3. Distribution of Methane in the Northern Indian Ocean:

3.1. Introduction:

As compared to the terrestrial sources, the emission rate of CH$_4$ to the atmosphere from the oceans appears to be quite modest, ranging from 0.40 Tg yr$^{-1}$ (1 Tg = 10$^{12}$ g) by Bates et al. (1996) to 11-18 Tg yr$^{-1}$ by Bange et al. (1994). These represent 0.1-4% of the total atmospheric flux of CH$_4$ from all natural and anthropogenic sources (Crutzen, 1991). However, the atmospheric emission of CH$_4$ from the oceans are not uniformly distributed geographically with the continental shelves and estuaries, which occupy a small area of the world oceans, accounting for as much as 75% of the total oceanic CH$_4$ emission (Bange et al., 1994).

Previous studies on CH$_4$ in the northwestern Indian Ocean have revealed that its concentrations in surface waters and consequently its flux to the atmosphere from this region are several folds higher than the oceanic averages (Owens et al., 1991; Patra et al., 1998). It has been proposed that the high CH$_4$ supersaturation in surface waters could be sustained at least in part by the release of CH$_4$ from sediments along the Indian continental margin (Karisiddaiah and Veerayya, 1994, 1996). On the other hand, the Arabian Sea is a highly productive area which also contains one of the most intense and thickest O$_2$ minima in the world oceans the upper portion of which (~150-500 m) is strongly reducing (Qasim, 1982; Sen Gupta and Naqvi, 1984; Naqvi, 1994). These conditions are expected to favour *in situ* production of CH$_4$ in the upper water column (Owens et al., 1991). Finally, the coast of the Indian subcontinent is indented by numerous backwaters and estuaries endowed with extensive growth of mangroves. The contribution of these wetlands, potentially important sites of CH$_4$ production, to CH$_4$ cycling in the coastal zone has not been investigated. An
assessment of the relative importance of these sources in regulating the CH$_4$ distribution in this region forms the principal objective of the present study.

Most of the data used in this study were collected during two cruises of FORV Sagar Sampada (SS141 and SS158) undertaken in April-May, 1996 and August-September, 1997, corresponding to the premonsoon and southwest monsoon seasons, respectively. Some observations were also made in the estuary (in both seasons) and along a short shallow section just north of the mouth of the river Mandovi in Goa during the monsoon (September 1997). Station locations are shown in Fig.3.1. The stations occupied during SS141 formed an east-west transect off Goa extending well into the suboxic (denitrifying) zone of the open central Arabian Sea (Naqvi, 1991). This section was repeated, up to the shelf break, during SS158 as well. However, the primary objective of the latter cruise was to investigate the effect of upwelling off the southwest Indian coast (Banse, 1968), and for this purpose four additional cross-shelf sections were worked at between Quilon in Kerala and Karwar in Karnataka.

Results and Discussion

3.2. Methane Distribution in Waters over the Continental Shelf:

Concentrations of CH$_4$ recorded in coastal surface waters during the monsoon cruise ranged from 2.6 to 20.3 nM, corresponding to saturations of 140-1091%. The near-bottom shelf waters at some stations were characterised by significant CH$_4$ enrichment relative to the surface; at other stations particularly those forming the shallowest parts of the sections the maximal concentrations were found at the surface or mid-depth (Fig. 3.2a-e). The most conspicuous feature seen in all the sections is the strong onshore-offshore gradients at all the depths with the concentrations decreasing rapidly offshore.
Fig. 3.1. Station location for methane studies
The three possible factors that could combine to produce the observed distribution are (a) supply from the sediments, (b) production in the water column, and (c) inputs from the coastal wetlands.

3.3. Sedimentary Supply:

Sedimentary supply of CH₄ may occur through bacterial degradation of organic matter (biological source) at shallow depths in sediments and also by thermal cracking of kerogens (geological source) (Floodgate and Judd, 1992). Seepage from the geological source may be limited to specific regions, but the biological source is expected to be more widespread given an adequate supply of organic matter and an availability of suitable reducing sites. Conditions conducive for the biological production of CH₄ in the sediments and at the sediment-water interface appear to exist along the shelf off the west coast of India due to copious supply of organic carbon to the sediments from land as well as overlying water column (Paropkari et al., 1987) where, as will be seen later, very high rates of primary production are supported by coastal upwelling during the monsoon. Moreover, the upwelled water covering the shelf sediments is extremely depleted in O₂ (Banse, 1968). The supply and preservation of organic matter in the present inner shelf region should have been even higher during the late Pleistocene-early Holocene when the sea level was lower and the monsoon had greatly intensified in response to the precession-related peak in the northern hemisphere summer insolation centred around 11,000 years Before Present (Van Campo, 1986).
Fig. 3.2. Distribution of methane (nM) during SW monsoon along five transects on the shelf off SW India.

Karisiddaiah and Veerayya (1994, 1996) have hypothesised that this organic matter could have served as the main biogenic source for the accumulation of \( \text{CH}_4 \) within the shallow inner shelf sediments. Presence of such gas-charged sediments a few metres below the seafloor, inferred from the
occurrence of acoustic maskings during seismic surveys, is also supported by limited chemical measurements in sediments (Siddiquie et al., 1981). The total inventory of CH$_4$ trapped in the gas charged sediment of the inner continental shelf off western India has been estimated as 2.6 Tg (Karisiddaiah and Veerayya, 1994, 1996). These authors also proposed that the diffusion of CH$_4$ from the sediments to the overlying water column, estimated as 0.039 Tg y$^{-1}$ [very nearly the same as the net atmospheric flux from the Arabian Sea reported by Owens et al. (1991)], could be important in sustaining high CH$_4$ saturation in the Arabian Sea surface waters. However, given the above estimates the sedimentary CH$_4$ inventory would be depleted in just (2.6/0.039=) 67 years, and so the estimated sedimentary CH$_4$ flux, if real, must be supported presently by a high rate of methanogenesis. It is pointed out here that while some near-bottom CH$_4$ enrichment is generally seen off Goa both during the monsoon (Fig. 3.2e) and premonsoon (Fig.3.3) seasons, with lower levels occurring during the latter period, these concentrations (5-6 nM) are in no way anomalously high. Indeed, as it will be shown later, these are generally lower than the maximal CH$_4$ concentrations in the open Arabian Sea (also see Owens et al., 1991; Patra et al., 1998). It is possible that the supply from the gas-charged sediments is episodic or that the seepage occurs at specific locations. Moreover, the diffused gas may be rapidly consumed by micro-organisms through aerobic (Rudd and Taylor, 1980) and anaerobic (Alperin and Reeburgh, 1984) oxidation. In any case, the present results clearly show that the sedimentary inputs from the eastern Arabian Sea do not produce large CH$_4$ anomalies in the overlying water column such as those seen in areas of known hydrocarbon seepage (e.g. Cynar and Yayanos, 1991).
3.4. **Land Drainage and In-situ Production**

As stated above, the coastal zone off the central and southwest coasts of India experiences intense upwelling during the monsoon. The physical processes that cause this upwelling appear to be complex. Studies by Shetye et al. (1990) led them to conclude that it was largely forced by local winds. But it is now generally recognised that while the wind stress may be an important contributing factor, particularly in the southern region, it cannot by itself account for the observed upwelling intensity, and that a remote forcing by winds in the Bay of Bengal may be equally, if not more, important (McCreary et al., 1993). In addition to the unique physical forcing, the other interesting aspect of the hydrography of this region is that the upwelled water is invariably capped by a thin (5-10 m) lens of fresher water which originates in part from the local precipitation and in part from runoff from the narrow coastal plain that receives heavy monsoon rainfall. The combination of upwelling and precipitation plus land runoff results in the property
Fig. 3.4. Distribution of temperature, salinity, dissolved oxygen and nitrate off Candolim (Goa) during the SW monsoon.

distributions shown in Fig.3.4a-d along the transect off Goa which is typical of all transects occupied during SS 158. Large vertical and horizontal gradients in all the properties are conspicuous in these sections. The low-salinity lens extending ~80 km from the coast of Goa was characterised by sharply decreasing CH₄ concentrations offshore indicating that the CH₄-rich surface waters originated from the land or at the land-ocean boundary. In order to investigate this
phenomenon in detail, observations were carried out at five closely-spaced stations along a short transect perpendicular to Candolim beach just north of the mouth of the river Mandovi (Fig. 3.1 inset). As expected, the highest CH$_4$ concentration (47.6 nM corresponding to a saturation of 2521%) was associated with the lowest salinity (25.3) (Fig. 3.5a). Further support for the large riverine inputs of CH$_4$ is provided by the data collected within the estuary during the same season (Fig. 3.6). The average CH$_4$ concentration at the river mouth was 57.9±12.7 nM.

Fig. 3.5. Distribution of (a) salinity and (b) methane (nM) off Candolim (Goa) during the SW-monsoon.
Fig. 3.6. Plot of methane saturation (%) versus salinity in the Mandovi estuary (Goa)

(3334±712% saturation); these are almost twice the corresponding values during the premonsoon (32.6±25.2 nM and 1818±1396%, respectively). The highest values were recorded at the freshwater-end of the estuary (248.1 nM and 13133%) decreasing almost conservatively towards the seawater-end (Fig. 3.6) during the monsoon season. Thus, it is evident that large amounts of CH₄ are added to coastal waters from the adjacent wetland ecosystems, which comprise extensive mangroves, during the wet season. However the effect of this is not felt a long distance offshore.

The fresher water "lid" occurring during the monsoon season causes strong stratification and prevents the upwelled water from reaching the sea surface, except at very shallow depths and presumably under very turbulent conditions. However, since the thermocline is very shallow, the upwelled waters, which are highly enriched with nutrients, should still be well lit by the Sun (Fig.
3.4d) supporting high rates of biological production. Measurements of primary productivity made at seven coastal stations during SS 158 by the $^{14}$C uptake method yielded an average value of $\sim 300$ mgC m$^{-3}$ d$^{-1}$ at the surface and about twice as much at $\sim 10$ m depth (J. Kurien, unpublished data). The consequently high biological demand in the stratified subsurface layer in conjunction with the already low O$_2$ content of the upwelled water leads to the development of suboxic conditions in the water column very close to the sea surface (Fig. 3.4c). The high primary production is expected to support rich zooplankton biomass and provide conducive conditions for in situ production of CH$_4$ in the water column as well as at the sediment water interface through availability of suitable sites for methanogenesis. The suboxic conditions would further aid the development of microenvironments within particles within which CH$_4$ could be produced (Karl and Tilbrook, 1994). Moreover, the shallow depths and high turbulence would keep these particles in suspension (the CTD-light transmission data showed the occurrence of thick bottom nepheloid layers at all these stations), resulting in their recycling and presumably greater release of CH$_4$ from their interiors. This might account for the generally high CH$_4$ concentrations with frequent subsurface maxima observed during the monsoon. However, it should also be pointed out that as the CH$_4$ oxidation is favoured by high combined nitrogen levels (Rudd et al., 1976; Harrits and Hanson, 1980), its rate is also expected to be high in the upper layers of the eastern Arabian Sea during the monsoon. This together with a vigorous air-sea exchange aided by strong winds may be responsible for the rapid offshore decline in CH$_4$ concentration.

3.5. Methane Distribution in the Open Arabian Sea

Profiles of CH$_4$ at four open ocean stations in the central Arabian sea are shown in Fig.3.7. Two CH$_4$ maxima were observed in almost all the profiles. The weakly-developed primary maximum was located in the upper 50 metres while the more pronounced secondary maximum was found between 150 and 200 m depths. CH$_4$ concentrations invariably decreased below 200 m at all the stations.
Oceanic surface waters are supersaturated with respect to atmospheric CH$_4$ the world over presumably due to its production through *in situ* biological processes (Sieburth, 1987). Since the bacterial production of CH$_4$ cannot take place in oxic environments (Wolfe, 1971), it is believed to be formed mostly within the reducing interiors of particles; evidence for existence of such a source has been provided by Owens et al. (1991), Karl and Tilbrook (1994) and Marty et al. (1997) through incubation experiments. However, since CH$_4$ is oxidised by bacteria and also lost to the atmosphere through gas exchange, the shape of its vertical profile must be determined by the balance between *in situ* biological production and consumption, and its inputs and removal by physical processes of diffusion, advection and gas exchange. Thus a “typical” CH$_4$ profile in the ocean with a subsurface peak normally found within the pycnocline (e.g., Brooks and Sackett, 1973; Scranton and Farrington, 1977; Brooks et al., 1981; Burke et al., 1983; Owens et al., 1991; Patra et al., 1998) can be explained by a decrease in CH$_4$ production rate with depth (Karl and Tilbrook, 1994) coupled with a high loss rate in the surface layer which could overwhelm the high potential CH$_4$ production rate at shallow depths (Burke et al., 1983). Possible departures from this “typical” profile in the Arabian Sea might be caused by its unique geographical setting (leading to, for example, a greater quasi-horizontal transport) and the resultant unusual biogeochemistry (for example, widespread suboxia at mid-depths) that distinguishes this region from most other parts of the open ocean.
For most parts, however, the vertical distribution of CH\textsubscript{4} in the Arabian Sea is qualitatively typical of the open ocean. The subsurface CH\textsubscript{4} maximum (the deeper maximum in this case) is, of course, the most important feature generally occurring close to the top of the pronounced O\textsubscript{2} minimum (Fig. 3.8; also see Owen et al. (1991) and Patra et al. (1998)). The available data seem to suggest that the CH\textsubscript{4} concentration at this maximum may be affected by the intensity of the O\textsubscript{2} minimum and associated denitrification in this layer. Of the four open ocean stations occupied during the course of this study, the highest concentration (~4 \mu M) of nitrite (NO\textsubscript{2}\textsuperscript{-}), an indicator of the denitrification intensity - see Naqvi (1991) was recorded at the most offshore Sta. 3741; the concentration of CH\textsubscript{4} at this station was also maximal at this site similar intensification of the CH\textsubscript{4} maximum within the denitrifying layer, not recognised previously, could be seen in the earlier data sets as well. For example, Fig. 2 of Owens et al. (1991) shows a deepening and intensification of the CH\textsubscript{4} maximum at Stas. 5-7 which were located within the denitrifying zone (Mantoura et al.,
1993). Similar trend is discernible at Stas. 6-15 in Patra et al.'s (1998) Fig. 2. Finally, the two stations (4 and 5) worked by Burke et al. (1983) in the eastern tropical North Pacific's suboxic zone also show elevated CH$_4$ levels within the suboxic layer, although the absolute CH$_4$ concentrations were lower than those in the more oxygenated waters at Sta. 3 which was located in the frontal zone immediately to the north of Sta. 5. There are two possible explanations for this relationship. First, the denitrifying layers are invariably associated with pronounced suspended particle maxima (e.g., Fig. 3.8) in the two regions (Garfield et al., 1983; Naqvi et al., 1993). Bacteria, which show a biomass maximum at these depths (Ducklow, 1993; Ward et al., 1998) are believed to constitute a very significant part.

![Graph](image)

Fig. 3.8. Vertical profiles of methane, DO, NO$_2$, and beam attenuation at station 3441 (15°N 69°E)
of this "particulate" matter. But elevated CH$_4$ levels may be expected if some of these "particles" support methanogenesis. A relationship between water turbidity (represented by the beam attenuation coefficient) and CH$_4$ is suggested by the present data (Fig. 3.9), but the relationship is not always one-to-one in that peaks in the beam attenuation coefficients and CH$_4$ do not always coincide (also see Burke et al., 1983). The second, more likely, explanation is that, owing to the extremely low O$_2$ contents of the NO$_2^-$ bearing waters (<0.02 ml/l as measured colorimetrically by S.W.A. Naqvi during the US JGOFS Process Study), the activity of CH$_4$ oxidisers may be greatly constrained. This view is reinforced by the rapid decreases in CH$_4$ concentration just above the suboxic (denitrifying) zone where the O$_2$ concentrations rise rapidly (Fig. 3.8). In any case, it would appear that the main subsurface CH$_4$ maximum in the Arabian Sea, as in other oceanic environments, is produced in situ (Owens et al., 1991) rather than being formed as a result of advection from the shelf. The latter
possibility was favoured by Patra et al. (1998) who proposed that the CH$_4$ maximum was associated with the Arabian Sea high salinity surface water (ASHSW) formed in the northern Arabian Sea. However, this hypothesis is not subscribed on several counts. First, it requires unreasonably high volume of ASHSW production. Secondly, the depth of CH$_4$ maximum in the central Arabian Sea is too deep for the ASHSW. Thirdly, as stated earlier, the maximal CH$_4$ concentrations in the central Arabian Sea are actually higher than those found in the near bottom waters of the continental margin off India making it unlikely that the CH$_4$ is supplied into the ocean interior from the marginal sediments.

The cause of the shallower CH$_4$ maximum observed during the present study [which was also occasionally observed by Patra et al. (1998)] is less certain. One possibility is that the waters with higher CH$_4$ concentrations may be sandwiched between two layers where the rate of CH$_4$ loss is higher: above this horizon (at the sea surface) CH$_4$ may be lost rapidly through exchange with the atmosphere while below it (within the thermocline) its oxidation may be favoured by high combined nitrogen concentrations. At or just above the subsurface chlorophyll maximum (SCM), however, high O$_2$ and relatively low nitrate (NO$_3^-$) concentrations may severely constrain bacterial oxidation of CH$_4$. Alternately, a higher rate of CH$_4$ production may occur at the SCM either due to phytoplankton metabolism (Scranton and Brewer, 1977) or in the guts of zooplankton (Scranton and Brewer 1977; Alldredge and Cohen 1987; Paerl and Prufert, 1987), which are expected to be concentrated in this layer for grazing. However, the correlation between the CH$_4$ maximum and SCM is quite patchy (Owens et al., 1991; Patra et al., 1998).

An interesting aspect of the present data is that the shallower CH$_4$ maximum was right at the surface at stations sampled at night. As diurnal variation at the same location could not be studied, all the surface saturation values were plotted against the sampling time (Fig. 3.10). It is possible that the
suggested trend, with the lowest saturation around noon and the highest around midnight may be real even though there is considerable scatter in the data, probably arising from the variable population density of the plankton. This aspect of CH$_4$ distribution warrants detailed investigation.

![CH$_4$ saturation at surface vs time of sampling](image)

Fig.3.10. Plot of surface methane saturation in the open ocean versus time of sampling

4.6. Conclusion:

In conformity with previous reports the results obtained during the course of this study also show higher-than-average CH$_4$ emissions from the Arabian Sea with a pronounced seasonal variability. While the waters over the continental shelf are significantly more enriched with CH$_4$ relative to the open ocean, particularly during the monsoon season when fairly intense upwelling takes place off the central and southwest coasts of India leading to the development of suboxic conditions at shallow depths, near-bottom methane anomalies such as those reported from other regions of known hydrocarbon seepage, are not seen in this region. Instead the maximal CH$_4$ concentrations are frequently seen either at the surface, associated with the low-salinity water
mass which caps the upwelled water, or at mid-depth, indicating that the major sources of high CH$_4$ saturation are the *in situ* production and supply from the land-sea interface. Extremely high CH$_4$ concentrations are observed in the Mandovi estuary presumably due to intense production in coastal wetlands. However, the large onshore-offshore gradients occurring during the wet season indicate rapid loss due to air-sea exchange and CH$_4$ oxidation.

The pronounced subsurface CH$_4$ maximum in the open ocean appears to occur within the upper portion of the suboxic (denitrifying) water close to the intermediate nepheloid layer supporting the view that the maximum is produced *in situ* from particulate matter at a depth where the vanishingly low O$_2$ levels might suppress the oxidative loss. An advective origin of the maximum, suggested previously, is not supported by the data. In addition, another weaker maximum is also seen in the upper well-oxygenated layer. It is speculated that this feature is formed either due to plankton metabolism or through a lower rate of CH$_4$ loss relative to the overlying or underlying waters. The shallower maximum may also show diurnal changes, but this aspect needs to be confirmed by future studies.