BIOGEOCHEMICAL CYCLING OF DIMETHYL SULPHIDE IN THE NORTHERN INDIAN OCEAN

THESIS SUBMITTED TO GOA UNIVERSITY
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DOCTOR OF PHILOSOPHY
IN
MARINE SCIENCES

BY
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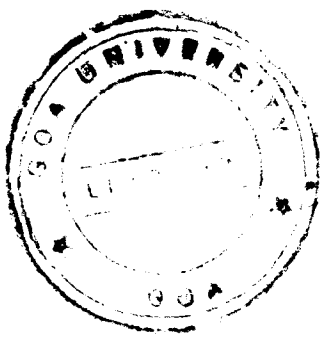

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CERTIFICATE

This is to certify that the thesis entitled **"BIOGEOCHEMICAL CYCLING OF DIMETHYL SULPHIDE IN THE NORTHERN INDIAN OCEAN"** submitted by **Mr. Damodar M. Shenoy** for the award of the degree of Doctor of Philosophy in Marine Sciences is based on his original studies carried out by him under my supervision. The thesis or any part thereof has not been previously submitted for any other degree or diploma in any university or institution.

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This is to certify that the suggestions made by the examiners are incorporated in the Thesis.

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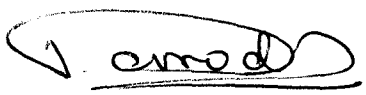
STATEMENT

As required under the University ordinance 0.19.8 (vi), I state that the present thesis entitled "**BIOGEOCHEMICAL CYCLING OF DIMETHYL SULPHIDE IN THE NORTHERN INDIAN OCEAN**" is my original contribution and the same has not been submitted on any previous occasion. To the best of my knowledge the present study is the first comprehensive work of its kind from the area mentioned.

The literature related to the problem investigated has been cited. Due acknowledgements have been made wherever facilities and suggestions have been availed of.



(Damodar M. Shenoy)

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Damodar M Shenoy

dedicated

to my Parents

CHAPTER 1

Introduction

Chapter 1

Introduction

1.1 General Scenario

The envelope of air around the solid Earth supports life by sustaining warm climate. An average temperature of ~15°C at the surface of the Earth is facilitated by greenhouse warming caused by air constituents such as moisture, carbon dioxide, etc. Otherwise, the surface temperatures should have been about –19°C [*Halmann and Steinberg,* 1999]. Unfortunately, the greed of humans for betterment of life style and comforts led to rapid industrialization since 1850's. This development together with exponential increase in vehicular traffic resulted in large emissions of carbon dioxide and other greenhouse gases. For example carbon dioxide in air has increased from the pre-industrial level of 280 ppmv to the present concentration of 360 ppmv [*Halmann and Steinberg,* 1999]. Therefore, an increase of over 25% in the concentration of carbon dioxide in air occurred between 1850 and 2000 AD that accounts for two-thirds of the increased radiative forcing. Fig. 1.1 depicts percent changes in the radiatively important atmospheric species since industrialisation. Major changes have occurred in respect of methane and sulphur species due to the burning of fuel (coal and oil).

1.2 Why study dimethyl sulphide (DMS)?

Dimethyl sulphide discovered in seawater by *Lovelock et al.* [1972] is the most dominant reduced sulphur gas found in surfacelayers of the ocean. It

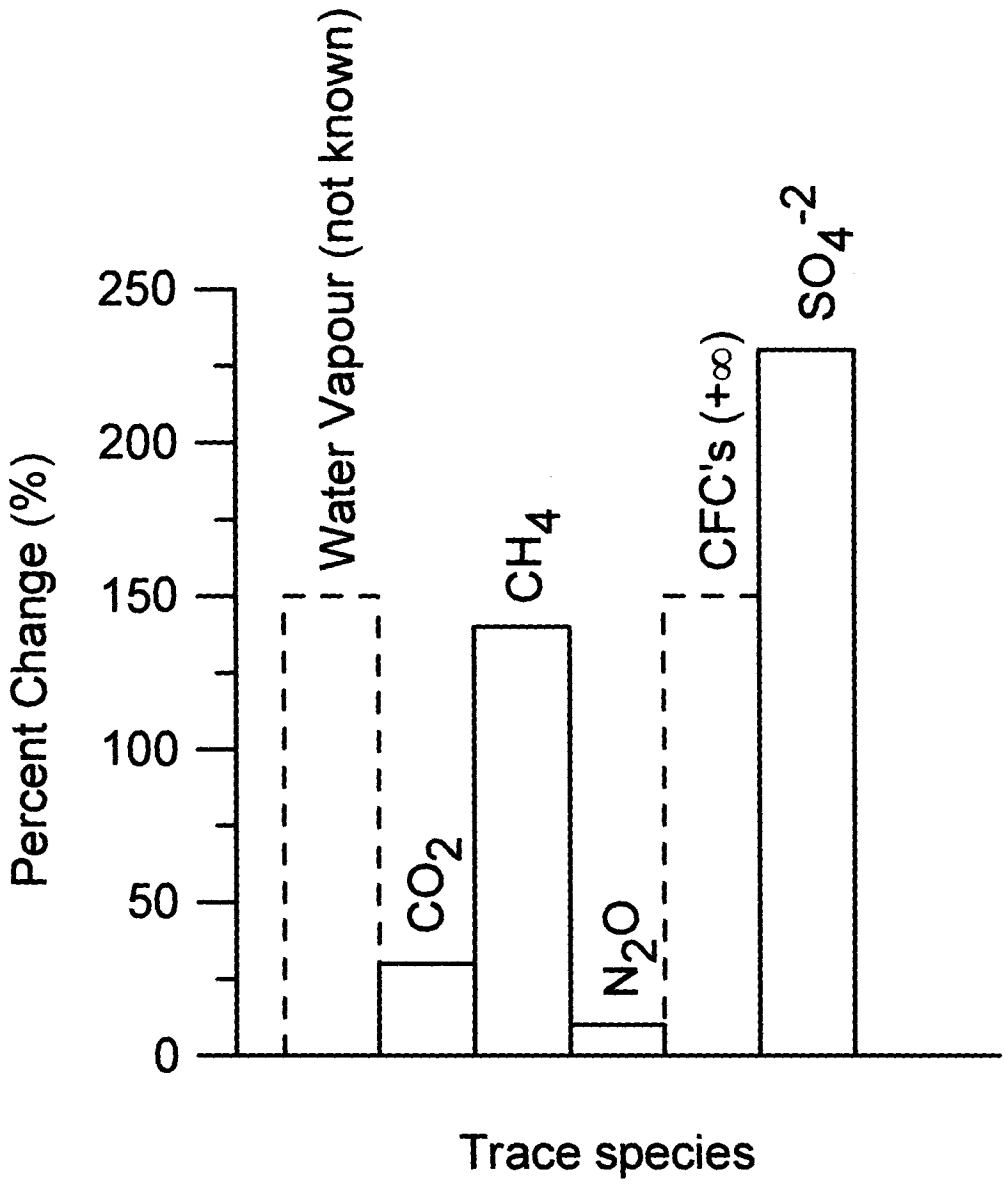


Fig. 1.1. Radiatively important trace species in the atmosphere and their percent change in flux measured relative to the pre-industrial time. (Data from *Charlson et al.*, 2000).

is produced from dimethylsulphoniopropionate (DMSP) according to the following reaction.

$$(H_3C)_2S^+ — CH_2 — CH_2 — COO^- \rightarrow (CH_3)_2S + CH_2CHCOOH$$

(DMSP) DMS Acrylic Acid

DMSP is in fact a product of biochemical reactions in algae involving methionine [*Andreae,* 1990]. The DMS thus produced in surface layers of the ocean is released to the atmosphere across the air-sea interface. The emission of dimethyl sulphide gas is expected to balance the excess sulphur deposition over the remoter oceans [*Charlson et al.,* 1992]. In the atmosphere DMS reacts with hydroxide and nitrate radicals leading to its oxidation to sulphur dioxide (Fig. 1.2). Sulphur dioxide then combines with moisture in air to yield sulphate aerosols. These aerosol particles form condensation nuclei, which also reflect a part of the incoming solar radiation back into space, and thus cause an indirect atmospheric cooling. Thus DMS counters the effect of greenhouse gases and hence is known as an anti-greenhouse gas. *Charlson et al.* [1987] proposed a hypothesis, now known as CLAW hypothesis connecting DMS emissions to changes in albedo. Increased production of DMS due to global warming is expected to lead to more sulphate aerosols and subsequently to more cloud condensation nuclei (CCN) that can enhance back radiation.

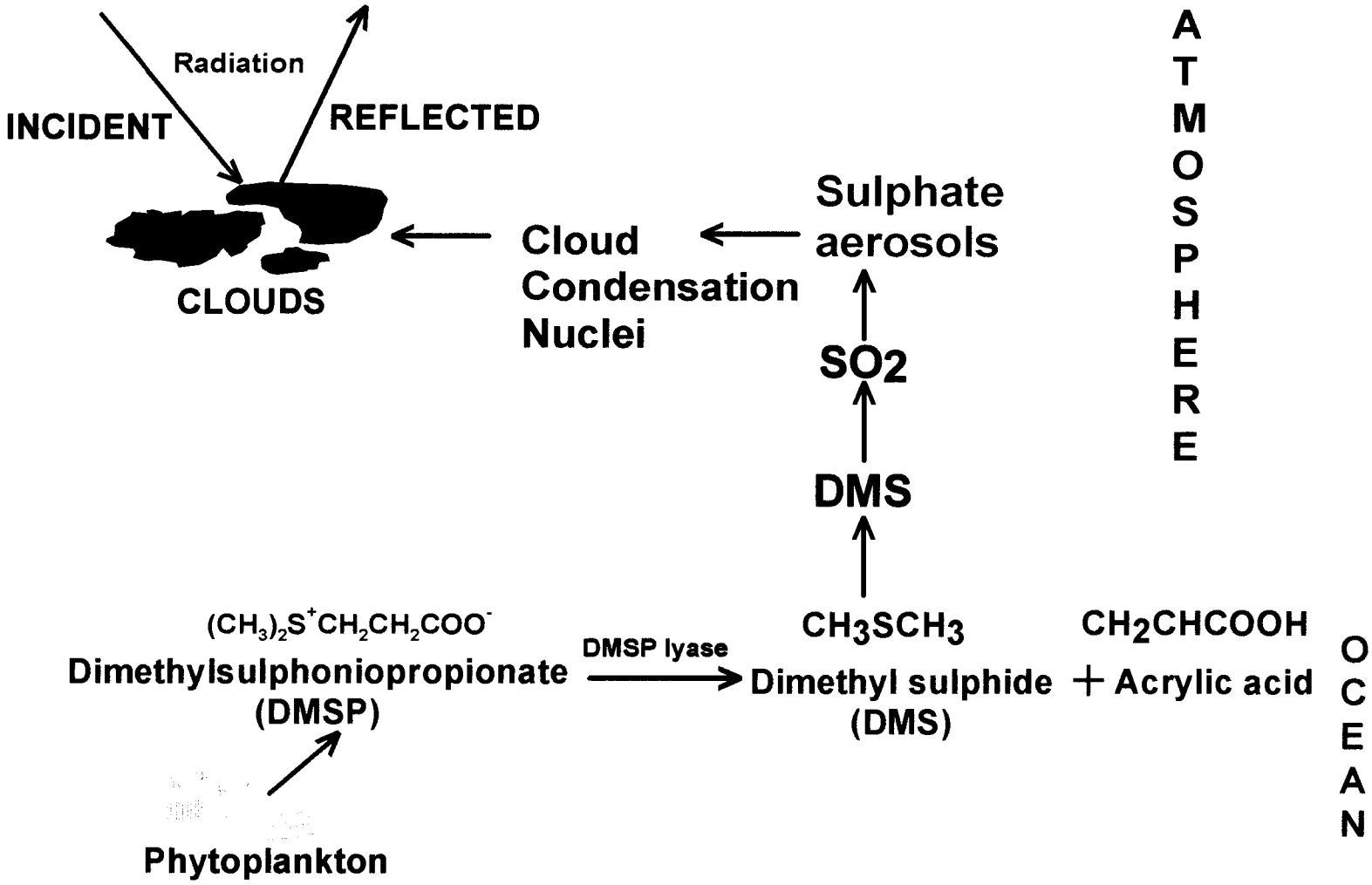


Fig. 1.2 Schematic layout of DMS production in the Ocean and its atmospheric feedback.

1.3 Biogeochemistry of DMS in the ocean

DMS is lost from the sea surface to the atmosphere due to diffusive flux. In seawater DMS can also be lost as a result of photochemical and bacterial oxidation to dimethyl sulphoxide (DMSO). *Hatton et al.* [1996] reported the occurrence of DMSO at deeper depths and concluded that DMSO may act as an important sink for DMS. Other removal mechanisms include photolysis and biological removal. *Brugger et al.* [1998] found out the DMS photolysis to follow pseudo first-order kinetics with the rate constant directly dependent on the irradiance intensity. The photolysis rates are also found to be directly dependant on dissolved organic carbon concentration (DOC). On the other hand *Slezak et al.* [2001] found that the biological removal rates of DMS were lower under light conditions than in dark. This has been attributed to partial inhibition of microbial consortia, which is responsible for DMSP and DMS turnover. Conversion of DMSP to methanethiol as one of the major processes has been shown by *Kiene* [1996]. *Simo and Pedros-Alio* [1999] have reported two major pathways of DMSP degradation. The first one leads to DMS and is carried out by both algal and bacterial enzymes (DMSP cleavage) and the second one in which bacteria play the major role and utilise DMSP (DMSP assimilation) for other purposes and thus does not lead to DMS formation.

The exact mechanism of DMS production from DMSP nor the real purposes of DMSP synthesis by plankton are still not clear [*Stefels,* 2000; *Kiene et al.,* 2000]. Many algal species are found to contain DMSP [*Ackman*

et al., 1966; *Tocher et al.*, 1966; *Craigie et al.*, 1967; *White,* 1982]. Despite attempts to correlate DMSP with chlorophyll no consistent relations are found between the two [*Turner et al.*, 1988; *Andreae,* 1990; *Malin et al.*, 1993; *Kettle et al.*, 1999]. Single species of phytoplankton are found to be responsible for most of the DMSP production in seawater [*Barnard et al.*, 1984; *Holligan et al.*, 1987; *Belviso et al.*, 1990; *Malin et al.*, 1993]. Hence different species of marine phytoplankton have varying capacities to produce DMSP. According to *Liss et al.* [1993] the production of DMSP follow the order:

Coccolithophores > Phaeocystis > Dinoflagellates > Diatoms

Kwint and Kramer [1996] studied DMS production by phytoplankton communities in mesocosm experiments and observed DMS concentrations to be highly variable between days and under identical conditions. They also observed that a significant quantity of DMS is released in to the waters during the senescent phase. *Dacey and Wakeham* [1986] found enhanced production of DMSP when zooplankton grazed on phytoplankton. Similarly *Wolfe and Steinke* [1996] also found increase in the production of DMS when *Emiliania huxleyi* was subjected to grazing by zooplankton. Marine plankton use strong DMSP lyase activity as a chemical defence against protozoan predators. Under the influence of high DMSP-lyase activity higher amounts of acrylic acid are produced which, have very good antibacterial properties, and therefore protozoan predators usually prefer grazing on strains with low enzyme activity [*Wolfe et al.*, 1997].

Another physiological role of DMSP in phytoplankton is proposed to be osmoregulation [*Dickson et al.,* 1980; 1982; *Vairavamurty et al.,* 1985]. Glycine betaine (BGT) a nitrogen analog of DMSP, is responsible for osmoregulation in plant cells [*Wyn Jones and Storey,* 1981]. Since the surface waters in most oceanic regions are nitrate depleted phytoplankton could use sulphate in seawater and produce DMSP for osmoregulation. *Grone and Kirst* [1992] found an increase in DMSP content in unicellular alga (*Tetraselmis subcordiformis*) in response to nitrogen deficiency. However, *Keller et al.* [1999a,b] did not find any difference in the production of DMSP under nitrogen increased conditions but GBT production enhanced to some extent.

Although DMS occurs largely in surface layers of the oceans its presence in the sea surface microlayer is not well known. Among these *Nguyen et al.* [1978] was the first to report DMS enrichment up to five times in the microlayer compared to that in the bulk water while *Yang* [1999] reported an average DMS enrichment of 1.95 in the South China Sea. On the other hand *Andreae et al.* [1983] and *Turner and Liss* [1985] reported no such enrichment.

As discussed above extensive measurements on DMS and DMSP have been done in different parts of the world's oceans [*Kettle et al.,* 1999 and references therein] including estuarine and lagoon waters [*Iverson et al.,* 1989; *Moret et al.,* 2000]. A few studies have been made in the Indian Ocean, which, include [*Hatton et al.,* 1999] and some unpublished data in eastern Indian Ocean [of T.S. Bates as mentioned by *Kettle et al.,* 1999] and for

Amsterdam station [*Nguyen et al.*, 1990, 1992]. However only the work of *Hatton et al.* [1999] represent the Indian Ocean.

1.4 Why study DMS in Indian Ocean?

The Indian Ocean unlike the Pacific and the Atlantic has landmass as its northern boundary and thus is smaller (74.9 x 10^6 km^2) than the Pacific (179.7 x 10^6 km^2) and the Atlantic Ocean (106.2 x 10^6 km^2). The north Indian Ocean is climatically very dynamic region and comprises of the Arabian Sea and the Bay of Bengal and the Southern Indian Ocean.

In the southern Indian Ocean the winds are from the southeast throughout the year with physical characteristics similar to the Pacific and the Atlantic Ocean. The wind pattern in the Northern Indian Ocean is unique and experiences seasonal reversal. Between November and February the winds are from the northeast, whereas between June and September the winds change from northeasterlies to southwesterlies. The change in the wind direction is driven by the existence of land mass in the north. Even though the Arabian Sea and the Bay of Bengal occupy nearly the same latitude range they have entirely different characteristics. The Arabian Sea lies between 8°N and 25°N and between 50°E and 80°E and occupies an area of 6.225 x 10^6 km^2 while the Bay of Bengal lies between 80°E and 100°E and occupies an area of 4.2 x 10^6 km^2. The Arabian Sea is an area of negative water balance where evaporation exceeds precipitation and river runoff, except off the west coast of India where annual precipitation and river runoff exceed evaporation (<20 cm) [*Venkateshwaran,* 1956]. The Arabian Sea is connected to the

Persian Gulf through the gulf of Oman and to the Red Sea through the Gulf of Aden. Surface salinities in this region are among the highest in the world. This together with winter cooling phenomenon leads to the formation of high-density water mass [*Dietrich,* 1973]. In the Arabian Sea this leads to the formation of high saline water mass known as the Arabian Sea High Saline Water mass (ASHSW). This is the only water mass, which originates in the Arabian Sea. Other water masses present in the intermediate and deeper depths with origin outside the Arabian Sea are Antarctic Intermediate Water (AIW), Circumpolar Water (CW) and Antarctic Bottom Water (ABW) [*Wyrtki,* 1973]. The Red Sea and the Persian Gulf lie in arid regions and thus experience intense evaporation. High density waters from these regions out flow into the Arabian Sea as the Red Sea Water (RSW) and the Persian Gulf Water masses (PGW) at intermediate depths. To balance this outflow inflow of Arabian Sea surface waters occur into the Red Sea and the Persian Gulf [*Grasshoff,* 1969, 1975; *Morcos,* 1970; *Hartmann et al,* 1971].

The seasonal reversal of winds drives the entire physical and biological processes of the Arabian Sea. During the summer monsoon the southwesterly winds drive the longshore currents along the coast of Somali and Oman, which cause upwelling off these coasts. Upwelling also occurs off the southwest coast of India. In addition, open ocean upwelling is caused by the Findlater jet. The resultant introduces nutrients in the surface layers over large parts of the open Arabian Sea [*Naqvi,* 2001]. During winter monsoon cool dry wind from the Asian subcontinent blows in the northeasterly direction over the

Arabian Sea. These cool dry winds enhance the surface evaporation thereby increasing the density of water thus setting up a convection process. This phenomenon dominantly occurs north of 15°N. In addition to the above processes there is a continuous supply of nutrients from below the thermocline as the nutrient gradients is very steep across the thermocline. And sometimes during the intermonsoon periods when the MLD is thin the thermocline with high nutrient levels falls in the euphotic zone and thus induces production. This gives rise to a subsurface chlorophyll maxima where photosynthetic rates are found to higher compared to surface [*Naqvi,* 2001]. The nutrients brought to surface by these processes induce biological high productivity in these waters and inturn makes the Arabian Sea as one of the most productive regions of the world oceans [*Qasim,* 1977]. The Arabian Sea is well known for oxygen minimum zone. Between 150 m and 1200 m the oxygen levels are below 0.5 ml lit^{-1}. Under these circumstances bacteria use nitrate as an alternative source of oxygen thereby causing denitrification. In addition the Arabian Sea also serve as a perennial source of carbon dioxide [*Sarma,* 1998].

On the other hand the Bay is known to receive large amounts of fresh water from some of the largest rivers in the world. Annual discharge from rivers bordering the coastline exceeds 1.6 x 10^{12} m^3 with Brahmaputra, Irrawaddy, Ganges and Godavari contributing on an average 0.510, 0.422, 0.493 and 0.092 (10^{12}) m^3 sec^{-1} respectively [*Subramanian,* 1993] in which most comes during and following the southwest monsoon. *Lakshmana Rao*

and Veena Devi [1985] found that anomalies in net radiation are an important factor for rainfall. In the Bay negative anomalies have been found to yield a good monsoon year and positive anomalies lead to poor rainfall. Annual rainfall in the Bay of Bengal is in excess of 2 m. All this discharge of fresh water in to the basin is responsible for the low saline cap in the Bay, which is one of its characteristic features.

During the summer monsoon there is a fall in surface temperature over the entire Bay and this is caused mainly by I) fall in air temperature ii) cloud cover and iii) high wind speeds [*Banse,* 1990]. Circulation in the Bay is mostly eastward under the influence of the southwesterlies. Along the east coast of India the circulation is towards the north in contrast to that during the NE monsoon. The northward coastal circulation during the SW monsoon brings high saline waters from the Arabian Sea into the Bay and the southward coastal circulation during the NE monsoon introduces low saline waters from the Bay into the Arabian Sea. This circulation along the east coast is mostly due to the local winds and does not include any remote forcing [*Shetye et al.* 1991] and is quite different from the southward coastal circulation along the west coast of India which is driven by both local winds and also influenced by remote forcing [*Shankar and Shetye,* 1997]. These western boundary currents cause upwelling along these shores where isopycnals from intermediate depths reach surface [*Shetye et al.* 1991, *Murty et al.* 1992]. *Krishna and Sastry* (1985) reported that upwelling off the east coast of India occurs only to

south of Vishakapattanam. Towards the north in spite of favourable winds upwelling is suppressed by the discharge of fresh waters from rivers.

Surface productivity (1 m) in the Bay of Bengal is greater than that of the Arabian Sea, but the column productivity of the Arabian Sea is greater than that of the Bay of Bengal [*Qasim,* 1977]. *Bhattathiri et al.* [1980] measured inshore and off shore primary productivity in the western Bay of Bengal. They reported average surface and column production of 69.4 mgC m^{-3} d^{-1} and 0.98 gC m^{-2} d^{-1} respectively. Inshore values were higher than offshore values and the average primary productivity of Bay during August-September of 1978 was found to be higher than that of many areas in the Arabian Sea. In spite of its land locked nature the Bay of Bengal is not an active site of denitrification. *Rao et al.* [1994] studied the hydrochemistry of the Bay of Bengal and found higher sinking rate of particulate organic matter to be responsible for this. On the other hand the Arabian Sea is an active site for denitrification in the oxygen minimum zone (OMZ) from 150 m to 1200 m. The only other site for denitrification among the world's oceans is the eastern tropical Pacific. *Naqvi et al.* [1996] found much lower ETS (electron transport system) activities in subsurface waters of the Bay of Bengal than those in the Arabian Sea. Even the renewal rates of waters from intermediate depths are lower than those of the Arabian Sea. In the Bay the sinking rate of POM is so high that there is not enough time to oxidize the organic matter thus making the Bay free from active denitrification in comparison to the Arabian Sea. Interestingly, nitrous oxide is higher in intermediate waters of the Bay as there

is no denitrification (sink) as it is in the Arabian Sea. This suggests a faster turnover of nitrogen species in the Arabian Sea. Unlike the Arabian Sea the Bay acts a seasonal sink for carbon dioxide [*Sarma,* 1998].

The Central Indian Ocean shows surface circulation similar to the Pacific and the Atlantic. North of equator exists the north equatorial current (NEC), also called as the northeast monsoon current (NMC) [*Shenoi et al.,* 1999]. The NMC has a westward flow. It is also fed by the East India coastal current (EICC) and thus NMC introduces into the area the low saline waters from the Bay of Bengal. South of the equator lies the south equatorial current (SEC) which also has a westward flow. The SEC on approaching the landmass of Madagascar bifurcates into northern and southern branches called as the East Africa coastal current (EACC) and East Madagascar current (EMC) respectively. During the NE monsoon the Somali current (SC) moves towards the equator and is milder unlike during the monsoon during which it has pole ward movement and behaves like the other western boundary current viz. the Gulf Stream and the Kuroshio. The equatorial counter current lies in between the NMC and SEC. It has a eastward flow and is fed by the EACC and EMC. During the intermonsoons (April – May and November – December) the scenario becomes further complicated with the appearance of eastward flowing Equatorial Jet (EJ). The ECC/EJ has higher salinity in comparison to the NMC and SEC.

In comparison to the Arabian Sea and the Bay of Bengal the Central Indian Ocean has lower primary productivity. This is primarily due to the

existing winds in the area, which are predominantly meridional and during the transition seasons the westerly winds generate convergence thereby inducing down-welling. During the summer season the western part of the equatorial Indian Ocean experiences high primary productivity as a result of the Somali upwelling. This region also experiences haze events during the southwest monsoon. Thus the nutrients from upwelling and trace metals from the haze explain the highest productivity observed. In contrast to this the eastern equatorial Indian Ocean neither experiences strong upwelling nor has any haze events and thus has low productivity. *Chavez and Smith* [1994] have reported the equatorial Atlantic to have twice the chlorophyll concentration of the equatorial Pacific, which in turn has twice the chlorophyll of the equatorial Indian Ocean. In the present work central Indian Ocean has been covered during the successive winters of 1998 (FFP) and 1999 (IFP) as part of Indian Ocean experiment (INDOEX).

1.5 Objectives

As mentioned above sparse data on DMS are available for the Indian Ocean. *Hatton et al.* [1999] found elevated concentrations of DMS, DMSP and DMSO in the eutrophic area (Arabian Sea) just after the SW monsoon. In addition DMSO concentrations were found to correlate with near surface DMS and DMSP. In Amsterdam island (southern Indian Ocean) *Nguyen et al.* [1990, 1992] found covariation between oceanic and atmospheric DMS and atmospheric SO_2, wet deposition of methane sulphonic acid (MSA), NSS SO_4^{-4}, and rain acidity.

While the behaviours and cycling of carbon dioxide and nitrogen species have been known in the Indian Ocean the information on sulphur species is sparse. DMS and associated sulphur compounds are climatically important, particularly in a dynamic area such as the Northern Indian Ocean. Great diversity in physical and associated biological regimes in the Indian Ocean together with dynamic climate offers an interesting region to study the DMS cycling and to understand controlling factors of its abundance. Therefore, the study has been undertaken to study DMS and DMSP in the Northern Indian Ocean with the following specific objectives.

1. To understand the DMS and DMSP variability
2. To find the regulating factors of DMS and DMSP in seawater
3. Transport of DMS to the atmosphere and
4. To evaluate the importance of sea-air flux of DMS from the northern Indian Ocean to global emissions.

CHAPTER 2

Materials and methods

Chapter 2

Materials and Methods

Sampling for this study was done keeping in view the large spatial and temporal variability in the biogeochemical processes in the Indian Ocean. Importantly strategies and experiments have been under constant modifications based on the results obtained from time to time.

Data were collected for temperature, salinity, fluorescence, dissolved oxygen, nutrients (nitrate and nitrite), chlorophyll a, phytoplankton speciation and enumeration (at time series station in Goa) and bacterial counts (total) and DMS and DMSP in seawater, sea surface micro layer and in aerosols. Besides, data were also collected for weather (particularly wind speeds and atmospheric temperature). Data on UV radiation were retrieved from NASA's Goddard Space Flight Centre, Greenbelt, Maryland, USA (*http://jwocky.gsfc.nasa.gov*).

2.1 Experimental strategies and Sample Collection

The sampling strategies followed in this study are:

i) Oceanic and coastal expeditions

ii) Time series measurements and

iii) Laboratory experiments.

2.1.1 Oceanic Expeditions

Fig. 2.1 depicts the area covered under the present study in the Indian Ocean. Oceanic expeditions were undertaken on boards ORV Sagar Kanya and FORV Sagar Sampada (Table 2.1).

At most of the regular stations data were collected from the upper 200 m of the water column since our preliminary investigations revealed concentrations of DMS and DMSP to be below detection limits in deep waters (shown in chapter 4). We also sampled surface water for chemical analyses at many locations besides regular stations. A Sea Bird CTD (conductivity-temperature-depth) system was used to collect physical variables (Temperature and salinity) and seawater samples. Seawater samples were collected using a rosette attached to the CTD system, fitted with 12 Niskin bottles of 1.8/10 litre capacity. Sub-sampling of water was done in the order: dissolved oxygen, DMS, DMSP, nutrients, salinity, chlorophyll a, bacterial counts and phytoplankton. Care was taken while sampling dissolved gases so as to avoid trapping of bubbles.

2.1.2 Time series measurements

These experiments were conducted in different ways in various locations: (1) diurnal variability experiments lasting 12 to 40 hours were done at two locations (7° and 10°N along 88°E) during SK 138C, (2) longer time experiment (nearly a month) was done at 17.5°N and 89°E during SK147A&B. (3) seasonal variability experiments, at a coastal station in Dona Paula bay, Goa from December 1999 to January 2001 (Fig. 2.2), (4) another seasonal

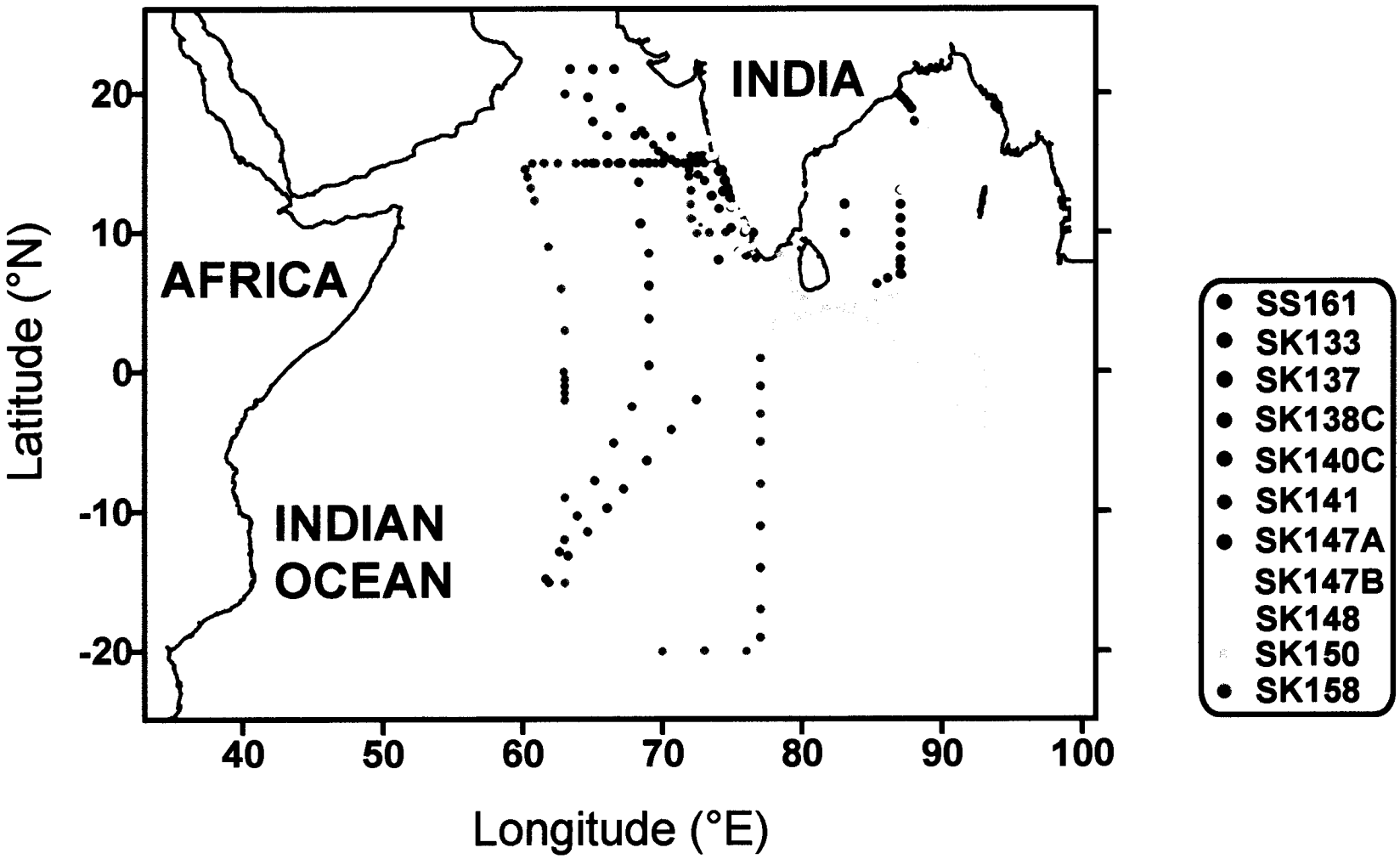


Fig. 2.1 Station locations for dimethyl sulphide studies in the present study.

Table 2.1 Details of cruises undertaken in this study.

Cruise No	No. of Stations/cruise	Area covered	Season	Duration
SS161	25	Northern Arabian Sea	North-east monsoon	2-22nd Jan 1998.
SK133	22	Central Indian Ocean	North-east Monsoon	18th Feb to 29th March 1998.
SK137	32	Arabian Sea (coastal)	South-west Monsoon	20thJuly to 17th Aug 1998.
SK138C	20	Bay of Bengal	Fall Inter-monsoon	23rd Oct to 12th Nov 1998.
SK140	19	Arabian Sea	North-east monsoon	1st to 28th Dec 1998.
SK141	51	Central Indian Ocean	North-east monsoon	20th Jan to 12th March 1999.
SK147A	44	Bay of Bengal	South-west monsoon	16th July to 8th Aug, 1999.
SK147B	53	Bay of Bengal	South-west monsoon	10th to 31st Aug, 1999.
SK148	27	Arabian Sea (coastal)	South-west monsoon	4th Sept. to 11th Oct 1999.
SK150	42	Southern Bay of Bengal	North-east monsoon	24th Jan to 22nd Feb 2000.
SK158	17	Arabian Sea	Fall Inter-monsoon	1st to 23rd Nov 2000.
Total No. of stations	352			

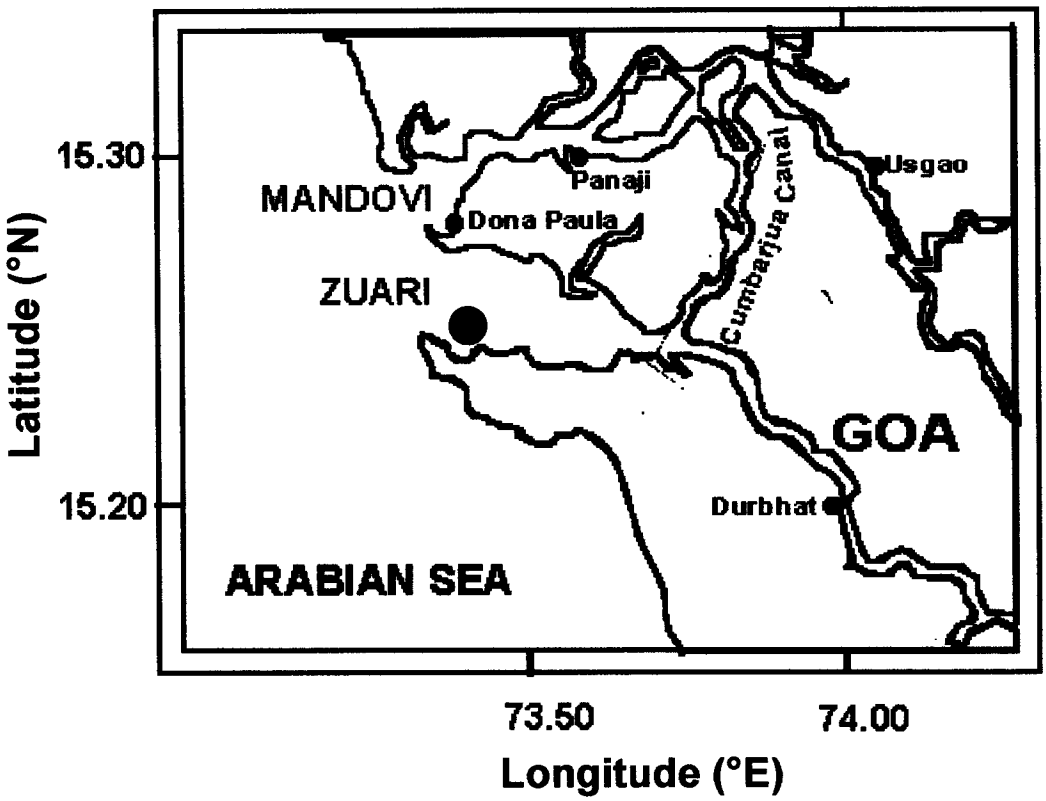


Fig. 2.2 Location of Time series station in Dona Paula Bay in the Zuari estuary (Goa)

variability experiment in Goa involved periodic collection of DMS data along a section off Candolim (Fig. 2.3), particularly during and after the southwest monsoon, and (5) two cruises (SK133-first field phase (FFP) and SK141-intensive field phase (IFP)) were undertaken in the Central Indian Ocean to find the inter-annual variability of DMS in that region. The coastal and estuarine sampling was done using mechanised boats.

2.1.3 Laboratory Experiments

Laboratory experiments were conducted on board the vessel ORV Sagar Kanya (cruise SK138C) and in the shore based laboratory in Goa. In the shore based laboratory experiments an attempt was made to study the role of changes in salinity in DMSP production by phytoplankton. In these experiments plankton (*Skeletonema Costatum* (Greville) Cleve) cultures were subjected to predetermined salinity shocks by changing the physical conditions of the ambient medium and to find changes in DMS and DMSP (i.e. Cultures grown at a salinity of 35 were subjected to salinity shocks by reducing the salinity to 32.5, 30, 27.5, 25, 22.5 and 20 through dilution). Moreover, as the rate of DMSP production by plankton could be dependent on the stage and health of the cells these experiments were conducted at two different stages of cultures, once on a two days old culture and the other when it was 11 days old and in stationary stage.

Shipboard (laboratory) experiments were conducted to understand the stability of DMSP in marine air and in seawater. Known amounts of DMSP were loaded on to a number of GF/F filter papers that were exposed to marine

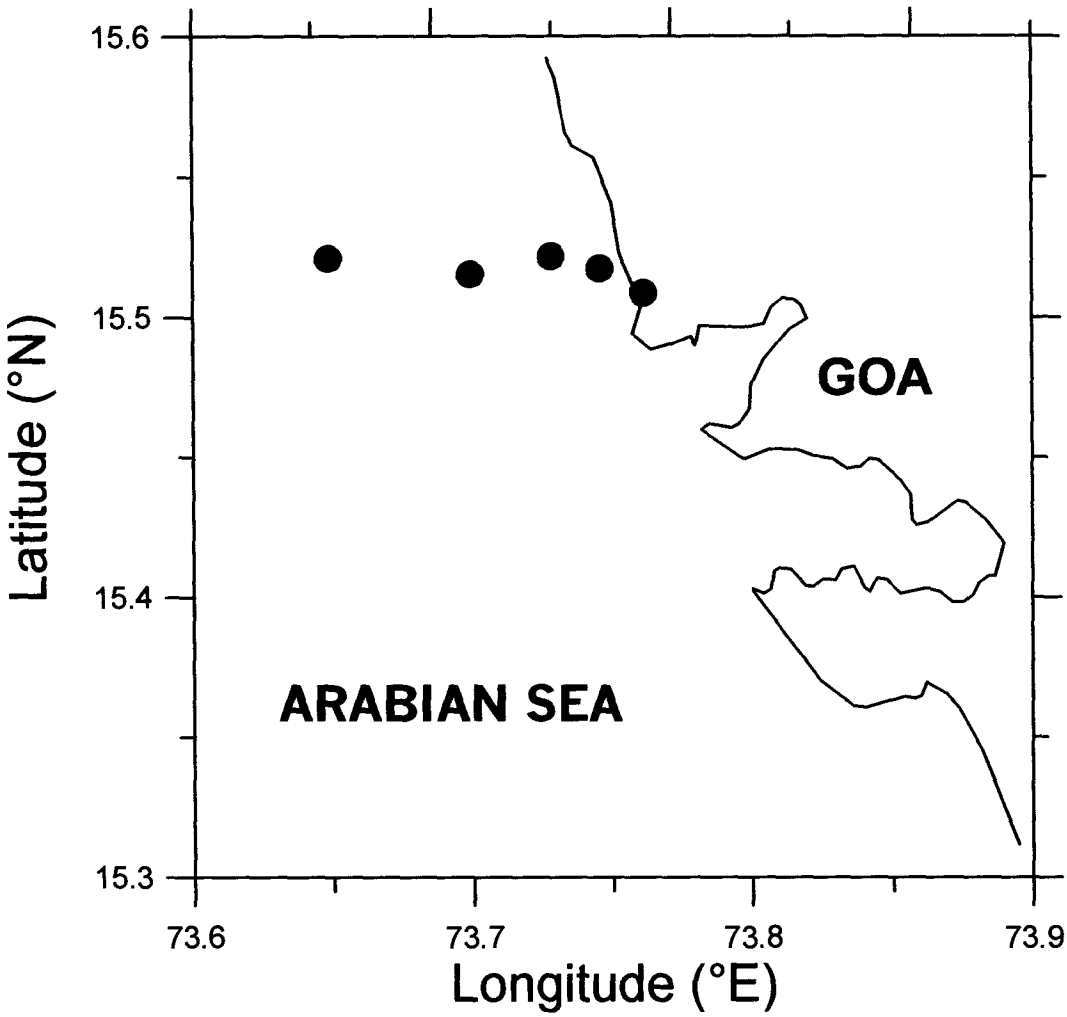


Fig. 2.3 Station locations off the Candolim coast in Goa

air. These were periodically removed and the remaining DMSP was measured. In addition to the above experiment DMSP stability (at the air-sea interface) experiments were also conducted in seawater. Known amount of DMSP was introduced in a litre of seawater in an open beaker. Atmospheric air was pumped through the beaker by means of a syringe. The beaker was periodically sub-sampled and measured for DMSP.

2.2 Methodology - Experimental

2.2.1 Temperature, Salinity and fluorescence

Temperature, salinity and fluorescence were measured using respective sensors fitted to the Sea-bird CTD system (Table 2.2). Temperature sensed by the probe was periodically checked using reversible thermometers. Temperature measurement during estuarine sampling was done with a mercury thermometer. Salinity computed from the conductivity probe measurements were calibrated against those made using an Autosal salinometer (model 8400).

Salinity measurements for the estuarine samples were done by determining the chloronity using the Mohr Knudsen method. The salinity is later calculated according to the formula:

$$S = 1.80655 * Cl$$

Where, S= salinity

Cl= chloronity

Florescence was measured using an Aquatrack III submersible Fluorimeter (Chelsea Instruments). The instrument uses a dual-beam,

Table 2.2 Details of major properties measured, methods used and associated precisions.

S. No.	Parameter	Method	Precision
1	Temperature	Temperature probe	0.01°C
2	Salinity	Conductivity probe	0.001 psu
3	Dissolved Oxygen	Winkler Titration method	0.02 µM
4	Nitrate	Azo-dye method	0.02 µM
5	Dimethyl sulphide	Gas Chromatography	10 %

ratiometric method for measurements. A Xenon lamp provides a light source having a high ultra content, which is applied to two paths: a reference path and a sample path. The measured reference and sample signals are transmitted to a ratiometer circuit. In this circuit, the ratio of returned (sample) signal to reference signal is computed and scaled logarithmically. In each cruise a few stations were sampled for chlorophyll a measurements for calibrating the florescence sensor.

2.2.2 Dissolved Oxygen

The dissolved oxygen was analysed by Winkler titration method. In this method dissolved oxygen is made to react with Manganese (II) hydroxide in a strongly alkaline medium.

$$2\ Mn(OH)_2 + 1/2O_2 + H_2O \rightarrow 2Mn(OH)_3$$

The manganese hydroxide precipitate is dissolved through acidification to a pH of less than 2.5 with 50% HCl. Under these conditions the fixed oxygen is released and is equivalent to amount of iodide that gets oxidised to iodine,

$$2Mn(OH)_3 + 2I^{-1} + 6H^{+} \rightarrow 2Mn^{+2} + I_2 + 6H_2O$$

which later forms a complex by reacting with the surplus iodide.

$$I_2 + I^{-} \leftrightarrow I_3^{-1}$$

This complex was titrated with sodium thiosulphate using starch as an indicator.

$$I_3^{-} + 2S_2O_3^{-2} \rightarrow 3I^{-} + S_4O_6^{-2}$$

Thiosulphate used in the sample analysis was standardized using KIO_3. The standardization reaction is based on a reaction of iodide with iodate resulting in the formation of iodine under acidic conditions,

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + H_2O$$

which in turn was bound by the formation of the iodide-iodine complex by reacting with surplus iodide. The iodide complex was titrated against thiosulphate according to the reactions shown above.

2.2.3 Nutrients (Nitrate)

Nitrate was measured using the SKALAR (model 5100-1) autoanalyser (segmented flow analysis). In this the nitrate was reduced using a Cu-Cd reductor column to nitrite, which was then made to react with sulphanilamide and N-(1-napthyl)- ethylenediamine dihydrochloride to form an azo dye. The extinction of the dye solution so formed was measured at 540 nM. Sets of standard have been run both before and after with each batch of samples.

2.2.4 Chlorophyll a

A known volume of seawater sample (0.5 to 1 litre for coastal and estuarine samples or 2 to 3 litres for open ocean samples) was filtered through Whatman GF/F filters under low vacuum. Chlorophyll pigments on the filter paper were then extracted in 10 ml of 90% acetone in dark under refrigeration for 24 hours. Fluorescence was measured using a Hitachi spectrofluorometer [*UNESCO,* 1994]. The chlorophyll data obtained through the acetone extraction method were used to calibrate the fluorescence sensor that was utilized for continuous profiling along with the CTD system.

2.2.5 DMS and DMSP in seawater, aerosols and sea surface microlayer

2.2.5.1 Standardization of DMS measurements

A semi-automated sampling system (Fig. 2.4) was used, to avoid atmospheric exchange during sub-sampling, similar to the one designed for total carbon dioxide analysis [*Sarma*, 1998] during the Joint Global Ocean Flux Study (India) Programme. A known volume of standard or seawater was purged (15 min) using dry nitrogen and the released sulphur gases were passed through moisture traps (ice bath, glass wool and potassium carbonate). These traps were replaced very frequently. The sulphur gases were cryogenically (liquid nitrogen) trapped in Teflon column. The column was then transferred to a water bath, maintained at >80°C, for elution of the trapped gases. Separation was done on a Teflon column packed with Chromosil 330 [*Turner et al.*, 1990; *Shenoy et al.*, 2000]. The oven and detector temperatures were 40°C and 150°C, respectively. The carrier gas flow was 35 ml min^{-1}. DMS retention time was found to be about 3 minutes under these conditions.

A DMS primary standard was made gravimetrically using DMS liquid (Merck) and ethanol (Fluka). Subsequent dilutions were done in Milli-Q water (20 megohm). The calibration curve was run for a DMS concentration range of 0.0044 to 0.65 nmol (Fig. 2.5). The detection limit for DMS measurements, found as twice the standard deviation from regression analysis for values <0.1 nmol, was 0.012 nmol. The accuracy (recovery checked with known standards), on an average, at lower DMS levels of <0.1 nmol was 86%

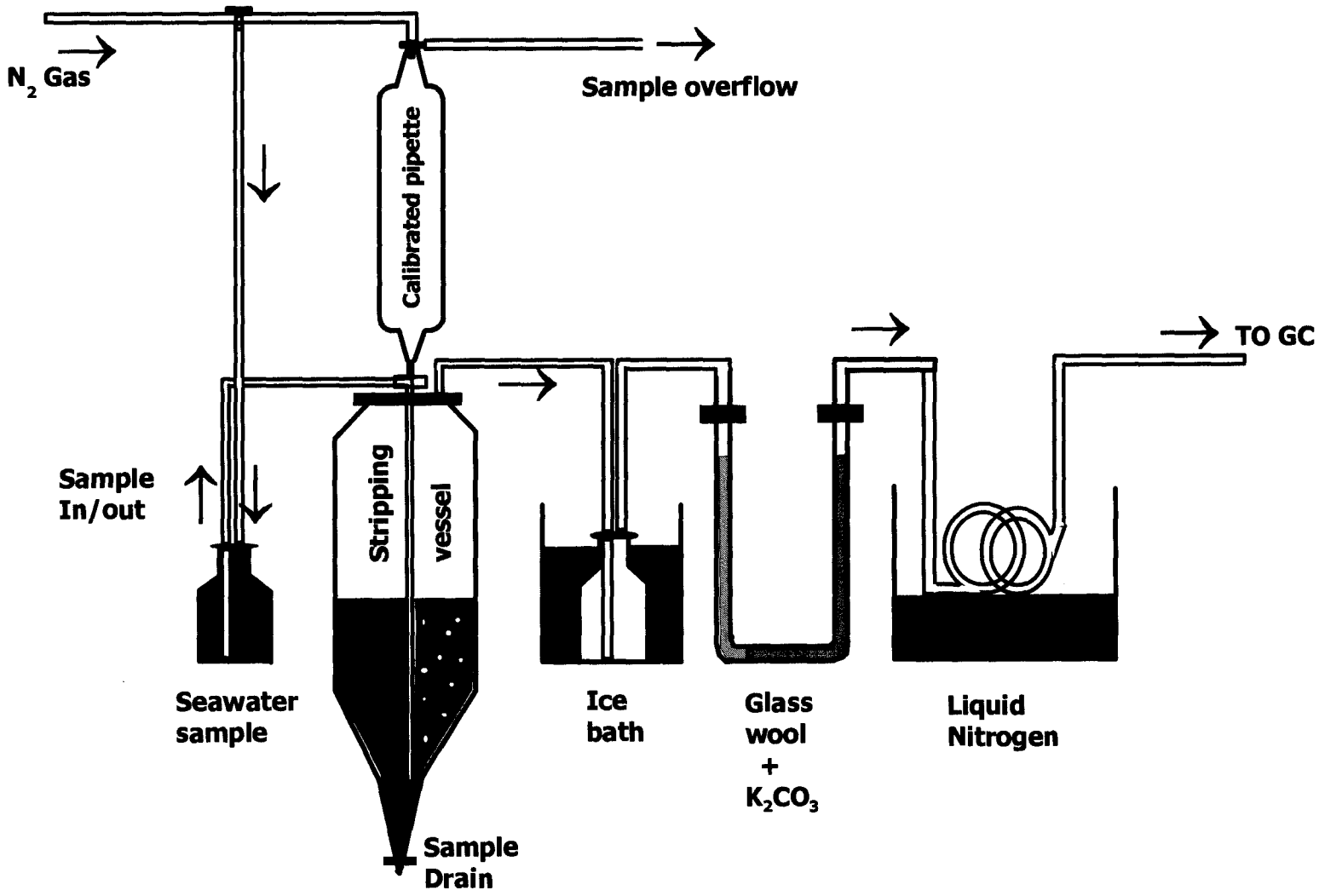


Fig. 2.4 Schematic diagram showing semi-automated device used in DMS and DMSP analysis

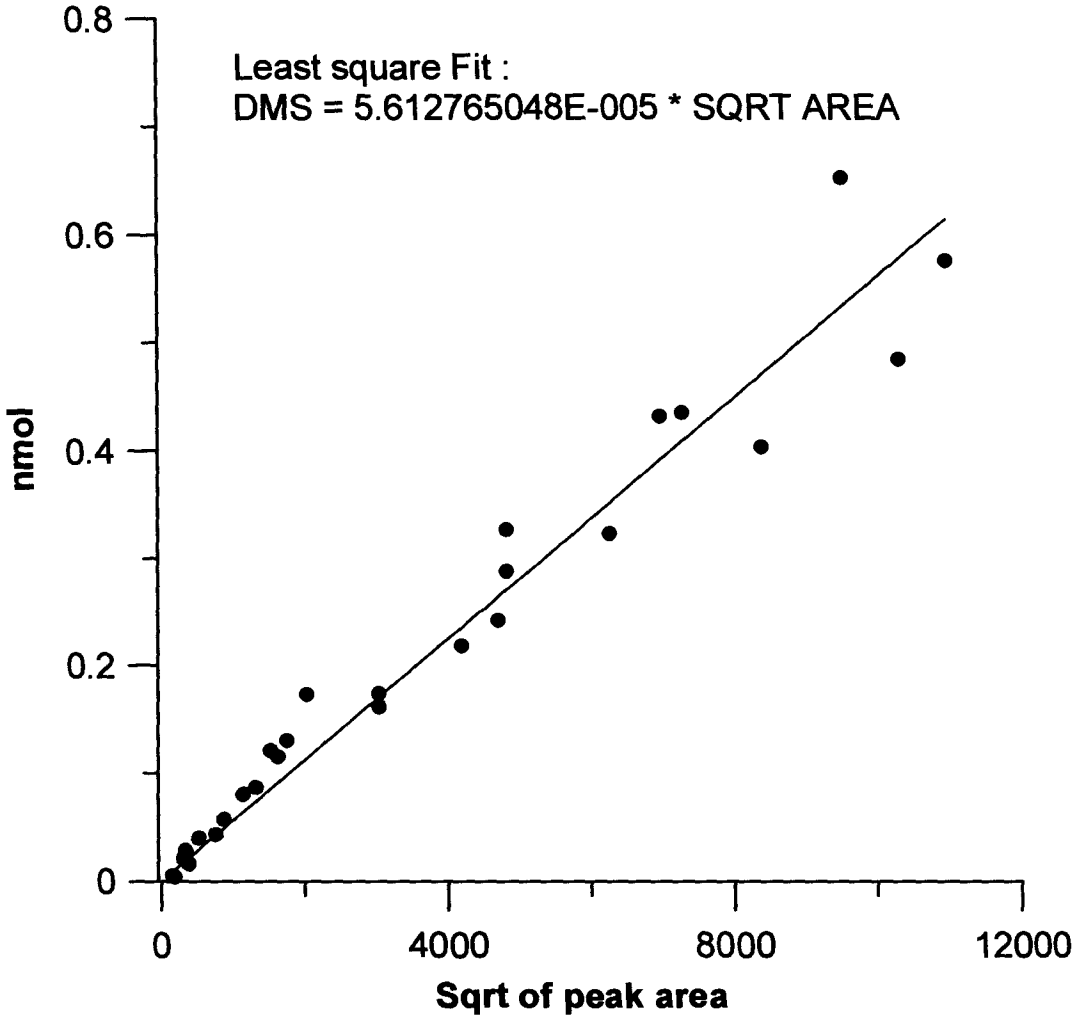


Fig. 2.5 Calibration curve found between dimethyl sulphide concentrations and square roots of the peak areas under the experimental conditions detailed in the text.

whereas it was about 93% for levels up to 0.7 nmol. Precisions (reproducibility determined from replicate analyses of same standard) in DMS measurements were found to be 6% for standards.

2.2.5.2 DMS and DMSP in seawater

Water samples for DMS and DMSP analyses were collected, from Niskin bottles, in to separate 60 ml dark ground glass bottles. Water samples were not filtered for two reasons: first even with extreme care DMS losses cannot be prevented during the filtrations, and second the filtration can alter the contents of DMSP in plankton and/or in water due to cell rupture under vacuum. Thus the concentrations reported here refer to total DMS and DMSP. Following collection the DMS samples were immediately preserved in the dark at 4°C. Starting of analysis immediately after the collection, in fact, enabled us complete the DMS and DMSP analyses within 10 hours. DMS was measured [*Shenoy et al.*, 2000], using a Hewlett Packard 5890 Series II Plus Gas Chromatograph fitted with a flame photometric detector (FPD). Immediate repeat analysis of an analysed aliquot showed no detectable signal of DMS indicating its negligible production from DMSP, if any, during the stripping process. DMSP was measured after hydrolysing the unfiltered water sample for six hours using 10 M NaOH (1 ml) [*Turner et al.*, 1990; *Shenoy et al.*, 2000], which was added immediately after sample collection. Alkali hydrolysis resulted in the cleavage of DMSP into DMS and acrylic acid. DMSP concentrations were read from the DMS calibration curve. Tests revealed 95%

conversion of DMSP to DMS during the alkali hydrolysis for 6 hours. Precision of seawater DMS analysis is found to be 8-10%.

2.2.5.3 DMS and DMSP in sea surface microlayer

Sea surface microlayer samples were sampled using the glass plate technique [*Harvey and Burzell*, 1972; *Carlson*, 1982, 1983; *Hardy*, 1982]. A glass plate (28 x 28 x 5 cm) was dipped vertically through the water surface and withdrawn. The seawater adhered to the glass plate was scraped from both sides using an acrylic plate that has a plastic edge, for quantitative removal. The microlayer sample was drained into a bottle. The sampling was done as soon as possible to minimise the loss of DMS. The sea surface micro-layer thickness was calculated using the number of dips, total surface area of the glass plate and the total volume of seawater collected.

$$\text{Micro-layer thickness} = \frac{\text{Total volume collected from n number of dips}}{\text{Surface area of glass plate x total number of dips}}$$

The analyses for DMS and DMSP were performed as detailed above.

2.2.5.4 DMS and DMSP in aerosols

Aerosol samples were collected using GF/F Whatman filters (47 mm in diameter) under vacuum from a height of about 6 m above the sea surface. As both DMSP and DMS are natural in origin contamination of samples from ship's emissions does not occur. The aerosol samples, collected from known volumes (about 2 to 80 m^3) of air, were immediately transferred to the stripping vessel and analyzed first for DMS and later for DMSP [*Kumar et al.*, 2002]. To facilitate stripping the filter was wetted with Milli Q water. The DMS

analyses were performed using the method prescribed above. Subsequently the same aerosol sample was hydrolyzed with alkali (2 ml of 10 M NaOH) and analyzed for DMS again after purging for 20 minutes. The latter step yielded concentration of DMSP in terms of DMS. These methods were the same as those used for analyses of DMS and DMSP in seawater [*Turner et al.*, 1990; *Shenoy et al.*, 2000].

2.2.6 Phytoplankton speciation and enumeration

A known volume (500 ml for coastal samples and 1 litre for open ocean samples) of phytoplankton samples was fixed with Lugol's iodine for enumeration by sedimentation technique [*Hasle*, 1978]. The bottles were kept for sedimentation for >24 hours. The top part was decanted reducing the volume to 200 ml. Aliquots were sub-sampled for analysis by using light microscope.

2.2.7 Bacterial abundance

For enumeration of bacteria water samples were fixed with 1 ml of formaldehyde (2% final concentration) and refrigerated. In the laboratory, samples were stained with florescing DNA stain, 4,6-diamidino-2-phenylindole (DAPI). These samples were filtered onto black stained 0.2µm Nuclepore filters [*Porter and Feig*, 1980]. Up to 25 microscopic fields were counted for bacteria using non-fluorescent oil immersion objectives (100X) in an Olympus BH2 epifluorescence microscope.

2.2.8 Wind Speed

Wind speeds used in the DMS flux calculations were collected using automatic weather station (AWS) on board the research vessels and on top of the institute building. Wind speed was measured using Young's wind monitor (model 05103). The sensor is an 18 cm diameter 4-blade helicoid propeller moulded of polypropylene. The wind speeds were corrected for height (were brought to 10 m level) and direction.

2.2.9 UV (TOMS) data

Incident UV radiation (J m^{-2}) at sea surface was retrieved from the Total Ozone Mapping Spectrometer (TOMS) data made available by Ozone Processing Team (OPT) of NASA Goddard Space Flight Center, at *http://jwocky.gsfc.nasa.gov*. The UV listed by OPT is for 300-400 nm range that comprises full UV-A (400-320 nm) and two-third of UV-B (320-290). Averaging has been done for UV data (listed for every 1° latitude and 1.25° longitude) available at four corners bordering each oceanographic station for better representation of incident radiation over the region.

2.3 Methodology - Computational

2.3.1 DMS Flux

DMS fluxes were calculated using the formulations proposed by *Turner et al.* [1996] using the correction factors given by *Saltzman et al.* [1993]. The flux of DMS gas from sea to air is proportional to the concentration gradient across the air sea interface and is calculated according to the following equation.

$F_{DMS} = k \cdot \Delta C$

Where F_{DMS} = net flux of DMS

k = transfer (or piston velocity) and

ΔC = concentration gradient across the air-sea interface.

$\Delta C = C_w - (C_a \cdot H^{-1})$

Here C_w = concentration of DMS is seawater

C_a = concentration of DMS in air

H = Henry's law constant, expressed as the ratio of air to water concentrations at equilibrium.

As the concentration of DMS in air is very low (nearly three orders of magnitude less than that in water) C_a is generally considered to be zero and thus C_w is equal to ΔC.

2.3.2 Mixed layer depth (MLD)

Mixed layer depths were calculated based on temperature and density criteria. In case of temperature we have considered two temperatures (i.e. 1°C and 0.5°C) and defined the depths at which there were decreases in temperature by 1°C or 0.5°C with reference to the sea surface temperature. In case of density criterion MLD was defined as the depth at which density increased by 0.125 kg dm^3 with reference to that of sea surface.

CHAPTER 3

Hydrographic Features

Chapter 3

Hydrographic Features

This chapter discusses the distributions of hydrographic properties (temperature, salinity, density, dissolved oxygen and nitrate) during different seasons in the northern Indian Ocean

3.1 The Arabian Sea

3.1.1 Northeast monsoon (January, 1998; SS161)

During the northeast monsoon (November to February) the surface circulation in the Arabian Sea is quite similar to the circulation in the North Pacific and Atlantic. North of equator the flow is from the east to west. Close to the coast (west coast of India) the surface circulation is pole ward. The west India coastal current (WICC) is an extension of the East India coastal current (EICC) that brings in low saline waters from the Bay of Bengal into the southeast Arabian Sea [*Shetye,* 1998]. Off the coast of Oman and Somali the circulation is towards the equator.

During January 1998, the atmospheric temperature north of 17°N was less than 24°C. Such low atmospheric temperatures lead to low sea surface temperatures (SST) in the study region. The SST in the study region (Fig. 3.1) varied between 24.2 and 27.2°C with an average value of around 25.4°C. The winds during this period were mainly northeasterly with speeds varying from 2.5 to 7 m s^{-1} (average value of 4.4 m s^{-1}). These cool dry winds hold extra

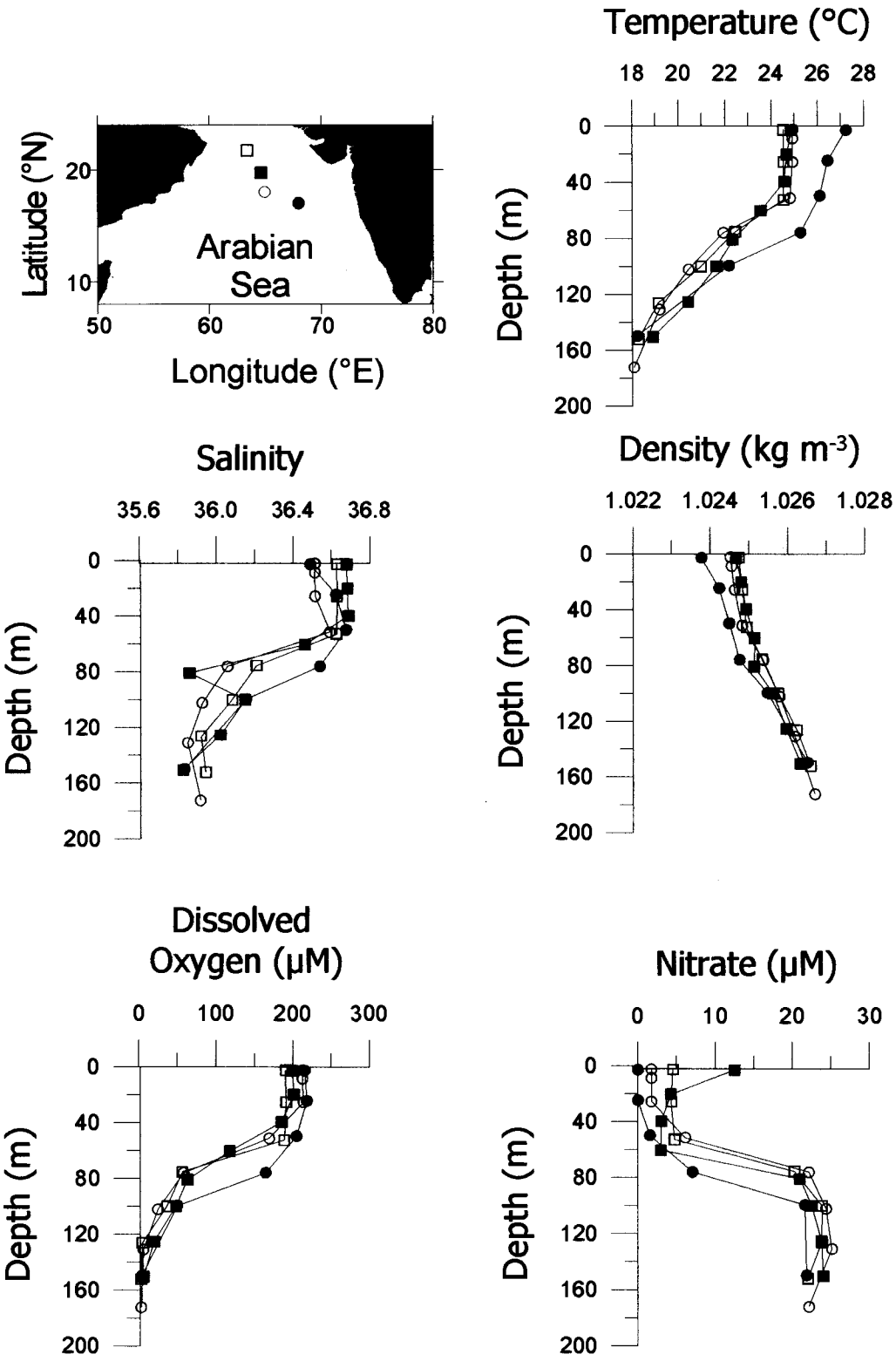


Fig. 3.1 Vertical profiles of temperature, salinity, density, dissolved oxygen (DO) and nitrate in the northern Arabian Sea during northeast monsoon (SS161).

moisture and heat that facilitate enhanced evaporation at the Arabian Sea surface leading to the occurrence of winter convection.

Fig. 3.1 depicts the signatures of winter convection in the study region. Temperature, density and dissolved oxygen profiles show clear differences between stations depending on the intensity of convection from south to north. The sea surface temperature and dissolved oxygen fell from 27.2°C to 24.5°C and from 215.8 µM to 191.1 µM, respectively, while the density increased from 1.0237 to 1.0247. Salinity structure showed higher values in the mixed layer of northern stations indicating intensification of evaporation and consequent sinking of high saline waters. This occurrence of winter convection facilitates the introduction of nutrients into the surface layers (Fig. 3.1). The surface nitrate levels varied between undetectable levels in the south (outside the winter convection zone) and 12.5 µM at 20°N and 65°E. The average surface nitrate in the area where convection occurred was found to be around 4.9 µM. Such high nitrate levels promote primary production. In concurrence with the above statement *Madhupratap et al.* [1996] and *Bhattathiri et al.* [1996] have observed column productivity of around 643 mgC m^{-2} d^{-1} in the northern Arabian Sea.

3.1.2 Southwest monsoon (July-August, 1998; SK137 and September-October, 1999; SK148)

Very high wind speeds are associated with the southwest monsoon. During the present study wind speeds varied between 0.5 and 5.2 m s^{-1} and between 1.3 and 7.9 m s^{-1} during SK137 and SK148 periods, respectively.

The observed wind speeds were in general lower than that expected since speeds > 10 m s^{-1} is common during this season [*Hastenrath and Lamb*, 1979]. Nonetheless upwelling is conspicuous during both the cruises. Figure 3.2 shows the hydrographic features observed near 15°N for SK137 as an example. Shoaling of isotherms is observed very close to the coast. The isotherm of 27°C shoals to 8m near the coast. The low saline cap formed from land runoff prevented surfacing of this isotherm. The upwelled high saline waters (~35.9) were accompanied by low dissolved oxygen (~90 µM) and high nitrate (4-12 µM).

At 8°N the upwelling was more pronounced with the surfacing of 25°C isotherm (Fig. 3.3). The salinity structure suggests mixing of low saline runoff with the high saline upwelled waters. Runoff also seems to bring in high amount of nitrate into the coastal area. In the present case the major part of nutrients was apparently introduced by the upwelled waters since the surface waters were found to contain low oxygen (<100 µM). If the nutrients were of land origin the oxygen levels should have been higher because of effective air-sea exchange.

Similar features were also noticed off 10°N and 12°N. Around 10°N surface temperature was 25.96°C with a salinity of 33.416 and a nitrate concentration of 10 µM while at 12°N surface temperature was 24.14°C with salinity of 34.552 having a nitrate concentration of 15.37 µM. Therefore the major observation during the southwest monsoon was the occurrence of upwelling all along the coast. Closer observation revealed that stations very

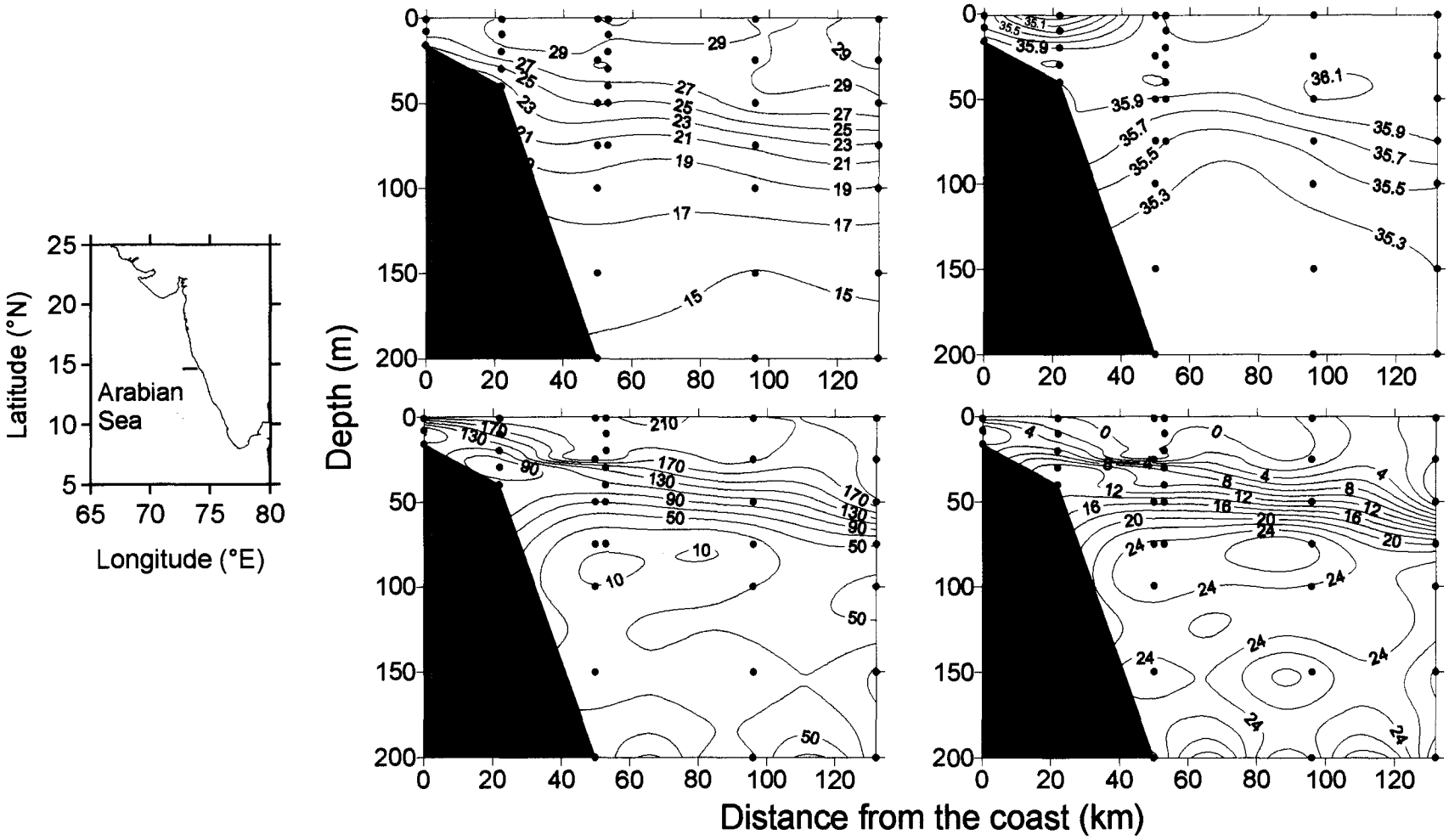


Fig. 3.2. Distributions of temperature, salinity, oxygen and nitrate near 15°N during the southwest monsoon of 1998 (SK137).

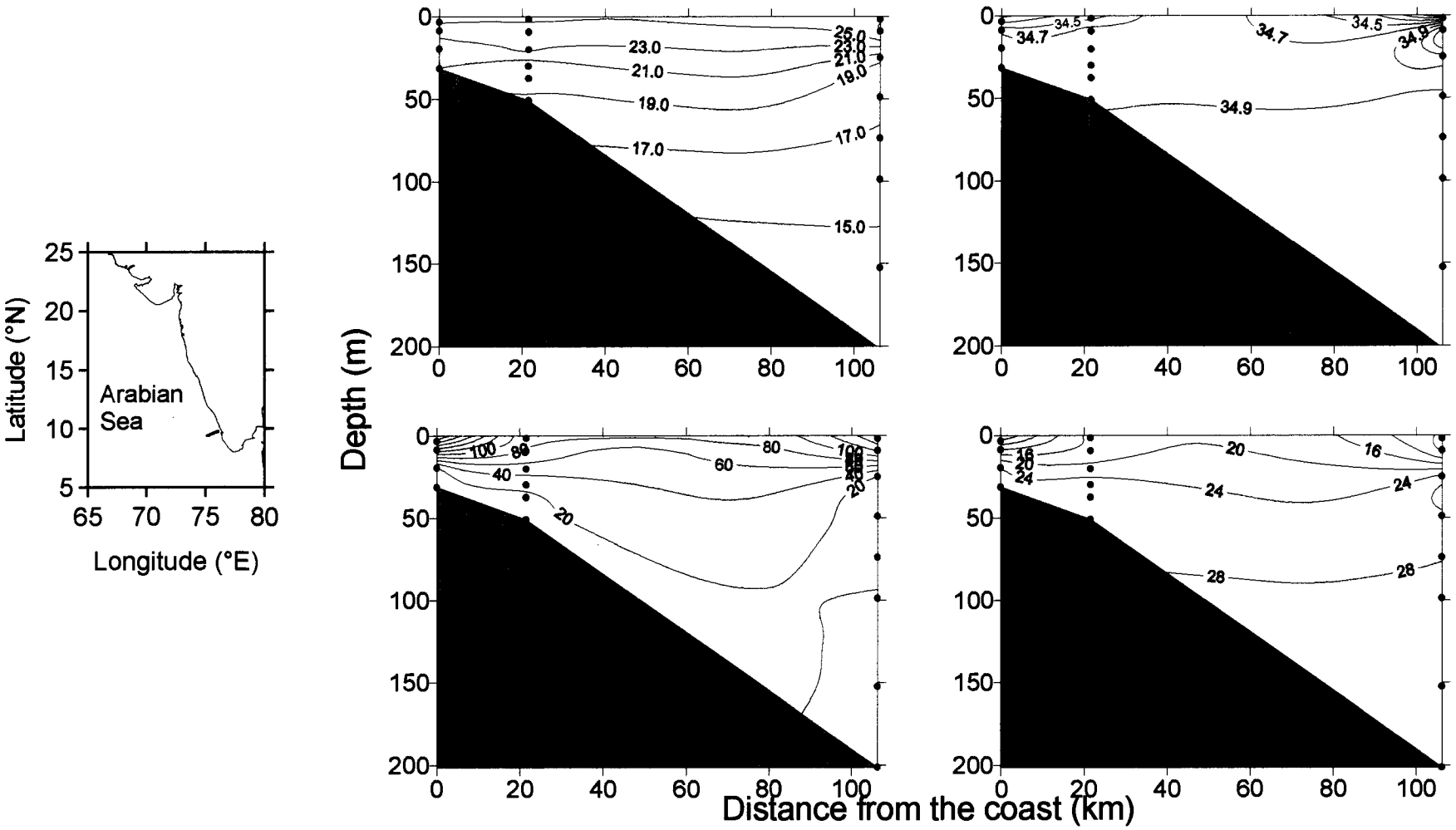


Fig. 3.3. Distributions of temperature, salinity, oxygen and nitrate along the section shown during the southwest monsoon of 1998 (SK137).

close to the coast did not show surfacing of isotherms representing sub-thermocline waters, but away from the coast (~ 20 km). This is caused by land runoff as discussed above. Though upwelled waters rich in nutrients may not have surfaced at many of the places along the coast, their occurrence within the euphotic zone favours intense biological production. Similar hydrographic features were also observed during southwest monsoon in the following year of 1999 (SK148). Study of the hydrographic features in different months of the southwest monsoon season exhibited the extent of temporal variability. The most interesting observation was that of chlorophyll. During SK137; the surface 50 m chlorophyll averaged to 0.6 mg m^{-3} whereas during SK148 it averaged to 2.2 mg m^{-3} indicating the importance of time lag for increased primary production after the monsoonal upwelling.

3.1.3 Fall-Intermonsoon (November, 2000; SK158)

Hydrographic data were presented for tracks near 15°N (Fig. 3.4) and along 72°E (Fig. 3.5). In coastal region wind speeds varied between 2.2 and 12.5 m s^{-1} while in the open ocean speeds varied between 1.8 and 10.2 m s^{-1}. Temperature contours show a stratified structure unlike in the SW monsoon, with the surface temperatures over 28°C (Fig. 3.4). The low temperature isotherms, indicating upwelling which surface during the SW monsoon, are now observed at deeper depths. The salinity distribution shows a low saline patch in surface waters between 50 and 100 km from the coast suggesting the runoff caused by post monsoon showers. Around 130 km from the coast high saline waters were noticed at a depth of 50 m. This shows the beginning of

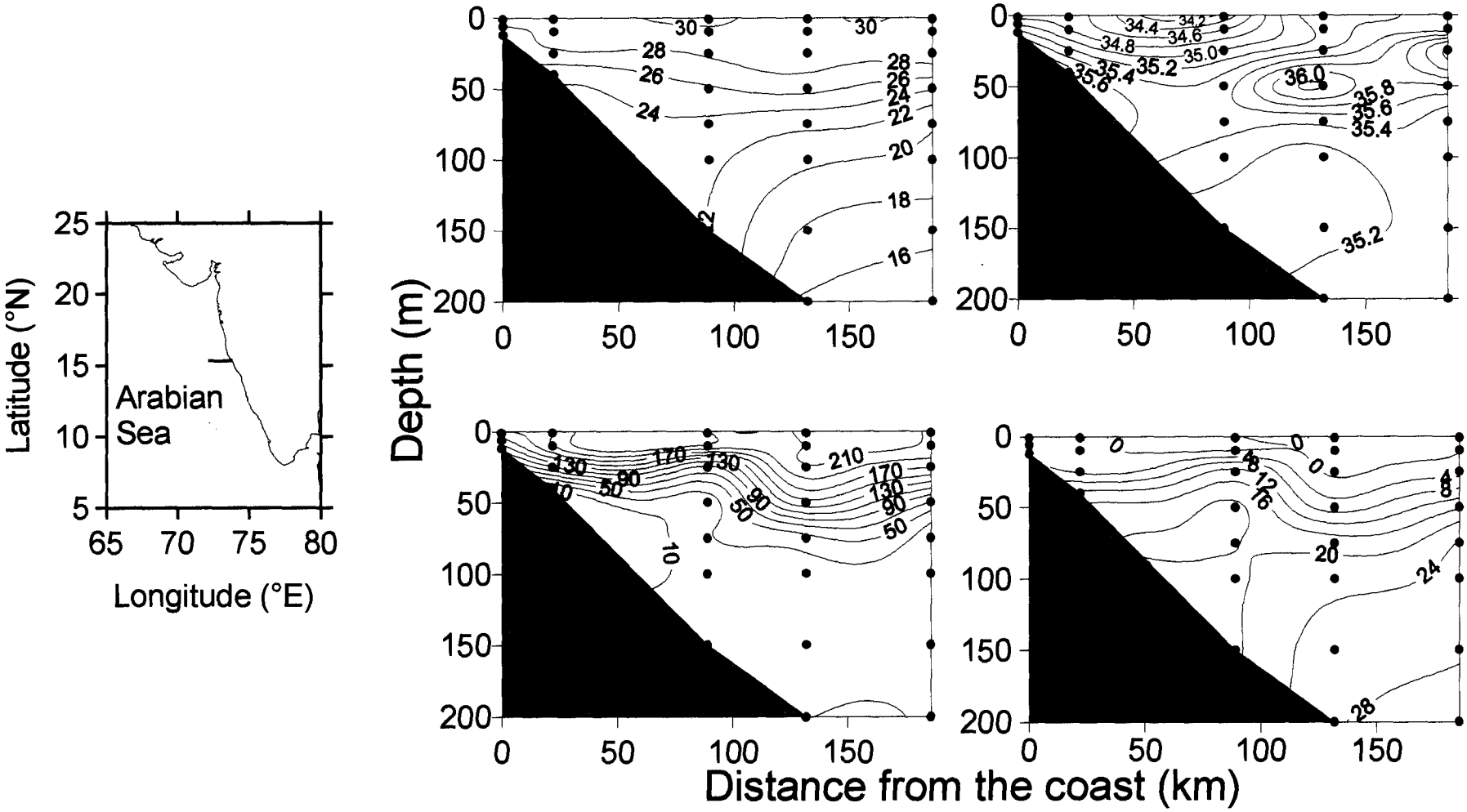


Fig. 3.4. Distributions of temperature, salinity, oxygen and nitrate near 15°N during the fall inter monsoon of 2000 (SK158).

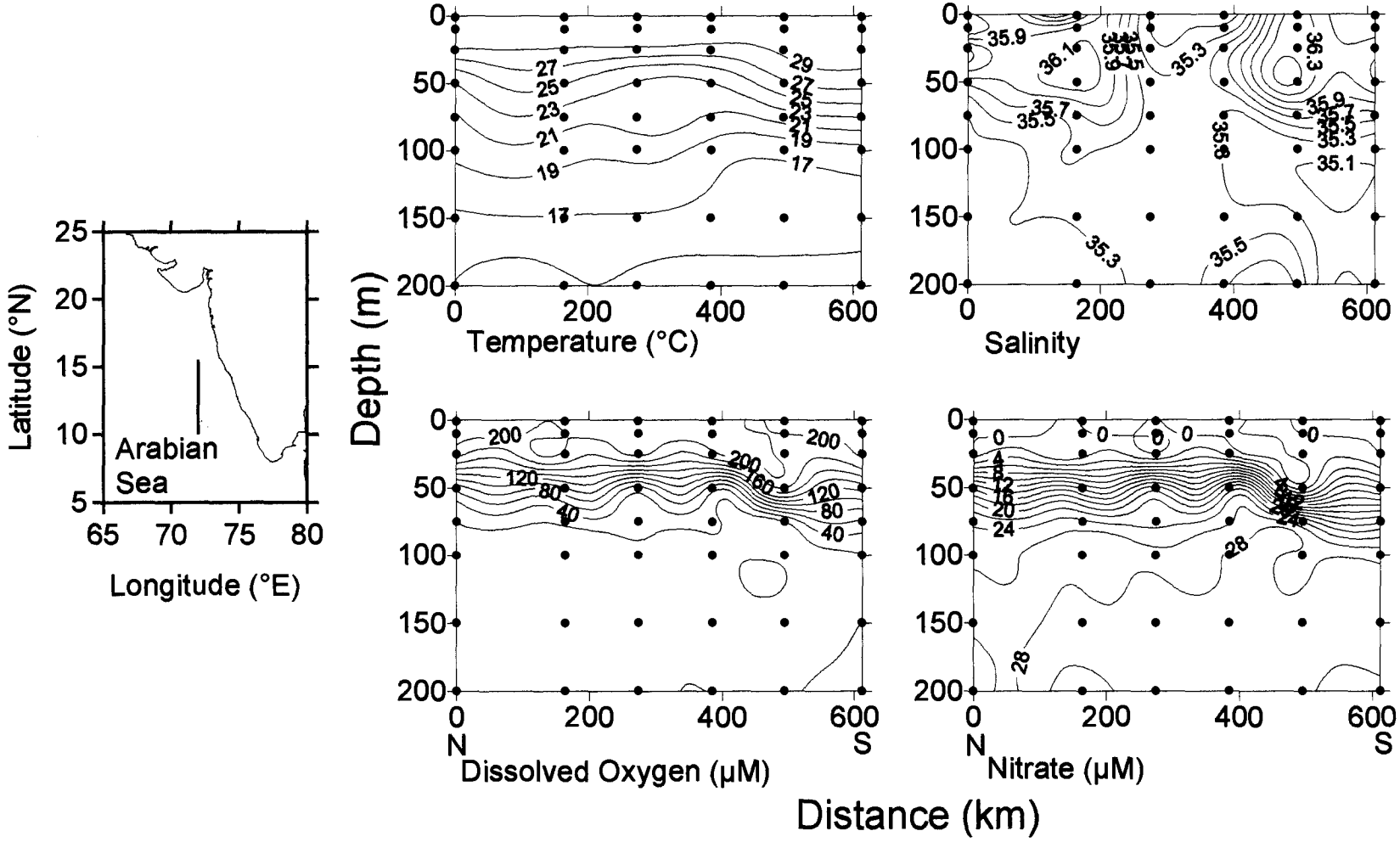


Fig. 3.5a. Distributions of temperature, salinity, oxygen and nitrate along 72°E during the fall intermonsoon of 2000 (SK158).

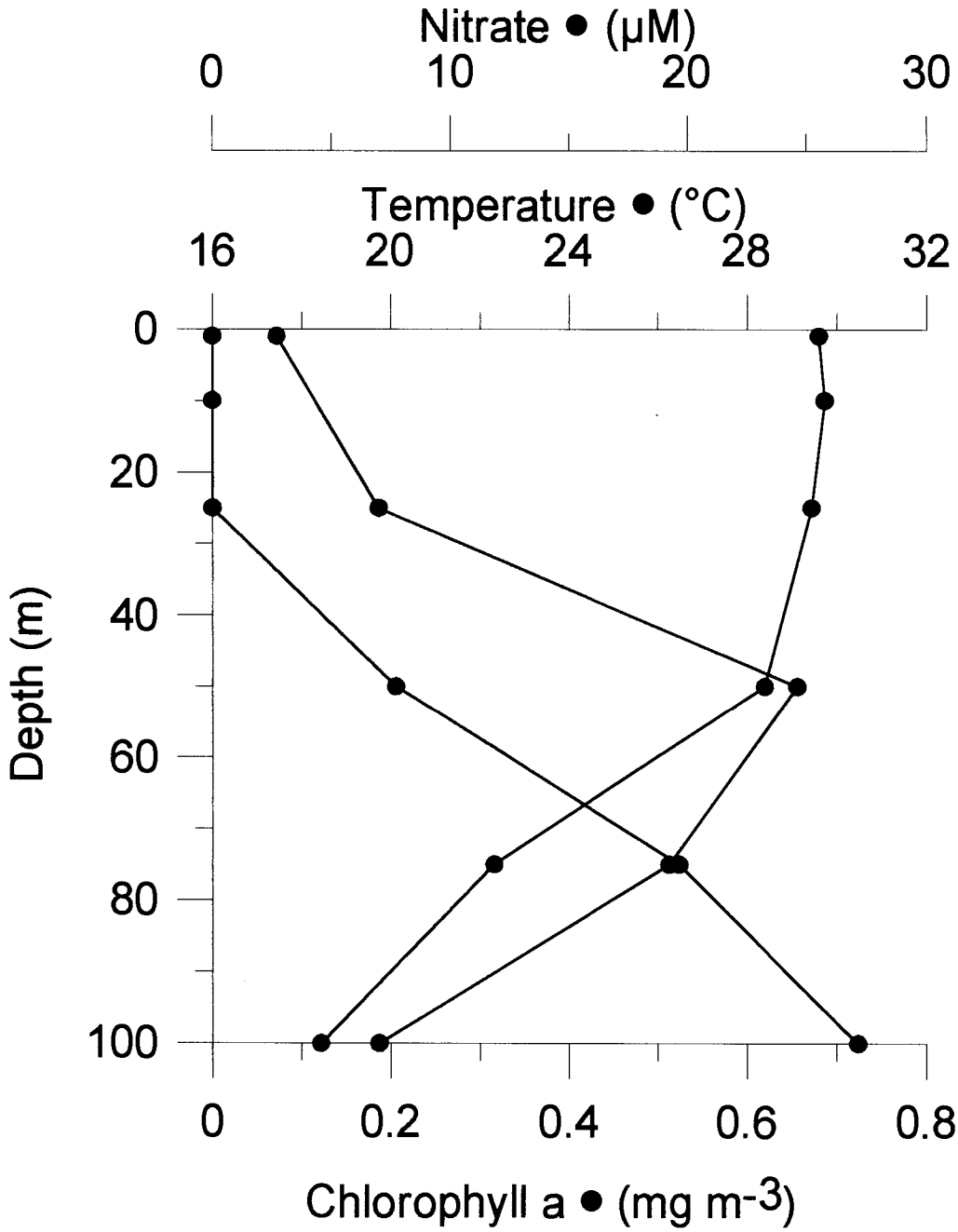


Fig. 3.5b Profiles of temperature, nitrate and chlorophyll (at 9.94°N, 72.44°E, SK158) showing subsurface chlorophyll maxima.

seasonal incursion of ASHSW mass into low saline coastal waters. The 4 µM nitrate isoline was found at 25 m depth (Fig. 3.4), whereas the same had surfaced during the southwest monsoon (Fig. 3.2).

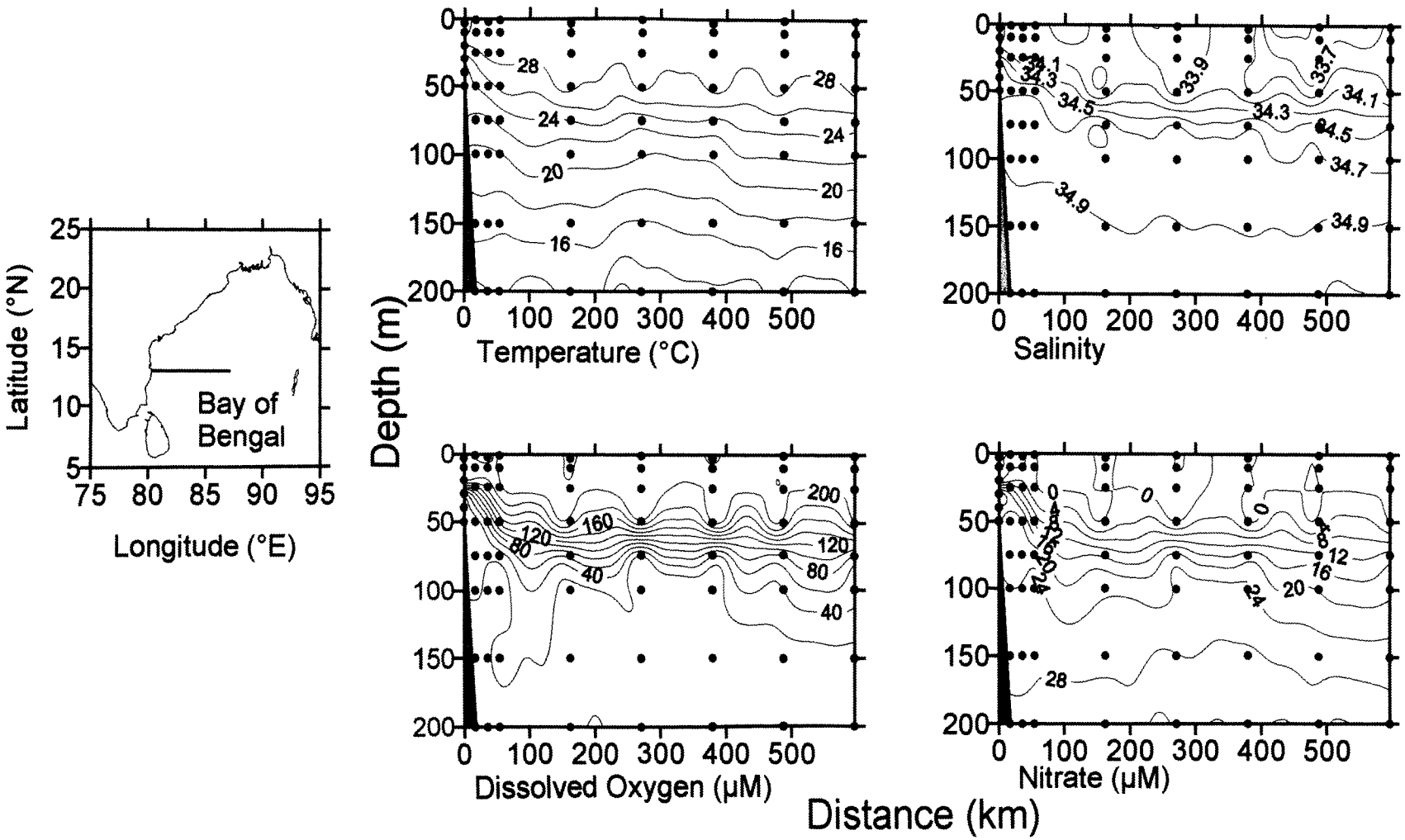
Temperature profile shows a stratified structure. In the upper 50 m the temperatures varied between 23.3°C and 29.7°C with the MLD deepening slightly towards the south (Fig. 3.5a). In contrast to the stratified temperature distribution salinity showed a low saline front at 12°N (35.300 at 300 km). Oxygen also shows a stratified structure with values at ~200 µM in the surface layers but decreased to around 80 µM around 50 m depth. There was no nitrate in the upper 10 m, but increased to the base of the MLD. One of the prominent features of the fall-intermonsoon was the occurrence of high nitrate levels near the base of MLD, but within the euphotic zone. This gives rise to subsurface chlorophyll maximum [SCM, *Bhattathiri et al.,* 1996]. In the present study the SCM was found to occur between 40 and 60 m (Fig. 3.5b).

3.2 Bay of Bengal

In the present study coastal regions off the east coast of India (off Chennai and Paradip) and a stationary position (time series measurement for nearly a month) in the northern Bay have been covered during the southwest monsoon (July-August, SK147) while open southern Bay of Bengal was occupied during fall-intermonsoon (October-November, SK138C).

3.2.1 Southwest monsoon (July-August, 1999; SK147)

The transect off Chennai (Fig. 3.6) shows surface stratification, which is reflected in all properties. Closer to the coast upward sloping in contours is



3.6 Distributions of temperature, salinity, oxygen and nitrate along 13°N during the southwest monsoon of 1999 (SK147B).

obvious that suggest surfacing of isolines The 28°C isotherm reached the surface near the coast, whereas the same was found at 40-50 m depth further from the coast. The lowest oxygen found in the upper within 50 m was 108.37 µM indicating the influence of possible upwelling, as can be seen from upward sloping in contours. This process during the southwest monsoon introduces nutrients into the euphotic layers. In the upper 50 m nitrate varied between undetectable levels and 23.3 µM.

In contrast to this the transect off Paradip (Fig. 3.7) shows a low saline cap with a salinity variation between 24.581 and 32.962 in the upper 25 m clearly indicating the influence of runoff during the SW monsoon season. The temperature showed clear layering all along the transect with no signs of upwelling near the coast. Surface oxygen levels were higher by 20 µM in comparison to the levels off Chennai coast. Nitrate profiles also showed a stratified structure with the nutricline occurred around 40 m.

The time series observation in the northern Bay was divided into two phases; Phase I was from 16th July to 8th of August and phase II was from 10th to 31st of August. Phase I was convectively more active in comparison to Phase II. This was due to a deep depression at the head Bay. Wind speeds varied between 6 and 18.2 m s^{-1} with an average value of 11 m s^{-1} in phase I while in phase II it varied from 4 to 12 m s^{-1} with a mean value of 7.8 m s^{-1}. Phase I also experienced good amount of cloud cover. Figure 3.8a shows variations in temperature, salinity and dissolved oxygen during the time series experiment. Temperature profiles did not show much variation exhibiting

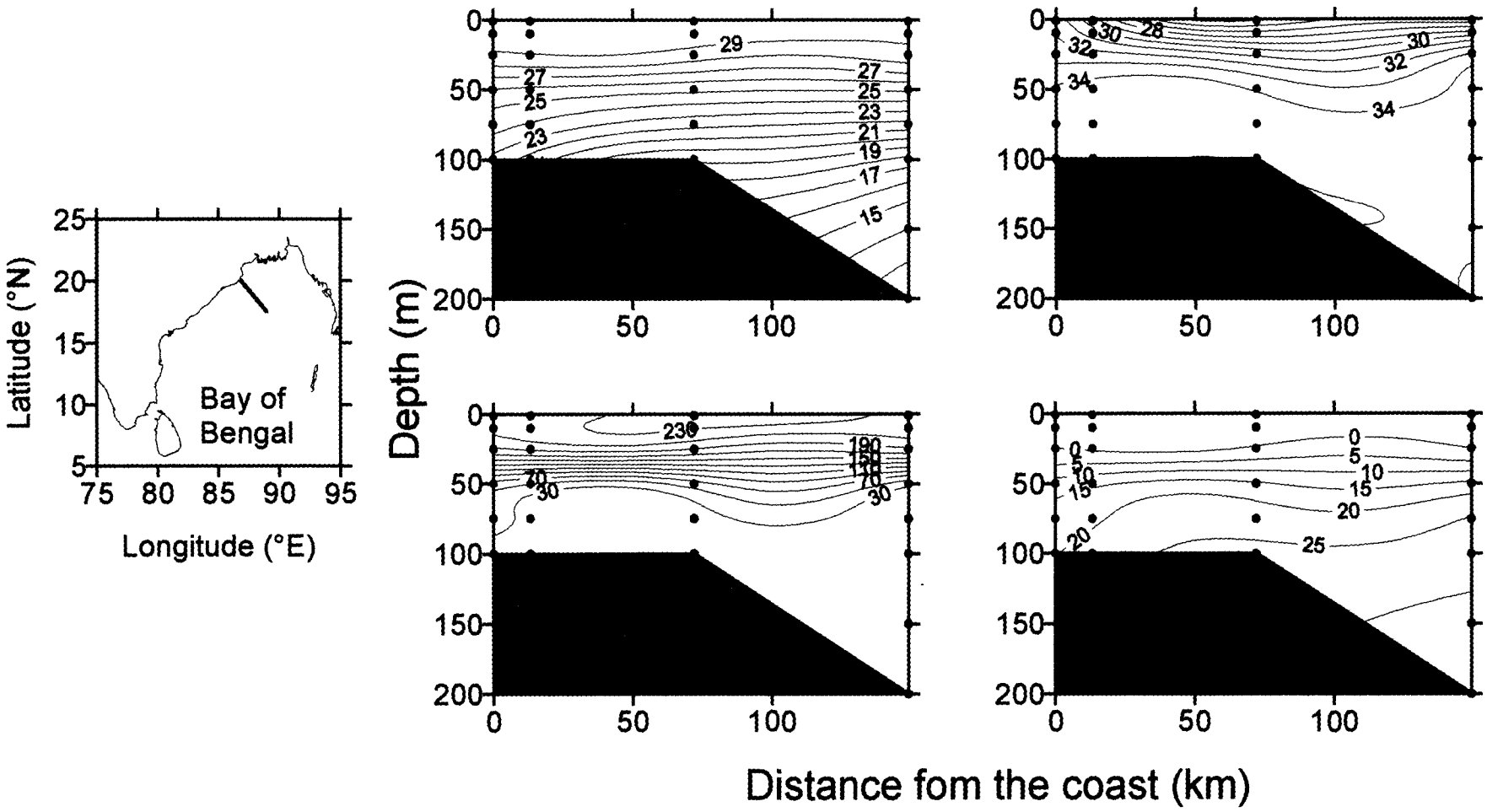


Fig. 3.7 Distributions of temperature, salinity, oxygen and nitrate off Paradip during the southwest monsoon of 1999 (SK147B).

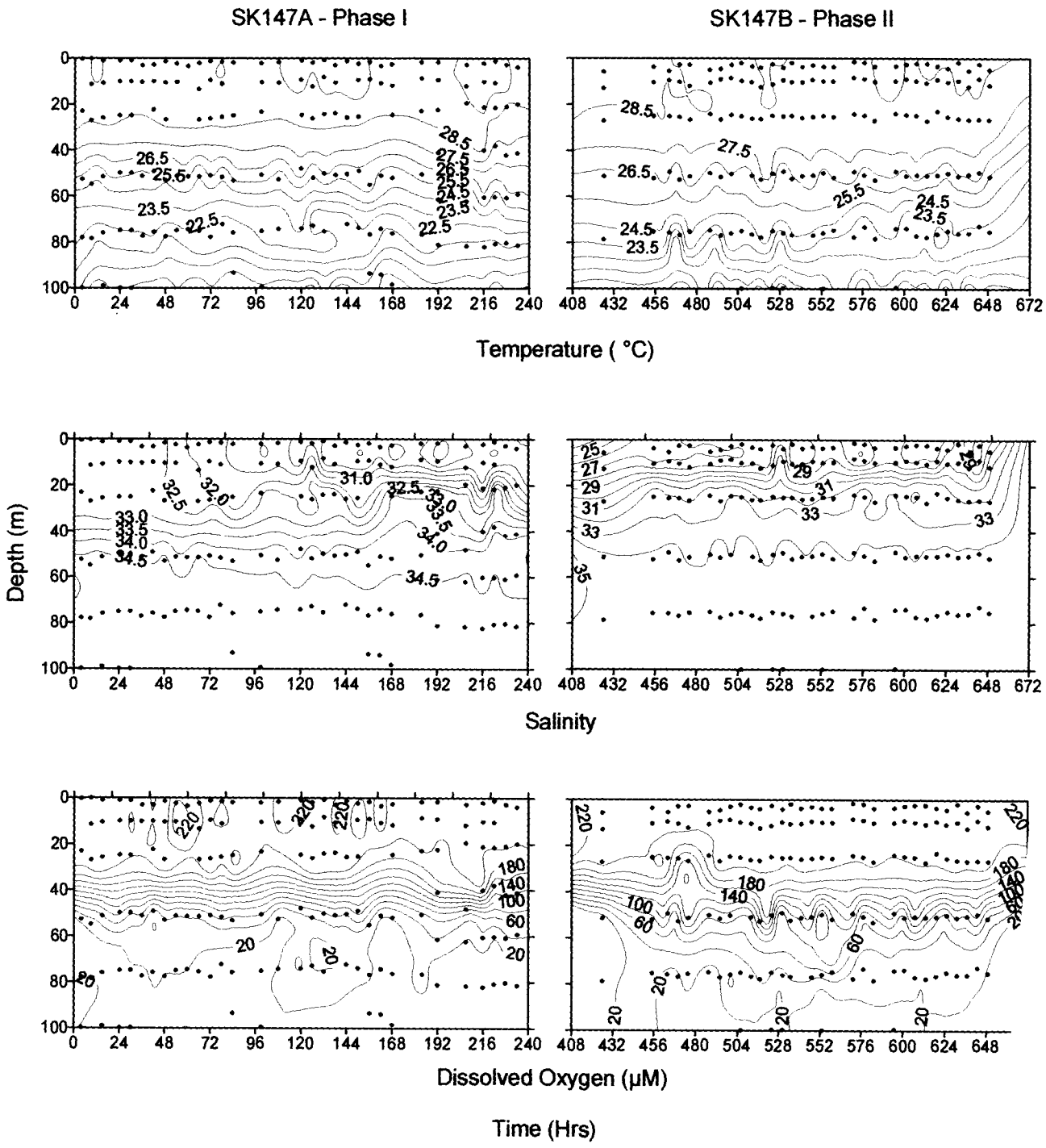


Fig. 3.8a Variations in temperature, salinity and dissolved oxygen at the time series station (17.5°N and 89°E) during the southwest monsoon of 1999 (SK147A&B). Station location is shown in Fig. 2.1.

persistent stratification. Surface (upper 20 m) temperatures were around 28.5°C during both the phases. On the other hand salinity exhibited significant variability. During phase I a flow of low saline water was found at the time series location at the beginning of the fourth day. Prior to the entry of these low saline waters the surface salinity (upper 20 m) in the study area varied between 32.586 and 32.648. With the incursion of the low saline water the salinity decreased to as low as 27.000. The low saline cap remained throughout phase II also, during which the surface salinity decreased further to 24.000. Associated along with the low saline cap were pockets of very high oxygen levels (~220 μM); which otherwise was around 200 μM. The high oxygen pockets were found to be associated with high wind speeds indicating the extent of turbulent mixing. According to *Vinaychandran et al.* [in press] the arrival of the fresh water plume divides the upper 30 m in to a two layer in which the top 15 m layer moves southward under the influence of Ekman flow and the lower geostrophic layer moves northward. Under these conditions upward pumping of nitrate occurred. Nitrate levels of ~10 μM were found at 10 m depth during phase I (Fig. 3.8b). This phenomena is responsible for upward pumping of nutrients throughout the first phase. Phase II also experienced a similar feature, but the extent is somewhat suppressed due to the existence of intense fresh water cap. Surface as well as mixed layer depth averaged chlorophyll levels were affected by changes in UV levels. Low levels of UV were associated with high chlorophyll and vice-versa (Fig. 3.9). Surface chlorophyll during phase I varied between 0.2 and 0.65 mg m^{-3} and between

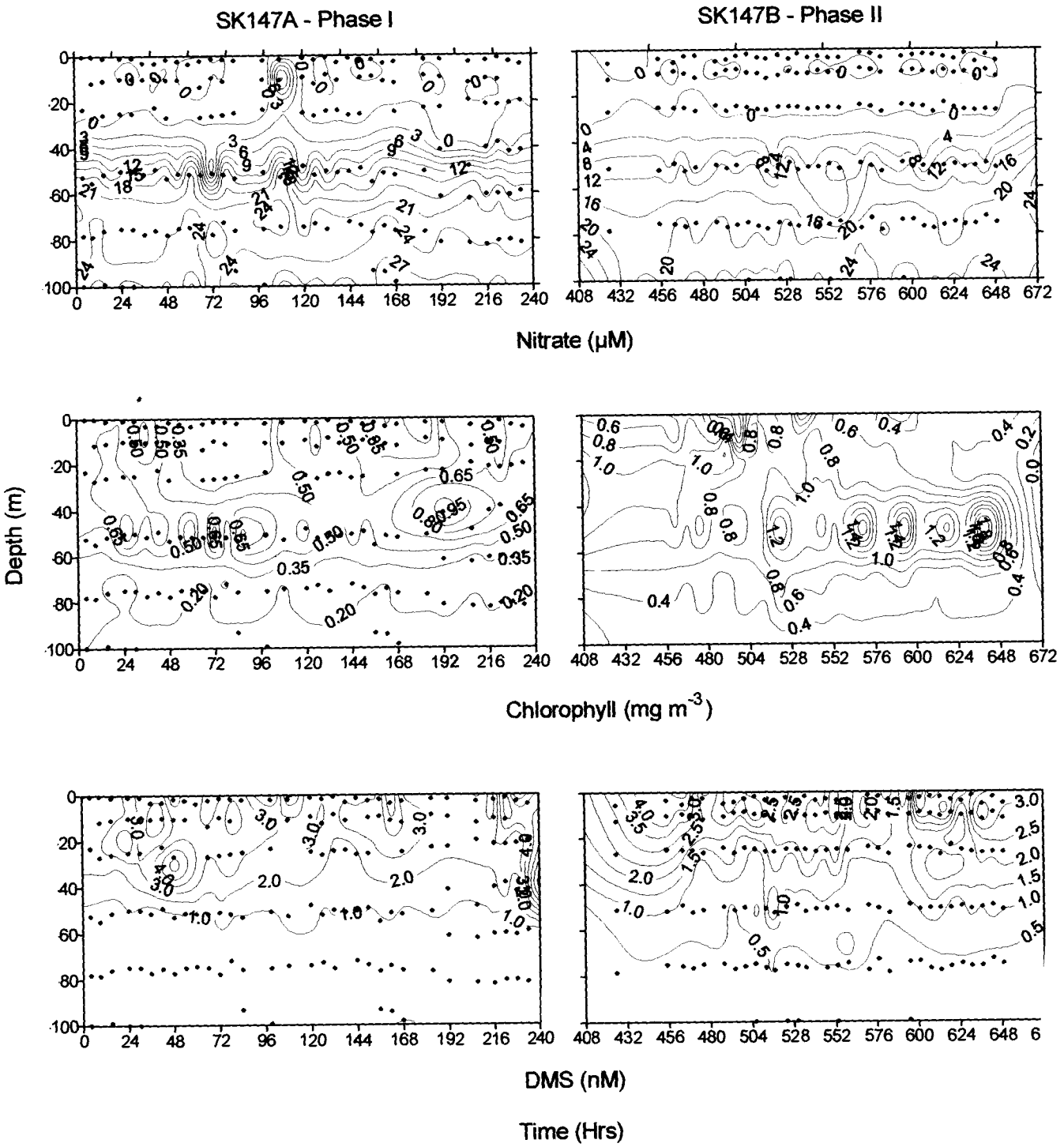


Fig. 3.8b Variations as in Fig. 3.8a but for nitrate, chlorophyll and DMS.

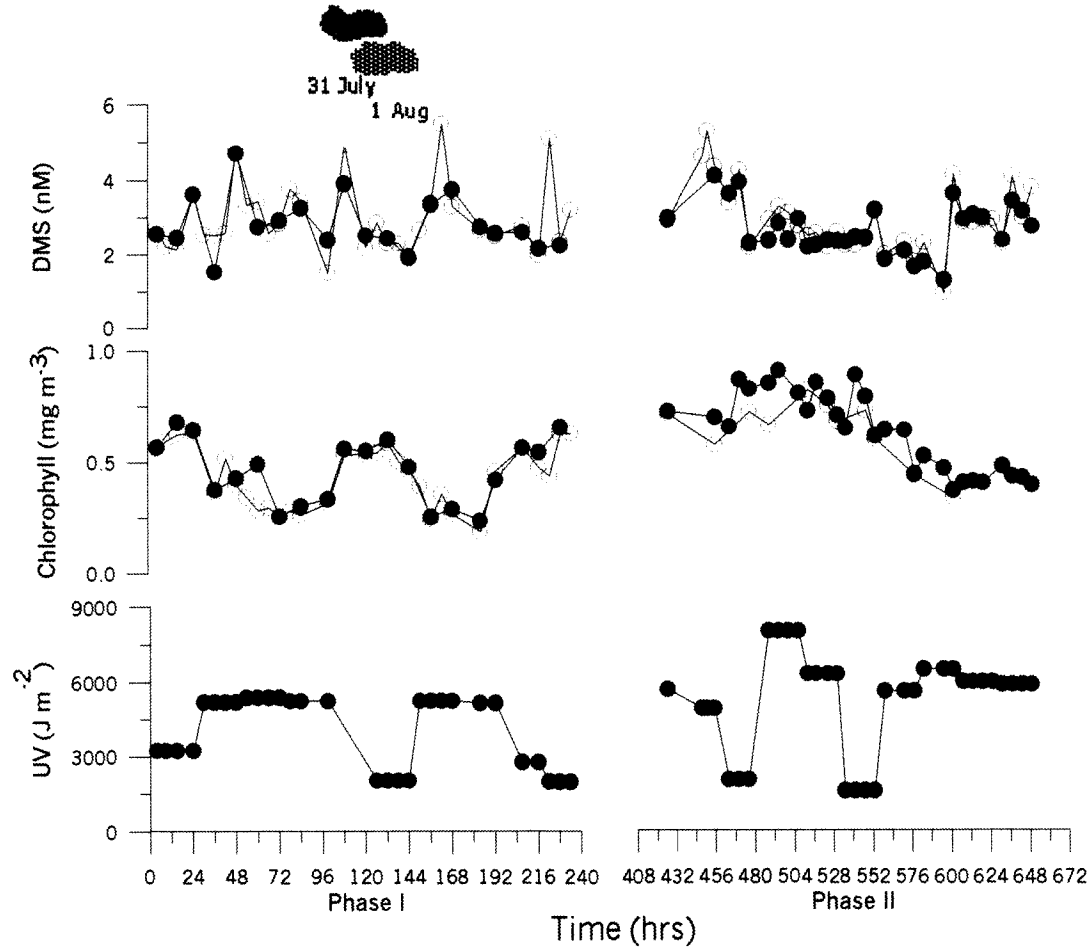


Fig. 3.9 Variations in DMS, chlorophyll and UV radiation at 17.5°N and 89°E during the southwest monsoon of 1999 (SK147A&B); open symbols indicate surface values and bold symbols indicate MLD averaged values. The weather was cloudy during 31 July – 1 August 1999.

0.3 and 0.83 mg m^{-3} in phase II. Chlorophyll maxima were found to occur between 40 and 60 m with higher levels during phase II than in phase I.

3.2.2 Fall-intermonsoon (Oct-Nov, 1998; 138C)

Figure 3.10 depicts variations in temperature, salinity, dissolved oxygen, nitrate and chlorophyll along 87°E in the southern Bay of Bengal. The temperature distribution shows more or less a stratified structure with a variation of 28 – 29.5°C at the surface (upper 25 m). Towards the north deepening of the MLD could be seen based on property distributions. Salinity profile showed the expected trend, i.e. a decrease in salinity towards north. Dissolved nitrate showed downward sloping towards the north. Low oxygen waters (~120 µM) with high nitrate (~8 µM) were observed to shoal upto 20 m at 7°N. The chlorophyll shows a typical high nitrate low chlorophyll (HNLC) situation at 20-40 m, at the southern end and an exactly opposite situation in the north.

3.3 Central Indian Ocean

3.3.1 Northeast monsoon (Feb-March, 1998, SK133; Jan-Feb, 1999, SK141)

One of the important features of hydrographic regimes in the Indian Ocean is the occurrence of a front that forms as a result of North and South equatorial current systems [*Wyrtki*, 1973]. During the period of First Field Phase (FFP '98) the water column hydrography seems to be well stratified (Figure 3.11a&b). Trough like features in temperature, oxygen and nitrate near equator appear to be related to the countercurrent moving from west to

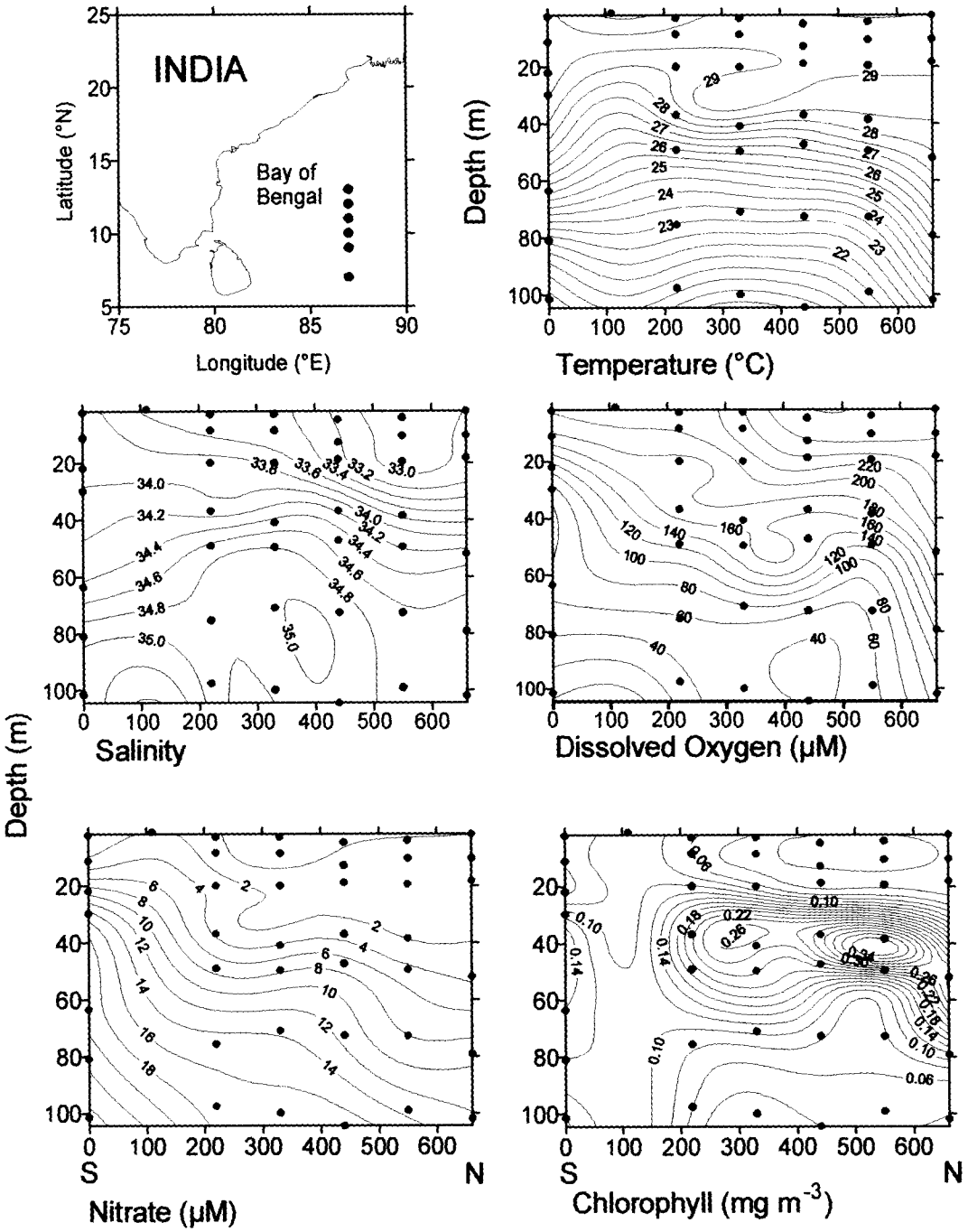


Fig. 3.10 Variations in temperature, salinity, dissolved oxygen, nitrate and chlorophyll along 87°E during the fall intermonsoon of 1998 (SK138C).

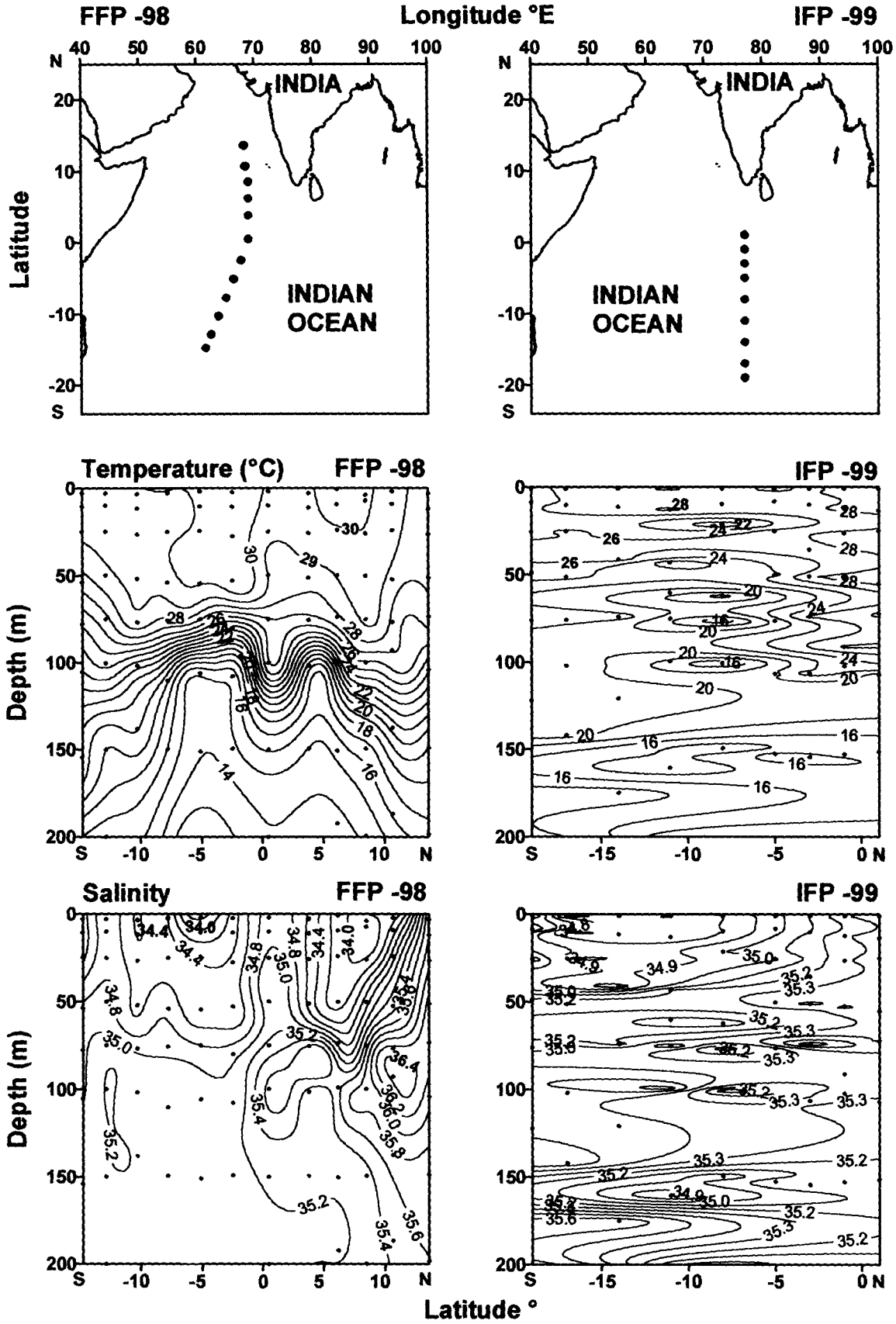


Fig. 3.11a. Variations in temperature and salinity during FFP - 98 and IFP - 99 of the INDOEX Experiment.

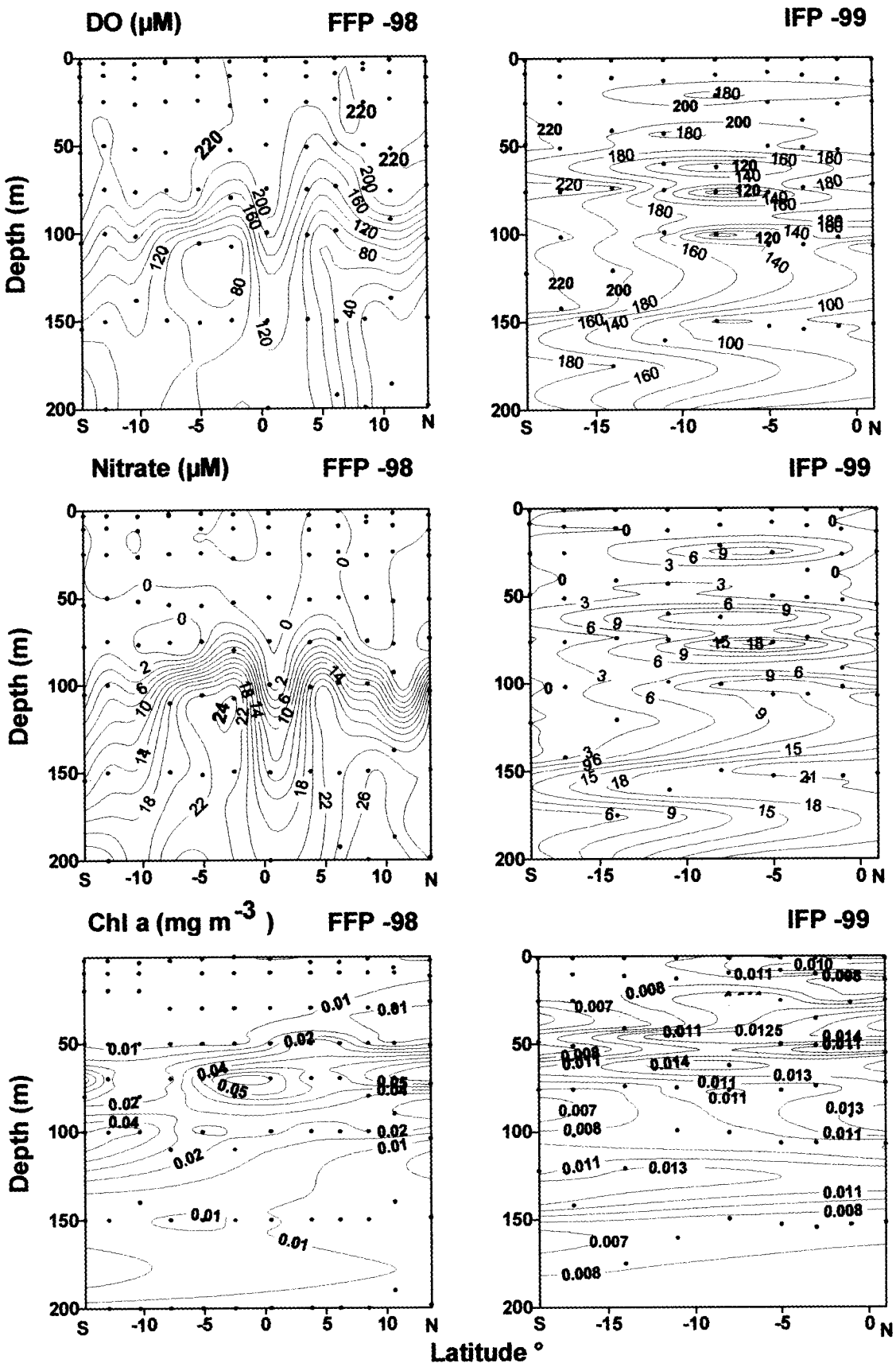


Fig. 3.11b. Variations in dissolved oxygen (DO), nitrate and chlorophyll during FFP - 98 and IFP - 99 of the INDOEX Experiment.

east. This trough also was marked by relatively higher salinities. Features of sub-surface (>100 m) hydrographic front could be seen in physico-chemical properties at 10° S. Temperature, salinity and oxygen exhibit the occurrence of a front in surface layers across the equator. On either side of the equator average salinity was lower (34.170 at 5°S and 34.182 at 9°N whereas it was 34.981 at the equator) in the upper 50 m due to the respective current systems flowing from east to west. The North and South equatorial current systems carry relatively low salinity waters from the eastern Indian Ocean to Madagascar [*Wyrtki*, 1973]. To the north of the equator (particularly >5°N) signatures of warm, low oxygen, high salinity and nitrate rich North Indian Ocean waters could be clearly seen below the thermocline (≥100m) in figure 3.11a&b. In contrast, no clear trends in these properties were found during Intensive Field Phase (IFP '99, Figure 3.11a&b). The usual hydrographic front at 10° S was not obvious. Physico-chemical properties (T, S, O_2 and NO_3^-) exhibited pocket like features that clearly indicated higher turbulence in waters due to higher wind speeds during IFP '99. Wind driven turbulence together with the frontal circulation should have caused vertical patches in distributions of these properties. Due to this turbulence temperature in the upper 50 m was lower by 2-3°C with concomitant higher salinities in 1999 than 1998. Stratification in FFP '98 and turbulence in IFP '99 have also led to significant differences in nitrate distributions observed between the two cruises. While nitrate occurred in the upper 50 m, to a maximum of ~9 μM, in 1999 it was mostly below detection limits, except just north of the countercurrent, in 1998.

3.4 Hydrographic features during a time series study in the Zuari estuary

The Zuari River stretches 50 upstream km in length and receives large amount of freshwater influx during the southwest monsoon. Being in the tropics the estuary experiences semi-diurnal tides and during the monsoons the tidal influx of salt water together with fresh water discharge leads to the formation of a salt wedge. The tidal amplitude remains unchanged up to nearly 40 kms upstream, but falls rapidly within the last 10 km due to river runoff [*Shetye* 1999 and references therein]. Heavy precipitation and land runoff from June to September bring about large changes in temperature, salinity, flow pattern, dissolved oxygen and nutrients since the estuary becomes freshwater dominated. The monsoon season (July-September) is followed by a recovery period during the post-monsoon season (October-January) and thereafter a stable period of the pre-monsoon season (February-May) when the estuary becomes marine dominated. Fig. 3.12 shows the monthly variations in temperature, salinity, dissolved oxygen and nitrate at the time series station (Fig. 2.2) at the mouth of the Zuari estuary.

Temperature showed high values during the month of March due to maximum solar insolation. The surface water temperature varied from 28°C to 33°C with an average value of 29.6°C whereas the bottom water temperatures varied from 22°C to 32°C with an average value of 28°C. Bottom water temperatures varied more than at surface. Figure 3.12 depicts low temperatures in bottom waters during June-August. These low values result from upwelling during southwest monsoon, which is intense in August. Afte

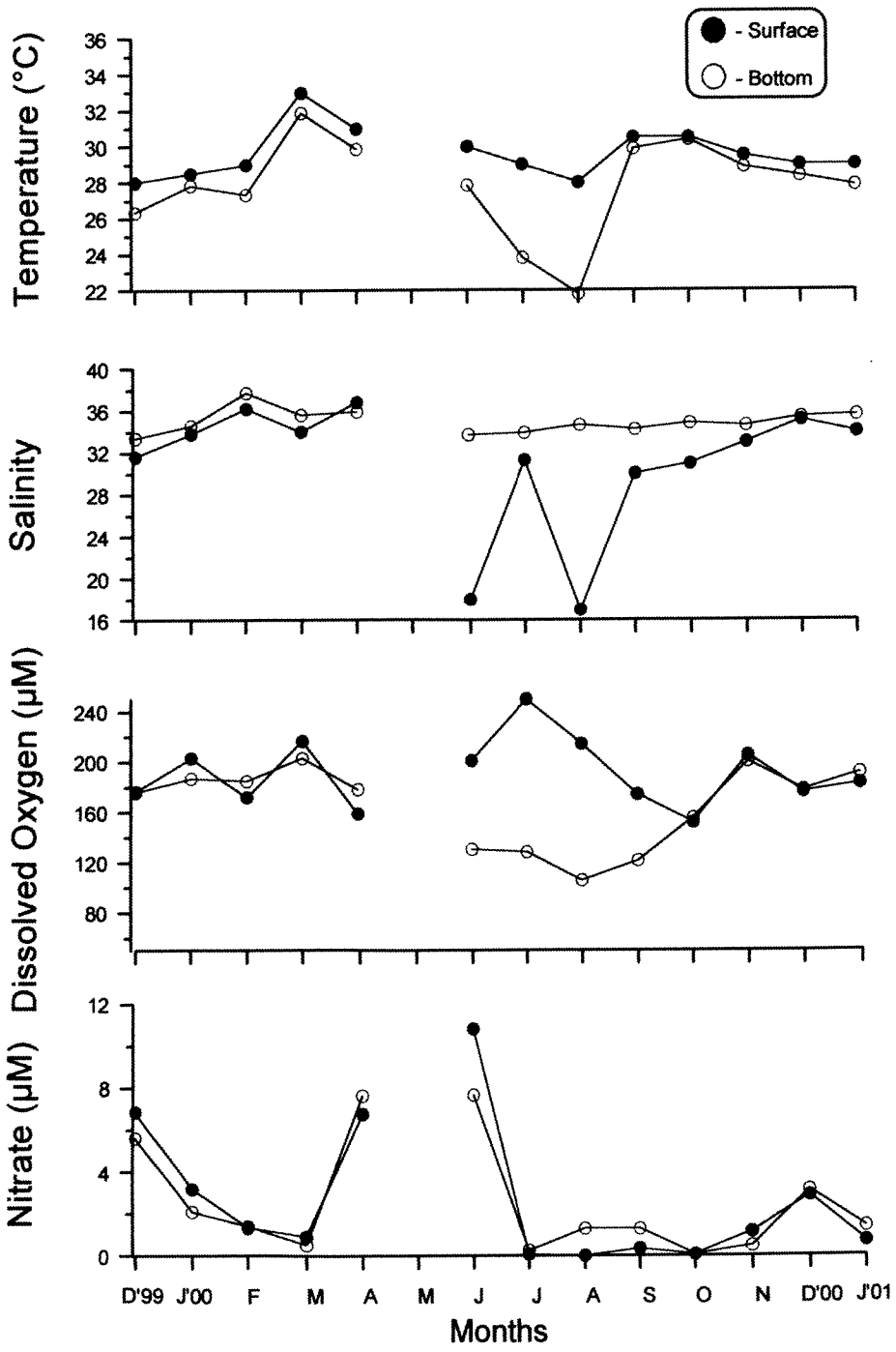


Fig. 3.12. Temporal variations in physicochemical parameters in the Dona Paula bay of the Zuari Estuary.

the monsoon the surface and bottom temperatures revert back to pre-monsoonal values. Similar variations were also seen in case of salinities. Both surface and bottom salinities did not show much variation throughout the year except during the monsoon where surface salinities fell drastically during June-August due to runoff. Due to a break in monsoon rainfall in July surface salinity almost equaled the bottom value.

The maximal variations in dissolved oxygen were seen during the southwest monsoon as in the case of temperature and salinity (Fig. 3.12). During this period bottom oxygen values decreased. A significant difference of 129.5 μM occurred between the surface and bottom values during July. The surface as well as bottom oxygen average to about 178.6 μM except during June to September when the bottom DO values average around 111.6 μM. As the bottom was occupied by upwelled waters the oxygen was low and nitrate was high in SW monsoon. This signature was pronounced during June. On the other hand high nitrate can be accompanied by high oxygen in estuaries since freshwater discharge supplies nutrients In the present study the maximal oxygen was observed in June 2000 during which the nitrate was about 10.8 μM. Surface and bottom nitrate values were nearly the same except at the beginning of the monsoon (June) when the surface nitrate was higher than the bottom nitrate. From August to September the bottom nitrate was higher. The inputs of nitrate into the study area were seen not only during the monsoon season particularly during November and December (Northeast monsoon) period. This was seen in two consecutive years (i.e. December of

1999 and 2000) and was thus not a mere coincidence. In addition a surface and bottom high of ~7μM was also observed during the April 2000. *Nair,* [1980] observed two peaks in zooplankton production in the Zuari estuary, one in November and the other in March/April. Higher zooplankton results in higher fecal matter, rich in ammonia. This ammonia in the presence of oxygen might undergo nitrification and thus results in high nitrate observed in the study area during these months. Similar observation from the study area *Qasim and SenGupta,* 1981] suggested these high concentrations to be of local origin.

The salient features of hydrography during the study period are:

1) In the Arabian Sea winter convection during the northeast monsoon and upwelling during the southwest monsoon introduces nutrients into the euphotic zone thereby inducing high productivity. The fall inter-monsoon showed oligotrophic conditions.
2) Runoff suppressed upwelling along the coasts of Chennai and Paradip during southwest monsoon.
3) Atmospheric depression in the head Bay caused nutrient pumping into the euphotic zone that affected biological production. .
4) Cloud cover reduced incident UV radiation but promoted high production.
5) Central Indian Ocean showed marked differences in the hydrographic features between 1998 and 1999 with higher levels of nutrient input and production in 1999.

6) Seasonal circulation resulted in maximal nutrient concentrations in the southwest monsoon in the Zuari estuary.

Chapter 4

Variability in Dimethyl Sulphide Species

As the DMS and its compounds are biogenic in origin their concentrations in seawater would be highly variable depending on day-night and physico-chemical conditions, biological domains and atmospheric forcings. The present chapter discusses variations in the distributions of DMS and DMSP in the Indian Ocean. Changes in concentrations can be treated in various ways. In this attempt variability is treated in terms of vertical, spatial and temporal changes in properties.

4.1 Vertical distributions

Both DMS and DMSP showed very clear trends in their vertical distributions. For instance, concentrations of DMS were very low in waters deeper than 200 m in the Indian Ocean (Fig. 4.1), which is also the case with DMSP. Therefore, DMS sampling was restricted to the top 200 m of water column for detailed study. Vertical distributions of DMS and DMSP in the coastal and open ocean waters of the Arabian Sea (AS) and in the Central Indian Ocean (CIO) are shown in Fig. 4.1. In the coastal waters of the Arabian Sea (76°E, 10.19°N) maximal concentrations of DMS and DMSP were found at shallow depths. In the present study the highest values of 525 nM of DMS and 916 nM of DMSP were found, respectively, at a station off Candolim and at a location off Mangalore (10.19°N, 76°E, SK148). In the open Arabian Sea (65°E, 18°N), a DMSP maximum of 15.5 nM occurred at 10 m whereas the

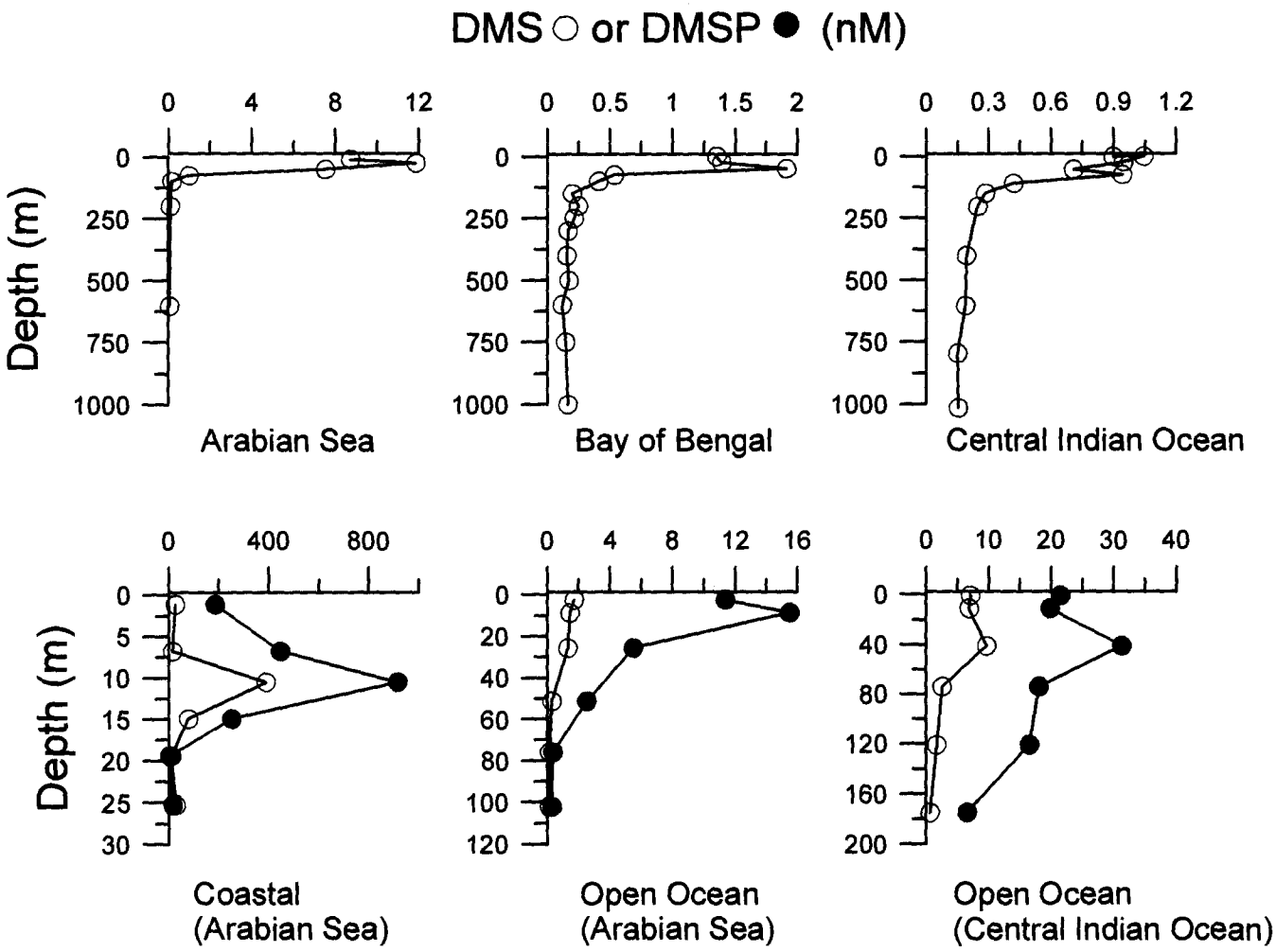


Fig. 4.1 Vertical distributions of DMS and DMSP in different domains of the Indian Ocean.

peak DMS of 1.7 nM was found at the sea surface. Therefore, depths of occurrence of maximal levels of DMS and DMSP not necessarily coincide at all stations but the higher abundances mostly occurred closer to the surface. The DMS and DMSP concentrations rapidly decreased to undetectable levels below about 120m. Similar behaviors were observed in their vertical distributions in the coastal and open ocean waters of the Bay of Bengal. In the Central Indian Ocean, however, peaks in DMS (9.7 nM of DMS at 41 m) and DMSP (DMSP maximum of 31.3 nM) were found around a depth of 40 m (Fig. 4.1). Further, DMS and DMSP levels were detectable up to 150 – 175 m. This occurrence of DMS at deeper depths is unique to the central regions of the Indian Ocean (because of deep mixed layers) and contrasts with that in the Arabian Sea and the Bay of Bengal.

The vertical distributions of DMS and DMSP in the Indian Ocean were similar to that reported elsewhere in the world Oceans. *Andreae and Barnard* [1984] reported maximum concentrations of DMS closer to surface in the Atlantic Ocean. *Holligan et al.* [1987] also observed higher concentrations of DMS in the top 50 m of the water column that in some cases coincided with higher chlorophyll. Maximal DMS concentrations have been found between 30 and 75 m in the South China Sea [*Yang et al.,* 1999]. Our results are in good agreement with that of *Hatton et al.* [1999] who observed highest DMS and DMSP concentrations in the 20 - 45 m range of the central and western Arabian Sea.

4.2 Spatial variations

Fig. 4.2 depicts the variation of DMS in the Arabian Sea, along a section near 15°N (off Goa), during January, July, October and December of 1998. Very clear coastal to open ocean trends were observed. In January (winter), the DMS concentrations varied between 6 nM and 12 nM within 50 m of the water column near the coast but between 200 and 400 km away from the shore the concentrations ranged between 2 and 4 nM before increasing to 10 nM further offshore. During the summer (July 1998) DMS values were higher near the bottom of coastal waters (29 nM) that decreased towards the open ocean. Features similar to those in summer were seen October 1998 when DMS concentration levels near the coast varied between 15 and 40 nM while in offshore waters these were low. In December 1998 coastal DMS concentrations were around 30 nM but decreased offshore. Thus in the eastern Arabian Sea high DMS concentrations were found closer to the coast.

Fig. 4.3 exhibits zonal variations of DMS in the Bay of Bengal. Near Paradip (86.87°E, 19.98°N) DMS concentrations varied between 0.5 and 3.3 nM in coastal waters that showed little change with increasing distance from the coast. Similar features were noticed off Chennai as well. Here, DMS varied from 0.5 to 3.2 nM. Thus the zonal variability trends of DMS were contrasting between the Arabian Sea (with clear inshore-offshore gradients) and the Bay of Bengal (with no significant variation).

In the Central Indian Ocean a different scenario is seen. Fig. 4.4 depicts the variation of DMS in the Central Indian Ocean observed during the

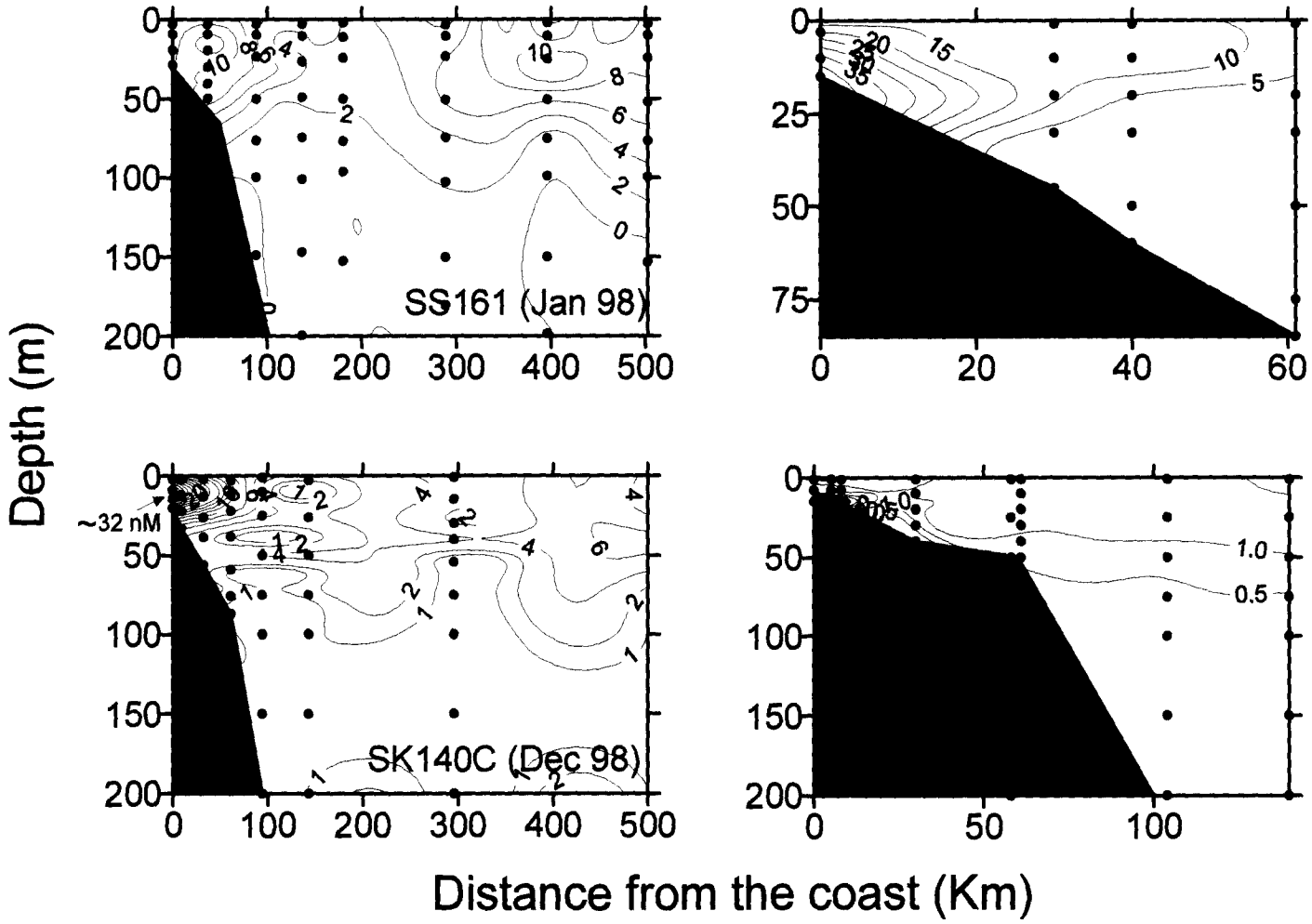


Fig. 4.2. Longitudinal variation of DMS off Goa in different seasons.

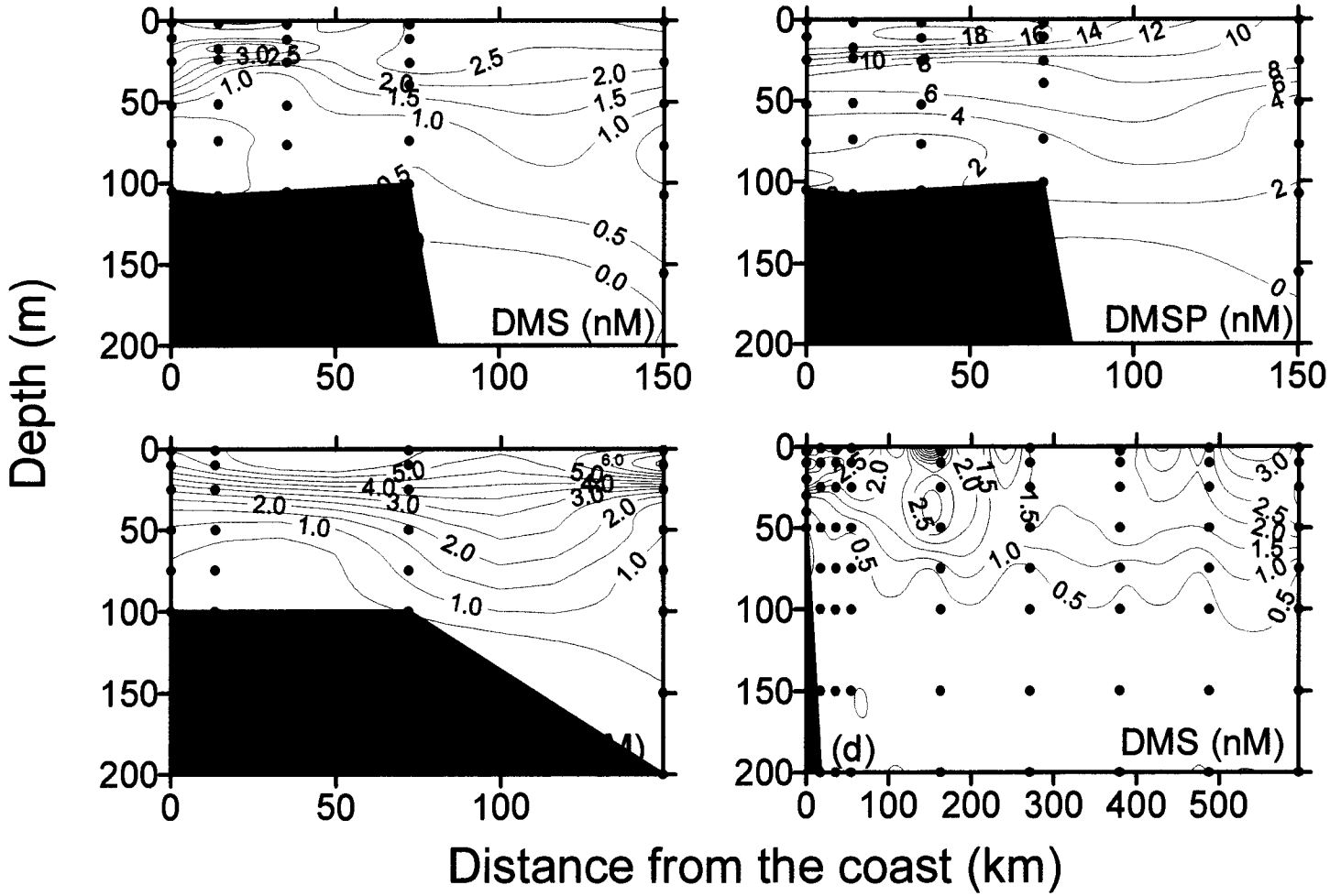


Fig. 4.3. Variations in DMS and DMSP off the coasts of Paradip (a,b (SK147A); c (SK147B)) and Chennai (d (SK147B)).

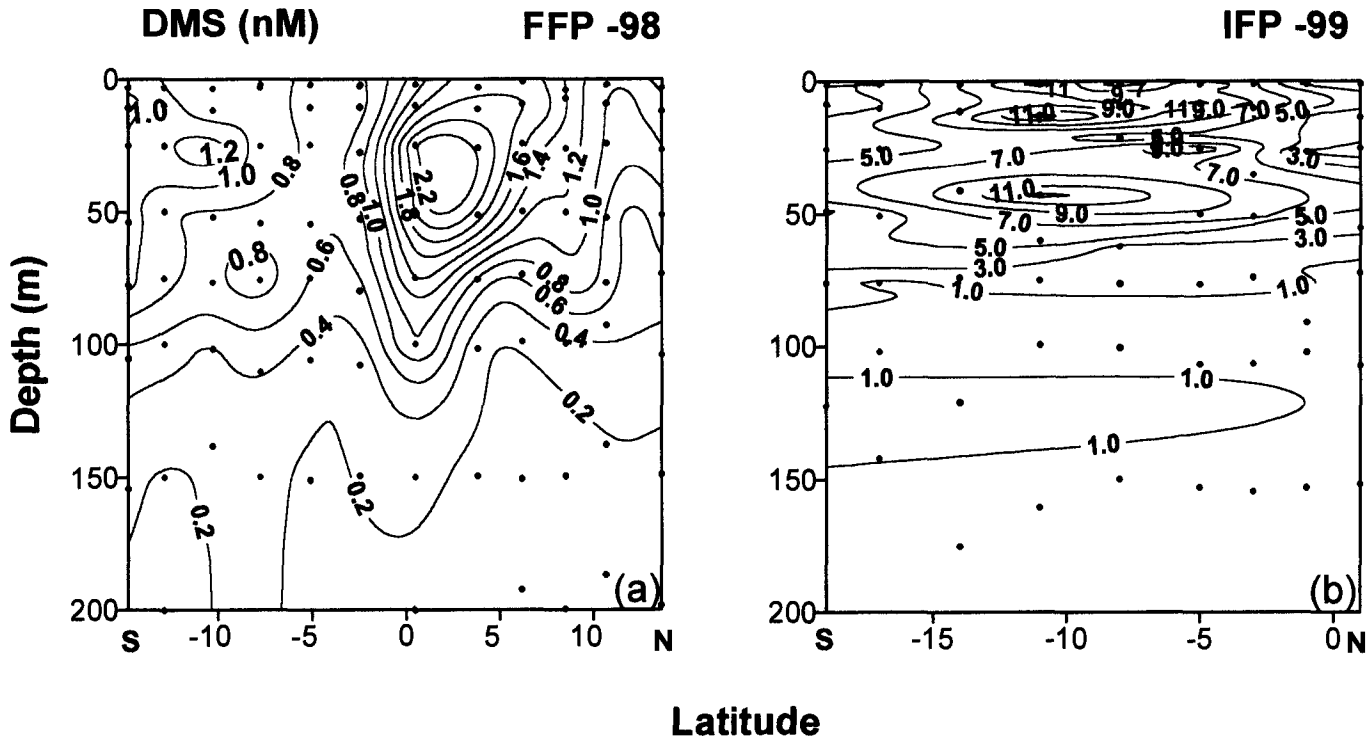


Fig. 4.4. Variations in DMS in the Central Indian Ocean during FFP - 98 and IFP - 99 of the INDOEX Experiment.

INDOEX cruises of 1998 and 1999. High DMS concentrations (0.1 to 13.9 nM) were observed between 5°S and 15°S in 1999 (Fig. 4.4b). These were observed as pockets between surface to 75 m with detectable concentrations up to 100 to 150 m. While away from these latitudes viz. between 0° and 5°S, and 15°S and 20°S DMS concentrations, in the same depth range, as mentioned above varied between 1 and 5 nM. DMS levels were lower in 1998 with strong latitudinal gradients (Fig. 4.4a).

Thus DMS in the Indian Ocean exhibits very high spatial variability. Besides the strong vertical variability DMS in the Indian Ocean exhibited very significant spatial variability in which higher concentrations were observed near to the coast and lower concentrations in the open Ocean. Further, DMS concentrations on an average, all the data points put together in respective areas, showed a gradual increase from the Bay of Bengal 1.8 nM to the central Indian ocean 2.2 nM to the Arabian Sea 5.5 nM.

4.3 Temporal variations

4.3.1 Diurnal variation

A time series station (7°N, 87°E) was occupied in the Bay of Bengal for 40 hours during which DMS concentrations showed distinct variations. At the beginning of the time series (3.30 AM) abundances were marked with lower DMS and high DMSP concentrations. Towards late afternoon the situation reversed when higher DMS and lower DMSP levels occurred (Fig. 4.5). However DMS exhibited lower concentrations on the following day while DMSP was low during the intervening night (14-26 hrs). Higher DMSP

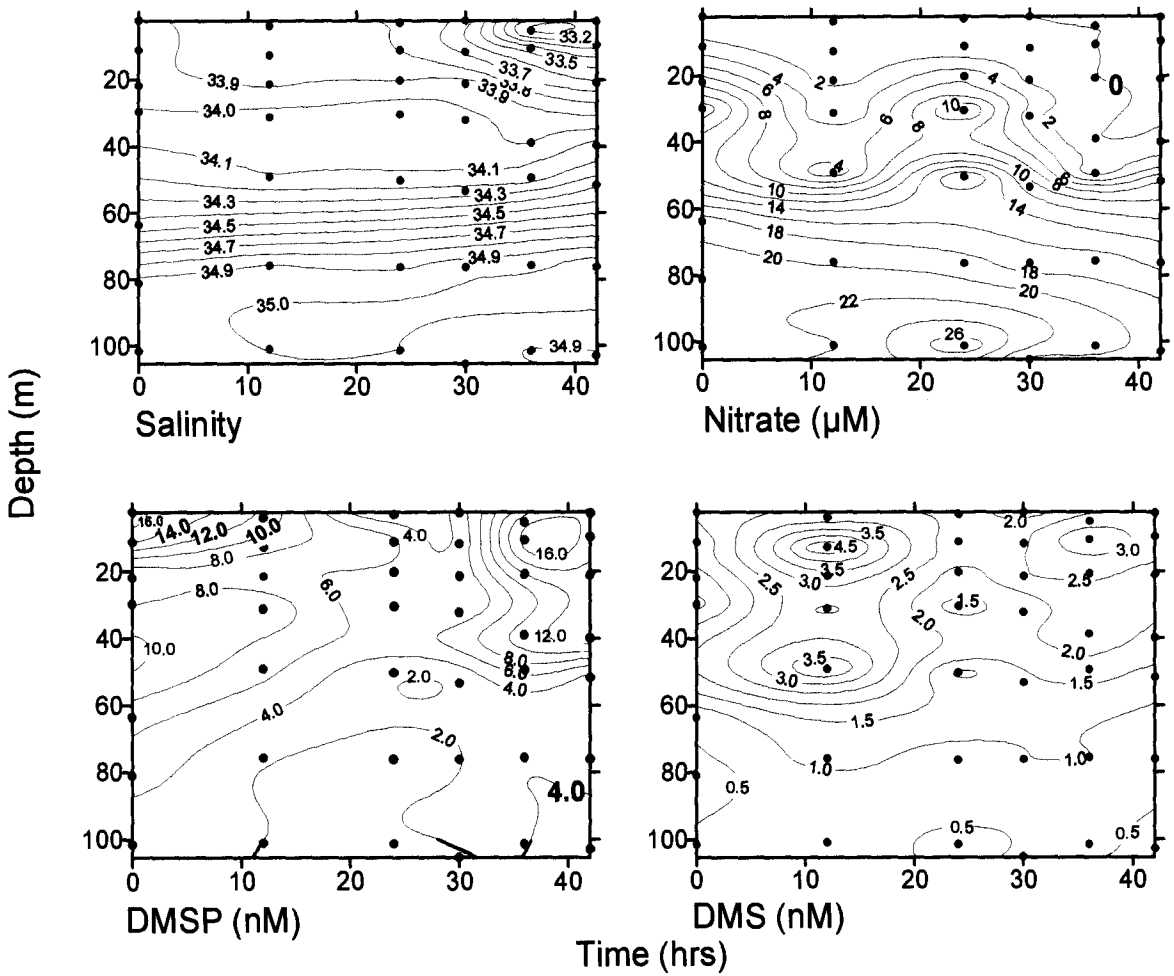


Fig. 4.5. Variations in salinity, nitrate, DMSP and DMS at the time series station (7°N, 87°E) during the BOBMEX Pilot Experiment. Zero hours refer to 03.30 AM on 30 October 1998.

concentrations were again observed towards the end (~7.30 PM on the following day) of the experiment. The high DMSP during the beginning of the time series could be due to intense grazing activity by the zooplankton [*Dacey and Wakeham*, 1986; *Wolfe and Steinke*, 1996], which leads to the subsequent increase in DMS on the following day. These features reveal that DMSP did not exhibit consistent day-night variations. Chlorophyll *a* was found to exhibit diurnal variability with maximum values occurring around late afternoon. The secondary DMS maximum of ~3.5 nM (at 50 m) coincided with the chlorophyll *a* maximum. The DMS concentrations during the time series observations varied from 0.2 to 5.1 nM with an average of 1.8 nM in the upper 100 m, whereas DMSP ranged from 1.4 to 17.6 nM with a mean value of 7.2 nM. DMS showed maximum concentrations around the late afternoon but this trend was not consistent, as the maximum was not observed on the following late afternoon. In addition to this DMS and DMSP maximal concentrations were decoupled from each other.

4.3.2 Variability during a cyclone

A long-term time series experiment (spanning over a month) was undertaken in the Bay of Bengal at 17.5° N and 89° E during the summer monsoon of 1999. The experiment was carried out in two phases wherein weather and oceanographic conditions were remarkably different between the two. Phase I (SK147A) was atmospherically more convective than phase II (SK147B). Variations in DMS, chlorophyll *a* and UV radiation are shown in Fig. 3.9. Surface as well as MLD averaged chlorophyll levels showed marked

variations. The highs in chlorophyll correspond to the lows in UV radiation thereby exhibiting inverse relation between the two. This relation was observed during both the phases, but phase I shows distinct inverse relation which is not so evident in phase II. The DMS variability was found to be very high during phase I in response to intense atmospheric convection. Phase I shows spikes in surface as well as MLD averaged DMS. In comparison to phase I, phase II does not show any such spikes in DMS. Stress is considered to be one of the reasons for enhanced DMS production [*Keller*, 1998]. Intense convection results in rough sea states and rapid changes in physico-chemical conditions, which may have led to higher DMSP production by phytoplankton, which in turn results in higher DMS production. During phase I surface DMS varied between 1.5 and 5.5 nM with an average of 3 nM, while in phase II it varied between 1 and 5.3 nM again with an average of 3 nM. The column DMS (0-200 m) in phase I ranged between undetectable levels and 6.3 nM with an average value of 1.4 nM and in phase II it varied from below detection limits to 5.3 nM with a mean of 1.2 nM.

4.3.3 Seasonal variation in waters off Goa

4.3.3.1 Off-Candolim

Data obtained through periodic sampling along a small transect (~13 km) off the Candolim coast (Goa) enabled us find the extent of seasonal variability in DMS and DMSP. During the premonsoon (March) season of 2000 (Fig. 4.6a) concentrations of DMS and DMSP varied, respectively, from 0.3 to 6.1 nM with an average value of 2.5 nM and between 3.2 and 38.7 nM

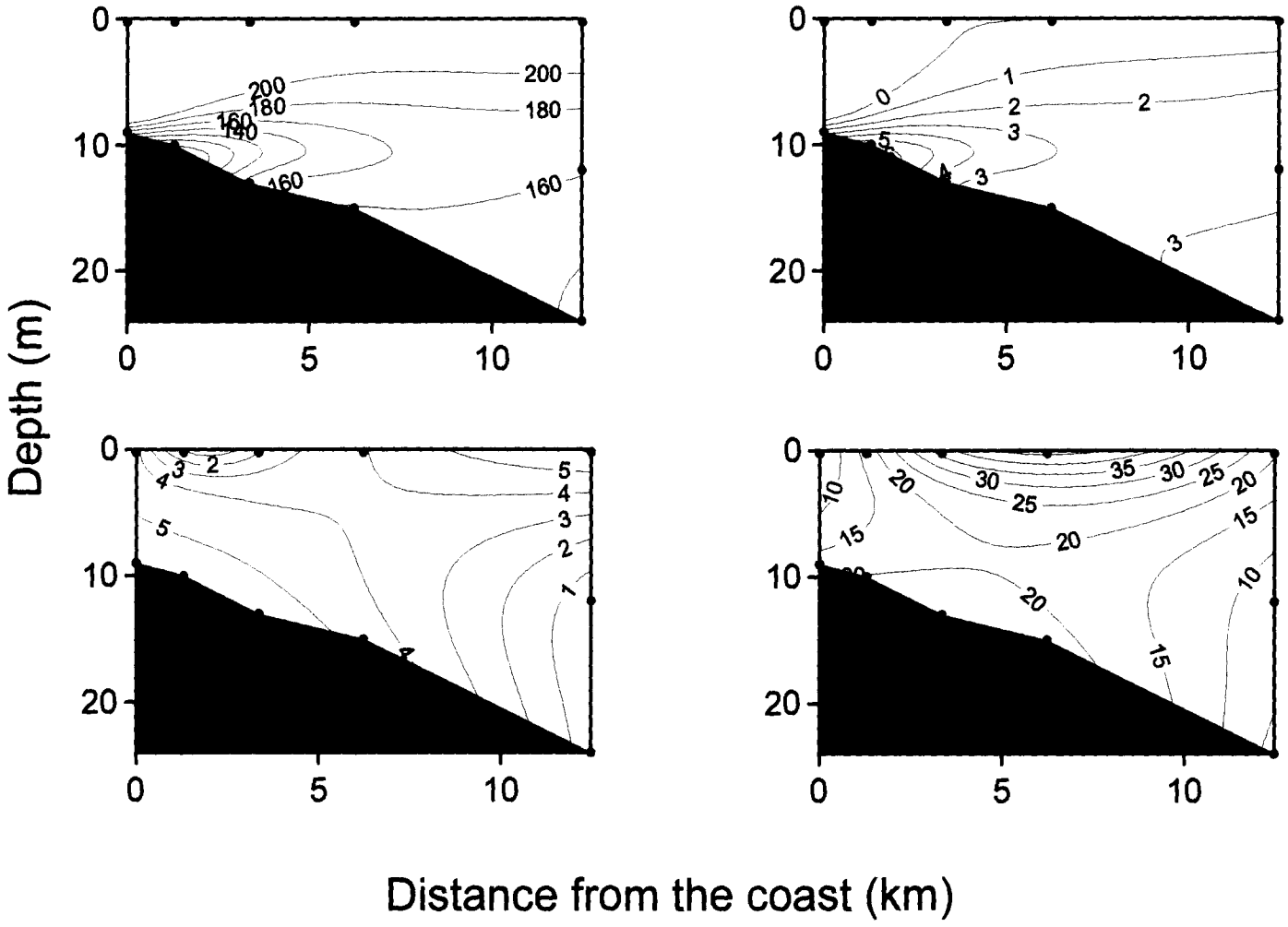


Fig. 4.6a. Variations in oxygen, nitrate, DMS and DMSP off Candolim in Goa on 30/3/2000

with a mean of 12.1 nM. A repeat observation in March 2001 (Fig. 4.6b) showed even lower concentrations of DMS and DMSP. DMS varied between undetectable levels and 1 nM while DMSP occurred between undetectable levels and 3 nM. Nitrate concentrations, however, were higher in March 2001 (Fig. 4.6b) than in March 2000 (Fig. 4.6a). Fig. 4.6a suggests a positive relation between nitrate and DMS production during organic matter regeneration in coastal sediments. However, DMSP is negatively related to nitrate distribution (Fig. 4.6a,b). These conditions were found to change in SW monsoon (Fig. 4.6c,d). On 12th September 2000 the surface oxygen varied between 140 and 190 µM whereas its concentrations reduced by 8 – 9 times at depths ~ 10 m. Substantial nitrite was observed wherever there was a fall in the oxygen levels indicating active upwelling and biological activity. DMS and DMSP are, in general, higher at surface because of intense biological activities at surface. Within three weeks the conditions (Fig. 4.6d) were found to be quite different with relatively higher oxygen but only traces of nitrate. These conditions indicate the consumption of nitrate during the intense biological production when oxygen is produced in the water column. Such intense photosynthetic fixation and the presence of traces of nitrate seems to have aided higher production of DMSP (9-113 nM) and DMS (13-132 nM). The DMS levels found in these coastal waters in 29 September 2000 are about 100 times more than that occurred in March 2001. On the other hand, the highest values for DMS were detected very close to the coast in November (1999). A maximal DMS of 525 nM was observed (Fig. 4.6e).

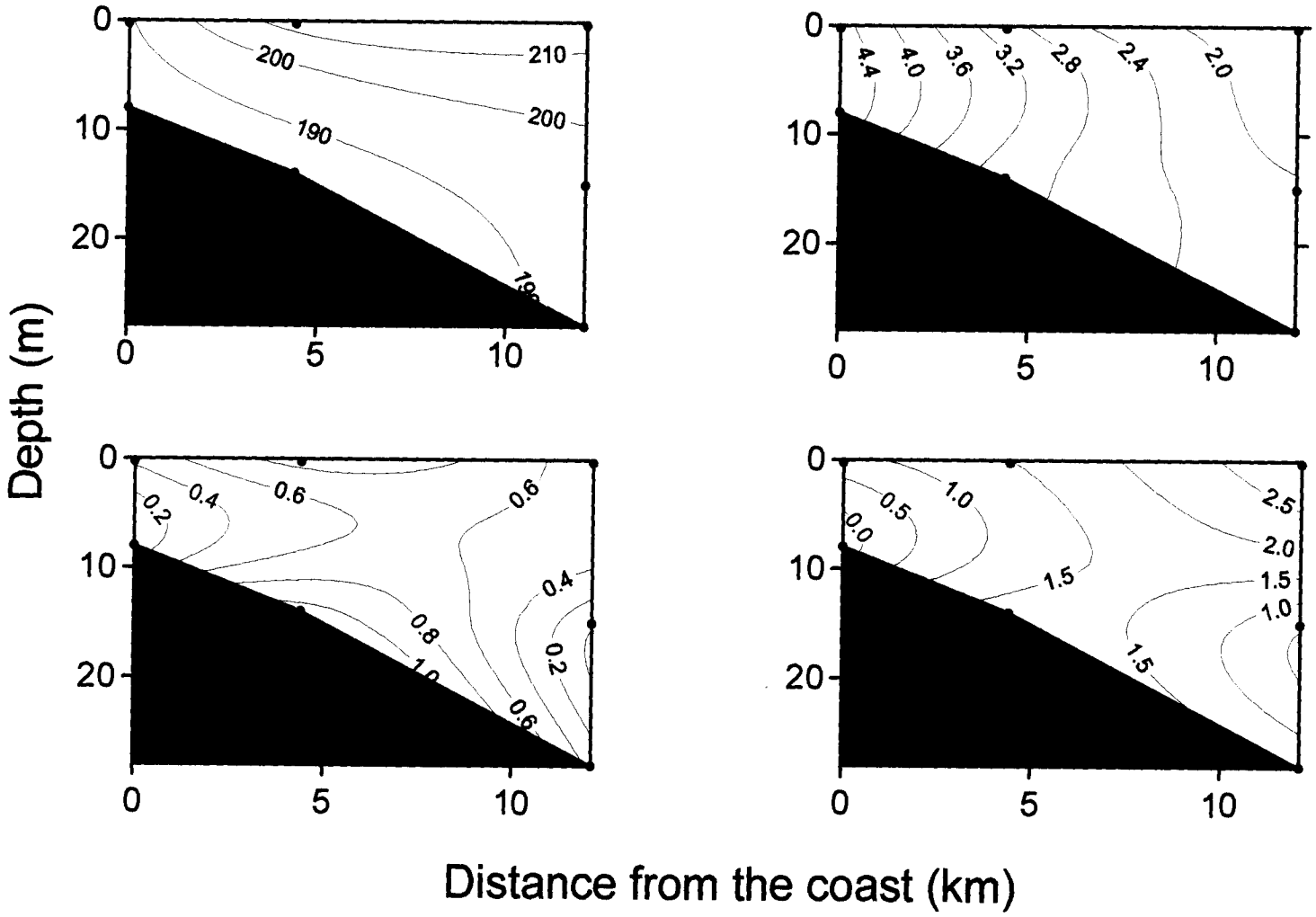


Fig. 4.6b. Variations in oxygen, nitrate, DMS and DMSP off Candolim in Goa on 28/3/2001

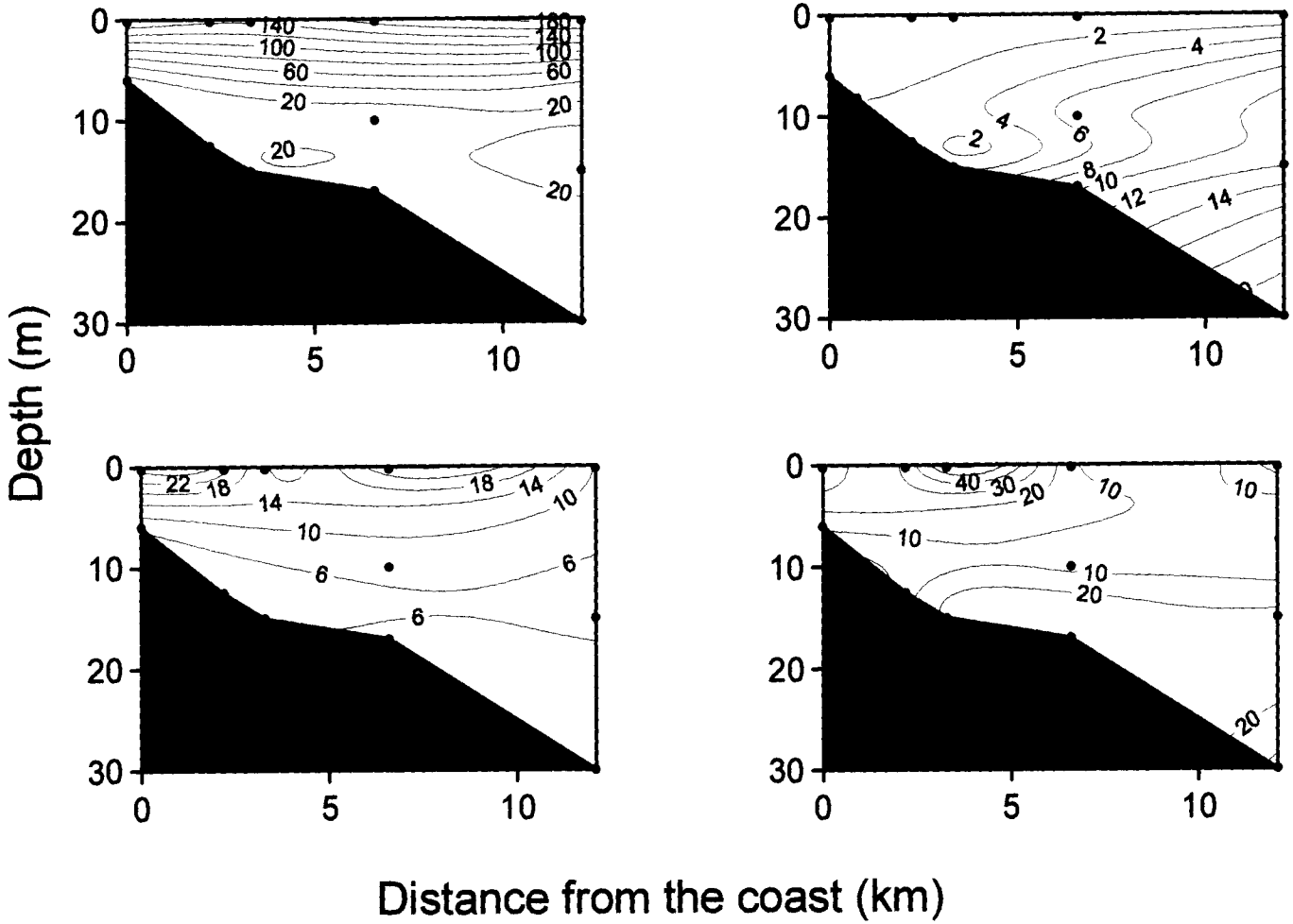


Fig. 4.6c. Variations in oxygen, nitrate, DMS and DMSP off Candolim in Goa on 12/9/2000

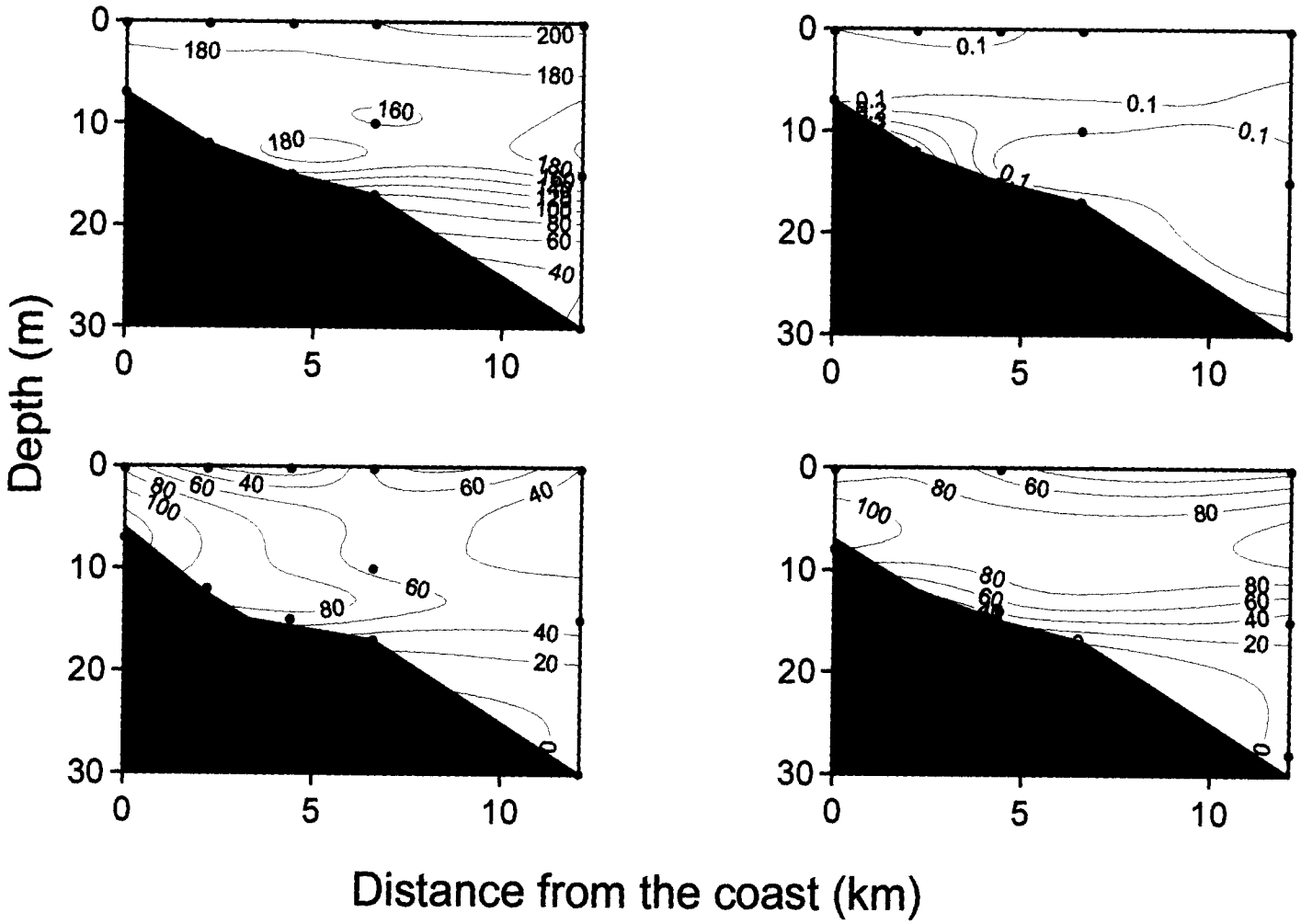


Fig. 4.6d. Variations in oxygen, nitrate, DMS and DMSP off Candolim in Goa on 29/9/2000

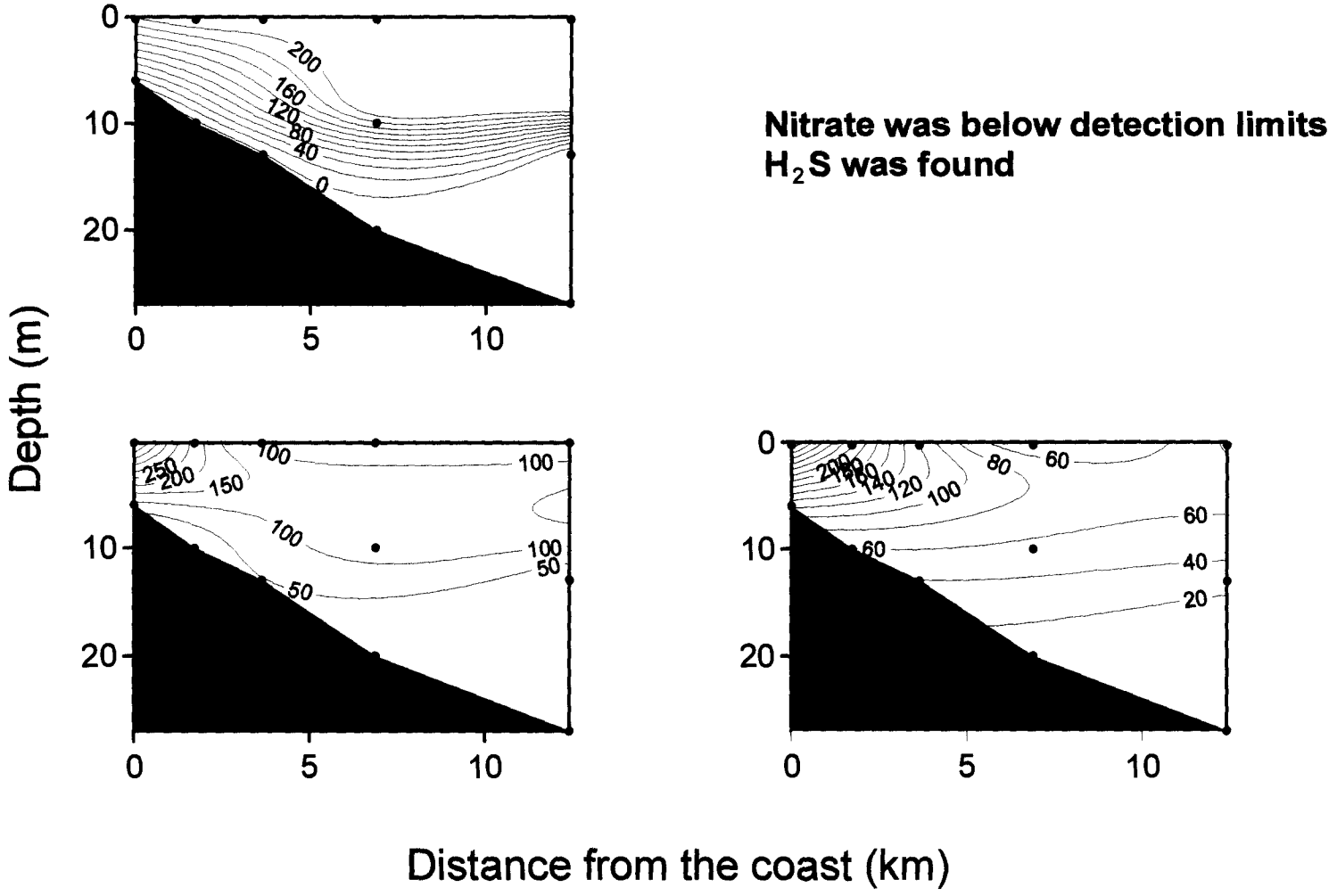


Fig. 4.6e. Variations in oxygen, nitrate, DMS and DMSP off Candolim in Goa on 11/11/1999.

Surface oxygen was very high (221 μM) indicating very high photosynthetic activity at the surface. The steep gradient in oxygen, between the surface and bottom (<μM) in these shallow waters, together with the presence of hydrogen sulphide and undetectable nitrate indicates intense biological activity including intense microbial degradation of organic matter. DMS levels ranged from 6 nM to 525 nM while DMSP varied between 8 nM and 339 nM. Coinciding with this trend extremely high DMSP values were found in the same season in Zuari estuary (~419nM) and in western continental marginal waters off Mangalore (~916 nM). Thus, DMS varied from ~0.1 nM in premonsoon season to 525 nM in fall-intermonsoon (or post-SW monsoon) season exhibiting a variability by 5000 times in coastal waters of Goa. Such behavior could be occurring in many places along the west coast of India since the oceanographic conditions are nearly the same.

4.3.3.2 Dona Paula Bay

Both surface and bottom DMS and DMSP concentrations, at a location in Zuari estuary in Goa (Fig. 2.2) showed periodic changes (Fig. 4.7). Surface DMS and DMSP showed higher values during December 1999, February and April (only DMS), July and November 2000. Bottom DMS and DMSP also showed almost similar trends. The highest DMS values were observed in April and July. During June to September the surface DMS varied between 0.3 and 12.8 nM with an average value of 5.8 while surface DMSP varied from 1 to 419.5 nM with an average value of 111.4 nM. Bottom DMS varied from undetectable to 28.3 nM with an average value of 8.5 nM while bottom DMSP

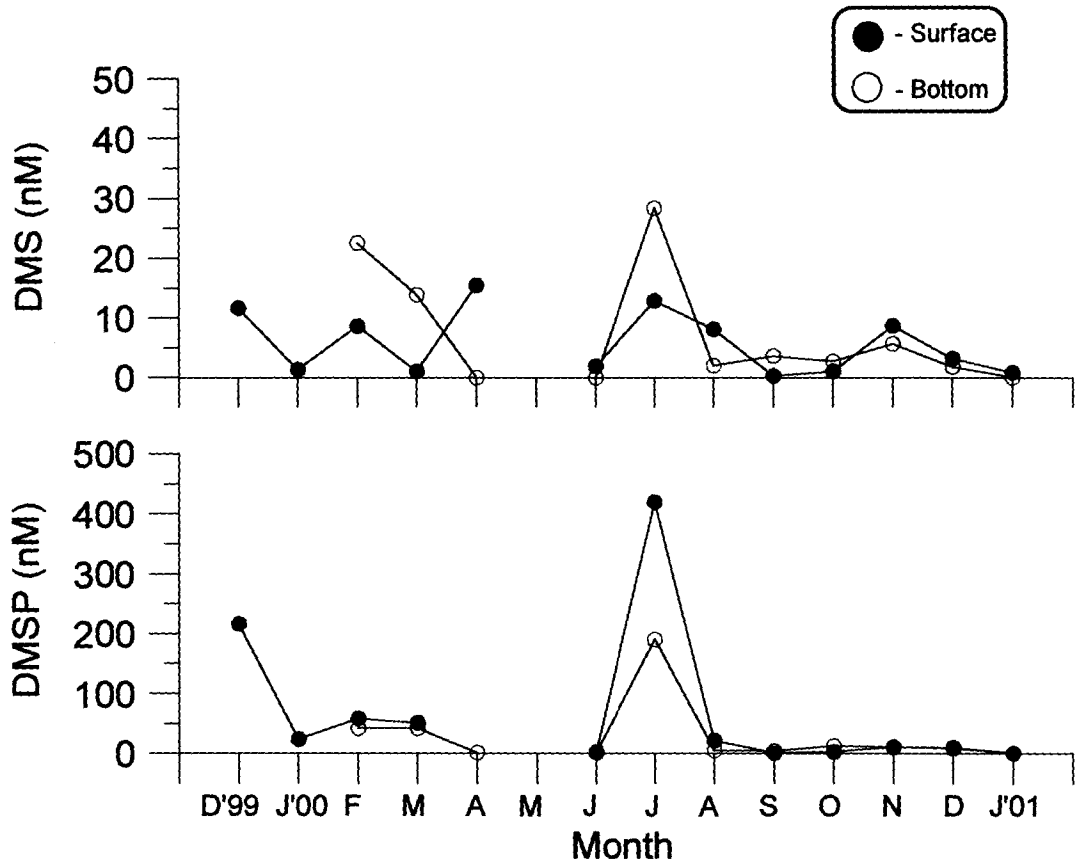


Fig. 4.7. Monthly variations in DMS and DMSP in the Zuari estuary.

varied between 1.4 and 190.6 nM with a mean of 50.5 nM. In general, DMS and DMSP peaks followed phytoplankton and chlorophyll peaks with a lag of one month except during July - August (Fig. 4.8). Nearly 99% of the phytoplankton consisted of diatoms between June and August except in July when diatoms contributed to ~85% with the remaining largely present in the form of dinoflagellates (Fig. 4.9). Chlorophyll *a* also exhibited peak levels in July. These data reveal species dependency of DMS and DMSP and that dinoflagellates contribute significantly to the production of these sulphur compounds. Enhanced DMS and DMSP in December 1999 and November 2000 also coincide with the increase in phytoplankton. However the values during the December 1999 (11.6 for DMS and 216.1 nM for DMSP) were greater than the values observed during November 2000 (8.7 nM and 11.3 nM DMS and DMSP, respectively). *Moret et al.* [2000] reported surface DMS to be between 0.4 nM and 16.3 nM, with an average value of 3.7 nM, from surface waters of two time series stations in Venice Lagoon. They found maximal DMS levels to occur during phytoplankton and macro-algal blooms. *Turner et al.* [1996] have found a monthly mean of around 25 nM in May and coincidence of higher DMS with blooms of *Phaeocystis*. The present results confirm that DMS not only shows significant temporal variation but also exhibits species dependency.

4.3.4 Inter-annual variability

Fig. 4.4 shows the variations in DMS in subsequent years during the INDOEX (FFP- 1988 and IFP-1999). A clear increase (nearly five times) in

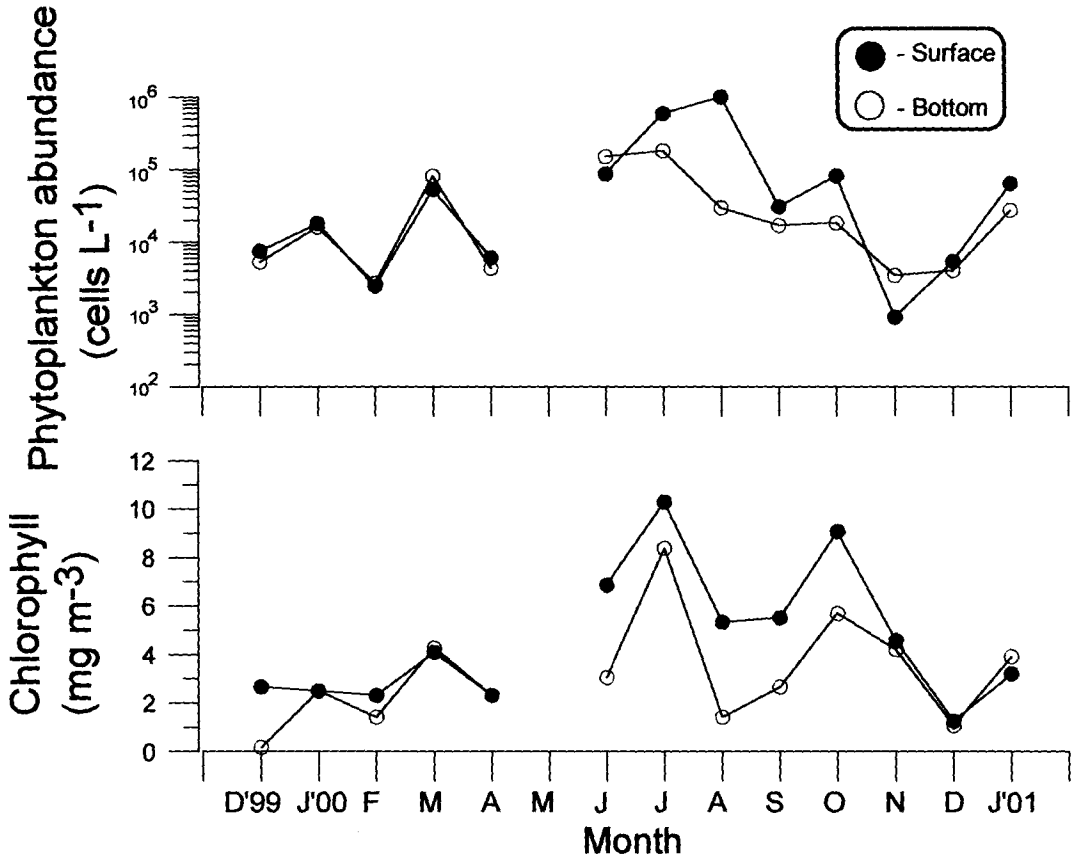


Fig. 4.8. Monthly Variability in phytoplankton abundance and chlorophyll in the Zuari estuary.

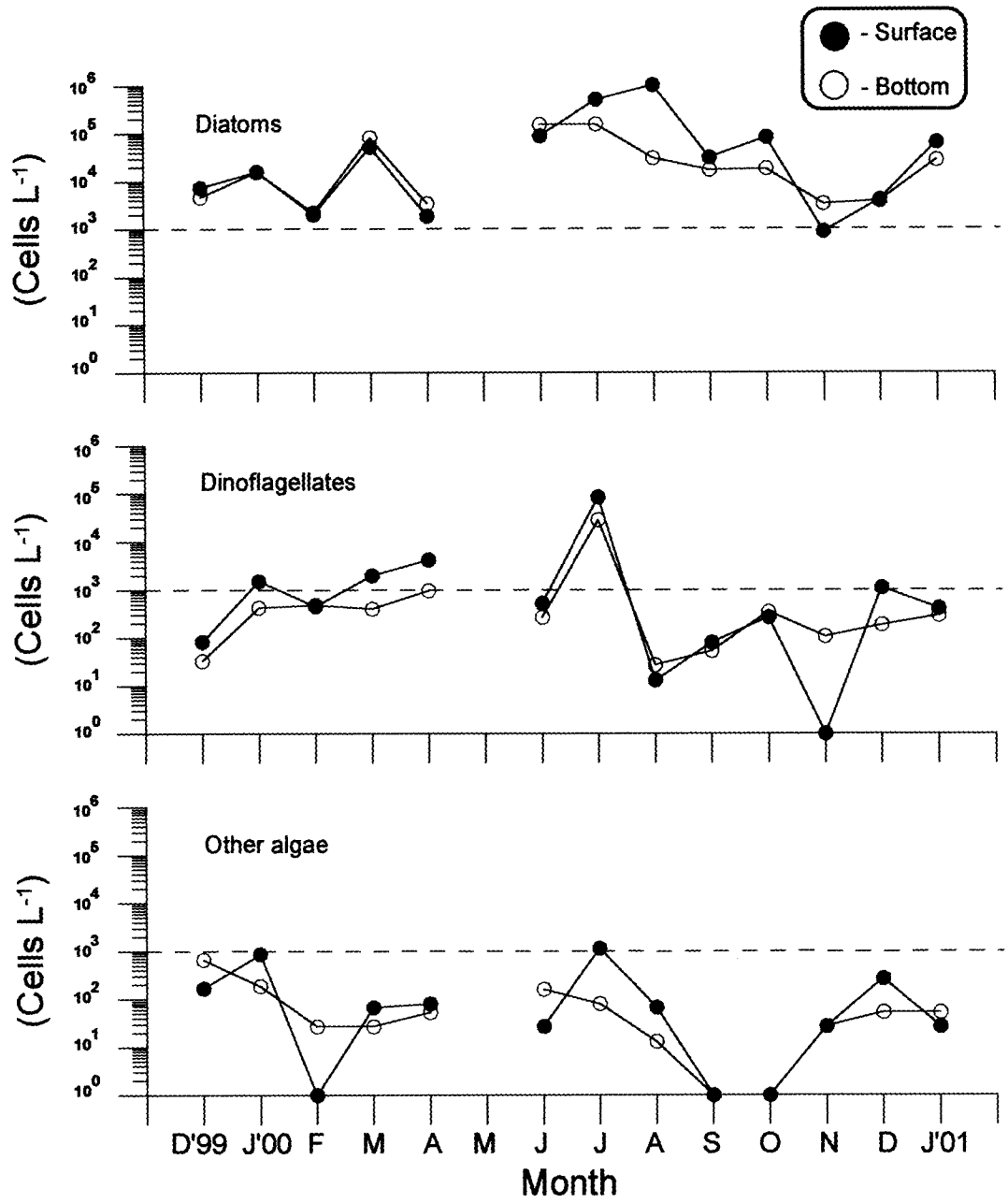


Fig. 4.9. Monthly Variability in diatoms, dinoflagellates and other algae in the Zuari estuary.

DMS concentrations was found in 1999 in comparison to that in 1998. During FFP the DMS concentrations in the upper 100 m varied between 0.4 and 2.6 nM with an average value of 0.6 nM whereas during IFP DMS concentrations varied between 0.1 nM and 13.9 nM with an average of 3.4 nM. This high degree of inter-annual variability is due to differential production during the two years. In spite of low chlorophyll contents in 1999 than in 1998 DMS abundance was higher in 1999 perhaps due to active biology supported by atmospheric disturbance and the consequent upward nutrient supply. On the other hand, higher chlorophyll found in 1998 might have been remnants of high production off Sumatra, following El Nino upwelling, as the nitrate supply from deep seem to not have been favoured (Fig. 3.11a,b). Thus DMS has shown significant inter-annual variability in response to oceanographic and atmospheric forcings.

Salient features of DMS distribution in the Indian Ocean are:

1. Maximal concentrations in DMS and DMSP occurred close to sea surface in the Arabian Sea and the Bay of Bengal whereas in the Central Indian Ocean these were found at deeper depths.
2. Zonal distribution indicated strong coastal to offshore gradients in DMS and DMSP in the Arabian Sea but not so in the Bay of Bengal.
3. Diurnal variability in DMS suggested peak abundance in the late afternoon.

4. Chlorophyll *a* is negatively related to incident UV radiation during stormy conditions in the Bay of Bengal but their influence on DMS was not clear since both the ocean and atmosphere were very turbulent.
5. The DMS in coastal waters of the western India exhibited very strong seasonality with the highest concentrations (~100 to 5000 times) occurring the late and post- southwest monsoon periods compared to that in pre-monsoon season.
6. Strong inter-annual variability in DMS was found in the Central Indian Ocean with five times higher abundance in 1999 than in 1998.

CHAPTER 5

Experimental Results on DMSP and DMS

Chapter 5

Experimental Results on DMSP and DMS

5.1 Influence of salinity shock on DMSP production by plankton

As detailed in section 2.1.3 a diatom species (*Skeletonema Costatum*) was subjected to salinity shock by adjusting the salinity of the ambient medium through the addition of deionised water. In order to follow the effect of state of growth on DMSP production plankton cultures of two days (young and in active growing phase) and eleven days (almost near stationary growth phase) old plankters were used in this experiment. The cultures were grown at a salinity of about 35 and temperature of 28°C. Shock experiments were conducted over a salinity range of 20 to 35. In addition to DMSP (total, includes dissolved and particulate), phytoplankton cell numbers and chlorophyll *a* were also measured. Samples were subjected for DMS and DMSP analyses within 5 minutes of giving the salinity shock. Fig. 5.1 depicts the variations in these parameters in response to the amount of deionised water added. In spite of the overall decreasing trends in both DMSP observed ($DMSP_{obs.}$) and DMSP expected ($DMSP_{exp.}$, based on dilution) with increasing dilution the former is higher than the latter; with more or less equal difference particularly when added water was more than 10 ml (Fig. 5.1). This implies that salinity shock (or sudden gradient in salinity) is more important, than the extent of dilution, for the production of $DMSP_t$ by the diatom. More significantly, the trend in increased DMSP production does not seem t

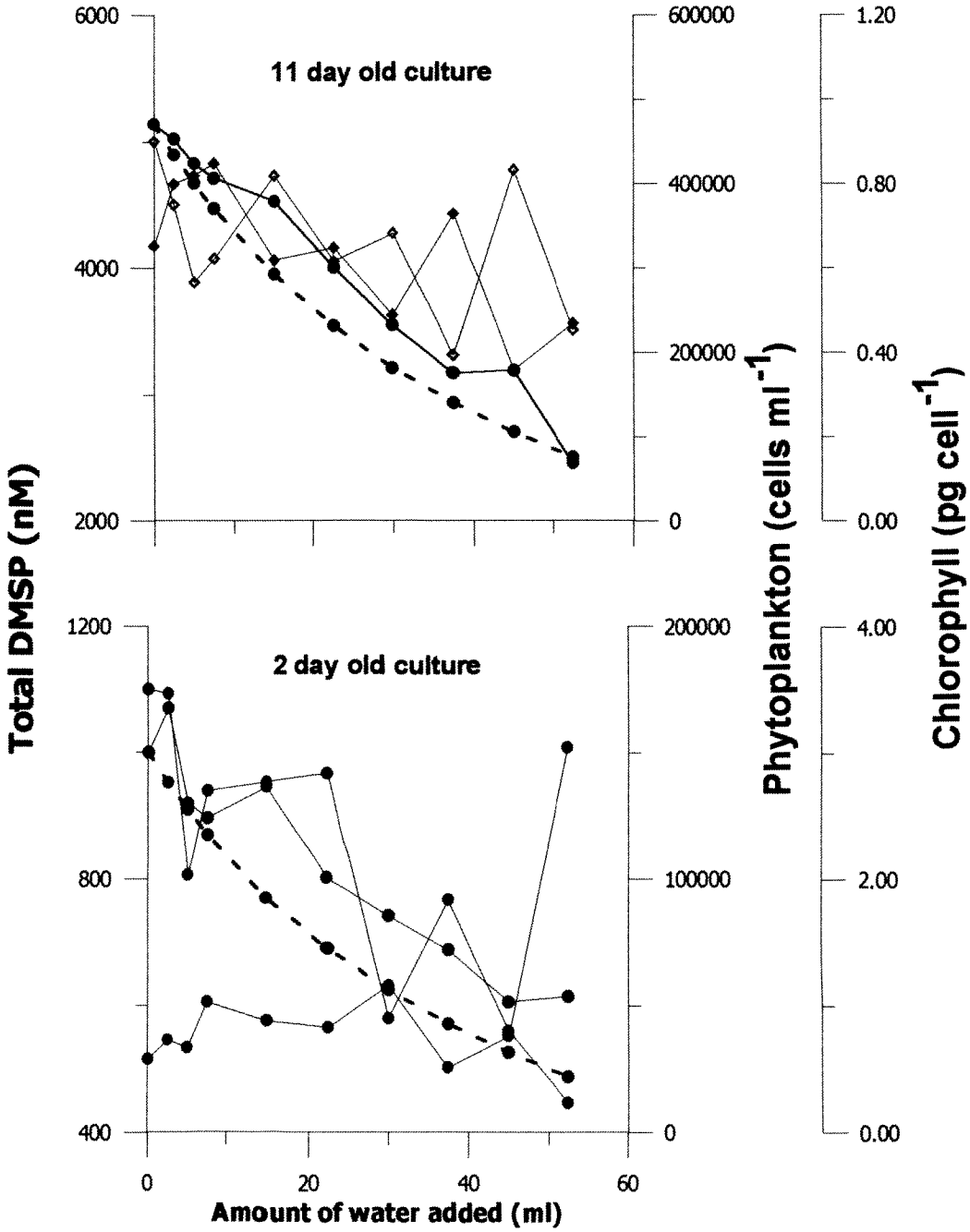


Fig. 5.1. Behaviours of DMSP expected (dashed line) and actual (continuous line) concentrations, and phytoplankton cell counts and chlorophyll during a salinity shock experiment on diatom in the laboratory. Blue symbols are for diatom cell numbers and green are for chlorophyll.

depend on the age of the diatom. However, aged (eleven day old) diatoms seem to be more sensitive and produce 3-5 times DMSP compared to that by younger ones (two day old). Even if we correct the total DMSP production to plankton cell basis, the aged plankton is evaluated to produce about twice than the young culture (Fig. 5.1). The hike in DMSP production occurs despite decreased phytoplankton cell numbers with dilution in both the cases. While chlorophyll in the two-day-old culture did not show no clear trend it decreased in the aged culture. The DMSP is known to function as an osmolyte in plankton cells [*Dickson et al.,* 1980, 1982; *Vairavamurthy et al.,* 1985]. Thus in order to maintain the osmotic pressure inside the body the phytoplankton produces DMSP to circumvent sudden changes in salinity, positive or negative. The above experiment reveals that changes in salinity are more important in the production of DMSP by plankton than the simple salinity of the ambient medium in which they grow. For instance, *Stefels and Dijkhuizen* [1996] reported negligible increase in the total DMSP content in the first 6 hours in cultures grown under different salinities ranging from 0 to 50 ppt. Thus we propose that it is the stress that leads to enhanced DMSP production. In the present case that stress was manifested in the form of sudden changes in salinity.

5.2 DMSP degradation

5.2.1 Decomposition in marine air

In the first experiment several membrane filter papers loaded with DMSP of 0.34 nmol were exposed to marine air at a height of 6m above the

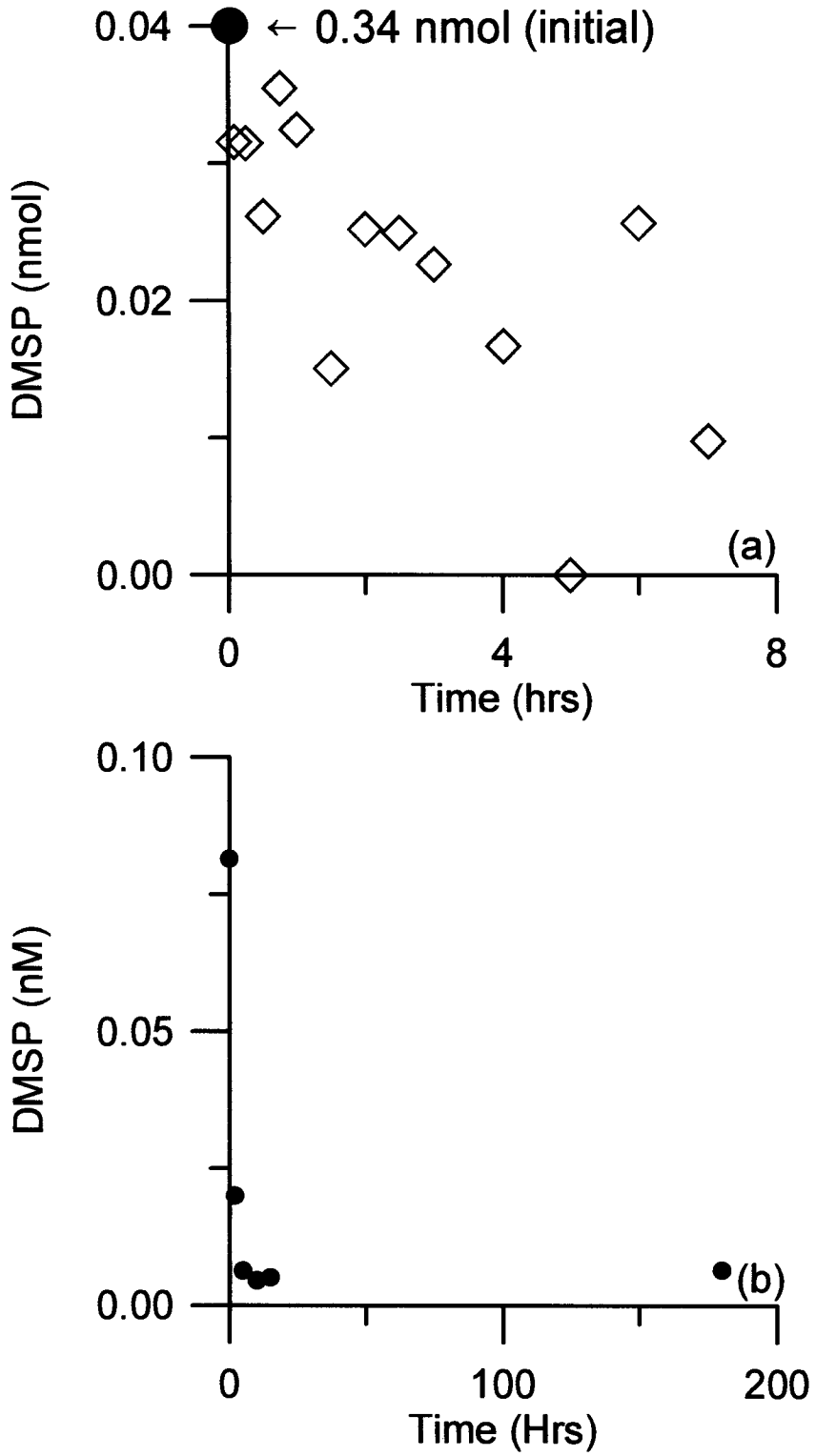


Fig. 5.2. Loss of DMSP with time from a) loaded membrane filters in air and b) in seawater.

sea level. These filters were periodically removed and analysed for DMSP. Fig. 5.2a shows the degradation of DMSP in air. Results revealed a decreasing trend in DMSP with time; drastic fall occurred in the first 5 minutes of exposure (the minimum time we could allow between loading and analysis). A loss of over 90% in 5 minutes suggests that significant portion of ejected aerosol DMSP could be rapidly lost to atmosphere. The loss rate might have been underestimated because the allowed 5 minutes may have been longer for 90% decomposition of DMSP. The DMSP loss thereafter was relatively slow as 30% of 0.035 nmol, present after 5 minutes of exposure, was found on filters at 7 hours.

5.2.2 Decomposition in seawater

In the second experiment 0.081 nM of DMSP was introduced in a litre of seawater in a beaker. Before the experiment, the seawater sample (collected from surface) was exposed to ultraviolet radiation to deactivate microbial populations. Blank runs were made on the seawater sample prior to the addition of DMSP. The spiked seawater sample was exposed to sunlight, adjacent to the laboratory, on the main deck of the ship. The sample was periodically subjected to purging with air using syringe, in order to simulate the introduction of atmosphere species (chemical species, eg. Nox, hydroxyl radicals etc.) and possibly including bacteria. Aliquots of the seawater sample were periodically sampled and analysed for DMSP after alkali hydrolysis. Even here, as in filter experiments briefed above, a rapid fall in DMSP was found (Fig. 5.2b). The DMSP analysis here would represent the sum of DMS

and DMSP present in the seawater sample. Our results suggest that a compound (probably methanethiol) with a retention time of 1.5 min, was formed in significant concentrations during the hydrolysis. As the alkali hydrolysis of DMSP is expected to lead only to the formation of DMS and acrylic acid, the appearance of peaks with 1.5 min retention time indicates that the DMSP decomposition in seawater is possibly resulting in an intermediate compound, which upon hydrolysis yields methanethiol. Formation of such compound may also be possible during DMSP decomposition in air. The unknown intermediate compound should be studied in detail and characterized in order to understand the dynamics of dimethylsulphur compounds in the marine environment.

During a declining phase of *Emiliana huxleyi*, *Levasseur et al.* [1996] found decrease in DMSP concentrations coinciding with a sharp increase in bacterial abundance and growth. The rapid loss of DMSP, as in our experiments, indicated the involvement of bacteria. Bacteria have been found to utilize DMSP and convert it to methanethiol. The methanethiol is later converted to methionine and taken up in the amino acid pathway [*Simo and Pedros-Alio,* 1999]. The above fall in the levels of DMSP on the filter paper and in seawater can thus be attributed to the rapid removal by photolytic and chemical reactions or possibly bacterial degradation.

The salient features from laboratory experiments are:

1. Salinity shock enhances DMSP production in phytoplankton.
2. DMSP production during the shock experiments does not depend on exposure time and salinity of medium.
3. DMSP is unstable in marine air and seawater and can be decomposed by chemical species, photolysis or bacteria.
4. During the DMSP decomposition to DMS there appears to be an intermediate product, which upon alkali hydrolysis possibly yields methanethiol.

CHAPTER 6

Factors Regulating DMSP and DMS in Seawater

Chapter 6

Factors regulating DMSP and DMS in seawater

Maximal concentrations of DMS and DMSP occur closer to sea surface (Chapter 4). Such occurrence facilitates higher emission of DMS to atmosphere than otherwise. Interestingly, even though these compounds are biogenic in origin their maximal concentrations do not always coincide with those of chlorophyll *a* (Chapter 4). Therefore, it is important to understand what factors control the abundance of these compounds in the water column with particular reference to their maximal abundance near the surface. This chapter examines the roles of salinity, chlorophyll, nitrate, mixed layer depth (MLD) and Ultra-Violet radiation (UVR) as factors responsible for regulation of DMS and DMSP levels in Indian Ocean.

6.1 Salinity as a controlling factor

Salinity of seawater plays a very important role in the physiological functions of marine organisms. The changes in salt contents in the body fluid and ambient seawater medium can result in osmotic pressure imbalance. The imbalance is likely to put the cell under stress. In order to maintain the required osmotic pressure, for the cell to remain in equilibrium with the surrounding seawater, the plankton said to produce DMSP [*Reed,* 1983*; Kirst et al.,* 1991], although the DMSP may also serve other functions as well [*Kiene et al.,* 2000]. Therefore, salinity could be one of the factors responsible for the extent of production of DMSP by phytoplankton. The DMS in seawater

results from the degradation of this DMSP and hence we examine their relations with salinity to understand its role in controlling their abundances.

The Arabian Sea region is the source of high salinity waters in the North Indian Ocean. Water masses such as the Arabian Sea High Saline Watermass (ASHSW), Persian Gulf water (PGW) and Red Sea Water (RSW) masses are important in the top 1000 m. Fig. 6.1 shows the typical vertical distributions of salinity, DMS and DMSP in the upper 100 m of the water column of the southern Arabian Sea. Profiles show general high salinity near the surface that decreases below. Salinity variation was between 34.560 and 36.570. DMS and DMSP were higher closer to the surface and decreased with depth. Weak positive relations for salinity with DMS and DMSP can be seen in Fig. 6.1. Thus an attempt was made to check if these relations are influenced by similarities in behaviours of the properties considered. Fig. 6.2a depicts the relations between vertical gradients in salinity (differences in property between any two depths at each station, d Salinity) with those in DMS (d DMS) and DMSP (d DMSP). Both DMSP and DMS gradients show somewhat positive relations with changes in salinity despite considerable scatter. It is possible, however, that these relations might be influenced by vertical behaviors of these properties. Therefore, horizontal gradients were evaluated (based on differences between properties at similar depths of two neighboring stations) and the consequent relations are shown in 6.2b. Here changes in DMSP and DMS showed unclear relations with that in salinity.

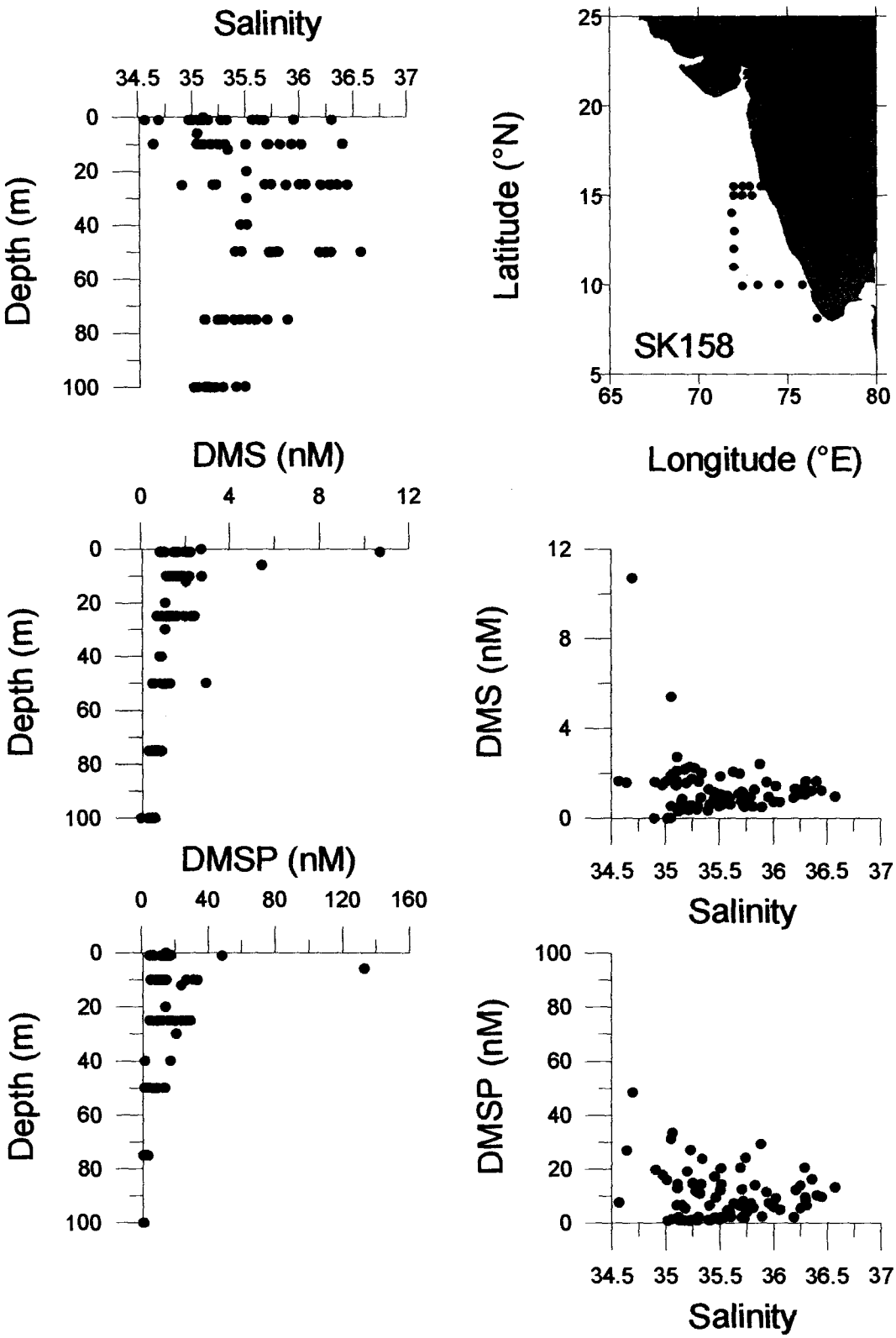


Fig. 6.1 Vertical variations in salinity, DMS and DMSP, and relations for salinity with DMS and DMSP in the Arabian Sea.

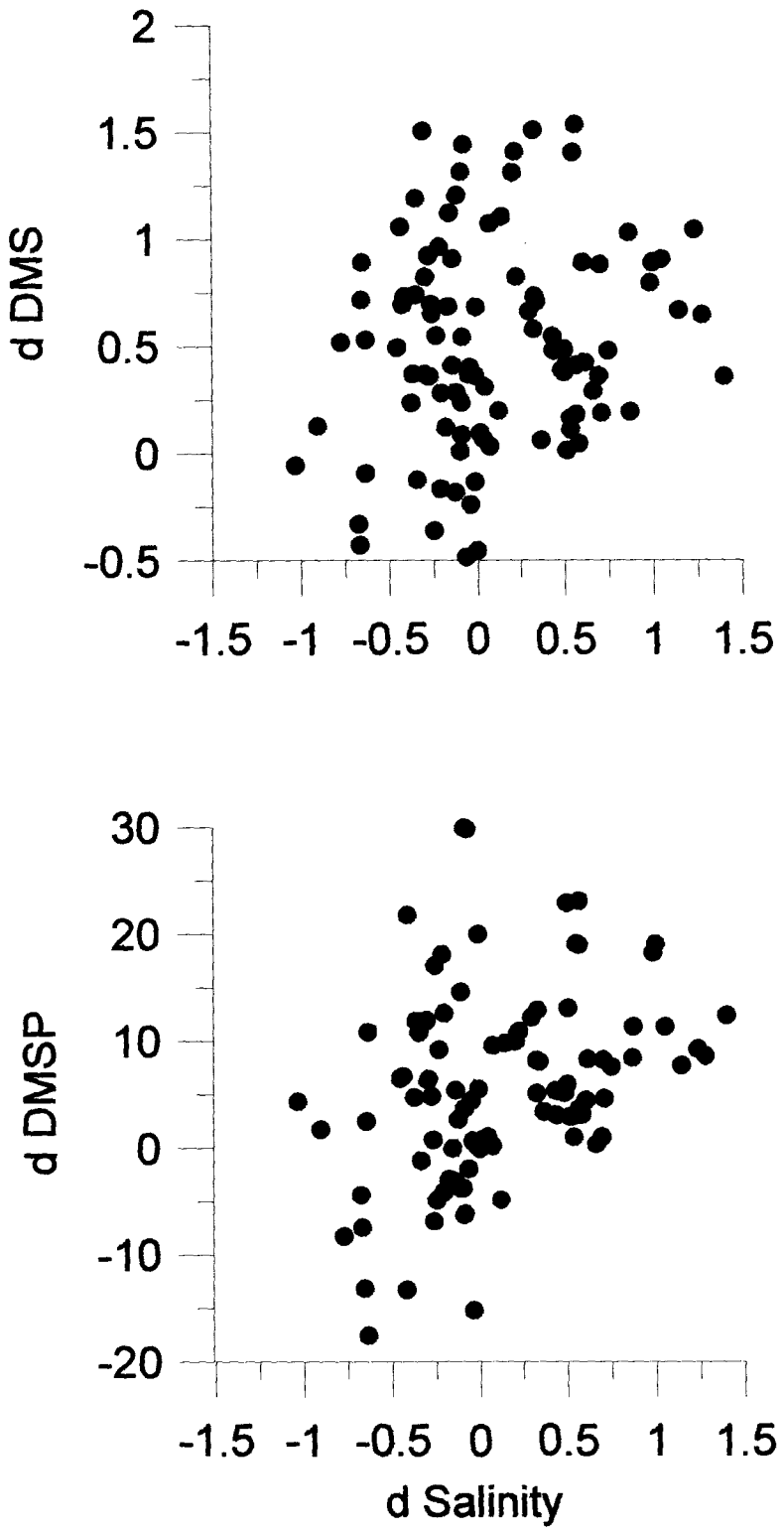


Fig. 6.2a. Relations between vertical gradients in salinity (based on differences between any two depths at each station) with those in DMS and DMSP in the Arabian Sea.

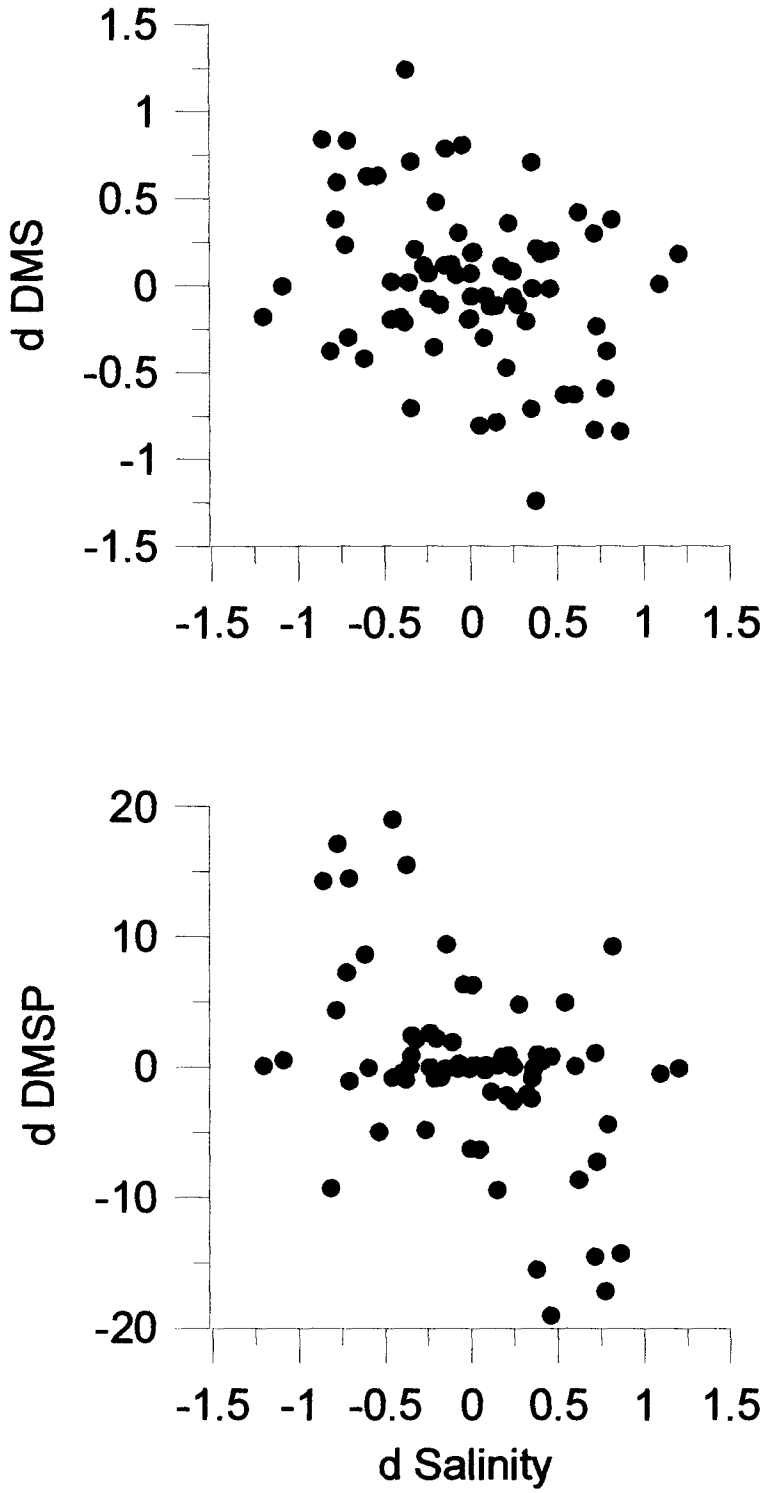


Fig. 6.2b. Relations between horizontal gradients in salinity (based on differences at a specific depth between two neighbouring stations) with those in DMS and DMSP in the Arabian Sea.

From this it is not clear whether changes in salinity influence the concentrations or production of DMSP and DMS in the Arabian Sea.

The Bay of Bengal is a region of positive water balance with strong salinity gradients. In contrast to that in the Arabian Sea, salinity in the Bay of Bengal (Fig. 6.3) shows an increase with depth. The Bay receives enormous amounts of fresh water from a few of the world's largest rivers. This together with monsoonal rain forms a low saline cap at the surface. During a time series study (SK 147A, see Fig. 3.8a,b) the salinity varied between 26.630 and 35.020 in the upper 100 m with higher values in the deep. The DMS and DMSP exhibited decreases in abundance with increasing depth with maximal values occurring in the upper 20 m. A few higher values were found around 40 m. The relations for DMSP and DMS with salinity were negative. This behaviour is in apparent contrast with the relations found in 6.1 for the Arabian Sea. The differences between 6.1 and 6.3 could be a result of contrasting vertical behaviour of salinity between the two regions. Relations between vertical gradients in salinity and that of DMSP and DMS revealed that enhanced DMSP and DMS levels are favoured where salinity decreased (Fig. 6.4a). As this relation may also be a biased result from vertical behaviors we considered horizontal gradients again (Fig. 6.4b). The obvious negative relations in Fig. 6.4b have important implications since horizontal gradients in this case were deduce from the variations at the same location but with changes in properties with time. Fig. 3.8a clearly indicates the incursion of low salinity waters into the study area. Although the negative relation appears not

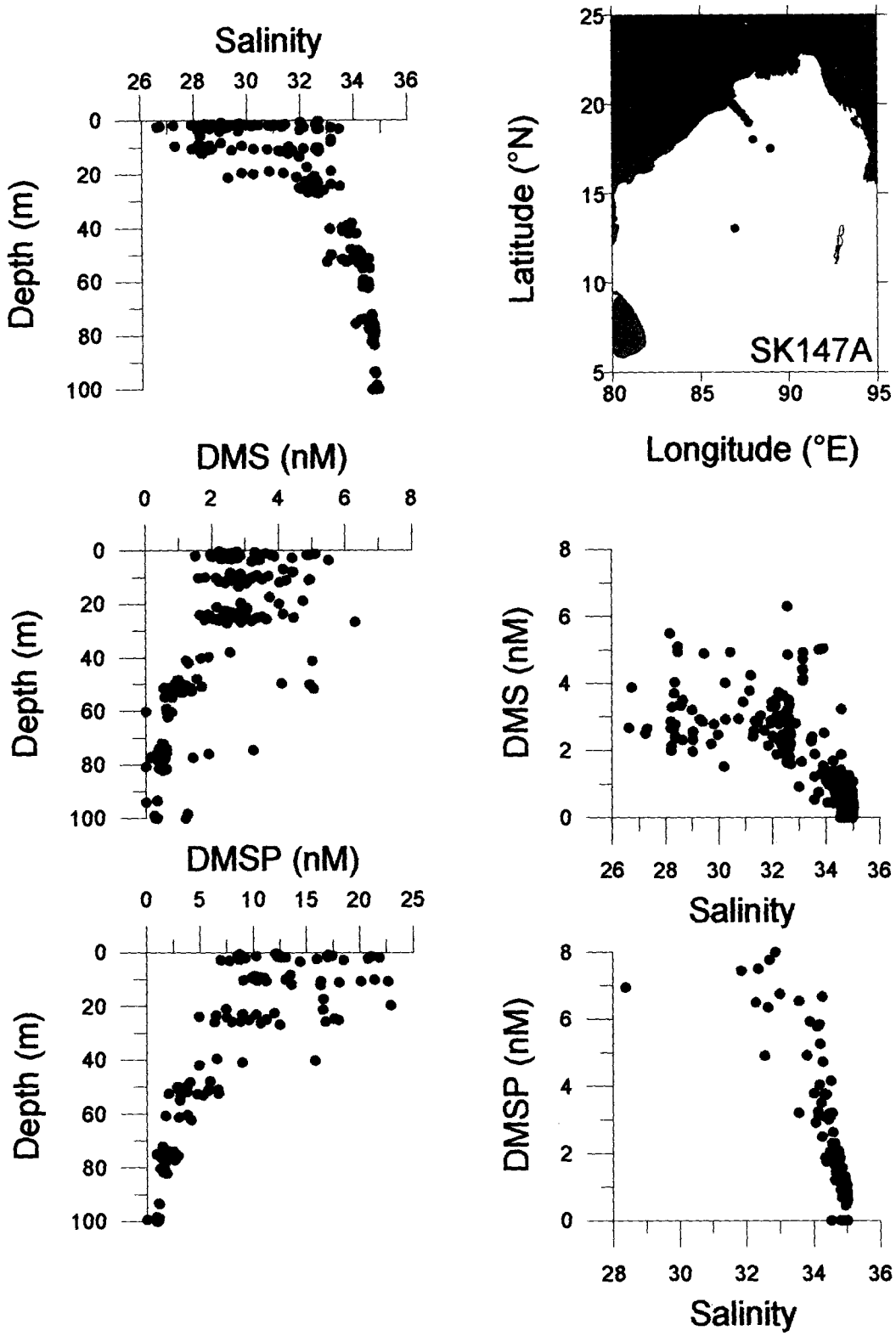


Fig. 6.3. Vertical variations in salinity, DMS and DMSP; and relations for salinity with DMS and DMSP in the Bay of Bengal.

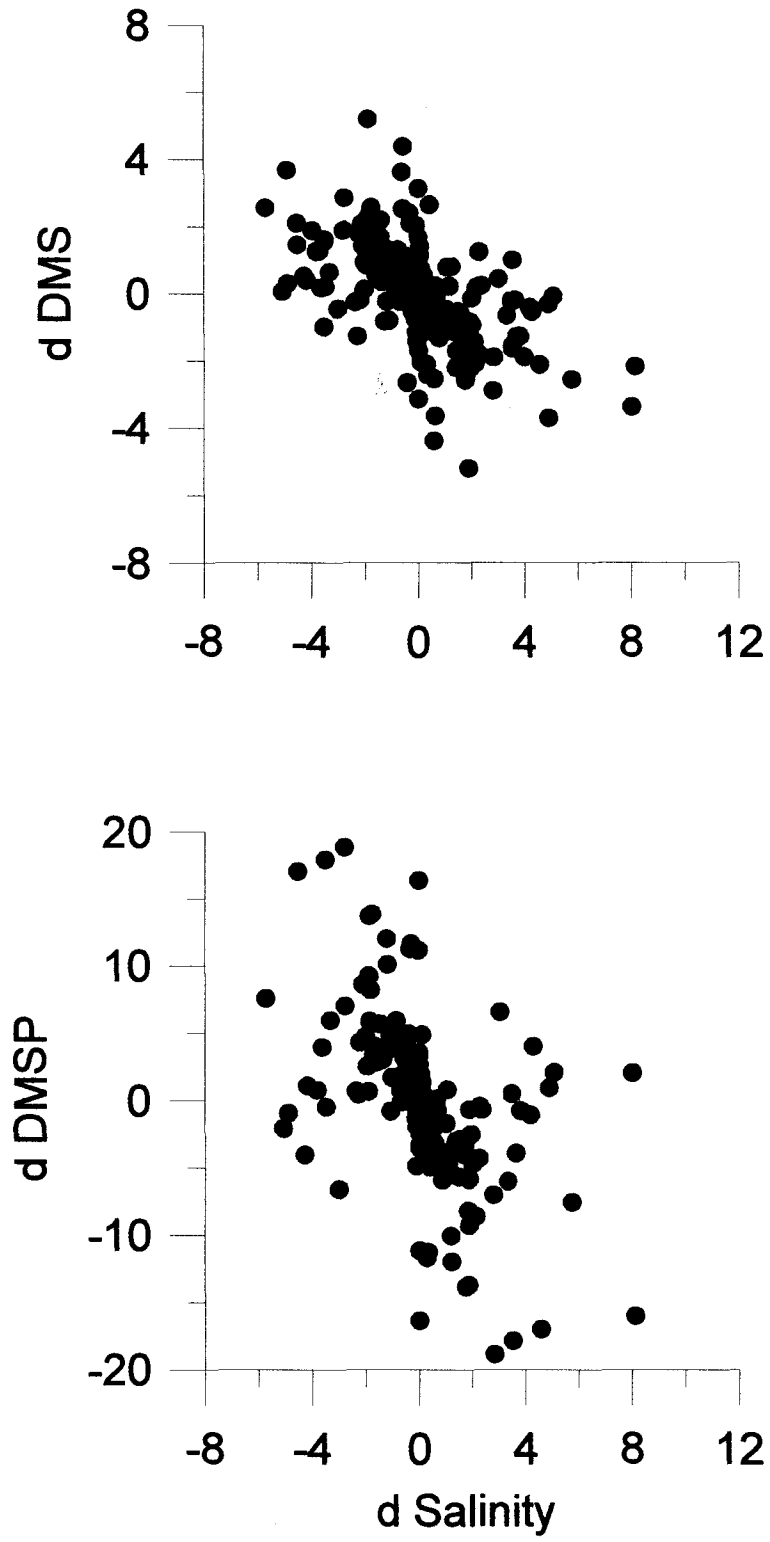


Fig. 6.4a. Relations between vertical gradients in salinity (based on differences between any two depths at each station) with those in DMS and DMSP in the Bay of Bengal.

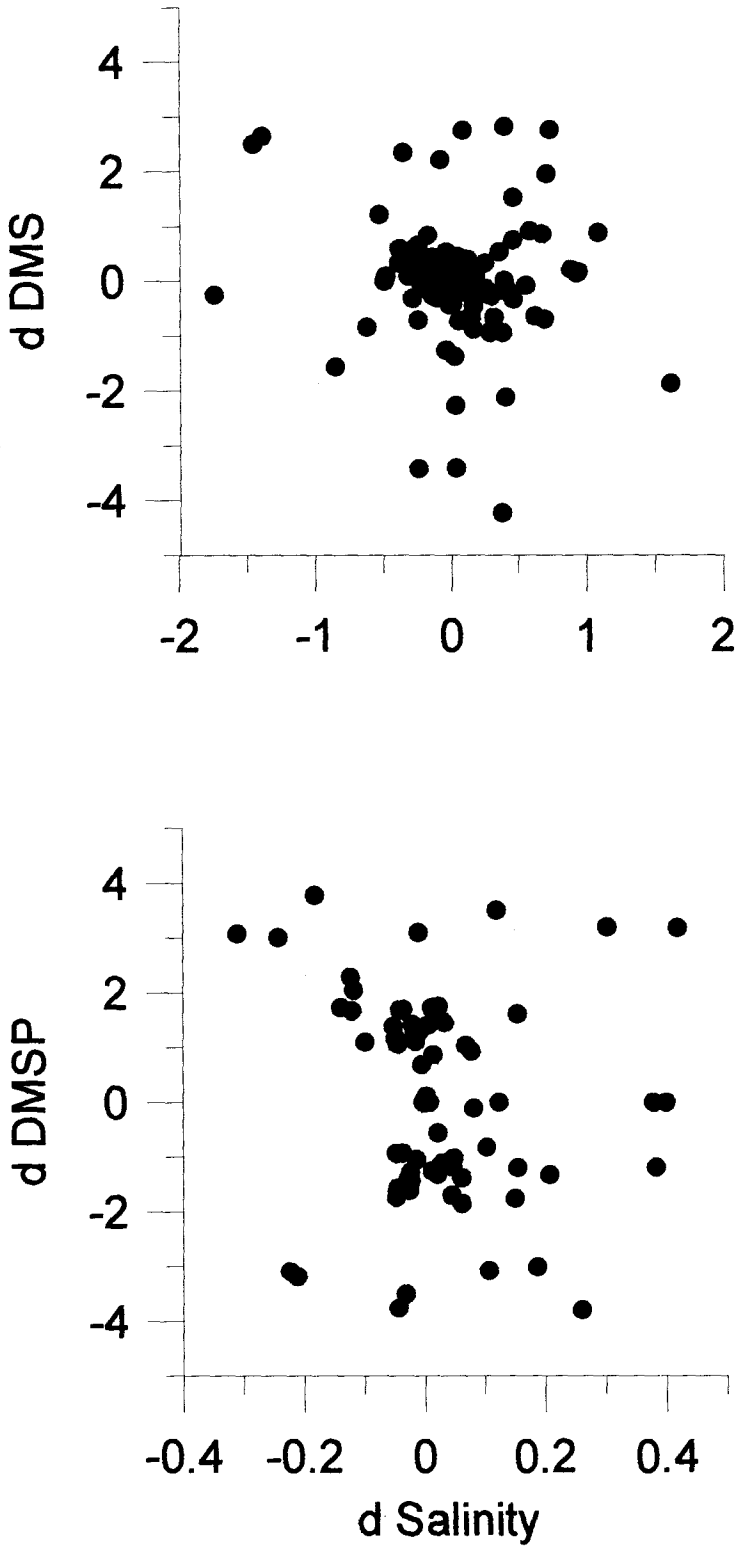


Fig. 6.4b. Relations between horizontal gradients in salinity (based on differences at a specific depth between two neighbouring stations) with those in DMS and DMSP in the Bay of Bengal.

well resolved it indicates to the possibility that a decrease in salinity can lead to an increase in DMS. This is clear from the dense number of points. In the case of DMSP the negative relation is more obvious. These relationships (Fig. 6.4b), in fact, prompted us conduct laboratory experiments (see chapter 5 and Fig. 5.1) in which our experiments unequivocally confirmed that plankton (diatoms) produce more DMSP when subjected to sudden changes in salinity.

Fig. 6.5 depicts the vertical distributions of salinity, DMSP and DMS and also the relations for salinity with DMSP and DMS in the central Indian Ocean. Vertical distributions of the properties in question are nearly similar to that in the Bay of Bengal (Fig. 6.3) but with changes in trends between relations. Detectable levels of DMS and DMSP occurred even below 100 m that differ with the vertical behaviours both in the Arabian Sea and the Bay of Bengal. Salinity varied between 34.620 and 36.440 in the upper 150 m of the Central Indian Ocean. Vertical gradients in salinity and DMS are clearly related negatively but not that involving DMSP (Fig. 6.6a). The relations are not clear also with respect to horizontal gradients (Fig. 6.6b).

Iverson et al. [1989], in a study on DMSP and DMS production in estuarine and coastal waters, found positive correlations between concentrations of these biogenic sulphur species and salinity. On the other hand, experiments performed on axenic cultures of *Phaeocystis sp.*, revealed that production of DMSP and its cleavage by DMSP lyase are not related to short-term regulation of the osmotic potential based on salinity changes [*Stefels and Dijkhujizen,* 1996]. *Nianzhi et al.* [1999] found no correlation

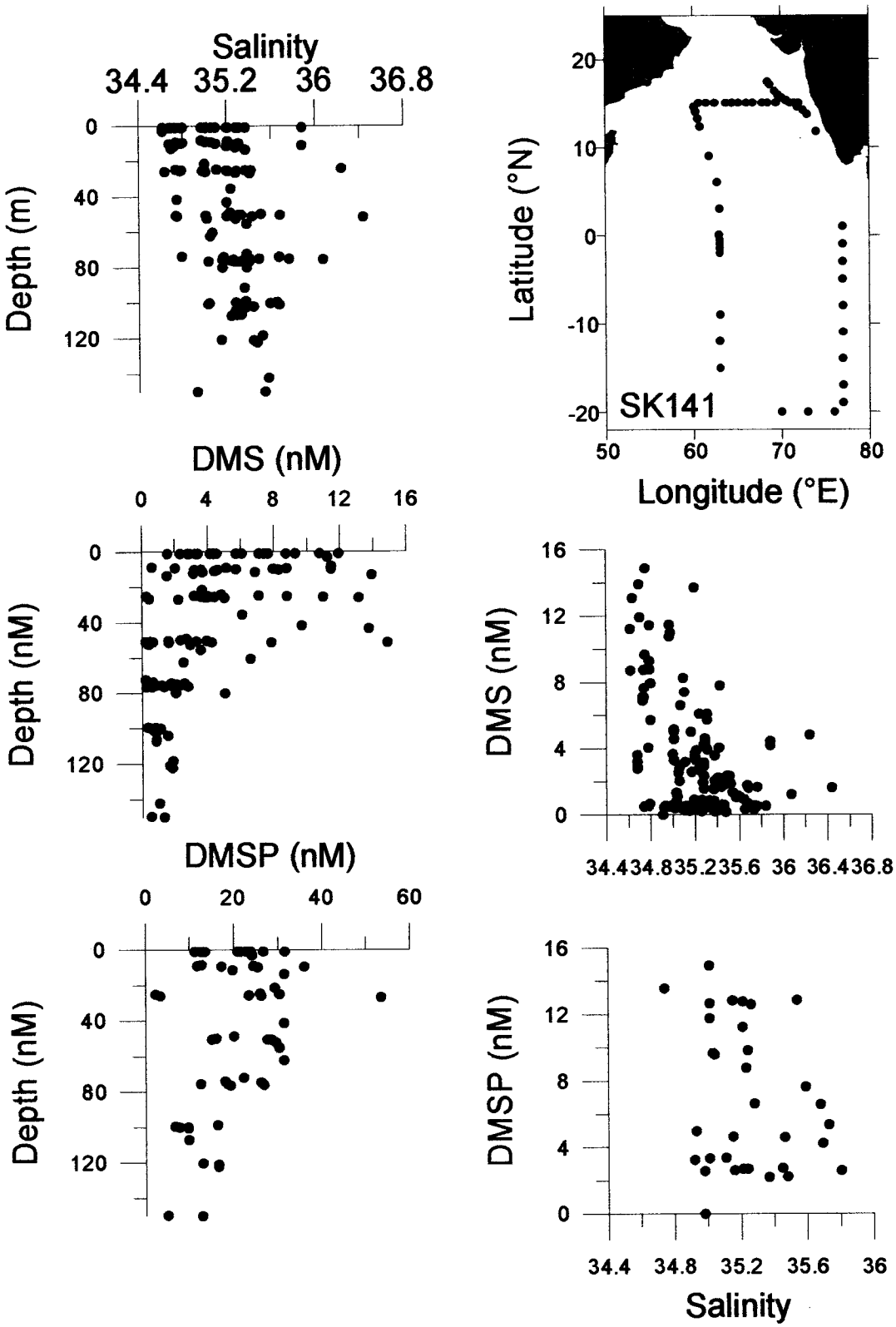


Fig. 6.5. Vertical variations in salinity, DMS and DMSP; and relations for salinity with DMS and DMSP in the Central Indian Ocean.

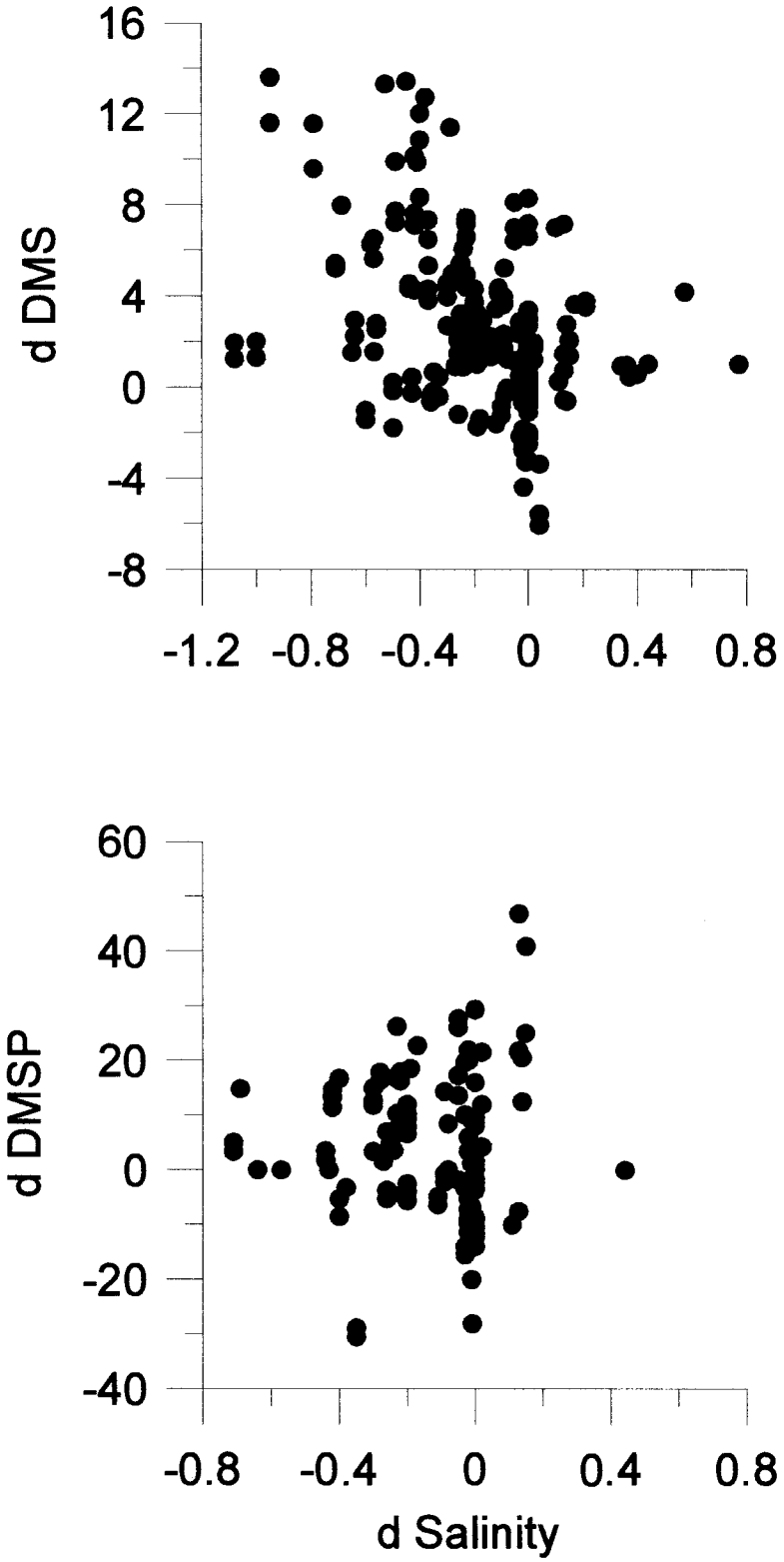


Fig. 6.6a. Relations between vertical gradients in salinity (based on differences between any two depths at each station) with those in DMS and DMSP in the central Indian Ocean.

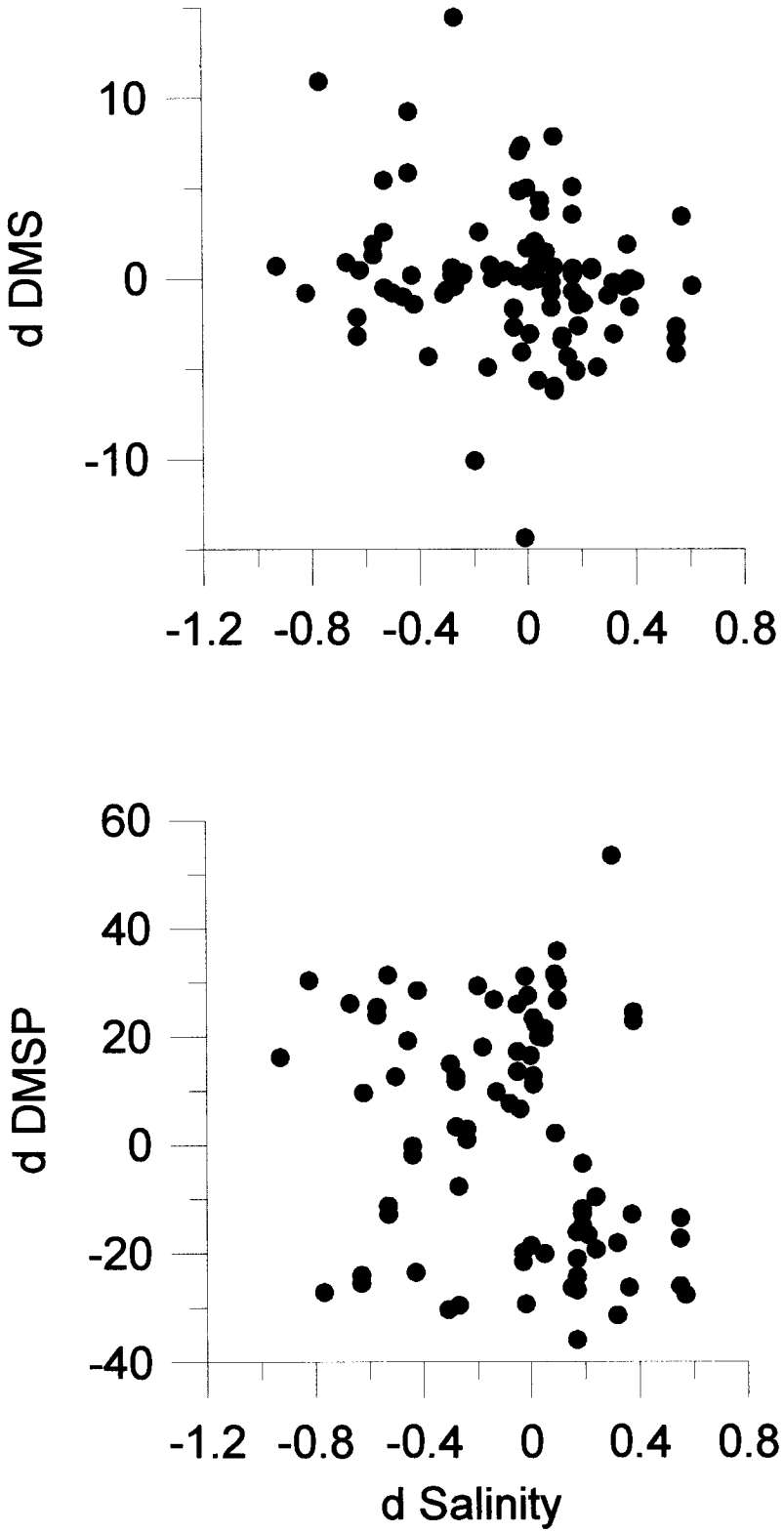


Fig. 6.6b. Relations between horizontal gradients in salinity (based on differences at a specific depth between two neighbouring stations) with those in DMS and DMSP in the Central Indian Ocean.

between DMSP and salinity in the East Chine Sea. *Stefels* [2000] opined that due to very slow plankton adaptation while changing its intracellular DMSP concentration in relation to ambient salinity changes DMSP need not be considered as an osmolyte, but rather as a constitutive compatible solute. Nevertheless, our field, particularly from the Bay of Bengal (Figs. 6.3 and 6.4) and experimental results (detailed in chapter 5) clearly establish the following: (i) salinity shocks (spontaneous dilution in salinity) do increase the $DMSP_t$ content in phytoplankton, (ii) extent of DMSP production depends on age of the plankton and (iii) the laboratory results appear to be of limited applicability in the field because of the fact that the expected sudden changes in salinity (as those in the diatom salinity shock experiment) may not occur in natural conditions. Thus salinity may not have a direct control over DMSP and DMS production in the Indian Ocean except to some extent in the Bay of Bengal due to intense vertical and horizontal salinity gradients aided by sudden changes in circulation driven by extreme climatic events.

6.2 Chlorophyll and phytoplankton speciation

Chlorophyll represents the biomass of mainly the phytoplankton origin. Since plankton largely produces DMSP the concentrations of DMSP and DMS might depend on phytoplankton productivity. The chlorophyll *a* is a measure of phytoplankton productivity even though the measured pigment is fresh or that accumulated over sometime. Although a fraction of that comprises the dead materials chlorophyll *a* is a good indicator of primary production in the immediate past, and therefore, this section attempts to explore the possible

relations for DMSP and DMS with chlorophyll. Both DMSP and DMS did not appear to exhibit clear relations with chlorophyll as the most number of Arabian Sea data appear to cluster near the point of origin in a linear plot (left panels) in Fig. 6.7, except for DMSP at concentrations > 2 nM. It could be seen from the scales that the variations in these parameters ranged by three-four orders of magnitude. The Arabian Sea is the most productive region in the Indian Ocean and the data used in Fig. 6.7 represent coastal, including SW monsoonal upwelling regions along the west coast of India, and open ocean data. When these data are plotted on log-scales the linear relations are well resolved both for DMS and DMSP. Interestingly, linearity is consistently found in different seasons and cruises. Very high concentrations in Fig. 6.7 were found along the Indian coast during and after the SW monsoonal upwelling. Thus phytoplankton production seems to have a direct influence on the levels of DMSP and DMS in the Arabian Sea despite the fact that one to one correlation with chlorophyll is not seen in their vertical distributions. Although DMSP and DMS levels seem to depend on phytoplankton production in the Arabian Sea occurrence of their maximal concentrations very close to surface cannot be explained with these relations.

Fig. 6.8 shows the relations as in Fig. 6.7 for the Bay of Bengal. As in Fig. 6.7 the simple linear plots did not clearly indicate the relations but the log plots did show weak positive relations compared to those in the Arabian Sea. Significantly, despite the widely variable chlorophyll contents between cruises and seasons both DMSP and DMS levels are almost the same. Increased

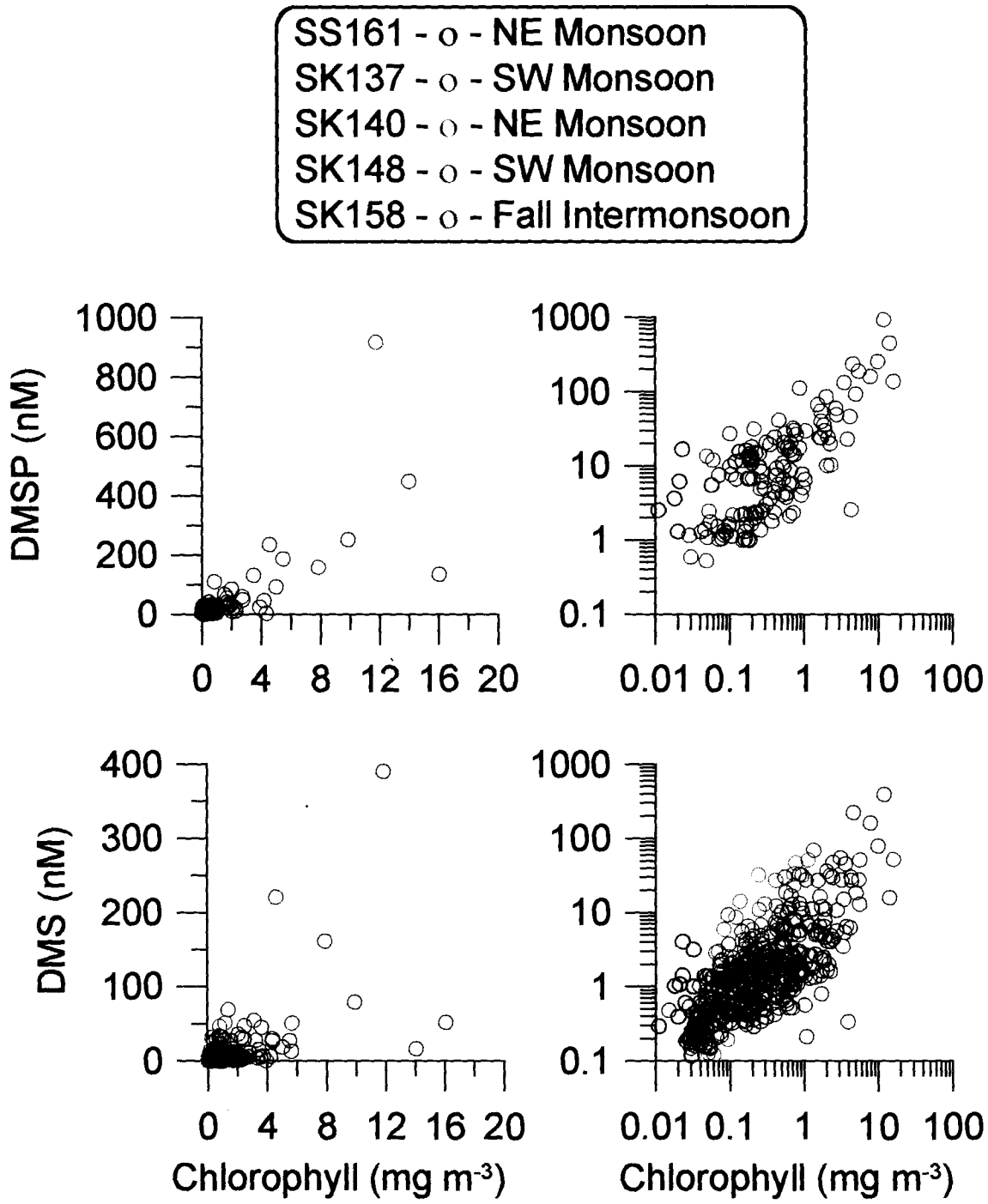


Fig. 6.7. Relations for DM S and DMSP with chlorophyll in the Arabian Sea.

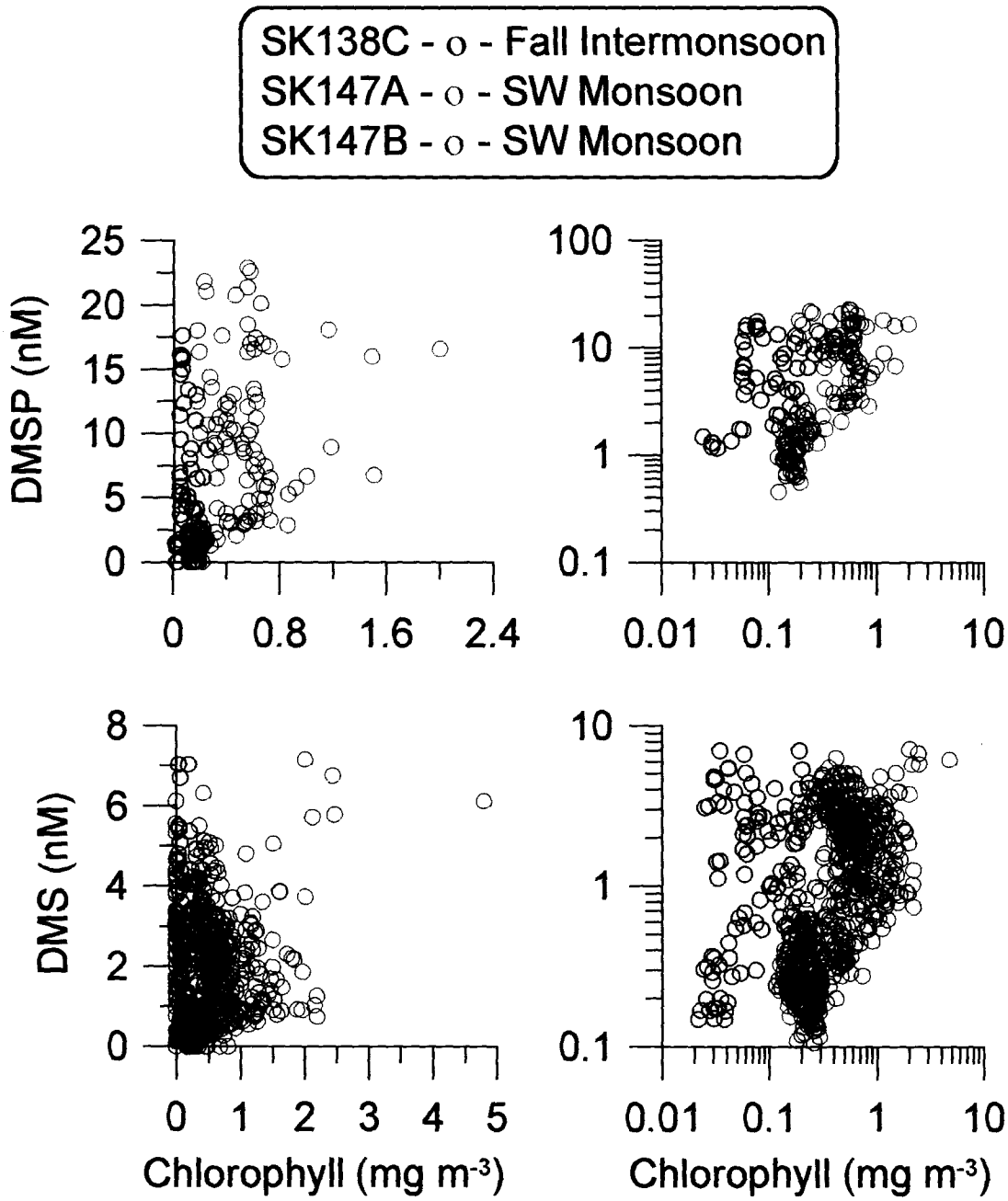


Fig. 6.8. Relations for DMS and DMSP with chlorophyll in the Bay of Bengal.

chlorophyll in the second phase of BOBMEX time series experiment (SK 147B) is striking. This has been a result of pumping of nutrients into the surface due to the turbulence created by storm in the first phase. On the other hand, chlorophyll does not show any specific trends in both linear and log plots with DMSP and DMS in the Central Indian Ocean (Fig. 6.9). The data distribution resulted in scattered diagrams although are well separated with respect to chlorophyll abundance. The eastern Central Indian Ocean (SK150) is found to have the least chlorophyll *a* levels (Fig. 6.9). Therefore, unlike in the Arabian Sea, DMSP and DMS do not show clear dependency on phytoplankton production in the Bay of Bengal and the Central Indian Ocean. One obvious reason, however, is the range of chlorophyll concentrations observed; 0-1 mg m^{-3} in the Central Indian Ocean, 0-10 mg m^{-3} in the Bay and 0-100 mg m^{-3} in the Arabian Sea. Nevertheless, DMSP and DMS levels are higher in the Central Indian Ocean than in the Bay of Bengal. Therefore, it is possible that factors other than phytoplankton production might be dominating in the regulation of DMSP and DMS abundances in the Bay of Bengal and Central Indian Ocean whereas biological dynamics seem to have a significant role in the Arabian Sea.

Presently attempts are being made to establish global relations between chlorophyll *a* and DMS so as to facilitate mapping of DMS through satellites imageries [*Liss et al.,* 1993; *Kettle et al.,* 1999]. *Yang et al.* [1999] and *Yang* [2000] have found positive correlations between DMS and chlorophyll for the South China Sea. *Turner et al.* [1988] found positive

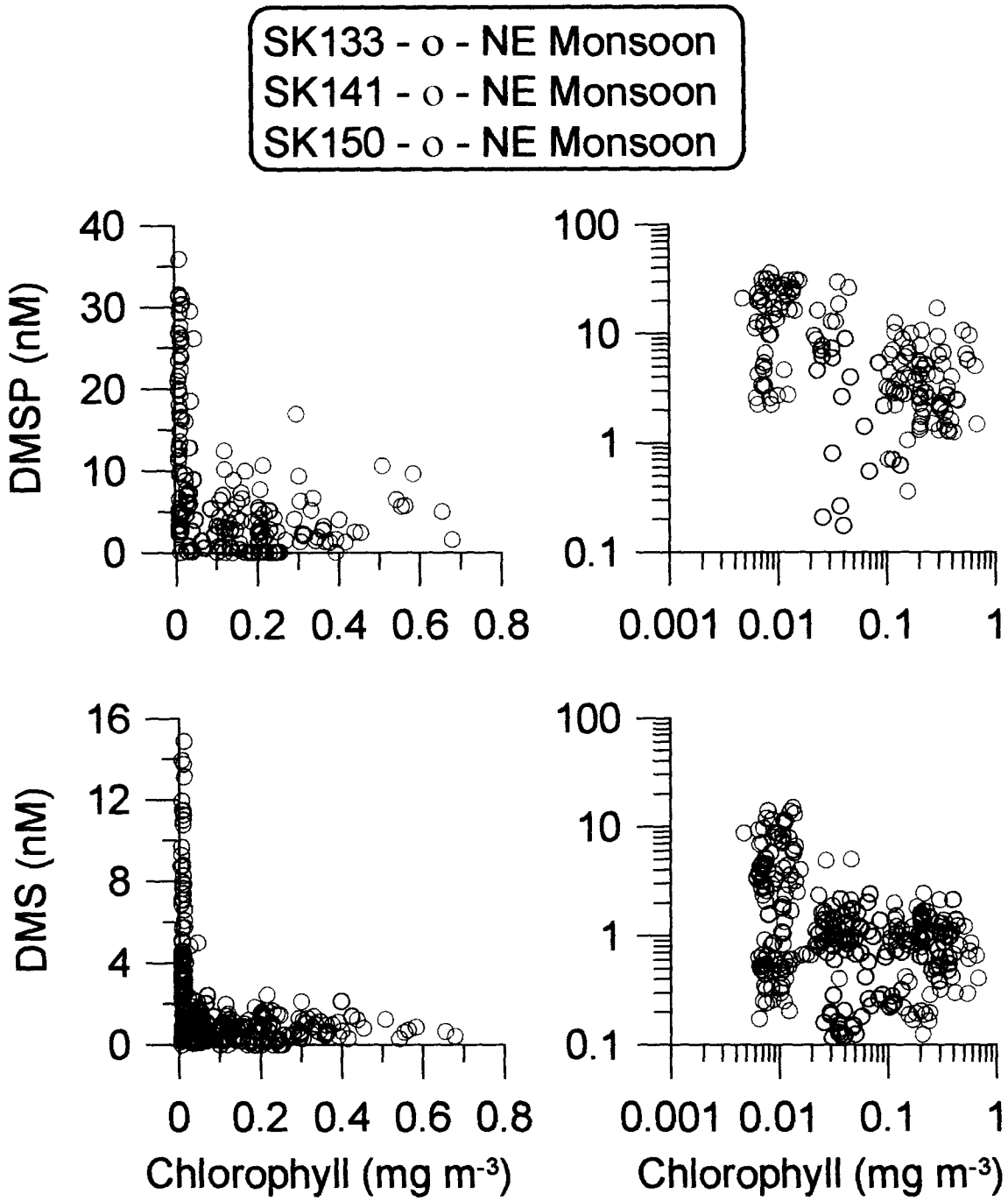


Fig. 6.9. Relations for DMS and DMSP with chlorophyll in the Central Indian Ocean.

correlations after segregation based on independent taxonomic groups in coastal waters of the United Kingdom but not when the data have been considered in toto. Use of global data sets by *Kettle et al.* [1999] did not show any clear relations between DMS and Chlorophyll. Our results on chlorophyll relations with DMS and DMSP in the Arabian Sea agree with that of *Yang et al.* [1999]. On the other hand, our results for the Bay of Bengal and the Central Indian Ocean agree with most of the other observations [see *Kettle et al.,* 1999; and references therein].

To study the species dependency of DMS and DMSP in this region time series measurements were made in the Dona Paula Bay (see Chapter 4). Blooms of diatoms occurred during SW monsoon season (see Fig. 4.9). In July a mixed bloom comprising mainly of diatoms and dinoflagellates was found. Even though dinoflagellates made up merely about 15% of the bloom biomass they appeared to significantly contribute to DMS and DMSP abundances since the highest levels of these compounds (DMSP of 419 nM and DMS of 12.8 nM) occurred in this month. Thus, DMSP and DMSP abundances showed a very clear species dependency in coastal waters of India.

6.3 Nitrate

In the presence of nitrate production of DMSP by phytoplankton has been found to decrease [*Turner et al.,* 1988] because of the lesser energy involved in nitrate conversion to glycinebetaine (GBT) than sulphate to DMSP [*Wyn Jones and Storey,* 1981; *Turner et al.,* 1988]. On the contrary, laboratory

experiments have revealed DMSP levels produced by plankton to be independent of nitrate concentrations available [*Keller et al.,* 1999a,b]. One of the main limiting factors of primary production in the northern Indian Ocean is nitrate unlike the Southern Ocean where iron is the limiting nutrient. Figs. 6.10, 6.11 and 6.12 give the relations between nitrate, and DMS and DMSP for the Arabian Sea, Bay of Bengal and the Central Indian Ocean respectively. Here, only the data from the top 50 m have been used to avoid sub-thermocline (where nutrients start increasing with depth) effects. The illustrations do not exhibit clear trends in relations. In general, DMSP and DMS occurred in measurable quantities at low concentrations of nitrate, which seem to be a result of differences in their vertical behaviours. However, these were found in higher abundance even at higher nitrate concentrations in upwelling regions in the Arabian Sea (Fig. 6.10), under turbulent conditions when nutrients are pumped into surface layers in the Central Indian Ocean and the Bay of Bengal (Figs. 6.11, 6.12). The bay also experiences shallow mixed layers where nutrient rich sub-thermocline waters are sunlit. Our observations, therefore, reveal no one to one correlations between nitrate, and DMSP and DMS abundances in the Indian Ocean.

6.4 Mixed layer depth

Mixed layer depths play a very important role in controlling biological processes in the surface ocean. For instance, the Arabian Sea has deeper MLDs during the monsoons due the higher wind speeds while lower wind speeds lead to shallow MLDs during the inter-monsoons. Shallower MLDs

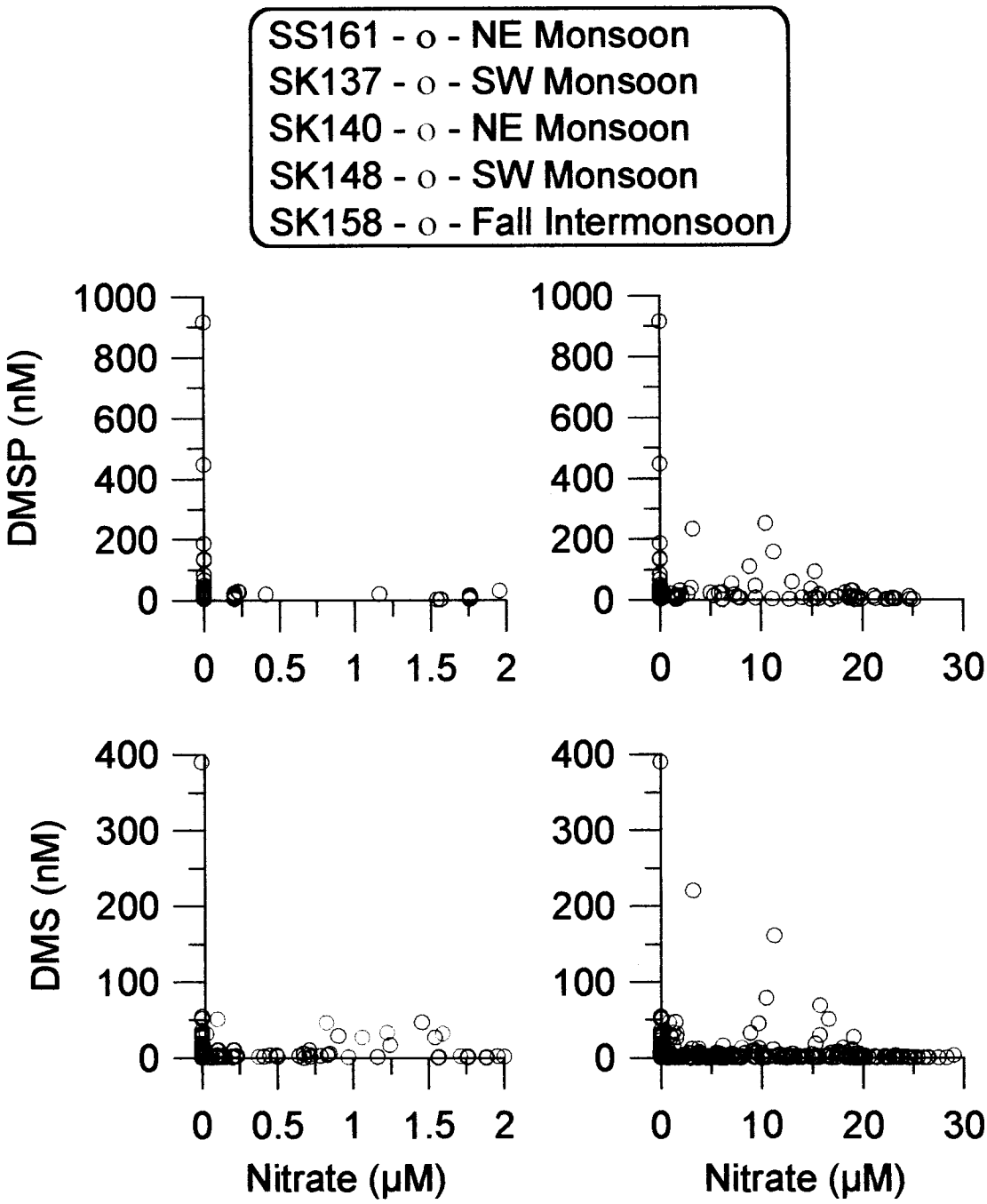


Fig. 6.10. Relations for DMS and DMSP with nitrate in the Arabian Sea; left panels - when nitrate is < 2µM and right panels - in the upper 50 m.

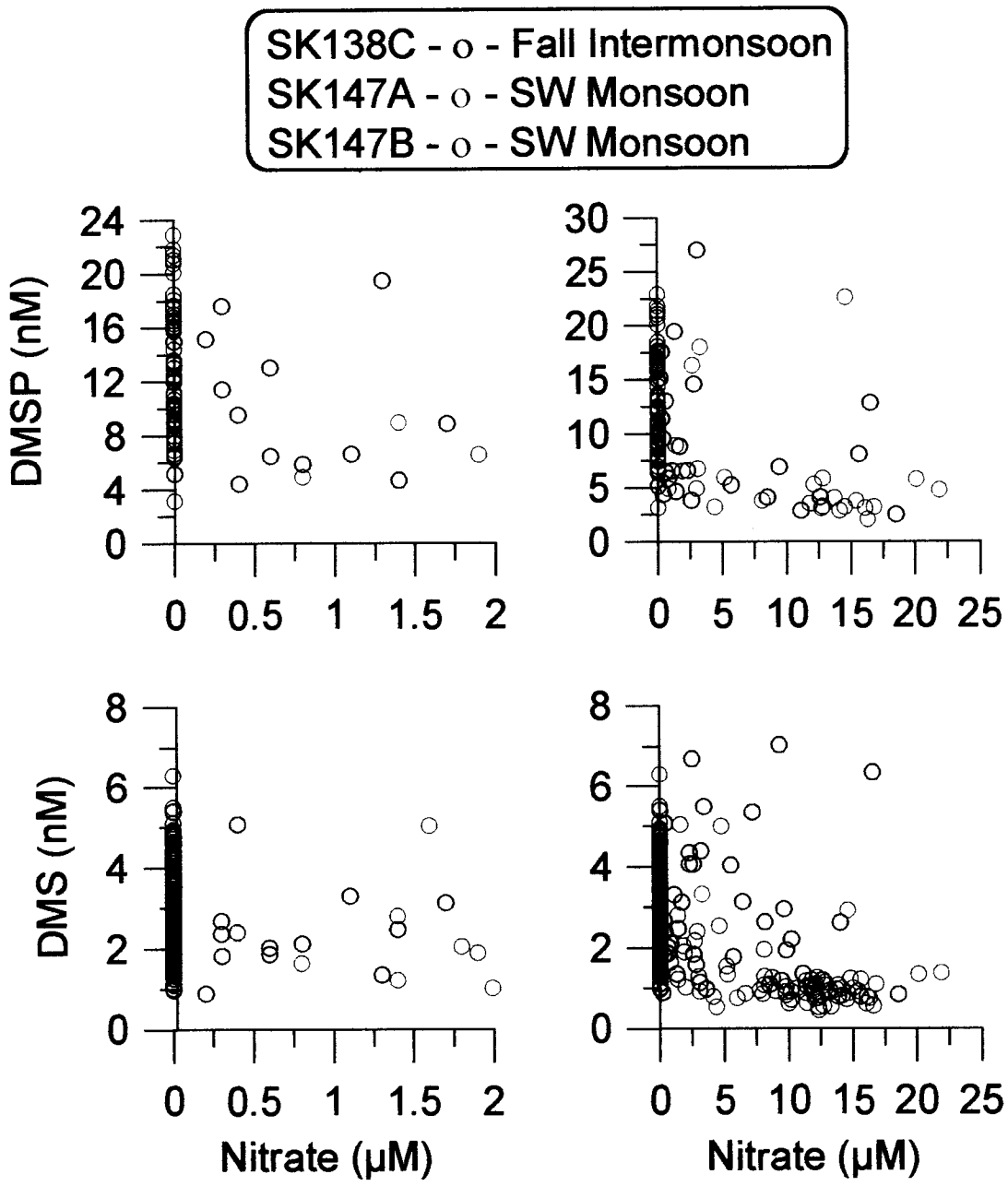


Fig. 6.11. Relations for DMS and DMSP with nitrate in the Bay of Bengal; left panels – where nitrate is < 2 μM and right panels – in the upper 50 m.

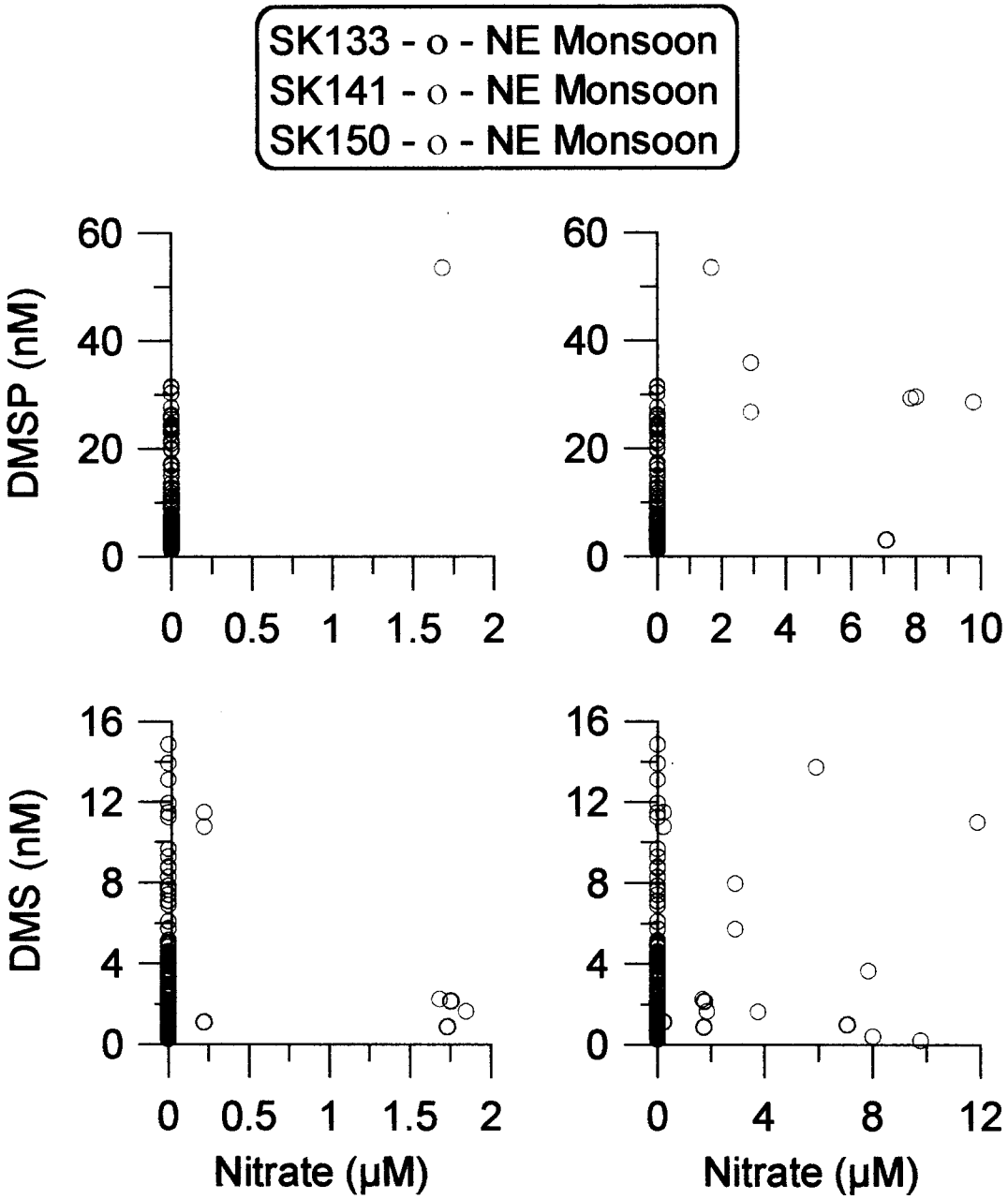


Fig. 6.12. Relations for DMS and DMSP with nitrate in the Central Indian Ocean; left panels - where nitrate is < 2 µM and right panels - in the upper 50 m.

imply shallower nutricline, which results in the availability of nutrients within the euphotic zone and helps in increased primary production (secondary chlorophyll maximum) during the inter-monsoons [*Naqvi,* 2001].

Deep MLDs of over 80 m occurred during SS161 (Arabian Sea) and SK141 (Central Indian Ocean in 1999) but were less deep in SK133 (Central Indian Ocean in 1998) in winter (Fig. 6.13). MLD of about 120 m occurs in Arabian Sea due to winter convection [*Madhupratap et al.;* 1996] whereas the deep ones in Central Indian Ocean during SK141 are due to intense mixing driven by strong winds, located near the Inter Tropical Convergence Zone (ITCZ, between equator and 10°S). MLDs, on the other hand, were much shallower in SK158 due to strong stratification, which is characteristic of inter-monsoon periods. The ML-DMS range was lower in SK133 (0.9 – 2.3 nM) than in SK141 (1.5 – 13.4 nM) exhibiting significant inter-annual variability since the study period (winter) and area (Central Indian Ocean) were the same but occupied in subsequent years (1998 and 1999). On the other hand, ML-DMS levels were low in inter monsoon (0.9-1.9 nM; SK158) than in winter (0.4-11.3 nM; SS161). These are compared for ML-DMS values evaluated based on 1° drop consideration. This is because of minimal effects of MLD computational considerations on MLD-DMS, in general, that further suggests improved negative relationship (decreased scatter) between MLD and ML-DMS when temperature drop (particularly 1°C) were used. Therefore three points emerge from Fig. 6.13: a) striking inter-annual variation in ML-DMS averages in Central Indian Ocean, b) vastly different ML-DMS values between

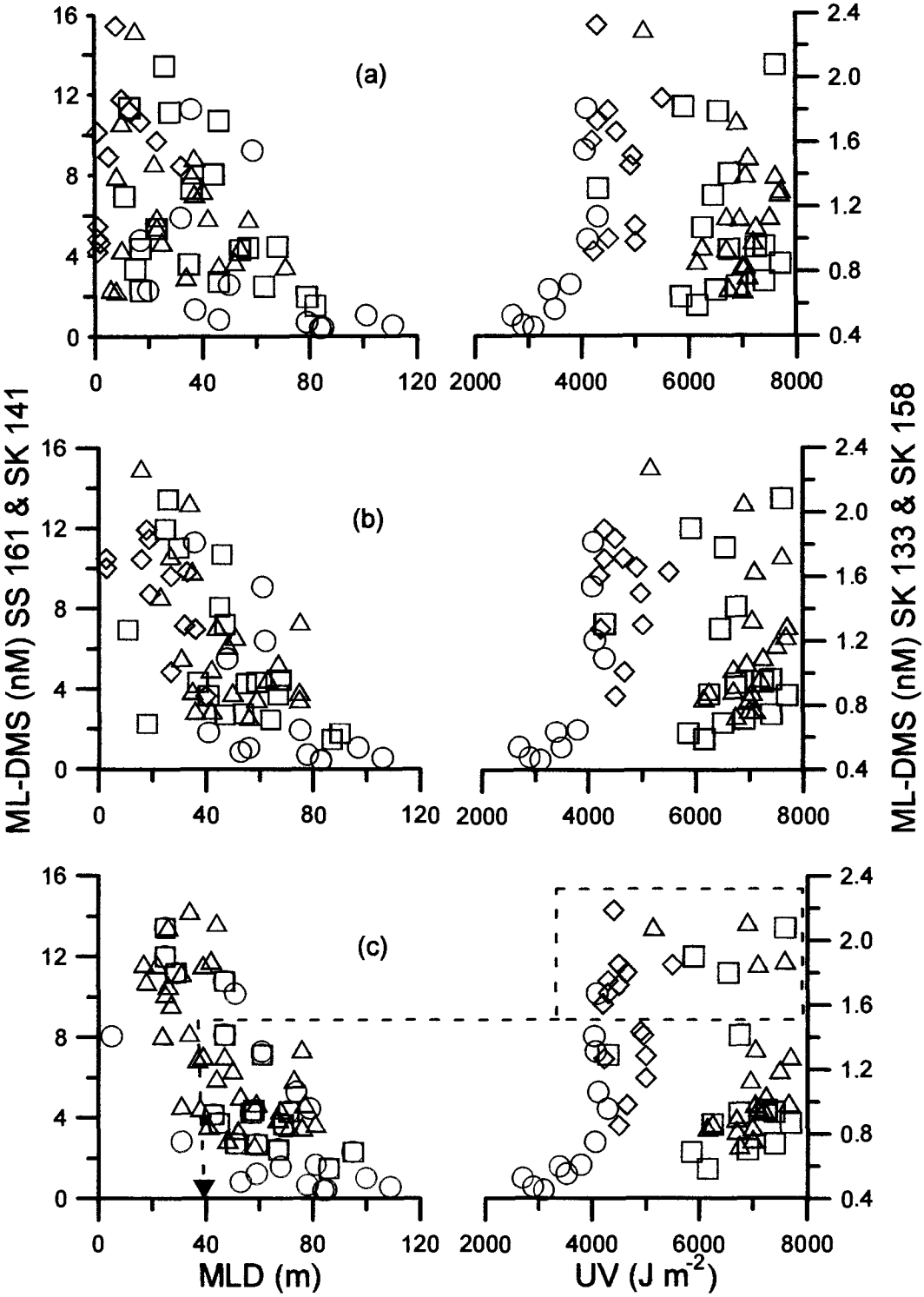


Fig. 6.13. ML-DMS relations with MLD and UV (TOMS) in the Indian Ocean. Symbols indicate: ○ - SS 161, △ - SK 133, □ - SK 141 and ◇ - SK 158 cruises. The three vertical panels are for MLDs computed based on the considerations of (a) 0.125 kg dm^{-3} hike, and (b) 0.5°C and (c) 1.0°C drops compared to that at the surface.

winter and fall inter-monsoon seasons in the Arabian Sea revealing strong seasonal variability and c) negative relation between ML-DMS and MLD irrespective of season and area of study. The relations observed between DMS yields and MLDs through *in vitro* incubation experiments [*Simo and Pedros-Alio,* 1999] seem to be at variance with those in Fig. 6.13. The incubation experiments showed a negative relation up to MLD of 15-20 m but a positive one thereafter. Despite the consistent negative relations in Fig. 6.13 wide variations in magnitudes of ML-DMS averages between regions and seasons indicate that MLD is not the sole factor in determining the magnitudes of DMS concentrations in the surface Ocean.

6.5 Ultra-violet (UV) radiation

Chlorophyll levels are found to be affected by UV radiation in the Bay of Bengal (Fig. 3.9). The maximal DMS concentrations in surface layers of the Indian Ocean are generally decoupled from peaks of chlorophyll [*Shenoy et al.,* 2002] suggesting that near surface processes are important in DMS formation of which radiation could be significant. Fig. 6.13 (right panels) suggests that intensity of ultra-violet radiation (300-400 nm) exhibited zonal bands; higher intensity occurred in Central Indian Ocean than in Arabian Sea. In Arabian Sea the difference in incident UV radiation between winter (when cloud cover is expected) and fall inter-monsoon (clear sky) seems to be insignificant. As in the case of MLD the strength of relationships (in left panels of Fig. 6.13) became better from (a) to (c) with clear positive relations between UV and ML-DMS, particularly at lower concentrations. Relations between

intensity of UV radiation and ML-DMS averages suggest: a) trends in relations remained unchanged even though higher incident radiation occurred in Central Indian Ocean than in Arabian Sea, b) in both regions ML-DMS increased with UV intensity irrespective of different DMS magnitudes (at lower ML-DMS levels) and c) higher ML-DMS values in all the cruises do not exhibit strong dependence on UV intensity. These observations suggest, as in the case of MLDs, that incident radiation alone does not lead to different ranges of ML-DMS observed.

Higher ML-DMS averages, which did not seem to depend on UV intensity mostly correspond to shallow MLDs (≤40 m; see Fig. 6.13c) indicating that a strong coupling between incident UV and shallow MLDs facilitated the occurrence of higher DMS concentrations. This is in excellent agreement with a near 100% DMS yield from DMSP in shallow MLDs [*Simo and Pedros-Alio,* 1999]. Shallower MLDs will receive intense UV radiation in comparison to deeper MLDs.

Non-dependence of high ML-DMS values on UV intensity when MLDs were ≤40 m is complimented by the observation [*Morrow and Booth,* 1997] of penetration of the most damaging UV-B (305 nM) radiation up to 40 m in clear equatorial waters off the coast of Nauru in the Pacific Ocean. Trends in Fig. 6.13 are, in general, consistent with penetration of UV of 320 and 340 nm radiation down to levels over 60 and 90 m, respectively [*Morrow and Booth,* 1997]. UV penetration, however, could be a strong function of dissolved organic matter that will undergo photolysis after absorption [*Herndl et al.,*

1997]. Signatures of ML-DMS formed in short-term mixed layers appear to be preserved even in seasonal MLDs in Fig. 6.13. Accordingly, the relation of MLDs with ML-DMS in particular, improved from density increment (indicative of wind and salinity forcing, (a)), to temperature drop (reflects seasonal mixed layer, (c)), respectively, considerations in MLD calculations. This indicates that effect of UV radiation on ML-DMS could be realized on a short-term scale (days) whereas that of MLD on a seasonal scale. Thus MLD and UV radiation complement each other in fine-tuning the DMS levels in the mixed layers of the Ocean but do not seem to account for large regional, seasonal and inter-annual variability in ML-DMS inventories observed.

If both the UV and MLDs do not account for DMS variations the only other possible mechanism would be biological. Following the iron injection in water DMS reached higher levels after 13 days during the Southern Ocean iron-release experiment (SOIREE) [*Boyd et al.,* 2000]. A combination of prymnesiophytes and microzooplankton is believed to have led to increased DMSP and DMS levels though diatom blooms are also found to be significant. In the days following iron/nutrient injection phytoplankton blooms occur and will have a large proportion of cells with sound physiology. Winter convection pumps nutrients into the surface layers and promotes biological production in the Arabian Sea. An important biological feature in the Arabian Sea is the occurrence of abundant zooplankton throughout the year [*Madhupratap et al.,* 1996] and is known as 'zooplankton paradox'. Hence, higher production of DMS could be expected following nutrient injection into the surface layers

(driven by physical forcing) and subsequent increase in phytoplankton aided by the presence of perennial zooplankton in the Arabian Sea. Nearly doubled (Table 6.1) ML-DMS (average = 2.9 nM) concentrations were observed, in the Arabian Sea, in winter than in fall- intermonsoon (mean = 1.5 nM) even though the ML-DMSP values were lower in the former season (6.8-7.4 nM, average 7.1 nM) than in the latter (6.5-28.9 nM, mean of 15.0 nM). In the central Indian Ocean, however, both the DMSP and DMS were higher in 1999 (Table 6.1) due to turbulent conditions driven by strong winds. Such an intense mixing led to an upward transport of nutrients in 1999. The upper layers were stratified down to 200 m in 1998 when nutrient pumping from sub-surface has been minimal [*Shenoy et al.,* 2002]. Although the measured chlorophyll *a* values in 1999 (SK 141) were lower than found in 1998 (SK 133) the freshly produced phytoplankton might have dominated biological community. Chlorophyll *a* found in 1998 might actually represent aged and decaying plankton in the central Indian Ocean, following the anomalous high biological production off Sumatra in October-November 1997 due to the occurrence of El Nino in 1997-98 [*Murthugudde et al.,* 1999], in contrast to that freshly produced in the Arabian Sea. Interestingly, while the Arabian Sea waters contained higher levels of DMSP and DMS in January 1998 these were lower in February-March of the same year in the central Indian Ocean. The winter convection was active in the Arabian Sea when the equatorial waters were well stratified. Hence, assuming that DMSP lyase activity is higher in surface waters in Indian Ocean also, as observed elsewhere

[*Steinke et al.,* 2002], more DMSP produced by plankton activity account for larger DMS levels in 1999 (ML-DMS average of 5.8 nM; ML-DMSP= 9.9 – 25.1 nM with a mean of 21.1 nM) than in 1998 (ML-DMS average of 1.2 nM; ML-DMSP= 3.4 – 6.5 nM with 4.7 nM) in the central Indian Ocean. From the foregoing discussion it is evident that the variability of DMS in the Indian Ocean is largely regulated by efficiency in biological and radiative conversion of DMSP to DMS and not necessarily by DMSP levels.

We undertook measurements of chlorophyll *a* and bacterial population along with DMS and DMSP in intermonsoon in the Arabian Sea (SK 158) to check the influence of physical factors on biological and DMS species production. Though the levels of chlorophyll *a* and bacterial populations decreased with increasing UV intensities (Fig. 6.14) the dominance of bacteria over phytoplankton in intermonsoon, as discussed above, might have led to lower DMS concentrations. The DMSP levels were higher in intermonsoon (Fig. 6.15) than found in winter (SS 161). Simultaneous decreases in the ML-DMSP and ML-DMS with enhanced MLD in Fig. 6.15 clearly reveal that a significant part of DMSP may be converted to non-DMS compounds (e.g. an increase of 25 nM of DMSP against an increase of only 1.6 nM of DMS).

If we have to realistically predict DMS concentrations in the surface ocean it is important that parameters representing DMSP lyase and bacterial activities (in forms of relevant pigments etc.) have to be incorporated in the algorithms besides the MLDs and UV intensities.

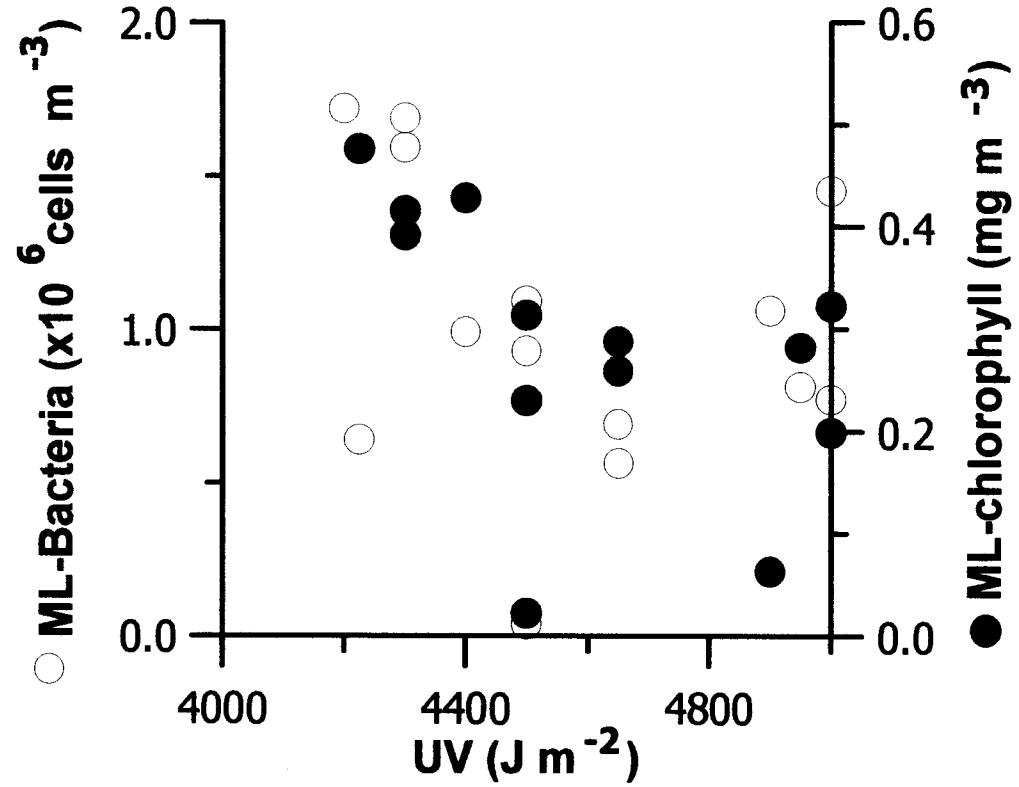


Fig. 6.14. Decreases in ML-chlorophyll and ML-bacterial abundances (SK 158) with increase in incident UV radiation (TOMS) in the Arabian Sea.

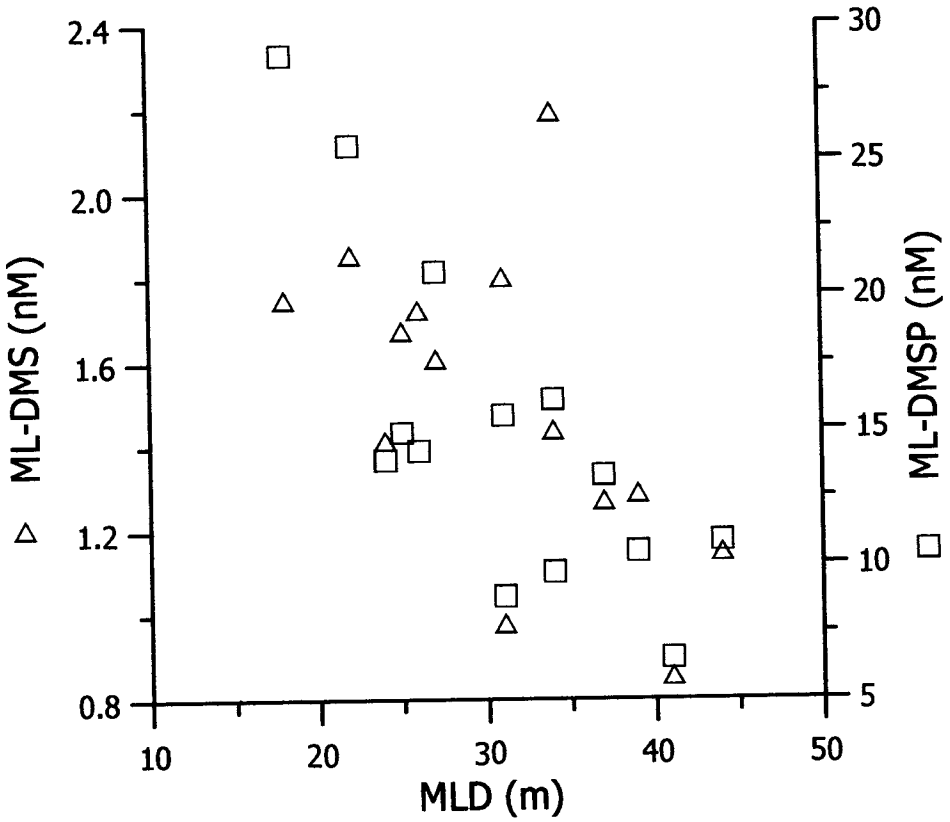


Fig. 6.15. Relationships for mixed layer DMS and mixed layer DMSP with mixed layer depth).

6.6 A hypothesis

Correlating physical variables, temperature and salinity or even nutrients, found at the time of sampling, to the DMSP and DMS will be of limited use since magnitudes of these sulfur compounds are associated with the extent and changes in trophic levels that follow the physical forcing with a time lag (i.e., the biological processes are manifestations of physical forcing occurred sometime before). Changing relations between DMSP and nitrate are the best examples in this context. Higher nitrates in surface waters, due to winter entrainment as indicated by low mixed layer temperatures, trigger photosynthetic production during which the DMSP production is not proportional to nitrate (Table 6.1). The DMSP content was higher in the central Indian Ocean (SK 141) than in the Arabian Sea (SS 161) despite the stronger nitrate supply at higher latitudes. During the winter bloom formation nitrate in water is consumed but the DMSP release might be significantly occurring in the intermonsoon. Once the nitrate supplied by circulation and mixing is (nearly) exhausted through primary production (i.e., in winter) its further supply occurs through regeneration processes (e.g., in intermonsoon) in the photic zone. At this stage (intermonsoon) the extent of primary production will depend on trace levels of nitrate available in water when the DMSP release will also be significant because of the presence of grazers in abundance. This situation might have led to a positive relation between DMSP and traces of nitrate (Table 6.1, except in SS 161). Hence, while the physical forcing determines the extent of photosynthetic production the magnitudes

TABLE 6.1. Means of incident UV radiation, mixed layer depth and mixed layer (ML) averages of properties in Indian Ocean

Area	Cruise No.	UV ($J\ m^{-2}$)	MLD (m)	T (°C)	NO3 (µM)	DMSP (nM)	DMS (nM)
CIO	SK 133	6939	56	29.4	0.25	4.7	1.2
CIO	SK 141	5563	49	27.1	0.50	21.1	5.8
AS	SS 161	3681	71	26.4	2.72	7.1	2.9
AS	SK 158	4638	31	29.0	0.47	15.0	1.5

and nature of trophic levels/succession are mainly responsible in maintaining DMS seasonal inventories in seawater.

The salient features of this chapter are:

1. Salinity does not seem to have a direct control over the production of DMS and DMSP except in the Bay of Bengal where the sharp gradients in salinity facilitate higher DMS and DMSP production to some extent
2. Chlorophyll seems to correlate well with DMS in the Arabian Sea, but not in the Bay of Bengal and the Central Indian Ocean.
3. Nitrate does not correlate with either DMS or DMSP in the Indian Ocean.
4. Mixed layer depth shows a clear negative relation with DMS but does not seem to be a prime controlling factor on its own. MLD together with UV radiation appears to control the DMS inventories on short-term scales.
5. Biological processes, not the physical variables, are hypothesized to regulate seasonal DMS and DMSP abundances in the Indian Ocean.

CHAPTER 7

Sea-to-air Fluxes of DMS in the Indian Ocean

Chapter 7

Sea-to-air fluxes of DMS in the Indian Ocean

The envisaged indirect global cooling by DMS products depends on its quantum emitted from the ocean. One of the major aims of the present study is to estimate the emissions of DMS from the Indian Ocean. The flux of a gas across the air-sea interface is a function of concentration gradient between air and water for the gas in question and of wind speeds. Therefore, in this chapter we discuss on the abundances of DMS at the sea surface in the Indian Ocean, changes in wind speeds and the derived DMS emissions to atmosphere. It is assumed that DMS in air over the Indian Ocean is negligible compared to that in seawater and therefore the concentration difference used in the flux calculation is essentially equals to DMS concentration in seawater (Chapter 2). This assumption is consistent with that generally made in DMS flux calculations since DMS in air is about three orders of magnitude less that in seawater [*Turner et al.,* 1996]. In addition to diffusive DMS flux this chapter also deals with the occurrence of DMSP in marine aerosols and in sea-surface microlayer and its export fluxes to atmosphere. Finally, budget evaluations were made so as to understand the magnitudes of DMS emissions in comparison to its abundance and reservoir sizes in the Indian Ocean.

7.1 Variations in surface DMS

Variations in surface DMS in coastal and open sea areas of the Indian Ocean are shown in Figs. 7.1 and 7.2, respectively. During the Northeast monsoon the surface DMS in coastal waters of the Arabian Sea (central and southern regions of the west coast of India) varied between 0.7 nM and 31.7 nM with an average of 6.3 nM while the open ocean it was between 0.03 nM and 16.8 nM with a mean of 4.5 nM. The average DMS concentrations between the coastal and the open ocean regions were comparable. During the SW monsoon the surface DMS in coastal waters varied between 0.5 nM and 220.5 nM (the highest value not shown in Fig. 7.1) with an average value of 10.3 nM. The highest value was found in near shore waters of Goa due to very high primary production driven by coastal upwelling and the associated biological processes. In contrast, the intermonsoon, which is a slack period for primary production but rich in bacterial production, experienced low concentrations of DMS. The coastal surface DMS varied between 0.9 nM and 10.7 nM with an average concentration of 2.6 nM when the open ocean surface DMS varied between 0.9 and 1.7 nM (average of 1.3 nM) in this season. In agreement with the DMS distributions in the water column (Chapter 4) the mean DMS concentrations at surface were greater in SW monsoon (~10 nM) followed by winter (~4-6 nM) and intermonsoon (~1.5 nM). The annual surface DMS average, in general, for the coastal Arabian Sea was 8 nM whereas it was 3 nM for the open Arabian Sea. Thus the surface DMS in the Arabian Sea shows very high spatial and temporal variability.

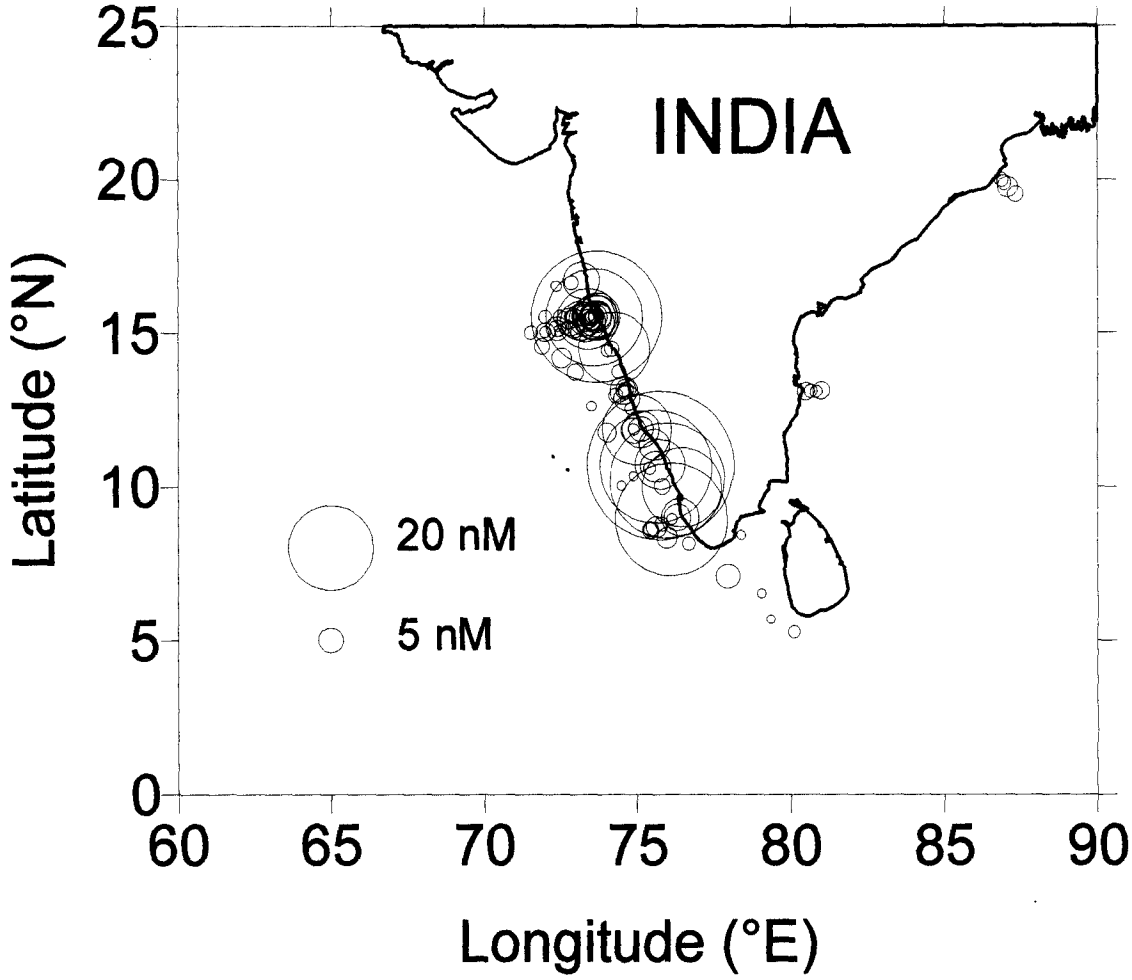


Fig. 7.1. Surface variability in DMS concentrations in coastal areas of the peninsular India.

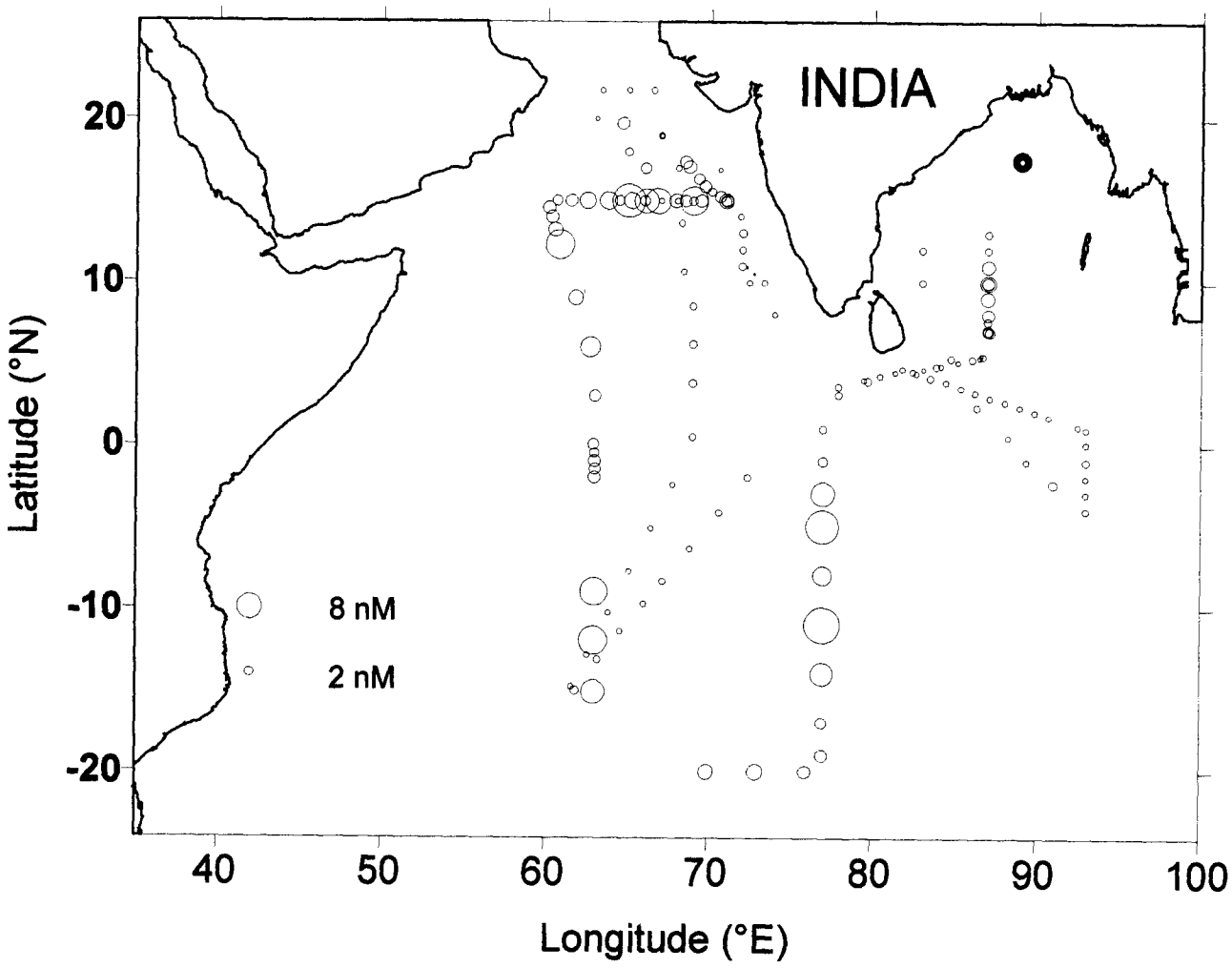


Fig. 7.2. Surface variability in DMS concentrations in open ocean areas in the Indian Ocean.

On the other hand, surface DMS concentration in the coastal waters (off the Paradip in the north and Chennai in the south) in the western Bay of Bengal varied from1.9 to 3.9 nM with an average of 2.7 nM during the SW monsoon when the central Bay waters contained the surface DMS concentrations of 1-5.5 nM having a mean of 3 nM. Thus surface DMS concentrations are almost the same between the coastal and open Bay of Bengal, as was the case in Arabian Sea in winter. The most possible reason for the open ocean concentration to equal that of coastal one could be the enhanced DMS production in the open ocean under cyclonic conditions (Fig. 7.3, and see Chapter 4). During intermonsoon, the southern and central deep Bay of Bengal exhibited surface DMS concentrations ranging between 1.4 and 4.7 nM with a mean of 2.9 nM. The overall surface average DMS concentration in the Bay of Bengal was 2.9 nM.

In the Central Indian Ocean the range of surface DMS was from 0.2 to 11.9 nM during the northeast monsoon the with an average concentration of 2.2 nM. All the observations made in the Central Indian Ocean were in winter due to the non-availability of ship in other seasons. Thus the surface DMS of the Arabian Sea was nearly double to that in the Bay of Bengal and thrice than that of the Central Indian Ocean. Figs. 7.1 and 7.2 show that the surface DMS concentrations in coastal waters were remarkably higher than in the open ocean. The overall average of surface DMS for the entire Indian Ocean was found to be 4.4 nM.

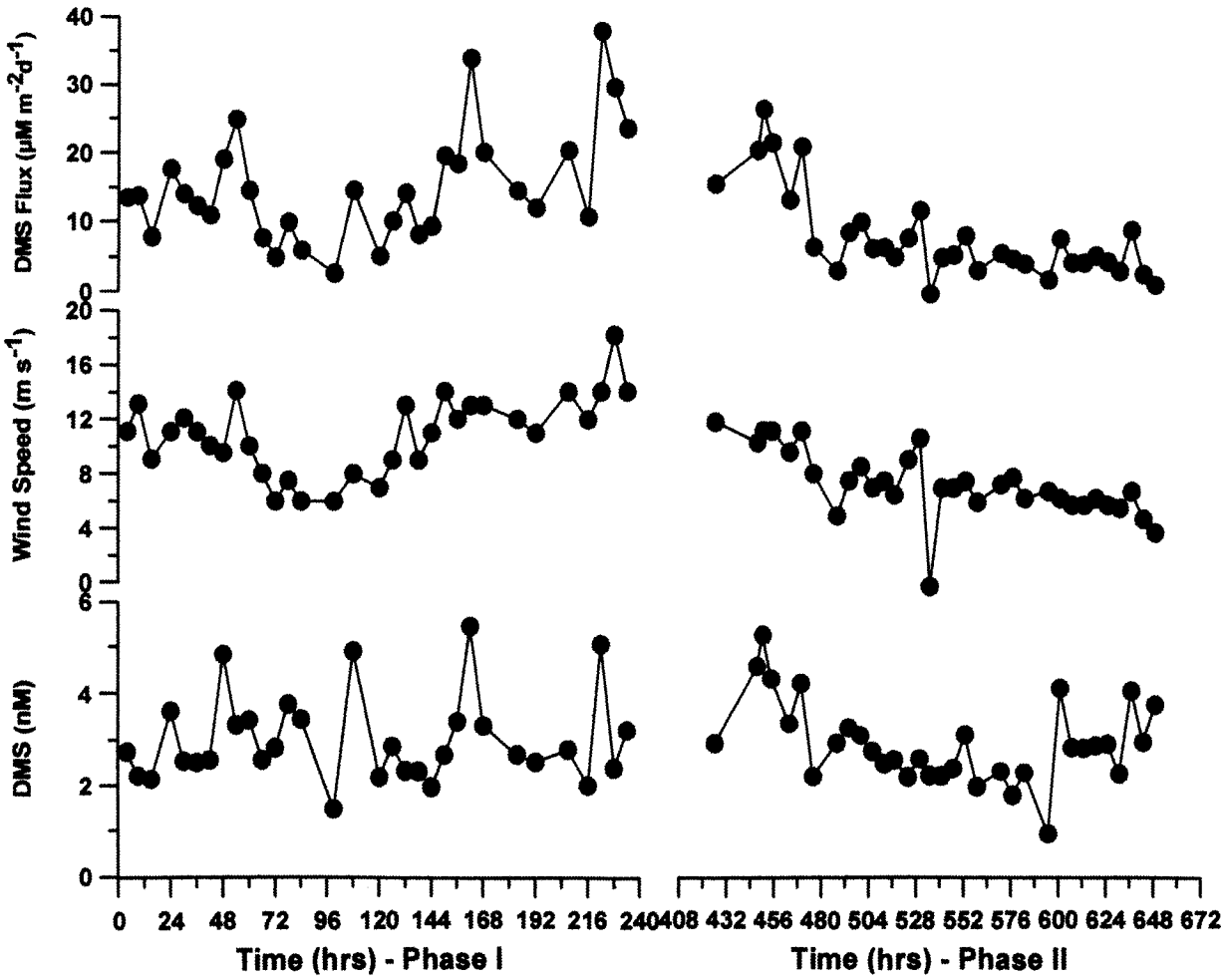


Fig. 7.3. Variations in surface DMS, wind speed and DMS flux at the time series location (17.5°N, 89°E) during the BOBMEX ~~~riment in the Bay of Bengal.

Barnard et al. [1982] reported a surface DMS range of 0.55-23.22 nM with a mean of 2.8 nM for the Atlantic Ocean. Area weighted summer and winter surface DMS concentrations in the North Pacific Ocean are 2.2 and 1.3 nM, respectively [*Bates et al.*, 1987b]. Highly seasonally variable surface DMS concentrations are found in the southern North Sea with minimal concentrations of 0.13 nM in winter to a mean of 25 nM in May, which coincided with large blooms of *Phaeocystis pouchetti* [*Turner et al.*, 1996]. In the Arctic Ocean surface DMS is found to vary between 0.04 and 12 nM with the highest values occurring along the ice edge [*Leck and Persson,* 1996]. Surface DMS concentrations in waters around North America have been detected to range between 0.1 and 12.6 nM with an average of 2.2 nM where the highest values occurred in the western Arctic and off the US east coast near the Sargasso Sea [*Sharma et al.*, 1999]. Surface DMS concentrations have been found to range between 0.002 to 4.63 nM with a mean of 2.6 nM in the South Chine Sea, and from 1.8 to 5.7 nM (a mean of 3.4 nM) for the East Chine Sea, where the highest concentrations occurred in shelf waters and DMS showed strong correlation with chlorophyll [*Yang et al.*, 2000]. *Uher et al.* [2000] studied highly variable surface DMS concentrations in the European western continental margin. In September 1994 it ranged between 0.6 and 33.4 nM (mean of 2.8 nM) while in July 1995 it varied from 2.9 to 38.5 nM (an average of 7.2 nM). It is apparent from the above comparisons that the Indian Ocean surface DMS average is nearly double than that of the Atlantic, the Pacific and the other seas in the Northern hemisphere and is also marginally

greater than the surface DMS concentrations reported for the China Sea. On the other hand it is also comparable to the July 1995 average for the European western continental margin. The higher surface DMS concentration in the Indian Ocean are a clear reflection of intense biological activity in the Indian Ocean in comparison to the other oceanic areas, except possibly under bloom conditions.

7.2 Winds

Wind is an important driving force in air-sea interaction processes that result in exchanges of heat and materials. The Indian Ocean experiences seasonally variable winds. During the northeast monsoon wind speeds along the coastal Arabian Sea were between 0.7 and 10.4 m s^{-1} with an average speed of 4.2 m s^{-1} while in the open ocean it varied from 0.03 to 16.8 m s^{-1} with a mean of 4.9 m s^{-1}. During the SW monsoon the winds along the coastal Arabian Sea were weaker and varied between 0.5 and 8 m s^{-1} with an average speed of 3.1 m s^{-1}. In intermonsoon, it ranged between 1.8 and 12.5 m s^{-1} and 3.7 and 6.3 m s^{-1} with average wind speeds of 5.8 and 5.2 m s^{1} for the coastal and the open ocean, respectively. Thus maximum wind speeds in the Arabian Sea were encountered during the intermonsoons, i.e. just before the onset of SW monsoon. Along the east coast of India winds varied between 1.9 and 4 m s^{-1} with an average speed of 2.7 m s^{-1} during the SW monsoon while in the open bay very high winds of 4 and 18.2 m s^{-1} were associated with a low pressure system (Fig.7.3) with an average speed of 9.4 m s^{-1}. During the intermonsoons, however, winds in the open bay varied between

1.6 and 8.6 m s^{-1} (an average of 3.8 m s^{-1}). In the Central Indian Ocean the winds showed a variation from 1.1 to 12.7 m s^{-1} (with a mean of 5.7 m s^{-1}). These wind speeds were higher in 1999, than in 1998, because of the development of stormy conditions, associated with the Inter Tropical Convergence Zone, in the former year. Thus maximal average wind speeds occurred in the Bay of Bengal during the study period. The measured wind speeds were in general agreement with the climatological winds given in *Hastenrath and Lamb* [1979].

7.3 Sea-to-air fluxes

7.3.1 Diffussional fluxes of DMS

Figs. 7.4 and 7.5 depict variations in surface DMS flux, respectively, in the coastal and open Ocean areas of the Indian Ocean. The DMS fluxes from the coastal Indian Ocean is lesser than that in the open Ocean. Higher DMS fluxes in the deep Indian Ocean are largely associated with high wind speeds. In the coastal areas of the Indian Ocean the DMS flux varied between 0.04 µmol m^{-2} d^{-1} and 34.4 µmol m^{-2} d^{-1} with an average value of 3.4 µmol m^{-2} d^{-1} while in the open Ocean it varied from 0.03 µmol m^{-2} d^{-1} to 41.1 µmol m^{-2} d^{-1} having a mean DMS flux of 6.5 µmol m^{-2} d^{-1}. Table 7.1 lists the fluxes of DMS in the Indian Ocean both on seasonal and regional basis. Average DMS fluxes were higher in the northeast monsoon season than in other both in Arabian Sea regions. In the intermonsoon, open Arabian Sea fluxes were nearly half of that in winter (Table 7.1). Comparatively low winds were found when the measurement made in coastal waters of the Arabian Sea in summer

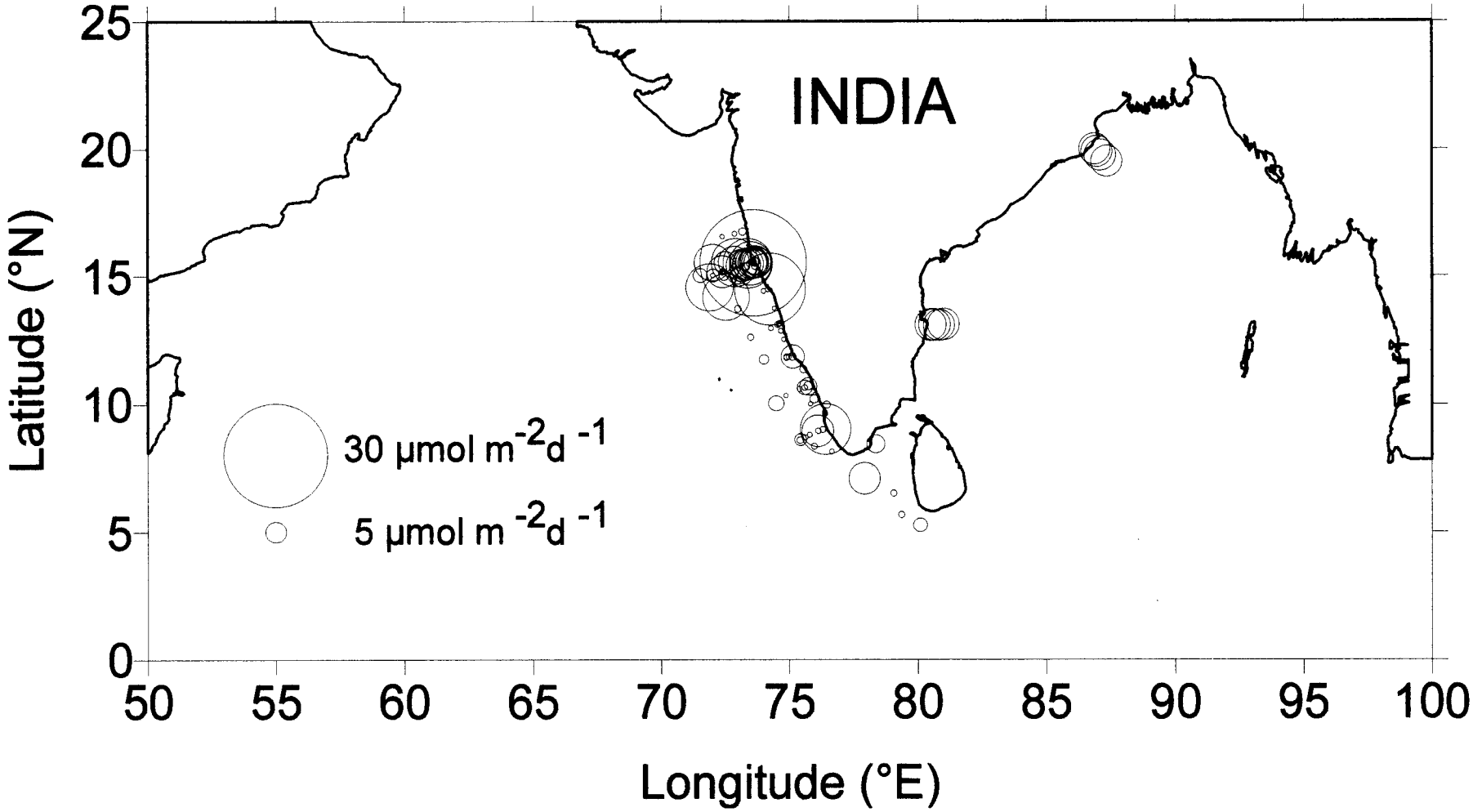


Fig. 7.4. Variability in DMS Sea to air flux in coastal areas around the peninsular India.

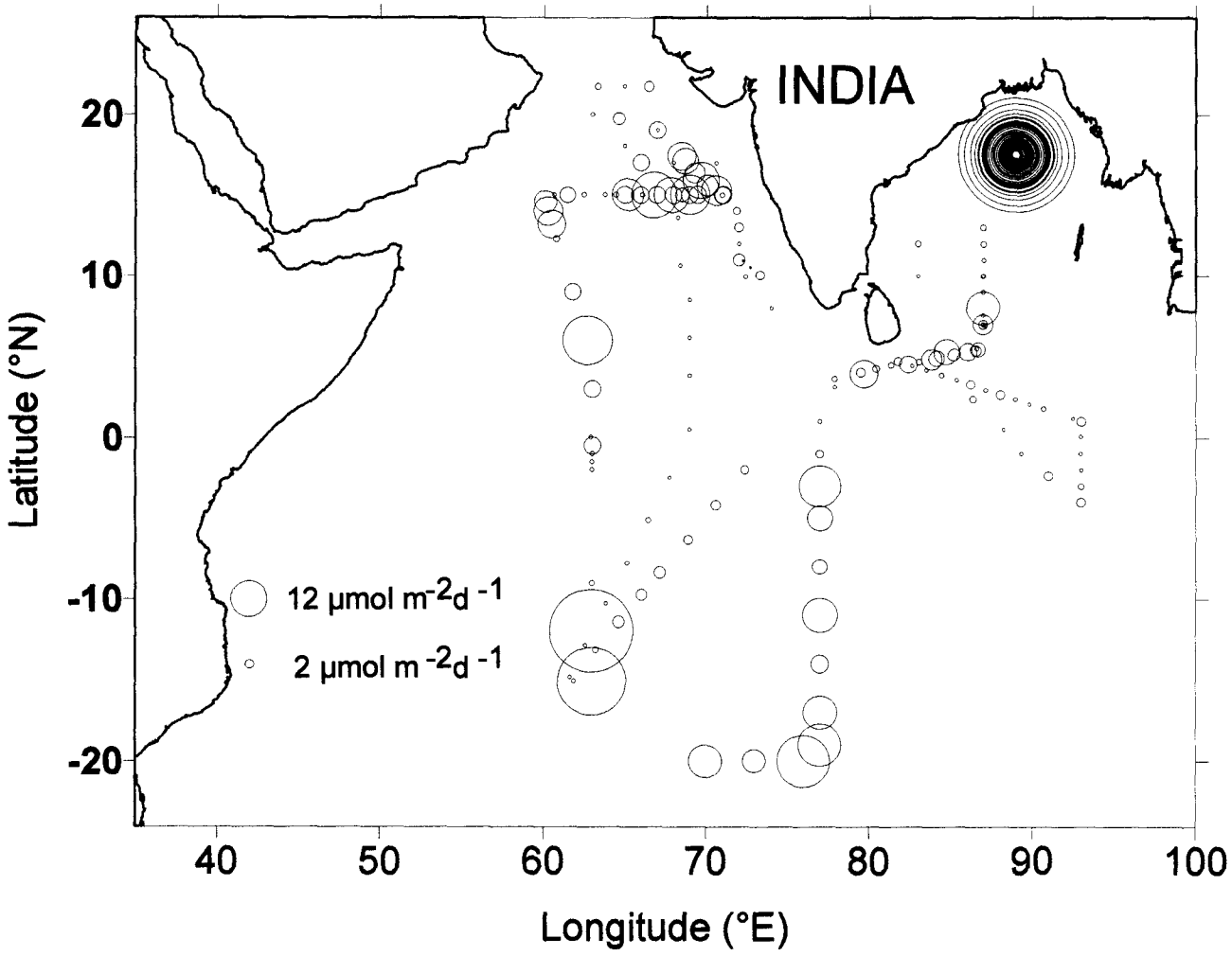


Fig. 7.5. Variability in DMS Sea to air flux in open ocean areas in the Indian Ocean.

Table 7.1. Sea-to-air fluxes of DMS (μmol S m^{-2} d^{-1}) in the Indian Ocean*

Area/Season	Coastal Ocean			Open Ocean			Total		
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
Arabian Sea									
NE Monsoon	0.1	34.4	4.7	0.03	16.8	4	0.03	36.4	4
SW Monsoon	0.04	31	2.6	-	-	-	0.04	31	2.6
Intermonsoon	0.1	13.1	3.9	0.4	3.1	1.6	0.1	13.1	2.9
ANNUAL	0.04	34.4	3.4	0.03	16.8	3.8	0.03	36.4	3.5
Bay of Bengal									
SW Monsoon				1.65	41.1	12.84	1.65	41.1	12.84
Intermonsoon	-	-	-	0.16	10.9	1.63	0.16	10.9	1.6
ANNUAL				0.16	41.1	10.71	0.16	41.1	10.71
Central Indian Ocean									
NE Monsoon				0.1	29.1	3.5	0.1	29.1	3.5
ANNUAL				0.1	29.1	3.5	0.1	29.1	3.5

*Wherever data are not available for coastal/open Ocean regions or seasons the listed values were assumed to be the same other regions/seasons in deriving annual fluxes.

monsoon. The annual coastal mean DMS flux was 3.4 μmol m^{-2} d^{-1} while the open ocean mean flux was 3.8 μmol m^{-2} d^{-1} resulting in an average flux for the Arabian Sea of 3.5 μmol m^{-2} d^{-1}. Fluxes in the Bay of Bengal were higher in the SW monsoon than in intermonsoon. Higher fluxes (average of 10.7 μmol m^{-2} d^{-1}) during the BOBMEX time series experiment were facilitated by the enhanced production of surface DMS due to increased biological activity triggered by turbulent conditions and strong winds that resulted from low pressure system in the study area. In the Central Indian Ocean the DMS flux varied between en 0.1 and 29.1 μmol m^{-2} d^{-1} with an average value of 3.5 μmol m^{-2} d^{-1}. Thus the Bay of Bengal exhibited the maximal DMS fluxes during the present observational period with nearly three times to that in the Arabian Sea and in the Central Indian Ocean. The overall DMS flux for the entire Indian Ocean is estimated to be 5.5 μmol m^{-2} d^{-1}.

Table 7.2 gives a comparison between the DMS diffusive flux from the Indian Ocean (this study) with those observed elsewhere. It is evident that flux from the Indian Ocean is higher than in many regions of the world Oceans, e.g. the Pacific, the Atlantic, the North Sea and the Arctic Polar Ocean. The only DMS estimate for the Indian Ocean, available from the earlier studies, is that of *Nguyen et al.* [1990] near the Amsterdam Island situated near 38°S, which is nearly one-half of the flux calculated in the present work. However, our flux estimate agrees well with that made by *Yang* [2000] for the South China Sea. Importantly, Table 7.3 suggests no relationships not only between bulk and microlayer DMSP concentration but also in relation to DMS

Table 7.2. Comparison of DMS flux with the rest of the world.

Source	**Area**	**Average Flux μmol m^{-2} d^{-1}**
Bates et al. (1987b)	Subantarctic Pacific Ocean	3.98
Bates et al. (1987b)	Coastal Pacific Ocean	3.0
Sharma et al (1999)	North Pacific Ocean	2.3
Berresheim et al (1991)	Western North Atlantic Ocean	3.4
Turner et al (1996)	North Sea	3.84
Leck and Persson (1996)	Arctic Polar Ocean (summer)	2.0
Nguyen et al (1990)	Amsterdam Island (Indian Ocean, 38°S)	2.1
Yang G. P. (2000)	South China Sea	5.5
Yang et al. (2000)	East China Sea	3.4
This Study	Arabian Sea	3.5
	Bay of Bengal	10.7
	Central Indian Ocean	3.5
	Indian Ocean (total)	5.5

Table 7.3. DMS and DMSP in sea surface micro layer.

Longitude	Latitude	DMS nM (surface)	DMSP nM (surface)	DMS nM (micro layer)	DMSP nM (micro layer)
93 °E	0.08 °N	1.0	1.4	0.0	78.8
93 °E	0.99 °S	1.4	10.6	0.0	5.1
93 °E	3.00 °S	1.0	2.9	0.7	1.6
93 °E	2.38 °S	2.0	7.0	0.0	20.8
89.34 °E	1 °S	1.1	5.3	1.0	19.9

abundances. This explains why strong relations are not found for DMS species because of their different reactivities and regulating mechanisms.

7.3.2 DMSP and DMS in the surface microlayer

Table 7.3 shows the concentrations of DMS and DMSP in the sea surface micro layer in the Central Equatorial Indian Ocean. On an average sea surface microlayer thickness was evaluated to be 16 μm. DMS was mostly below the detection limits. On the other hand DMSP exhibited variable enrichments in the sea surface microlayer. One of the reasons for the absence of DMS in the microlayer might be its escape during the sampling. The DMSP showed a mean enrichment factor of 10. Whilst we did not find enrichment of DMS in the microlayer it was detected elsewhere [*Yang,* 1999; *Nguyen et al.,* 1978]. For instance, *Yang* [1999] found a DMS enrichment of 1.95 in the surface microlayer of the South China Sea.

7.3.3 Export fluxes of DMSP

DMSP was found to occur in marine aerosols from below detection limits to 4.7 pmol m^{-3} (Fig. 7.6) with an average of 0.92 pmol m^{-3}. Higher DMSP concentrations (1.5 – 4.7 pmol m^{-3}) were found in aerosols over the Central Indian Ocean in 1999 (INDOEX) when its abundance was also higher in seawater (11.2 – 31.6 nM) than during other seasons and in other areas (Table 7.4). This is the first ever detection of DMSP occurrence in aerosols. The fact that DMSP is unstable in surface seawater, through its susceptibility to photolysis and biological decomposition, makes its detection in marine aerosols significant. These decomposition processes can occur in

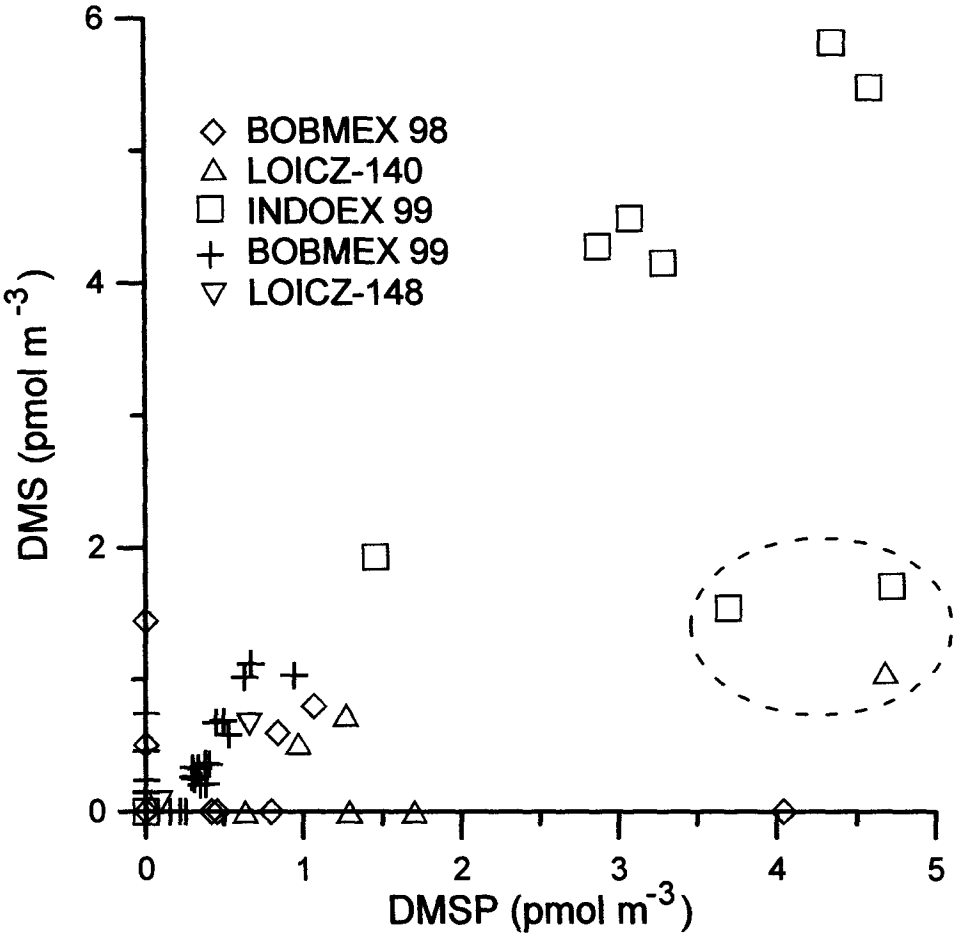


Fig. 7.6. Relationship between DMSP and DMS in marine aerosols over the Indian Ocean.

Table 7.4. Abundance of DMSP (nM) and DMS (nM) in surface seawater and sea-to-air diffusive flux of DMS (μmol m^{-2} d^{-1})

Cruise	**Area**	**DMSP range**	**DMSP average**	**DMS range**	**DMS average**	**DMS Gas flux Average**
BOBMEX 1998 SK 138C	Bay of Bengal	5.2-17.6	14.3	1.4-4.7	2.9	1.6
LOICZ 1998 SK 140	Central eastern Arabian Sea	-	-	0.9-31.7	7.0	4.78
INDOEX 1999 SK 141	Central Indian Ocean	11.2-31.6	20.6	1.6-11.9	4.4	7.26
BOBMEX 1999 SK 147	Bay of Bengal	6.9-21.8	13.4	1.5-5.5	3.0	16.3
LOICZ 1999 SK 148	South East Arabian Sea	-	-	0.6-220	19.3	5.13

troposphere (marine boundary layer) so also in surface microlayer and produce non sea-salt (NSS) substances. The relationship between DMSP and DMS in aerosols is positive and linear (Fig. 7.6). However, DMS values (0 – 5.8 pmol m^{-3}) need to be treated with caution since the aerosol samples were collected under vacuum. These DMS compounds are also susceptible to decomposition on filters during the sample collection; and hence the values reported in Fig. 7.6 might be underestimates. Notwithstanding such artifacts there is a striking proportionality between DMSP and DMS (Fig. 7.6), which is not a chance occurrence since these measurements were made in different seasons and regions of the Indian Ocean. An important point in favour of this argument is the detection of higher DMS concentrations where DMSP levels were also higher not only in aerosols but also in surface seawater of the Central Indian Ocean (Table 7.4; Fig. 7.6). On the other hand, DMS concentrations in aerosols do not seem to be a function of the extent of its concentrations in surface seawater or diffusive DMS fluxes across the interface. For instance, maximum diffusive flux occurred during the BOBMEX 1999 and maximal surface water DMS concentrations were found in LOICZ cruises in the Arabian Sea but higher DMS in aerosols occurred during INDOEX 1999 (Table 7.4; Fig. 7.6).

Relations of DMS and DMSP in aerosols with winds (Fig. 7.7) suggest that variability and abundance of these compounds decreased with an increase in wind speed. Low levels of DMSP and DMS in aerosols at higher wind speeds might have been due to effective decomposition of DMSP and

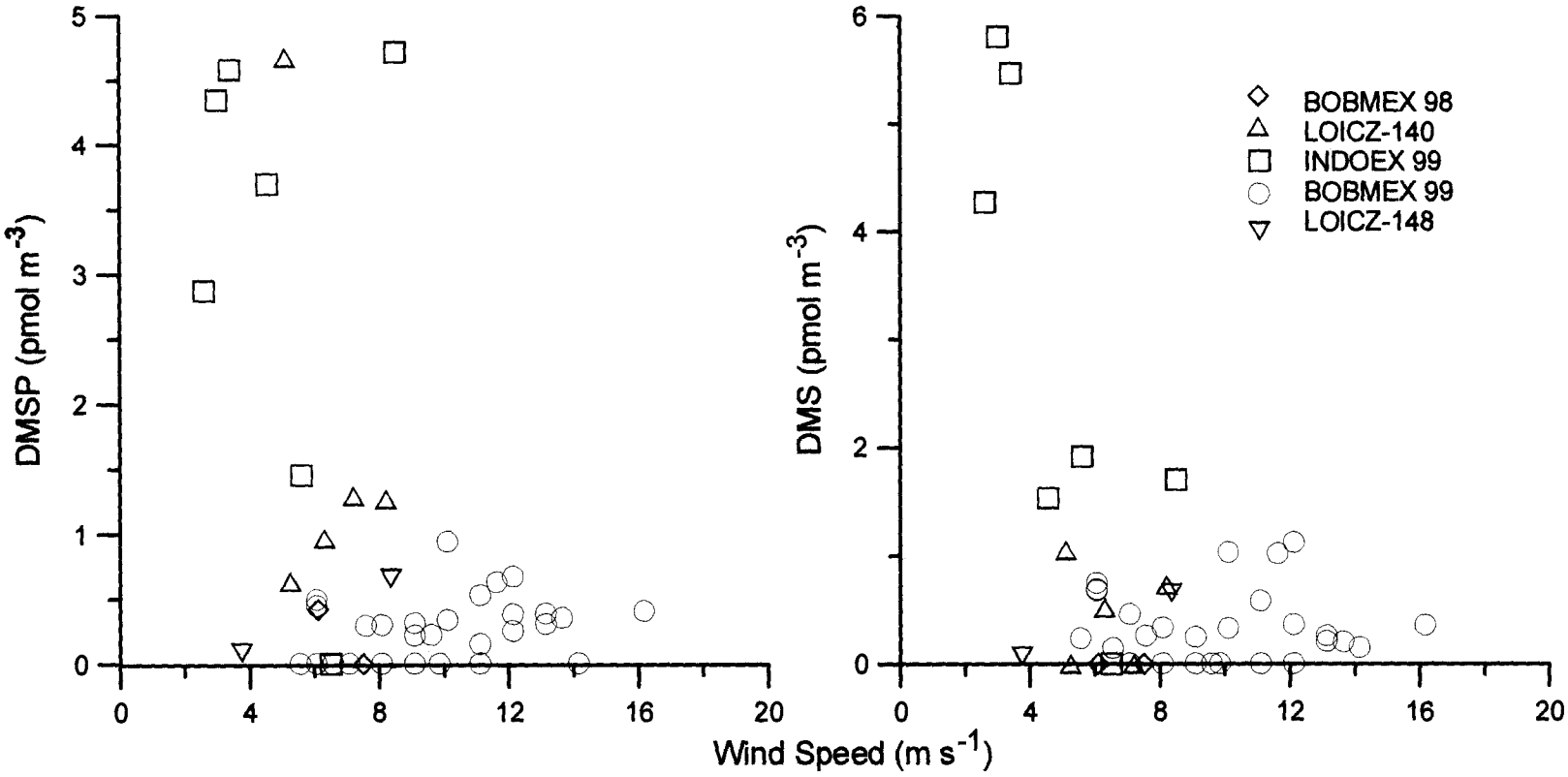


Fig. 7.7. Dependence of DMS and DMSP concentrations in aerosols on wind speeds.

subsequent rapid evasion of NSS gases from aerosols. The escape will greatly be facilitated across the aerosol-air interface in turbulent winds. The observed ratio of about one for DMS/DMSP contrasts that (~0.2) in seawater (Table 7.4). As seawater is the source of aerosols in the remote marine atmosphere a ratio of 0.2 should have been maintained in these aerosols also, which is not the case. This suggests that a rapid DMS formation from DMSP is favoured in aerosols than in seawater.

Sea salt particle production rate at air-sea interface is reported to be 100 cm^{-2} s^{-1} [*Hobbs,* 2000]. The total production at the sea surface, over the world ocean area of 10^{14} m^2, would be 10^{20} s^{-1}. Assuming a droplet (from which a salt particle is produced) radius to be 10 μm each droplet volume works out to be 4.2 x 10^{-12} dm^3. Therefore, annually a total volume of 1.32 x 10^{16} dm^3 of seawater appears to be ejected as aerosols. Considering an average DMSP of 10 nmol dm^{-3} in seawater, from the ranges listed in Table 7.3, the total aerosol export flux of DMSP amounts to 0.42 x 10^{10} g S y^{-1}.

Direct efflux of NSS gases produced from DMSP decomposition in the microlayer (similar to the mode of loss from DMSP loaded on filters, see Chapter 5 and Fig. 5.2a) should be added to the above aerosol flux. If we consider the surface film thickness to be 10 μm and DMSP abundance in seawater to be 10 nmol dm^{-3} (320 μg S m^{-3}) the DMSP inventory in the global oceanic microlayer will be 0.32 x 10^6 g S. Since Fig. 5.2a suggests 90% loss in 5 minutes of exposure the estimated DMSP loss from global oceanic surface will be 3 X 10^{10} g S y^{-1}. Direct loss of DMSP products from the

microlayer seems to contribute 7-8 times more than that by aerosol export to atmospheric NSS sulphur. The total DMSP loss (3.4×10^{10} g S y^{-1}) to atmosphere is two to three orders of magnitude lower than by DMS diffusive flux ($16\text{-}25 \times 10^{12}$ g S y^{-1}). However, the DMSP flux could potentially become an important one under stormy conditions since aerosol DMSP loss to air seems to be near quantitative at higher wind speeds (Fig. 7.7). This situation is similar to spray contribution to mass transfer at the air-sea interface. *Pattison and Belcher* [1999] found a small contribution of water droplets to the global mass transfer flux but recognized their contribution to be significant under rough conditions. The above evaluations suggest a global lifetime of 6 hrs for aerosol DMSP in the lower 1 km of the marine troposphere. Therefore, methanesulphonic acid or NSS sulphur with a residence time of 36 hrs. [*Charlson et al.,* 1992] live six times longer than that by DMSP in air. Our present DMSP export calculations should be considered conservative since the measured DMSP in aerosols and its losses from loaded filters in marine air are likely underestimates.

The total flux of DMS compounds from the north and Central Indian Ocean is, therefore, amounted to 1×10^{12} g S y^{-1}. This agrees well, although slightly higher flux seems to occur in the Indian Ocean, with the global DMS emission rates of $16\text{-}25 \times 10^{12}$ g S y^{-1}.

7.4. DMS budget for Indian Ocean

Table 7.5 gives the inventories of DMS and DMSP in the upper 100m of the Indian Ocean. Highest reservoir sizes of DMS and DMSP occurred in

Table 7.5. Inventories of DMS and DMSP in the upper 100 m of the Indian Ocean*

Area/Season	**Mean DMS** (nM)	**DMS** (TgS)	**Mean DMSP** (nM)	**DMSP** (TgS)
Arabian Sea				
NE Monsoon	3.5	69	8.7	162
SW Monsoon	9.5	187	63.5	1241
Intermonsoon	2.8	55	15.3	303
ANNUAL	5.5	110	26.4	527
Bay of Bengal				
SW Monsoon	1.76	23	7.3	94
Intermonsoon	2.3	29	8.8	113
ANNUAL	1.8	23	7.4	96
Central Indian Ocean				
NE Monsoon	2.2	49	9.8	220
ANNUAL	2.2	49	9.8	220

*Annual fluxes were calculated as in Table 7.1.

SW monsoon in the Arabian Sea amounting to 187 and 1241 TgS, respectively. These were about 3 times for DMS and 4-6 times for DMSP of that in NE and Intermonsoon seasons. The annual reservoir sizes, on average, were 110 and 527 (Table 7.5). There do not seem to be significant seasonal changes in the Bay of Bengal where the annual reservoirs were found to be about 5 times less than those in the Arabian Sea both for DMS and DMSP. On the other hand, the Central Indian Ocean contained a DMS of 49 and DMSP of 220 TgS that were comparatively lower than in the Arabian Sea but higher than in the Bay of Bengal. Interestingly, DMS abundance and sizes were one-fifths of DMSP averages revealing that only 20% of the DMSP produced by plankton was converted to DMS in the Indian Ocean. In winter, however, the conversion seems to be more efficient, when DMSP was only >2 times that of DMS, due to higher plankton production, more lyase availability and large biodiversity. This indicates that relatively more DMSP was being converted to reduced sulphur compounds other than DMS in winter.

Sea-to-air fluxes of DMS (Table 7.1) did not show a great seasonal variability in the Arabian Sea over the entire basin that has an annual ejection of 0.26 TgS (Table 7.6). While the Central Indian Ocean also seem to efflux almost the same the Bay of Bengal supplies 3 times more (Table 7.6) to atmosphere. A comparison of these fluxes with the standing stocks of DMS in Indian Ocean reveals that hardly less than 1% of the DMS available in the 100 m water column is lost to atmosphere per year both in the Arabian Sea and the Central Indian Ocean. On the other hand, about 3% is lost from the Bay of

Table 7.6. DMS inventories in the Indian Ocean and its diffusive loss to atmosphere*

Area/Season	DMS inventory (TgS) 100 m	DMS Efflux (TgS y^{-1})	% loss to the atmosphere
Arabian Sea			
NE monsoon	69	0.1	0.15
SW monsoon	187	0.007	0.04
Intermonsoon	55	0.07	0.13
ANNUAL	110	0.26	0.24
Bay of Bengal			
SW monsoon	23	0.94	4.1
Intermonsoon	29	0.12	0.4
ANNUAL	23	0.78	3.4
Central Indian Ocean			
NE monsoon	49	0.26	0.52
ANNUAL	49	0.26	0.52

*Annual fluxes were calculated as in Table 7.1.

Bengal. These results clearly indicate that 97-99% of the DMS produced in the Indian Ocean is recycled or lost to other forms in seawater.

Highlights from the above discussions are:

1) Surface DMS showed very high spatial and temporal variability in the Indian Ocean.
2) While maximal surface DMS concentrations were observed in the Arabian Sea, maximal diffusive fluxes were found in the Bay of Bengal.
3) DMSP is found to occur in marine aerosols that contradicts earlier notion that NSS is lost to atmosphere only in the form of DMS diffusive flux.
4) Under stormy conditions transport of NSS sulphur through aerosols could be very significant.
5) The enrichment of NSS sulphur compounds in the sea surface micro layer will further enhance efflux of these compounds.
6) Arabian Sea is a large reservoir of DMS and DMSP in comparison to the Central Indian Ocean and the Bay of Bengal.
7) Less than 3% of the DMS formed in the surface layers is emitted to the atmosphere and the rest is recycled or lost to some other forms.
8) The DMS emission from the Indian Ocean is consistent with the global oceanic sulphur fluxes.

CHAPTER 8

Summary and Recommendations

Chapter 8

Summary and Recommendations

The Indian Ocean experiences seasonal reversal in the wind system, which is unique to this area. The wind induced current system causes upwelling and subsequently results in high primary productivity. This region is one of the most productive regions among the world's oceans. DMS is an important gas with implications to climate change. The Indian Ocean is climatically and biogeochemically dynamic but no systematic studies had been made on reduced sulphur gas before this study was undertaken. This study is aimed to understand the distribution and factors controlling DMS and DMSP in the Indian Ocean, and to quantify the emission of non-sea salt sulphur to atmosphere. A total of 11 oceanic expeditions were undertaken in the Arabian Sea, Bay of Bengal and the Central Indian Ocean covering 352 stations. Time series observations were carried out at specific coastal and open sea locations and a few laboratory experiments were conducted to study the stability of DMSP in air and seawater. The highlights of this present study are as follows.

8.1. Summary

Intense spatial variability in DMS has been found in the North Indian Ocean.

- ***Extremes in DMS*** – Very high DMS and DMSP are generally found in coastal waters of the Arabian Sea from non-detectable to over 526 nM and 916 nM, respectively.
- ***Low DMS in intermonsoons*** – DMS concentrations are low in the intermonsoons in the Arabian Sea when bacteria seem to dominate the biological regimes. This is because of large siphoning of DMSP to form methanethiol.
- ***Higher DMS with a time lag after nutrient pumping*** – We found a time lag between the occurrences of higher biological production driven by nutrient pumping to surface layers, resulting from winter convection or southwest monsoonal upwelling, and maximal DMS concentrations in seawater. This is primarily because of the time required for secondary producers (grazers) to arrive on the scene.
- ***Very high DMS in coastal domains of sub-oxia*** – Intense biogeochemical activity following very high biological production after the southwest monsoonal occurrence appears to lead to the maximal concentrations (DMSP= 916 nM and DMS = 526 nM) in coastal waters off the west coast. These are among the highest values known to occur in the world oceans.
- ***Lower DMS in the Bay of Bengal*** – We found lower DMS values to occur in the Bay of Bengal compared to that in the Arabian Sea and Central Indian Ocean. This might have been due to relatively less

biological production and trophic diversity in the bay as also can be seen from generally lower DMSP levels in the bay.

Very strong time series variability of DMS has been found from diurnal to inter-annual time scales.

- ***Higher DMS values in the afternoon*** - Diurnal variability studies have shown that DMS values peaked in the water column in the after-noon. The variability is ≥ 50%.
- **Enhanced DMS/DMSP levels under stormy conditions** – Studies during a storm in the Bay of Bengal revealed higher contents of DMSP and DMS because of the upward pumping of nutrients from subsurface layers that resulted in higher biological activities.
- **Cloud cover influenced chlorophyll production** – Time series study during a cyclonic storm on board ORV Sagar Kanya revealed that the cloud cover enhanced chlorophyll production under the conditions of nutrient availability. There was a clear negative relation between the incident UV radiation and chlorophyll in seawater.
- ***Strong monthly variability*** - DMS in Dona Paula bay showed strong seasonal variability with higher values occurring in southwest monsoon season. This is because of the increase in biological activity during the southwest monsoon driven by upwelling.
- ***Significant inter-annual variability*** – Studies in the Central Indian Ocean during the winter season of 1998 and 1999 showed clear annual variations in DMS and DMSP concentrations in the water column,

which were higher in 1999 due to changes in biology triggered by turbulent mixing.

The factors regulating DMS in seawater were found to be multiple.

- ***Pulses of salinity*** – Sudden changes in salinity in the ocean are found to induce enhanced DMSP and DMS production in plankton cells. This has been confirmed by our laboratory experiments.
- ***DMSP production does not depend on nitrate availability*** – Relations between DMSP and nitrate have not revealed any specific dependency of the former production on the latter. Although negative relation could be seen between these two parameters this appears to result from differences in vertical behaviours.
- ***Decoupling found between chlorophyll and DMS maxima*** – Although chlorophyll at times shows positive relationship with DMS the vertical profiles of the two show a clear decoupling. While peak in DMS occurs closer to the sea surface that of chlorophyll is deeper. This implies that at a given location the DMS content in seawater is not a function of biological activity alone.
- ***Shallow mixed layers favour higher DMS levels*** – The results revealed that shallower mixed layer depths in the ocean are favourable to DMS production.
- ***Higher UV radiation lowers phytoplankton and bacterial populations*** – We found evidence for the suppression of

phytoplankton and bacterial counts at higher intensity of incident UV on the sea surface.

- ***Higher UV incidence enhances DMS production*** – Higher DMS concentrations in the surface ocean were found to be favoured by increased incident UV radiation since bacterial activity is suppressed when exposure is intense.

Export fluxes of sulphur compounds are important from Indian Ocean since this is one of the most turbulent regions, with regular occurrence of monsoons, in world oceans.

- ***DMSP in marine aerosols*** – Ours is the first report on the occurrence of DMSP in marine aerosols.
- ***Export of DMSP derived NSS gases*** – Export of non-sea salt sulphur gases, resulting from break down of DMSP in marine aerosols and surface microlayer, could be comparable to DMS diffusive fluxes, particularly under rough weather conditions.
- **Normal diffusive DMS fluxes** - Diffusive fluxes of DMS from the Indian Ocean are comparable to other regions of the world.

8.2. Recommendations for future research

- ***Role of DMSP in biochemical and biophysical functions of plankton cells*** - Many workers have found that plankton cultures supplemented with nitrate concentrations produced less DMSP in comparison to those which were nitrate deficient. One possible reason is that there could be production of glycinebetaine (GBT), which is an

alternative to DMSP. Production of GBT requires lesser energy in comparison to that to be spent for DMSP synthesis. Conflicting views about this assumption are, however, known. Our knowledge of real functions of DMSP in plankton cells is not satisfactory and should be unraveled.

- ***Long term time series measurements*** - Actually a time series study is needed in this area where one can study right from the input of nutrients in the surface waters to increase in primary production and then how these changes in the water column characteristics bring about changes in DMSP and DMS concentrations with respect to phytoplankton population and speciation.
- ***Phaeocystis occurrence and role to be probed*** - The Ocean's micro algae play a key role in the cycling of elements that determine to a large extent the global climate. Prymnesiophyceae is a family of marine algae of which Phaeocystis is one of the most important species involved in biogeochemical cycles. This species is found to occur in the central Arabian Sea during southwest monsoon and might play an important role in cycling of materials. Therefore, investigations should be carried out to study DMS in the Arabian Sea during the prevalence of Phaeocystis blooms since the research elsewhere revealed higher DMS abundance associated with this species.
- ***DMS – an essential ingredient in ocean-atmosphere interactions*** – Since DMS has a major source in the ocean with implications to

indirect atmospheric cooling this should find focus in all national and international programmes in the Indian Ocean since this region is one of the most dynamic in regard to ocean atmosphere interactions.

- ***Coastal investigations have to be intensified*** – Since DMS variability is too large and the influence of biological variability along the coast is not very well known it is important that future DMS studies should be closely linked to carbon dioxide and biological studies.
- ***Mechanisms of DMSP decomposition in seawater and air*** – The pathways of DMSP decomposition is not fully known. Whether the degradation pathways in seawater and air are the same or different are unknown. This is the most demanding and challenging aspect in understanding the dynamics of DMS compounds in nature and therefore needs to be given top priority.

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