CHAPTER 3
Chapter 3

HYDROGRAPHY AND BIOGEOCHEMICAL CHARACTERISTICS
OF THE CORING SITES

3.1 Introduction

This chapter provides the background information on oceanographic processes on the central and eastern Arabian Sea. Some of the information included is based on the published data for which appropriate references are made. The other data were generated by the biogeochemistry group of which the author was a participant. It may be added that collection of diverse data used in the study cannot be obtained by a single individual.

In order to understand the hydrographical and biogeochemical processes of the Indian Ocean, it is essential to consider its unique geographical setting and geomorphological features that have already been alluded to, in Chapter 1. The presence of land mass that limits the northern expanse of the Indian Ocean to a latitude \(\sim 25^\circ\)N, give rise to the monsoonal climate. The word “monsoon” is derived from the Arabic “mausam”, meaning the climate. It is believed to have been used by the sailors in the context of the seasonally reversing winds and oceanic currents that they made use of, for sailing to and from India, from the middle-eastern and east African ports. There are actually two monsoons, the Northeast (NE) or winter monsoon and the Southwest (SW) or summer monsoon, both identified by the dominant direction, the winds blow from during December-March and June-September,
Figure 3.1: Modern sea surface temperature (°C) and general wind pattern during SW and NE monsoon period. The thick arrow represents the axis of Findlater Jet. The dashed line over Asia indicates elevations >3,000 meters. Dashed arrow indicates direction of relatively weak winds during NE monsoon period (modified from Prell, 1984a).
respectively. Following the scheme currently in use, the transition periods between the two monsoons are called the Spring Intermonsoon (April-May) and Fall Intermonsoon (October-November).

The winter (NE monsoon) season is characterized by high pressure over the Asian landmass which results in the northeasterly winds over the Arabian Sea (Figure 3.1). The formation of low pressure over the Asian landmass is due to the low seasonal insolation and relatively high albedo due to seasonal snow cover (Clemens et al., 1991). On the other hand in summer, as a result of the differential heating of the continent and oceanic regions, a low atmospheric pressure develops over the Asian landmass with relatively high atmospheric pressure over the cooler southern Indian Ocean. This drives southwesterly winds over the Arabian Sea including a strong low-level atmospheric jet, called the Findlater (or Somali) Jet (Smith et al., 1991) that extends from the Somali coast to the northwest coast of India (Figure 3.1). The moisture-laden winds bring about widespread rainfall over the whole of South Asia (Clemens et al., 1991).

Most of the rainfall over the Arabian Sea occurs during the SWM and along its eastern shores where it exceeds ~3000 mm y\(^{-1}\). The precipitation declines towards the northwest. The balance between evaporation and precipitation is the highest off the Arabian coast and the lowest off Southwest India. The Arabian Sea receives much smaller river runoff than the Bay of Bengal with the combined discharges by the Indus, Narmada and Tapi being < 200 km\(^3\) y\(^{-1}\). However, there are numerous smaller rivers originating in the Western Ghats whose combined annual discharge (mostly during the SWM)
has been estimated to be about 150 km$^3$ (Naqvi et al., 2003). Due to the large rainfall and land runoff precipitation and runoff exceed evaporation over a narrow belt off the west coast of India. The net water balance is negative elsewhere in the Arabian Sea. Therefore, surface salinity shows a marked increase from the southeastern to the northwestern parts of the Arabian Sea (Wyrtki, 1971).

3.2 Circulation and water masses

The most remarkable feature of the surface circulation in the Arabian Sea, as indeed for the Indian Ocean as a whole, is the reversal of surface currents every six months. Because, the North Indian Ocean is a small ocean basin located essentially in the tropics, coastal and equatorial Kelvin waves and equatorial Rossby waves, that have both annual and sub-annual periods and are generated by changes in the monsoon winds, can propagate rapidly through the region, thereby strongly influencing circulation far away from their origins (Shetye and Gouveia, 1998). The combination of such remote forcing and local wind forcing produces features of surface circulation not observed in other regions.

Figure 3.2 shows the generalized surface circulation in the northern Indian Ocean during the two monsoon seasons. In general, surface currents in the Arabian Sea flow clockwise during the SWM and counter-clockwise during the NEM. The SWM currents are the most energetic in the western Arabian Sea, especially off Somalia, where the northbound seasonal Somali Current (SC) attains a volume transport which is comparable to that of the
Figure 3.2: Surface circulations in the Indian Ocean during the SW and NE monsoon period (after Wyrtki, 1973). MC — Monsoon Current, SC — Somali Current, SEC — South Equatorial Current, NEC — North Equatorial Current, ECC — Equatorial Counter Current.
The Somali Current system includes three major anticyclonic eddies - the Southern Gyre (SG), the Great Whirl (GW) and the Socotra Eddy (SE); because of which most of the northward coastal flow by the SC is deflected to the east and south around 4° and 10 °N latitudes to feed the Southwest Monsoon Current (SMC). The offshore divergence causes intense upwelling at these latitudes, especially around 10 °N. Even more widespread upwelling occurs further north off the Arabian coast, especially off Oman. However, the currents here do not exhibit an organized pattern and seasonality expected from the wind stress except close to the coast (e.g. the Ras-al-Hadd Jet off northwestern Oman). Instead, the flow is dominated by meso-scale eddies that account for the bulk of the kinetic energy (Flagg and Kim, 1998). The filaments and plumes carrying the cold, nutrient-rich upwelled waters extend up to ~1000 km from the coast, fertilizing a large volume of the surface layer and resulting in intense phytoplankton blooms (Naqvi et al., 2003).

Along the Indian coast, the southward flowing West India Coastal Current (WICC) induces upwelling, but this process is much weaker compared with the upwelling off Oman or Somalia and the upwelled water does not spread as far offshore. The thermocline does shoal up over a large area, though, all along the coast and in the region of the Lakshadweep Low (LL), a seasonal cyclonic eddy. Moreover, the upwelled water is overlain by a thin (~10 m) warm, fresher lens because of which the signatures of upwelling are not discernible in the satellite data. It may be noted that the upwelling period (May-November) extends well beyond the SWM season indicating that
the process cannot be forced entirely by local winds. This is supported by results of numerical modeling which shows that, remote forcing from the Bay of Bengal plays a major role in driving the WICC (McCreary et al., 1993).

During the NEM, the SMC is replaced by the Northeast Monsoon Current (NMC) that flows westward. Surface currents in the northern and western Arabian Sea are weaker and less organized, but circulation in the eastern Arabian Sea is best developed during this season. This current is the broadest off the SW coast of India, where the LL is replaced by the Lakshadweep High (LH), and gradually narrows as it flows northward (Shetye et al., 1991a). The warm, low-salinity waters of the WICC exert a major control on biogeochemical cycling as they do not allow convective mixing to occur along over most of the western continental shelf of India. This certainly is the case off Goa.

The subsurface water movement in the northern Indian Ocean is poorly known, but is also greatly impacted by the existence of the low latitude northern boundary. As the isotherms within the thermocline do not outcrop in the North Indian Ocean, the subsurface layers in the region are ventilated mostly from the south. The Arabian Sea does receive dense outflows from the Persian Gulf and Red Sea; however, their combined volume transport is only about $0.64 \times 10^6$ m$^3$ s$^{-1}$, an order of magnitude lower than the volume transport for intermediate waters of the southern origin (Warren, 1994). These waters enter the Arabian Sea only along its western boundary and during the SWM (Swallow, 1984) such that most of the mid-depth water renewal in the Arabian Sea (and in fact the entire North Indian Ocean) occurs in the western
Based on the temperature and salinity distribution in the water column, three different kinds of water masses can be distinguished for the Indian Ocean; those that are generated within the open Indian Ocean by subduction, those that are mixing products of other water masses, and those that enters from outside (Wyrtki, 1971; Tomczak and Godfrey, 1994, Tomczak and Godfrey, 2003). Winter cooling in the northern Arabian Sea leads to the formation of a very shallow subsurface water mass called the Arabian Sea High Saline Water (ASHSW) (Shetye et al., 1994). Being denser, this water spreads as a salinity maximum just beneath the surface mixed layer (Morrison, 1997; Schott and Fischer, 2000). Another northern salty near-surface water mass, found at a depth of about 250–300 m which is clearly distinct from ASHSW, is the Persian Gulf Water (PGW). The influence of PGW does not extend very far beyond the northern Arabian Sea; it loses its identity due to mixing with waters of the southern origin as it moves southward (You and Tomczak, 1993; Kumar and Prasad, 1996). The third and the densest water formed in the region is the Red Sea Water (RSW) which is encountered at a water depth of 500-600 m; the salinity maximum corresponding to this water is rarely seen north of latitude 17 °N. Of the water masses coming from the Southern Hemisphere, the Subantarctic Mode Water (which has about the same density as the PGW) but is characterized by an oxygen maximum and a salinity minimum, is the most prominent (Sen Gupta and Naqvi, 1984). The oxygen maximum corresponding to this water vanishes at about 12 °N, the southern limit of the suboxic zone (Naqvi et al., 1993).
The Lower Circumpolar Deep Water (CDW) enters the deepest parts of central Indian Ocean (Toole and Warren, 1993). However its direct entry is generally obstructed by the deep ridges. The deepest water in the Arabian Sea is derived through a western boundary current that passes through a chain of western basins and enters the Arabian Basin through the Owen Fracture Zone (Naqvi and Kureishy, 1986). The Indian Deep water (IDW) mass which is presumably formed due to deep upwelling of the CDW flows just above the CDW. The IDW mass is oxygen-poor and has high salinity as a result of its mixing with older intermediate waters above while in the southwest, it has the characteristics of diluted North Atlantic Deep Water, which has higher oxygen and salinity (Mantyla and Reid, 1995).

3.3 Upwelling/vertical mixing, productivity and the oxygen minimum zone

The effect of monsoonal forcing in the Arabian Sea is evident in the seasonal sea surface temperature (SST) maps that also reflect the circulation pattern (Figure 3.1). The lowest SSTs in the Arabian Sea paradoxically occur in summer in the western Arabian Sea, obviously caused by upwelling. As already mentioned, upwelling also occurs along the west coast of India during the SWM, though far less vigorously than in the western Arabian Sea. This is because, the strong wind blowing with the Somali and Arabian coasts to its left results in rapid and large scale Ekman transport. The volume of water upwelled is very large as is the area of the Arabian Sea over which it spreads. In the eastern Arabian Sea, the process is much slower. The thermocline
shoals up to very shallow depths (with the upwelled water often prevented from reaching the surface by the low salinity cap) in response to the large scale circulation with the local winds contributing only part, to the upwelling. The process introduces copious amounts of nutrients to near-surface waters sustaining high primary productivity (PP).

Nutrient enrichment also occurs in the Arabian Sea during the NEM. This is because, the cold dry winds blowing from the continent over the ocean increase the density of surface waters resulting in convective overturning which reaches and erodes the upper portion of the thermocline over a large area in the northern and central Arabian Sea. The high biological productivity arising from the nutrient enrichment is accompanied by a high rate of organic matter input and its oxidation in the water column. As pointed out earlier, the renewal of intermediate waters is largely through advection from the south and these waters lose much of their oxygen content by the time they reach the Arabian Sea. The circulation in the equatorial Indian Ocean also plays an important role in maintaining low oxygen concentrations in the Arabian Sea. The flow of waters in the upper kilometer in the equatorial belt is mostly zonal, such that cross equatorial exchange of water is only confined to the western Arabian Sea (Swallow, 1984). According to Swallow, “The equatorial region between, say, 5 °N and 5 °S seems likely to act as a holding tank, in which the dissolved oxygen of the relatively new intermediate water decays and is reduced by mixing with the older water”. Thus, the development of an intense and thick (150-1200 m) OMZ in the Arabian Sea is a result of the combination of limited oxygen supply to the intermediate layers through water renewal and
a moderately high rate of oxygen consumption (Swallow, 1984; Naqvi, 1987; Olson et al., 1993; Warren, 1994).

The acute oxygen depletion causes the heterotrophic bacterial population to switch over to alternate electron acceptors for organic matter degradation (Richards, 1965). The most abundant of such species in the water column is NO$_3^-$: For NO$_3^-$ to be utilized as an oxidant, the dissolved oxygen concentrations must cross a threshold value which is probably well below 1 μM (Morrison et al., 1999; Codispoti et al., 2001; Naqvi et al., 2003). This threshold is deduced based on the observation that NO$_2^-$ accumulation in oxygen-poor waters, taken as a diagnostic tool for denitrification, only occurs when the precisely measured oxygen concentrations are below this level. Note that the corresponding Winkler oxygen concentrations may be higher by 2-3 μM. The threshold oxygen levels appear to reach in only upper 1/3 or so of the OMZ in the Arabian Sea in the vertical within a zone that is well defined and does not seem to have changed much since it was first delineated by Naqvi (1991) from the climatology of NO$_2^-$ data then available. It is remarkable that despite the presence of a large volume of water with oxygen levels just above the nitrate reduction threshold, the open-ocean denitrification (suboxic) zone remains fairly stable over decades, that too with the “global change” reportedly already underway (Goes et al., 2005).

3.4 Processes for the formation of coastal and open-ocean suboxic zones

The most intense OMZ, as inferred from the occurrence of the SNM is
located in the generally most productive northwestern part of the Indian Ocean. However, within the Arabian Sea itself, suboxic conditions are not associated with the upwelling systems of Somalia and Arabia; instead, the SNM zone extends toward the southwest into the central Arabian Sea from the northwestern Indian shelf, a region of relatively low PP (Figure 3.3). This is believed to arise from a more effective subsurface-water renewal along the Arabian Sea's western boundary through advection from the south (given that the cross-equatorial exchange of subsurface waters is largely confined in the western Indian Ocean – Swallow, 1984) as well as from the Red Sea and the Persian Gulf. Moreover, the dominance of upper-layer flow by meso-scale eddies, which account for the bulk of the kinetic energy (Flagg and Kim, 1998) and extend to the core of the suboxic zone, may facilitate greater downward diffusion of $O_2$ from the surface in the west. In contrast, the SNM coincides with the zone of the lowest kinetic energy and reduced vertical penetration of the eddy field (Kim et al., 2001). In addition to these physical factors, the availability and utilization of nutrients by phytoplankton and the subsequent vertical flux of organic matter must also contribute to the observed $O_2$ distribution. Kim et al. (2001) opined that the route of offshore transport of the nutrient-rich upwelled water (occurring predominantly through filaments and plumes) is such that the denitrification zone receives more nutrients/organic matter than the region located to its south and west. They emphasized the importance of the Ras al Hadd Jet that transports upwelled water first along the northeast Omani coast and then away from the coast off the cape, it has been named after. Nutrient distributions during the upwelling season (e.g. for
Figure 3.3: Map of Arabian Sea demarcating the OMZ region in terms of secondary nitrite (NO$_2$) maxima and oxygen (O$_2$) concentrations (μM). Hatched areas represent zones of upwelling off Arabia (A), Somalia (B) and Southwest India (C). Figure modified from Naqvi (1991).
NO$_3^-$; Figure 3.4) do indeed indicate long-distance ($\geq$1000 km) transport of the upwelled water reaching well within the region of the most intense O$_2$ deficiency, but the generally-observed gradual offshore decrease in surface nutrient concentration is not supportive of this view.

Recent results of modeling (Wiggert et al., 2006) as well as observations (Naqvi et al., submitted) suggest that, contrary to the prevalent belief, PP in the western Arabian Sea might sometimes be limited by iron (Fe) instead of nitrogen during the SWM. These results have important implications for the composition of phytoplankton and the vertical scale of organic matter degradation. Iron deficiency has been known to cause an increase in ratio of Si:N uptake by diatoms (Hutchins and Bruland, 1998) facilitating greater offshore transport of NO$_3^-$. A more rapid depletion of silicate is expected to cause a shift in phytoplankton community structure with increasing abundance of smaller autotrophs offshore, which is in accordance with observations (Garrison et al., 1998). During the northeast (NE) monsoon the central Arabian Sea experiences convective mixing that penetrates, at the most, to a depth of 125 m (Banse, 1984, 1987). The depthwise nutrient distribution in the region is such that vertical mixing brings up substantial amounts of NO$_3^-$ to the euphotic zone but not much silicate, thereby limiting diatom productivity (Naqvi et al., 2002). Thus, PP in the open central Arabian Sea seems to be dominated by small, non-diatomaceous autotrophs during both the SWM and NEM. The organic matter produced by these organisms would be degraded at shallower depths relative to that produced by diatoms. Therefore, one would expect the average depth of remineralization of material
Figure 3.4: (a) Cruise track (+) of U.S. JGOFS cruise TN050 (August-September) (b) Distribution of NO$_3^-$ (nitrate data from U.S. JGOFS cruise TN050) indicating long distance (>1000km) transport of upwelled waters reaching well within the OMZ region. (Figure adapted and modified from Naqvi et al., 2006b).
exported from the surface layer to shoal up with increasing distance from the coast, such that more material is degraded close to the core of the O$_2$ minimum zone in the offshore region. This is consistent with the observed O$_2$ distribution (Naqvi et al., submitted).

The development of suboxic conditions over the Indian shelf is related in a general way to the prevalence of large-scale, mesopelagic, open-ocean O$_2$ deficiency, because the latter is the source of water that upwells over the Indian shelf during the SWM. Nevertheless, the open-ocean and coastal suboxic zones are not contiguous. This is due to the presence of the West India Undercurrent (WIUC) that flows northward while the surface flow is toward the south. The WIUC may be identified just off the continental shelf/slope from the distribution of temperature (upward sloping of isotherms at the top of this feature and downward tilt close to its bottom; Figure 3.5a), and even more clearly from those of salinity and O$_2$ (Figure 3.5b,c). Note that the water derived from the south has lower salinity and slightly higher O$_2$ content. As judged by the 35.400 salinity contour, the influence of the undercurrent, at its peak, extends vertically down to approximately 400 m depth and horizontally up to 200 km from the continental slope at 15°N latitude (Figure 3.5b). Even though seasonally variable, the WIUC is very important for determining the redox status of subsurface waters since it is a source of O$_2$ to the otherwise suboxic mesopelagic zone that prevents the water from turning denitrifying off the continental margin probably as far north as 17 °N latitude. Consequently, as reflected by the distribution of NO$_2^-$ (Figure 3.5d), denitrification intensifies away from the coast. This pattern is
Figure 3.5: Distribution of (a) temperature, (b) salinity, (c) $O_2$, and (d) $NO_2^-$ in the upper 1 km off Goa (see inset in (b) for station locations) during December 1998. Adapted from Navqi et al. (2006b).
opposite to that observed in the two other major oceanic suboxic zones, especially off Peru-Chile, where the poleward undercurrents, in fact, support bulk of the denitrification (Codispoti et al., 1989). This difference probably owes to a lower respiration rate within the WIUC, which, in turn, may be caused by two factors. First, unlike its counterpart off Peru-Chile the WIUC does not occur over the shelf but along the continental slope, and secondly, except in the most southern part, upwelling along the west coast of India is by and large confined to a narrow strip over the inner shelf such that surface waters directly overhead of the WIUC are not very productive. As the water upwells and moves shoreward, rapid increase in respiration depletes its already low O$_2$ content, culminating in the seasonal development of reducing conditions [denitrification followed by sulphate (SO$_4^{2-}$) reduction] over the mid-and inner-shelf regions (refer the following section of 3.5) covering a wide latitudinal range (between at least 12 °N – 20 °N, probably extending further north to the Pakistani coast).

3.5 Biogeochemical conditions prevailing over the shallow coring sites

Cores CR-2, SaSu-1 and SaSu-3B were raised from the inner- and mid-shelf regions off Goa (Figure 3.6). Hydrographic and chemical data along a coast-perpendicular section off Goa for the core sampling period (late SWM/early SI) are plotted in figure 3.7 whereas figure 3.8 provides the same information for the NEM season. In order to demonstrate the evolution and demise of the oxygen deficient conditions on an annual cycle, the data
Figure 3.6: Section showing the sampling transect (G2-G9) off Goa, along with the CaTS and coastal core (SaSu-1, SaSu-3B) locations with bathymetry.
collected at the CaTS station are also presented and discussed.

3.5.1 Cross shelf sections off Goa during two seasons

As stated above, the southward flowing WICC induces upwelling along the west coast of India. Figure 3.7, based on measurements made in September 2002, shows this feature and also depicts the changes that occur in the upwelling water as it moves up the shelf. The upsloping of isotherms (Figure 3.7a) toward the coast are obviously due to upwelling which begins sometime in April-May and lasts till October/November. The other striking feature of the hydrographic data is the presence of the previously mentioned low-salinity lens that overlies the cold, saline upwelled water, especially near the coast (Figure 3.7b). This fresher water lens is produced as a result of intense rainfall in the coastal zone (in Goa, the annual rainfall is in the vicinity of 3000 mm, but most of it is concentrated during the SWM).

Around the shelf break, near-bottom water has low oxygen concentration, but it is oxidizing (DO is well above the detection limit of the Winkler procedure, NO$_3^-$ content is high and NO$_2^-$ is undetectable, see figures 3.7c,d,e). However, as this water ascends over the shelf, it quickly loses the residual oxygen that leads to sequential reduction of other oxidized chemical species: First, denitrification sets in over the mid-shelf region as evidenced by the depletion of NO$_3^-$ and build up of NO$_2^-$ (Figure 3.7e), and once NO$_3^-$ and NO$_2^-$ are fully consumed, SO$_4^{2-}$ reduction is initiated over the inner-shelf, as reflected by the accumulation of H$_2$S (Figure 3.7f). These conditions are typical for the period (late summer/early autumn) although some variations do
Figure 3.7: Vertical sections of temperature, salinity, oxygen (O2), nitrate(NO₃⁻), nitrite(NO₂⁻) and hydrogen sulphide (H₂S) along a coast-perpendicular section off Goa (sampling transect as shown in figure 3.6) during late SWM (September 2002).
occur from one year to another (Naqvi et al., 2006a).

The conditions are quite different during the NEM when the WICC carries warmer, fresher waters of equatorial origin towards the north (Figure 3.8). The low concentrations of nutrients coupled with downwelling associated with this flow result in lower productivity and relatively deep mixed layers so that the shelf waters are generally well oxygenated. Observations made during the NEM season of 2002 accordingly show higher temperatures (~27-28 °C) than those observed during the SWM season (Figure 3.8a) while low salinity (< 34) persists to a depth of at least ~ 40m (Figure 3.8b). NO$_3$ levels are much lower even when the denitrification does not occur due to the prevalence of high oxygen concentrations throughout the water column (Figures 3.8c).

### 3.5.2 Climatology at the CaTS site

The time-series station, named as the Candolim Time Series (CaTS), (15°31'N, 73°39'E) lies approximately 10 km off the coast from the village of Candolim (Figure 3.6). This site is being monitored since 1997. These observations are of great relevance to the present study because, the three short cores examined here come from the same general area and also because it is the most suitable data set to provide the background information on seasonal changes in the hydrographic and biogeochemical environment today with which, one can compare the core top proxy data and make inferences as to the past changes. The data for 7 years (1997-2004) have been pooled and averaged for various depth intervals on a fortnightly basis for
Figure 3.8: Vertical sections of temperature, salinity, oxygen (O₂), nitrate(NO₃⁻), and nitrite(NO₂⁻) along a coast-perpendicular section off Goa (sampling transect as shown in Figure 3.6), for the NEM season (February, 2002)
August-December and on a monthly basis for the remaining period. Figure 3.9 gives variations of various properties on a depth-time plot that reveals well-defined annual cycles of the measured variables.

The temperature record (Figure 3.9a) shows a bimodal distribution pattern that is well known to exist in this region (e.g. Banse, 1959). The highest values are recorded during the SI while the lowest values occur during the late SWM extending into the early FI, obviously due to upwelling. The water column during the NEM is homogenous but the salinity changes considerably (Figure 3.9b) presumably related to the northward flow of WICC that brings fresher waters from the south, especially in February. Like temperature, salinity also reaches its maximum (≥ 36.000) during the SI season. With the onset of upwelling and almost simultaneous formation of the low salinity cap strong vertical gradients in salinity (and temperature) develop that persist from June/July to October/November (Figure 3.9).

The oxygen deficiency apparently persists for a much longer period than one would expect from the temperature record (Figure 3.9c). Naqvi et al. (2006a) speculated that the decay of *Trichodesmium* blooms during the SI could sometimes result in O₂ depletion in the near bottom water even before the onset of upwelling. However, near-bottom O₂ concentrations do not reach suboxic (< 10 μM) levels until July/August. NO₃⁻ concentrations increased during the early stages of upwelling, but decrease once suboxic conditions develop in near-bottom waters (Figure 3.9d). This is associated with the accumulation of NO₂⁻ (Figure 3.9e). Within about one month of its onset, denitrification reaches completion (i.e. NO₃⁻ and NO₂⁻ are fully consumed). It
Figure 3.9: Monthly/fortnightly averaged records showing annual cycle of (a) Temperature (b) Salinity (c) Oxygen (d) Nitrate (e) Nitrite and (f) Hydrogen Sulphide at the Candolim Time Series (CaTS) site (15°31' N, 73°39' E) based on observations from 1997-2004. Figure modified from Naqvi et al. (2006a).
may be noted that in addition to the build-up of NO$_2^-$ in suboxic waters during denitrification, some accumulation of NO$_2^-$ also takes place at shallower depths in oxygenated waters (Figure 3.9e); this is due to assimilatory reduction of NO$_3^-$ by phytoplankton, nitrification or denitrification in sediments (Naqvi et al., 2006a).

Reduction of SO$_4^{2-}$ as indicated by the appearance of H$_2$S (Figure 3.9f) begins only after the complete removal of the oxidized N species from the water column. Such (anoxic) conditions prevail during the months of September and October (Figure 3.9). During this period, cross-shelf sections north of about 12°N latitude (e.g. Figure 3.10), exhibit all three types of redox environments (oxic over and beyond the outer shelf, suboxic over the mid-shelf and anoxic over the inner shelf). Such a well-organized sequence with a remarkable regularity is not known to occur along any other open coast. However, it is believed that a few decades ago complete anoxia in this region was not as frequent, if it existed at all, as it is now (at the CaTS site it has been recurring every year since 1998). For the region off Karwar and during the upwelling period, Naqvi et al. (2006a) compared oxygen data generated in recent years (1997-2004) with those collected in the 1970s, and found the recent values to be significantly lower. According to these authors, oxygen deficiency in this region seems to have intensified as a consequence of enhanced nutrient loading and this might account for the development of completely anoxic conditions.
Figure 3.10: Vertical sections of temperature, salinity, oxygen, inorganic species and hydrogen sulphide off Goa during October 1999. Station locations are the same as shown in figure 3.6.
3.6 Biogeochemical conditions prevailing within the suboxic zone of the open ocean

As already stated, the seasonal suboxic zone over the western continental shelf of India is not contiguous with the perennial deeper suboxic zone of the open ocean. In figure 3.11, the boundaries of the perennial suboxic zone along with the climatological maximal nitrite concentrations reported by Naqvi, (1991) are shown along with the locations of the two open ocean coring sites (AAS-42/15 and AAS-42/12A). The two sites are clearly in the region that experiences intense denitrification today. A brief account of the hydrographic and biogeochemical attributes of the water column at this site is as follows:

Three stations were selected to provide representative profiles of hydrographic and chemical parameters. Two of them (3201 and 3202), occupied during the FORV Sagar Sampada cruise SS119 in April 1994, and are very close to the location of the core AAS-42/15 (17.07°N, 68.01°E). Station 3201 was sampled down to ~1.5 km, but 3202 was sampled down to 3 km. However, since the T, S and O₂ profiles converge at ~1.5 km, the profiles at 3202 can be taken to apply, to the core-top at this coring site and to the AA-42/12A site as well (horizontal gradients in properties at depths > 2 km are negligible between the two locations).

Vertical profiles of temperature, salinity and oxygen and of oxygen, nitrate and nitrite at the two stations are presented in figure 3.12a and 3.12b, respectively. A pronounced OMZ is conspicuously seen at both the sites between 150-1000 m, with the lowest oxygen values occurring in the upper
Figure 3.11: Geographical limits of the perennial suboxic zone, demarcated by 0.5 \( \mu \text{M} \) nitrite contour, along with location of open ocean cores (denoted with empty circles) and bathymetry.
Figure 3.12a: Vertical profiles of temperature, salinity and oxygen at the two stations 3201 and 3202 sampled during the FORV Sagar Sampada cruise SS119 in April 1994. Station 3201 was sampled down to ~1.5 km [data points marked with plus (+)], but 3202 was sampled down to 3 km [data points marked with filled circles (●)].
Figure 3.12b: Vertical profiles of oxygen, nitrate and nitrite at the two stations 3201 and 3202 sampled during the FORV Sagar Sampada cruise SS119 in April 1994. Station 3201 was sampled down to ~1.5 km [data points marked with plus (+)], but 3202 was sampled down to 3 km [data points marked with filled circles (•)].
portion of the OMZ, as already mentioned. It is within this layer that the main secondary nitrite maximum is located and also nitrate profiles exhibit a pronounced minimum, indicative of denitrification. Note that the nitrite maximum is not confined to a specific water mass. At 3201, salinity remains high and relatively invariable throughout the nitrite maximum whereas at 3202 the most intense nitrite maximum includes the transition from a salinity minimum to a salinity maximum. The oxygen concentration rises at depths exceeding 1 km where both T and S decreases steadily. At the depths, the two cores were raised from the oxygen concentrations are >100 μM. In other words, both core sites are presently bathed by fairly oxygenated waters.

Similar results are also observed at another location slightly (by 2°Latitude) to the north of the coring sites. This location (19°N, 67°E) was sampled repeatedly during the United States Joint Global Ocean Flux Studies (U.S. JGOFS) Arabian Sea Process Study (1994-95) and thereafter during cruises conducted by the National Institute of Oceanography. The oxygen data collected during the US JGOFS cruises following either the automated Winkler titration or colorimetric procedures are more accurate, as the nitrite build-up was almost always noticed when oxygen fell below 1 μM (Figure 3.13a). This was also where nitrous oxide (N₂O) concentrations were the lowest indicating that like NO₃⁻ and NO₂⁻, N₂O was also being used by bacteria as an electron acceptor (Figure 3.13a, b). At the boundaries of the secondary nitrite maximum, however, N₂O accumulates in high concentrations due to production by nitrification, denitrification or a coupling between the two processes (refer Figure 4 from Naqvi and Noronha, 1991).
Figure 3.13: Vertical profiles of oxygen (O₂), nitrate (NO₃⁻), nitrite (NO₂⁻) and nitrous oxide (N₂O) at 19°N, 67°E (data from TN039 cruise of U.S. JGOFS – station 18; during October 1994). (a) O₂ (circles) and NO₃⁻ (triangles); (b) N₂O (circles) and NO₂⁻ (triangles); (c) NO₃⁻ deficit according to Codispoti et al. (2001) are shown with dots connected by solid line, “excess nitrogen (N₂)” calculated from the N₂/Ar ratio (larger unconnected symbols – crosses for the data collected on two different cruises from this station and triangles for those from other stations also located within the denitrification zone) and N* according to Gruber and Sarmiento (2002) (small filled triangles connected by dashed line). N/Ar data are from Devol et al. (2006a).
In addition to the routine hydrographic and chemical data, specialized measurements made at this site included the \( \text{N}_2/\text{Ar} \) ratio. This ratio exhibits a strong increase within the secondary nitrite maximum zone, and by subtracting the background ratio (at the same density level but outside the suboxic zone), it is possible to calculate the excess nitrogen biologically produced in these waters. Surprisingly at its maximum, the excess nitrogen far exceeds even the most generous estimates of nitrate deficit (Figure 3.13c). Some of this discrepancy might be accounted by the contribution by anammox, with the rest mostly caused by the non-Redfieldian (\( \text{N}:\text{P} >> 16 \)) composition of organic matter, produced by nitrogen fixers, that is supplied to and degraded within the OMZ (Codispoti et al., 2001; Devol et al., 2006). In any case, it would appear that the current estimates for \( \text{N}_2 \) production in the open-ocean suboxic zone should be conservative.

### 3.6.1 Nitrogen Isotope composition

Discrimination by denitrifying bacteria between the two stable isotopes of nitrogen (\( ^{14}\text{N} \) and \( ^{15}\text{N} \)) has been known for quite some time (Wada and Hattori, 1991, and references therein). Brandes et al. (1998) were the first to demonstrate that, this effect leads to marked enrichment of the heavier isotope in residual nitrate in the open-ocean suboxic zone of the Arabian Sea. Their data came from the one of the stations (3201) for which the hydrographic and chemical data have been presented and discussed above (see Figure 3.12). Deep waters (2500 to 3000 m) at this site are found to have \( \delta^{15}\text{N} \left( ^{15}\text{NO}_3^- \right) \) of \(-6\%\) which is close to the values \((-5\%\) \) observed in other
areas (Wu et al., 1997; Sigman et al., 1997). However the $\delta^{15}$N values increases to 15% within the core of the denitrifying layer (Naqvi et al., 2006b; Brandes et al., 1998; Figure 3.12) because of the preferential reduction of $^{14}$NO$_3^-$ over $^{15}$NO$_3^-$ in seawater (Cline and Kaplan, 1975). Concurrently, the $\delta^{15}$N of N$_2$ was found to decrease from $\sim$0.6%o to $\sim$0.2%o in the denitrifying layer of the central Arabian Sea (Brandes et al., 1998). Brandes et al. (1998) computed the isotope fractionation factor ($\varepsilon$) using the measured $\delta^{15}$N in NO$_3^-$ and the nitrate deficits computed following Naqvi and Sen Gupta (1985). The estimated values for $\varepsilon$ for the Arabian Sea (22 - 25%o) were similar to those calculated for the eastern tropical North Pacific. These estimates were also well within the range ($\varepsilon = 17$ to 29%o) obtained by Delwiche and Steyn, (1970), Mariotti et al. (1981) and Barford et al. (1999) in laboratory cultures of denitrifying bacteria.

The isotopic distribution pattern observed in the coastal suboxic zone is quite different, and more variable, from that described above, even though the data are rather limited (Naqvi et al., 2006b). These data come from two sets of observations - in August 1997 off Mangalore (Station SS 3939; isotopic analysis carried out following Brandes et al., 1998) and in September 2000 off Goa (Stations G3, G4 and G5; isotopic analysis carried out following Tanaka and Saino, 2002). On both occasions the sub-pycnocline water column had experienced significant losses of NO$_3^-$. The NO$_3^-$ profile at Station 3939 exhibited a mid-depth maximum below which concentrations decreased while the NO$_2^-$ concentrations showed a concomitant increase with depth (Naqvi et al., 2006b). NO$_3^-$ deficit also increased with depth, reaching the peak value of
just under 15 μM in the deepest sample (27 m). While all the above parameters exhibited expected depth wise changes, the profile of δ¹⁵N-NO₃⁻ deviated greatly from the expected one. That is, given the high NO₃⁻ deficit in subsurface waters, the δ¹⁵N-NO₃⁻ values should have ranged between 17 and 26‰ if the isotopic fractionation factor reported for the open ocean suboxic zone (~25‰) was also applicable to the shallow suboxic zone. The values measured were consistently lower. In fact, all samples taken from within or below the pycnocline yielded δ¹⁵N-NO₃⁻ values (6.65 to 7.41‰) that were quite close to the oceanic average with no depth wise variability. NO₃⁻ in the only sample taken from the surface layer was even lighter (3.43‰).

Several possibilities could be invoked to explain the above observations: (1) Processes responsible for the observed NO₃⁻ losses in the coastal suboxic zone may be different from those in its open ocean. A likely scenario is that a substantial fraction of the loss may occur within the sediments, and the much smaller isotopic fractionation associated with sedimentary denitrification (Brandes and Devol, 2002) could then account for the low δ¹⁵N-NO₃⁻ values. The few data on sedimentary denitrification, measured mostly during the upwelling period following the acetylene block technique, have yielded values ranging from 0.23 to 1.25 mmol NO₃⁻ m⁻² d⁻¹, which are generally within the range of values from other areas (Naik and Naqvi, 2002). Estimates based on the isotope pairing method are comparable with these values (Naqvi et al., manuscript in preparation). These rates by themselves appear to be inadequate to account for the observed NO₃⁻ loss in the water column. The other processes that may bring about NO₃⁻ removal are
anammox, dissimilatory reduction of NO$_3^-$ to NH$_4^+$ (which may also be coupled to anammox) and/or autotrophic denitrification (e.g. reduction of NO$_3^-$ by species such as S$^2-/HS^-, Fe^{2+}$ and Mn$^{2+}$; Luther et al., 1997). Of these at least anammox is expected to be quite important in view of the above-mentioned results from other regions, more so over the Indian shelf where very high NO$_2^-$ concentrations (maximum 16 μM) are expected to be matched by a high rate of diffusive supply of NH$_4^+$ from the sediments (Naqvi et al., 2000). (2) Apparently low $\delta^{15}$N-NO$_3^-$ relative to the NO$_3^-$ deficit could be produced by mixing involving anoxic water. (3) It has been found recently that the reduction of NO$_3^-$ to NO$_2^-$ involves huge isotopic discrimination, such that $\delta^{15}$N of NO$_2^-$ in the suboxic zone of the eastern tropical North Pacific is quite low (Casciotti, in press). The procedures followed to measure isotopic composition of NO$_3^-$ did not differentiate between NO$_3^-$ and NO$_2^-$, and therefore the measured values would be dependent on the ratio between NO$_2^-$ and NO$_3^-$ concentrations. This ratio is generally much higher in the coastal zone than in the open ocean, and that could contribute to lower $\delta^{15}$N of the combined NO$_3^-$ and NO$_2^-$ pool. (4) Finally, it is also possible that if and when the NO$_3^-$ loss is through heterotrophic denitrification, the fractionation factor associated with the process may not be the same in the coastal and offshore regions.

Unlike the observations off Mangalore, isotopic data off Goa do show substantial enrichment of the heavier isotope in residual NO$_3^-$ (Naqvi et al., 2006a). For these samples the fractionation factor was calculated using a simple advection-reaction model that ignores diffusion. The $\varepsilon$ value so obtained was 7.7‰. Inclusion of data from Sta. SS 3939 led to little change in
ε (7.21‰). At the first glance these results appear to support the notion of lower fractionation factor in the coastal suboxic zone. However, as discussed above, the possibility of other factors being also responsible for pulling down the δ¹⁵N value of NO₃⁻ of coastal waters cannot be ruled out. In fact, it is quite likely that all the factors mentioned above may be in operation, their relative importance varying in space and time. Such a dynamic environment which contrasts the relatively more stable conditions of the open ocean system offers both challenges and opportunities to gain further insights into the pathways of oceanic nitrogen cycling.

3.7 Conclusions

The water column data along the off Goa transect clearly indicates the existence of an enhanced suboxia turning to anoxia. This leads to the inference that the coastal cores (SaSu-1 and SaSu-3B) collected along the same transect and the core (CR-2) just below this transect were all overlain with low oxygen waters during the time of collection. For the open ocean gravity cores, from the data presented in vicinity to core locations, confirms the bottom waters to be oxygenated with denitrification occurring in the intermediate water column.