Coast Current (EACC), Somali Current (SC), Southern Gyre (SG), Great Whirl (GW), Socotra Eddy (SE), Ras al Hadd Jet

(RHJ), West India Coast Current (WICC), Laccadive High and Low (LH and LL), East India Coast Current (EICC), Southwest and Northeast Monsoon Current (SMC and NMC), South Java Current (JC) and Leeuwin Current (LC). 'A', 'B' and 'C' are sites of subsurface water formation in the Red Sea, Persian Gulf and northern Arabian Sea, respectively. Adapted and modified from Schott and McCreary (2001).

In contrast to the Arabian Sea, seasonal (SWM) upwelling along the east coast of India, in the Bay of Bengal, is much weaker (Shetye *et al*., 1991), due to a combination of weaker winds and enormous river runoff from the Ganges-Brahmaputra system (Naqvi *et al*., 2006a; Chamarthi *et al*., 2008). Upwelling is not known to occur along the northeastern boundary of the Indian Ocean (*e.g*., off Myanmar; Naqvi *et al*., 2006a). As a result of this, in contrast to the Pacific and Atlantic Oceans, surface temperatures in the eastern Indian Ocean are generally higher than in the western Indian Ocean at low latitudes. However, this pattern, which also drives an opposite atmospheric Walker circulation, reverses in some years. This phenomenon, equivalent to El Niño-Southern Oscillation (ENSO) in the Pacific, is called the Indian Ocean Dipole (Saji *et al*., 1999). During strong dipole years such as 1997 upwelling is quite intense off the west coasts of Java and Sumatra (Murtugudde *et al*., 1999).

(2) The porous boundary between the Indian Ocean and the Pacific Ocean constituted by the Indonesian archipelago is the only low latitude connection between any two major ocean basins. This connection is of global significance because it allows flow of low salinity water (the Indonesian Throughflow) from the Pacific Ocean to the Indian Ocean close to the surface (Gordon, 1986), constituting a key component of the global thermohaline circulation, popularly known as the Great Ocean Conveyor Belt (Broecker, 1991). It may be noted that before the Isthmus of Panama was formed a few million years ago, exchanges of water and heat also occurred between the Atlantic and the Pacific at low latitudes, and ocean circulation and climate were very different at that time (*e.g*., Keigwin, 1982; Haug and Tiedemann, 1998). On the other hand, a closure of the Indonesian seaway 3–4 million years ago has been suggested to have drastically altered ocean circulation and climate (Cane and Molnar, 2001). The Indonesian Throughflow is responsible for the anomalous poleward surface flow off Western Australia (Fig. 2.1) in sharp contrast to equatorward currents off the west coasts of Africa and South America in South Atlantic and South Pacific; unlike these currents, which are wind driven, the Leeuwin Current off Australia is forced by the large density gradients arising from Indonesian Throughflow (thermohaline forcing; Godfrey and Weaver, 1991). Thus, conditions off Western Australia are not favourable for intense upwelling, making this region far less productive than the eastern boundary systems in the Atlantic (off Namibia) and Pacific (off Peru and Chile). Consequently, an ODZ is conspicuous by its absence off the Australian coast.

As a result of the above mentioned anomalies, subsurface waters in the Indian Ocean progressively age northward at all depths, and lose their oxygen content. An abrupt change occurs across the Hydrochemical Front located

around 10 °S (Wyrtki, 1973), which coincides with the South Equatorial Current and separates the oxygen-depleted waters of in the north from more oxygenated waters to its south (Sen Gupta and Naqvi, 1984).

Subsurface circulation in the upper kilometre or so in the northern Indian Ocean is complex and poorly known. As stated above, cross-equatorial exchange of intermediate waters only occurs off the African coast, where the relatively oxygenated Indian Central Water/Subantarctic Mode Water flows northward during the SWM. This flow can be seen in property distribution off the Arabian coast. The general northward tilt of oxygen contours north of the Hydrochemical Front in Wyrtki's (1971) maps of oxygen distribution (*e.g.*, at 300 m, reproduced in Fig. 2.2) reflects this flow. In addition, the western Arabian Sea also receives warm, saline outflows from the Persian Gulf and the Red Sea, the cores of which are characterised by $\sigma_\theta$ values of ~26.5 (~200–350 m) and ~27.1 (~500–800 m), respectively (Wyrtki, 1971). Both these waters, distinguished by salinity maxima, ventilate the thick oxygen minimum zone ($O_2 < 5$ µM) of the northwestern Indian Ocean, which lies between ~100–150 m and up to 1200 m, with the former occurring where the oxygen minimum is the most intense (Deuser *et al*., 1978; Codispoti *et al*., 2001). The Bay of Bengal does not receive any such outflow. However, flow of intermediate waters does occur from the Arabian Sea to the Bay of Bengal, as evident from a very broad salinity maximum at intermediate depths in the latter region (Rao *et al*., 1994). Moreover, due to a large excess of precipitation and river runoff over evaporation (positive water balance), the surface layer in the Bay of Bengal is much fresher as compared to the Arabian Sea (where the water balance is negative), producing a very strong thermohaline stratification, which greatly inhibits downward oxygen supply from the surface layer (Naqvi *et al*., 2006a). Thus, from physical considerations alone, the Bay of Bengal should be expected to experience a more pronounced oxygen deficiency compared to the Arabian Sea, particularly in its northeastern part.

An opposite pattern is expected from primary productivity. In addition to summer upwelling, the euphotic zone in the Arabian Sea is also fertilised by convective mixing in the winter. This convective mixing erodes the upper thermocline and causes nutrient entrainment and consequent phytoplankton blooms over a fairly large area in the northern/northwestern Arabian Sea (Banse, 1968, 1984; Banse and McClain, 1986; Madhupratap *et al*., 1996; Naqvi *et al*., 2002). Such blooms do not occur in the Bay of Bengal because the strong stratification persists despite sea surface cooling in winter (Naqvi *et al*., 2006a). One must also consider variations in re-mineralisation depths of particulate organic carbon (POC) sinking from the surface layer (Al Azhar *et al*., 2017) that may depend on the nature of POC, size of sinking particles and their ballast. In the zones of intense coastal upwelling of the western Arabian Sea, availability of silicate favours the growth of diatoms, and as silicate is utilised, the nitrate/silicate ratio in upwelled water being transported offshore decreases, causing a shift in phytoplankton community from diatoms to smaller photoautotrophs (Garrison *et al*., 1998). As discussed later, Naqvi *et al*. (2010b) suggested that such a shift is further supported by an increase in silicate to nitrate uptake ratio by diatoms in

waters experiencing deficiency of iron (Fe). Moreover, in the winter convection regime, diatom productivity is also limited by low silicate concentration in the entrained water (Naqvi *et al.*, 2002). The combined effect is that POC sinking from the surface may be re-mineralised more extensively at shallower depths offshore from the upwelling centres of the western Arabian Sea, causing an offshore intensification of the OMZ, consistent with observations (Wyrtki, 1971). Results of modeling studies also support such intensification (McCreay *et al.*, 2013; Al Azhar *et al.*, 2017).

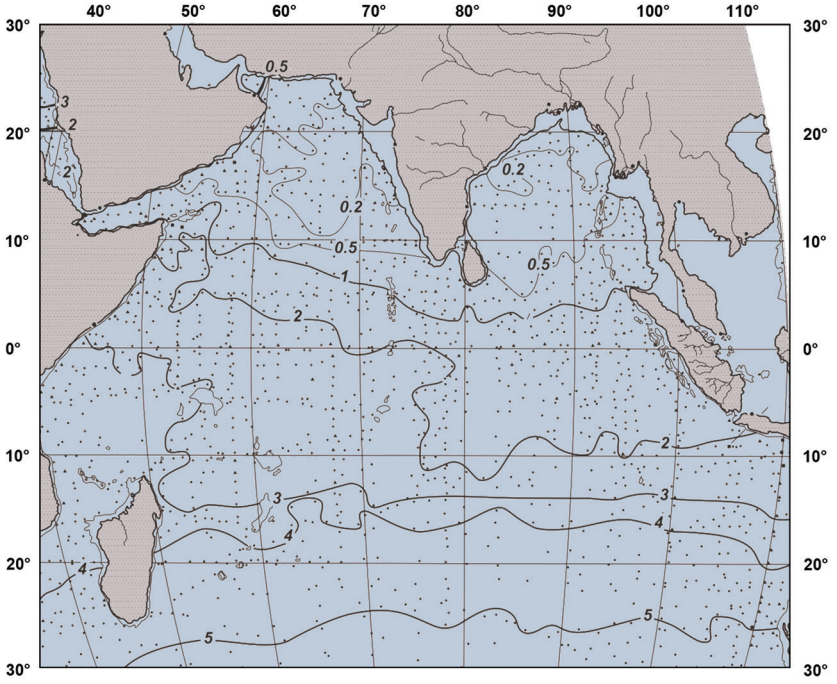



**Figure 2.2** Distribution of dissolved oxygen at 300 m in the Indian Ocean. From Wyrtki (1971).

Oxygen distribution shown by Wyrtki's (1971) atlas (*e.g.*, Fig. 2.2), although based on the classical Winkler data, shows that the OMZ in the Bay of Bengal is *slightly* less intense than that in the Arabian Sea. In view of what has been discussed above, this is a major anomaly which will be dealt with in some detail later.

# 3. NITROGEN CYCLING IN OPEN OCEAN ODZS

## 3.1 Oxic Versus Anoxic Degradation of Organic Matter

Heterotrophic organisms derive energy by oxidising organic matter produced by autotrophs. There are a number of chemical species dissolved in seawater that may serve as electron acceptors (oxidants) for this purpose. The most important of these are oxygen, nitrate (and other oxidised forms of nitrogen), manganese (IV), iron (III) and sulfate. The energy gained by the heterotrophs using these electron acceptors varies widely with the oxidation involving oxygen being the most profitable while that based on sulfate providing the least energy (Table 1). These electron acceptors are sequentially utilised in the order of decreasing energy yield with little overlapping, underlying the strict thermodynamic control on biologically mediated redox transformations in water and sediments (Froelich *et al*., 1979). However, in addition to the energy yield, one must also consider the relative abundance of these species. Concentrations of both oxygen and nitrate in seawater are quite variable but are usually below 350 µM and 40 µM, respectively. Mn and Fe are trace constituents occurring in nanomolar levels (in the oxidised states these metals occur mostly in particulate/colloidal forms). Sulfate is by far the most abundant of all electron acceptors, being a major constituent of seawater (~28 mM). Since Mn occurs in such low concentrations and nitrate is seldom fully utilised, biogeochemistry of ODZs is dominated by nitrogen, but in the sediments Mn, Fe and sulfate reduction make important contributions to the oxidation of organic matter (Jørgensen, 1983).

**Table 3.1** Free energy change associated with the oxidation of organic matter by different electron acceptors (from Froelich *et al*., 1979).

| Electron acceptor | Reduced product | Free energy change ($\Delta G^o$) KJ (mole glucose)$^{-1}$ |
|---|---|---|
| $O_2$ | $H_2O$ | -3190 |
| Mn (IV) | Mn (II) | -3090 to -2920 |
| $NO_3^-$ | $N_2$ | -3030 |
| Fe (III) | Fe (II) | -1410 to -1330 |
| $SO_4^{2-}$ | $S^{2-}$ | -380 |

## 3.2 Nitrogen Cycle

Nitrogen is an essential element for life, being a constituent of many key biochemical molecules such as amino acids (building blocks of proteins) and nucleic acids. Nitrogen is a polyvalent element that occurs in oxidation states ranging from –3 to +5 (Fig. 3.1) with molecular nitrogen ($N_2$, oxidation state 0) being by far the most abundant species, accounting for about 78 % by volume of the Earth's atmosphere. Unlike the atmosphere, the Earth's crust contains very little nitrogen, which underscores the importance of processes that are responsible for gaseous nitrogen production.

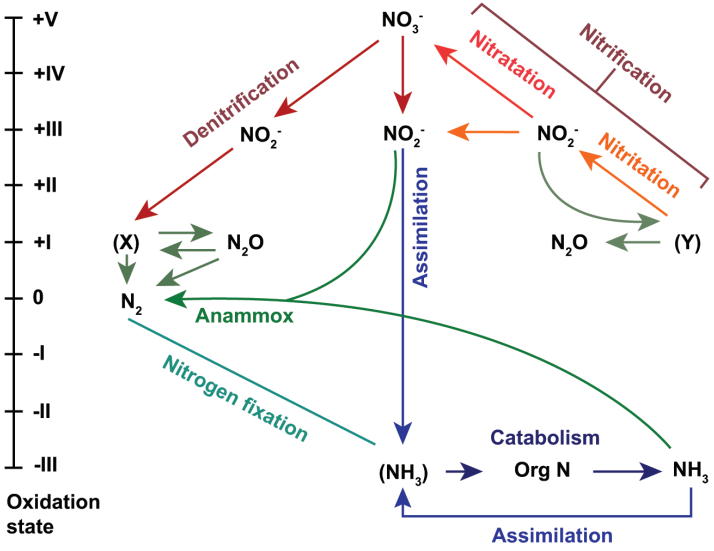



**Figure 3.1** The nitrogen cycle (from Naqvi, 2006). The three most important components of the cycle are nitrogen fixation, nitrification and denitrification. Nitrogen fixation (reduction of atmospheric $N_2$ to $NH_3$, predominantly by the diazotrophic bacteria) is the main source of combined nitrogen on Earth. In the oxidising part of the cycle (nitrification), $NH_3$, the most reduced form of nitrogen which is assimilated by plants and regenerated from the organic matter during its decay/respiration, is terminally oxidised to $NO_3^-$, with $NO_2^-$ as an intermediate and $N_2O$ a by-product. The reducing part of the cycle is mostly comprised of denitrification (utilisation of $NO_3^-$ as an electron acceptor by heterotrophic microbes to oxidise organic matter, leading to production of $N_2$ with $NO_2^-$ and $N_2O$ as intermediates). Some heterotrophs reduce $NO_3^-$ to $NH_4^+$, known as the dissimilatory nitrate reduction to ammonium (DNRA), not shown here. $N_2$ can also be produced in anoxic environments from anaerobic ammonium oxidation (anammox) by $NO_2^-$. When $NO_3^-$ is used as a nutrient, plants reduce it to $NH_3$ (assimilatory reduction), which also proceeds with $NO_2^-$ as an intermediate. In addition to organic matter, oxidised nitrogen species can also oxidise reduced species like $CH_4$ (not shown here but discussed in the text). (X) and (Y) are intra-cellular intermediates that do not accumulate in water (Codispoti and Christensen, 1985).

Despite the large atmospheric $N_2$ inventory, photosynthesis is generally limited, both in the ocean and on land, by the availability of nitrogen. This is because the strong triple bond between the two nitrogen atoms makes $N_2$ nearly inert and only a few prokaryotes have the capability to fix nitrogen from the atmosphere (converting $N_2$ to ammonia ($NH_3$)). The enzyme (nitrogenase) that catalyses this reaction is inhibited by oxygen, and so the diazotrophs ($N_2$ fixing bacteria) must maintain anaerobic conditions within their cells for this enzyme to function. This represents a major constraint on biological nitrogen fixation. Still the total natural biological nitrogen fixation rate exceeds 200 Tg N $yr^{-1}$ (1 Tg = $10^{12}$ g), with almost equal contributions coming from terrestrial and marine environments; in comparison the rate of abiotic nitrogen fixation (through lightning) is much lower (3-10 Tg N $yr^{-1}$; Galloway *et al.*, 2004). In the absence of a process to resupply it, natural nitrogen fixation would remove all $N_2$ from the atmosphere (3.92 x $10^9$ Tg; Yeung *et al.*, 2017) in <20 million years. Therefore, in order to keep the atmospheric nitrogen inventory constant, $N_2$ must be produced from the combined[2] nitrogen pool.

Since the Earth's surface environment is oxidising, the reduced nitrogen (oxidation state -3) fixed by diazotrophs and present in the biological tissues gets oxidised to nitrate (oxidation state +5) when liberated from the cell. This process (nitrification) proceeds with nitrite (oxidation state +3) as an intermediate and nitrous oxide ($N_2O$, oxidation state +1) a by-product (Fig. 3.1).

The above mentioned production of $N_2$ must occur through the reduction of nitrate. It had long been believed that the sole process responsible for converting nitrate to $N_2$ was heterotrophic denitrification that proceeds with nitrite, nitric oxide (NO, oxidation state +2) and $N_2O$ as intermediates (Fig. 3.1). However, close to the end of the last century it was demonstrated that autotrophic microbes could also produce $N_2$ through anaerobic ammonium oxidation (anammox) by nitrite (Strous *et al.*, 1999). As will be discussed below, this process appears to be more important than heterotrophic denitrification in the marine ODZs. It must be noted that most of the nitrite involved in the anammox reaction probably comes from the reduction of nitrate.

Thus, the entry and exit of nitrogen to and from the bioavailable combined nitrogen pool are catalysed by two key enzymes (nitrogenase and nitrate reductase, respectively). I call them *Chowkidar* (Urdu/Hindi for gatekeeper) enzymes. The activity of both enzymes is inhibited by oxygen, which obviously plays the key role in the nitrogen cycle as schematically shown in Figure 3.1.

2. Also referred to as the reactive or fixed nitrogen, combined nitrogen includes dissolved inorganic nitrogen (DIN) species ammonia, nitrate and nitrite and the bio-assimilable organic forms like urea. However, due to their low concentration, the organic forms are not significant for the mass balance.

## 3.3 Nitrogen Cycling in ODZs

### 3.3.1 Historical background

Interest in the ODZs as potential sites of combined nitrogen loss to $N_2$ and, to a smaller extent, to $N_2O$ essentially arose from observations made by early workers (Emery *et al*., 1955; Eriksson, 1959; Holland 1973), which indicated that the combined nitrogen inputs to the oceans by the rivers and from the atmosphere far exceeded its loss to the sediments (by $10^{12}$-$10^{13}$ g $yr^{-1}$) even though the extent of marine biological nitrogen fixation (~1 x $10^{14}$ g $yr^{-1}$, as stated above) was not fully appreciated at that time. In fact, even before that, the very first systematic study of nitrogen cycling in an ODZ made in the Arabian Sea by Gilson (1937) during the John Murray Expedition had generated data that should have been interpreted to support such as loss. It was on this expedition that a nitrite maximum, known as the secondary nitrite maximum (SNM), was first observed within an ODZ along with the more ubiquitous primary nitrite maximum found close to the base of the well-oxygenated euphotic zone (Gilson, 1937). Gilson erroneously attributed the primary nitrite maximum to the activity of nitrate reducing bacteria; we now know that it arises from a combination of nitrite excretion by phytoplankton and the oxidation of ammonium (the first step in nitrification; Fig. 3.1) (Lomas and Lipschultz, 2006, and references therein). Surprisingly, Gilson did not explicitly invoke this mechanism (dissimilatory nitrate reduction) for the formation of the SNM.

It was left to Wilhelm Brandhorst from Institute für Meereskunde, Kiel, to make what now appears to be an obvious connection between the oxygen deficiency and combined nitrogen loss, when he observed a similar feature in the ETNP during cruises undertaken in 1956 and 1957 (Brandhorst, 1959). In this paper, Brandhorst also included nitrite profiles from the Arabian Sea ODZ taken during the John Murray Expedition. Later, the SNM was also found to occur in the ODZ of the eastern tropical South Pacific (ETSP) by Wooster *et al*. (1965) and in the eastern South Pacific off Namibia by Calvert and Price (1971).

Brandhorst (1959) found waters within the SNM to be apparently deficient in nitrate relative to those above and below this feature. Thomas (1966) made the first attempt to quantify these deficits using the average nitrate to phosphate ratio in waters immediately below the SNM. This approach is essentially based on the classical work by Alfred Redfield from Woods Hole Oceanographic Institution who found the N:P ratio in plankton to be quite constant and almost the same as the average ratio of the concentrations of nitrate and phosphate in seawater (Redfield, 1934). Incidentally this paper by Redfield, which forms a pillar of ocean biogeochemistry, was published in a memorial volume, for which Redfield would perhaps not get any credit from most scientific and academic institutions today as the volume had an "impact factor" of zero. The original Redfield ratios (C:N:P:1 = 140:20:1) were later revised to 106:16:1 (Redfield, 1958). Assuming that these elements were present in constant oxidation states in organic matter,

the ratios of oxygen consumption/production to regeneration/uptake of carbon, nitrogen and phosphorus during respiration/photosynthesis were postulated to be $\Delta O_2$:$\Delta C$:$\Delta N$:$\Delta P$ = -138:106:16:1 (by moles) by Redfield *et al.* (1963).

Cline and Richards (1972) developed a much more refined method to compute nitrate deficits within the ODZ in the ETNP based on Redfield stoichiometry. They computed nitrate concentrations expected in a parcel of subsurface seawater if there were to be no losses as the sum of the oxidative and pre-formed fractions[3]. While the observed linear regression between the apparent oxygen utilisation (AOU) and nitrate was used to compute the oxidative fraction from AOU, the pre-formed nitrate fraction was quantified from pre-formed phosphate utilising its linear relationship with pre-formed nitrate in the region. The amount of "nitrate deficit" could then be quantified as the difference between the expected and observed nitrate (plus nitrite) concentrations.

Cline and Kaplan (1975) made the first measurements of natural abundance of the two stable isotopes of nitrogen ($^{15}N$ and $^{14}N$) in dissolved nitrate in the ETNP. Of the two isotopes, $^{14}N$ is far more abundant in nature, accounting for 99.6 % of all nitrogen. Their results showed that the $^{15}N/^{14}N$ ratio was significantly higher within the ODZ than above and below this zone, indicating that the process(es) occurring within the ODZ discriminated between the two isotopes, with preferential loss of $^{14}NO_3^-$. The only process responsible for the nitrogen loss was then believed to be heterotrophic denitrification. The extent of $^{15}N$ enrichment in residual nitrate, expressed as $\delta^{15}N$ with reference to atmospheric $N_2$, has been found to correlate with the amount of combined nitrogen lost, *i.e.* the nitrate deficit.

At about the same time, Codispoti and Richards (1976) followed a different approach to quantify denitrification in the ETNP. This approach involved computing the export of nitrate deficits, mainly through horizontal advection, but also through diffusion, from the ODZ. These workers introduced a term called "equivalent nitrate" defined as the sum of the observed nitrate and nitrite concentrations and the product of the observed oxygen concentration and the Redfieldian ratio between nitrate regeneration and oxygen consumption ($\Delta NO_3^-/\Delta O_2$ = 16/138). This property was mapped at selected density surfaces, and nitrate deficits were calculated as the difference between the expected nitrate concentration based on the property distribution south of the ODZ and the "equivalent" nitrate concentration computed for individual samples. The deficits so obtained agreed reasonably well with those derived from the approach

3. The "pre-formed" fraction is the concentration of a nutrient in a parcel of water at the time the water mass was formed (*i.e.* just before the water parcel had left the sea surface). The "oxidative" fraction is the additional amount of nutrient regenerated from organic matter since the water parcel had left the surface. It is assumed that the water parcel was 100 % saturated with respect to atmospheric oxygen when it was at the surface. The oxidative fraction may then be calculated from the apparent oxygen utilisation (AOU, the difference between the saturation and measured concentrations) and the ratio between oxygen utilisation and nutrient regeneration (Redfield *et al.,* 1963). The pre-formed concentration is obtained by subtracting the oxidative fraction from the total (measured) concentration.

of Cline and Richards (1972) described above. The total export of nitrate deficits out of the ODZ of the ETNP (area ~3 x $10^6$ $km^2$), which under a steady state should equal the rate of denitrification, was estimated to be ~20 Tg N $yr^{-1}$ (Codispoti and Richards, 1976). This was the first reliable basin scale estimate of the rate of nitrogen loss from any ODZ. This value compared well with another independent estimate that involved measurements of activity of the respiratory electron transport system (ETS). This method was developed by Ted Packard, another student of Francis Richards at the University of Washington (Packard, 1971). In using this method, ETS activity provides a measure of respiration rates that can be converted to denitrification rates using a suitable conversion factor, assuming that denitrification is the dominant respiratory process within the ODZ.

The SNM of the ETSP, first reported by Wooster *et al*. (1965), was investigated in greater detail by Fiadeiro and Strickland (1968). This nitrite maximum was also believed to result from anaerobic (dissimilatory) nitrate reduction. As in case of the ETNP, nitrate losses to gaseous nitrogen seemingly occurred from this system as well, with the early estimates of denitrification rate varying from 3–7 Tg N $yr^{-1}$ (Tsunogai, 1971) to 18–26 Tg N $yr^{-1}$ (Elkins, 1978). More extensive measurements of ETS activity by Codispoti and Packard (1980) allowed them to make a robust estimate of the denitrification rate in the ETSP as ~20 Tg N $yr^{-1}$, which was well within the range reported previously by Elkins (1978).

Thus, until the mid-1970s research on nitrogen cycling in oxygen deficient waters was almost entirely confined to the ETNP and ETSP, and relatively little was known about the ODZs of the Indian Ocean. However, the Arabian Sea was widely recognised as a region where water column denitrification occurred (*e.g.*, Richards, 1965; Cline and Richards, 1972; Deuser, 1975). As stated earlier, Brandhorst (1959) had pointed out the similarity between his measurements in the ETNP with the observations made by Gilson (1937) in the Arabian Sea during the John Murray Expedition. Moreover, Russian researchers had not only confirmed the occurrence of a SNM in the Arabian Sea (Rozanov and Bykova, 1964), but had also reported the presence of hydrogen sulfide ($H_2S$) in traces within the oxygen-depleted layers of both the Arabian Sea and Bay of Bengal (Ivanenkov and Rozanov, 1961).

By the 1970s the centre of gravity of research on ODZs had clearly shifted to the US, where researchers were primarily focussing on the ODZs of the Pacific Ocean, with Francis Richards' group at the University of Washington providing the lead. This is now a fairly crowded research area with amazingly rapid strides having been made in this millennium by groups scattered all around the world, not only on chemical transformations but also ecology of microbes that mediate them. Back in the early 1970s, one could count the number of people working on marine ODZs on her/his fingertips. The community of European researchers in this field had shrunk after WWII and was mostly confined to institutions located around the Baltic Sea. One such group was in Gothenburg. This group included stalwarts like Stig Fonselius, who had spent a lifetime studying anoxia in the Baltic, and an Indian: Rabin Sen Gupta. Having worked on the biogeochemistry

of the Baltic, including nitrogen cycling for his Ph.D. (Sen Gupta and Koroleff, 1973), Sen Gupta was well trained and eager to pursue similar research in the Indian Ocean after he returned to India and joined NIO in 1973.

### 3.3.2 My involvement in research on anoxia

When I joined NIO in November 1974, I had no training in Oceanography. In fact, until then I had not even seen the sea. So, I had a lot to catch up with. There was, of course, no Internet at that time for online learning. Fortunately, NIO had an excellent library, and everyone in the Institute was keen to help a young lad who wanted to pursue a career in Marine Science without knowing much about it. The good thing was that I had lots of interest and enthusiasm.

Despite its success, the IIOE was implemented in exploration mode with few researchers involved in projects with clear-cut scientific objectives. As a result, although a large volume of data was collected, the science was not question driven, and not many process studies were undertaken. Thus, there were a number of important scientific issues to be addressed, including many related to water column anoxia. However, the lack of adequate resources (research funds and infrastructure such as analytical facilities and research vessels) was the major constraint at that time for pursuing research on these topics. For example, the problem for which CSIR had awarded me a fellowship was: why chemical precipitation of $CaCO_3$ does not occur from seawater in spite of surface waters being highly saturated with respect to both calcite and aragonite, especially in the tropics? It was a nice scientific problem chosen for me by the then Head of Chemical Oceanography Division, C.V. Gangadhara Reddy, a very knowledgeable person, who passed away very early. However, after working for a few months on this topic, I realised that NIO simply did not have analytical facilities needed for this work.

As it turned out, I did not have to stick to this topic because in early 1976 I accepted a regular position (a Junior Scientific Assistant) in the Institute, giving up the CSIR fellowship. It was the lowest entry level position that a person with a Master's degree was given at that time. The basic salary was only INR 485 *per* month. But it was a stable job that my family members including my uncle strongly encouraged me to go for. I was destined to serve NIO/CSIR for 44 more years!

By this time I had developed a real interest in marine anoxia, mainly because of interactions with Dr. Sen Gupta who, as described below, was already working on the IIOE and the Indian Naval Ship *Darshak* data. However, even in this case, not having access to a research vessel meant that new measurements could not be made. Fortunately, NIO acquired a research vessel in December 1975, named *Gaveshani* (Fig. 3.2). *Gaveshani* was not originally built as a research vessel. Having a flat bottom and single hull, she was a hopper barge operating in the Hooghly River. She was converted to research vessel at a very modest cost. Therefore, she had some inherent shortcomings. For example, although she was

quite large (68.5 m in length), the deck and lab spaces were severely limited. The Chemistry Lab where I spent most of my time was less than 15 square metres in area. Also, the deck and lab equipment were quite obsolete. There was no satellite position-fixing equipment on board and the coordinates were determined using a sextant. There was an unforgettable occasion in 1977 when we were doing a cruise in the Bay of Bengal. The weather turned stormy, and our position could not be fixed for several days. The sea was so rough that the vessel had to be sealed. We were convinced that we would not survive. The ship was very uncomfortable under such conditions. Still the acquisition of *Gaveshani* was a historic event for NIO as this enabled us to venture out to the open ocean (Fig. 3.3). A large part of my early research was done using data collected by *Gaveshani.*

**Figure 3.2** India's first Research Vessel *Gaveshani*. Converted from a hopper barge, the ship was commissioned in December 1975 and remained in service till 1994.

**Figure 3.3** Participants of R.V. *Gaveshani* Cruise #86 conducted in January–February, 1981, for exploring polymetallic nodules in the central Indian Ocean. The cruise was led by Dr. S.Z. Qasim, the then Director of NIO (standing, fourth from the right) with Dr. H.N. Siddiquie, then Head, Geological Oceanography Division (standing, second from the right), as the Deputy Leader. I am on extreme right in the sitting row. Both Dr. Siddiquie and I had the privilege of leading the Institute later.

Fortunately, the situation started improving rapidly in the 1980s both regarding funding and infrastructure including modern, well equipped ships. Thus, I believe I was very fortunate to have been at the right place at the right time. One problem still remained, though. I was finding it very hard to enrol for a Ph.D. degree. This was because unlike today, CSIR was then not recognised as a degree awarding organisation, and while NIO was recognised as a centre for research by a number of universities across the country, these universities would only allow their own degree holders to enrol/register for a Ph.D. Goa University was not yet established, and Lucknow University, from where I had obtained both of my degrees (B.Sc. and M.Sc,), did not recognise NIO. So, I was quite frustrated and even contemplated moving abroad. I wrote to Wolfgang Seiler, who was then the Group Leader of Trace Gases at the Max Planck Institute for Chemistry in Mainz, Germany. Prof. Seiler kindly accepted to guide me, but then suddenly I got a break. On the initiative of Appasaheb Pant, whose daughter Aditi Pant was a colleague and close friend of mine, Poona University recognised NIO as a research centre and Sen Gupta as a research guide in the Department of Chemistry, enabling me to finally secure a Ph.D. registration. Still, I could only submit my dissertation in July 1986 and had to wait for 10 more months to be awarded a Ph.D. degree.

### 3.3.3 Previous work on Indian Ocean ODZs

Soon after returning from Sweden, Sen Gupta started working on ODZs of the Indian Ocean. Using data collected during the *Meteor* cruise in 1965 as a part of the German IIOE programme, Sen Gupta *et al*. (1976) computed nitrate deficits essentially following Cline and Richards (1972). Positive deficits reaching up to a maximum of ~25 μM were seen within a wide depth range (~150–1,000 m), and denitrification was inferred to occur north of 4–5 $^{o}$N latitude.

A dedicated cruise of R.V. *Atlantis II* was undertaken in January 1977 by Werner Deuser from Woods Hole to address the Arabian Sea denitrification problem. The data generated were used to compute nitrate deficits (Deuser *et al*., 1978). The basic premise of this study was that denitrification was largely confined to the layer that received the Persian Gulf Water, such that the "expected" nitrate concentrations could be calculated from the observed linear (inverse) relationship between nitrate and salinity close to the core of the Persian Gulf Water. The computed deficits were quite modest (maximum ~5 μM), and were also restricted only to the region north of ~15 $^{o}$N latitude. Assuming that the deficits accumulated over a period of 3–30 years (residence of water in the denitrifying layer), the denitrification rate in the Arabian Sea was estimated to range between 0.1 and 1 Tg N yr$^{-1}$, one to two orders of magnitude smaller than the above mentioned estimates for denitrification in each of the two ODZs of the eastern tropical Pacific (ETNP and ETSP).

## 3.3.4 Our contributions; Arabian Sea

### a. Denitrification

In view of the large mismatch between the two studies (Sen Gupta *et al*., 1976, and Deuser *et al*., 1978), I was convinced that the extent of denitrification had been vastly overestimated in one study and underestimated in the other. So, I decided to recalculate nitrate deficits. Like Sen Gupta, I also followed Cline and Richards' approach with some refinement, but unlike Sen Gupta, I used fresh, self-collected data from the Arabian Sea, designed to test the key assumption made by Deuser *et al*. (1978) *i.e*. the association of denitrification with the Persian Gulf Water. As I had expected, I ended up with deficits that were intermediate of the two earlier studies of the Arabian Sea. I prepared my first manuscript on denitrification (Naqvi *et al*., 1982) and communicated it to *Deep-Sea Research*, which was then being edited by none other than Francis Richards. To my extreme delight, the reviews were mostly positive, but Richards himself had quite a bit to say on its contents including, "*I can take care of the non-idiomatic English, but your meanings must always be clear*". He was known (feared!) for editing manuscripts mercilessly (in red ink) - I have not seen another editor like him - and he did that with my manuscript as well, perhaps more than usual. In the end he said, "*Another good estimate of denitrification in the Arabian Sea will be a welcome addition to the literature*". As it turned out, however, it was not a good estimate in terms of the rate. It was not because the estimated deficits were widely off the mark, but because of the wrong choice of the residence time: We had chosen a value of 30 years, the upper end of range used by Deuser *et al*. to arrive at an estimate of 3.2 Tg N $yr^{-1}$. Had we chosen the value (3 years) at the lower end of their range, our estimate would have been closer to what I now believe is the most likely value (25–30 Tg N $yr^{-1}$). The popular view at that time was that intermediate waters in the northern Indian Ocean were stagnated (Qasim, 1982). Soon afterwards, Swallow (1984) demonstrated that such was not the case.

Because the range of estimated residence times of water in the denitrifying layer was very wide, leading to a corresponding uncertainty in computed denitrification rates, the next logical step was to follow approaches that did not involve residence time. Moreover, oxygen measurements are generally more accurate than phosphate measurements, when data from multiple sources are used, and so we strived to do away with the use of phosphate data for computing nitrate deficits. We achieved this by using the tracer "NO" (note it is not nitric oxide) introduced by Broecker (1974) and defined as the sum of oxygen concentration and nitrate concentration times the ratio between the apparent oxygen utilisation (AOU) and nitrate regeneration during oxic respiration:

$$NO = O_2 \text{ (obs)} + NO_3^- \times \Delta AOU/\Delta NO_3^-)$$

As pointed out by Broecker (1974), NO should behave conservatively as long as nitrate is not lost.

Taking the $\Delta AOU/\Delta NO_3^-$ to be 8.65 (by moles), we examined the relationship between NO and potential temperature ($\theta$) in the Arabian Sea for samples not affected by denitrification (*i.e.* not containing secondary nitrite) and found NO to vary approximately linearly in two ranges (Fig. 3.4) within the depth range of our interest with a discontinuity at ~15 °C (Naqvi and Sen Gupta, 1985). It may be pointed out that this relationship should actually be non-linear, reflecting the variability of oxygen solubility with temperature, if we ignore the variability of 'pre-formed' nitrate. For our purpose though, a linear approximation seemed adequate. This approach was also based on Redfield stoichiometry, Its suitability lay in the fact that the "expected" nitrate could be computed simply from potential temperature. This method was applied to the large amount of data then available enabling the quantification of nitrate deficits. The nitrate deficits were then used along with dynamic computations and reasonable values of diffusion constants to work out advective and diffusive exports of the deficits from the zone of denitrification. The net export of nitrate deficits, which under steady state should equal denitrification rate, came to 29.5 Tg N $yr^{-1}$ (Naqvi, 1987).

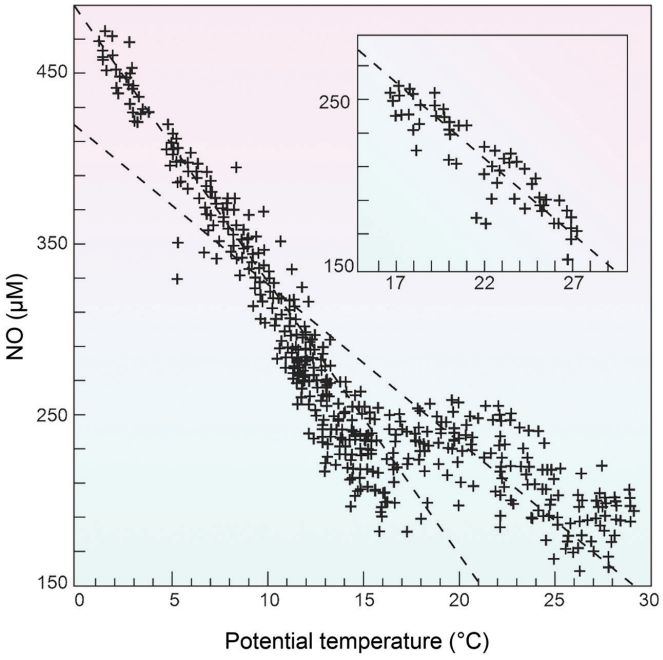



**Figure 3.4** Plot of 'NO' ($[O_2] + 8.65[NO_3^-] + 8.65[NO_2^-]$) *versus* potential temperature for the eastern Arabian Sea (between ~12 °N and 17 °N latitudes, east of 67 °E longitude). The straight lines give the least squares fits for two subsets of data: The relationship in deeper waters (line with the steeper slope) was derived using all data with $\theta \leq 9$ °C. For shallow and intermediate depths

(line with less steep slope), which included most of the waters affected by denitrification/anammox, samples which had potential temperature within the range $17 \leq \theta \leq 27$ °C and also did not contain secondary nitrite (shown in the inset) were only considered. Loss of combined nitrogen is evident from low 'NO' values, especially between $\theta$ values of ~10 °C and 20 °C. From Naqvi (1994).

This work formed the core of my Ph.D. thesis (Naqvi, 1986). I sent a copy of the thesis to Lou Codispoti, who was then at Bigelow Laboratory for Ocean Sciences. I met Lou personally in 1990 when I visited Lamont Doherty Geological (now Earth) Observatory (L-DEO) of Columbia University as a C.V. Raman Fellow. That was the beginning of our long friendship. During this visit, I also met most other former students of Francis Richards and nearly everyone else in the U.S. engaged in research on ocean anoxia. My own research was greatly influenced by their work in the Pacific. So much so that I considered myself to be a disciple of Francis Richards, with whom I had maintained contacts until his death in 1984, in the same way as Eklavya considered Dronacharya as his guru in Indian mythology. Over a period of time, I developed close scientific collaboration with quite a few American scientists, including an informal participation in the Arabian Sea Process Study (1994–1995) of U.S. JGOFS (Joint Global Ocean Flux Study). Being a relatively small community, everyone then personally knew everyone else and kept close contacts with each other (Figs. 3.5, 3.6).

Our findings that denitrification in the Arabian Sea had been severely underestimated, and that its rate appeared to be comparable, if not more, than the published estimates of rates in each of the two Pacific ODZs, were confirmed by subsequent work. Measurements of ETS activity made by us yielded a very similar denitrification rate (24–33 Tg N $yr^{-1}$; Naqvi and Shailaja, 1993). Using data taken during the World Ocean Circulation Experiment (WOCE), Howell *et al.* (1997) combined nitrate deficits, estimated from an isopycnal mixing model and assuming Redfield stoichiometry, with water mass ages derived from the distribution of chlorofluorocarbon (CFC-11). Their estimate was a little bit lower ($21 \pm 7$ Tg N $yr^{-1}$), but another estimate derived from a 3-dimensional ecosystem model (26.2 Tg N $yr^{-1}$) was very close to our value (Anderson *et al.*, 2007). The short ventilation time (a few years) of waters within the SNM zone (Somasundar and Naqvi, 1988) implied by a high denitrification rate was supported by short term (seasonal) variability of chemical parameters reported by Naqvi *et al.* (1990), Morrison *et al.* (1999), Banse *et al.* (2014), and Shenoy *et al.* (2020).

Utilising all the nitrite data then available with the NIO Data Centre, I could demarcate the zone of denitrification in the Arabian Sea (Naqvi, 1991). This zone (Fig. 3.7) was estimated to cover an area of $1.37 \times 10^6$ $km^2$. It nicely corresponds to the zone of minimum oxygen in the northeastern and central Arabian Sea, as inferred from Wyrtki's (1971) maps (Fig. 2.2).


**Figure 3.5** **(a)** A gathering of old friends and collaborators in NIO in December 2015 for celebrating the Golden Jubilee of NIO. **(b)** The 'Nitrogen Gang' (left to right: Don Canfield, Bo Thamdrup, Bess Ward, Lou Codispoti and myself).

Data along two transects, one extending from the Indian coast to the Omani coast and the other from the south-central Arabian Sea to the Gulf of Oman, give an idea of spatial extent of the SNM (Fig. 3.8). The north-south sections of oxygen and nitrite were constructed using data from a US JGOFS cruise on board R.V. *Thompson* in October 1994. In this case, oxygen measurements in low oxygen waters were made by me following the colorimetric method of Broenkow and Cline (1969). From these data, higher oxygen levels in the northwestern Arabian Sea could be clearly seen, with the Persian Gulf Water injecting oxygen into the ODZ in the northwestern Arabian Sea and the

Gulf of Oman. The SNM was found to be largely confined to waters having dissolved oxygen below 1 μM. However, as stated earlier, the SNM zones are actually functionally anoxic, as also documented by Lam *et al.* (2009) for the Arabian Sea ODZ, based on measurements using the STOX sensor that yielded values < 90 nM (note that the detection limit was higher on that cruise as compared to that of current sensors). As compared to the north-south section, the data used for the east-west oxygen section are less reliable and more variable in the low range. This section was constructed by combining observations made in the summer of 1995 on a US JGOFS cruise of R.V. *Thompson* in the western half of the basin and on a cruise of R.V. *Sagar Kanya* in its eastern half. Oxygen values were determined by manual Winkler titrations on *Sagar Kanya* and the interference by nitrite was not supressed. The more accurate Thompson data, generated by automated titrations, were found to be only marginally higher within the oxygen minimum layer than those obtained with the colorimetric method (Morrison *et al.*, 1999). This inter-cruise difference is masking subtle variations in oxygen concentrations at its minimum. In actuality, as we will also see later (in Section 8), while the nitrite-free waters in the western Arabian Sea contain detectable oxygen, the nitrite-bearing ODZ in the central and eastern parts of the section is functionally anoxic. In any case, concentrations of oxygen at its minimum are below 5 μM all along this section at these latitudes. There are two other noteworthy features discernible in the east-west oxygen and nitrite sections: coastal upwelling and offshore deepening of the oxycline in the west (off Oman) and a poleward undercurrent transporting relatively more oxygenated (nitrite-free) water in the east (off India).

**Figure 3.6** With some pioneers in marine ODZ research; Francis Richards' students at a meeting in Gran Canaria in June 2006 (left to right: myself, Lou Codispoti, Gayle Devol, Al Devol and Ted Packard).

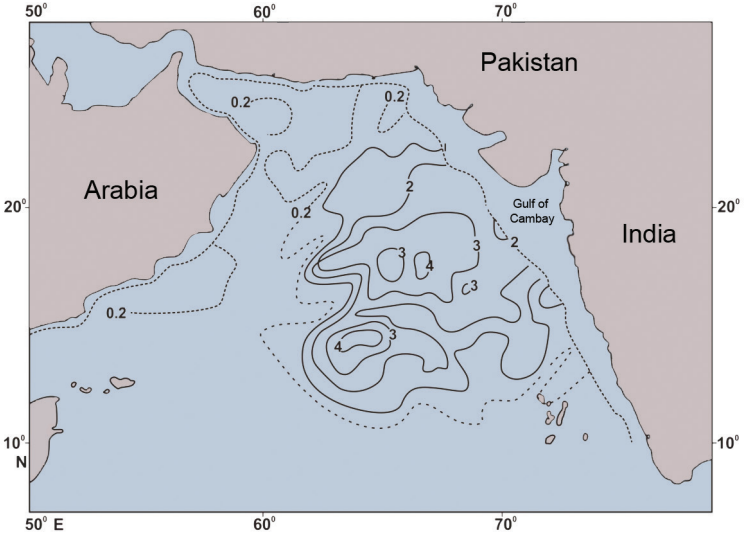



**Figure 3.7** Distribution of nitrite (μM) at the secondary maximum averaged for each 1° square using all the data available in 1989. The 200 m depth contour is also shown. From Naqvi (1991).

The distribution of nitrite shown in Figure 3.7 is generally consistent with the geographical variability reported by Rozanov and Bycova (1964). In 1990 I was not aware of this work that had appeared in Russian literature, but it is now available online as English translation by the U.S. Naval Oceanographic Office (https://apps.dtic.mil/sti/pdfs/AD0651200.pdf). Considering these data in conjunction with Gilson's measurements during the John Murray Expedition (Brandhorst, 1959), it would appear that the SNM zone has been fairly stable over a multi-decadal time scale with perhaps the largest variability occurring in the western Arabian Sea due to advection of waters from the south (Rixen *et al.*, 2014) as well as from the Persian Gulf (Codispoti *et al.*, 2001; Banse *et al.*, 2014). We will see later that the SNM is a good indicator of the occurrence of nitrate reduction in the water column.

## b. Nitrous oxide cycling

Denitrification produces inert $N_2$, and to a smaller extent, $N_2O$, a strong greenhouse gas (Elkins, 1978; Elkins *et al.*, 1978; Codispoti and Christensen, 1985). The distribution of $N_2O$ within the OMZs of the Pacific was well known following the works by Cohen and Gordon (1978) and Pierotti and Rasmussen (1980). These studies revealed relatively low (<10 nM) concentrations, except at the boundaries of the SNM where maxima in $N_2O$ concentrations (tens of nM) were located. The SNM itself was associated with an $N_2O$ minimum, indicating that $N_2O$ was being consumed within this layer.

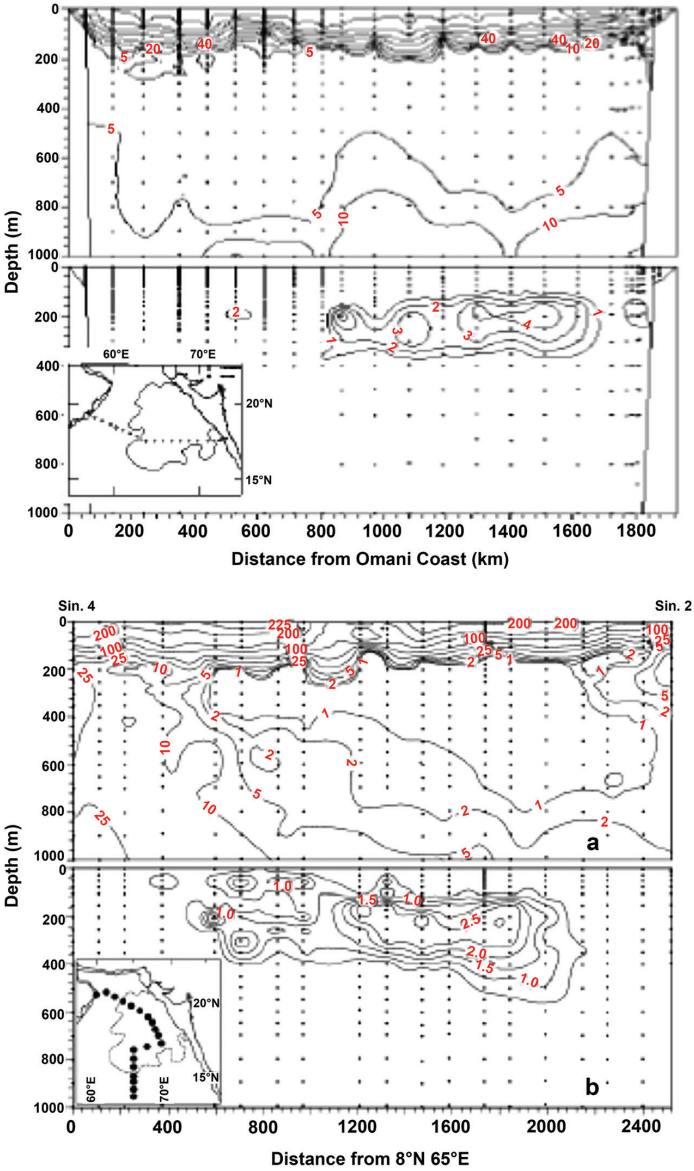



**Figure 3.8** Vertical sections of oxygen (μM, upper panels) and nitrite (μM, lower panels) in the upper kilometre showing their variations in roughly east-west and north-south directions. Insets show station locations and the boundary of the secondary nitrite maximum (SNM) zone according to Naqvi (1991).

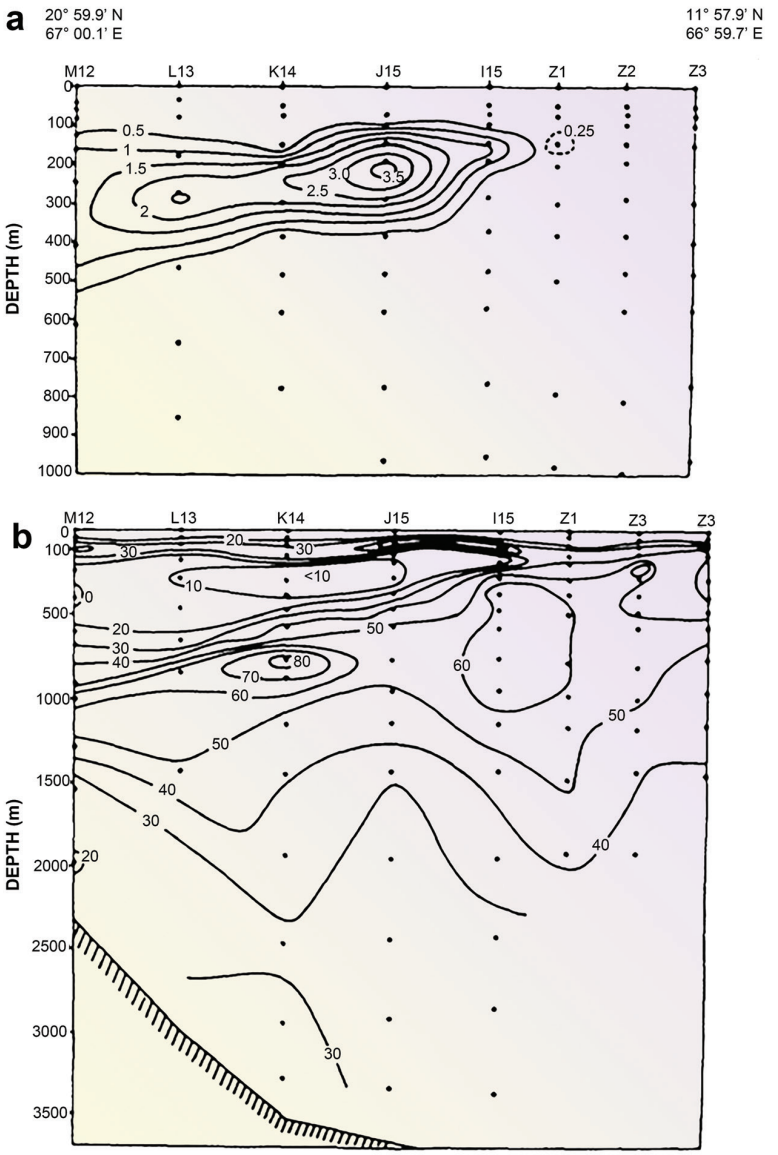



**Figure 3.9** Vertical sections of nitrite (μM, upper panel) and nitrous oxide (nM, lower panel) along 67 °E longitude in the Arabian Sea. Note that only the secondary nitrite maximum is shown. From Naqvi and Noronha (1991) with permission from Elsevier.

These days $N_2O$ analysis is done on an almost routine basis, but back in 1980s it was not trivial, and we had to build in house expertise for this purpose. Following Yoshinari (1976), we rigged up the extraction and analytical system that required about 1 litre of sample (as compared to few millilitres today) and involved tedious purge and trapping before analysis with a gas chromatograph. Analysis of each sample would take close to an hour, and the chromatograms had to be manually integrated.

My colleague Ronnie Noronha and I made our first measurements of $N_2O$ on a cruise of *Sagar Kanya* in December 1988. The results (Fig. 3.9) were similar to those reported from the ETNP by Cohen and Gordon (1978), but the concentrations in the surface layer were higher. We prepared a manuscript and submitted it to *Deep-Sea Research*. One of the reviewers was unjustly critical. She/he expressed doubts about our ability to measure $N_2O$ properly: according to her/him it was "a shame" that we had not analysed air to show that we had the capability to make reliable $N_2O$ measurements. Fortunately (or unfortunately), while this manuscript was in review, a paper appeared in *Nature* reporting high surface saturation of $N_2O$ in the Arabian Sea (Law and Owens, 1990); the average saturation (186 %) reported by these authors was exactly the same as derived from our data. We brought it to the notice of John Milliman, the then editor of *Deep-Sea Research*. He was convinced and immediately accepted the manuscript (Naqvi and Noronha, 1991). I must add that this was among the very few instances in my long career where I saw a bias against researchers from the developing world.

## c. Collaborations with groups outside India

Starting in the 1990s, we began to collaborate with several American groups on nitrogen cycling in Indian Ocean ODZs. In 1994, the Office of Naval Research (USA) approved a project under the US-India Fund that involved collaboration between our group and a number of American researchers including Bess Ward, from University of California, Santa Cruz, CA (who later moved to Princeton University), Lou Codispoti, from Monterey Bay Aquarium Research Institute, Monterey Bay, CA (who moved to Horn Point Lab, University of Maryland), Al Devol, from University of Washington, Seattle, WA, and Tadashi (Ted) Yoshinari, from Wadsworth Centre and State University of New York at Albany, NY. One of the objectives of this project was to make direct measurements of denitrification rate using $^{15}N$-labelled nitrate. The incubation experiments were conducted both *in situ* by directly injecting the labelled tracer into the sample and by keeping the bottle suspended in ODZ waters for the duration of the experiment, as well as *in vitro* on board ship in 1 litre amber coloured bottles (Devol *et al*., 2006). Rates derived from these experiments averaged 9.1 ± 1.0 nmol. $l^{-1}$ $d^{-1}$ in the open ocean and 33.3 ± 12.4 nmol. $l^{-1}$ $d^{-1}$ over the Indian shelf. Extrapolation of these rates to appropriate volumes of ODZ water yielded a total rate of 41 ± 18 Tg N $yr^{-1}$, somewhat higher than the above mentioned rates based on stoichiometric calculations and ETS activity (Devol *et al*., 2006).

An earlier attempt to measure denitrification rate through the application of the $^{15}N$ tracer technique in the ETNP (Goering, 1968) apparently overestimated $N_2$ production because of the bottle effect (*i.e.* generally accelerated rates due to the proliferation of bacteria on the inner surface of containers when incubations are carried out in small volumes; Cline and Richards, 1972), but the same technique had surprisingly failed to detect $N_2$ production in the ODZ off Peru (Goering and Dugdale, 1966). In our case, the rates were determined, in a majority of cases, using only two points (initial and final). In limited cases (14 out of 33 incubations), where 3–4 time series incubations were done, the $N_2$ production was found to be nearly linear with time, indicating little bottle effect. It must be pointed out that only $^{29}N_2$ was measured in this study, so the production through heterotrophic denitrification and anammox (more on anammox below) could not be differentiated (Devol *et al*., 2006).

We also wanted to investigate the fate of ammonia released during the anaerobic oxidation of organic matter with nitrate. Amal Jayakumar (now in Princeton) and I incubated a few samples with $^{15}N$-labelled ammonium. Jay Brandes, then a graduate student of Al Devol, who analysed these samples saw lots of labelled $N_2$ production and mistakenly thought that he might have inadvertently forgotten to add the preservative ($HgCl_2$) to the "eggs" (evacuated glass containers to which the samples were transferred after incubations) while preparing them for our use, and discarded the data. Anammox was yet to be discovered at that time, but would have been a fine explanation for these results!

We also measured $N_2$/Ar ratio in water at a number of stations in the Arabian Sea/western Indian Ocean located both within and outside the denitrification zone (Devol *et al*., 2006). This approach had been followed by Richards and Benson (1961) to quantify denitrification (and the $N_2$ it produces) in two different land locked basins (the Cariaco Basin in the Caribbean and Dramsfjord, Norway), but it was used for the first time in an open ocean ODZ to compute "excess" $N_2$ produced by denitrification and/or anammox. In the western Indian Ocean outside the denitrification zone, the $N_2$/Ar ratios, normalised by dividing with the equilibrium saturation values, did not show significant geographical variability, but increased from 1.000 at the surface to 1.014 at 2,500 m, similar to the trend observed elsewhere in the ocean, attributed to bubble injection and differential non-equilibrium conditions existing during water mass formation (Hamme, 2003). In contrast to the profiles outside the SNM zone, $N_2$/Ar values within the SNM were greatly elevated with the maximum in the ratio (1.030–1.035) almost coinciding with the SNM (Fig. 3.10), Taking the best non-linear fit to the combined data from the stations located outside the SNM zone as the background, and considering the solubility of $N_2$ in seawater, the absolute excess of dissolved $N_2$ within the OMZ could be computed. This amount was roughly of the same magnitude, in fact slightly higher, than the computed nitrate deficits (Fig. 3.11). The excessive $N_2$ was attributed to the re-mineralisation of organic matter having higher than usual N:P ratio produced by diazotrophs in the Arabian Sea (Devol *et al*., 2006).

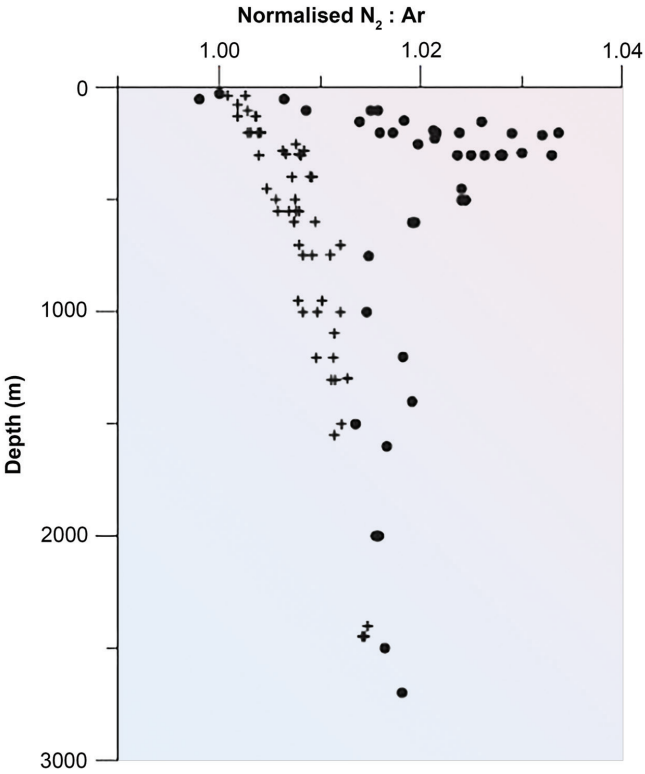



**Figure 3.10** $N_2$/Ar ratio normalised by equilibrium saturation values within (circles) and outside (crosses) of the denitrification zone. Note that stations outside the denitrification zone covered a wide latitudinal range (from 29 °S to 8.5 °N) in the western Indian Ocean. Adapted and modified from Devol *et al.* (2006).

With Al Devol's group we also obtained the first data set on natural abundance of nitrogen isotopes in nitrate and molecular nitrogen from the ODZs of the ETNP and Arabian Sea. These data showed large enrichment of $^{15}N$ in nitrate (increase in $\delta^{15}N$ of nitrate from 6 ‰ (*vs.* atmospheric $N_2$) at 2,500 m to 15 ‰ close to the SNM, similar to the previously mentioned results from the ETNP (Cline and Kaplan, 1975); the $\delta^{15}N$ of $N_2$ concurrently decreased from 0.6 ‰ to 0.25 ‰ (Brandes *et al.*, 1998; Naqvi *et al.*, 1998a; Figs. 3.12, 3.13). It may be noted that the station where $\delta^{15}N$ of $N_2$ was measured was located at the periphery of the SNM zone, and $^{15}N$ depletion within the core is expected to be greater. The data from the Arabian Sea and the ETNP were used to compute the average global isotopic fractional factor associated with denitrification as 27 ± 3 ‰.

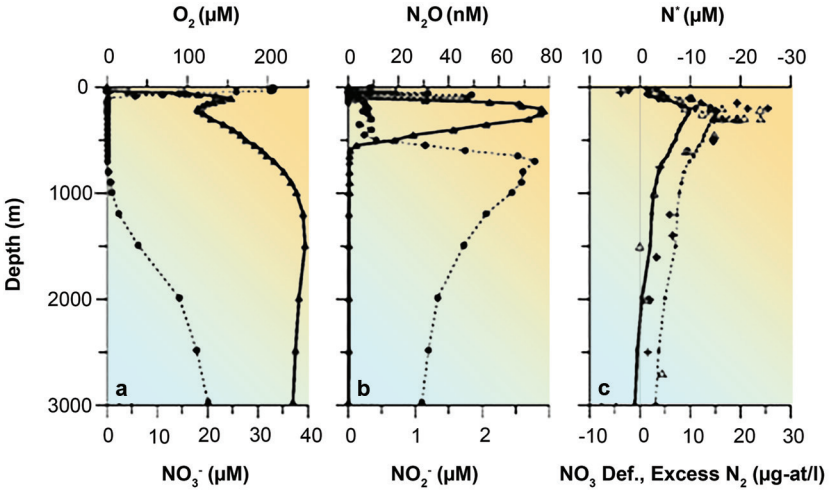



**Figure 3.11** Vertical profiles of properties at 19 °N, 67 °E. **(a)** $O_2$ (circles) and $NO_3^-$ (triangles); **(b)** $N_2O$ (circles) and $NO_2^-$ (triangles); **(c)** nitrate deficit according to Codispoti *et al.* (2001) (dots connected by the solid line), N* according to Gruber and Sarmiento (2002) (small filled triangles connected by the dashed line), and "excess $N_2$" calculated from the $N_2$/Ar ratio (larger unconnected symbols: crosses for data collected on two different cruises from this site and triangles for those from other stations also located within the denitrification zone). $N_2$/Ar data are the same as shown in Figure 3.10; all other data are from sampling during a US JGOFS cruise on 1–2 October 1994. From Naqvi *et al.* (2006b).

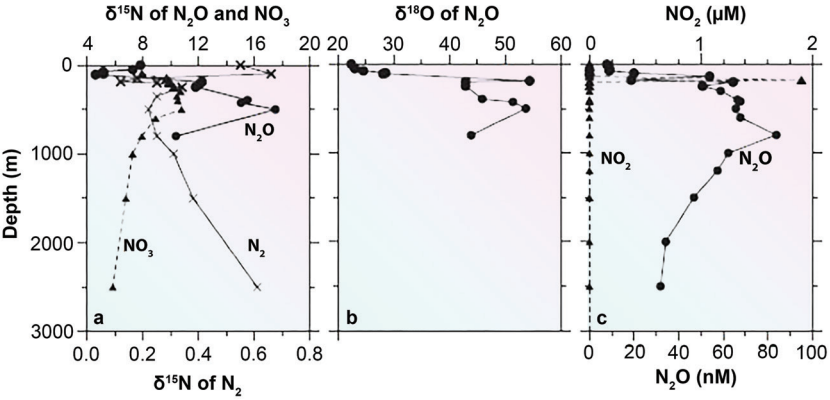



**Figure 3.12** Vertical profiles of **(a)** $\delta^{15}N$ of $N_2$, $NO_3^-$ and $N_2O$ (‰ *vs.* air), **(b)** $\delta^{18}O$ of $N_2O$ (‰ *vs.* air) and **(c)** concentrations of $NO_2^-$ (μM, triangles) and $N_2O$ (nM, circles) at 19.75 °N, 64.62 °E. From Naqvi *et al.* (1998a).

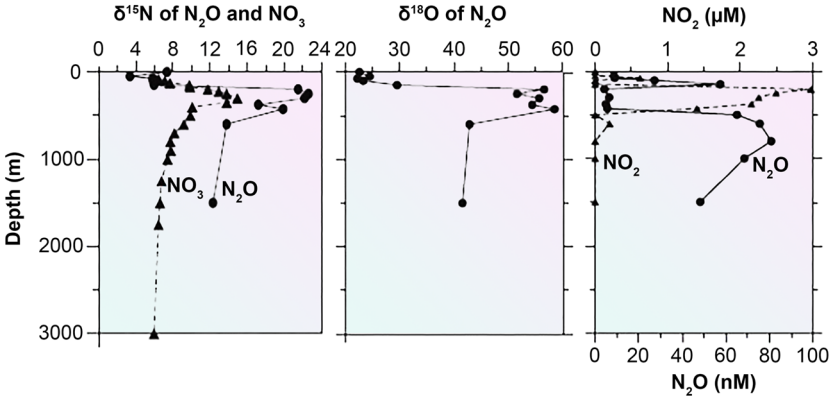



**Figure 3.13** Vertical profiles of **(a)** $\delta^{15}N$ of $NO_3^-$ and $N_2O$ (‰ *vs.* air), **(b)** $\delta^{18}O$ of $N_2O$ (‰ *vs.* air) and **(c)** concentrations of $NO_2^-$ (μM, triangles) and $N_2O$ (nM, circles) at 17 ºN, 68 ºE. From Naqvi *et al.* (1998a).

An interesting feature of the vertical profiles of $\delta^{15}N$ of nitrate is the decrease by ~9 ‰ from the maximum within the ODZ to the shallowest depth where nitrate was present. Similar to the trend observed in the ETNP (Cline and Kaplan, 1975), this decrease requires a source of isotopically light nitrogen close to the surface. This is contrary to expectation because the phytoplankton preferably use $^{14}NO_3^-$, and so $\delta^{15}N$ of nitrate is expected to increase, not decrease, toward the surface. Brandes *et al.* (1998) argued that nitrogen fixation, which produces isotopically light combined nitrogen, is the most likely cause of this anomaly. They estimated that ~40 % of the nitrogen at ~80 m was supplied by this process. This is consistent with the higher "excess" nitrogen derived from the $N_2$/Ar ratios than the computed nitrate deficits[4] (Devol *et al.*, 2006; Naqvi *et al.*, 2006b). The Arabian Sea has long been known to be a hot spot for nitrogen fixation, as one would expect in a region with "excess" phosphate in the surface layer due to the combined nitrogen loss within the ODZ (Deutsch *et al.*, 2007; Naqvi, 2008). However, the quantity of combined nitrogen lost is several fold higher than that added by nitrogen fixation (Naqvi, 2008).

The dual isotopic composition of $N_2O$ in the Arabian Sea (both N and O) was also determined by us, both in the open ocean and over the Indian shelf during anoxic periods. This work was in collaboration with Ted Yoshinari and Mark Altabet (who was then at Woods Hole). Ted had built a system for extracting $N_2O$ from water directly from Go-flo water samplers. Due to the low (often < 10 nM) $N_2O$ levels within the SNM, relatively large volumes of

4. Degradation of high N:P organic matter produced by diazotrophs will release N:P in a non-Redfieldian proportion (excess of N over P), and so the nitrate deficits computed from the phosphate concentration assuming Redfield stoichiometry will be lower than the excess $N_2$.

water were required to extract sufficient amounts of gas for isotopic analysis. As the sampling was done manually using large (20 litre) samplers mounted on a hydrowire (Fig. 3.14) and the extraction (purging with He and trapping on Molecular Sieve columns) was time consuming, sampling and processing of water from a single station would take over 24 hours without a break. Thus, the shipboard work was quite back breaking, but the results were worth the effort (Yoshinari *et al.*, 1997; Naqvi *et al.*, 1998a,b).

We found wide variations in isotopic compositions of both nitrogen and oxygen in $N_2O$ in the open ocean (Figs. 3.12, 3.13, 3.15 and 3.16). The low $N_2O$ concentrations within the SNM were expectedly associated with very large enrichment of both $^{15}N$ and $^{18}O$, evidently due to reduction of lighter $N_2O$ to $N_2$ in anoxic water, as previously reported from the Pacific Ocean (Yoshida *et al.*, 1984), but the magnitude of $^{15}N$ enrichment in the Arabian Sea ODZ was much more pronounced (Figs. 3.12, 3.13 and 3.15). Interestingly, $N_2O$ accumulating at the upper and lower boundaries of the SNM had different isotopic signatures, indicating different formative mechanisms. The isotopic data could not be explained by production through nitrification or denitrification alone, and a coupling between the two processes was proposed to be an important mechanism of $N_2O$ production.

**Figure 3.14** Water sampling with Amal Jayakumar on board R.V. *Sagar Sampada* in 1994 for measurement of isotopic composition of $N_2O$.

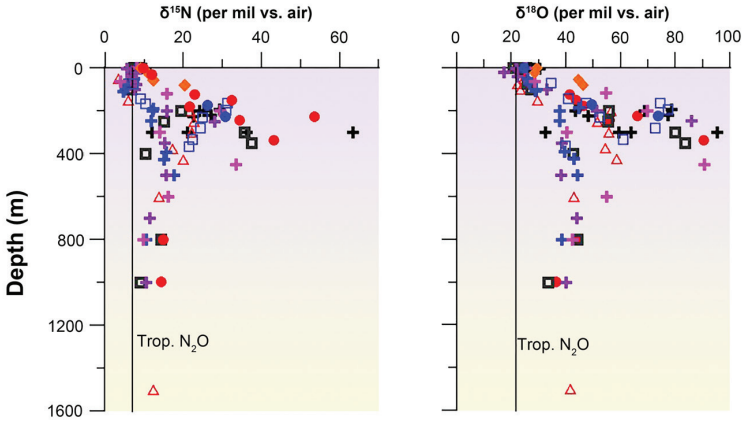



**Figure 3.15** Dual isotopic composition of $N_2O$ in the open Arabian Sea. Different symbols represent different stations that were all located within or at the periphery of the SNM zone (from Naqvi *et al.*, 1998a,b; Naqvi *et al.*, 2006b; and some unpublished data).

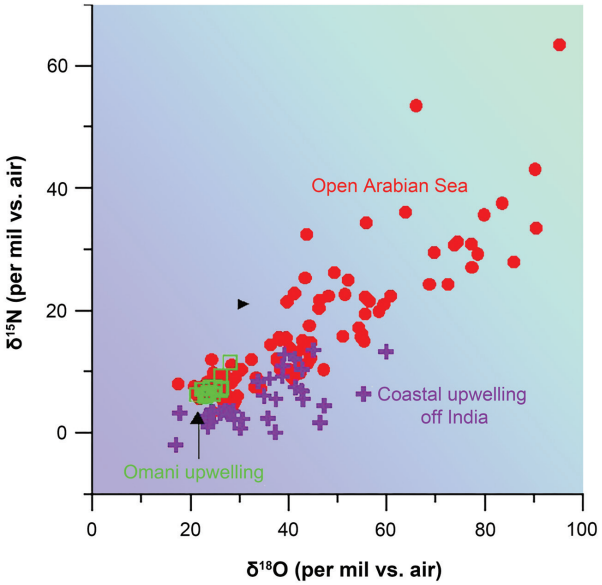



**Figure 3.16** Plot of $\delta^{15}N$ *versus* $\delta^{18}O$ in the open Arabian Sea and coastal upwelling zone over the western Indian continental shelf (from Naqvi *et al.*, 1998a,b; Naqvi *et al.*, 2006b; and some unpublished data).

Nitrous oxide is produced as a by-product during nitrification through decomposition of hydroxylamine ($NH_2OH$) or through the reduction of nitrite (nitrifier denitrification). The well known enhancement of $N_2O$ yield *via* nitrification in low oxygen waters (Goreau *et al.*, 1980) suggests the dominance of nitrifier denitrification close to the boundaries of the anoxic zones (Figs. 3.9, 3.11). $N_2O$ is also an intermediate of denitrification and may accumulate in denitrifying waters under certain conditions (Codispoti, 2010; Ji *et al.*, 2018). However, since nitrification and denitrification have common intermediates, especially nitrite from which most of the $N_2O$ is probably produced in low oxygen environments, the exchange of these intermediates (nitrification-denitrification coupling) may greatly affect the isotopic composition of $N_2O$.

The isotopic composition of nitrite is probably very variable; nitrite within the SNM has been found to be highly depleted in $^{15}N$ due to the inverse isotope effect associated with its oxidation to nitrate (Casciotti, 2009, 2013, 2016; Gaye *et al.*, 2013; Martin and Casciotti, 2017). Such exchanges of intermediates are expected to be more important in the spatially and temporally more variable coastal environment such as the Indian shelf, where despite the prevalence of more extreme redox conditions, described in detail later, the ranges of isotopic values for $N_2O$ are relatively narrow (–2 to 13 ‰ for $\delta^{15}N$ and 17 to 60 ‰ for $\delta^{18}O$) than in the open ocean (3 to 81 ‰ for $\delta^{15}N$ and 17 to 95 ‰ for $\delta^{18}O$) (Fig. 3.16). The exchange of intermediates between nitrification and denitrification introduces complexity in interpretation of isotopic data. Analysis of isotopomer ratios (site preference of $^{15}N$ in the linear $N_2O$ molecule) provides deeper insights into the mechanisms of $N_2O$ formation (*e.g.*, Yoshida and Toyoda, 2000; Yamagishi *et al.*, 2007), but such data are not available from the Arabian Sea.

Together with Bess Ward's group from Princeton University, we investigated the diversity and distribution of *nirS* genes, which encode cytochrome $cd_1$-containing nitrite reductase (NirS), over the western Indian shelf in October 2001. Note that NirS is one of the two functionally equivalent enzymes (the other being NirK, which contains copper) that catalyse the reduction of nitrite to NO, a key step in denitrification. At the time of sampling, almost the entire shelf off Goa experienced strongly reducing conditions below a thin surface layer. This was the first study of nitrite reductase sequences from any pelagic denitrifying system (Jayakumar *et al.*, 2004). The *nirS* genes could be amplified from DNA extracted from anoxic samples that contained high concentrations of nitrite, but rarely from well-oxygenated or sulfidic waters. The sequences, most of which did not show a high level of identity with the then known sequences from marine and estuarine sediments, formed 12 clusters. Rarefaction analysis, based on sequence and restriction fragment length polymorphism (RFLP) data, showed high diversity in samples containing secondary nitrite, suggesting that the chemical environment exerted key control on functional diversity.

Diversity and community composition of the microbial population involved in denitrification were also studied by incubating samples collected from the ODZ in gas-tight bags (Jayakumar *et al.*, 2009). Denitrifying assemblages varied

greatly with time with striking changes in diversity occurring as denitrification progressed in incubated samples. In this case, diversity decreased with time, leading to dominance of one or a few phylotypes; this is in conflict with the *nirS* data mentioned above. These results imply that a few microbes, forming blooms under suitable environmental conditions such as the availability of labile organic matter and the complete absence of oxygen, may mediate a large part of reductive nitrogen transformations in nature.

Incubations of water samples from the ODZ were also carried out under trace metal clean conditions to investigate the response of the denitrifying community to additions of copper and organic matter (while organic matter fuels denitrification, one of the two nitrite reductases (nirK) contains copper, as mentioned above). The results (Ward *et al*., 2008) indicated that in the ETNP and ETSP, denitrification was limited by organic carbon, but such was not the case in the Arabian Sea. Copper was not found to limit denitrification in any region. Given that the Arabian Sea is less productive than the ETSP, the inferred insensitivity of denitrification to organic carbon is intriguing. It is quite possible that sampling in the Arabian Sea was done during a productive season, and that organic carbon may limit denitrification during oligotrophic periods (*e.g.*, Spring Intermonsoon).

The discovery of anammox as a major process of $N_2$ production in anaerobic aquatic systems led to a re-evaluation of marine nitrogen cycle in the early part of the present century (Dalsgaard *et al*., 2003; Kuypers *et al*., 2003). Contrary to expectation, appreciable denitrification could not be detected in a vast majority of studies from various ODZs: anoxic water samples spiked with $^{15}N$-labelled nitrate or nitrite did not show significant production of $^{30}N_2$ as would be expected from the pairing of two $^{15}N$ atoms in dinitrification. On the other hand, anammox was detected by the production of $^{29}N_2$ in almost all incubations of samples spiked with $^{15}N$-labelled ammonium when nitrite was present (Kuypers *et al*., 2005; Hamersley *et al*., 2007; Lam *et al*., 2009; Canfield *et al*., 2010; Lam and Kuypers, 2011). Note that in this case $^{15}N$ of ammonium pairs with $^{14}N$ of nitrite to form $^{29}N_2$. However, large production of $^{30}N_2$ does usually occur in relatively long incubations (~48 hr and longer), presumably due to the aforementioned bottle effect (*e.g.*, Kuypers *et al*., 2005). Our unpublished results also show a similar effect, indicating that the organisms present were capable of heterotrophic denitrification, which was further confirmed by molecular analyses.

Extensive incubations and molecular work during a cruise of R.V. *Meteor* in September–October, 2007, failed to establish either denitrification or anammox as significant pathways of $N_2$ production within the SNM of the Arabian Sea. Dissimilatory nitrate reduction to ammonium (DNRA) was also not found to be significant (Lam *et al*., 2011). Note that unlike denitrification, DNRA does not cause direct loss of combined nitrogen, but the ammonium it produces may support anammox. In contrast to insignificant rates of $N_2$ production, rates of nitrite oxidation were found to be quite high by Lam *et al.* (2011). These authors

concluded that nitrite accumulated within the ODZ without getting further reduced to $N_2$; as discussed in detail in Section 8, this interpretation is inconsistent with all other data. However, on the same cruise, significant $N_2$ production was observed at a station located off Oman outside the main secondary nitrite zone shown in Figure 3.7; this was ascribed to a coupling between DNRA and anammox (Jensen *et al.*, 2011), as also observed in the ETSP by the same group (Lam *et al.*, 2009).

In sharp contrast to the results of Lam *et al.* (2011), rate measurements made by Bess Ward in collaboration with us on a *Roger Revelle* cruise yielded fairly high rates of $N_2$ production through heterotrophic denitrification with anammox being much less important; these results were supported by the gene abundance data (Ward *et al.*, 2009). However, similar measurements in the ETSP by these authors showed an opposite trend (*i.e.* a dominance of anammox), consistent with previous reports, mentioned above. The difference between the two ODZs was attributed to geographic and temporal variability in carbon supply to the ODZs. However, considering that the two studies in the Arabian Sea (Ward *et al.*, 2009; Lam *et al.*, 2011) were undertaken at exactly the same time (September–October, 2007; the fag end of the SWM), it is hard to reconcile differences between their results.

Subsequent work has shown that heterotrophic denitrification may sometimes be more important than anammox in the ETSP as well. Dalsgaard *et al.* (2012) found both anammox and dentrification to occur in waters where oxygen levels were below detection of the highly sensitive STOX (Switchable Trace amount Oxygen) sensor. Although anammox was detected more often than denitrification, when the latter did occur its rates could be an order of magnitude higher than anammox rates. Overall, denitrification was found to account for 72 % of $N_2$ production in this study. The greater variability/patchiness in denitrification, probably arising from differences in the organic carbon availability and an apparent requirement of functional anoxia (when the ambient oxygen levels are below detection of the currently available sensors and the SNM is present), may also explain the above mentioned contrasting results from the Arabian Sea. Moreover, the possibility of methodological artefacts cannot be completely ruled out. A time lag of several hours before the appearance of labelled $N_2$ is not uncommon in the widely used procedure for estimating rates of anammox/denitrification/DNRA in various aquatic systems (Sarkar *et al.*, 2020, and references therein). Sarkar *et al.* (2020) suggested that this time lag might arise from oxygen contamination during sample handling and processing. In view of the apparent sensitivity of denitrification to sub-micromolar oxygen concentrations (Jensen *et al.*, 2008; Thamdrup *et al.*, 2012; Dalsgaard *et al.*, 2012), $N_2$ may not be produced until all oxygen has been consumed. Moreover, De Brabandere *et al.* (2014) reported that significant diffusion of oxygen may occur through the butyl septa of Labco exetainers often used for incubations. This oxygen contamination may prevent $N_2$ production through denitrification in incubations where such septa are used.

### 3.3.5 Our contributions; Bay of Bengal

As noted above, researchers from NIO did not have access to an ocean going vessel until *Gaveshani* was commissioned in December 1975. However, the Indian Navy organised a few cruises in the northern Indian Ocean during 1973–1975 using its survey ship *Darshak.* Rabin Sen Gupta, along with a few other colleagues from NIO, participated in these cruises. The cruise in the western Bay of Bengal was conducted in March–April 1975. The limited data taken on this cruise did not show the occurrence of a SNM. Surprisingly, though, nitrate concentrations were much lower than expected. Following the procedure of Sen Gupta *et al.* (1976), nitrate deficits reaching up to ~15 μM were computed and attributed to denitrification (Sen Gupta *et al.*, 1977).

My very first cruise happened to be in the northern Bay of Bengal during the SWM of 1976. I was extremely sea sick for two days after the ship came out of the Hooghly, which convinced me that I was unfit for Oceanography. But I was still obliged to work as the other chemists, including our group leader Gangadhara Reddy, were in no better shape than me. Feeling miserable and oblivious to what was happening around me as I was running the samples, I was still amazed by the absence of dissolved oxygen below the thermocline not far below the surface; yet there was no SNM. Since then, I have been to Bay of Bengal on numerous occasions, including a major seasonal basin wide survey in 1991. I know of only one instance where the SNM was recorded within the oxygen minimum; this was at one station sampled during the Bay of Bengal Process Study. This station was located near the northern end of a meridional section. Otherwise, there is no clear evidence of large scale combined nitrogen loss in this region (Rao *et al.*, 1994). This is contrary to the conclusions of Sen Gupta *et al.* (1977). This issue will be discussed in greater detail in Section 7.

A particle maximum or an intermediate nepheloid layer, ubiquitous of all reducing ODZ is also conspicuous by its absence in the Bay of Bengal. Also, a minimum in $N_2O$ concentration is invariably sandwiched between two maxima in a typical ODZ (Naqvi *et al.*, 2010c). This $N_2O$ minimum is not seen in the Bay of Bengal; instead a broad $N_2O$ maximum is found to coincide with the oxygen minimum (Fig. 3.17; Naqvi *et al.*, 1994). This pattern is typical of all low oxygen systems where the SNM does not occur (*e.g.*, Gulf of California; Yamagishi *et al.*, 2007). It may be pointed out that there has been one study that reported departures from this well defined trend, including lesser accumulation of $N_2O$ in the oxygen-depleted waters (Hashimoto *et al.*, 1998a). However, this data set is inconsistent with our observations that comprise hundreds of vertical profiles including from a time series station in the northern Bay of Bengal (Hema Naik, unpublished data).

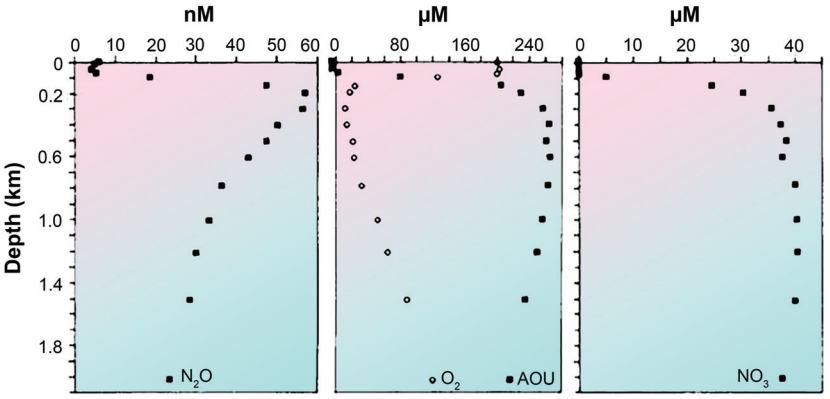



**Figure 3.17** Vertical profiles of nitrous oxide ($N_2O$), dissolved oxygen ($O_2$), apparent oxygen utilisation (AOU) and nitrate ($NO_3^-$) at a station located at ~11 °N, 83 °E in the Bay of Bengal. From Naqvi *et al*. (1994) with permission from Elsevier.

# 4. REDOX SENSITIVE ELEMENTS OTHER THAN NITROGEN

## 4.1 Previous Work

As stated earlier, in addition to nitrogen, several other polyvalent elements also undergo redox transformations in anoxic waters (Table 1). Studies in the Arabian Sea undertaken prior to JGOFS had focussed on manganese (Mn), iron (Fe) and cerium (Ce) (Saager *et al*., 1989; German and Elderfield, 1990). These authors observed concentration maxima in dissolved Mn, Fe and Ce (operationally defined as the fractions passing through a 0.4 µm filter) at mid-depths within the oxygen minimum layer. The dissolved Mn and Fe concentrations peaked in the lower part of the oxygen minimum layer, but these maxima were not associated with a nitrite maximum. Within the shallower nitrite-bearing ODZ, sharper maxima in dissolved Mn, Fe and Ce clearly coincided with the nitrite maximum. Although these maxima were thought to result mostly from lateral flow of water masses, especially those originating in the Red Sea and Persian Gulf (Saager *et al*., 1989), *in situ* mobilisation (reduction of Ce (IV) to Ce (III)) from particulate matter was also recognised in the case of Ce (German and Elderfield, 1990).

The observed accumulation of Fe and Mn in the lower part of the oxygen minimum layer is most likely due to lateral inputs from the continental margin. However, the persistence of these features in waters that contain oxygen, albeit in traces, is intriguing. This is because Fe (II) is oxidised in a biologically catalysed reaction when oxygen is present in traces (Moffett *et al*., 2015). The association of Fe maximum with the SNM is also not to be expected because, as stated earlier, reduction of Fe (III) to Fe (II) is energetically much less favourable than nitrate reduction (Froelich *et al*., 1979).

Subsequent work by Lewis and Luther (2000) as a part of the Arabian Sea Process Study of US JGOFS also confirmed the occurrence of two maxima in Mn at depths of 200–300 m and around 600 m. The deeper maximum was associated with oxygen levels <~2 µM, and was proposed to arise from lateral inputs of dissolved Mn from highly reducing sediments over the Pakistan margin, instead of the Oman Margin as suggested by Saager *et al*. (1989). The dissolved Mn maximum at 200–300 m coincided with the SNM and the accompanying turbidity maximum, to be discussed later. It was concluded that *in situ* microbially mediated processes were the predominant source of dissolved Mn within the SNM zone.

The importance of horizontal processes in transporting reduced chemical species was best demonstrated by the results of George Luther's group on iodine cycling in the Arabian Sea during JGOFS. Farrenkopf *et al*. (1997) and Farrenkopf and Luther (2000) showed that like nitrate, iodate also undergoes dissimilatory reduction to iodide by bacteria within the ODZ of the Arabian Sea. In fact, the spatial extent where the iodate reduction occurs appears to be larger than that

of nitrate reduction. That is, the iodide maximum was not only found to be vertically broader than the SNM, its horizontal extent was also larger in that the iodide maximum occurred at some locations in the western Arabian Sea where the SNM was not present (Farrenkopf *et al.*, 1997). Maximal accumulation of iodide was coincident with the secondary nitrite and dissolved Mn maxima within the denitrifying layer, where the total iodine (iodide plus iodate) concentration far exceeded that computed from its normally rather constant ratio with salinity. Notably, only about 4 % of the excess total iodine was estimated to come from re-mineralisation of iodine from particulate organic matter sinking from the surface layer with the remainder being supplied to the ODZ horizontally, most likely from marginal sediments off India. These horizontal processes may also supply organic matter to the ODZ, in part driving a high rate of dentrification that does not seem to be supported entirely by the export of particulate organic matter from the surface layer (Naqvi and Shailaja, 1993).

As a part of the US JGOFS programme in the Arabian Sea, fairly extensive Fe measurements were made in surface waters by Measures and Vink (1999), covering different seasons including the SWM. Dissolved Fe concentrations were always found to be in excess of 0.7 nM, high enough to meet the requirement of phytoplankton. This led to the conclusion that primary production in the macronutrient replete upwelling zones of the western Arabian Sea was controlled by grazing, not Fe limitation (Marra and Barber, 2005). In fact, due to the high rates of Fe supply then believed to occur through deposition of dust from the atmosphere, the Arabian Sea was regarded as "Mother Nature's iron experiment" (Smith, 2001).

## 4.2 Our Contribution: Iron Cycling in the Arabian Sea and its Possible Link with Nitrogen Cycle

Post-JGOFS research in the Arabian by Jim Moffett (then at Woods Hole) in collaboration with our group provided further insights into Fe cycling in the Arabian Sea. We considered total dissolved Fe as the fraction that passed a 0.2 µm filter. Of this, the amount occurring in the ferrous form (Fe (II)) was determined on board ship using a FeLume II system, whereas the total dissolved Fe was measured in Woods Hole in filtered, acidified samples using an inductively coupled plasma mass spectrometer (ICP-MS), as described in Moffet *et al.* (2007, 2015).

The association of a dissolved Fe maximum with SNM was confirmed by observations made on a cruise of *Sagar Kanya* conducted in September, 2004 (Moffett *et al.*, 2007). This study sampled the SNM zone of the central Arabian Sea along a roughly east-west transect that also covered the Omani shelf. Fe (II) was found to account for about half of dissolved Fe at its maximum. As Fe (II) is thermodynamically unstable in the presence of even minor traces of oxygen, the dissolved Fe maximum could only result from active *in situ* biological reduction

of Fe (III) (Moffett *et al*., 2007). It was proposed that dissolved Fe may meet the high Fe requirement associated with the metalloenzymes for nitrate and nitrite reduction within the SNM.

We did not adequately sample surface waters for Fe over the Omani shelf on that cruise because we were expecting Fe replete conditions in the region based on the results of Measures and Vink (1999). We were, therefore, quite surprised to observe very low surface chlorophyll *a* (Chl. *a*) concentration (<0.1 mg $m^{-3}$) with a correspondingly low rate of primary production (280 mg C $m^{-2}$ $d^{-1}$) over the central Omani shelf off Ras al Madrakah; these values contrasted with much higher surface Chl. *a* and primary production (5.42 mg $m^{-3}$ and 1903 mg C $m^{-2}$ $d^{-1}$) off Ras al Hadd over the northern shelf of Oman (Naqvi *et al*., 2010b). Both areas experienced intense upwelling, as evident from low sea surface temperatures (<23 °C) and high surface nitrate concentrations (>11 μM), and with comparable mixed layer depths (Fig. 4.1). Samples for Fe analysis were not taken at the station where very low Chl *a* and primary production were recorded, but a sample from a nearby station yielded a dissolved Fe concentration of 1 nM which, although still representing Fe replete conditions, was considerably lower than the dissolved Fe concentrations (4-7 nM) measured off Ras al Hadd during the same cruise. Qualitatively, this pattern was similar to that reported by Measures and Wink (1999) during late SWM. The lowest dissolved Fe concentration measured on our 2004 cruise (0.23 nM) was at a station located offshore that was still affected by the transport of nutrient-rich upwelled water. The high nutrient, low chlorophyll condition strongly pointed to potential limitation of primary production by Fe, consistent with the prediction of a model published later (Wiggert and Murtugudde, 2007).

As a follow up of this work, a cruise focussing on potential Fe limitation of primary production in the western Arabian Sea was planned in August–September, 2007, on board the *Roger Revelle*. Unfortunately, we did not get permission from the Omani Government to work within their exclusive economic zone. However, even in the open ocean, well outside the Omani exclusive economic zone, surface concentrations of dissolved Fe at a number of stations were low enough (minimum 60 pM at Sta. 16: Lat. 14.26 °N, Long. 58.67 °E) to limit primary production (Moffett *et al*., 2015). Iron limitation of primary production was confirmed by the results of deck incubations of surface samples enriched with Fe. Conducted under trace metal-free conditions, these incubations resulted in up to 6 fold increase in Chl *a*. Interestingly, surface silicate concentrations at these stations were mostly close to or below the detection limit (<1 μM) even though nitrate and phosphate were present in fairly high amounts. This feature is typical of marine environments where primary production is Fe limited; it arises from an increase in the uptake ratio of silicate to nitrate by diatoms subjected to Fe stress (Hutchins and Bruland, 1998). The relative distribution of nitrate, phosphate and silicate observed on this cruise conformed to the previously reported trend from the western Arabian Sea during late SWM (Morrison *et al*., 1999; Naqvi *et al*., 2010b). In the absence of silicate, diatoms did

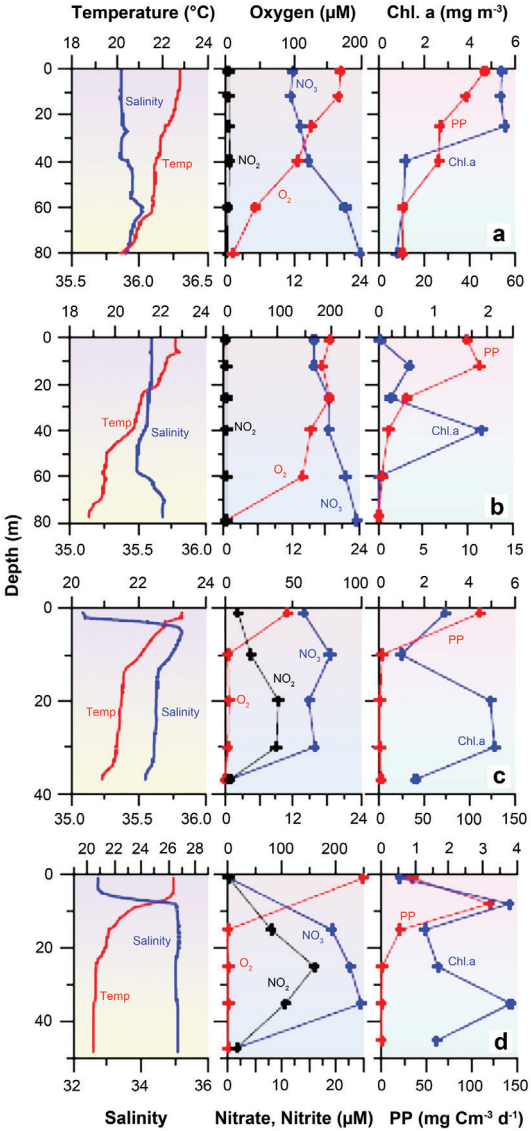



**Figure 4.1** Contrasting vertical profiles of temperature, salinity, dissolved oxygen, nitrate, nitrite, chlorophyll and primary production in the western and eastern Arabian Sea based on cruises of *Sagar Kanya* in August–September 2004. While Stas. SK209/07 **(a)** and SK209/16 **(b)** were located over the Omani shelf, Stas. SK208/M03A **(c)** and SK208/G6 **(d)** were located over the Indian shelf. From Naqvi *et al*. (2004).

not grow in incubated samples; instead, Fe enrichment benefitted *Phaeocystis*, a bloom-forming algae that produces dimethyl sulfide (DMS), an anti-greenhouse gas (Moffett *et al*., 2015).

Similar to the observations made in 2004 (Moffett *et al*., 2007), strong enrichment of dissolved Fe and Fe (II) within the ODZ was also observed in 2007 (Fig. 4.2 from Moffett *et al*., 2015). However, the dissolved Fe enriched zone did not extend as far westward along these latitudes (~15 $^{o}$N) as the SNM. Fe (II) was strongly associated with SNM in the eastern and central parts of the basin. The western boundary of the SNM zone has been reported to expand westward during the SWM (Rixen *et al*., 2014). The 2007 data suggest that dissolved Fe probably does not keep up with this westward expansion of the SNM, implying that dissolved Fe may have a longer residence time than nitrite (Moffett *et al*., 2015). Moreover, a decoupling of dissolved Fe and nitrite might also result in part from the supply of dissolved Fe from reducing sediments of the Indian continental margin, as against *in situ* production of nitrite within the ODZ (Moffett *et al*., 2015). The offshore transport of Fe from the Indian margin in the upper water column may support higher vertical export fluxes of Fe into the ODZ/SNM. Additionally, complexation with organic substances has been suggested to stabilise Fe against removal through scavenging onto sinking particles (Witter *et al*., 2000).

Iron limitation of primary production in the western Arabian Sea has some potentially important ecological, biogeochemical and climatic implications (Naqvi *et al*., 2010b; Moffett *et al*., 2015). As mentioned earlier, a more rapid depletion of silicate than nitrate in waters being transported offshore from the upwelling centres of the western Arabian Sea would favour the growth of phytoplankton other than diatoms that, on account of being smaller in size and lighter, would sink to and get degraded at shallower depths. The offshore shoaling of the depth of mineralisation of organic matter would produce a stronger ODZ offshore, consistent with the observations (Naqvi *et al*., 2010b). Moreover, a change in the phytoplankton community structure may also directly affect climate through proliferation of the DMS producing *Phaeocystis* (Moffett *et al*., 2015). Finally, our results introduce an additional complexity in the response of oceanic ecosystems to human activities. For example, it has been reported that the ongoing decrease in seasonal snow cover over Eurasia as a consequence of global warming may lead to intensification of upwelling in the western Arabian Sea (Goes *et al*., 2005). Our results imply that effects of any changes in upwelling on ecosystems and biogeochemistry, including the impact on the ODZ processes, will strongly depend on changes in Fe supply to the region. Therefore, models developed to predict the response of the Arabian Sea biogeochemistry to climate change must consider effects on Fe inputs (Moffett *et al*., 2015).

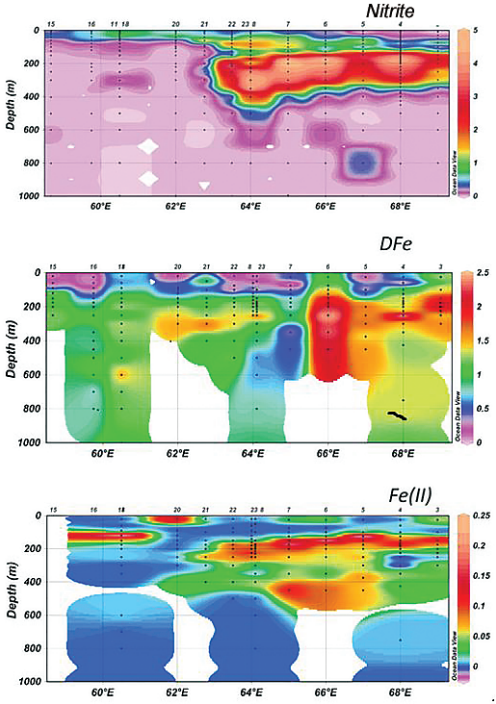



**Figure 4.2** Distribution of nitrite, dissolved iron and reduced iron (Fe (II)) along a roughly east-west section (Lat. ~15 ºN) in the Arabian Sea. From Moffett *et al.* (2015) with permission from John Wiley and Sons.

# 5. SEASONAL ANOXIA OVER THE WESTERN CONTINENTAL SHELF OF INDIA

In addition to the perennial ODZ in the open ocean, anoxic conditions also develop seasonally over the western Indian continental shelf. This phenomenon was first discovered in the 1950s by Karl Banse who came to India in 1958 to pursue research on tropical plankton. He was then a young man, having obtained a Ph.D. in Oceanography/Zoology from University of Kiel in 1955 followed by a post-doc at Institut für Meereskunde. At that time Cochin (now Kochi) was the most important centre for marine research in India, and Karl was based at what was then a sub-station of the Central Marine Fisheries Research Institute (CMFRI) in Ernakulam. It must have been quite a change for Karl moving from Kiel to Cochin. In addition to managing with a rudimentary infrastructure for marine research, which India had at that time, the hot and humid climate of Cochin must have been unbearable to him (there was no air conditioning then!). What was worse is that he soon realised that the sea off Cochin was not what he had planned to work on; it was not a typical tropical region: We now know that the seasonally reversing West India Coast Current flows poleward (Fig. 2.1), opposing the wind, during the winter, when the sea surface temperature is the highest; the surface temperature is at its minimum in summer. Karl learnt this only after he had settled in Cochin. Anyway, now that he was in India, he tried to make the most out of the opportunity.

Karl designed a time series study off Cochin, carrying out monthly observations at two stations, including temperature, salinity and oxygen in addition to the plankton collections he was mainly interested in. His study spanned well over a year. This was, in fact, the first systematic time series study of Indian coastal waters, which provided the baseline data that have now become even more valuable as we are struggling to evaluate the changes brought about by human activities (Gupta *et al*., 2016). Karl's seminal work not only provided the first account of seasonal upwelling along the west coast of India, but it also revealed the associated low oxygen conditions. Unfortunately, he was ill advised to publish his results in a local biology journal (Banse, 1959), and in the journal's very first issue! For this reason, his work went largely un-noticed (in fact, for many years after joining NIO, I was not aware of it). Another paper published in *Nature* (Carruthers *et al*., 1959) at about the same time with fewer observations reporting prevalence of low oxygen conditions in coastal waters off Bombay (now Mumbai) drew a lot more attention.

After staying in India for two years, Karl took up a faculty position in University of Washington. However, he remains interested in the Arabian Sea to this day, continuing to write some outstanding papers (Banse, 1968, 1984; Banse and McClain, 1986; Banse *et al*., 2014). Karl has mentored many younger Indian researchers, and I am privileged to be one of them (Fig. 5.1). Before the advent of the Internet, he used to regularly update me by post about new publications that he thought would be of interest to me.

**Figure 5.1** With Karl Banse in Director's Office, NIO in December 2015.

Karl takes strong exception to the fact that many people do not count the southwest coast of India among the eastern boundary upwelling systems. During the SWM, the region does behave like an eastern boundary upwelling system with an equatorward surface flow, a poleward undercurrent and coastal upwelling (Shetye *et al*., 1990). One major characteristic of this region, however, is that upwelling is not entirely forced by local winds. It is far less intense than upwelling in the western Arabian Sea. It is also confined to belt that is just a few tens of kilometres wide, except in the south (off Sri Lanka and Kerala) where the winds are upwelling favourable and the process is more intense. Another unique feature of this region is that, unlike the four major eastern boundary upwelling systems in the Pacific and the Atlantic oceans, the coastal zone off western India receives heavy rainfall during the SWM that is orographically forced by the Western Ghats (a chain of mountain ranges bordering the western coastal plain on its east). The cold, saline upwelled water is usually not allowed to break to the surface as it gets capped by a thin (5–10 m) warm, low salinity lens produced by freshwater inputs. This creates extremely strong thermohaline stratification very close to the sea surface (Banse, 1968; Naqvi *et al*., 2000, 2006a,b,c, 2009). As a result, although primary production is not very high, oxygen depletion below a shallow pycnocline is extremely severe.

For quite some time after Banse's seminal work, not much attention was paid to coastal upwelling and associated oxygen deficiency over the Indian shelf, with the exception of intensive surveys carried out during 1971–75 under the UNDP/FAO supported Integrated Fisheries Project (IFP). These surveys involved

repeated occupation of several coast-perpendicular sections (Naqvi, 2006). The scarcity of data during the SWM period was not only because of the difficulty in making observations due to rough seas; it was also due to a lack of interest: frankly we prided ourselves to be deep sea oceanographers after we had acquired an ocean going vessel. It was not until the 1990s that interest in coastal upwelling was rekindled. In the summer of 1995, we secured ship time to investigate this phenomenon in some detail, and the results were so interesting that our focus shifted to shelf anoxia. In 1997, we set up a coastal quasi-time series station off Goa. We named it CaTS (Candolim Time Series) as it was located off Candolim, a coastal village in North Goa that is famous for its beach. Over the past 25 years, my colleagues at NIO have been monitoring this site and the data generated have provided very useful insights into coastal processes, the development of shelf anoxia, and how they are being impacted by climate change (*e.g.*, Naqvi *et al*., 2006b,c, 2009).

Our work established the seasonal hypoxic[5] zone over the Indian shelf (Fig. 5.2) to be the largest shallow water hypoxic system in the world, covering an area about 10 times the area of the famous "dead zone" in the Gulf of Mexico (Rabalais *et al*., 2002). The sulfidic conditions observed by us in the bottom water over the inner shelf had not been documented previously, including during the above mentioned sustained surveys conducted in the 1970s under the IFP, even though near zero oxygen concentrations have been known to persist since the 1970s, as stated earlier. Therefore, it was suggested that such conditions could arise from human induced intensification of oxygen deficiency (Naqvi *et al*., 2000; 2006c). Subsequently, CaTS data confirmed frequent occurrence of sulfidic conditions in late summer/early autumn, including the most recent observations in 2022 (Damodar Shenoy, personal communication). However, the data do not show a clear increase in $H_2S$ since the late 1990s. The inter-annual variations in the intensity of oxygen deficiency are large, but irregular (Naqvi *et al*., 2009). For example, conditions were extremely severe in 2001, when the entire shelf off Goa was covered by sulfidic bottom water, drastically (negatively) impacting demersal fish landings all along the Indian west coast. The exact driver of these changes has not been identified, but it is probably a basin scale phenomenon. From a coupled physical-biogeochemical regional simulation with 1/4° resolution over the 1960–2012 period, Vallivattathillam *et al*. (2017) found oxycline fluctuations over the shelf to be strongly influenced by the Indian Ocean Dipole with positive dipole events associated with weaker anoxia.

5. Hypoxia is traditionally defined by the threshold oxygen concentration of 2 mg $l^{-1}$ (~1.4 ml $L^{-1}$, 62.5 µM), below which animal behaviour is believed to be affected. However, this threshold is known to vary greatly among various groups of marine organisms and even within the same group (Vaquer-Sunyer and Duarte, 2008).

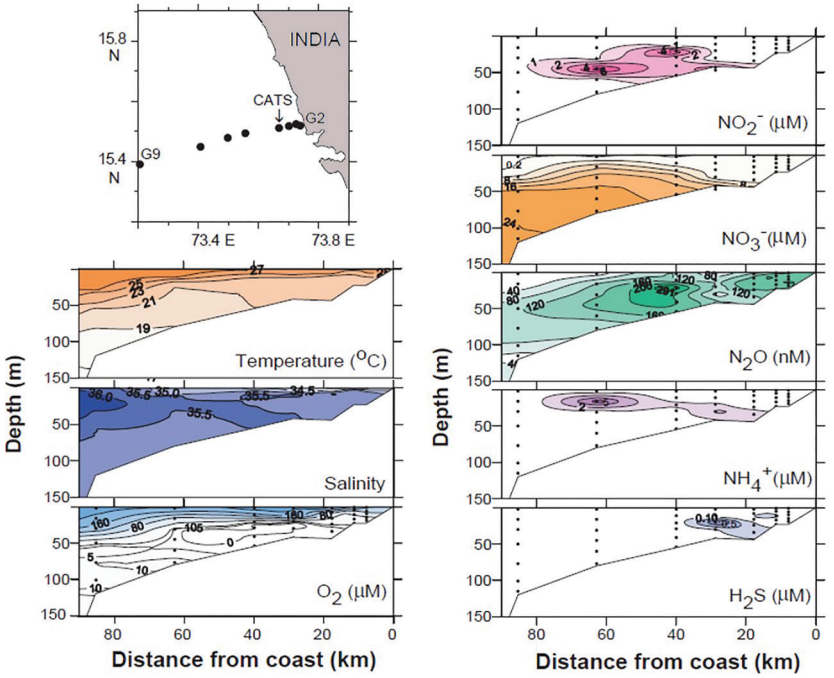



**Figure 5.2** Vertical sections of temperature, salinity, dissolved oxygen, nitrate, nitrite, ammonium and hydrogen sulfide off Goa during 9–10 October 1999. Station locations are shown in the map. From Naqvi *et al.* (2006b).

Despite strongly reducing conditions prevailing in bottom waters over the Indian shelf, this system exhibits some distinct differences from the two other coastal eastern boundary environments where sulfate reduction has also been found to occur in the water column; off Namibia in the Benguela Current system (Brüchert *et al.*, 2006; Lavik *et al.*, 2009) and off Peru in the Humboldt Current system (Schunck *et al.*, 2013). These differences are as follows.

(1) Seasonal ODZ over the Indian shelf is not contiguous with the open ocean ODZ, unlike in the other eastern boundary systems (Peru and Namibia), with the undercurrent keeping the waters just off the shelf slightly oxygenated, enough to prevent the onset of nitrate reduction (Naqvi *et al.*, 2006b). However, the undercurrent, which is invariably rich in oxygen to begin with, also occurs in other eastern boundary upwelling systems, but in these other systems, dissolved oxygen gets quickly exhausted due to high demand such that in areas like the ETSP, the most intense nitrogen loss actually occurs within the undercurrent itself (Codispoti *et al.*, 1989).

(2) While $H_2S$ builds up to fairly high levels (up to 14.1 μM) at very shallow depths over the Indian Shelf (in 2000 it occurred in concentrations ~5 μM just 5 m below the surface off Mangalore), its accumulation in porewaters of sediments of the inner shelf is not very large (<3 μM; Naik *et al*., 2017). This may in part be due to the removal of sulfide as insoluble FeS in sediments owing to large Fe supply from land. Moreover, sedimentary sulfate reduction rates in the region (0.066–0.46 mol $m^{-2}$ $yr^{-1}$) are much lower than those reported from other coastal environments experiencing upwelling (Naik *et al*., 2017). The lack of free sulfide build-up in sediments explains the absence of sulfur bacteria such as *Thiomargarita, Thioploca* and *Beggiatoa* that are known to oxidise sulfide with nitrate and are commonly found off Peru-Chile and Namibia (Fossing *et al*. 1995; Schulz *et al*., 1999).

(3) As compared to other systems, especially the Namibian shelf where methane ($CH_4$) concentrations exceeding 5 μM have been observed (Brüchert *et al*., 2006), $CH_4$ accumulation in the anoxic bottom waters over the Indian shelf is relatively modest: concentrations exceeding 100 nM are extremely rare (Jayakumar *et al*., 2001; Shirodkar *et al*., 2018; Sudheesh *et al*., 2020). Anaerobic oxidation of $CH_4$ (*e.g*., by sulfate and nitrite) has been invoked to explain the relatively low $CH_4$ values in anoxic waters over the Indian shelf (Sudheesh *et al*., 2020). There is no information on the extent of $CH_4$ oxidation by sulfate, but its oxidation by nitrite does not appear to be significant in anoxic waters over the Indian shelf, as will be discussed later. It is likely that a more subdued $CH_4$ production through non-competitive methanogenesis rather than enhanced methanotrophy is mainly responsible for the lack of large $CH_4$ accumulation. Moderate $CH_4$ levels (5–62 μM in the upper 17 cm) in porewaters at the CaTS location are consistent with this view (Araujo, 2018).

The above mentioned differences between the Indian shelf with similar systems off Peru-Chile and Namibia can be explained by a smaller organic loading due to a much lower primary production over the Indian shelf (Pitcher *et al*., 2021). This is also reflected by the lower organic carbon content of sediments over the inner Indian continental shelf (<4 %; Shirodkar *et al*., 2018) than off Namibia and Chile (10–40 %; Fossing, 1990; Fossing *et al*., 1995; Brüchert *et al*., 2006). It would thus appear that the relative importance of biology and physics in the formation of shallow water anoxic zone over the western Indian shelf may be different from that in the other two eastern boundary coastal anoxic zones. That is, large organic loading may be the main driver of anoxia off Namibia and Peru/Chile. Over, the Indian shelf, on the other hand, where the lower productivity allows the undercurrent to remain slightly oxygenated, a longer residence time of upwelled water may be a more important contributor to the development of anoxic conditions (Naik *et al*., 2017; Pitcher *et al*. 2021).

Perhaps the most important aspect of biogeochemistry of the coastal ODZ is an accumulation of $N_2O$ at hundreds of nM level. Such high concentrations were unprecedented at that time (Naqvi *et al*., 2000), but similar build-up of $N_2O$ has since been observed also in the ETSP off Peru (Arévalo-Martínez *et al*., 2015).

An example of this phenomenon is provided in Figure 5.2, which shows vertical sections of several physico-chemical variables including $N_2O$ off Goa in October 1999. Clear zonation in redox conditions over the shelf is usually seen around this time off the Konkan and northern Malabar coasts: slightly oxic conditions prevail over the outer shelf; denitrifying conditions are seen over the mid-shelf and sulfidic conditions develop over the inner shelf. The highest $N_2O$ concentrations mostly occur at mid-depths in association with very high nitrite concentrations (reaching up to 16 μM) and very low nitrate concentrations (Naqvi *et al*., 2000, 2006a,b,c, 2009). $N_2O$ concentrations decrease in sulfidic waters, apparently due to $N_2O$ reduction to $N_2$. Transient $N_2O$ accumulation to micromolar levels was also seen in anaerobic incubations of water samples (Naqvi *et al*., 2000). These results strongly point to $N_2O$ production through denitrification over the Indian shelf, in contrast to the net consumption within the SNM in the open ocean, as discussed above. The greatly enhanced $N_2O$ production was attributed to the regulation of $N_2O$ reductase activity by frequent oxygenation of water arising from turbulence in shallow, rapidly denitrifying systems (Naqvi *et al*., 2000). The large production of $N_2O$ at shallow depths maintains high $N_2O$ concentrations in the surface layer (5–436 nM, mean 37.3 nM), in turn resulting in a large atmospheric efflux (0.05–0.38 Tg $N_2O$ $yr^{-1}$) (Naqvi *et al*., 2006c).

As already mentioned in Section 3, $N_2O$ over the shelf exhibited a different stable isotopic composition in the coastal ODZ than in the open ocean, which was attributed to greater exchange of common intermediates, especially nitrite, having variable isotopic composition between nitrification and denitrification over the shelf. An alternative explanation could be that fractionation patterns of isotopes in the two systems may be different. Measurements of isotopic composition of nitrate also revealed different degrees of heavy isotope enrichment between the coastal and open ocean ODZs (Naqvi *et al*., 2006b; Bardhan and Naqvi, 2020). The relatively limited data used by Naqvi *et al*. (2006b) from two stations (one each off Goa and Mangalore) provided the $\delta^{15}N$ of the combined nitrate and nitrite pool. The overall range of measured values was 3.43–22.5 ‰, but with a large geographical variability. The $\delta^{15}N$ varied within a surprisingly narrow range off Mangalore (3.43–7.41 ‰) despite large nitrate deficits occurring below the shallow pycnocline (up to ~15 μM). The isotopic fractionation factor computed assuming Raleigh distillation was 7.21–7.7 ‰, much lower than estimates for the open ocean ODZs: 27 ‰ by Brandes *et al*. (1998) for the ETNP and the Arabian Sea and 25.6 by Gaye *et al*. (2013) for nitrate + nitrite for the Arabian Sea. Relatively low fractionation factors (10–15 ‰) have been reported for denitrification at the cellular level based on experiments with cultured denitrifying bacteria (Kritee *et al*., 2012). However, even these values are significantly higher than those derived by us from the Raleigh model over the Indian shelf.

A larger data set on dual isotopic composition of nitrate with better geographical coverage (from Calicut in the south to Mumbai in the north) has been generated more recently by Bardhan and Naqvi (2020). The range of values reported by these authors is wider (1.9–30.7 ‰ for $\delta^{15}N$ and 1.5–36.2 ‰ for $\delta^{18}O$). The slope (0.9) of the linear relationship between $\delta^{18}O$ and $\delta^{15}N$ deviated

significantly from the expected 1:1 trend, implying that other processes such as nitrite oxidation to nitrate were important in determining the isotopic composition of nitrate. However, it must be noted that nitrite present in the samples was removed in this study before isotopic analysis. Since nitrite in the ODZs is highly $^{15}N$-depleted due to the inverse isotope effect associated with nitrite oxidation to nitrate (Casciotti, 2009; Casciotti *et al*., 2013; Gaye *et al*., 2013), the $\delta^{15}N$ values reported by Bardhan and Naqvi (2020) should be higher than those reported by Naqvi *et al*. (2006b). Nonetheless, the fraction factor estimated by these authors was also quite low (6.1 ‰). Assuming that the low fractionation value arose from denitrification in the sediments that has only a small isotope effect, if any (Brandes and Devol, 2002; Zhang *et al*., 2020), Bardhan and Naqvi (2020) estimated that sedimentary denitrification could account for about half of the nitrogen loss over the Indian shelf. In addition to the isotopic influence of sediment denitrification, Naqvi *et al*. (2006b) mentioned other possible reasons for the apparently low fractionation factor for denitrification in the coastal ODZs (not only in the Arabian Sea but in many several other areas as well; Bardhan and Naqvi, 2020, and references therein). These are (1) the extent of nitrogen isotope fractionation in coastal ODZs may actually be lower than in the open oceanic ODZs, (2) low fractionation values could be an artefact of mixing between anoxic waters (that would have lost all nitrate and nitrite) and freshly upwelled waters, and (3) processes other than heterotrophic denitrification (*e.g.*, anammox, DNRA coupled to anammox, and autotrophic denitrification) may also be important in the reduction of nitrate.

More recent work has enabled us to estimate the rates and evaluate relative importance of various processes that reduce nitrate in anoxic waters (Sarkar *et al*., 2020). Rates of denitrification, anammox and DNRA were measured using the isotope dilution technique (Holtappels *et al*., 2011) at a number of stations located off Goa, Karwar and Mangalore during the anoxia season (late August to late September) in three consecutive years (2008, 2009 and 2010). Addition of $^{15}NH_4^+$ resulted in low to moderate production of $^{29}N_2$, indicating anammox in about half of the incubations of anoxic waters. In contrast, incubations with $^{15}NO_2^-$ led to production of $^{30}N_2$ in almost all incubation experiments (*e.g.*, Fig. 5.3), yielding rates of denitrification (up to 10.03 ± 1.70 μmol $N_2$ $l^{-1}$ $d^{-1}$) that are among the highest reported from any aquatic environment. As stated earlier, the production of $^{30}N_2$ indicates denitrification by microbes. These microbes could be either heterotrophic (those which oxidise organic matter using nitrate/nitrite as electron acceptors) or autotrophic (those which oxidise reduced inorganic species such as $H_2S$ with nitrate/nitrite to synthesise organic matter (Lavik *et al*., 2009). Our results cannot differentiate between these pathways. However, since nitrate was often present in anoxic waters, as also evident by substantial production of $^{29}N_2$ through pairing of $^{15}N$ and $^{14}N$ of nitrate/nitrite, it appears that heterotrophic denitrification should be more important. When detected through production of $^{15}NH_4^+$ in incubations involving $^{15}NO_2^-$, DNRA rates were much lower than denitrification rates. Time series data from fixed coastal sites show that, following the onset of dentrification, it takes about a month for

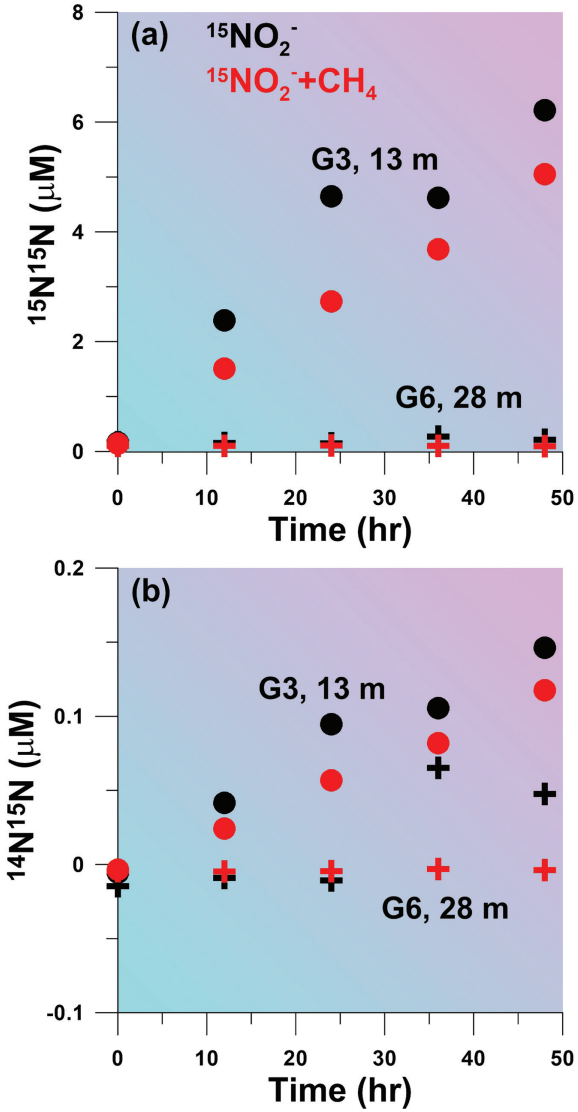



**Figure 5.3** Changes in concentrations of **(a)** $^{15}N^{15}N$ and **(b)** $^{14}N^{15}N$ with time in anoxic water samples collected from two stations located off Goa that were incubated with $^{15}N$-labelled nitrite in the absence (black symbols) and presence (red symbols) of $CH_4$. Sta. G3 (circles), 15.526 °N., 73.718 °E; depth 14 m; sampled on 19.09.2011; Sta. G6 (crosses), 15.498 °N, 73.582 °E; depth 39 m; sampled on 17.09.2011.

nitrate with an initial concentration of ~24 µM to be fully consumed (Naik, 2003). The measured denitrification rates are even higher than derived from these data, requiring source(s) of nitrate in addition to inputs by upwelling. These results clearly show that denitrification is the dominant pathway of combined nitrogen loss in the seasonal ODZ over the Indian shelf.

Another possible pathway of $N_2$ production is the nitrite dependent anaerobic methane oxidation (n-damo), the significance of which in nitrogen loss from marine environments is not fully known (Thamdrup *et al*., 2019; Rogener *et al*., 2021). In order to investigate such a linkage between denitrification and methanotrophy, we also carried out incubations with $^{15}N$-labelled $NO_2^-$ in the presence of $CH_4$. Addition of $CH_4$ had no discernible effect on labelled $N_2$ production (Fig. 5.3). This may be because of low ambient $CH_4$ levels as a result of which microbes that mediate $CH_4$ oxidation by nitrite, detected elsewhere in the ocean (*e.g,*. Thamdrup *et al*., 2019), may not be present over the Indian shelf.

Large spatio-temporal variations (including interannual changes) in redox conditions seem to occur in this region, controlling rates of different nitrogen transformations. Higher denitrification rates were recorded off Mangalore and Karwar as compared to Goa. The rates also decreased rapidly offshore from the inner shelf (Fig. 5.3). Extrapolation of the average $N_2$ production rates ($2.45 \pm 0.6$ µmol $N_2$ $l^{-1}$ $d^{-1}$ through denitrification and $0.06 \pm 0.004$ µmol $N_2$ $l^{-1}$ $d^{-1}$ through anammox) over the volume of anoxic waters ($1.2–3.6 \times 10^{12}$ $m^3$) yielded estimates of annual nitrogen loss ranging from 3.70 to 11.1 Tg N, roughly three times the previously reported estimate (1.3–3.8 Tg $yr^{-1}$). Thus, the shallow ODZ may account for a significant fraction of the total nitrogen loss from the Arabian Sea (Sarkar *et al*., 2020).

Similar anoxic conditions are not known to develop over the continental shelves in the Bay of Bengal (Naqvi *et al*., 2006a). This is surprising as this region receives enormous amounts of freshwater by numerous rivers that drain thickly populated and intensely cultivated lands with large utilisation of synthetic fertilisers (Naqvi, 2008). So, the riverine inputs of nutrients (nitrogen and phosphorus) into coastal waters of Bay of Bengal are expected to be very high. Employing a model called "Global NEWS" (Global Nutrient Export from WaterSheds; Mayorga *et al*., 2010), Pedde *et al.* (2017) estimated that 7.1 Tg of N (4.1 Tg of DIN) and 1.5 Tg of P were brought to the Bay of Bengal by rivers in the year 2000. These high fluxes constitute significant fractions of the total amounts of chemical fertilisers used globally for agriculture (~82 and 14 Tg $yr^{-1}$ in the same year)[6]. Future projections showed that while phosphorus fluxes may not change much, those of nitrogen will rise to 8.6 Tg N $yr^{-1}$ (6 Tg DIN $yr^{-1}$) by 2050. The Ganges-Brahmaputra and Irrawaddy river systems are the main contributors to these fluxes, and both these river systems discharge onto wide continental shelves. Thus, coastal "dead zones" such as those found in the Gulf of Mexico and Black Sea (Rabalais *et al*., 2010) are expected to form off the mouths of these

6. https://www.statista.com/statistics/438967/fertilizer-consumption-globally-by-nutrient/).

rivers, which is not the case (Naqvi *et al*., 2006a). There is a report by Satpathy *et al*. (2013) on the occurrence of nearly anoxic water (Winkler $O_2$ ~4.5 µM) over the shelf (at 59 m depth) off the southeast coast of India in September 2010 (the upwelling season), which was attributed to land based pollution; however, an examination of data presented by these authors points to an offshore origin of these waters (as discussed later, subsurface waters in the Bay of Bengal are also severely oxygen-depleted, although not anoxic). Thus, the absence of naturally formed coastal ODZs is most likely due to weaker upwelling in the Bay of Bengal as compared to the Arabian Sea. The absence of large anthropogenically driven coastal dead zones in the Bay of Bengal strongly indicates that the model-derived nutrient inputs may be too high (Naqvi, 2008; Krishna *et al*., 2016). It seems that the terrestrial ecosystems efficiently remove these nutrients, particularly nitrogen (Naqvi *et al*., 2018). This will be discussed in some detail in Section 9.

# 6. GLOBAL EFFORT TO ASSESS OCEAN DEOXYGENATION: TRENDS IN THE INDIAN OCEAN

Human activities are affecting oxygen distribution in the ocean in two major ways (Keeling *et al*., 2010; Breitburg *et al*., 2018; Naqvi, 2020). (1) Rising levels of greenhouse gases in the atmosphere are also causing ocean warming, with as much as 93 % of the extra energy being retained by the planet going into the oceans. Warming may affect the oxygen balance of subsurface waters through a decrease in oxygen supply from the surface by altering thermohaline circulation and strengthening near surface stratification, and by decreasing oxygen solubility in seawater. (2) Over the past few decades there has been a large increase in fluxes of nutrients to the ocean, especially nitrogen, by land runoff, and to a smaller extent, atmospheric deposition. The main sources of these nutrients are agriculture, municipal sewage and fossil fuel combustion. Nutrient inputs promote photosynthesis by phytoplankton, and the degradation of this plankton is an oxygen sink. While the effect of warming is global, impacting the ocean as a whole, the impact of eutrophication is largely confined to coastal waters where most of the extra nutrient loading occurs.

Development of hypoxic conditions in coastal waters due to eutrophication has been known since the early 1970s, with the coastal hypoxic (dead) zone of the Gulf of Mexico having been most extensively studied (Diaz and Rozenberg, 1995, 2008; Rabalais *et al*., 2002). Human induced deoxygenation in the open ocean was recognised more recently (Stramma *et al*., 2008; Keeling *et al*., 2010; Helm *et al*., 2011). This realisation has led to a great deal of concern, especially because the oceans are also subject to other anthropogenic changes such as warming and acidification (Gruber, 2011). Subsequent work has demonstrated that the ocean has already lost over 2 % of its oxygen content since 1960 (Schmidtko *et al*., 2017). The Intergovernmental Oceanographic Commission (IOC) of UNESCO constituted a group under a new initiative called the Global Ocean Oxygen Network (GO2NE) in 2015 of which I have been a member since its formation. The aim of this Network is "to improve observation systems, identify and fill knowledge gaps, as well as develop and implement capacity building activities worldwide" (https://en.unesco.org/go2ne). Research outputs of this group include two review/synthesis publications (Breitburg *et al*., 2018; Pitcher *et al*., 2021). Moreover, the group members have also contributed to the report prepared by the International Union for the Conservation of Nature (IUCN) on ocean deoxygenation (Laffoley and Baxter 2019). My contribution to this report deals with the Indian Ocean (Naqvi, 2019), an updated summary of which is as follows.

Analyses of global data sets revealed considerable inter-basin variability in deoxygenation with the highest rate of oxygen loss occurring in the equatorial Pacific while the lowest rate of loss was found in the Indian Ocean (Stramma *et al*., 2008; Schmidtko *et al*., 2017). Results of studies focussing on the northern Indian Ocean, especially the northwestern part, have been somewhat contradictory.

Utilising data collected during 53 cruises in the western Arabian Sea from 1960 to 2008, Piontkovski and Al-Oufi (2015) detected fairly large decadal changes in the upper 300 metres; warming by ~1.5 $^{o}$C over five decades and decrease in the oxygen concentration at ~100 m depth by ~90 µM over the same period. During this period the oxycline shoaled by a rate of ~19 m per decade. These changes were especially pronounced during the SWM, when waters of the southern hemisphere ventilate the oxygen-depleted zone. A subsequent study by Queste *et al.* (2018) in the Gulf of Oman made use of time series data from automated gliders carrying oxygen sensors. This study showed that the minimum oxygen concentrations have fallen from ~6–12 µM in the 1960s to < 2 µM in recent times. Another study by Banse *et al.* (2014) focussed on the more oxygen-depleted waters within the depth range 150–500 m in central Arabian Sea (along 65 and 67 $^{o}$N longitudes and between 8 and 21 $^{o}$N latitudes). Oxygen data alone showed mixed trends that might result, at least in part, from analytical errors at near zero oxygen levels. Banse *et al.* (2014) also used the nitrite concentration within the SNM as a proxy of the severity of oxygen deficiency (Naqvi, 1991). Repeat measurements at two locations (19.75 $^{o}$N, 64.62 $^{o}$E, going back to 1977, and ~15 $^{o}$N, 68 $^{o}$E, going back to 1979) showed large inter-annual variability but no secular long term trend. There are not enough measurements to investigate the systematic shift, if any, of the western boundary of the SNM zone to the west.

Lachkar *et al.* (2021) have recently simulated the evolution of dissolved oxygen in the Arabian Sea from 1982 to 2010. Their results show that deoxygenation in the northern Arabian Sea may result mainly from local warming of surface waters and also warming of waters within the Persian Gulf. Their results also suggest that an intensification of SWM would lead to further deoxygenation in the Arabian Sea.

Reliable oxygen data from the northeastern Indian Ocean are even more sparse for evaluating the trends of oxygen changes in the Bay of Bengal and Andaman Sea. Nevertheless, a comparison by Naqvi (2019) of oxygen data from a cruise of R.V. *Anton Bruun* at about 18 $^{o}$N latitude and 89 $^{o}$E longitude collected in April 1963 with measurements made on a cruise of R.V. *Roger Revelle* in April 2007 indicate a decrease in oxygen levels within the core of its minimum (200–400 m) from 8.33 ± 2.11 µM to 2.63 ± 0.26 µM. It may be mentioned that while oxygen measurements on *Anton Bruun* were made by Winkler titration with manual end point detection, analysis on *Roger Revelle* was automated with potentiometric end point detection. However, even if we allow for the consistent offset between the two sets of measurements (*i.e.* manual titrations yielding higher values by 1.8 µM; Banse *et al.*, 2014), the decrease would still be significant. This decline is roughly of the same magnitude as the decline documented by Queste *et al.* (2018) in the Gulf of Oman. Its importance owes to the fact that, as will be discussed later, the Bay of Bengal may be on verge of turning fully anoxic and therefore even minor decreases in oxygen levels here may drive large shifts in its biogeochemistry and ecology.

A more recent analysis by me of data from the Andaman Sea enable a more robust evaluation of oxygen change at a deeper depth (~1.4 km) in the northeastern Indian Ocean (Naqvi, 2021). The Andaman Sea, a marginal basin with maximum depths exceeding 4,000 m, is separated from the Bay of Bengal by a sill at ~1,400 m depth at the Great Passage (Naqvi *et al*., 1994). The Andaman Sea has an estuarine circulation, and so the basin below the sill depth is filled by water from the Bay of Bengal at the sill depth. The remarkably uniform thermohaline characteristics and AOU (which is indistinguishable from that in the Bay of Bengal at the sill depth) imply that deep water in Andaman Basin is renewed very rapidly with little oxygen consumption (Naqvi *et al*., 1994; Naqvi, 2021). Fortunately, a large amount of data is available from the Andaman Sea from the IIOE; in this case, there is a paucity of modern data as the region is entirely covered by the exclusive economic zones of the littoral countries. The most recent data from this region come a cruise of R.V. *Knorr* along the WOCE Line I01 (~10 ºN latitude) in October 1995, *27 years ago*.

At depths exceedingly 1.5 km, the mean (±s.d.) concentrations for the IIOE (1961–1964) and WOCE (1995) cruises were 79.73 ± 2.77 µM and 78.40 ± 1.37 µM, respectively. The difference between the two data sets is statistically significant, but comparable to the above mentioned offset between manual and automated titrations.

In conclusion, with the exception of data from the western Arabian Sea that show large, consistent decreases in oxygen over the past five decades, especially during the SWM (Piontkovski and Al-Oufi, 2015), the magnitude of shifts in oxygen levels in other parts of the northern Indian Ocean, although in the same direction, is far smaller than documented for the Pacific Ocean (Schimidtko *et al*., 2017). However, the likelihood of large changes occurring in the near future is very high, as demonstrated by modelling studies (Lachkar *et al*., 2019, 2021).

# 7. SOME OUTSTANDING ISSUES CONCERNING INDIAN OCEAN'S OXYGEN DEFICIENT ZONES

Despite huge advances over the past few decades in our understanding of the biogeochemistry of ODZs, there are still a couple of fundamental, inter-related questions that remain to be satisfactorily answered, with one of them more specific to the North Indian Ocean.

(1) Can substantial combined nitrogen loss through heterotrophic denitrification and anammox occur in the presence of oxygen in traces, and outside the secondary nitrite maximum zones?

(2) Why such loss does not occur in areas like the Bay of Bengal?

I offer below my perspective on these issues largely based on some hitherto unpublished data.

## 7.1 Can Substantial Nitrogen Loss Occur in the Presence of Oxygen in Traces and Outside the SNM zones?

It has long been recognised that oxygen depletion is required for anaerobic metabolic pathways to become operational, but the oxygen threshold for this to happen was not explicitly stated by most early workers. For example, according to Richards (1965), "When all, or nearly all, of the free dissolved oxygen has been consumed, nitrate ions are the most abundant source of free energy for the oxidation of organic matter". At that time, it was not possible to quantitatively define *nearly all* due to uncertainties in Winkler oxygen measurement at near zero levels. Therefore, ODZs were very often operationally defined as those with Winkler oxygen concentrations below 4.5 µM (*e.g.*, Codispoti and Christensen, 1985). Froelich *et al.* (1979) coined the term 'suboxia' to that zone *within the sediments* where anaerobic transformations that precede sulfate reduction (reduction of nitrate, Mn (IV) and Fe (III)) occurred. As pointed out by Canfield and Thamdrup (2009), this term has been often misused for pelagic ODZs where denitrification has been believed to be the dominant respiratory process, including the layer lying just above the sulfidic deep waters in enclosed basins such as the Black Sea and Cariaco Basin (*e.g.*, Murray *et al.*, 1995). Thus, it was implied that 'suboxic' transformations, including denitrification, could occur when oxygen was present in traces.

A high resolution study of the ODZ off northern Chile showed that while the highest rates of $N_2$ production, mostly through anammox and to a smaller extent denitrification, occurred within the anoxic nitrite-bearing core of the ODZ, significant $N_2$ production was also found to occur in the lower oxycline (De Brabandere *et al.*, 2014). However, as these authors pointed out, this was probably due to a combination of intrusion of water parcels from the anoxic zone (that contained denitrifying and anammox bacterial communities) and the fact

that the incubations were done in anoxic environments (*i.e.* traces of oxygen were removed during sparging with helium). Manipulation experiments of samples collected from the ODZs off Namibia and Peru have shown that anammox, the major process responsible for $N_2$ production in these systems, may occur at oxygen concentrations up to ~20 µM (Kalvelage *et al.*, 2011). There have also been some studies that explicitly reported denitrification in oxygenated environments (Robertson *et al.*, 1995; Gao *et al.*, 2010; Ji *et al.*, 2015). However, the significance of aerobic denitrification in the oceanic ODZs is yet to be convincingly demonstrated. The oxygen sensitivity of processes that produce $N_2$ is especially relevant for modelling studies that use 'critical oxygen concentrations' below which nitrate reduction and denitrification take over from oxygen as the principal processes responsible for the mineralisation of organic matter. For example, Anderson *et al.* (2007) chose a critical oxygen concentration of 11 µM in their 3 dimensional hydrodynamic ecosystem model to investigate and quantify denitrification in the Arabian Sea. This threshold would make almost the entire Bay of Bengal denitrifying, which, as we will see later, is not the case.

Cline and Richards (1972) were the first to determine oxygen levels with the colorimetric method of Broenkow and Cline (1969) in an ODZ (ETNP); this procedure is more suitable for measuring oxygen in the low concentration range. Their results revealed that within the SNM oxygen concentrations were below 0.5 µM. Similar results were later obtained in the Arabian Sea using the colorimetric method (Naqvi, 1987; Naqvi and Jayakumar, 2000; Codispoti *et al.*, 2001; Fig. 3.8). With the development and *in situ* deployment of STOX (Switchable Trace OXygen) sensors, it turned out that even these concentrations were too high: the true oxygen levels associated with the SNM are below the detection limit of these sensors (~10 nM; Revsbech *et al.*, 2009; Thamdrup *et al.*, 2012). It has been reported that sub-micromolar oxygen concentrations suppress process rates and gene expression of both denitrification and anammox in seawater (Dalsgaard *et al.*, 2014), which is in conflict with the results of Kalvelage *et al.* (2011), mentioned above. Because waters containing secondary nitrite are functionally anoxic, 'suboxic zone' is a misnomer (Canfield and Thamdrup, 2009); consequently, the ODZs are increasingly being referred to as anoxic marine zones (AMZs; Ulloa *et al.*, 2012) or anoxic oxygen minimum zones (A-OMZs; Canfield and Kraft, 2022).

It must be pointed out, however, that the absence of nitrite accumulation just above the ODZs does not necessarily mean that nitrite is not being produced from nitrate reduction; instead, it may be due to rapid oxidation of nitrite. High rates of nitrate reduction to nitrite have been reported from almost all ODZs, where it is now considered to be the dominant pathway of organic matter degradation (Lipschultz *et al.*, 1990; Lam *et al.*, 2009, 2011; Kalvelage *et al.*, 2011). Above the ODZ, while the nitrate reduction rate has been found to generally decrease with an increase in oxygen concentration, complete inhibition of nitrate reduction was not seen even at oxygen levels as high as 25 µM (Kalvelage *et al.*, 2011). Nitrite is known to be oxidised at a very rapid rate not only in low oxygen waters but also within the upper ODZ where oxygen concentrations are below the

detection limit of STOX sensors, presumably because of the high oxygen affinity (low values of the Michaelis-Menten constant, $K_m$) of the enzymes involved. In fact, the transition zone between the oxygenated surface waters and anoxic ODZ is believed to support both aerobic and anaerobic nitrogen transformations for the same reason (Canfield and Kraft, 2022, and references therein). This implies a high bacterial biomass within this transition zone, which is not the case as we will see later.

Results of numerous studies in the ODZs of the ETNP, ETSP, Arabian Sea, and over the continental shelf of Namibia have shown that the SNM is a hotspot of microbially mediated anaerobic processes. In addition to what has been described in Section 3, especially the enrichment of $^{15}N$ in nitrate and its depletion in $N_2$, marked increase in the $N_2$/Ar ratio, and depletion of $N_2O$, the SNM layer is also distinguished by the following features: (a) an elevated microbial biomass that probably contributes dominantly to (b) a turbidity maximum *a.k.a.* the intermediate nepheloid layer (Spinrad *et al.*, 1989, and references therein; Naqvi *et al.*, 1993), (c) a particle protein maximum (Garfield *et al.*, 1983; Naqvi *et al.*, 1993), and (d) high respiration rates as inferred from an ETS maximum (Codispoti and Packard, 1980; Naqvi and Shailaja, 1993; Naqvi *et al.*, 1993, 1996). Therefore, despite low rates of labelled $N_2$ production through denitrification and anammox in incubations, reported by Jensen *et al.* (2011) and Lam *et al.* (2011), it is very hard to contest the long held view that most, if not all, of the combined nitrogen loss occurs within the SNM (De Brabandere *et al.*, 2014).

The reduction of nitrate to nitrite is a key step that also provides substrates (nitrite and $NH_4^+$) for anammox. Whether or not an accumulation of nitrite so produced necessarily occurs in all aquatic environments experiencing denitrification and/or anammox is not absolutely clear. We have evidence, presented in Section 9, which shows that nitrite does not accumulate in several freshwater dam-reservoirs in India, the hypolimnia of which turn anoxic during the summer (Naqvi *et al.*, 2018). However, as we will see later, combined nitrogen loss in these $CH_4$-rich systems is predominantly through coupled denitrification-methanotrophy. In aquatic systems where $CH_4$ does not accumulate, as is the case with the open ocean ODZ and the seasonally anoxic western Indian shelf, nitrite always accumulates in anoxic waters as long as they are not sulfidic. Why such accumulation occurs in the first place is perhaps due to the location of nitrate reductase in the bacterial cell, in the outer aspect of the bacterial cell wall (Haddock and Jones, 1977) such that nitrate reduction essentially occurs outside the cell (Anderson *et al.*, 1982). Moreover, bacteria may gain enough energy by reducing nitrate to nitrite, and further reduction to $N_2$ may only be favoured when the nitrate to nitrite ratio falls substantially in water (De Brabandere *et al.*, 2014). However, as we have seen earlier, the SNM is invariably associated with an $N_2O$ concentration maximum and huge enrichment of $^{15}N$ in $N_2O$, strongly pointing to an active reduction of $N_2O$ to $N_2$.

The sensitivity of nitrite build-up to the ambient oxygen concentration is demonstrated by hitherto unpublished data taken during the same cruises of *Roger Revelle* in 2007 on which the above mentioned studies on denitrification and anammox rates (Ward *et al.*, 2009) and iron (Moffett *et al.*, 2015) were carried out. Profiles of temperature, salinity, beam attenuation coefficient, oxygen (measured by automated Winkler titrations), nitrite, heterotrophic nanoflagellates and bacteria (counted after staining with DAPI) at three stations (4, 20 and 23) are shown in Figures 7.1–7.3. Stas. 4 and 23 were located within the SNM zone, as demarcated by Naqvi (1991), with Sta. 23 being closer to its more dynamic western boundary (Rixen *et al.*, 2014). Sta. 20 was located outside this zone (Fig. 7.1, inset).

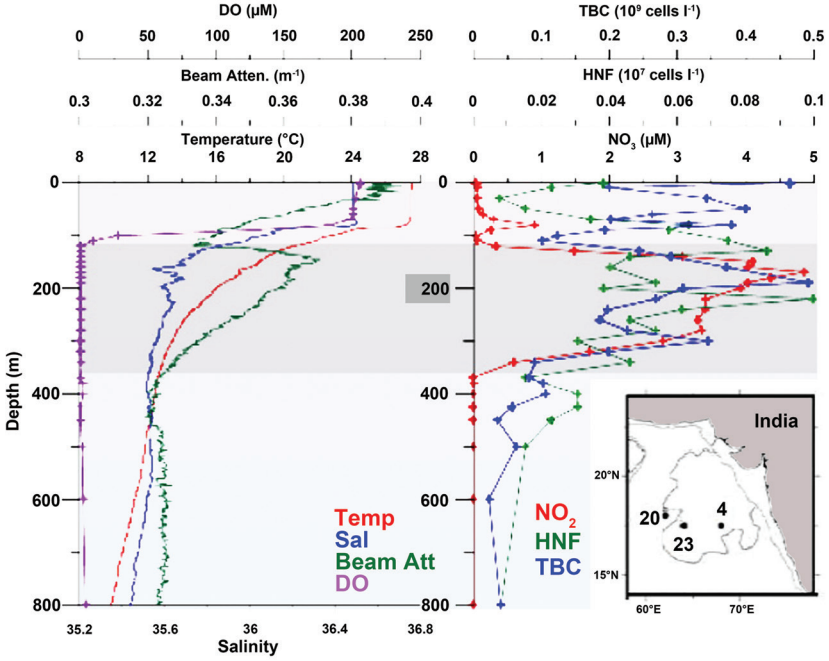



**Figure 7.1** Vertical profiles of temperature, salinity, dissolved oxygen (DO) and beam attenuation coefficient (left panel); and nitrite, total bacterial counts (TBC) and heterotrophic nanoflagellates (HNF) (right panel) at the *Roger Revelle* Sta. 4 worked on 27–28 August 2007. Station location is shown in the inset where denitrification zone as demarcated by the 0.5 μM nitrite contour by Naqvi (1991) is also shown. The shaded zone is the depth range (ODZ) where the secondary nitrite maximum (SNM) is located. The TBC and HNF data were kindly provided by Mangesh Gauns of NIO.

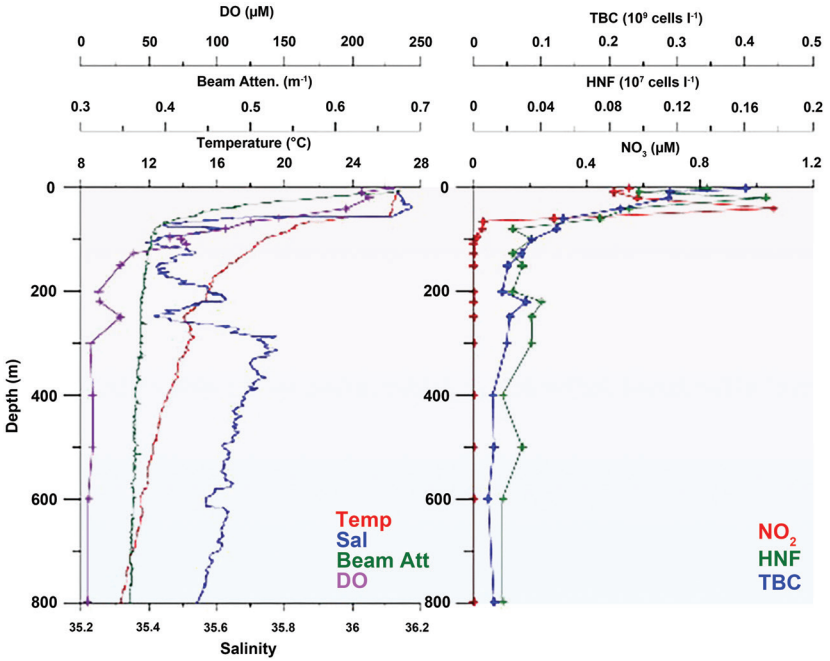



**Figure 7.2** Vertical profiles of temperature, salinity, dissolved oxygen (DO) and beam attenuation coefficient (left panel); and nitrite, total bacterial counts (TBC) and heterotrophic nanoflagellates (HNF) (right panel) at the *Roger Revelle* Sta. 20 worked on 10 September 2007. Station location is shown in the inset of Figure 7.1. The TBC and HNF data were kindly provided by Mangesh Gauns of NIO.

Some salient features of these profiles are as follows.

(1) Sta. 4 had a pronounced SNM extending downward from slightly below 100 m to about 350 m depth with the highest nitrite concentration just under 5 μM. A turbidity (beam attenuation coefficient) maximum occurred remarkably within the same depth range (shaded zone) having the same shape as the SNM. The total bacterial count profile was also very similar to those of SNM and beam attenuation coefficient, albeit showing more variability. What was surprising is that the heterotrophic nanoflagellates, which feed on bacteria, were much more abundant within the SNM than outside this zone. Subdued grazing and associated "repackaging" by zooplankton in an inhospitable (anoxic) environment has been previously invoked as a possible mechanism for the formation of the turbidity maximum/intermediate nepheloid layer off Peru (Pak *et al.,* 1980). Our data show that such is not the case. Obviously these protists are capable of anaerobic respiration (*e.g.,* Orsi and Edgcomb, 2013).

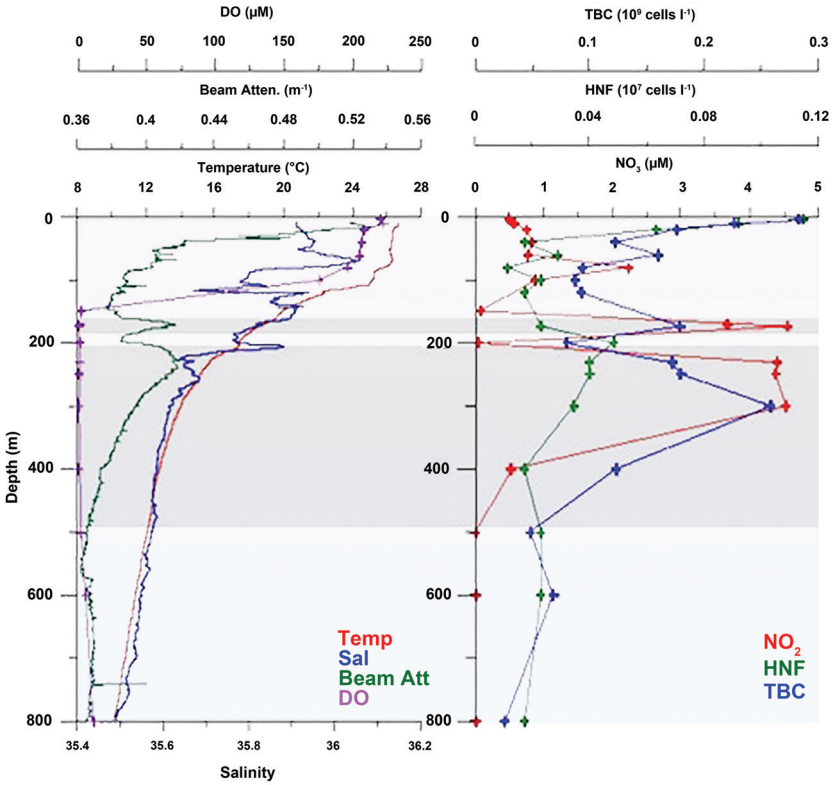



**Figure 7.3** Vertical profiles of temperature, salinity, dissolved oxygen (DO) and beam attenuation coefficient (left panel); and nitrite, total bacterial counts (TBC) and heterotrophic nanoflagellates (HNF) (right panel) at the *Roger Revelle* Sta. 23 worked on 12 September 2007. The shaded zones are the depth ranges (ODZ) where the secondary nitrite maxima (SNM) are located. Station location is shown in the inset of Figure 7.1. The TBC and HNF data were kindly provided by Mangesh Gauns of NIO.

Going upward from the core of the oxygen minimum, the beam attenuation coefficient, and total bacterial and heterotrophic nanoflagellate counts show clear minima at the top of the shaded zone where nitrite disappears. Such "clear zones" are invariably found in all ODZs (*e.g.,* Pak *et al.*, 1980, and Spinrad *et al.*, 1989, in the ETSP; Garfield *et al.*, 1983, in the ETNP; Naqvi *et al.*, 1993, and Wojtasiewicz *et al.*, 2020 in the Arabian Sea), but they have not been paid due attention. This zone is thus highly unlikely to support elevated microbial activity, including very high nitrite turnover. These results are also consistent with relatively low organic carbon mineralisation rate around the oxic-anoxic transition zone (Canfield and Kraft, 2022).

(2) The oxygen minimum at Sta. 20 was clearly more oxygenated and did not have the SNM (Fig. 7.2). Consequently, the associated maxima in beam attenuation coefficient, total bacterial counts and heterotrophic nanoflagellate counts were also conspicuously absent at this site, with a lower overall microbial biomass in the low oxygen waters. Higher oxygen levels appeared to result from advection of waters from the south, as mentioned previously. Such a flow of water from the south is indicated by a layer of low salinity and high oxygen with its core at ~250 m (corresponding to the Subantarctic Mode Water). This flow split the broad salinity maximum representing the North Indian Ocean High Salinity Intermediate Water (Wyrtki, 1971) into two.

(3) Despite being in close proximity to Sta. 20, conditions at Sta. 23 were very different (they were quite similar to those described above for Sta. 4) underlining the sharp horizontal gradients that occur across the oxic-anoxic boundary located between the two stations (Fig. 7.3). The most interesting feature observed at this station was the splitting of the SNM and the associated maxima in beam attenuation coefficient and bacterial counts. This splitting most likely resulted from horizontal advection of more oxygenated water from the west/south, similar to what was seen at Sta. 20, but at slightly shallower depth (~200 m). An intrusion of fresher water is also evident from the salinity profile. Oxygen concentrations at this nitrite-free depth were practically indistinguishable from those in the overlying and underlying nitrite-bearing strata. These data not only demonstrate the remarkable association of the SNM with the intermediate nepheloid layer having an elevated microbial biomass, but also underline their co-variability on short time scales (probably sub-seasonal) close to the boundary of the SNM.

The above observations may be interpreted as follows.

(a) Nitrate reduction that provides nitrite for denitrification and anammox, consequently controlling these processes, is inhibited by oxygen at sub-micromolar levels. This is consistent with the measurements made elsewhere with STOX sensors (Thamdrup *et al*., 2012; Dalsgaard *et al*. 2014).

(b) Active nitrogen loss in oceanic water columns is always associated with the accumulation of nitrite. Where such loss was detected outside the main SNM zone (*i.e*. off Oman by Jensen *et al*., 2011), weak secondary nitrite maximum occurred in an isolated pocket. Occurrence of such pockets in the western Arabian Sea is indicated by historical data (Naqvi, 1991).

(c) The transition from well oxygenated conditions in the surface layer to the anoxic zone characterised by the SNM occurs through a layer that is unsuitable for both aerobic and anaerobic metabolisms. This is what Don Canfield calls a 'metabolic hole' (Canfield and Kraft, 2022). Within this zone, low overall respiration rates may result from a combination of kinetic and thermodynamic factors. That is, while oxygen levels are too low to sustain vigorous aerobic decay of organic matter (kinetic control), they are high enough to inhibit the onset of nitrate reduction (thermodynamic control). This layer is, therefore, relatively sterile and remarkably "clear". Once oxygen is fully used up, however, anaerobic organisms can access the large pool of nitrate, proliferating and thereby

contributing to the formation of the intermediate nepheloid layer, which should be produced *in situ* rather than originating at the continental margin (Spinrad *et al*., 1989; Naqvi *et al*., 1993).

(d) Areas such as the Bay of Bengal, Gulf of California, and California Borderland basins, where very low oxygen concentrations are maintained and complete anoxia is seldom reached, for whatever reasons, may be considered as large scale analogues of the "clear" zones (metabolic holes) observed over the SNM in all ODZs. Conditions in the Bay of Bengal are examined in a greater detail below.

## 7.2 Why Does Large Scale Combined Nitrogen Loss not Occur in the Bay of Bengal?

Explanations of why the water column in the Bay of Bengal does not turn strongly reducing (supporting large loss of combined nitrogen; Rao *et al*., 1994; Howell *et al*., 1997; Naqvi *et al*., 2006a) have involved either low biochemical oxygen demand (Rao *et al*., 1994; McCreary *et al*., 2013; Al Azhar *et al*., 2017) or re-oxygenation of the oxygen minimum zone through physical processes (Johnson *et al*., 2019). The notion of low oxygen demand is supported by measured respiration rates that are much lower in the Bay of Bengal as compared to the Arabian Sea (Naqvi *et al*., 1996). These estimates are based on ETS activity measured using the same protocol, and so the uncertainties associated with the conversion of ETS activity to respiration rates should be similar for the two basins. Two possible reasons have been proposed (Naqvi *et al*., 2006a) for lower oxygen demand/ respiration rates in the Bay of Bengal: first, the Bay of Bengal is less productive than the Arabian Sea because of very weak upwelling and strong thermohaline stratification (Qasim *et al*., 1977), and second, organic matter sinks rapidly through the water column as a result of ballast imparted to particle aggregates by the lithogenic matter brought in by the rivers (Ittekkot *et al*., 1992; Rao *et al*., 1994).

On the other hand, the idea that re-oxygenation by physical factors such as eddies can maintain minimum oxygen levels just above anoxia most of the time (Sarma and Bhaskar, 2018) seems to be supported by the data collected by Argo floats equipped with biogeochemical sensors that were deployed in the Bay of Bengal for five years (Johnson *et al*., 2019). The eddies have also been proposed to play an important role in determining the location of the SNM zone in the Arabian Sea in that the SNM zone coincides with the area of minimal eddy activity (Kim *et al*., 2001). However, conventional wisdom dictates that the magnitude of oxygen supply to intermediate waters should be smaller in the Bay of Bengal than in the Arabian Sea. This is because the upper layers in the Bay of Bengal are very strongly stratified due to the aforementioned unusually large excess of precipitation and river runoff over evaporation in the north-eastern Indian Ocean. Therefore, most of the ventilation/ reoxygenation should be through horizontal processes. However, since in the upper kilometre the Bay of Bengal does not directly receive intermediate waters from south of the equator

and that the northeastern part of the Bay of Bengal is the farthest from the region (off Africa) where these waters cross the equator during the SWM (Swallow, 1984), horizontal processes are not expected to supply more oxygen to the Bay of Bengal than to the Arabian Sea.

The unusual biogeochemical status of Bay of Bengal has intrigued many researchers including Don Canfield from University of Southern Denmark. Don gathered a multi-disciplinary team from several institutions, including Marcel Kuypers' group at Max Planck Institute for Marine Microbiology (MPI), Bremen, and organised a cruise of *Sagar Kanya* in January–February 2014 on which oxygen was measured using the STOX sensor. The results (Bristow *et al*., 2017) showed that while at its minimum, oxygen concentration sometimes fell below the STOX detection limit (~10 nM), and at one station in the northern Bay of Bengal, a weak (150 nM) SNM was detected, traces of oxygen (up to 200 nM) were frequently present. Indeed, pronounced concentration spikes were striking features of most oxygen profiles, indicating its lateral inputs. The persistence of these layers with low but detectable oxygen can only be due to lower oxygen demand. In the biologically productive western Arabian Sea, oxygen content of such layers gets quickly depleted (Figs. 7.2, 7.3), but off the western continental margin of India, where productivity is lower, the signature of higher oxygen content of the poleward undercurrent is preserved, as discussed earlier. Respiration rates in the Bay of Bengal are expected to be even lower than those in the latter region.

On this cruise, rates of anammox, denitrification and DNRA were measured through on board incubations, and samples were also taken for molecular work, and for measurements of $N_2$/Ar ratio and isotopic composition of nitrate. Molecular data revealed the presence of both denitrifying and anammox microbial communities, and incubation experiments yielded low rates of $N_2$ production through these processes. The $N_2$/Ar and isotope data were consistent with these results, pointing to low but significant nitrogen loss. It was concluded that the availability of oxygen, although in very small amounts, was sufficient to oxidise nitrite, not allowing it to be converted on a large scale to $N_2$ by the denitrifiers and anammox bacteria. As argued above, however, the very presence of traces of oxygen probably owes to very low oxygen consumption rates.

I believe there is one other reason (a geochemical one) that can explain why the Bay of Bengal cannot sustain extensive nitrogen loss in the long run. This is related to the geography of the Bay of Bengal, as well as its hydrography and climate. Both the Arabian Sea and Bay of Bengal are semi-enclosed basins, bounded by landmasses on three sides and exchanging water with the rest of the Indian Ocean only through their southern boundaries. The budgets of combined nitrogen in both basins should therefore be predominantly controlled by net inputs of combined nitrogen through these exchanges. There is no published estimate of nitrogen budget from the Bay of Bengal, but for the Arabian Sea, three estimates are available in the literature (Somasundar *et al*., 1990; Naqvi *et al*., 1992; Bange *et al*., 2000). The budget from Bange *et al*. (2000) for the region north of 6 $^{o}$N latitude is reproduced in Table 7.1. The two most important components

of this budget are the net input through water exchange across the southern boundary and the loss through water column denitrification. Considering the uncertainties in estimates (*e.g.*, possible over-estimation of nitrogen input from the south), the net input is almost of the same magnitude as the net loss.

**Table 7.1** Reactive nitrogen budget of the Arabian Sea (north of 6 °N) (reproduced from Bange *et al.*, 2000).

| Sources | Tg N $yr^{-1}$ |
|---|---|
| Atmospheric wet and dry depositions of $NO_3^-$ and $NH_4^+$ | 1.6 |
| Pelagic $N_2$ fixation | 3.3 |
| Inputs from marginal seas (Red Sea and Persian Gulf) | 1.1 |
| Dissolved inorganic N inputs from rivers | 1.2 |
| Northward transport | 38 |
| Sinks | |
| Pelagic denitrification | 33 |
| Sedimentary denitrification | 6.8 |
| N sedimentation | >0.22 |
| $N_2O$ loss to the atmosphere | 0.25 |
| $NH_3$ loss to the atmosphere | 0.05 |
| ΣSources - ΣSinks | 4.9 |

This is what one would expect for a semi-enclosed basin where a steady state must be achieved over a sufficiently long time scale (probably a few years, comparable with the renewal time of the ODZ) in order to keep the nitrogen inventory constant. Intense upwelling in the western Arabian Sea probably plays an important role in determining the steady state through its participation in water circulation constituting the meridional overturning cell: Formation of intermediate waters in the Subantarctic Zone that advect northward, bringing nutrients to the tropical and subtropical regions, upwell and return southward close to the surface. This process, of course, results in high productivity that drives high particulate organic matter export from the surface layer. Degradation of this organic matter promotes nitrogen loss through creation of anoxic conditions needed for both anammox and denitrification processes to occur. As a corollary of the steady state achieved by such a cycling is that, should the amount of nitrogen brought into the Arabian Sea increase (or decrease) as a result of changes in circulation, the loss term would also increase (or decrease), associated with a more (or less) intense upwelling.

Canfield (2006) investigated the processes responsible for the formation of ODZs by using a simple 5 box model, the results of which highlighted the key role of upwelling, in that ODZ developed only when the upwelling rate exceeded a critical value (0.17 cm $hr^{-1}$). Notably, in this model upwelling was linked to or fed by lateral advection of intermediate waters to the ODZ from outside this zone. Other model simulations also show a link between denitrification and SWM intensity (Lachkar *et al*., 2021), which controls upwelling, in the Arabian Sea. There is palaeoceanographic evidence showing that such changes occurred in the geological past. For example, during the early Holocene (Kessarkar *et al*., 2018) and at other times when the SWM intensified due to orbital forcing and productivity was higher, denitrification in the Arabian Sea was more intense than it is today; on the other hand, it was much less intense during the last glacial maximum when the SWM was weaker (Altabet *et al*., 1995, 1999, 2002).

The other important result of Canfield's ODZ model is that nitrate cannot be completely removed from the ODZ through denitrification even at very high upwelling rates unless diazotrophs avail full benefit of the excess phosphate in the surface layer arising from denitrification in the ODZ. In the Arabian Sea, nitrogen fixation does not keep pace with denitrification (Bange *et al*., 2000; Naqvi, 2008). One must also consider here the difference in ratios of organic carbon production to nitrogen uptake by phytoplankton (6.6, by atoms) in the surface layer, and of organic carbon oxidation to nitrate consumption (1.1, by atoms) by denitrifiers, as *per* the Redfield stoichiometry (Richards, 1965). As a result of this, difference, organic carbon exported from the surface layer to an anoxic zone can potentially remove six times as much nitrate-nitrogen than the amount of nitrogen that was used for its production (Codispoti *et al*., 2001). The counter intuitive persistence of sufficient nitrate in the ODZs even at very high upwelling rates was attributed by Canfield (2006) to an internal feedback mechanism wherein changes in denitrification and new production are tightly coupled. This internal feedback mechanism is similar to what was proposed by McElroy (1983) and Codispoti (1989) for the global ocean, except that in Canfield's model it operates on a regional scale.

Even in the absence of a published combined nitrogen budget, it is logical to expect steady state to prevail in the Bay of Bengal as well, and given the much smaller nitrogen loss in the water column, the net input of nitrogen through circulation must also be comparatively small. This difference between the two basins probably arises from the fact that as compared to the Arabian Sea the Bay of Bengal experiences much milder upwelling (Naqvi *et al*., 2006a). Consequently, one would expect not only a smaller exchange of combined nitrogen between the Bay of Bengal and the rest of the Indian Ocean to its south, but the export of organic matter from the surface layer, which indirectly controls nitrogen loss, would also be lower in the Bay of Bengal. In other words, a less energetic exchange at mid-depths with the rest of the Indian Ocean implies that a large loss of combined nitrogen cannot be sustained in the Bay of Bengal for a long time. This is consistent with Canfield's model results.

It must be noted that low oxygen demand at mid-depths that does not allow the establishment of complete and persistent anoxia is perfectly compatible with the proposed long term biogeochemical control because, as pointed out above, upwelling links the subsurface water exchange and respiration rates. If and when complete anoxia does develop, as mentioned earlier there is one clear instance of the occurrence of SNM in the available data base, the feedback mechanism outlined above would ensure that such episodes are short lived.

In conclusion, an ODZ does not develop in the Bay of Bengal primarily because of a low rate of upwelling which is most likely linked to a greatly subdued exchange at intermediate depth with the rest of the Indian Ocean. A strong stratification of the upper water column probably also contributes to lower diffusive flux of nitrate into the surface layer. The persistent presence of oxygen in traces probably results in low organic matter degradation rates (kinetic control) with the ballast driven faster sedimentation of the particulate organic matter removal of organic matter being another potentially important factor. Finally, the presence of oxygen, albeit in traces, prevents large scale denitrification (thermodynamic control). This is consistent with the conclusions of Canfield *et al*. (2019). In view of these, for the Bay of Bengal to turn anoxic and intensely denitrifying on a sustained basis, a major change in climate causing an intensification of the upwelling favourable longshore winds will be needed. Alternatively, riverine inputs of DIN must increase drastically. This later is unlikely to happen due to an efficient removal of combined nitrogen in the terrestrial aquatic environments, as discussed in Section 9.

I would like to flag an important issue here that needs to be resolved by future research. In my opinion, we are still not quite sure how oxygen affects activities of key enzymes mediating nitrogen transformations when it is present at sub-micromolar levels (see Canfield and Kraft, 2022). Specifically, it is not clear to what extent the results of oxygen manipulation experiments (*e.g.*, Kalvelage *et al*., 2011) are representative of conditions prevailing in the natural environment. That is, it is quite possible that an enzyme like nitrate reductase, the activity of which was found to decrease only moderately even when the oxygen concentration of the ODZ water was raised to 25 µM, might continue functioning for a while after being exposed to oxygen. Also, the Km values of the enzymes (or the microbes possessing them) are variable (Canfield and Kraft, 2022) and how they vary from one environment to another is not clear. These questions are of great significance in the context of ongoing ocean deoxygenation, and also considering the large volume of waters with "near zero" oxygen concentrations that lie just outside the ODZs.

# 8. OCEANOGRAPHY OF MARGINAL SEAS OF THE NORTHWEST INDIAN OCEAN

The Northwestern Indian Ocean contains two marginal seas: the Red Sea and the Persian Gulf. Located in a highly arid region, these seas experience negative water balance (large excess of evaporation over precipitation and river runoff) resulting in very high salinities and Mediterranean-type (anti-estuarine) circulation *i.e.* net flow of fresher seawater into these basins close to the surface and outflow of dense high salinity waters close to the bottom (Morcos, 1970; Sheppard *et al.*, 2010). As stated earlier, these dense water masses enter the Arabian Sea *via* the Gulf of Aden and the Gulf of Oman, respectively, and spread along density ~27.1 and 26.5 $\sigma_\theta$ surfaces (Wyrtki, 1971), significantly affecting mesopelagic water mass structure and biogeochemical cycling in the northwestern Indian Ocean (Naqvi *et al.*, 2006a).

While experiencing similar climate, the two seas exhibit marked geomorphological differences, reflecting tectonic processes responsible for their formation (Naqvi, 2021). The Red Sea is much deeper (average depth 491 m; Morcos, 1970) than the Persian Gulf (average depth 36 m; Sheppard *et al.*, 2010). The central axial trough of the Red Sea is its deepest part where the maximal depth exceeds 3,000 m. However, the sill at the Bab-el-Mandeb Strait, which separates the Red Sea from the Gulf of Aden, is only 137 m deep (Lambeck *et al.*, 2011). The dense deep water that fills the Red Sea basin below sill depth is quite uniform in temperature and salinity (Naqvi, 2021). The residence time of deep water, produced through cooling and deep convection in the northern region including the Gulf of Suez and the Gulf of Aqaba, is fairly long (36–90 yr; Cember,1988; Woelk and Quadfasel, 1996). The long residence time results in a significant depletion of oxygen and the accumulation of nutrients within the basin. However, despite the highly isothermal and isohaline characteristics of deep water, the deep water oxygen concentration is not constant, with a well defined oxygen minimum occurring at mid-depths (Naqvi, 2021).

The Persian Gulf covers an area (251,000 $km^2$; Sheppard *et al.*, 2010) that is about half of the area of the Red Sea (438,000 $km^2$; Morcos, 1970). The deepest part of the Persian Gulf, where water depth barely reaches ~90 m, is off the Iranian coast. Unlike the Red Sea, the Persian Gulf does not have a sill at its entrance (the Hormuz Strait). Accordingly, the residence time of water within the Persian Gulf is short (~1.2 yr; Al-Said *et al.*, 2018). Except in the southern and central parts, the water column in the Persian Gulf is generally well mixed, especially in the winter (Grasshoff, 1976; Brewer and Dyrssen, 1985). Therefore, under pristine conditions that existed until a few decades ago, the Persian Gulf Waters were generally well oxygenated with little build-up of nutrients (Al-Yamani and Naqvi, 2019, and references therein).

I had an opportunity to visit the Red Sea in May 1983 when India acquired R.V. *Sagar Kanya.* The ship, which was operated by NIO for 15 years and on which I did a large part of my research, was built in Germany and I was a member of a

joint Indo-German research team that brought the vessel to India, making observations in the Red Sea during this voyage. I teamed up with Hans-Peter Hansen from Institut für Meereskunde, and Tariq Kureishy from NIO to make chemical measurements. Some of the results from this cruise have been published (Naqvi *et al.*, 1986; Naqvi, 2021).

In 1990–1991 I spent eight months in Rick Fairbanks' laboratory at Lamont Doherty Earth Observatory (L-DEO) of Columbia University, Palisades, New York, as a CV Raman Fellow. The Core Laboratory of L-DEO has some of the best collections of cores from the Indian Ocean, some of which were used by me. Among other things, we looked at the sedimentary record to reconstruct changes in the Red Sea Outflow over the last glacial-interglacial transition (Naqvi and Fairbanks, 1996).

I also got an opportunity to work in the Persian Gulf after my superannuation from NIO in 2016 (Fig. 8.1). I was offered a Consultant position by the Kuwait Institute of Scientific Research (KISR), where I was involved with the ongoing monitoring programme of their Oceanography Group led by Faiza Al-Yamani in Salmiya to investigate the ongoing human induced changes in the northwestern Persian Gulf (Al-Said *et al.*, 2018, 2019; Al-Yamani and Naqvi, 2019; Ahmed *et al.*, 2022; Yamamoto *et al.*, 2022). A brief summary of these studies is provided below.

**Figure 8.1** Water sampling with Ayaz Ahmed on a KISR research boat in the northwestern Persian Gulf (November, 2017).

## 8.1 Red Sea

The *Sagar Kanya* observations in 1983 revealed some interesting features. The observed relative changes in the molar $O_2$:N:P ratios in water (230:21:1) were significantly different from Redfield values (138:16:1). From these data, the atomic C:N:P ratios in the biomass were estimated to be 188:21:1. Departure from open ocean "Redfield" values indicated an overall phosphate deficiency, despite the fact that the waters flowing into the Red Sea from the Gulf of Aden/Arabian Sea are enriched in phosphate relative to nitrate as a result of the large scale nitrogen loss within the Arabian Sea ODZ, discussed above. In other words, the high $\Delta N0_3$:$\Delta P0_4$ ratio observed in the Red Sea implied that when normalised to phosphate, more nitrate is exported out of the Red Sea by the high salinity outflow than the amount added by the inflowing current. This nitrogen could only be added through $N_2$ fixation by diazotrophs. The absence of significant river runoff and little anthropogenic perturbation at that time allowed estimation of net nitrogen fixation in the Red Sea from the known volumes of inflows and outflows assuming phosphate conservation. This came to 0.74 Tg N $yr^{-1}$ (Naqvi *et al.*, 1986). Thus, on a *per* unit area basis nitrogen fixation rate in the Red Sea may be five times as much (1.7 x $10^6$ gN $km^{-2}$ $yr^{-1}$) as in the oceans as a whole (0.33 x $10^6$ gN $km^{-2}$ $yr^{-1}$; Codispoti *et al.*, 2001; Galloway *et al.*, 2004; Gruber, 2008). However, this is not unexpected given the prevailing high temperatures and generally calm weather conditions persisting within the Red Sea for most part of the year that should favour nitrogen fixation (Devassy *et al.*, 1978). The region has been known for blooms of *Trichodesmium*, and it was from here that this genus was first described by Ehrenberg (1830). It is also believed that the Red Sea derives its name from the red colour imparted to seawater by such blooms (Naqvi *et al.*, 1986).

It may be pointed out that the above estimate for $N_2$ fixation rate in the Red Sea is based on the assumption that phosphate supply to the Red Sea is entirely by the inflowing currents (note that in summer, June–September, the inflow through Bab-el-Mandeb occurs at mid-depths sandwiched between a weak surface outflow and the deep outflow of dense water; Murray and Johns, 1997). In absolute terms, there also occurs a net export of phosphate out of the Red Sea, so there must be additional sources of this nutrient in the region. Dissolution of phosphorites in the sediments has been proposed by Grasshoff (1969) as a possible additional source, but atmospheric deposition may also be important, as will be discussed in the case of the Persian Gulf. In any case, this estimate may be treated as a conservative lower limit.

In view of the anthropogenic perturbations this land locked region has recently been subjected to, the natural steady state in the Red Sea has probably been substantially impacted. Satellite derived data indicate rapid warming of surface waters at a rate that exceeds the global trend (0.17–0.45 $^oC$ $decade^{-1}$) from 1982 to 2015 (Chaidez *et al.*, 2017). The limited data available also suggest oxygen loss from Red Sea waters (Naqvi, 2021). Coastal waters receiving sewage from Jeddah City have been reported to experience severe oxygen depletion

including sulfidic conditions and high concentrations of $CH_4$ (Orif *et al.*, 2016). Even in the open Red Sea, oxygen concentrations below 400 m appear to have fallen substantially in 2015–2017 relative to the *Sagar Kanya* observations made in 1983 (Naqvi, 2021). However, it may be noted that the recent data used for the comparison were only available for the southern half of the Red Sea, and a more detailed data set with time series observations is needed to confirm the reported trend.

The ongoing human induced changes such as warming are not only expected to affect oceanographic processes, including biogeochemistry and ecosystem functioning, within the Red Sea, but may also potentially impact water exchange with the Indian Ocean, including characteristics of the Red Sea Outflow, thereby impacting mesopelagic oxygen distribution in the Arabian Sea (Lachkar *et al.*, 2019).

On my visit to L-DEO we conceived of a novel approach to investigate changes in exchanges between the Red Sea with the Indian Ocean. This approach was based on the large differences in stable carbon isotopic composition ($^{13}C/^{12}C$ ratio expressed as $\delta^{13}C$ with respect to the PDB standard) of dissolved inorganic carbon (DIC) of waters within and outside the Red Sea, with the $\delta^{13}C$ values of deep waters within the Red Sea being substantially higher (Ostlund *et al.*, 1987). Calcareous shells of some benthic foraminifera (*Cibicidoides* sp.) are known to reflect $\delta^{13}C$ of bottom waters, and where bottom water is affected by the Red Sea Outflow, this proxy could be used to reconstruct changes in the outflow. This was done in Naqvi and Fairbanks (1996) using a sedimentary core from the inner Gulf of Aden from a depth that presently receives the outflow. Radiocarbon dating by accelerator mass spectrometry showed that this record, having an average sampling resolution of ~800 years, covered the past 27,000 years (*i.e.* going back beyond the last glacial maximum (LGM) that occurred ~20,000 years ago).

The much lower sea level (by ~120 m) during the LGM as compared to today apparently resulted in greatly reduced outflow from the Red Sea as indicated by low $\delta^{13}C$ values. However, as the sea level rose, the Red Sea appears to have been vigorously flushed for approximately 2,000 years before a major monsoon intensification and associated freshening of the upper water column caused the cessation of deep water formation from 15,500 to 7,300 yr BP, as evidenced by the increase, and then an abrupt decrease, in $\delta^{13}C$. This record enabled an evaluation of the timing of monsoon intensification in response to insolation increase in the northern hemisphere. It revealed that the monsoon intensification lagged behind insolation until 15,500 yr BP. However, the time lag did not persist thereafter, and the humid interval over which the outflow was interrupted persisted for 8,000 years, coinciding with the period of peak solar insolation in the northern hemisphere. This is in conflict with previous reports of a lag in monsoon response behind solar forcing by a few thousand years, attributed to the ice sheet overprint or the effect of cross-equatorial transport of latent heat (Van Campo *et al.*, 1982; Prell, 1984; Clemens *et al.*, 1991).

## 8.2 Persian Gulf

As in the case of the Red Sea, biogeochemistry of the Persian Gulf, a similarly land locked sea, is also strongly controlled by water exchange with the Indian Ocean, driven mainly by excessive evaporation over precipitation and river runoff. Low salinity surface water flows in from the Gulf of Oman through the Hormuz Strait whereas near bottom export of dense water occurs in the opposite direction.

There are several features, however, that differentiate the Persian Gulf from the Red Sea. (1) Despite the highly negative water balance, the Persian Gulf receives substantial runoff from rivers flowing through Turkey, Iraq and Iran (Sheppard *et al*., 2010), which makes the Persian Gulf more susceptible to human induced alteration of fluxes of freshwater and chemicals, especially nutrients. (2) Endowed with vast petroleum deposits, all eight Persian Gulf countries are very prosperous, resulting in a great deal of "development" along its shores including large expansion of urban and industrial centres over the past few decades. In fact, the Persian Gulf is among the most anthropogenically impacted marine environment in the world (Sheppard *et al*., 2010). (3) Because its average depth is only 36 m, benthic processes are expected to play an important role in biogeochemical cycling. (4) While, as in the case of the Red Sea, the inflowing water (from the Gulf of Oman) has high P:N ratio, unlike the Red Sea, the relative change in N:P in the Persian Gulf is very close to the Redfield value (Hashimoto *et al*., 1998b; Al-Yamani and Naqvi, 2019). What causes this difference between the two basins is not quite clear, but sedimentary cycling may have a role (*i.e.* nitrogen loss through denitrification and/or anammox is expected to occur in sediments that are reducing beneath a very thin surface layer).

Considering nutrient distribution in the Hormuz Strait (Grasshoff, 1976; Brewer and Dyrssen, 1985), Al-Yamani and Naqvi (2019) pointed out that the quantities of combined nitrogen and phosphorus exported from the Persian Gulf with the high salinity outflow far exceed their inputs by the inflowing surface current. This implies that there must be some hitherto unknown local sources of these macronutrients. The riverine inputs alone cannot account for the observed anomaly. As in the case of the Red Sea, nitrogen fixation must be important in the Persian Gulf as well, although it does not produce departures in the N:P ratio, as for the Red Sea mentioned above.

Reduction of river runoff due to diversion of waters and enhanced loading of nutrients through sewage and industrial/agricultural wastes are the two most important ways by which human activities are impacting the marine environment of the Persian Gulf (Al-Yamani and Naqvi, 2019). The effect of salinity change is most pronounced in the northwestern part of the Persian Gulf, which receives runoff from the Shatt al-Arab River. This region is one of the two areas where dense waters are produced in the Persian Gulf (Swift and Bower, 2003); the other one is the southwestern region off the coast of the United Arab Emirates (Brewer and Dyrssen, 1985). When compared with the data collected in the 1970s, surface water salinities off Kuwait have increased by ~10 psu during

winter, the time when the deep water formation occurs, making these waters now the densest found anywhere in the Persian Gulf (Al-Said *et al*., 2018). This is expected to significantly alter water circulation in the Persian Gulf, potentially affecting the characteristics of the Persian Gulf Outflow.

Unlike salinity, increases in nutrient loadings through sewage discharge are not readily evident from historical data sets. Based on monthly measurements of nitrate, nitrite, ammonium and phosphate during 2002–2015 at three time series stations located in coastal waters of Kuwait, Al-Said *et al*. (2019) found considerable inter-annual variability, broadly related to fluctuations in the Shatt-al-Arab discharge, but a lack of secular trend despite the long term decline in the discharge. These observations are generally consistent with the results of Devlin *et al*. (2015) who examined a longer record (1983–2013) but from sites closer to the Kuwaiti coast. The data set analysed by Devlin *et al*. also included chlorophyll, which surprisingly showed a slight decreasing trend over this time period, which was ascribed to a community shift to small phytoplankton taxa arising from inhibition of nitrate uptake by diatoms in the presence of ammonium, the predominant form of nitrogen in sewage. Such an inhibition has been observed elsewhere in the ocean (*e.g*., by Dugdale *et al*. (2007) in San Francisco Bay). However, the following results of our studies do not support this interpretation.

(1) At the coastal sites investigated by Al-Said *et al*. (2019), ammonium concentrations neither increased with time nor were they high enough (>4 µM) to inhibit nitrate uptake by diatoms (Dugdale *et al*., 2007). Moreover, although inhibition of nitrate uptake by ammonium has not been found to be very consistent (Dortch, 1990; Gilbert *et al*., 2016), if it were to occur in our study area, then the nitrate concentration would have shown an increasing trend with time, which is not the case (Devlin *et al*., 2015; Al Said *et al*., 2018).

(2) Water samples collected from several locations in different seasons, spiked with different combinations of nutrients and incubated *in situ* in KISR Marina revealed rapid nitrate uptake, chlorophyll build-up and growth of diatoms, even in the presence of ammonium, as long as other macronutrients (phosphate and silicate) were present (Al-Said *et al*., 2019; Ahmed *et al*., 2022). These experiments also indicated that primary production was mostly nitrogen limited.

(3) Phytoplankton also responded quickly to natural addition of nutrients from land as a result of a series of flash floods that swamped urban drainage systems of Kuwait in November–December 2018, as inferred from rapid increases in chlorophyll *a* and net community production (Ahmed *et al*., 2022).

An efficient utilisation of nutrients of anthropogenic origin would result in an overall increase in biological productivity of the Persian Gulf. This is reflected by an increase in the frequency of occurrence of phytoplankton blooms in the region (Al-Yamani *et al*., 2012). Why the increase in productivity is not being reflected by an increase in phytoplankton biomass (Chl. *a*) is most likely due to rapid consumption of the photosynthesised organic matter by the heterotrophs

(Al-Said *et al.*, 2019). Measurements of net community production and respiration made at several stations off Kuwait following the light and dark bottle oxygen method yielded very high rates (up to 1103 mg C $m^{-3}$ $d^{-1}$ and 2196 mg C $m^{-3}$ $d^{-1}$ under bloom conditions) indicating both rapid production and respiration of organic matter (Al-Said *et al.*, 2019; Ahmed *et al.*, 2022). An analysis of phytoplankton community structure following the aforementioned flash floods revealed the dominance of diatoms and the photosynthetic ciliate *Myrionecta rubra*. Results of field observations as well as microcosm experiments suggested that although the phytoplankton growth was stimulated by the nutrient supply, microzooplankton grazing controlled their outbursts (Ahmed *et al.*, 2022).

The increased loading of carbon and its respiration are also reflected by the available data on total organic carbon (TOC, which consists of both dissolved and particulate organic matter including biomass) and the recent emergence of hypoxia in waters of the Persian Gulf. The TOC measurements, although restricted in geographical (Kuwait's coastal waters) and temporal (2014–2016) coverage, yielded concentrations ranging from 101.0 to 318.4 µM, with a mean value of 161.2 µM, which is fairly high for oceanic surface waters, including marginal seas (Al-Said *et al.*, 2018, and references therein). Much higher TOC levels (336.7–543.3 µM) were measured in the inner Kuwait Bay during episodic phytoplankton blooms in the spring of 2017. The TOC was found to be significantly related to chlorophyll, which reached values as high as 96.2 mg $m^{-3}$ under bloom conditions. These data suggest that the TOC is most likely produced locally by phytoplankton.

Historical data show the prevalence of generally well oxygenated conditions in the water column due to the short residence time of water within the Gulf (Grasshoff, 1976; Brewer and Dyrssen, 1985). Al-Ansari *et al.* (2015) were the first to report the development of hypoxic conditions in the Persian Gulf. In the autumn of 2000, these authors measured a minimum oxygen concentration of 38 µM in the bottom water at a station located north of the Qatar peninsula. Comparing these results with observations made at about the same time of the year in 1968 by R.V. *Lesnoye* in the southern half of the Persian Gulf, Al-Said *et al.* (2018) demonstrated that hypoxia in the Persian Gulf was of recent origin (Fig. 8.2). Since then, utilising a more extensive data set generated during cruises conducted in 2018–2019, Saleh *et al.* (2021) have mapped the hypoxic zone in the region in detail. Occurring below about 50 m water depth, this zone was reported to develop in late winter and was found to be most intense during mid-autumn, when it was estimated to cover 50,000 $km^2$ of the seafloor (about a fifth of the total area of the Persian Gulf!) with a minimum observed oxygen concentration of ~27 µM.

As mentioned earlier, the Persian Gulf Water is an important component of the intermediate water mass structure in the northwestern Indian Ocean. In fact, it is the only freshly formed water mass in the world that directly advects into the heart of an ODZ. Historically, this water mass has been slightly oxygenated to begin with, and so it generally inhibits processes that bring about

combined nitrogen loss in the Gulf of Aden and in the northwestern Arabian Sea (Codispoti *et al.*, 2001; Banse *et al.*, 2014). Any changes in its characteristics may have a potentially large impact on $N_2$ production rate in the Arabian Sea. This can happen in three possible ways.

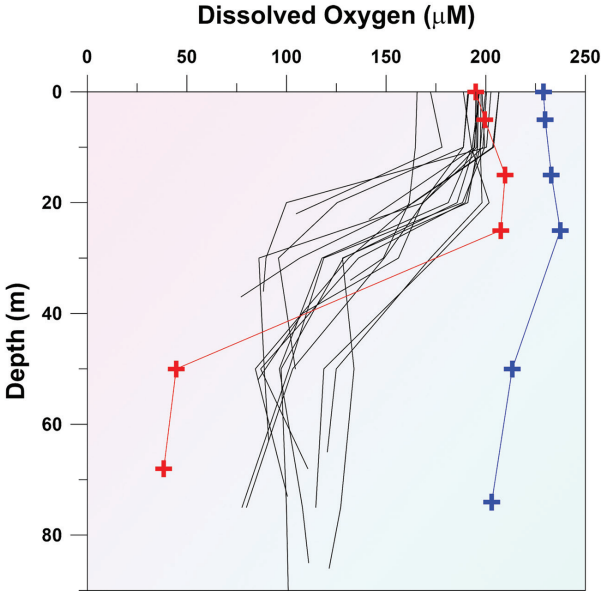



**Figure 8.2** Comparison of an oxygen profile from central Persian Gulf obtained from the northern periphery of Qatar's EEZ in the autumn of 2000 (red line and crosses; blue line and crosses show profile at the same station in winter) from Al-Ansari *et al.* (2015) with oxygen profiles in the same region and at the same time of the year taken by R.V. *Lesnoye* in 1968 (Al-Said *et al.*, 2018), The inferred development and intensification of hypoxic conditions in the Gulf have been confirmed by Saleh *et al.* (2021). From Al-Yamani and Naqvi (2019).

(1) Changes in thermohaline characteristics: The Persian Gulf, like any other region, is experiencing ocean warming. An analysis of time series data from Kuwaiti waters yielded a long term trend of increasing sea surface temperature at a rate of 0.38 °C decade$^{-1}$ (Al-Yamani *et al.*, 2017), which is higher than the global average (0.11 °C decade$^{-1}$; Rhein *et al.*, 2013). Model simulations by Lachkar *et al.* (2019) show that such warming can strongly alter the volume and intensity of the Arabian Sea ODZ by making the Persian Gulf Water lighter (Lachkar *et al.*, 2019). This would result in an intensification of the ODZ. However, the model also predicted that if too much nitrate is lost from the ODZ, as expected from strong warming (*e.g.*, by 4 °C), it would provide a negative feedback to the ODZ intensity through a decrease in nitrate supply to surface waters, with a consequently lower productivity and lower respiration rates at depth (Lachkar *et al.*, 2019).

This internal feedback has already been discussed in Section 7. As stated above, surface water salinities have risen drastically in recent years in the northwestern Gulf, the effect of which on the density of Persian Gulf Water will be in the opposite direction. However, the model results suggest a less important role of changes in salinity than those in temperature in the Persian Gulf in controlling deoxygenation in the Arabian Sea (Lachkar *et al*., 2019).

(2) Increase in pre-formed TOC in Persian Gulf Water: Even though there were no data available on TOC from the Persian Gulf prior to the study by Al-Said *et al*. (2018), as stated earlier the TOC concentrations reported by these authors are quite elevated and their apparent relationship with phytoplankton biomass, especially during algal blooms, suggests an ongoing increase in TOC concentrations as a consequence of increasing biological production. Arguably, part of the excess TOC being produced has resulted in the development of hypoxia, but a significant fraction may also escape degradation and get exported out of the Gulf. It is not clear what fraction of the TOC that is labile/semi-labile is transported into the Arabian Sea ODZ and decomposed on time scale of its renewal (a few years).

Measurements of TOC by Hansell and Peltzer (1998) under the US JGOFS programme yielded a TOC concentration of ~54 µM associated with the Persian Gulf Water salinity maximum at a station in the Gulf of Oman, where the Persian Gulf Water had probably already been modified by mixing. This value is considerably higher than the background concentrations of 44–46 µM at comparable depths at other stations in the Arabian Sea experiencing lesser influence of the Persian Gulf Water. Any increase in the pre-formed TOC of this water mass could therefore have a potentially large impact on $N_2$ production. According to Al-Said *et al*. (2018), an increase in labile TOC content of Persian Gulf Water by 10 µM, could potentially enhance the denitrification rate by 0.9 Tg N $yr^{-1}$. This assumes that the additional TOC will be anaerobically degraded. However, even if a part is aerobically respired, it would consume oxygen, still causing an expansion of the ODZ.

(3) Decrease in pre-formed oxygen: Expansion of the ODZ to the west/northwest should also be expected from the irrefutable evidence of ongoing expansion of hypoxia in the Persian Gulf presented above, and crucially also in the Hormuz Strait where the characteristics of the outflow are modified by mixing (Saleh *et al*., 2021). One may argue that as hypoxia in the Persian Gulf occurs seasonally, this effect may be limited. However, it must be considered that the outflow itself does not show seasonal changes (Johns *et al*., 2003), the annual decrease in oxygen inputs to the northwestern Indian Ocean by Persian Gulf Water are expected to be significant.

It is difficult to evaluate the relative importance of above factors. However, in view of large ongoing changes in the Persian Gulf, its rapid flushing, and relatively quick renewal of the ODZ waters in the Arabian Sea, intensification/expansion of ODZ of the northwestern Indian Ocean in the near future, seems inevitable, if it is not already happening. Long term monitoring of the redox state of intermediate waters in the Gulf of Oman is extremely desirable.

# 9. THE TERRESTRIAL CONNECTION

The National Academy of Sciences of the USA organised a Symposium on Nutrient Over-Enrichment in Coastal Waters in October 2000 in Washington, D.C. This was a fairly large meeting, which I also attended. Christine Todd Whitman, the then Governor of New Jersey, inaugurated the Symposium. I remember her because in her inaugural address she jokingly questioned why the area of the infamous dead zone in the Gulf of Mexico was always compared with the area of her state. Our paper on the seasonal hypoxic zone off the Indian west coast (Naqvi *et al*., 2000) had just been published, and it occurred to me that if we were to make a similar comparison, the estimated area of this system would be about 50 times the size of Goa.

Sybil Seitzinger from Rutgers (now at University of Victoria) was a keynote speaker at this meeting. The highlight of her talk was the large anthropogenic input of combined nitrogen to the ocean by rivers (her estimates were subsequently published in a special issue of *Estuaries*; Seitzinger *et al*., 2002). The estimated runoff from South Asia was 4.2 Tg N $yr^{-1}$. Even though not much was known about the DIN load of major South Asian rivers at that time, the data I was aware of (from the Mandovi-Zuari river system in Goa) were not alarmingly high. I also had access to data from the Bay of Bengal including the region just off the mouth of the Hooghly that were collected during numerous cruises undertaken by NIO. Surface DIN concentrations were always close to the detection limit. Therefore, I felt that Sybil's estimate was too high. I told her about it but failed to convince her. Every time we have met thereafter (she also visited NIO once), we discussed this issue, ending up with disagreement. Subsequent estimates utilising the growing data base have since confirmed that actual DIN inputs by Indian rivers are indeed quite modest (Naqvi, 2008; Singh and Ramesh, 2011; Krishna *et al*., 2016). However, this has raised the question as to where the enormous amount of combined nitrogen released to the environment mainly from agriculture, sewage discharge and fossil fuel combustion is going? This question is of great relevance to possible emergence of new hypoxic systems in coastal waters of the region, especially in the Bay of Bengal and Andaman Sea, and intensification of the naturally produced seasonal anoxic zone over the western continental shelf in the future.

In order to answer this question, we started visiting some dam-reservoirs (Selaulim in Goa, Tillari in Maharashtra, Markandeya and Supa in Karnataka) that were easily accessible to us (Fig. 9.1). Even though these reservoirs are located at low latitudes, we found that they experienced marked seasonal physico-chemical changes: in all cases, the water column became stratified in summer leading to anoxic conditions in late summer and autumn. What really surprised us was that DIN concentrations in the reservoirs, many of which were located in areas with intensive farming utilising synthetic fertilisers, were quite modest (a few tens of micromolar at the most). Intrigued by these observations, we extended our work to a few more systems. Some of these reservoirs

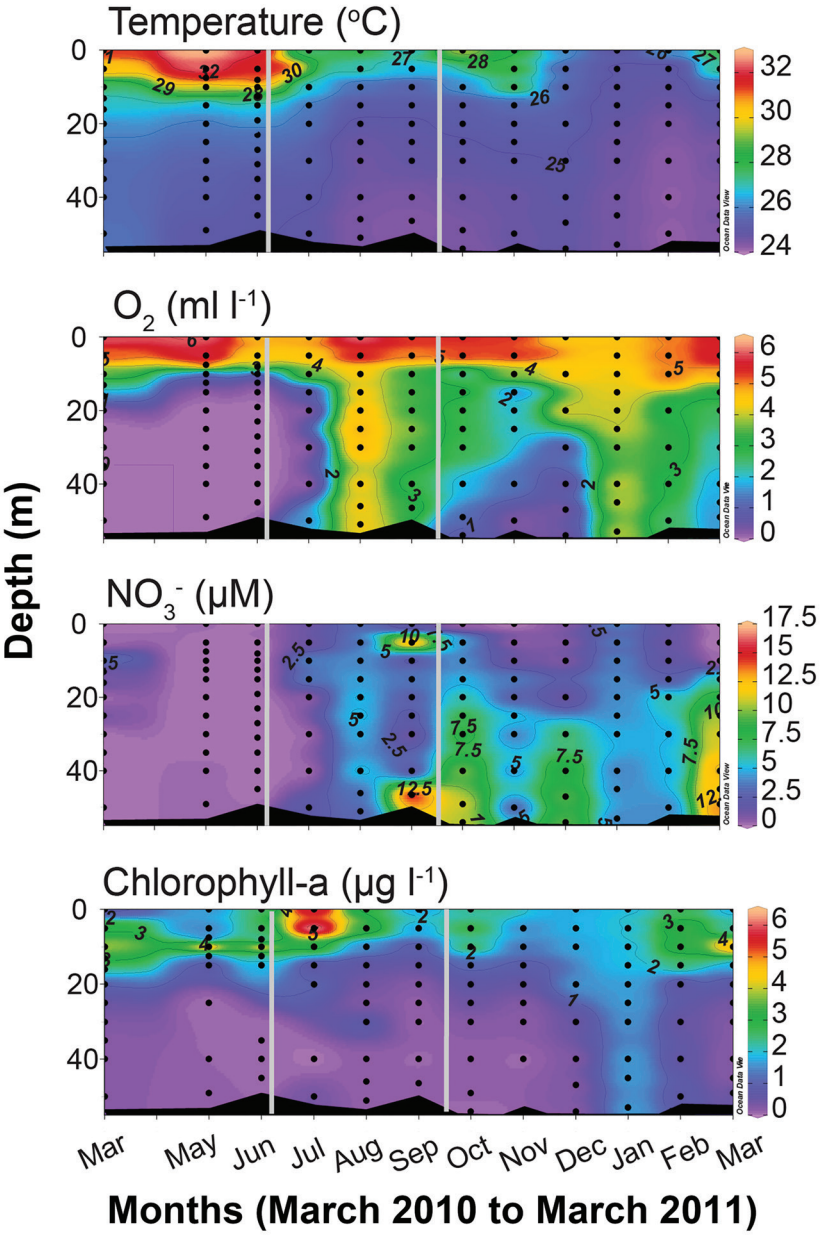
**Figure 9.1** Sampling fresh/brackish water ecosystems: Lonar Lake (upper panel) and Idukki Reservoir (lower panel). The late Pradeep Narvekar is seen on a barge that was used for sampling in the Idukki Reservoir.

(Idukki in Kerala, and Koyna in Maharashtra) are located in the Western Ghats, others further inland (Nagarjuna Sagar and Srisailam in Andhra Pradesh, Sardar Sarovar and Ukai in Gujarat, Hirakud in Orissa, Rihand in Uttar Pradesh, Rana Pratap Sagar in Rajasthan, Tehri in Uttarkhand and Bhakra-Nangal in Himachal Pradesh) (https://static-content.springer.com/esm/art%3A10.1038%2Fs41467-018-03607-z/MediaObjects/41467_2018_3607_MOESM1_ESM.pdf).

The trends seen in Tillari, Markandeya and Supa were also observed in all reservoirs with the exception of Tehri and Bhakra Nangal. The latter two reservoirs are located in or at the foothill of the Himalayas and fed by glacial melt waters. Summer stratification is not strong enough and/or oxygen consumption rates not high enough to result in the development of anoxic conditions in these systems.

The physical processes regulating the annual cycle in these reservoirs are discussed in detail by Shenoy *et al*. (2021) taking Tillari as an example, where time series data based on monthly observations are available for several years. Data for the period 2010–2011 are presented in Figure 9.2. Briefly, winter cooling is strong enough even in the tropics to bring about convective mixing and the bottom water gets isolated in spring following the establishment of thermal stratification. Waters of the hypolimnion (the layer lying below the thermocline) turn anoxic in the spring/early summer leading to an apparent loss of combined nitrogen, as indicated by a decrease in nitrate concentration, often followed by sulfate reduction (appearance of $H_2S$ and accumulation of $NH_4^+$ when all nitrate had been used up; Shenoy *et al*., 2021). Measurements of $N_2$/Ar ratios in four reservoirs revealed high values within the anoxic hypolimnia, pointing to combined nitrogen loss to $N_2$ (Naqvi *et al*., 2018). In reservoirs located in/close to the Western Ghats where intense rainfall associated with strong winds occurs during the SWM, the water column gets vertically homogenised and oxygenated to varying extents during this season as well (Fig. 9.2). Oxygen concentrations in the hypolimnion drop again in the following autumn but the water does not become fully anoxic. However, periods of anoxia could be more prolonged in reservoirs located in areas where the SWM is less intense.

Apart from the low DIN concentrations, an intriguing aspect of nitrogen cycling in Indian freshwater reservoirs is the generally low concentrations of nitrite and $N_2O$, as evident from Figure 9.3 (a scatter diagram constructed using all data). The nitrite concentration was often below or close to the detection limit and only in 27 samples out of a total of 815 (3 % of the total) did it exceed 0.5 µM (maximum 1.35 µM). Similarly, the $N_2O$ concentration was below 20 nM in 681 cases (84 % of the total). Concentrations in excess of 100 nM (maximum 357.2 nM) were recorded only in 34 samples (4 % of the total). None of the samples with elevated $N_2O$ content came from the epilimnion (oxygenated surface layer lying above the thermocline); most of them also had elevated nitrite and low oxygen (22.3 µM; Fig. 9.3). The less frequent high nitrite-high $N_2O$ values were confined to a few reservoirs; Markandeya (4 trips), Tillari (3 trips), Idukki and Koyna (1 trip each), all sampled during the summer.


Temperature (°C)
O2 (ml l-1)
NO3- (µM)
Chlorophyll-a (µg l-1)
Depth (m)
0
20
40
Mar
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
Jan
Feb
Mar
Months (March 2010 to March 2011)

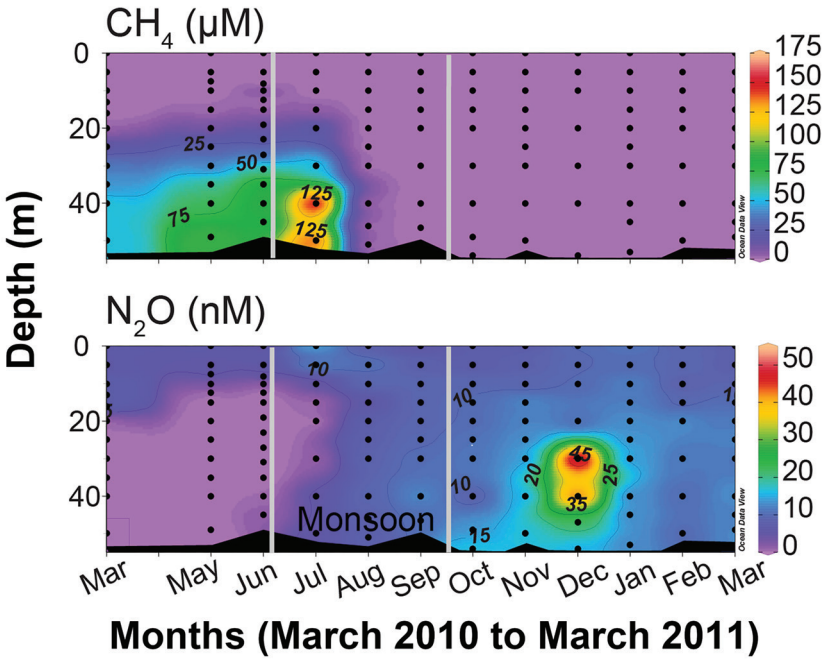



**Figure 9.2** Annual cycles of physico-chemical variables in Tillari Reservoir. The south-west monsoon period (June–September) is demarcated by white vertical lines. Longer term records from this site are presented elsewhere (Shenoy *et al.*, 2021). From Naqvi *et al.* (2018).

Methane also showed relatively modest accumulation (Fig. 9.2; also Shenoy *et al.*, 2021). The maximum concentration was ~207 μM from Tillari Resevoir. Like $N_2O$, information on $CH_4$ from Indian reservoirs did not exist prior to our work. However, even in the absence of any data, it had been postulated that Indian reservoirs served as a large source (33.5 Tg $yr^{-1}$) of atmospheric $CH_4$; our measurements, first reported by Narvenkar *et al.* (2013), show that this was a gross overestimate.

We carried out measurements of rates of the processes potentially responsible for combined nitrogen loss to $N_2$ (denitrification and anammox) and conversion of nitrate to ammonium (DNRA) following the isotope pairing method (Holtappels *et al.*, 2011). This work was done in collaboration with Marcel Kuypers' group at MPI Bremen, Germany. While the incubations were carried out at the dam sites, mass spectrometric measurements of labelled nitrogen ($^{14}N^{15}N$ and $^{14}N^{15}N$) produced were made in at the MPI Bremen. For this purpose, I made several trips to Bremen, which included a 24 month assignment as a Marie Curie Incoming Fellow during 2008–2011.

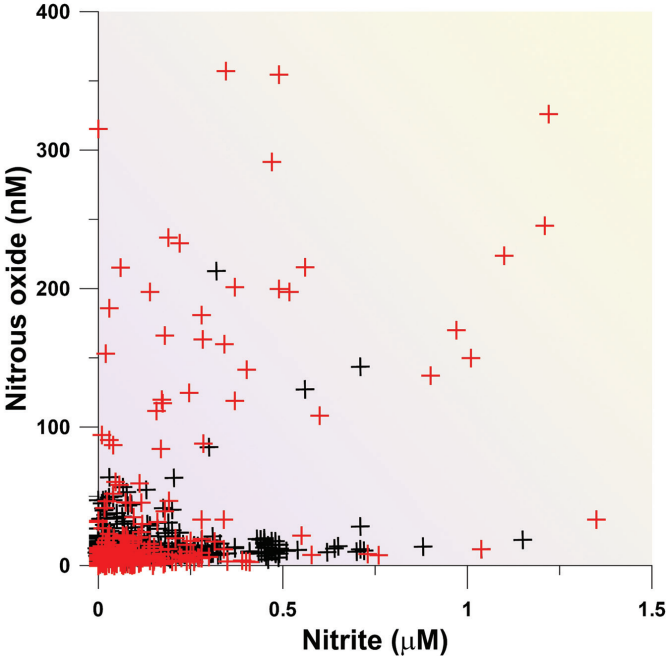



**Figure 9.3** Plot of nitrous oxide *versus* nitrite in all reservoirs. Red and black symbols denote samples with dissolved $O_2 \leq 22.3$ μM, and >22.3 μM, respectively. From Naqvi *et al.* (2018).

Five reservoirs were chosen for rate measurements; Koyna and Selaulim (once each); Idukki and Markandeya (three times each); and Tillari (five times). Although the choice of these reservoirs was dictated by logistical convenience, they also happened to differ in terms of the extent of anthropogenic impact, with Tillari being the most pristine and Markandeya the most perturbed.

Measured rates of both denitrification and anammox were quite low with one exception; Markandeya Reservoir in May 2007. On this occasion, high dentrification rates were measured throughout the anoxic hypolimnion in samples incubated with $^{15}NO_2^-$. Rates of $^{15}N^{15}N$ and $^{14}N^{15}N$ production reached maximum values of 832.1 and 111.4 nmol $N_2$ $l^{-1}$ $d^{-1}$, respectively, with an average total denitrification rate of 1371 ± 368 nmol $N_2$ $l^{-1}$ $d^{-1}$ as compared to the average value of 53.2 ± 149.9 nmol $N_2$ $l^{-1}$ $d^{-1}$ for all other observations (Naqvi *et al.*, 2018). Anammox rates determined from $^{14}N^{15}N$ production from $^{15}NH_4^+$ and $^{15}NO_2^-$ averaged only 3.98 ± 8.82 nmol $N_2$ $l^{-1}$ $d^{-1}$ and 12.62 ± 22.47 nmol $N_2$ $l^{-1}$ $d^{-1}$, respectively. Rates of DNRA derived from the production of labelled $NH_4^+$ from incubations with $^{15}NO_3^-$ or $^{15}NO_2^-$ in four reservoirs were also very low, averaging 9.70 ± 11.16 and 8.71 ± 13.44 nmol N $l^{-1}$ $d^{-1}$, not including Selaulim

Reservoir, where high rates (70.97–162.14 nmol N $l^{-1}$ $d^{-1}$) were obtained in incubations with $^{15}NO_2^-$ on one summer visit (Naqvi *et al*., 2018).

The Marie Curie Fellowship proposal was focussed on the fate of anthropogenic nitrogen in Indian freshwater ecosystems. Among other things, it aimed to reconcile the anomalous observations mentioned above, *i.e.* relatively low rates of denitrification and anammox, with large apparent loss of combined nitrogen from the anoxic hypolimnia as indicated by data on DIN and excess $N_2$ derived from the $N_2$/Ar ratio (Naqvi *et al*., 2018). For this purpose we revisited in 2011–2012 the two most frequently sampled reservoirs; Tillari and Markandeya. In addition to repeating incubation experiments previously conducted with $^{15}N$-labelled nitrate, nitrite and ammonia, we also measured labelled $N_2$ production in samples that were incubated with $^{15}NO_3^-$ and $^{15}NO_2^-$ along with $CH_4$ to evaluate the role of then recently discovered nitrite dependent anaerobic methane oxidation (n-damo; Ettwig *et al*., 2010) in nitrogen loss. Subsequent work has indicated widespread occurrence of the microbes that mediate n-damo (*Methylomirabilis oxyfera*' and its relatives in the phylum NC10) in different environments (*e.g.*, Shen *et al*., 2015). However, when we carried out these experiments, the potential contribution of this process to nitrogen cycling in anoxic freshwater ecosystems was unknown.

Observations in Tillari and Markandeya during the 2011–2012 (Fig. 9.4; Naqvi *et al*., 2018) conformed to the previously observed trends in these reservoirs, including low nitrate and nitrite concentrations in anoxic waters (Narvenkar *et al*., 2013). The rate of labelled $N_2$ production was again found to be quite low in incubations of samples spiked with $^{15}NO_2^-$ alone, but this rate increased dramatically (by a factor of ~12) when $CH_4$ was added to the samples (Fig. 9.4). It should be noted that almost all samples originally contained $CH_4$ in concentrations that were comparable to those in amendment experiments with $CH_4$. However, since the procedure followed involved sparging of samples with helium to lower $N_2$ background prior to $^{15}N$ label additions, $CH_4$ originally present in samples had also been removed from samples that were incubated with $^{15}NO_2^-$ alone. Therefore, production of $N_2$ would also have occurred at a high rate in unamended samples, as probably happens in the natural environment, had the $CH_4$ originally present in the samples not been removed. These results strongly indicated that denitrification coupled to methanotrophy was the dominant pathway of combined nitrogen loss from Indian freshwater reservoirs (Naqvi *et al*., 2018). It is most likely that the denitrification- methanotrophy coupling observed by us is a general phenomenon occurring in all those aquatic ecosystems, including reservoirs globally, where $CH_4$ occurs in high concentrations.

We also investigated microbial community structure in Markandeya Reservoir in summer using molecular techniques (Naqvi *et al*., 2018). Although *M. oxyfera*-type methanotrophs belonging to the NC10 phylum were present, their abundance was quite low (0.003–0.022 %). The previously considered aerobic methanotrophs were much more abundant, not only in oxygenated waters but also in the anoxic hypolimnion, accounting for nearly 14 % of the microbial community at the oxycline (12 m).

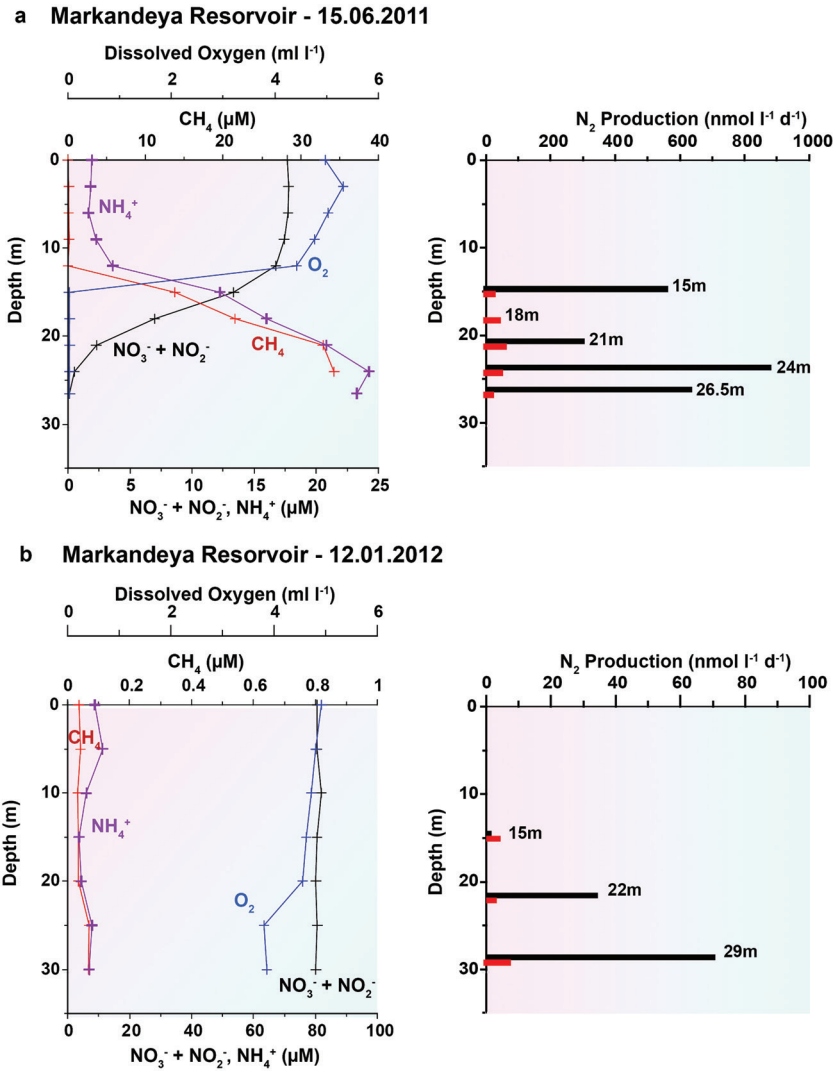



**Figure 9.4** Vertical profiles of dissolved oxygen, nitrate (+ nitrite), ammonium and methane, and total denitrification rates on 15.06.2011 (upper panel) and 12.01.2012 (lower panel). $N_2$ production rates were measured by the isotope pairing method using $^{15}N$-labelled nitrite, with methane (black bars) and without methane (red bars). From Naqvi *et al.* (2018).

Although, the microbial community included all types of methanotrophs (Type I, Type II, and Type III), it was usually dominated by Type I *Methylococcaceae*, of which *Methylocaldum* and *Methylomonas* could be identified. Type II methanotrophs, especially *Methylocystaceae*, were more abundant in the anoxic hypolimnion, whereas Type III *Methylacidiphilales* was more common within the epilimnion. Phylogenetic analyses of biomarker gene encoding the cd1-containing nitrite-reductase (*nir*S) indicated a highly diverse community of dentrifiers with most sequences obtained closely related to sequences from other $CH_4$-rich environments such as rice paddy soils and freshwater sediments. One of the *nir*S clusters was associated with the Type I methanotroph *Methylomonas* sp. 16a. From these observations we concluded that even though NC10 bacteria were present, performing n-damo, the much more abundant conventional methanotrophs and, possibly also methylotrophs, were quantitatively more important for coupling denitrification with methanotrophy.

Oxidation of $CH_4$ by nitrate/nitrite may, at least in part, explain the less than expected $CH_4$ accumulation in the reservoirs examined by us. However, it did not easily explain the lack of a large build-up of $N_2O$. This is because while $N_2$ production through n-damo is known to bypass $N_2O$, conventional methanotrophs had been believed to be incapable of reducing $N_2O$ to $N_2$ (Naqvi *et al*., 2018). However, recent work has provided evidence for the oxidation of $CH_4$ by $N_2O$ in wetland sediments (Cheng *et al*., 2021). These authors inoculated sediments from a Chinese wetland in an enrichment reactor that was continuously fed with $CH_4$ and $N_2O$ for 500 days, resulting in 800 fold increase in $CH_4$ oxidation rate, presumably producing $N_2$ from $N_2O$. Species of *Methylocaldum* were greatly enriched during the experiment, eventually to become the predominant methanotroph. Notably, this genus was also prominently present in Markandeya Reservoir, as mentioned above. Thus, it is most likely that methanotrophs present in Indian reservoirs actively convert nitrate/nitrite to $N_2$ without much $N_2O$ accumulation.

Naqvi *et al*. (2018) pointed out that the lack of a large accumulation of nitrite and $N_2O$ could be a common distinguishing feature of all aquatic systems where $CH_4$ builds up to high levels. This includes silled, land locked marine basins having estuarine circulation such as the Black Sea, Cariaco Basin and Saanich Inlet. The so called 'suboxic' zones lying above sulfidic waters in these basins have been known to possess a much weaker nitrite minimum, with the $N_2O$ maximum located at their upper boundary being much less pronounced than in the open ocean ODZs (Naqvi *et al*., 2010c). The isotopic composition of $N_2O$ has also been reported to be quite unusual in the Black Sea (Westley *et al*., 2006), indicating a different $N_2O$ cycling from the open ocean ODZs, presumably arising from the availability of $CH_4$. On the other hand, anoxic areas that do not show large $CH_4$ build-up, such as the western continental shelf of India, are characterised by high concentrations of both nitrite and $N_2O$ (in non-sulfidic waters). Naqvi *et al*. (2018) showed that addition of $CH_4$ to anoxic samples from these waters did not have a discernible effect on $N_2$ production, presumably because of the absence of the required microbes (Shirodkar *et al*., 2018). This is

not surprising considering that even during peak anoxia, when sulfidic concentrations develop over the inner shelf, $CH_4$ build-up in near bottom waters is quite moderate; generally <100 nM (Jayakumar *et al.*, 2001; Shirodkar *et al.*, 2018; Sudheesh *et al.*, 2020). Accordingly, the microbial community does not normally encounter elevated $CH_4$ concentrations. There is also an absence of nitrate/nitrite if the waters are sulfidic.

Thus, our results point to a potentially important role of $CH_4$ in nitrogen cycling in all aquatic systems having high $CH_4$ concentrations. This is a potentially important topic for future research. Although such a role is increasingly being recognised (*e.g.*, Thamdrup *et al.*, 2019; Rogener *et al.*, 2021), the recognition has been mostly limited to n-damo. The above mentioned emerging evidence of the involvement of 'conventional' methanotrophs such as *Methylocaldum* in denitrification and $N_2O$ removal, strongly supported by our work, further broadens the scope of coupled denitrification-methanotrophy.

As a part of the EC funded project we have also measured concentrations of DIN in a large number of groundwater samples, and determined rates of $N_2$ production by the isotope pairing method in a limited number of cases (Naqvi *et al.*, unpublished manuscript). Although India consumes an enormous amount (~20 Tg N $yr^{-1}$) of synthetic nitrogen fertilisers, a very large part of this consumption occurs in areas such as the northwestern states of Punjab and Haryana and western Uttar Pradesh that are not well drained. Consequently, much of the fertilisers getting washed off from farmlands should be expected to get into the groundwater. Most of the groundwater in the Indo-Gangetic Plain is anoxic beneath a thin upper stratum, supporting very high rates of denitrification (Naqvi *et al.*, unpublished manuscript). Notably these waters have very low $CH_4$ concentrations, and sometimes very high nitrite (tens of µM); $N_2O$ concentrations are quite variable, but may reach mM levels (Naqvi, unpublished data). Thus, in several respects nitrogen cycling in the groundwaters of this region is similar to that described above for the seasonally-forming coastal ODZ over the western Indian shelf. We propose that the high rate of heterotrophic denitrification and the frequent high build-up of $N_2O$ in groundwaters may primarily result from greater availability of organic matter and low $CH_4$ concentrations. In fact it is quite likely that the lack of $CH_4$ accumulation may itself be because of high nitrite concentrations that would remove all $CH_4$ through coupled denitrification-methanotrophy.

In addition to the environments investigated so far (freshwater reservoirs and groundwaters) nitrogen loss is also expected to occur in other ecosystems such as soils, rice paddies, wetlands, lakes/ponds and rivers. However, most surface waters are well oxygenated, so nitrogen losses in these ecosystems should be confined to anoxic benthic environments including riverbeds, probably stimulated by $CH_4$, as has been observed elsewhere (Hu *et al.*, 2014; Shen *et al.*, 2019). How combined nitrogen loss may occur in sediments even when the overlying water column is fully oxygenated is indicated by our data from Markandeya Reservoir (Fig. 9.4). During our trip to this site on 12.01.2012,

when the water column was well oxygenated, we measured low but appreciable $N_2$ production in the presence of $CH_4$ in near bottom waters. These samples were incubated under anoxic conditions with the dissolved oxygen having been removed through helium sparging, thereby allowing the reductive loss to occur. We suppose that the organisms that mediated $CH_4$-induced nitrogen loss came from the sediments where they are expected to be active.

In conclusion, there are several possible pathways by which combined nitrogen may be efficiently converted to $N_2$ in terrestrial aquatic ecosystems of South Asia, thereby accounting for its much smaller export to the ocean by rivers than what is expected from the enormous quantities of combined nitrogen being produced and consumed in the region due to human activities. A more detailed study is required to further explore these pathways.

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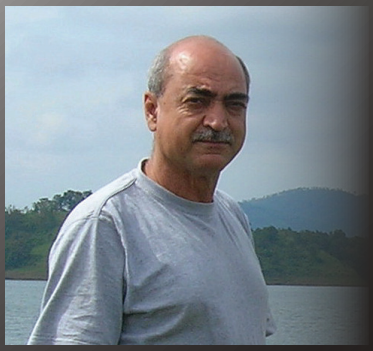

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