Biogeochemistry of trace metals in the Indian EEZ of the Arabian Sea and Bay of Bengal

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Certificate

I certify that the thesis entitled **"Biogeochemistry of trace metals in the Indian EEZ of the Arabian Sea and Bay of Bengal"** submitted by Rejo Mon George, Research Scholar (Register. No. 2395), National Institute of Oceanography, Regional Centre, Kochi -18, is an authentic record of research carried out by him under my supervision, in partial fulfilment of the requirement for the Ph.D degree of Cochin University of Science and Technology in the faculty of Marine Sciences and that no part thereof has previously formed the basis for the award of any degree, diploma or associateship in any university.

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Preface

Globally, trace metals have gained a high demand in marine environmental research owing to its role in the biogeochemical cycling and in turn, the ecology of oceans. Studies on trace metals in the water column from other world oceans so far reported have mainly concentrated on their behavior, for its quantification and possible exploitation. Even though, some preliminary attempts have been made in selected areas for the qualitative study of trace metals in the Indian EEZ of the Arabian Sea and Bay of Bengal, no comprehensive work has been reported to identify and assess the distribution or reactivity. The present study has been initiated to unravel the distribution of trace metals and its geochemical behavior in the Indian EEZ of the Arabian Sea and Bay of Bengal. Moreover this work also evaluates the bioaccumulation and biomagnification of trace metals in zooplankton samples collected from the Indian EEZ of the Arabian Sea and Bay of Bengal.

The study region for the investigation is the EEZ of the Arabian Sea and Bay of Bengal, sampled onboard under the Marine Research-Living Resource Programme (MRLR) funded by Department of Ocean Development (DOD). Water samples and zooplankton were collected from the Bay of Bengal during Cruises, 209 (6th November to 5th December, 2002) and from the Arabian Sea during the 217 (14th September to 18th October, 2003), 224 (10th April to 4th May, 2004) of FORV Sagar Sampada. The investigations in the Bay of Bengal (Cruise No.209) covered six transects perpendicular to the coast between 11°N to 20.5°N and in the Arabian Sea (Cruise No.217) along seven transects between 8°N to 21°N. A duplicate sampling was carried out in the northern Arabian Sea along transects 17°N to 22°N (Cruise No.224) so as to ascertain the trace metal contribution due to active winter cooling and convective mixing, a prominent feature of the area. Along each transect two coastal & two offshore stations were sampled from standard depths for metal analysis.

The thesis is presented in six chapters. The first chapter gives a general introduction regarding the importance of trace metal studies, its occurrence, fate and

transport in the sea. Review of previous works and objectives of present studies are also included in this chapter.

The second chapter deals with the materials and methods, description of the study area, analytical procedures for the estimation of dissolved & particulate trace metals, temperature, salinity, dissolved oxygen, nitrate, phosphate, silicate, primary productivity, chlorophyll a and particulate organic carbon. Dissolved trace metals were analysed using Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS, ZL-4110) whereas trace metals in particulate matter & zooplankton were analysed through Flame Atomic Absorption Spectrophotometer (FAAS, *PE AAanalyst 100*).

The third chapter deals with the hydrography, nutrients and biological characteristics in the eastern Arabian Sea and western Bay of Bengal. Physico-chemical characteristics and associated biological response of the entire EEZ of the Arabian Sea for the period of intermonsoon fall, northern Arabian Sea during intermonsoon spring and Bay of Bengal during winter monsoon are explained.

The fourth chapter deals with the dissolved and particulate trace metals in the eastern Arabian Sea and western Bay of Bengal. The geochemical behavior of trace metals in the water column of the both basins is addressed based on the concentration profiles and the partition coefficient obtained for each metal. The metal-nutrient slopes computed from the linear regression equations in the Arabian Sea and Bay of Bengal are compared with those reported in the Pacific and Atlantic oceans. The seasonal response of the Arabian Sea, its trace metal transport associated with physical forcings is also dealt with.

The fifth chapter deals with bioaccumulation of trace metals in zooplankton from the eastern Arabian Sea and western Bay of Bengal. The relationship between trace metal content in zooplankton and the seawater of both basins where it inhabits are established by means of bioaccumulation and biomagnification factors.

The sixth chapter deals with the summary and conclusion of the study. The list of references cited is given at the end of the thesis.

Acronyms and Abbreviations

AOU	Apparent Oxygen Utilization
AS	Arabian Sea
ASHSW	Arabian Sea High Salinity Water mass
baf	Bioaccumulation factor
bmf	Biomagnification factor
BOB	Bay of Bengal
CTD	Conductivity - Temperature – Depth
CMLRE	Centre for Marine Living Resources and Ecology
dFe	Dissolved Iron
dCo	Dissolved Cobalt
dNi	Dissolved Nickel
dCu	Dissolved Copper
dZn	Dissolved Zinc
dCd	Dissolved Cadmium
dPb	Dissolved Lead
DOD	Department of Ocean Development
DO	Dissolved Oxygen
E	East
e.g.	exempli gratia (Latin word meaning 'for the sake of example')
EEZ	Exclusive Economic Zone
EICC	East India Coastal Current
et al.	et alii (Latin word meaning 'and others')
etc	et cetera (Latin word meaning 'and other similar things; and so on')
FORV	Fishery & Oceanographic Research Vessel
GF/F	Glass Fibre/Filter
GLOBEC	Global Ocean Ecosystem Dynamics
HNLC	High Nutrient Low Chlorophyll
IIOE	International Indian Ocean Expedition
JGOFS	Joint Global Ocean Flux Studies
Kd	Partition Coefficient
MLD	Mixed Layer Depth
MR-LR	Marine Research - Living Resources
nM	nano moles
N	North
No.	Number
NE	Northeast
NS	Northsouth
NIO	National Institute of Oceanography
NO_2 - N	Nitrite - Nitrogen
NO_3 - N	Nitrate - Nitrogen
δN	Nitrate Deficit
µg/l	Microgram per litre
µg/g	Microgram per gram

μM	Micro moles
pFe	Particulate Iron
pCo	Particulate Cobalt
pNi	Particulate Nickel
pCu	Particulate Copper
pZn	Particulate Zinc
pCd	Particulate Cadmium
pPb	Particulate Lead
PGW	Persian Gulf Watermass
PO_4 - P	Phosphate - Phosphorus
PP	Primary Productivity
POC	Particulate Organic Carbon
psu	Practical Salinity Unit
ppb	Parts Per Billion
ppm	Parts Per Million
RSW	Red Sea Watermass
SiO_4 - Si	Silicate - Silicon
SMC	Southwest Monsoon Current
SST	Sea Surface Temperature
SW	Southwest
SPM	Suspended Particulate Matter
UNESCO	United Nations Educational Scientific and Cultural Organisation
viz	videlicet (Latin word meaning 'namely')
WICC	West India Coastal Current
WOCE	World Ocean Circulation Experiment

Contents

Chapter 1

Introduction

The mechanism of biogeochemical interaction among trace metals and planktonic organisms is one of the keys to elucidate the role of trace metals in the ecology of the oceans and the role of organisms in the bioaccumulation of metals. Trace metal accumulation in aquatic consumers is of interest to ecologists and environmentalists so as to understand the fate and effect of contaminants in the food web dynamics and the biogeochemical cycling of trace metals. It is well established that oceanic distribution of macronutrients such as nitrate, phosphate and silicate provide critical to biological growth and related geochemical processes. The extent to which the distribution of macronutrients and biological activity depends on the availability of trace elements and over what spatial and temporal scale this control manifests itself is far less clear. Iron has received a great deal of attention as a controlling element in certain ecosystems but links between other trace elements (example; zinc, cobalt, copper and manganese) and ecological and geochemical cycles are likely to be at least as complex and important. The degree to which multiple trace element processes serve to stabilize and/ or change oceanic ecosystems could provide insight into ecosystem response to global change. There is a need to identify and evaluate the complex trace element interactions between ecological and geochemical cycles and their relationship to changing oceanic conditions.

Metals of biological concern can be classified into three groups namely, (i) Light metals which are normally transported as mobile cations in aqueous solutions (e.g., Na^+ and K^+), (ii) Transition metals which are essential at low concentrations but toxic at higher concentrations (e.g., Iron, copper, cobalt and manganese), and (iii) Heavy metals or metalloids which are required for metabolic activity at low concentrations, but at higher levels toxic to the cell (e.g., Mercury, selenium, lead, tin and arsenic). Trace elements such as vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc and molybdenum play an important role in metal-requiring and metal-activated

enzyme systems which catalyze major steps in glycolysis, the tricarboxylic acid cycle, photosynthesis and protein metabolism (Bruland, 1983).

Trace metals enter into the oceans as a result of natural processes and human activities via; atmosphere, rivers, land runoff, dumping and from the seabed. Natural and human inputs of the trace metals to the sea are reflected in elevated concentrations at least in the immediate vicinity of the source especially in the coastal areas. Among the different compartment in the oceans, marine particulate matter is of considerable geochemical importance since it acts as a carrier phase for the transport of chemical constituents from seawater to the bottom sediments. Factors such as production, sinking and decomposition of particulate matter control to a large extent, the recycling and distribution of trace elements within the oceans. This involves uptake of dissolved trace metals by particulate phases and their subsequent regeneration when the latter undergoes oxidation and / or dissolution either within the water column or within the surficial sediments with subsequent diffusion into the water column. That is, dissolved trace metals are removed from seawater either actively by biological uptake or passively by adsorption onto detritus, and regenerated in the water column from their carrier phases. Variations in this general pattern may be caused by processes such as circulation, vertical mixing by advection, atmospheric fall out, continental input from rivers, diffusion from sediments and *in situ* production. In nearshore regions the situation may be much more complicated due to greater intensity of some of the above processes like atmospheric and fluvial inputs, biological activity and diffusive fluxes from sediments.

The concept of Exclusive Economic Zone (EEZ) is one of the most revolutionary features of the Convection on the Law of the Sea. It has already had a profound impact on the management and conservation of the resources of the oceans. The Exclusive Economic Zone (EEZ) is defined as the region, which extends into the ocean up to 200 nautical miles from the coastline, including those of island territories. The new regime for the oceans by giving all maritime nations exclusive rights over economic activities in a region came into force by the signing of the United Nations Conference on the Law of the Sea (UNCLOS), which came into force in 1994.

Overlapping territories are to go by mutual agreements on resources. The EEZ has very large implications for pursuing equity in the oceans. The EEZs cover about 8% of the earth's surface, 25% of global primary productivity and 90% of the total fish catch. The EEZ of India spans an area of 2.02 million square kilometers, representing two-thirds of India's land mass. Of the total area of the EEZ, the continental shelf (0-200m) occupies 20.54%, the continental slopes (200-500m) cover 1.29%, and the oceanic region covers 78.17%.

The EEZ concept provides to the coastal state the jurisdiction over the resources in the zone. To the coastal state falls the right and responsibility to exploit, develop, manage and conserve all resources, e.g. fish, oil, gas, sand and gravel, nodules, minerals, sulphur, to be found in the waters, on the ocean floor and in the subsoil of an area extending 200 nautical miles from its shore. The EEZ adds a new province to the country and provides for the possibility or potential of an added dimension to its development. About 90% of all known and estimated hydrocarbon reserves under the sea fall under some national jurisdiction as a result of the EEZ regulation. The most valuable fishing grounds are predominantly in coastal and hence within the EEZ waters. This is due to the dynamics of the effective primary biological production in the near shore area of the ocean. The non-conventional fishery resources distributed in the continental slope of the Indian EEZ offer a promising potential in the Indian fishery scenario, which can be further be improved by knowledge on the exploitable fishery resources of the EEZ.

Transition group of metals, especially those with half filled d-shells have a tendency to attach to donor atoms to undergo bioaccumulation. Metals in certain concentration are desirable for the growth of marine organisms but its over accumulation is hazardous. It has been observed that metals, belonging to the transition group, complex more easily with chelate-forming constituents of biomaterial than with synthetic chelating chemicals (Goldberg, 1965; Riley and Taylor, 1968). Near the coast and river mouths the chelating character of humus material can render many of these metals easily assimilable to marine organisms. Zooplanktons are one of the most abundant ecological group of organisms in the sea,

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which play an important role in the marine food chain. They mostly feed on phytoplankton and in turn form food for animals at higher trophic level. Thus, zooplankton may contribute to the transfer of metals to higher trophic levels and have been chosen as recommended groups for the baseline studies on metals in the marine environment. Fishes are located at the end of the aquatic food chain and may accumulate harmful metals and pass them to human beings through food causing chronic or acute diseases. In assessing environmental quality with respect to heavy metals in seawater, the bioavailable fraction of trace metals is of major importance, because toxicity depends on bioavailable exposure concentration. This bioavailable fraction cannot be detected directly by measuring metal concentrations, in the soluble phase and can be assessed by determining the amount of metal incorporated into organisms. Since trace metals are partitioned at different compartments in the water column the only way of understanding the dominant processes controlling metal concentration in coastal and offshore waters is to collect systematic data on their concentrations from different phases, namely dissolved phase, particulate phase and planktonic organisms.

The oceanic areas most intensively investigated so far are bordering the developed nations with well-established research centres. For example, the Atlantic and Pacific oceans have been subjected to intensive oceanographic studies, when compared with Indian Ocean. Investigation on the heavy metal aspects in Indian seas is very limited and sporadic. The earliest work on the trace metals in world oceans including that of Indian Ocean was that of Schutz and Turekian (1965). They developed methods for the determination of eighteen trace metals from seawater by neutron activation analysis. Geographical and vertical variations observed in the concentrations of Ag, Co and Ni in different oceans were attributed to several factors such as continental runoff, volcanic activity and organic productivity.

Topping (1969) analyzed dissolved trace metals (Mn, Co, Cu, Fe and Zn) from the northern Indian Ocean and the Arabian Sea. Higher values of these trace metals were found in the surface layers when compared with the bottom, and exhibited a decreasing trend in their concentrations with depth. Except copper all other metals

recorded higher values in inshore waters than in oceanic waters. An extremely low concentration of dissolved cobalt observed in northern Indian Ocean was attributed to its least occurrence in that area under certain conditions. Further, the author is of the opinion that the organic form of manganese in seawater plays a major role in its distribution in the marine environment.

Chester and Stoner (1974) reported concentrations of dissolved trace metals (Zn, Ni, Mn, Cd and Fe) in the surface waters from various regions of the world oceans. While the concentrations of manganese, zinc and cadmium were similar in open ocean surface waters from the south Atlantic and Indian Ocean, copper and nickel were higher in the former. They were used as "baselines" in order to evaluate trace metal enrichment in near shore regions. The enrichment factors follow a decreasing order such as Zn = Mn > Cd = Cu = Ni. Significant variations in the concentration levels of trace metals in near shore surface waters of different regions of world oceans are discussed in detail.

While studying the particulate trace metals (Mn, Cu, Co, Ga, V, Ba, Pb and Zn) and particulate organic carbon in the surface waters of the Indian Ocean, Chester and Stoner (1975) reported several sources of occurrence in the particulate material. For example manganese, cobalt and vanadium were probably present in continentally derived material and authigenic precipitates, and zinc in association with plankton. However barium showed partition between the two components.

Fondekar and Sen Gupta (1976) analyzed total arsenic content in seawater to evaluate the extent and magnitude of its occurrence in the Bay of Bengal, Gulf of Mannar and northeastern Arabian Sea. The results showed highest concentration in the Gulf of Mannar. It was found to be below the limit of detection in the oxygen minimum layer.

Qasim and Sen Gupta (1980) & Sen Gupta and Qasim (1985) reviewed the present state of marine pollution in the Indian Seas and has given an environmental overview of the Indian Ocean. In their extensive reviews they discussed the concentration levels of heavy metals in seawater, crustaceans, bivalves and muscles of certain fishes in the Indian Seas. The data indicates that the levels of metal

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pollution in the Indian Seas have not reached an alarming limit to cause any anxiety. They are of the opinion that localised problems, both short term and long term, however, do appear from time to time and their overall importance vary from place to place.

Danielson (1980) reported concentration levels of dissolved trace metals (Cd, Co, Cu, Fe, Pb, Ni and Zn) from five offshore stations of the Indian Ocean. Vertical profiles of cadmium, copper and nickel showed an increasing trend with depth indicating a nutrient-type distribution. However, iron profile showed an irregular depth distribution probably controlled by biogeochemical processes. While the concentrations of cadmium, cobalt, copper, iron and nickel in the open Indian Ocean agree with other open ocean regions, those of lead and zinc were found to be higher, the latter being attributed to the contamination during sampling. Atomic ratios of Cd : P, Cu : Si and Ni : Si were evaluated by regression equations.

Preliminary studies on trace metals of the Arabian Sea waters were from the Bhavanagar coast by Kappanna *et al.,* (1960; 1962). They had reported the concentration levels of fourteen trace metals and compared their values with similar data reported in the literature for other oceanic waters.

In view of its biological activity in natural waters, Sankaranarayanan and Reddy (1973) studied the distribution of copper in the inshore, estuarine and river waters around Goa coast. Higher copper concentrations observed at certain locations (>1.0 ppm) were attributed to land discharge from natural and artificial sources. George and Sawakar (1981) reported the concentration of organically associated copper in Mandovi and Zuari estuaries employing Anodic-stripping Voltammetry. They observed variations in the organically associated copper upto 46% in the Mandovi, and 60% in the Zuari estuary.

Estimation of arsenic content in the coastal and estuarine waters around Goa was reported by Fondekar and Reddy (1974). Arsenic content in the inshore waters was relatively higher than those reported for normal seawater. A higher concentration of arsenic in the estuaries especially during the monsoon period was attributed to land

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origin. A wide variation in concentrations at different locations was explained in terms of its precipitation and adsorption onto the sediments.

Vasanti and Pillai (1975) studied the concentration levels of zinc in water, sediments and various organisms around the estuarine environment of Bombay harbour. Their results indicate wide variations in its concentration in all the constituents. While seawater, suspended silt and bottom sediments in the harbour showed higher values of zinc, the shore sediments however, showed relatively low values. Among the organisms studied, barnacles and crabs showed higher concentration factors for zinc.

Kamat and Sankaranarayanan (1975a, 1975b) reported the distribution of iron in estuarine and coastal waters of Goa. Higher concentrations of dissolved and particulate iron were attributed to the river discharges flowing through iron ore bearing terrain. The concentration of particulate iron was high during the southwest monsoon when the river runoff was maximum. They also observed considerable decrease in its concentration from river mouth towards offshore which they attributed to flocculation and settling.

Zingde *et al.*, (1976) reported the concentration levels of arsenic, copper, zinc and manganese in marine flora and fauna of coastal and estuarine waters around off Goa. Among seaweeds, *Sagassam tenerimum* and *Padina tetrastromatica* were more efficient in the accumulation of trace metals. Among crustaceans highest values were found in crabs, while prawns, mussels and bivalves showed intermediate levels. The concentration of arsenic in fish was generally low. Though highest concentrations of copper and zinc were observed in oysters, they showed least preference for arsenic and manganese. Abnormally high levels of manganese observed in seawater were attributed to the iron-manganese ore bearing landmass and the mining operations. However, this was not reflected in its accumulation in marine organisms except in seaweeds, which exhibited higher concentrations.

Singbal *et al.*, (1978) reported the range and average concentrations of mercury in seawater collected at nine stations from the Arabian Sea. Surface values of mercury varied from 26 to 130 ng l^{-1} with an average of 77 ng l^{-1}. While studying the

concentrations of total mercury in the Laccadive Sea, Sanzgiri *et al.*, (1979) reported the range and average concentrations at different depths. Based on the data they are of the opinion that the Laccadive Sea is free from mercury pollution.

Sankaranarayanan and Rosamma Stephen (1978) reported the particulate trace metal concentrations of iron, manganese, copper and zinc in the Cochin backwaters. Higher metal concentrations observed at river mouth when compared with similar environments in other regions of India were attributed to the domestic and industrial pollution in the study area.

Concentration levels of particulate trace metals such as iron, copper, zinc, cobalt, nickel and manganese in the Arabian Sea were reported by Sen Gupta *et al.*, (1978). Higher concentrations at near-shore stations were attributed to their addition from land.

Sanzgiri and Moraes (1979) reported the distribution of trace metals like iron, copper, manganese, zinc, cobalt and nickel, both in dissolved and particulate forms, at five stations in the Laccadive Sea. While the dissolved copper showed a decreasing trend, iron and manganese showed a marked increasing trend with depth. The concentration levels of trace metals in Laccadive Sea were within the range reported for the other areas of the world oceans.

Vasanti *et al.*, (1981) reported the concentration levels of trace metals such as iron, zinc, copper and manganese in seawater, sediments and in some organisms of Bombay harbour Bay. The distribution coefficients (K_d) between suspended silt and bottom sediments were found to be higher than in organism and followed the order $Zn < Cu < Mn < Fe$. While zinc and iron showed preferential accumulation in finer fraction, copper and manganese showed preferential occurrence in coarser fraction of the sediment.

Zingde and Singbal (1983) while studying the characteristics of nearshore waters of Binge Bay (Karwar), observed relatively lower concentrations of soluble manganese, iron, copper and zinc than those of the Arabian Sea. Concentrations of arsenic, copper, zinc and manganese in marine algae, fish, crustaceans and molluscs were also reported. Their studies revealed highest concentrations of manganese in

marine algae (*Sargassum tenerimum*), and copper, zinc and arsenic in oysters (*Crassostrea cucullata*).

Concentration levels of dissolved and particulate metals (copper, zinc, cadmium, mercury and lead) were determined in surface waters from a series of coastal sites in Bahrain, United Arab Emirates (UAE) and Sultanate of Oman of Gulf, and Western Arabian Sea (Fowler *et al.*, 1984). Average dissolved copper concentration along the coast of UAE in general, was lower than those from either Bahrain or Oman. Higher values of cadmium and zinc were found in the waters from more polluted and industrialized northwest coast of Oman than those adjacent to the more open waters of the Arabian Sea. Possible reasons for the observed regional variations in trace metal concentrations in Oman were explained in terms of natural and anthropogenic input sources. Range of concentrations of trace metals such as copper, zinc, cadmium, mercury and lead in Gulf and Western Arabian Sea agreed with those reported for other oceanic areas indicating that coastal waters of this region are not affected by metal pollution. Further, the authors are of the opinion that the existing levels can be used as a point of reference (baseline) for future pollution studies.

George *et al.*, (1984) measured the labile and non-labile (organically associated) concentrations of cadmium, lead and copper in Mandovi estuary. The non-labile form varied from 0-50% of the total for cadmium, from 0-60% for lead, and 0-80% for copper. Higher concentrations of metals observed in Mandovi compared to other estuaries were believed to be due to their leaching from the near by mining zone and spillage during transportation of the ore by barges.

Distribution patterns of zinc, manganese, copper, iron, cobalt, nickel, cadmium, chromium, lead and tin in water, sediment and benthic species in Bombay harbour have been investigated by Patel *et al.*, (1985) in order to assess their possible impact on the harbour ecosystem. The concentration levels of these elements were within the range of nearshore and oceanic waters and were far below to adversely affect the life and quality of benthic communities. Further, the concentration levels neither revealed any spatial or temporal fluctuations nor reflected substantial increase in their total range during the past 8-12 years.

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Labile, non-labile and particulate forms of cadmium, lead and copper were determined from Wadge Bank area (George, 1986) and Lakshadweep lagoon waters (George, 1988). The results revealed higher concentrations of all the metals in Wadge bank region compared to those reported for coastal waters of the Gulf and the Western Arabian Sea. This is attributed to local geological and climatological conditions. Distribution of labile and non-labile forms of dissolved cadmium, lead and copper inside and outside the Lakshadweep lagoon indicates higher concentrations of all the metals with higher percentage of their non-labile form within the lagoon than outside which was attributed to the excretory/decay products of coral/sea grass. The restricted water movement in the lagoon might be responsible for higher concentration of metals and higher percentage of non-labile forms.

Concentration levels of manganese, zinc, copper, nickel and cobalt in seawater and seaweeds (green, brown and red) from Saurashtra coast were reported by Kesava Rao and Indusekhar (1986). The metal content in seaweeds follow a decreasing order Mn > Zn > Cu > Ni > Co. Further the concentration factor of the elements in seaweeds also followed the trend Mn > Zn > Cu > Co > Ni. The authors are of the opinion that shorter the residence time, more is the concentration factor of the elements in seaweeds. Kesava Rao (1986) reported the molybdenum content in seawater and seaweeds from Saurashtra coast. The observed differences in molybdenum to salinity ratios in seawater are attributed to its biological utilization.

George and Kureishy (1979) reported the trace metal concentrations in bulk collections of zooplankton from the coastal and offshore sites of the Bay of Bengal. They observed higher concentration of metals in the offshore samples than coastal samples, which might be due to the peculiar gyral circulation pattern of the Bay of Bengal. The results suggested building up of non-essential elements in the biota of the Bay of Bengal for which the reasons are unknown.

Jegatheesan and Venugopalan (1973) studied seasonal variation of trace metals (iron, copper, manganese, molybdenum, cobalt and vanadium) in the particulate matter collected from two stations in the Vellar estuary and one station in the near shore waters of the Bay of Bengal. Particulate iron showed no significant variation.

Lower concentration of particulate iron observed in the study region was attributed to its utilization by phytoplankton. Relative enrichment of particulate iron in bottom waters was explained in terms of terrigenous input and stirring of the bottom by the tide-induced current. Particulate copper showed well-defined seasonal variation and its higher content observed during November-December in the estuary was believed to be due to the monsoon floods. While particulate manganese showed an increase in its concentration, particulate molybdenum showed no such variation with depth. A marked seasonal variation in particulate vanadium was observed in the estuarine waters whereas no such variation was evident in inshore waters. Except in the months of April to July, particulate cobalt was found to be absent in the study area.

Subramanian *et al.*, (1979) observed a non-linear relationship between the rate of iron precipitation and salinity in the Vellar estuary. The study revealed that the inorganic fraction contributes only a small percentage (18.8%) to the total particulate iron and the role of sedimentary particles could not be neglected while considering the precipitation of iron in estuaries.

Rao *et al.*, (1974) studied the distribution of trace metals (iron, copper, manganese and cobalt) in coastal waters off Vishakapatnam and in different regions in the Bay of Bengal. They observed higher values of iron, copper, manganese and cobalt in August-November (monsoon) and lower values in March-April (pre-monsoon). While the higher values were attributed to contribution from rivers and storm water channels draining the areas of mineral deposits located at north of Vishakapatnam, the lower values were presumed to be due to their utilization by phytoplankton crop. Concentrations of iron, copper and manganese in surface waters of different regions of the Bay of Bengal revealed only slight variation during March-April, and showed an increasing trend away from south to north direction from the Nicobar area. The concentrations were found to be higher near the coasts and lower in the oceanic areas. Vertical distribution of iron and copper exhibited a decreasing trend with depth upto 500m followed by an increase upto a depth of 1000m.

Braganca and Sanzgiri (1980) estimated the concentration of dissolved and particulate fractions of trace metals (copper, iron, manganese, zinc, cobalt and nickel)

at different depths from nine stations in the Bay of Bengal. Concentrations of dissolved and particulate iron were fairly high at coastal stations, especially at river mouths. Though the concentration of copper at nearshore stations was high, no marked difference in its concentration was evident between nearshore and offshore stations so as to reflect the possibility of its river input. Dissolved zinc and nickel were low at the surface than in deeper layers contrary to manganese. Particulate fractions of iron and zinc were significant, whereas cobalt and nickel was not significant. Copper and manganese showed intermediate values.

Sanzgiri and Braganca (1981) estimated the concentration levels of dissolved and particulate trace metals (copper, cadmium, zinc, lead, iron, manganese, cobalt and nickel) from the Andaman Sea. They observed very low concentrations of cobalt and nickel in both dissolved and particulate fractions. Dissolved lead was higher at depth of 0-100m while particulate lead was higher at depths exceeding 500m. The results showed that copper, zinc and lead are more effectively removed onto particulate matter than cobalt, nickel and manganese.

Rajendran et al., (1982) reported concentration levels of trace metals (copper, zinc, manganese, iron, cobalt, nickel and lead) both in soluble and particulate forms in the upper 200m depths of the Western Bay of Bengal. They noticed higher concentrations of zinc, nickel and cobalt in both particulate and dissolved forms. Correlation between trace metal and the primary productivity was also reported in their study. Inshore waters showed higher concentrations of soluble zinc, nickel and cobalt than that normally found in river water. The concentration levels of zinc and nickel were found to be higher in offshore waters. Total suspended matter (TSM) recorded relatively higher values at river mouths. The higher values of total suspended matter extended off Godavari estuary as far as 500km away from the coast.

Satyanarayana et al., (1987) while studying the oceanographic features of the Bay of Bengal, reported the range and average concentrations of dissolved and particulate trace metals (iron, manganese, copper, nickel, zinc, lead, cadmium and cobalt) in the northern Bay of Bengal. Except lead, all other trace metals registered relatively higher values in coastal stations compared to the offshore stations. The range and average

concentration of trace metals obtained in their study in general, agreed with those reported earlier for the Western Bay of Bengal.

Pragatheeswaran *et al.*, (1988) reported the trace metal concentrations (copper and zinc) in water and sediments of Kodiyakkarai coastal environment. Concentrations were higher in water during northeast monsoon and during postmonsoon in sediments. Though the distribution was not uniform, higher concentrations were observed in swampy region.

Morley *et al.*, (1993) reported the dissolved trace metal concentrations (cadmium, copper, nickel, zinc and manganese) from a section in the southwestern Indian Ocean, extending from 7 to 27° S around the 56°E meridian. The overall distributions found are in conformity with those found in other oceans especially with cadmium, copper, nickel and zinc showing recycled, or nutrient-like behaviour, whereas manganese is enriched in the mixed layer relative to deepwater. Deep-water concentrations of the recycled elements are intermediate between those for the North Atlantic and North Pacific Oceans, as would be expected from known patterns of deep-ocean circulation.

Lewis and Luther (2000) studied the vertical and horizontal distributions of dissolved and particulate manganese in the Northwestern Indian Ocean during the spring intermonsoon period. In the oxygen minimum zone, two distinct dissolved manganese maxima were observed, at depths of 200-300m and 600m, respectively. This mid-depth maximum was associated with the low oxygen core of the oxygen minimum zone ($[O_2] \sim 2\mu M$), and appears to be maintained by a southward horizontal advective-diffusive flux of dissolved manganese from the highly reducing margin sediments off Pakistan.

Saager *et al.*, (1992) studied the vertical distribution of dissolved metals (cadmium, zinc, nickel and copper) in the Northwest Indian Ocean. None of the metals gets affected by the reducing conditions prevailing in the oxygen minimum zone. The slopes of Cd/PO_4 are found to be much higher than published for the deep North Atlantic and North Pacific Oceans. However, the slopes of Zn/Si are about the same as found in the Pacific Ocean. The copper profile shows evidence of surface

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water inputs, regeneration in intermediate and deep waters and benthic fluxes, and is further influenced by intensive scavenging, notably in surface waters.

It is evident from the above literature survey that studies so far carried out on trace metals in the water column of coastal and offshore sites of the Arabian Sea and Bay of Bengal are too inadequate. In view of this, the author has undertaken studies on trace metals in different phases (dissolved, particulate and zooplankton) of the water column of coastal and offshore waters of the Arabian Sea and the Bay of Bengal to assess the hydrological and biological factors affecting their concentration levels.

The main objectives of the study are:

1) To study the vertical variation (at standard depths) of trace metals in the dissolved and particulate phases along the inner shelf (~50m), outer shelf (~200m) and offshore sites (>1000m) of the Arabian Sea and the Bay of Bengal.

2) To study the bioaccumulation of trace metals in zooplankton from the Arabian Sea and the Bay of Bengal.

3) To compare the trace metal distribution in different phases (dissolved, particulate and zooplankton) from the Arabian Sea and the Bay of Bengal.

Chapter 2

Materials and Methods

2. 1. Description of the study area

2. 1a. Arabian Sea

The West Coast of India is environmentally unique because it is bordering one of the sensitive ecosystems in the world, the Arabian Sea which is strongly influenced by the Asian monsoons. It is a region of negative water balance, where the evaporation far exceeds precipitation and runoff; consequently the upper layers in this region are highly saline and weakly stratified. The semi-annual reversal of surface currents associated with the monsoon, water mass intrusions from marginal seas, and the absence of subtropical convergence or deepwater formation due to the Asian landmass, provide the Arabian Sea a peculiar thermohaline structure and circulation (Wyrtki, 1971; Morrison and Olson, 1992; Morrison *et al.*, 1998). The complex water mass is due to advection and formation of high-salinity waters in the Red Sea, Persian Gulf and northern Arabian Sea High Salinity Water Mass that sink to moderate depths in the central basin. The excess evaporation over precipitation eventually gives rise to several water masses (Sen Gupta and Navqi, 1984). Seasonal variation in the heating of the southern Asian continent produces a semi-annual reversal in the winds over the Indian Ocean. The monsoon winds have a direct influence on the upwelling, by enhancing the productivity of the area. Strong southwest winds blow across the northwest Indian Ocean during summer monsoon, forcing upwelling off southwestern margin of India (Wyrtki, 1973) leading to intense surface production. Primary productivity in this region fluctuates seasonally as a result of this upwelling and mixing, and the settling organic particles consumes much of the dissolved oxygen and hence the intermediate waters become suboxic leading to remineralization and high rates of denitrification (Saager, 1994). Primary production is high during the southwest monsoon (Qasim, 1982), which has been attributed to injection of inorganic nutrients to the euphotic zone (Ryther *et al.*, 1966). Productivity can remain

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high in the northeastern Arabian Sea during winter monsoon periods, because sea surface cooling drives convection processes that supply nutrients into surface waters (Madhupratap *et al.*, 1996).

The high biological production sustained throughout the year in northern Arabian Sea also results in very high rate of sinking organic particles at intermediate depth. As the oxidation of these particles requires oxygen, the subsurface waters exhibit acute deficiency in oxygen levels, which extents from 150m down upto 1000m in Arabian Sea. The OMZ intensifies northward from 10°N, reaching <10 μM north of 15°N. The OMZ is maintained by a balance between oxygen consumption by organic matter and ventilation at intermediate depths. Strong oxygen minimum zones have substantial impacts on pelagic organisms, which in turn, may have consequences for carbon cycling along with vertical fluxes of trace metals. Recent estimates show that the average renewal time of OMZ waters range from 4 to 20 years (Naqvi, 1987). Suboxic conditions in the OMZ, thus appear to be maintained by rapid biological consumption as the oxygen sink and by the input of Indian Central Water (ICW) from the south, a water mass already low in oxygen (Naqvi, 1987; Olson *et al.*, 1993; Swallow, 1984; You and Tomczak, 1993).

Thus Arabian Sea is a highly dynamic, characterized by a seasonally reversing monsoonal circulation pattern, high surface productivity, carbon fluxes, and a well-developed oxygen-minimum zone. In addition, because of the differential solubility of oxidized and reduced forms of metals, the subsurface, sub-oxic water of the region play significant role in moderating the geochemical distribution of metals from nitrogen and phosphorus during the remineralisation of organic matter.

2. 1b. Bay of Bengal

The Bay of Bengal is an embayment of the Indian Ocean, bounded by the Indian Peninsula and Srilanka to the west and by the Andaman and Nicobar Islands and Myanmar to the east. This semi-enclosed basin has an area of about 2.2×10^6 km^2, which is 0.6% of the world ocean (La Fond, 1966). The bathymetry of the open bay shoals from 4km at the southern end (~ 5°N) and about 2km near the northern end, at about 20°N (Shetye *et al.*, 1991). The continental shelf along the East coast of India is

very narrow (<45 km), but the shelf areas off the mouths of the Ganges, Irrawady and Salween are very wide (200 km). It is an area of positive water balance, where precipitation and river runoff exceeds evaporation leading to very low surface salinities. Its oceanography experiences seasonal changes controlled by the Asian monsoon system. Bay of Bengal is characterised by two dominant wind systems, the southwest and northeast monsoons. Strong winds from southwest lead to maximum rainfall over most parts of the Indian subcontinent from June to September (Southwest monsoon), whereas northeast winds during the December-February (northeast monsoon) brings in heavy rainfall only to southeastern India (Ramage, 1971). The uniqueness of the bay results from six major rivers that flow through various geological formations of the Indian subcontinent. These rivers introduce ~ 2.0 x 10^{15} g suspended particulate matter annually into the Bay, i.e. ~ 15% of the contemporaneous global discharge of fluvial sediments into the world oceans (Rao, 1985). This enormous supply of sedimentary material has resulted in the formation of one of the world's largest deep-sea fan. The average annual runoff from the rivers of India is about 2.0 x 10^{12} m^3 (Gill, 1982), and average annual rainfall over the Bay is in the order of 3.5 x 10^{12} m^3 (Qasim, 1977). The average annual discharges are high in the Northern Bay (10^{12} m^3 for Ganges and Brahmaputra), medium in the central Bay (8.5 x 10^{10}m^3 for Krishna and Godavari), and low in the southern Bay (Cauvery and Pennar) (UNESCO, 1988). Most of the fresh water influx into the Bay occurs during the southwest monsoon (May-September).

The seasonal changes in the direction of monsoonal winds influence the circulation in the northern Indian Ocean. With the onset of the southwest monsoon (May-September), an easterly current develops north of the equator, and coastal circulation becomes clockwise. The present study was under taken during the northeast monsoon (November-December), when the current becomes anticlockwise resulting a strong southerly flow along the coast (Suryanarayana, 1988). Large-scale circulation of currents equator-ward occurs of the east coast of India during September-January, which reverses during February-April to pole-ward (Cutler and Swallow, 1984). Upwelling and sinking along the east coast of India were first

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reported by La Fond, (1954). Based on isotherms, upwelling was noticed prominently during March-May and sinking during September-November. Moderate upwelling, induced by favorable currents and winds, also occur during southwest (June-September) monsoon season (Murty and Varadachari, 1968; Naqvi *et al.*, 1979). However, during southwest monsoon the high influx of freshwater dampens the upwelling of deeper water masses to the surface (Johns *et al.*, 1992, 1993; Shetye *et al.*, 1991).

Bay of Bengal is traditionally considered to have poorer biological productivity compared to Arabian Sea, due to the heavier cloud coverage during summer monsoon. However being a cyclone-prone region certain episodic events are likely to churn-up the area, injecting nutrients to the shallow euphotic zone (shallow due to cloud cover and turbidity arising from sediment influx) and there by enhancing production in upper layers.

Like other parts of the northern Indian Ocean, the Bay of Bengal also experiences intense depletion of dissolved oxygen at intermediate depths (Wyrtki, 1971). The suboxic conditions may lead to important transformation in redox elements in the water column. An oxygen minimum zone between 100 and 500m, less thick compared to Arabian Sea occurs in the Bay of Bengal (Olson *et al.*, 1993).

Suspended particles in seawater play a major role in regulating the distribution and deposition of trace metals released into the marine environment as a result of natural processes and human activities. This is particularly true in coastal waters where dissolved and particulate matter in runoff from rivers and coastal discharges interact with seawater by several physical, chemical, biological and geological processes. The immense river runoff into the northeastern Indian Ocean brought settling particles to the ocean surface, can act as a major vehicle for the vertical mass transport from the sea surface to the ocean interior, and thus expected to influence significantly the marine biogeochemical cycles. Their main source is the biological production in the surface layers with additional contribution from river inputs (Ittekkot *et al.*, 1991) and atmospheric fallout of terrestrial material (Nair *et al.*, 1989). In addition to supplying large amounts of dissolved and suspended matter, the

runoff may also affect the chemistry through controls on circulation and mixing. The lithogenic substances may strongly influence the sedimentation of biogenic matter (Ittekot *et al.*, 1992). Due to these specific characteristics, the study area of the Arabian Sea and Bay of Bengal depicts a unique setting to examine the interacting continental and oceanographic processes on the biogeochemical cycling of trace metals.

2. 2. Sampling and analytical procedures

Water samples were collected during the various cruises of FORV Sagar Sampada conducted under the ongoing MRLR Programme funded by Department of Ocean Development, Center for Marine Living Resources and Ecology (CMLRE), Kochi.This is a multi disciplinary programme, since 1998, with systematic seasonal coverage in the EEZ of India. The classifications of the seasons are in accordance with the JGOFS studies.

The hydrographic surveys conducted along the Arabian Sea and Bay of Bengal were at a one-degree longitudinal interval and two degree latitudinal interval. The station positions for hydrographic surveys in the EEZ of Arabian Sea for intermonsoon fall, northern Arabian Sea (north of 15°N) for spring intermonsoon and Bay of Bengal for winter monsoon are shown in Fig. 1. Together with hydrographic observations, trace metal studies in the water column and surface zooplankton of the Bay of Bengal and the Arabian Sea were studied for selected locations. Water samples and zooplankton were collected from the Bay of Bengal during the cruise No.209 (6th November to 5th December 2002) and from the Arabian Sea during the cruise No.217 (14th September – 18th October, 2003) & cruise No.224 (10th April- 4th May, 2004) of FORV Sagar Sampada. The investigation in the Bay of Bengal (Cruise No. 209) is based on the samples (Fig. 2) along six transects perpendicular to the coast at 11°N, 13°N, 15°N, 17°N, 19°N and 20.5°N and in the Arabian Sea (Cruise No. 217) along seven transects 8°N, 10°N, 13°N, 15°N, 17°N, 19°N and 21°N (Fig. 3). A duplicate sampling was done in the northern Arabian Sea (Fig. 4) along transects 17°N, 19°N, 21°N and 22°N (Cruise No.224). Trace metal studies were performed in all transects at two coastal (50m depth, inner shelf and at 200m depth,

outer shelf) & at two offshore stations (> 1000m depth) in the Arabian Sea and the Bay of Bengal.

In view of very low concentrations (μg l^{-1} or even less) of trace metals in seawater, extreme precautations were taken during their collection, storage and analysis. Water samples from standard depths 0, 10, 20, 30, 50, 75, 100, 150, 200, 300, 500, 750 and 1000m or more were collected using a PVC-coated new stainless steel CTD-rosette sampler with precleaned 5-litre Teflon coated Go-Flo bottles (General Oceanics). The rosette sampler was first sent down to obtain real-time hydrographic data and to flush the Go-Flo Bottles. Upon recovery, samples were filtered directly from the Go-Flo samplers, under nitrogen pressure, through preweighed and acid washed 0.45μm membrane (Millipore) filters mounted on Teflon filter blocks to separate them into dissolved and particulate fractions. The filtered water samples were stored in 2.5 litre acid cleaned polythene carboys after acidifying with pure 6N HCl (Merck) to p^H 3-4. Filters containing particulate matter were placed in a plastic petridish, dried, weighed and stored in a vacuum dessicator.

2. 2a. Dissolved trace metals

Owing to extremely low concentrations of trace elements, particularly transition metals in seawater, it is often necessary to preconcentrate them prior to their determination by Atomic Absorption Spectrophotometer. Further, direct determination of trace elements in seawater by Atomic Absorption Spectrophotometer will lead to erroneous results because of unspecific absorption effects due to high salt content. Solvent extraction procedures have been used extensively for preconcentration of trace metals from seawater as a preliminary to their determination by Atomic Absorption Spectrophotometer. Ammonium pyrolidine dithiocarbamate (APDC) is widely used for chelation of trace metals (Fe, Co, Ni, Cu, Zn, Cd and Pb) in seawater at p^H 3-4 and Methyl Isobutyl Ketone (MIBK) for extraction of metal chelates from the aqueous medium followed by their estimation using Atomic Absorption Spectrophotometer (Brooks *et al.*, 1967). However, though this method is sensitive, it suffers from the disadvantage that the metal chelates are not stable for a long time in Methyl Isobutyl Ketone (MIBK) and hence requires

immediate determination after preconcentration. To avoid this difficulty, the metal-APDC complexes were back extracted from MIBK into aqueous medium using repeated extraction with 4N HNO$_3$ (Jan and Young, 1978). As back extraction step offers greater stability for metal ions in aqueous solution, this has been adopted as the method prior to their determination in Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS, ZL-4110).

2. 2a1. Preconcentration of trace metals

An aliquot (800ml) of filtered seawater was placed in a Teflon beaker of 2.0-litre capacity and the pH was adjusted to 3-4 by adding 6N hydrochloric acid (Merck) solution drop wise. Then 10ml of 2% Ammonium Pyrrolidine Dithio Carbammate (APDC) solution was added and thoroughly mixed. To avoid any possible trace metal contamination, the APDC solution was purified by repeated extraction with MIBK prior to its use. The contents were transferred to a seperating funnel (2.0 litre), 15ml of freshly distilled MIBK was added (pre-equilibrated with Milli-Q water containing 10ml of 2% APDC solution) and thoroughly shaken for 5 minutes to attain equilibrium. The two phases were then allowed to separate and the lower aqueous layer was transferred into another 2.0 litre seperating funnel. This was again treated with 5ml of 2% APDC and 10ml of MIBK and thoroughly equilibrated for 5 minutes. The aqueous phase after second extraction containing only major elements, which do not form complexes with APDC and thus are extracted into MIBK, is used as trace metal free seawater for preparation of blanks and standards in AAS analysis.

The organic layers containing metal complexes obtained from the two successive extractions were combined, transferred into 60ml seperating funnel and treated with 15ml of 4N HNO$_3$ in order to back extract trace metals into the aqueous medium. The contents were thoroughly shaken for 5 minutes, and the two phases were allowed to separate and the aqueous phase was again transferred into the acid-cleaned 60ml screw capped polythene bottle. This aqueous phase containing the trace metals was stored in a deep freezer until their analysis using GFAAS.

2. 2a2.Preparation of standards

Stock standard solutions (1000µg/ml) of the elements (Fe, Co, Ni, Cu, Zn, Cd and Pb) obtained from Merck standards (Germany) were prepared using Milli-Q water, keeping the overall acidity of the solution 1N with respect to nitric acid.

A working solution (mixed standard of 5.0 ppm) was prepared by taking 5.0ml each of the above stock solution with a calibrated micropipette into 1000ml volumetric flask and diluting upto mark with Milli-Q water, keeping the overall acidity 1N with respect to nitric acid.

The combined aqueous phase (seawater left over in the APDC-MIBK extraction step) was treated with 20ml of MIBK for each 1 litre and brought to equillibrium for 5 minutes as described earlier and the aqueous phase is separated. The purpose of this operation was to ensure that the seawater is completely free from the trace metals and should not contribute any absorbance in AAS measurements.

Five aliquots (800ml) of trace metal free seawater (obtained as described above) were taken in five seperating funnels (2l capacity). They were then spiked with 0.8, 1.6, 2.4, 3.2 and 6.4 ml respectively of mixed standard solution (5.0 ppm) with a calibrated micropipette so that the resulting concentration of each trace metal is 5.0, 10.0, 15.0, 20.0 and 40.0 (μg l^{-1}) respectively. The pH of the solution was adjusted to 3-4, treated with APDC and extracted with MIBK. This is followed by their back extraction into aqueous phase (4N HNO_3) as described earlier in the preconcentration step. They were then collected in five precleaned 60 ml screw capped polythene bottles. Each solution (Sea water sample and standards) was analysed by Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS, ZL-4110). Concentration of dissolved trace metals in the seawater samples were computed using calibration curves constructed with standards above. It was found that the calibration curve (absorption versus concentration) constructed for each element was linear upto 40.0 ppb.

The procedure of dissolved metal was tested using the estuarine water reference material (SLEW-2), (n = 5) from the National Research Council of Canada (NRC), to check the analytical quality. Statistical parameters such as standard deviation,

coefficient of variation and relative error are evaluated and the data are presented in Table 1.

2. 2b. Particulate trace metals

Filters containing particulate matter and blank filters were treated with a mixture of (1ml each) concentrated perchloric acid and concentrated nitric acid (Merck, suprapure) and evaporated to dryness. The residue after cooling was dissolved and diluted to 25 ml with 1N HNO_3 and transferred to 60ml screw capped polythene bottle. This solution containing the particulate trace metals was stored in a deep freezer until their analysis in a Flame Atomic Absorption Spectrophotometer (*PE A Aanalyst100*).

The mixed standard solution (5.0 ppm) prepared as above was diluted with Milli-Q water into five 25 ml volumetric flasks so as to give final concentrations of 1.0, 2.0, 3.0 and 4.0 ppm respectively with regard to each element (Fe, Co, Ni, Cu, Zn, Cd and Pb) keeping the overall acidity 1N with respect to HNO_3. After calibration, the samples were then aspirated into AAS and the absorbance of each element was recorded as direct read out of the instrument. Samples were suitably diluted wherever necessary, so as to bring their concentrations below the linearity range. Concentrations were computed using calibration curves constructed using standards as above. It was found that the calibration curve (absorption versus concentration) constructed for each element was linear upto 5.0 ppm.

This procedure was also subjected to analytical quality test (n = 5) using a sediment reference material (BCSS-1). Statistical parameters such as standard deviation, coefficient of variation and relative error are evaluated and the data are presented in Table 2.

2. 2c. Trace metals in zooplankton

Zooplankton collected using a Bongo net was subjected to close visual observation, under a binocular microscope to ensure the absence of any foreign particles. The zooplankton samples were then placed in a small nylon sieve and thoroughly rinsed with Milli-Q Water for removing salts. Water adhering to the samples was removed by placing the sieve on good quality filter paper, without any

contamination. Subsequently, the samples were dried in an oven at 65°C and stored in a vacuum dessicator. Zooplankton samples were first powdered and aliquots of about 300mg were digested for 3 hours at 80°C with 300μl HNO_3 (65%, Suprapure, Merck) in tightly closed 2 ml Eppendorf reaction tubes. The digests were made upto 25ml with HCl (0.1N) and the samples were measured using a Flame Atomic Absorption Spectrophotometer (*PE A AanalystI00*). The precision and accuracy of analysis was checked by replicate measurements (n=5) of target metals in a standard reference material of marine biota sample (TORT-2, Lobster Hepatopancreas, National Research Council, Canada). Statistical parameters such as standard deviation, coefficient of variation and relative error are evaluated and the data are presented in Table 3.

Bioaccumulation factors (baf) were calculated for each metal and organism as the ratio of the metal concentration in the organism's body to its concentration in the respective dissolved phase. Biomagnification factor (bmf) was calculated for each metal and organism as the ratio of the metal concentration in the organism's body and its corresponding concentrations in the particulate phase. For the dissolved and particulate trace metals the concentration values in water samples are reported as both $\mu g \; l^{-1}$ and nM whereas in zooplankton the values are in $\mu g \; g^{-1}$ dry weight. Particulate trace metal data can be expressed in both ways, as $\mu g \; g^{-1}$ and $\mu g \; l^{-1}$. The former will help in establishing the composition of the particulates and thus contribute to identify their sources, and the latter will provide a measure of the total mass of particulate metal in the water sample and thus help in assessing the relative contributions of dissolved and particulate fractions.

2. 3. Suspended particulate matter (SPM)

Total suspended matter or suspended particulate matter is defined as the residue retained by a 0.45μm pore size filter on passing the sample, dried to a constant weight at 60°C. This was determined by filtering an aliquot (5.0 litre) of seawater through a preweighed 0.45μm Millipore membrane filter immediately after collection, washing the residue with Milli-Q water to remove the salts and weighing it after drying at 60°C in an air oven.

2. 4. Temperature and salinity

The sea surface temperature was measured using a bucket thermometer. The temperature-salinity profiles were also measured using the CTD probe (Sea Bird Electronics, Inc., USA, model: SBE-911 plus). The salinity values from the CTD were corrected using the values obtained from the Autosal (Guideline, model 8400A) onboard.

2. 5. Dissolved Oxygen

The dissolved oxygen was estimated by Winkler's method as described in Grasshoff (1983). In the dissolved oxygen estimation, the water sample (60ml) is allowed to react with (0.5ml each) Winkler A (manganese chloride) and Winkler B (alkaline potassium iodide) respectively. The precipitated manganese hydroxide is acidified (with 50% HCl) and the liberated iodine is titrated against standard sodium thiosulfate solution using starch as the indicator.

2 .6. Nutrients

Nutrients like nitrate, nitrite, phosphate and silicate were analysed onboard FORV Sagar Sampada using a SKALAR Segmented Flow Auto Analyzer.

2. 6a. Nitrate-nitrogen

The automated procedure for the determination of nitrate-nitrogen is based on the cadmium reduction method. The sample is treated with ammonium chloride solution and passed through a column containing granulated copper-cadmium to reduce the nitrate to nitrite. The nitrite (originally present plus reduced nitrate) is determined by diazotizing with sulfanilamide and coupling with N-naphthyl ethylene diamine dihydrochloride to form an intense coloured azo dye, which is measured photometrically at 540 nm. The concentration of nitrate in seawater samples was computed from the calibration curves constructed with standards. The efficiency of the reductor column was checked periodically using standard nitrate solution. Seawater samples and standards were subjected to identical treatment in each batch of samples.

2. 6b. Nitrite-nitrogen

The automated method for the determination of nitrite is based on the diazonium compounds formed by diazotizing of sulfanilamide by nitrite in sea water under acid conditions and coupled with N-naphthyl ethylene diamine dihydro chloride to produce a reddish purple color which is measured photometrically at 540 nm. The concentration of nitrite in seawater samples was computed from the calibration curves constructed with standards. Seawater samples and standards were subjected to identical treatment in each batch of samples.

2. 6c. Phosphate-phosphorus

The automated procedure for the determination of phosphate in seawater is based on the following reaction; ammonium molybdate and potassium antimony tartrate react in an acidic medium with phosphate to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue colored complex (molybdenum blue) by ascorbic acid. The absorbance of molybdenum blue is measured at 880nm. The concentration of phosphate in seawater samples was computed from the calibration curves constructed with standards.

2. 6d. Silicate-silicon

The automated procedure for the determination of silicate in seawater is based on the following reaction; the sample is acidified and mixed with ammonium molybdate solution forming molybdosilicic acid. This acid is reduced with ascorbic acid to a blue dye, which is measured at 810nm. Oxalic acid is added to avoid phosphate interference. The concentration of silicate in seawater samples was computed from the calibration curves constructed with standards.

2. 7. Biological parameters

2. 7a. Primary productivity

For measuring *in-situ* primary productivity, water samples from 7 depths:- surface, 10, 20, 50, 75, 100 and 120m were subjected to *insitu* incubation according to Indian JGOFS protocol (UNESCO, 1994) using ^{14}C- technique. Polycarbonate (Nalgene, USA) bottles were used for primary productivity incubations and the radioactivity was counted (*disintegration per minute*- DPM) in a liquid scintillation

system (Wallac 1409, DSA-Perkin Elmer-USA) (Plate 2.5). The daily production rate $(mg \ C \ m^{-3}d^{-1})$ at various depths was used to calculate the integrated water column production $(mg \ C \ m^{-2}d^{-1})$.

2. 7b. Chlorophyll a

For the estimation of chlorophyll a, 1.0 litre of water from each standard depth was filtered under low vacuum through GF/F (l pore size $0.7\mu m$) filters, added one or two drops of magnesium carbonate solution and kept in a refrigerator (Strickland and Parsons, 1972). The samples from the filter papers were extracted using 90% acetone, centrifuged and made up to 10ml using 90% acetone and the absorbance was measured using a spectrophotometer (Perkin-Elmer uv/vis) using 1cm cuvette against 90% acetone as blank at different wavelengths of 750, 664, 647 & 630 nm. Chlorophyll a calculated for each depth was integrated to obtain the column values.

2. 7c. Particulate Organic Carbon

For the determination of particulate organic carbon (POC), one litre of seawater was filtered through precombusted GF/F filter paper. The filters were later digested in chromic acid and back titrated with standard ferrous ammonium sulfate.

Table 1

Statistical data for trace metals in estuarine water reference material, (SLEW-2)

Element	Certified Concentration ($\mu g\ g^{-1}$)	Measured Concentration ($\mu g\ g^{-1}$)	Standard deviation	Coefficient of variation (%)	Relative error (%)
*Fe (%)	2.37± 0.37	2.51±0.15	0.15	5.97	5.90
Co	0.055±0.002	0.053±0.002	0.002	3.77	-3.63
Ni	0.709±0.054	0.67±0.036	0.036	5.37	-5.50
Cu	1.62±0.11	1.47± 0.11	0.11	7.48	-9.25
Zn	1.10± 0.14	1.09±0.006	0.006	0.55	-0.91
Cd	0.019±0.002	0.017±0.002	0.002	0.12	-10.52
Pb	0.027± 0.005	0.025±0.001	0.001	0.04	-7.40

Table 2

Statistical data for trace metals in a sediment reference material, (BCSS-1)

Element	Certified Concentration ($\mu g\, g^{-1}$)	Measured Concentration ($\mu g\, g^{-1}$)	Standard deviation	Coefficient of variation (%)	Relative error (%)
*Fe (%)	3.05±0.17	3.11±0.10	0.10	3.21	1.96
Co	11.4±2.1	11.64±1.39	1.39	1.19	2.10
Ni	55.5±3.6	54.74±3.85	3.85	7.03	-1.36
Cu	18.5±2.7	18.28± 2.34	2.34	12.8	-1.18
Zn	119± 12	123.6±11.9	11.9	9.62	3.86
Cd	0.25±0.11	0.24±0.006	0.006	2.5	-4.0
Pb	22.7± 3.4	22.26±2.42	2.42	10.9	-1.94

*(Fe concentration is only expressed in %)

Table 3

Statistical data for trace metals in TORT-2, Lobster Hepatopancreas

Element	*Certified Concentration (μg g -1)	Measured Concentration (μg g -1)	Standard deviation	Coefficient of variation (%)	Relative error (%)
Cu	106$\pm$ 10	109$\pm$ 5.03	5.03	4.58	3.58
Zn	180$\pm$ 6	182.4$\pm$ 4.78	4.78	2.62	1.33
Cd	26.7$\pm$ 0.6	27.6$\pm$ 1.1	1.1	3.98	3.37
Fe	105$\pm$ 13	107.5$\pm$ 3.13	3.13	2.91	2.38
Pb	0.35$\pm$ 0.13	0.377$\pm$ 0.033	0.033	8.75	7.71
Ni	2.5$\pm$ 0.2	2.69$\pm$ 0.20	0.20	7.43	7.6
Co	0.51$\pm$ 0.09	0.58$\pm$ 0.08	0.08	13.8	13.7

*(Certified by, National Research Council, Canada)

Figure. 1. Station locations in the Arabian Sea and Bay of Bengal for Primary Productivity, Secondary Productivity and hydrographic studies
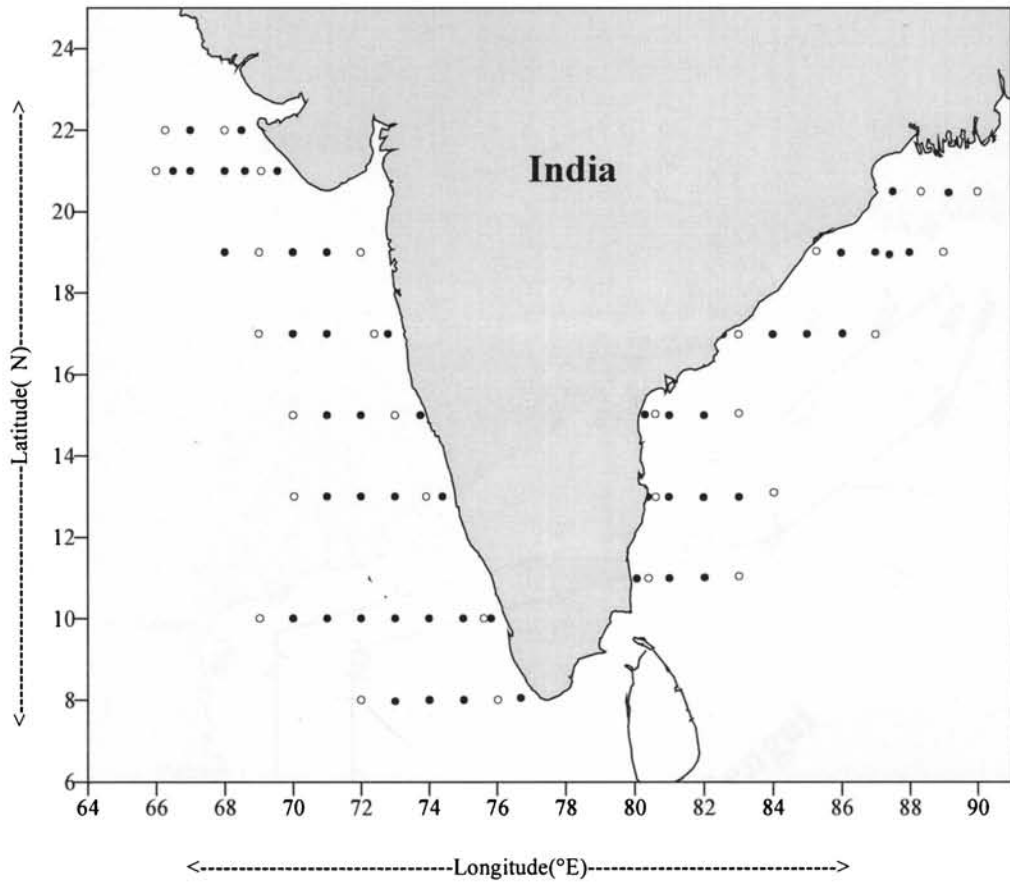
●- CTD stations
O- Primary Productivity stations

Figure. 2. Station locations in the western Bay of Bengal for trace metal studies during winter monsoon
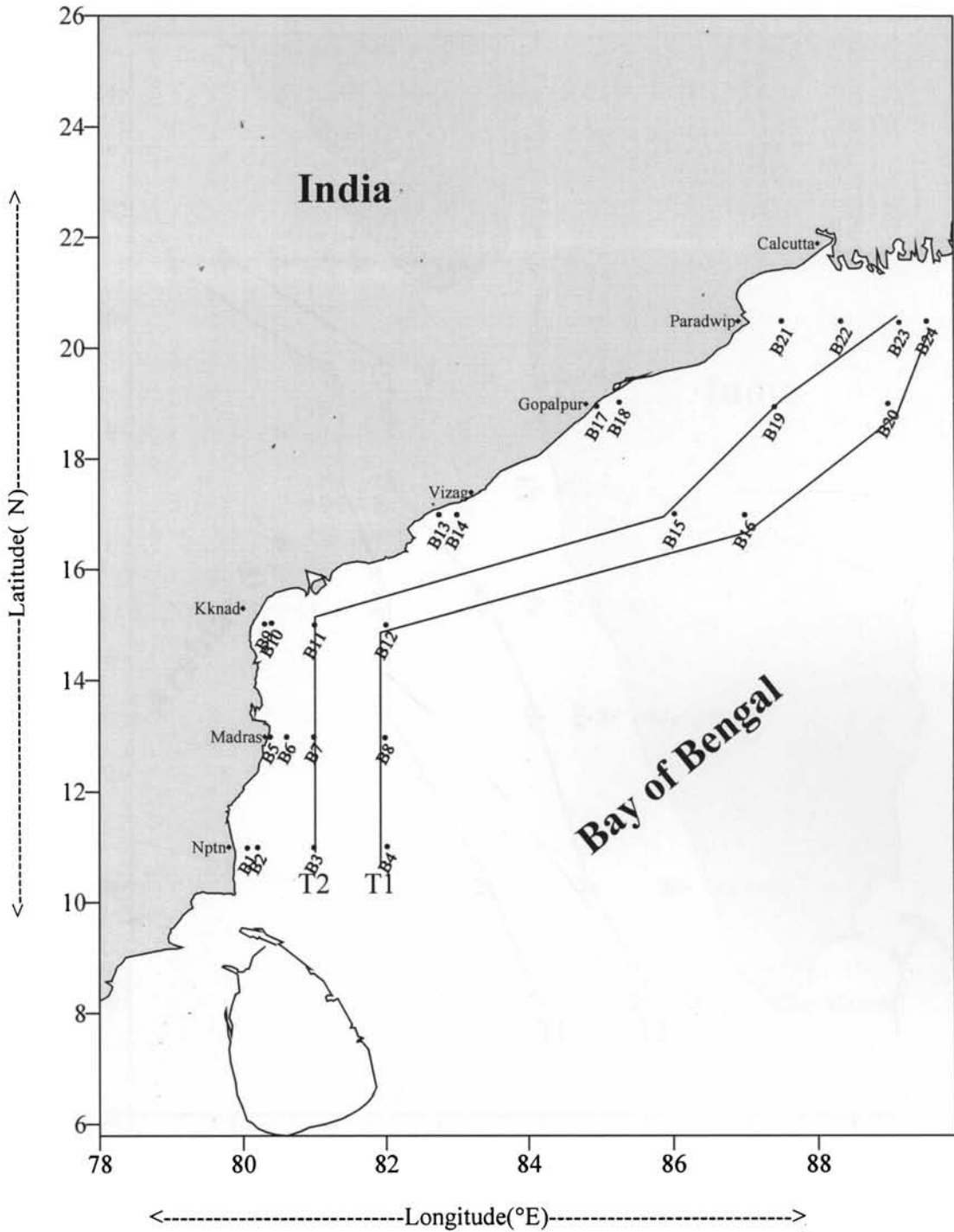
Figure. 3. Station locations in the eastern Arabian Sea for trace metal studies during intermonsoon fall
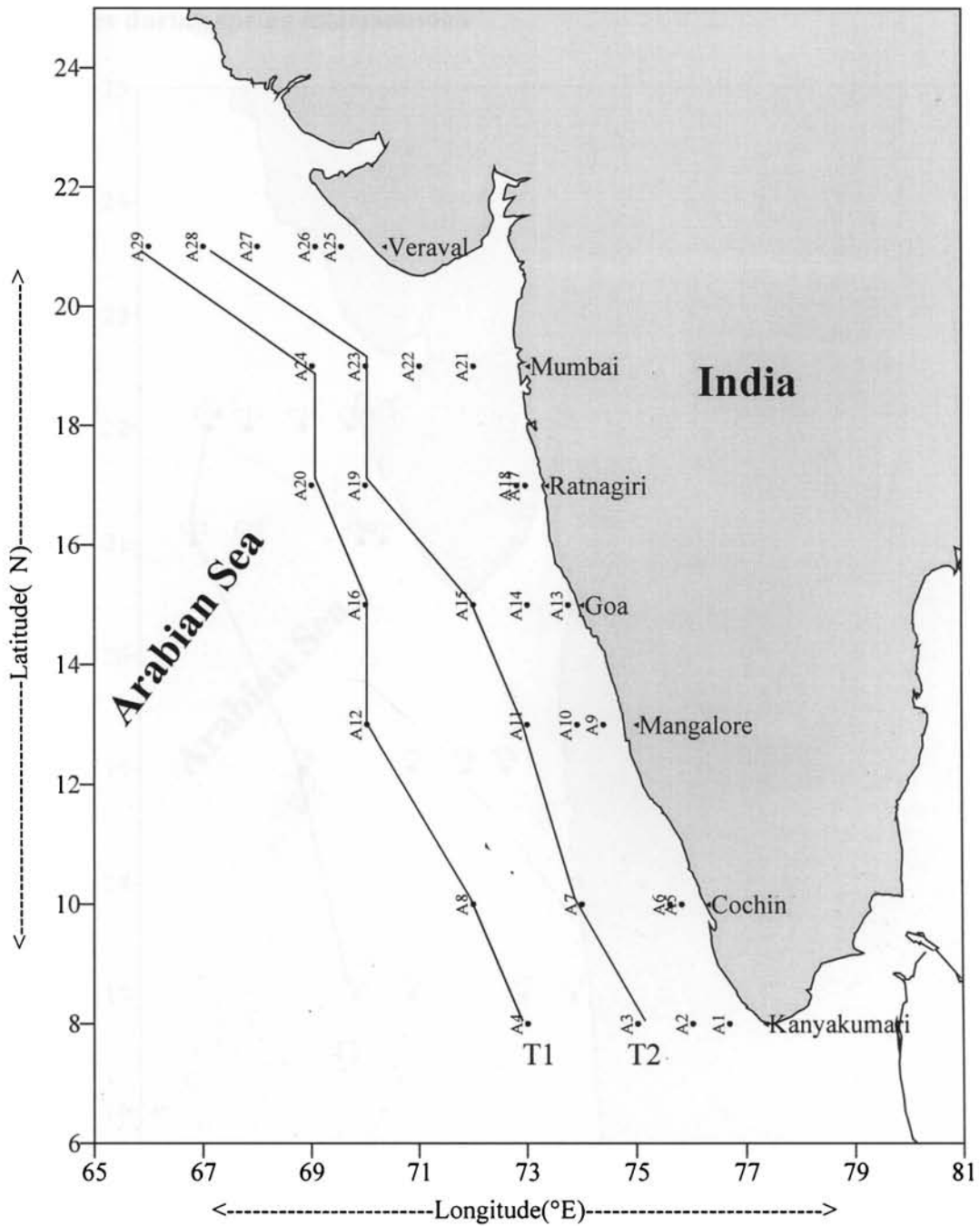
Figure. 4. Station locations in the northeastern Arabian Sea for trace metal studies during spring intermonsoon
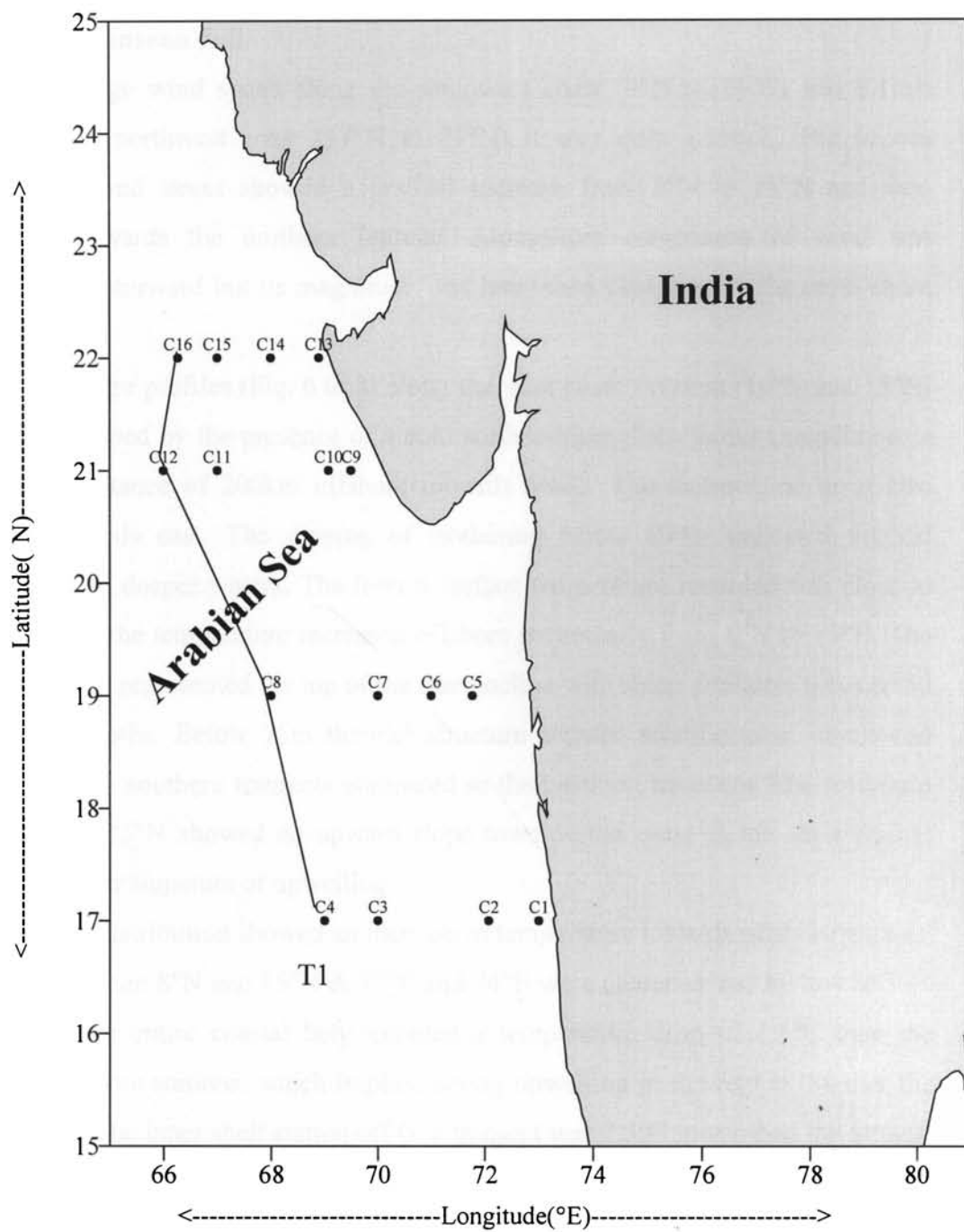
Chapter 3

3.Hydrography, nutrients and biological characteristics in the Eastern Arabian Sea and Western Bay of Bengal

3.1. Arabian Sea

3.1 a. Intermonsoon Fall

The average wind speed along the southwest coast (8°N to 15°N) was 8.1m/s while in the northwest coast (17°N to 21°N) it was only 3.15m/s. The *in situ* alongshore wind stress showed a gradual increase from 8°N to 15°N and then decreased towards the northern latitude. Alongshore component of wind was generally equatorward but its magnitude was less when compared to the cross-shore component.

Temperature profiles (Fig. 6 to 8) along the west coast between (10°N and 15°N) was characterised by the presence of a cold surface layer (75m thick) extending to a maximum distance of 200km offshore towards south. The thermocline layer also shoaled towards east. The dipping of isotherms below 100m indicated vertical movements of deeper waters. The lowest surface temperature recorded was close to the coast and the temperature increased offshore particularly from 8°N to 15°N. The 28°C isotherm represented the top of the thermocline with sharp gradients between 50 and 200m depths. Below 75m thermal structure showed stratification, which was stronger in the southern transects compared to the northern transects. The isotherms from 8°N to 15°N showed an upward slope towards the coast in the shelf region, which is a clear signature of upwelling.

The SST distribution showed an increase in temperature towards offshore regions. The area between 8°N and 15°N & 77°E and 74°E were characterized by low SST (< 28°C) and the entire coastal belt recorded a temperature drop of 1.5°C than the farthest off shore stations, which implied strong upwelling in the region. Further the SST value of the inner shelf station off Goa transect was 2.5°C lower than the farthest offshore station.

The MLD in the coastal waters was 26m along 8°N, which decreased to <10m in the middle transects (10°N –15°N) and deepened to >30m in the northern transects (17°N – 21°N). The MLD in the open ocean in all this transects were > 50m.

Sea surface salinity in the coastal waters off Kochi, Mangalore, and Goa were low (<34.4psu) whereas to the north off Goa it increased (>35.0psu). The eastward upslope of the isohalines at subsurface was at a lesser degree over the entire region (8°N to 15°N). The subsurface isohalines of the above latitudes showed a slight upward tilt from the offshore region towards the midsection and from there on no indication of upslope of contours towards the coast was seen. The salinity decreased from north to south and increased offshore from the coast. The highest surface salinity (>36.0psu) was found at the northeastern part of the Arabian Sea. Surface salinity near the coast in general, was 2.0 psu lower than the open ocean values. A tongue of high saline water (>36.00 psu) extending from the offshore region to the midshelf and with its core around 50m depth was observed in the vertical sections from 8°N to 15°N. Below 50m the salinity was gradually decreasing with depth to about 35.4 psu at about 300m depth. The upward tilt of the isohalines towards the coast in the shelf region also indicates upwelling.

A significant observation was the coastal upwelling, which is one of the major factors that govern the distribution of nutrients. Towards the end of summer monsoon (end of September, 2003) upwelling in the Arabian Sea has retreated from south (8°N), but still persisted in the coastal belt between 10°N and 15°N. Vertical isolines (Fig. 6 to 8) of chemical parameters along these transects showed a sharp cross-shelf upslopping of contours towards the coast. Near the coastal margins, colder (<28°C), less oxygenated (<190.0µM) subsurface waters (~75m deep) containing high nutrients enriched the surface layers. Thus, the contour of 2.0µM nitrate, 0.8µM phosphate and 4.0µM silicate was found to penetrate through the shelf waters to surface near the coast. The spatial distribution of nitrate, phosphate and silicate along these transects showed a decreasing trend in its concentration from coastal to offshore stations. However, the upward movement of isolines of nutrients was limited upto 15°N.

The concentration of nitrate in the study region varied from non-detectable levels to 4.0μM in the surface waters (in the upper 50m). Vertical distribution of nitrate in the northern transects (north of 15°N) showed that the upper 50m was almost devoid of 2.0 μM nitrate. This was followed by a marked increase in the intermediate and deeper layer nutrients, suggesting the existence of a permanent nitracline in the thermocline region. In regions of upwelling, a shoreward increase in gradient of the nitrate distribution was observed. Apart from upwelling, the rivers draining through agriculture fields in the coastal belt could also bring in considerable amount of nitrogen-based fertilizers, causing enrichment of coastal waters with nitrate (Fig. 6). Surface nitrate concentrations in the Kochi estuary were as high as 25.0μM during a period of heavy runoff in July 2003 and rainwater collected at the National Institute of Oceanography, Regional Centre, Kochi, contained an average of 10 μM nitrate. Thus, significant nitrogen loading occurs through rivers during the period, as evidenced by elevated 2.0μM surface nitrate in the off Kochi transect.

Phosphate also showed the effect of upwelling from off Kochi to off Goa transects (Fig. 6 to 8). At the offshore waters of these transects phosphate values were 1.0μmol at 75m depth but in the coastal areas this concentration was found in the upper 30m depth. The phosphate concentration in the deeper waters of the southern transects were higher (~3.0μM) than the northern transects. Here also in the upwelling regions, a coastward increasing gradient in the phosphate concentration was noticed.

Distribution of silicate also revealed the upwelling of deepwater with 4.0μmol contours along 70°E at 30m (Fig. 6 to 8), which shoaled sharply to the surface near the coast. However, the high silicate values corresponded with a lowering of salinity values which could be attributed to the large influx of river waters rich in silicate. Thus upwelling together with river water and land drainage seems to attribute to enhanced silicate and nitrate fractions during this period. Unlike nitrate and phosphate, silicate exhibited a continuous increase from near surface to bottom.

Along the northern transects (north of 17°N) the surface waters were nutrient depleted and seemed to be oligotropic in nature. Along off Mumbai and off Veraval

transects, the surface nutrients were below detectable levels with uniformly saturated dissolved oxygen concentration ($O_2 > 190.0\mu mol$). Surface water temperature in these transects (Fig. 10 to 11) increased gradually with distance towards offshore leading to more stratified, thermally stable oligotropic waters. Nutrient concentration increased sharply below 50m depths. In the deeper waters, (100-300m) there occurred an east-west decreasing gradient in the nutrient contours. Along 21°N, 26μmol contour of nitrate was observed at 300m at 66°E which could only be traced at 150m along 69°E.

Nitrite showed an unusually primary maximum at 20-50m depths of >1.5μM intensifying towards the inner shelf between Kochi and Ratnagiri (Fig. 12). A secondary nitrite maximum >3.0μM at 200-300m depths increasing towards offshore was also seen from Ratnagiri to Veraval (Fig. 12).

Vertical profiles of dissolved oxygen, nitrate, phosphate and silicate along a coastal transect parallel to the West Coast of India (Fig. 27, shown at the end of Chapter 4) was found to give a clear cut picture of the retreat of upwelling from the southern tip of India (8°N) towards the end of summer monsoon. Concurrently, the surface waters between 10°N and 15°N had comparatively low oxygenated waters (<190μmol), whereas the oxygen concentrations in the surface waters south of 10°N and north of 15°N were higher than 190μmol. In almost all the transects, waters below 100m showed suboxic condition ($O_2 < 20\mu M$) and towards the near shore waters, it was severely depleted ($O_2 < 10\mu M$).

As the north Indian Ocean responds to the seasonally reversing monsoons, its impact is also seen along the southwest coast of India, conspicuously as the seasonal upwelling. The climatological wind analysis (Muraleedharan, 1995) is also in support of the *in situ* wind measurements which shows that, alongshore component of wind during September appears to decrease from 8°N to 10°N and then increases upto 14°N. The shoaling of the isotherm with low SST off Kochi, Mangalore and off Goa indicated strong upwelling and was well correlated with the prevailing strong winds. Evidence of upwelling is seen from figures (5 to 8) as upward tilting of isotherms, isolines of nutrients and dissolved oxygen. At 8°N the upwelled waters has already

retreated from the surface layers whereas the regions between 10°N and 15°N were still under the grip of upwelling with nutrient rich (NO_3^- > 2.0µM, PO_4^{3-} >0.8 µM and SiO_4^{4-} > 4.0µM) and low oxygenated coastal waters (< 190.0 µM) in the surface. The offshore stations however, showed a deepening of isotherms and nitracline upto 75m depth along 69°E where surface waters remained oligotropic. The isotherms of > 20°C indicated a marked shoaling towards the coast along 8°N to 15°N. Further inshore, the region experiencing coastal upwelling had lower water temperature and enriched nitrate, phosphate and silicate concentrations. Previous studies at the peak of southwest monsoon season demonstrated a similar structure for phosphate concentrations in the upwelling areas (Sastry and D'Souza, 1972; Currie et al., 1973). It is evident from the thermal structure that the surface waters along the western shelf between 10°N to 15°N were colder compared either to north or south of the region due to different physical processes operating along the shelf. These anomalies are well explained in the context of active winds favoring sustained upwelling in the southwest coast (10°N to 15°N) compared to the northwest coast. From the vertical sections it can be inferred that waters from a depth of 75m reach the surface between 10°N and 15°N but is restricted to subsurface depths (~30 m) on either sides since the wind forcing here is weak. The upwelling signature is totally absent to the north of 17°N and can be concluded that since upwelling begins in the south with the onset of summer monsoon and slowly gets propagated to north, the retreat is initiated also from south to north.

The sea surface salinity decreases from north to south and increases offshore from the coast. High surface salinity values observed in the northeastern part of the Arabian Sea are due to high evaporation. Vertical salinity structure showed strong gradient in the upper 100m depth. In the surface layer, salinity was about 36.6 psu between 19°N and 21°N but reduced towards south to values less than 35.0psu. The salinity gradients close to inshore at 25m depth observed from the vertical sections off Kochi to off Mangalore (0.4psu) was weaker while that at off Goa (1.8 psu) was stronger indicating the signals of freshwater influx in the region. The low surface salinity values off the west coast of India south of 15°N can be due to land drainage.

Low oxygen values (< 20.0μM) were observed at the entire shelf break areas of the west coast of India probably because of higher rate of oxidation of organic matter associated with high productivity of overlying shelf and slope waters. The oxygen saturation is regulated by the supply of organic matter, which in turn depends on surface runoff and *in situ* production. For instance, along the transects 13°N, 15°N, 17°N and 19°N very low oxygen concentrations (< 10μM) with its intensity towards shelf areas observed were often associated with high nutrient concentrations indicating the land-derived organic matter depleting oxygen from the water column.

A shallow primary nitrite maximum (>1.5μM) at 20-50m depth intensifying towards the inner shelf, associated with hypoxic waters was observed between Kochi to Ratnagiri transects and was attributed to be due to denitrification (Naqvi *et al.*, 2000). They have identified this hypoxic region covering an area of about 180,000 km^2 in the western continental shelf of India. The along-shelf transects from off 8°N to 21°N in the present study showed the prevalence of reducing conditions (oxygen deficiency) over much of the shelf area with a progression from hypoxic to suboxic regimes which is more prominent between 10°N to 15°N, where the upwelled water moved up from the shelf break to the inner shelf (Fig. 13). This shallow suboxic zone is distinct from the deeper perennial suboxic layer of the central Arabian Sea (Naqvi, 1987). The intense oxygen depletion over the western Indian shelf has been brought about by an increased nutrient loading by the extensive consumption of nitrogen and phosphorus-based fertilizers in the coastal belt during the monsoon crops. Moreover, West coast of India represents one of the densely populated regions, implying that human activities have a direct impact on the coastal ecosystem.

A secondary nitrite maxima (>3.0μM) at 200-300m depth was evident in the OMZ where nitrate depletion intensified towards offshore between Ratnagiri and Veraval, indicating the denitrifying zones (Fig. 12). The build up was considered to be due to the active denitrification during mineralisation of sinking organic particles (Mantoura *et al.*, 1993). In the northern Arabian Sea the secondary nitrite maxima, which occurs in the layers between 200 and 300m corresponds to the depths of occurrence of Persian Gulf water. The high productivity of the northern Arabian Sea

(Krey, 1973) and Persian Gulf water at its source might be responsible for the suboxic conditions observed in the intermediate layers of the Arabian Sea leading to an intense denitrification.

Peaking of nutrient rich contours towards the surface waters between Kochi and Goa suggests the persistent upwelling during the period (Fig. 27, shown at the end of Chapter 4). Nutrient rich waters at the surface at the southern most transect (off Kanyakumari) during the onset of summer, shifts towards north upto off Goa during the end of summer monsoon. Upwelling characteristics were not evident north of 15°N possibly because the width of the continental shelf is narrower on the southern side and wider on the northern side (Gopinathan and Qasim, 1974). There is an apparent streaming up of nutrients at the bottom layers towards southern latitudes in the coastal transect probably due to sediment resuspension by the poleward under current succeeding the monsoon. Strong winds and the upwelling-induced, onshore bottom flow occurring during the southwest monsoon should enhance resuspension of sediments on the inner and outer shelf (Nittrouer, 1994). Resuspension of sediments results in faster recycling of nutrients, which increases nutrient availability for biological production in the surface water (Banse, 1984). On the outer shelf, these nutrients were entrained into the onshore bottom flow which carries already nutrient enriched subsurface water to the surface. On the inner shelf, resuspension supplies nutrients directly into the surface water (Nittrouer, 1994).

The vertical profiles of nutrients during the withdrawal phase of summer monsoon indicate the enrichment of coastal waters by the nutrients brought up from the sub-surface levels. This gives a picture of upwelling, which is further corroborated by the distribution of temperature. The present study indicates that the process of enrichment of nutrients at the surface waters is weak in the southern region of the west coast of India (8°N), but intensify towards north between 10°N to 15°N. The weak thermocline during this period probably favours vertical mixing of the waters and thus replenishes the surface layers with nutrients.

Upwelling in this region is characterised by the lifting up of the isotherms, with a shoaling and sharpening of the thermocline and the penetration of the low oxygen

water of less than 30μM over the entire shelf. Another feature is the lowering of sea surface salinity in the near shore region (10°N to 15°N) with associated land drainage. Upwelling may be coupled with undercurrents, which may carry the mud deposits from deeper areas to shallow regions (Gopinathan and Qasim, 1974). One effect of upwelling is to force fish and prawns to move closer to the shore to avoid the oxygen deficient waters.

Vertical sections of temperature, salinity and nutrients along the north-south open ocean transects (T1and T2), are shown in (Fig. 30, 31, 36 & 37, shown at the end of Chapter 4). The contours for this section are plotted at two depth intervals since the larger spatial features of a given water property are shown over the depth range 0-200m and hence given in the upper portion but property distribution at 200-1000m are given in the lower portion. Cold core eddies of comparable magnitude was present in both transects. The two eddies present at transect T1 were stronger but the one present at transect T2 was weaker. Two subsurface cold-core eddies were present at T_1 transect; with one of its diameter was approximately 240km at the 17°C isotherm, and for the other the diameter was approximately 480km at 15°C isotherm which was the dominant feature. The first eddy extends to a depth of about 100m while the second one extends to a depth of 200m. The center of the first eddy was between 8°N and 12°N while the center of second one was located between 13°N and 17°N. An upheaval of isotherms was noticed between 8°N & 12°N and then sinks, followed by upheaval of isotherms between 13°N & 17°N while north of it the isotherms shoaled towards 21°N. In the former case the 28°C isotherm shoaled from 30 to 10m, and thus the upper thermocline showed a vertical displacement of 20m, which tapered off towards the lower thermocline. But in the latter case the 28°C isotherm shoaled from 40 to 20m, thus shifting the upper thermocline by a vertical displacement of 20m, which tapered off towards the bottom of thermocline. This was clearly a signature of cold-core eddy, seen below 10m depth, which lowered the ambient temperature at 40m (27°C) by about 4°C. A warm surface layer (29°C isotherm), which extended to a depth of ~30m, lies over the two eddies. The horizontal variability in this layer was small over the eddy core region compared to that of the exterior frontal structure,

which partially surrounded the eddy system. Outside this region thermal fronts are found on either side of the eddy, which was weak in the north and strong in south. Vertical sections of salinity (Fig. 30) showed strikingly the same feature as that of temperature. For example, within the region of the eddy system, isotherms and isohalines exhibited a concave structure. In addition, the small-scale haline fronts that partially surround the eddy were more intense than the corresponding thermal fronts. Further the haline fronts were strongest in the southern region and weak in the northern region of both eddies.

Fig. 31 shows the north-south vertical sections of nitrate, phosphate and silicate in the open ocean transect (T1) at the eddy region. Pronounced nutrient fronts, spatially aligned with the strong thermal fronts were present in the north and south quadrant of the two-eddies system. Strong nitrate, phosphate and silicate fronts were present in southern side of the two-eddy system but are weak at the northern side. Interestingly the temperature contours (29°C) and isolines of 2.0µM of nitrate south of the two eddies shoaled upwards to the surface. The two cold-core eddies both of which were characterized by low temperature (<27°C), low dissolved oxygen (<100µM) and high nutrients ($NO_3^->10µm$, $PO_4^{3-}>1.2µm$ and $SiO_4^{4-}>8.0µM$) at 30m. The location and strength of these nutrient fronts were consistent with the isotherms of temperature and isohalines of salinity, which showed that water of deep oceanic origin, is preferentially entrained into the upper surface levels. The physical fronts showed uniformity of structure and intensity to the surface consistent with the isolines of nutrients, which had pronounced nutrient concentrations and got concentrated on the center of the cold-core region. However the eddy present in the middle open ocean transect (T2) did not bring out nitrate rich waters to surface even though it brought out 0.6µM phosphate and 4.0µM silicate respectively to the surface waters.

A significant feature observed from the thermal structure, along the open ocean transects was the presence of thermocline oscillations and cold-core eddy signatures. Under the influence of these eddies, cold waters enriched in nutrients were pumped into the surface layers. Consistent with the southward shoaling of isotherms and isohalines in the open-ocean section, nitrate, phosphate and silicate isopleths also

showed shoaling. Thus both eddies and shoaling of isotherms were induced by favourable wind, which leads to surfacing of nutrients.

Spatial variations of Primary Productivity, Chlorophyll a and Particulate Organic Carbon showed that maximum plant pigments (8.1 mgC/m^3/day, 0.38 mgC/m^3/day & 0.945 gC/m^3) are likely to be located along the frontal zone adjacent to the center of the first eddy and near the center of the upper portions of the cold core region. High chlorophyll a concentrations implied with high primary productivity and particulate organic carbon were observed within the cold-core eddy associated with nitrate injected to the upper layers due to eddy induced mixing. The anomalous chlorophyll a structure observed in the eddy region can be due to the enhanced vertical entrainment of subsurface nutrients into the euphotic zone resulting from prolonged surface cooling and deep convection from summer storms as the eddy moved away from its area of formation into waters with an overlying colder atmosphere might explain why productivity and chlorophyll a in the cold core eddy region was high.

During this period, the chlorophyll a, Primary productivity and Particulate organic carbon (POC) in both surface and column at the coastal transect was higher than that at the offshore transect (Table 4). In the outer shelf transect, the chlorophyll a in both surface and column at the southwest coast were higher than that at the northwest coast (Table 4). The surface PP, chlorophyll a and POC of coastal transect varied from 2.0 to 37.4 mgC/m3/day (average 11.34 mgC/m3/day), 0.02 to 0.75 mg/m3 (average 0.27 mg/m3) and 0.158 to 1.83 g/m^3 (average 0.635 g/m3), while in the offshore transect it was 2.0 to 8.4 mgC/m3/day (average 6.0 mgC/m3/day), 0.03 to 0.38 mg/m3 (average 0.22 mg/m3) and 0.158 to 0.945 g/m^3 (average 0.436 g/m3) respectively. The column PP, column chlorophyll a and POC of coastal transect varied from 179 to 1630 mgC/m2/day (average 501 mgC/m2/day), 5.9 to 60.70 mg/m2 (average19.4mg/m2) and 9.1 to 157.2 g/m^2 (average 61.3 g/m^2). The column PP, column chlorophyll a and column POC in the offshore transect was 199 to 490 mgC/m2/day (average 324 mgC/m2/day), 9.0 to 30.2 mg/m2 (average17.4mg/m2) and 25.8 to 84.5 g/m^2 (average 53.4 g/m^2).

During this season the nutrient concentration along the southwest coast are high and exhibit an intense cross shelf gradient, which are not observed along the northern coast. High surface nutrient concentrations are consistent with low SST and low MLD values in the southern area, suggesting stronger upwelling in the southwest coast. The nitrate distribution in the coastal transect showed that the nitracline shoaled south of 17°N resulting in a rapid increase of surface nitrate from 0.0 µM to 2.0 µM. Consistent with the nitrate distribution, chlorophyll *a* and primary productivity were higher than that at the northwest coast (Table 4). The effect of wind driven upwelling was clearly seen in the coastal transect along the southwest coast, which in turn have resulted in shoaling of isotherms and isolines of nutrients. The very high chlorophyll pigment concentration and primary productivity in the southwest coast was associated with nitrate injected to the upper layers due to upwelling. Thus wind-induced entrainment of nutrients together with surface runoff, favoured by the low mixed layer temperature, might explain why productivity and chlorophyll in the southwest coast were high as compared with the northwest coast.

However, the effects of the river plume were also evident in the region (10°N to 15°N) reducing the surface salinity of nearby coastal stations to <34.40 psu (Fig. 6 to 8). Hence, the lense of nutrients in the surface layers observed in the southwest coast of India may be attributed to combined effects arising as a result of coastal upwelling and the surface runoff. For instance salinity gradients close to inshore at 25m depth observed the vertical sections from off Kochi carries a nitrate of 2.0 µM and phosphate of 0.6µM to the outer shelf (Fig. 6). The reason for this anomaly might be due to the existence of rich benthic fauna of the area and the nutrient rich Kochi back waters draining in this zone. At the coastal station off Kochi where there was a combined effect of upwelling and surface runoff, chlorophyll *a (60.7* mg/m2*)*, and pp (1630 mgC/m2) were the highest. The triggering mechanism for enhanced productivity and chlorophyll *a* measured at the coastal station off Kochi might be related to nitrate repletion due to surface runoff rather than upwelling. The high productivity of the region was clearly a consequence of influx of nutrients into the euphotic zone due to upwelling coinciding with surface runoff.

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3.1 b. Intermonsoon Spring

Relatively weak winds (average 4m/s) predominating northwesterly were observed along the northwest coast of India during this period. SST indicated colder waters near the open ocean (27.6°C) along the northwest coast around 21°N & 22°N with slight increasing trend towards shelf areas and from north to south. Sea surface salinity ranged from 35.15 to 36.55 and showed a gradual increasing trend from 17°N to 22°N. The mixed layer depth ranged from 22-51m, with shallow MLDs near the open ocean and deeper MLDs (>40m) near the coast.

The vertical sections of temperature and salinity along 22°N, 21°N, 19°N and 17°N (Fig. 20 to 23) showed that the isotherms and isohalines either runs parallel or slope down towards the coast. The temperature profiles in the surface layer showed a decreasing trend northwards. Weak thermal gradients were observed in the mixed layer of all the transects. The waters below 50m were strongly stratified. Surface temperatures gradually increased from coastal to open ocean waters. Similar to the isotherms the isohalines showed down slopping characteristics towards the coast. The salinity decreased from north to south and increased offshore from the coast. High surface values are due to low precipitation and high evaporation. The highest surface salinity are found in the northeastern part of the Arabian Sea. In general the Arabian Sea High Saline Water mass (ASHSW) were observed at the 50m of these transects, whereas Persian Gulf Water mass (PGW) is observed between 300 to 500m depth.

These features may be the remnant of receding winter cooling present in the area during the previous months. The cooling of sea surface towards north, down slopping of isolines of temperature, salinity, deepening of MLD and thermocline towards the coast from 17°N to 22°N showed that the north western coast of Arabian Sea was still under the grip of the winter cooling processes.

The surface waters along 19°N, 21°N and 22°N were saturated with dissolved oxygen (Fig. 21 to 23) upto 50m. The 200 µM contour of dissolved oxygen observed was slightly upslopping towards the open ocean at 22°N transect whereas it was running parallel to the transect at 21°N and 19°N. Vertical section of nutrients from 19°N to 22°N is characterised by detectable levels of nutrients in surface layers.

Presence of nutrients ($NO_3^->1.0\mu M$, $PO_4^{3-}>0.8\mu M$ and $SiO4^{4-}> 2.0\mu M$) in the upper 50m north of 17°N during this period was due the effect of the receding winter cooling processes in the area. Nitrate concentration increased from $1.0\mu M$ at 19°N to $2.0\mu M$ at 22°N with its intensity increasing towards offshore. The transect wise vertical profile of nitrate portrayed the water column behaviour during spring where the upper 30m along the north west coast (north of 19°N) holds 1.0 to 2.0 μM with a eastward increase in gradients. In the 19°N and 21° N transect signals of surface overturning of nitrate were prominent. Silicate occupied a high concentration (~ $2\mu M$) in the surface water of the open ocean region of the three transects. The concentration of phosphate in the surface waters along 68°E was found to be $1\mu M$ whereas it reduced to ~ 0.6 μM along 21° N and 22° N.

Convective mixing in northern Arabian Sea during winter is strong enough to erode the upper portion of the thermocline and bring high concentration of nitrate, phosphate and silicate to surface layers. Vertical sections of temperature and nitrate in the open ocean transect showed a considerable shoaling of isotherms and nitracline towards northern latitudes. The water along the northern part of the Arabian Sea was well mixed and colder. The Arabian Sea High Saline Water (ASHSW), the Persian Gulf Water (PGW) and the Red Sea Water (RSW) make the Arabian Sea highly saline. Consequently the heat loss by the winter cooling process triggers convective mixing. The deepening of mixed layer from south to north in this study coincided with the intensification of winter. In the Arabian Sea, the winter cooling processes lead to densification of surface water, which resulted in convective mixing and deepening of the mixed layer. During winter the surface layers gets cooled, causing the water column less stable, and the surface layer mixing triggered by winter storms erode the thermocline, creating a well mixed homogenous water column. The atmospheric forcing that leads to the observed changes is a combination of enhanced evaporation under the influence of dry continental air from the north carried by the prevailing north easterly trades and reduction in solar radiation. Subsequent cooling and convective mixing injects nutrients into the surface layers from the base of the thermocline region.

Distribution of nutrients and dissolved oxygen and nutrients (Fig. 20 to 23) clearly revealed the northward decrease in the magnitude of convective mixing. Dissolved oxygen was saturated (>200μM) at surface layers and it decreased with depths to less than 10μM, at intermediate depths. The dissolved oxygen concentration between 150-1000m was observed to be less than 10μM along a large part of the north west coast of India, generating severe mid-depth oxygen deficiency in the northern Arabian Sea. This zone is characterised by intense denitrification. Distribution of nitrate at intermediate depths of the northern region during spring portraits a comparable reduction (Fig. 20 to 23). This reduction resulted by the drastic consumption of dissolved oxygen by the sinking organic mater, frames a pool of secondary nitrite ($NO_2^- > 2.0μM$) at intermediate depths (150-300m) along the northern region (17°N to 22°N). The existence of strong density gradient and poor horizontal advection due to semi-enclosed nature of the northern Arabian Sea restricts the supply of oxygen to the waters below the euphotic zone (Naqvi and Qasim, 1983).

A combination of predominant north-westerly winds and the continued convective overturning eventually enhanced the nutrient loading to the surface layers along the offshore regions of the northwest coast.

During this period, the chlorophyll a, and Primary productivity in both surface and column at the coastal transect was higher than that at the offshore transect (Table 5). The surface pp and chlorophyll a of coastal transect varied from 0.86 to 2.85 mgC/m3/day (average 1.92 mgC/m3/day) and 0.119 to 0.458 mg/m3 (average 0.259 mg/m3), while in the offshore transect it was 0.92 to 1.39 mgC/m3/day (average 1.1 mgC/m3/day) and 0.028 to 0.221 mg/m3 (average 0.126 mg/m3) respectively. The column pp and column chlorophyll a of coastal transect varied from 133 to 290.7 mgC/m2/day (average 189.7 mgC/m2/day) and 16.5 to 29.5 mg/m2 (average 22.2mg/m2). The column pp and column chlorophyll a in the offshore transect was 61.9 to 153.8 mgC/m2/day (average111.4 mgC/m2/day) and 7.5 to 16.8 mg/m2 (average11.0 mg/m2).

Thus, spring intermonsoon measurements showed the prevalence of winter conditions in the northeastern Arabian Sea. The effects of cooling due to evaporation

are supported by the presence of relatively cool saline waters along the northern region during spring (Morrison *et al.*, 1998). Consequently, the SST was relatively low (<28°C) with moderately deeper mixed layer (~ 40m). The convective process continues until the SST increases in late spring, with the commencement of winter cooling (Prasanna Kumar *et al.*, 2001). The availability of nutrients in the surface layers under improved light and weak wind conditions can favour the formation of spring blooms in the open ocean region. The winter scenario changes when the atmosphere starts warming up under the increased solar radiation during the late spring. The sea surface was warm (> 29°C) with thinner mixed layer (>30m) and increased stratification that restricted nutrient input to the surface layers (Madhupratap *et al.*, 1996a; de Souza *et al.*, 1996). This inturn could reduce the primary production in the region.

3. 2. Bay of Bengal

3.2 a. Winter monsoon

During this season, the surface winds were predominantly north easterly and the magnitude on an average was 5m/s. The open ocean region was having a stronger wind speed of 13m/s with respect to the coastal stations. SST showed about 2°C drop from south (28.8°C at 11°N) to north (26.8°C at 20.5°N). The variability of SST between the coastal and open ocean region was maximum along the southeast coast of India especially along 11°N and 13°N and in the rest of the region it showed minimum zonal variation. The depth of the mixed layer varied from 8 – 35m, which shallowed towards the coast where sea surface salinity was quite low, the lowest MLD at 13°N and 81°E (8m) and a maximum at open ocean regions of 11-14°N (35m) where sea surface salinity was high.

Vertical distribution of temperature and salinity in all the transects were characterized by an upslopping of contours towards open ocean (Fig. 14 to 19). The thermal structure along 11°N showed relatively deep isothermal surface layer in the open ocean region. But towards coastal areas, thermal structure showed an inversion of temperature that is notable below 30m. Another prominent feature observed was the doming of isotherms, which can be clearly seen below 50m, centered around

45

82°E. This feature was more conspicuous at 180m depth. This pattern continued along 13°N but here the eddy like signals were not so prominent as along 11°N transect. The profiles of temperature and salinity along 15°N showed the dome like feature between 81°E and 83°E, extending along 17°N and 19°N, which had the signature of a cold-core eddy.

Another feature in the thermal structure was the presence of warm waters first below the surface cold waters along 17°N and 19°N. This was obvious in the vertical sections of temperature in the inner and outer shelf area (Fig. 54 & 57, shown at the end of Chapter 4), which were characterized by cold waters in the surface followed by warm waters below it in the upper layers with its intensity increasing northwards. Thus the thermohaline properties along 20.5°N were characterized by strong thermal inversion and low saline surface waters. The amplitude of thermal inversion increased northward and the maximum (>2°C) was observed in the northern transects (17°N, 19°N and 20.5°N), while in the southern region (11°N, 13°N and 15°N) a small-scale inversion (<2°C) was observed.

The vertical thermal structure in the upper 300-meters in general showed an upheaval of the isotherms between the longitudes of 81°E and 83°E along the low latitudes (11°N, 13°N and 15°N), which got shifted to east at the northern parts (17°N and 19°N). This can be featured out as a signal of an eddy with a low temperature at the center than that of surroundings. The eddy seems to be centered along 15°N and spread northerly upto 19° N and southerly upto 12° N.

The vertical salinity structure in all transects (Fig. 14 to 19) showed strong gradient in the upper 75m. In the upper 50m the salinity showed a frontal pattern towards the coast indicating the fresh water influx from the continent. The salinity gradient in the upper 50m was 3.6 psu at 11°N, 2.8psu at 13°N, 2.4 psu at 15°N, 8.4 psu at 17°N, 8.4 psu at 19°N and 5.6 psu at 20.5°N, indicating strong fresh water influx towards the head of the Bay. From 100-300m depth, the water mass remained homogenous with a salinity of 35 psu. The vertical salinity distribution along the inner shelf and outer shelf showed strong salinity gradient in the upper layer of 35m thickness northwards. The low salinity along 19°N, 20.5°N and 15°N in the south east

coast of India are due to the freshwater influx from the Ganges-Mahanadi system in north and Krishna river in south. The riverine input also occurred during southwest monsoon, continued all the way through the post monsoon season, prompting a stratified layer in the upper ocean.

Consistent with thermal inversion and low saline surface waters, the nutrient characteristic in the area was different. The inner shelf (north of 17°N), waters were saturated with dissolved oxygen (200-220μM) and low in nutrients (nitrate ~ 0.2μM, phosphate ~ 0.2μM). However, the low salinity layer coincides with 2.6μM silicate, indicating the influence of fresh water in the northern transects. It is to be noted that the influx of freshwater do not seem to escalate the nitrate and phosphate levels in the surface layers. Moreover due to strong stratification, high concentration of nitrate and phosphate remained at greater depths. Stratification in the surface layer of the Bay is dominated by the salinity gradient rather than the temperature gradient (Shetye *et al.*, 1991).

The vertical profiles of dissolved oxygen and nutrients in different transects are characterized by upslopping of isolines towards open ocean. The surface water during winter was comparatively less saturated with oxygen (~ 180.0 μM) except at 20.5°N (~220.0μM) that was due to heavy fresh water input from the adjacent rivers. In almost all transects a slight down slopping of dissolved oxygen contours towards the coast was observed. The oxygen concentration within broad minimum (defined by 20μM contour) showed latitudinal variation in the outer shelf and open ocean transects (T1 & T2). The oxygen minimum zone (defined by 20μM contour) starts at the middle of the thermocline extending down to 600m. In both outer shelf and open ocean transects the oxygen minimum zone increases its thickness towards northern latitudes. The intermediate waters along the northern latitudes (20.5°N to 17°N) were found to be oxygen depleted with O_2 < 10.0 μM. A severe depletion in oxygen was observed along 20.5°N transect where a comparatively thick patch of 5.0μM oxygen waters were located between 100-150m throughout the transect. In the southern transects (11°N to 15°N), the intermediate waters were characterized by low oxygen waters (~ 20μM).

The nitrate and phosphate distribution (Fig. 14 to 19) revealed that the surface layer (50m) was devoid of nutrients (NO_3^- < 0.5µm, PO_4^{3-} < 0.4µM) and the enrichment of the nutrients (NO_3^- >30µM and PO_4^{3-} >2.6µM) at 200-250m signifies the presence of the eddy. Vertical distribution of nitrate in all transects showed that in general the upper 30-50m was devoid of 2.0 µM nitrate, along 11°N, 13°N, 15°N and 19°N. The nitracline was situated between 50 and 100m depth in almost all transects. In all transects, nitrate increased with depth reaching a maximum of 32.0µM at 300m. The concentration gradient of nitrate in the upper 100m was much higher than 200-300m water column in the offshore region. The nitrate isolines in the upper 200m showed a down slopping towards the coast from 13°N to 19°N. The down slopping of isolines of nutrients to the outer shelf extending to a depth of 200-250m at 13°N to 19°N substantiate the presence of an eddy in this region. Sankaranarayan and Reddy (1968) observed similar nitrate gradients in the northern Bay, which they related to differential rates of regeneration and some physical processes determining the accumulation. They were of the opinion that incursion of Persian Gulf and Red Sea waters at subsurface layers in the Bay favours the formation of internal waves at the boundary thus enhancing the eddy diffusion resulting in the above type of distribution. Sen Gupta et al., (1976) observed an inverse relationship in the depth profiles of inorganic nitrogen and total nitrogen in the western Bay of Bengal. They opined that the concentration of inorganic nitrogen in the water column depends on oxidation of organic matter as well as on possible denitrification processes. The vertical distribution of phosphate in all transects showed an increasing trend with depth reaching a maximum of 2.6µM at 250-300m depth, which was very much similar to that of nitrate. The characteristic strong down slope of the subsurface nitrate and phosphate gradients were due to differential rates of regeneration and disposal by the cold core eddy.

Vertical sections of temperature, salinity and nutrients along the north-south outer shelf and open ocean transects are shown in Fig. 57, 60, 61, 66 & 67 respectively (shown at the end of Chapter 4). Cold core eddies of comparable magnitude was present in the outer shelf, and in both the open ocean (T1 & T2) transects. Two

subsurface cold-core eddies were present at outer shelf and open ocean transect (T1); spread out to a diameters of approximately 480km with a 14°C isotherm in the open ocean transect (T1), and 17°C isotherm in the outer shelf, located at a depth of 200m. The center of both eddies were between 13°N and 17°N. The vertical sections of temperature in the upper 300m showed oscillation with in the thermocline (T1 transect). The upheaval of isotherms was noticed between 12°N and 17°N, while north of it the isotherms showed a gradual down slopping towards 20.5°N. The 28°C isotherm shoaled from 40m to surface on either side of the eddy, and the upper thermocline showed a vertical displacement of about 40m, which tapered of towards the lower thermocline. This was clearly a signature of a cold-core eddy, seen below surface, which lowered the ambient temperature at 40m (27°C) by about 1°C.

A warm surface layer (28°C isotherm), which extends to a depth of ~30m, overlay the eddies in the outer shelf and open ocean transects T1 and T2. The eddy in the outer shelf was characterized by an inversion in temperature of approximately 1°C than the overlying water. The horizontal variability of this warm surface layer in the open ocean transects (T1 &T2) was smaller in the core of the eddy core compared to that of the exterior frontal structure, which partially surrounds the eddy system but was relatively high in the outer shelf. Outside this region thermal fronts were found on either side of the eddy in the outer shelf and open ocean transects (T1 & T2), but at the open ocean transect (T1), it was weak in the south and strong in north. Vertical sections of salinity (Fig. 60) showed strikingly the same structure as that of temperature. For example, within the region of the eddy system isotherms and isohalines revealed a concave structure. In addition, the small-scale low saline fronts (Salinity < 30.00psu), which partially surround the eddy, were more intense than the corresponding thermal fronts. Further, the low saline fronts were strongest in the northern region and weak in the southern region of the eddy in the outer shelf, it was reverse in the case of open ocean transects (T1 & T2). The coastal characteristics of these frontal structures along the open ocean transects (T1 & T2) as evidenced by the low saline waters (salinity < 30.00psu) surrounding the eddy system support the

conclusion that surface waters of coastal origin can get entrapped into the surface layer and cold core region of the eddy.

However in the open ocean transect at mid section (T2 transect) the eddy shifted to northern latitudes. The subsurface cold-core eddy centered between 15°N and 19°N with a diameter of approximately 480km with 14°C isotherm was the dominant feature and it extended to a depth of about 200m. The vertical sections of temperature in the upper 300m showed oscillation within the thermocline (T2 transect). The upheaval of isotherms was noticed between 15°N and 19°N, while south of it, the isotherms showed a gradual shoaling towards 11°N. In the former case, the 27°C isotherm shoaled from 80 to 30m, and the thermocline showed a vertical displacement of about 60m, which tapered off towards the bottom of thermocline. This was clearly a signature of a cold-core eddy, seen below 20m depth, which lowered the ambient temperature at 60m (27°C) by about 5°C.

The vertical sections of temperature in the upper 200m showed oscillation within the thermocline of the outer shelf transects. The upheaval of isotherms was noticed between 12°N and 15°N, while north of it the isotherms showed a gradual shoaling towards 20.5°N. In the former case, the 28°C isotherm shoaled from below 50m. However, the low saline surface waters probably prevented its entry to the surface. Consistent with the isotherms the nitracline in the outer shelf also shoaled between 12°N and 15°N upto 50m.

Fig. 57, 61 and 67 shows the north-south vertical sections of nitrate, phosphate and silicate in the outer shelf and open ocean transects (T1 & T2) where eddies are identified. In the open ocean transects, the contours are plotted at two depth intervals since the larger features of a given water property are shown over the depth range 0-200m and hence given in the upper portion but property distribution at 200-1000m are given in the lower portion. Pronounced nutrient fronts, spatially aligned with the strong thermal fronts were present in the north and south quadrant of the eddy system. Strong nitrate, phosphate and silicate fronts were present towards the north of the eddy system in the open ocean (T1 transect), but were weak towards the south. Interestingly the isotherm (28°C) and isolines of 1.0 or 2.0 µM of nitrate north and

south of the cold core eddies in the outer shelf and open ocean transect (T1) were restricted to rise only upto 30m. But at the middle section of the cold core eddy at the open ocean transect (T2), the same isolines were found to shoal upwards to 20m. The two cold-core eddies of the open ocean transects were also characterized by low temperature (<27°C), low dissolved oxygen (<160μM) and high nutrients (NO$_3^-$ >2μM, PO$_4^{3-}$>0.8μM and SiO$_4^{4-}$>4.0μM) at 30m. The location and strength of these nutrient fronts at 30m depth were consistent with the isotherms of temperature and isohalines of salinity, which showed that water of deep oceanic origin, was preferentially entrapped into the upper 30m. The physical fronts show uniformity with the nutrients centered on the cold-core region. The depletion in dissolved oxygen and repletion in nutrients could be due to the rising up of deep waters, since cold core eddies are divergent.

During winter, along the northwestern Bay of Bengal, the atmospheric conditions are favourable for the winter cooling. The cold dry air (humidity < 45%) from the continents blows over the northwestern Bay and intensifies the evaporation leading to surface cooling. But the influence of river discharge freshens the surface layers in the northern Bay. As a result, the cold fresh water spreads over warm oceanic water causing a thermal inversion. The low saline waters compensate the static stability lost by the thermal inversion. Hence the heat loss caused by the winter cooling does not trigger convective overturning in the Bay, instead, it leads to strong thermal inversion.

Northwestern Bay of Bengal receives a discharge of 531 x 10^9 m^3 and 59 x 10^9 m^3 fresh water during summer and winter monsoons respectively. However, earlier studies in the Bay of Bengal reported small-amplitude thermal inversion during summer even if being influenced by maximum river discharge (Rao *et al.*, 1994). The winter cooling processes can be the major causative force for the large-scale inversion (amplitude>2°C) in the northern Bay of Bengal along with the strong salinity gradients in the surface. In this study it is confirmed that nitrate (2.0μM) injected to subsurface levels by the cold core eddy in the outer shelf was limited to 50m only, and the same situation follows in the open ocean transects but at transect T1 it comes

to 30m, but at transect T2 it rises to 20m. The absence of nitrate in the top 30m or 50m in the outer shelf is a clear indication of lack of any vertical mixing mechanisms (convective mixing) operating in this region. The surface cooling fails to impart it to the deeper waters owing to the lack of sinking or low efficiency of convective mixing to erode the thermocline. Maximum MLD values were obtained in the open ocean sections due to the absence of fresh water influx, being far away from the hinterland. Large-scale fluctuations in salinity in the upper 50m (gradients of 2.4 to 8.4 psu) in the Bay of Bengal are a clear evidence of the enormous quantity of freshwater that the northern Bay of Bengal receives from the Godavari-Mahanadi-Ganges-Brahamaputra river systems.

In the Bay of Bengal, winter cooling processes results in strong thermal inversion resulting in shallow mixed layer. A significant feature observed from the thermal structure, both along open ocean transects and outer shelf was the formation of cold-core eddies. Under the influence of these eddies, the nutrients were pumped into subsurface layers as evidenced by the shoaling of nitracline consistent with isotherms. But the surface low-salinity layer caused distinct stratification in winter resulting in an insulated layer. Both eddies and shoaling isotherms were capped by a low saline fresh water layer, leading to its failure of surfacing and prevented nutrients reaching the upper (20m or so) layers or restricting the chances of sinking by densification. Thus, neither did the river plume nor eddies bring in appreciable nutrients to surface in the shelf areas or open ocean regions of the Bay of Bengal, revealing the oligotropic nature that eventually leads to low biological production.

The Primary Productivity, Chlorophyll a and Particulate Organic Carbon in the outer shelf show that maximum plant pigments (10.5mgC/m^3/day, 0.69 mgC/m^3/day & 0.178 gC/m^3) are likely to be located along the frontal zone adjacent to the upper core portions of the cold core region. Similar to the outer shelf spatial variations of Primary Productivity, Chlorophyll a and Particulate Organic Carbon in the open ocean transect showed that maximum plant pigments (6.5 mgC/m^3/day, 0.22 mgC/m^3/day & 0.152 gC/m^3) were located along the frontal zone adjacent to the center of the upper portions of the cold core region. The values were comparable

between outer shelf and open ocean regions. Higher chlorophyll *a* concentrations implied with high primary productivity and particulate organic carbon were observed within the cold-core eddy in both outer shelf and open ocean regions. The observed chlorophyll pigment concentration and primary productivity in the outer shelf and open ocean transect associated with nitrate injected to the upper layers due to eddy induced mixing. The anomalous chlorophyll *a* structure observed in the eddy region can be due to the enhanced vertical entrapment of subsurface nutrients into the euphotic zone.

During this period, the chlorophyll *a*, Primary productivity and Particulate organic carbon (POC) in both surface and column at the coastal transect and offshore transect did not vary appreciably (Table 6). The surface PP, chlorophyll *a* and POC of coastal transect varied from 0.7 to 10.5 mgC/m3/day (average 4.4 mgC/m3/day), 0.01 to 0.69 mg/m3 (average 0.19 mg/m3) and 0.075 to 0.178 g/m^3 (average 0.123 g/m3), while in the offshore transect it was 1.0 to 6.5 mgC/m3/day (average 4.4 mgC/m3/day), 0.01 to 0.22 mg/m3 (average 0.14 mg/m3) and 0.056 to 0.152 g/m^3 (average 0.105 g/m3) respectively. The column pp, column chlorophyll *a* and POC of coastal transect varied from 26.0 to 433 mgC/m2/day (average 213.5 mgC/m2/day), 4.3 to 22.9 mg/m2 (average 11.2 mg/m2) and 7.3 to 11.5 g/m^2 (average 9.3 g/m^2). The column pp, column chlorophyll *a* and column POC in the offshore transect was 21.9 to 423.2 mgC/m2/day (average 230.1 mgC/m2/day), 5.6 to 17.4 mg/m2 (average 11.3mg/m2) and 6.9 to 17.2 g/m^2 (average 10.4 g/m^2) respectively.

Table 4: Spatial variation of primary productivity, chlorophyll a and particulate organic carbon in the coastal & offshore waters of the eastern Arabian Sea during intermonsoon fall

Coastal						
Latitude	S.PP	C.PP	S.Chl a	C.Chl a	S.POC	C.POC
(°N)	$mgC/m^3/day$	$mgC/m^2/day$	mg/m^3	mg/m^2	g/m^3	g/m^2
8	10.53	568	0.26	23.8	0.819	44.9
10	37.4	1630	0.75	60.7	1.827	157.2
13	2.0	292	0.22	17.5	0.504	57.8
15	8.4	311	0.36	9.1	0.158	64.9
17	8.8	218	0.02	5.9	0.567	53.1
19	8.1	308	0.12	13.1	0.378	9.1
21	4.2	179	0.15	6.0	0.189	42.1
Average	11.34	501	0.27	19.4	0.635	61.3
Offshore						
8	6.6	376	0.16	14.7	0.252	46.9
10	8.1	490	0.38	30.2	0.945	84.5
13	2.0	292	0.22	16.4	0.504	57.8
15	8.4	311	0.36	9.0	0.158	64.9
19	4.2	199	0.15	20.9	0.315	25.8
21	6.7	275	0.03	13.2	0.441	40.6
Average	6.0	324	0.22	17.4	0.436	53.4

Table 5: Spatial variation of primary productivity and chlorophyll a in the coastal & offshore waters of the northeastern Arabian Sea during intermonsoon spring

Coastal				
Latitude	S.PP	C.PP	S.Chl a	C.Chl a
(°N)	mgC/m^3/day	mgC/m^2/day	mg/m^3	mg/m^2
17	2.85	181.1	0.458	16.5
19	2.59	133.0	0.237	29.5
21	0.86	290.7	0.119	26.1
22	1.39	153.8	0.221	16.8
Average	1.92	189.7	0.259	22.2
Offshore				
17	1.12	87.2	0.135	7.5
19	0.92	61.9	0.028	10.0
21	0.97	142.6	0.119	9.8
22	1.39	153.8	0.221	16.8
Average	1.10	111.4	0.126	11.0

Table 6: Spatial variation of primary productivity, chlorophyll a and particulate organic carbon in the coastal & offshore waters of the western Bay of Bengal during winter monsoon

Coastal						
Latitude	S.PP	C.PP	S.Chl a	C.Chl a	S.POC	C.POC
(°N)	mgC/m3/day	mgC/m2/day	mg/m3	mg/m2	g/m^3	g/m^2
11	7.9	325.9	0.14	11.6	0.127	11.5
13	0.7	26.0	0.06	4.3	0.167	7.4
15	10.5	433.0	0.69	22.9	0.178	12.2
17	3.1	143.9	0.01	12.8	0.105	10.2
19	2.2	253.0	0.08	7.1	0.075	7.4
20.5	1.8	99.1	0.17	8.4	0.084	7.3
Average	4.4	213.5	0.19	11.2	0.123	9.3
Offshore						
11	3.2	320.0	0.12	10.6	0.152	11.1
13	5.8	285.3	0.12	12.6	0.145	12.9
15	6.5	423.2	0.22	17.4	0.152	17.2
17	4.3	237.3	0.18	13.6	0.056	7.0
19	1.0	21.9	0.01	5.6	0.069	7.4
21	5.9	93.0	0.18	7.9	0.057	6.9
Average	4.4	230.1	0.14	11.3	0.105	10.4

Figure. 5. Vertical section of physical and chemical parameters along 8°N in the Arabian Sea during intermonsoon fall

Temperature(°C) Salinity(psu) Dissolved oxygen(μM)

Nitrate-nitrogen(μM) Phosphate-phosphorus(μM) Silicate-silicon(μM)

<------------------------------Longitude(°E)------------------------------>
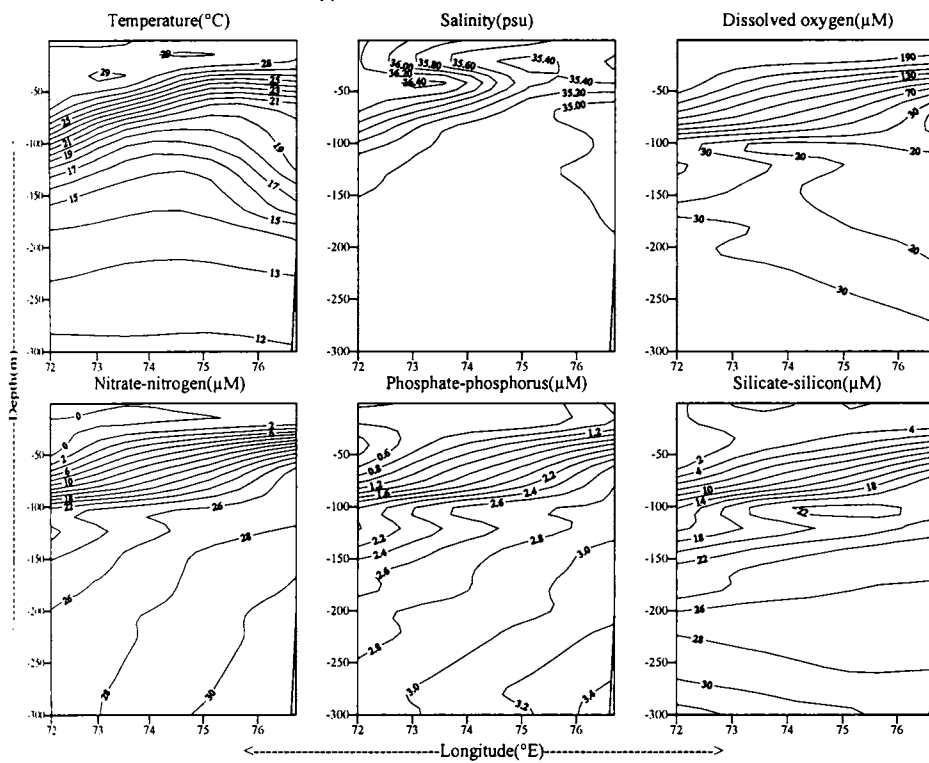
Figure.6. Vertical section of physical and chemical parameters along 10°N in the Arabian Sea during intermonsoon fall
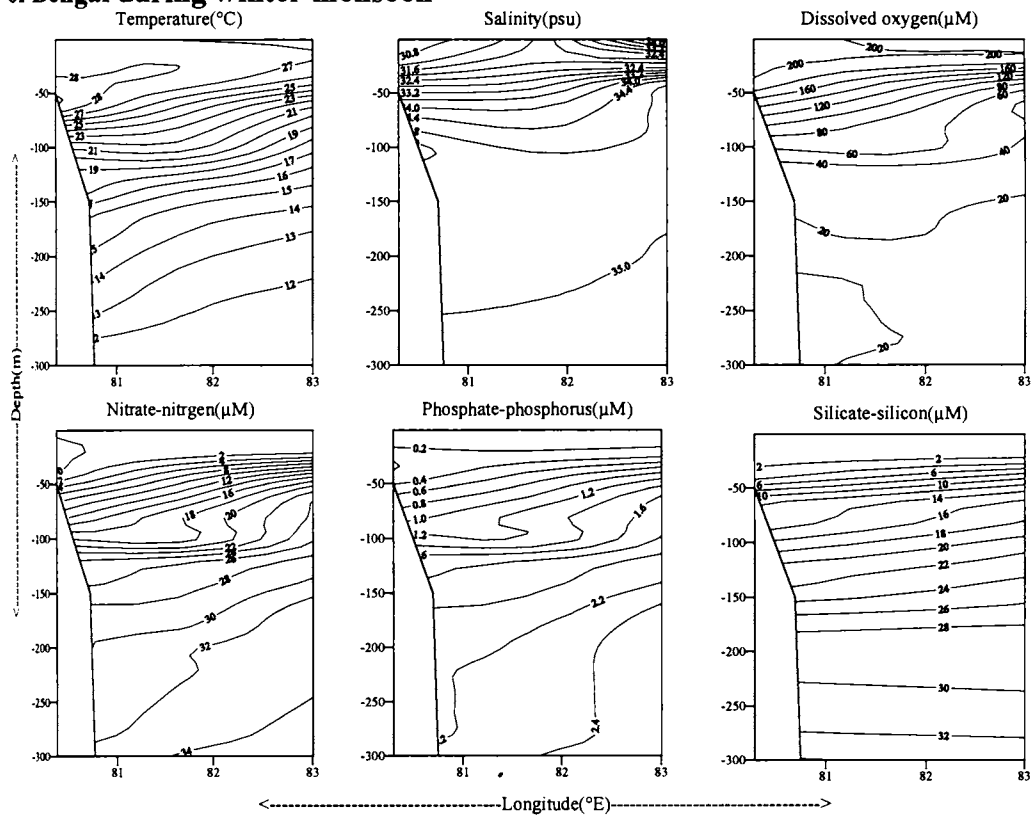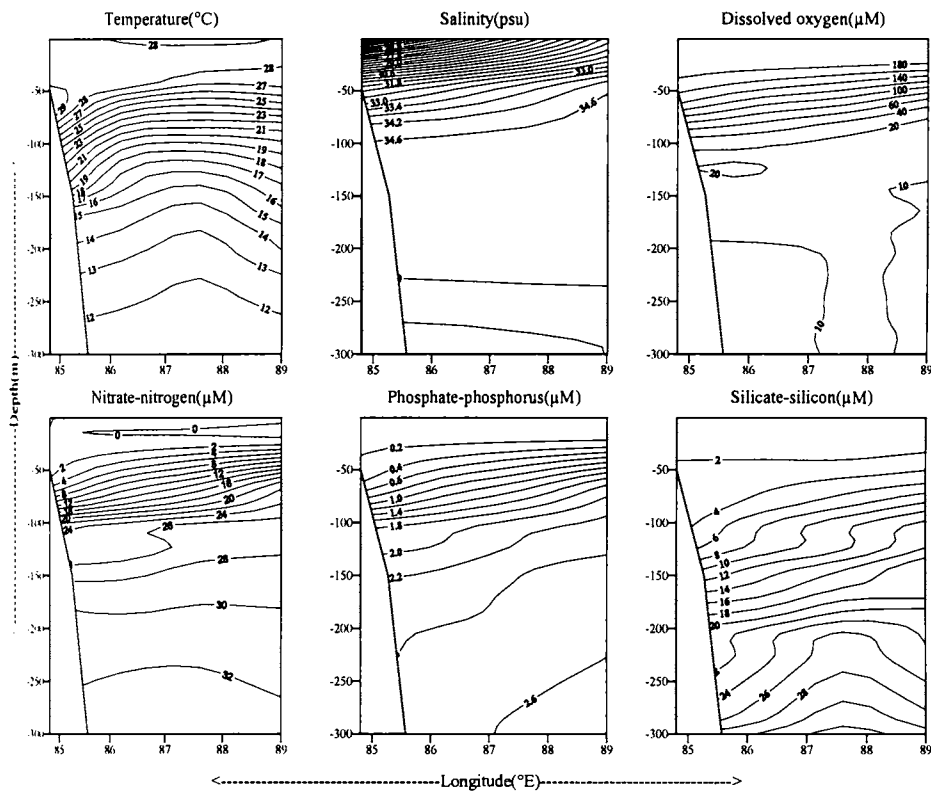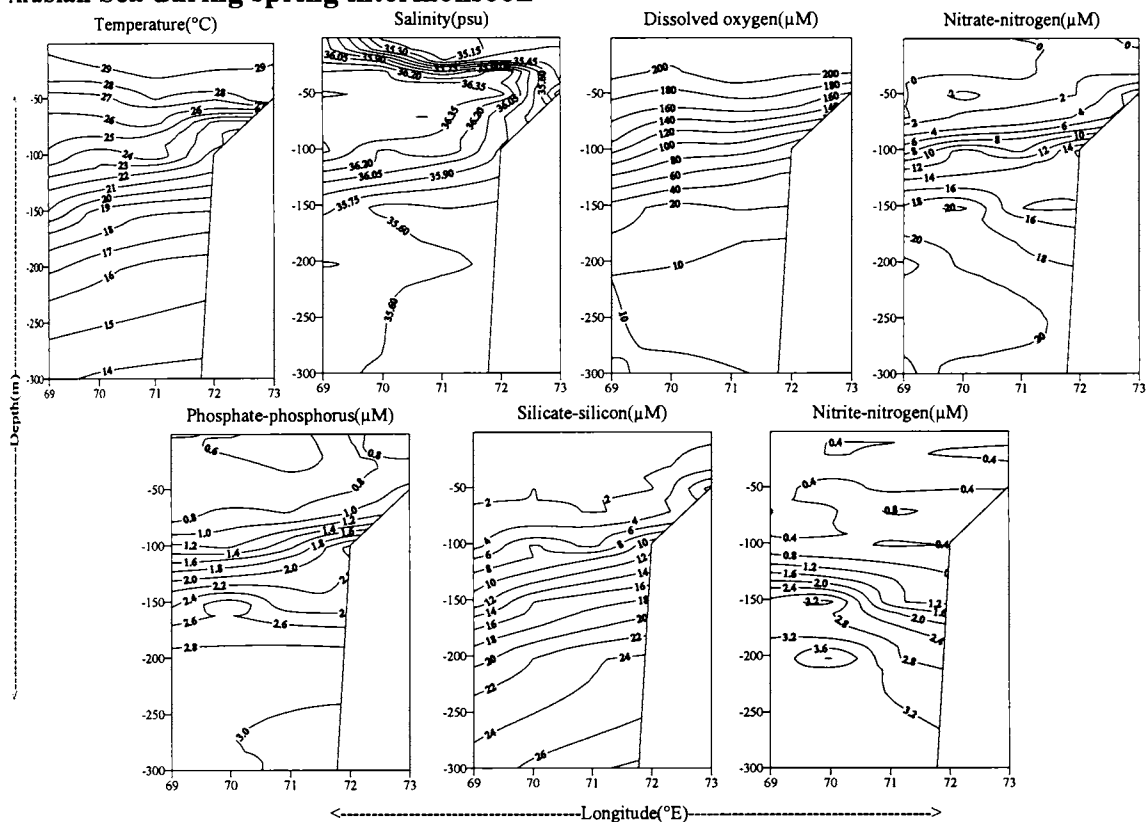
Temperature(°C) Salinity(psu) Dissolved oxygen(μM)

Nitrate-nitrogen(μM) Phosphate-phosphorus(μM) Silicate-silicon(μM)
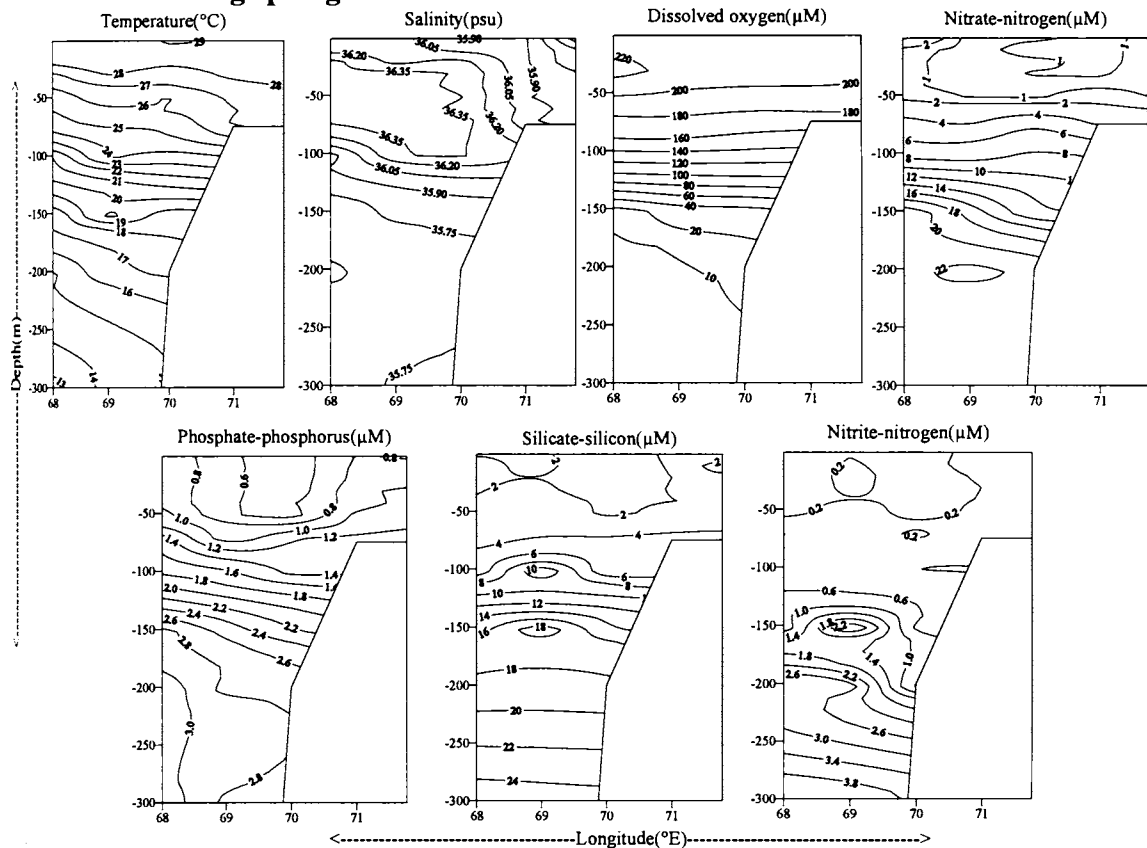
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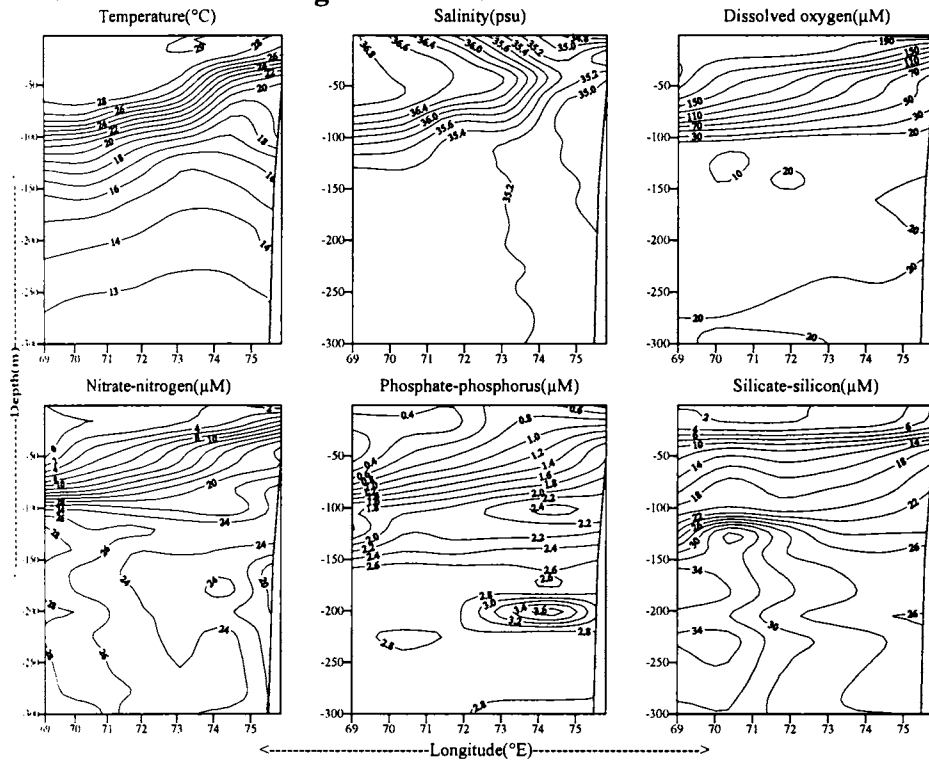
Figure.7. Vertical section of physical and chemical parameters along 13°N in the Arabian Sea during intermonsoon fall

Temperature(°C) Salinity(psu) Dissolved oxygen(μM)

Nitrate-nitrogen(μM) Phosphate-phosphorus(μM) Silicate-silicon(μM)

<-------------------------Longitude(°E)------------------------->
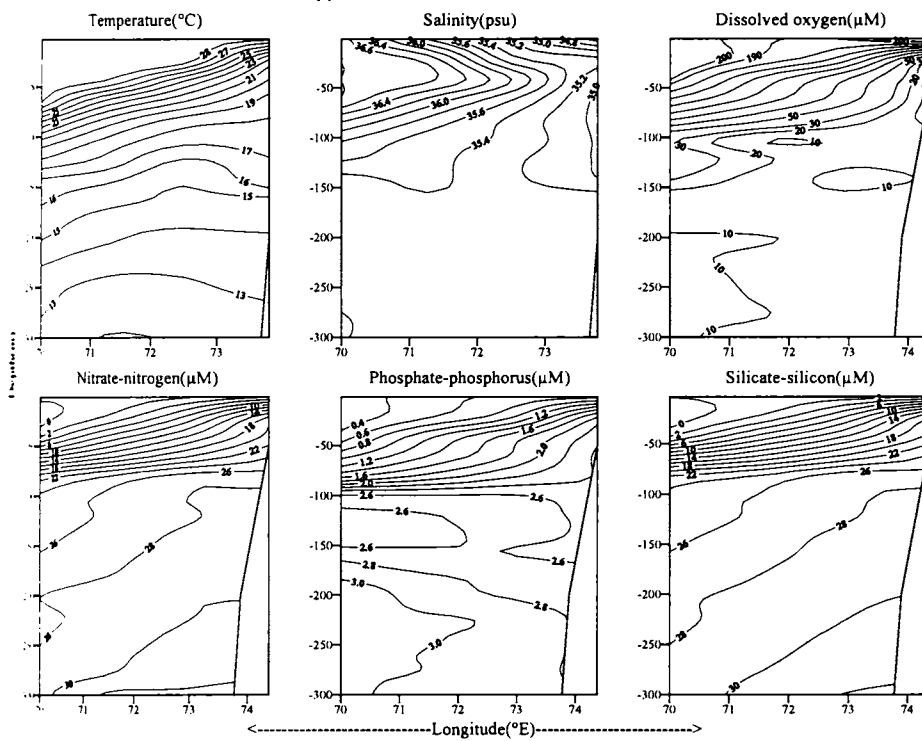
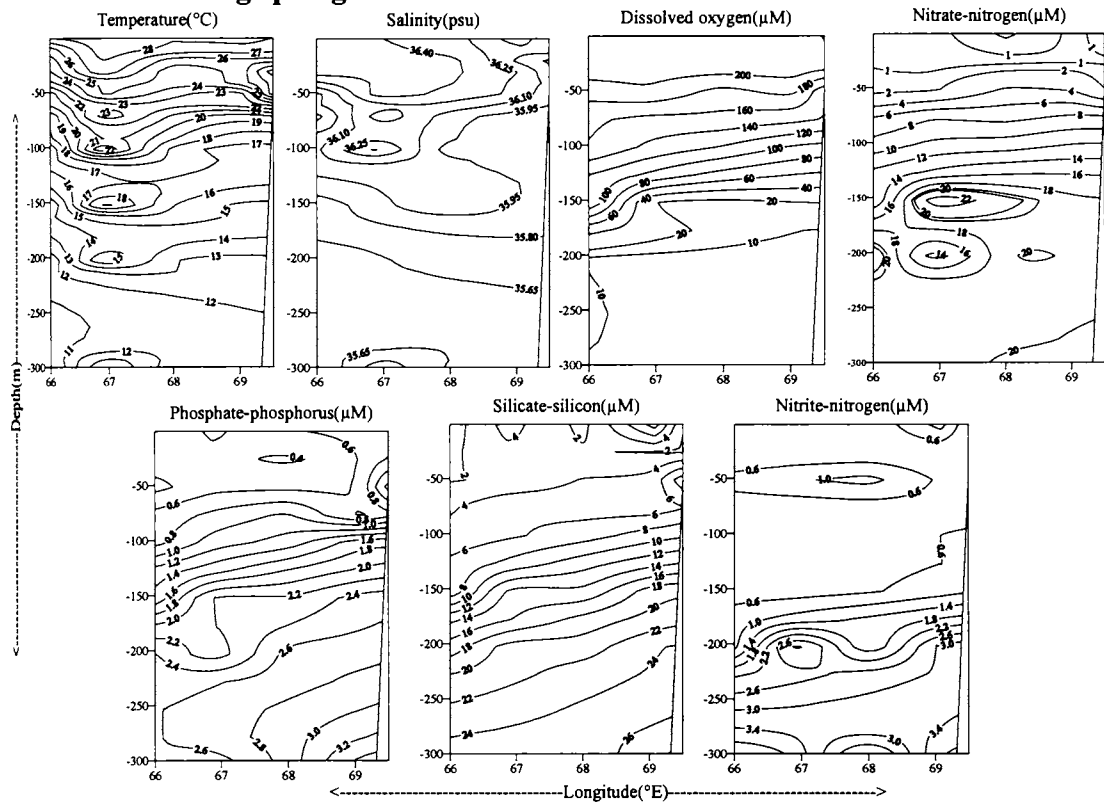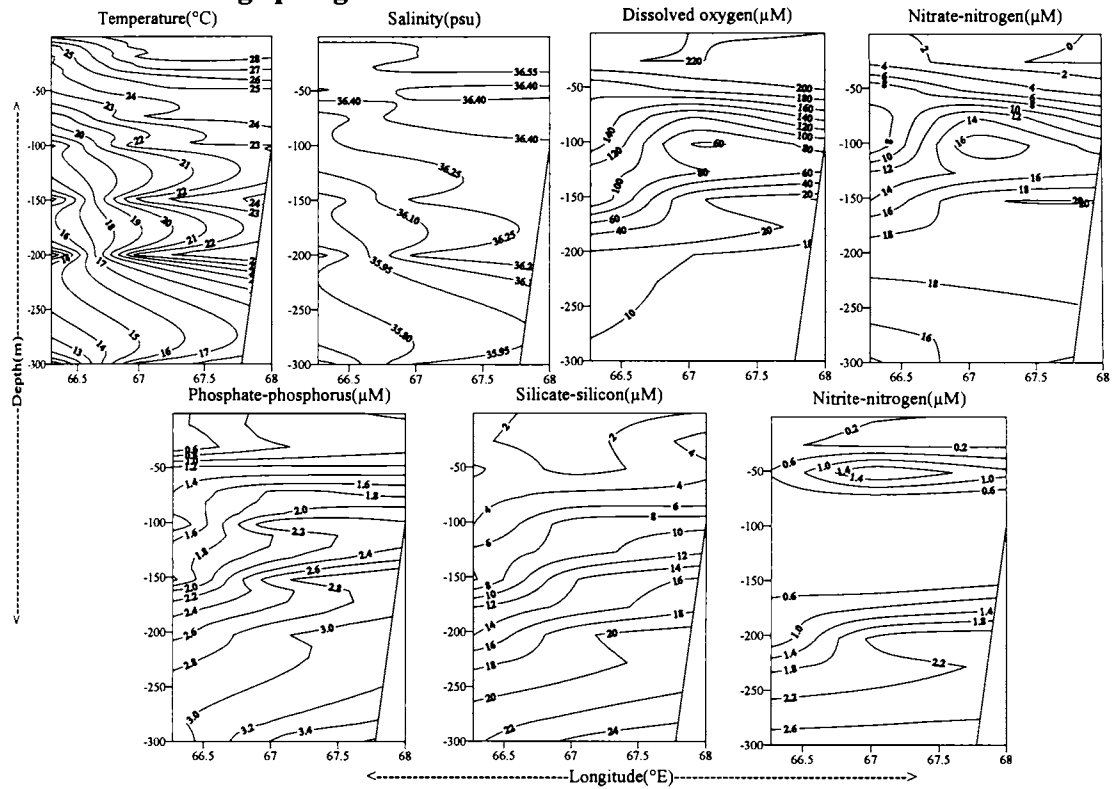**Figure.8. Vertical section of physical and chemical parameters along 15°N in the Arabian Sea during intermonsoon fall**

Temperature(°C) Salinity(psu) Dissolved oxygen(μM)

Nitrate-nitrogen(μM) Phosphate-phosphorus(μM) Silicate-silicon(μM)

<-------------------------Longitude(°E)------------------------->
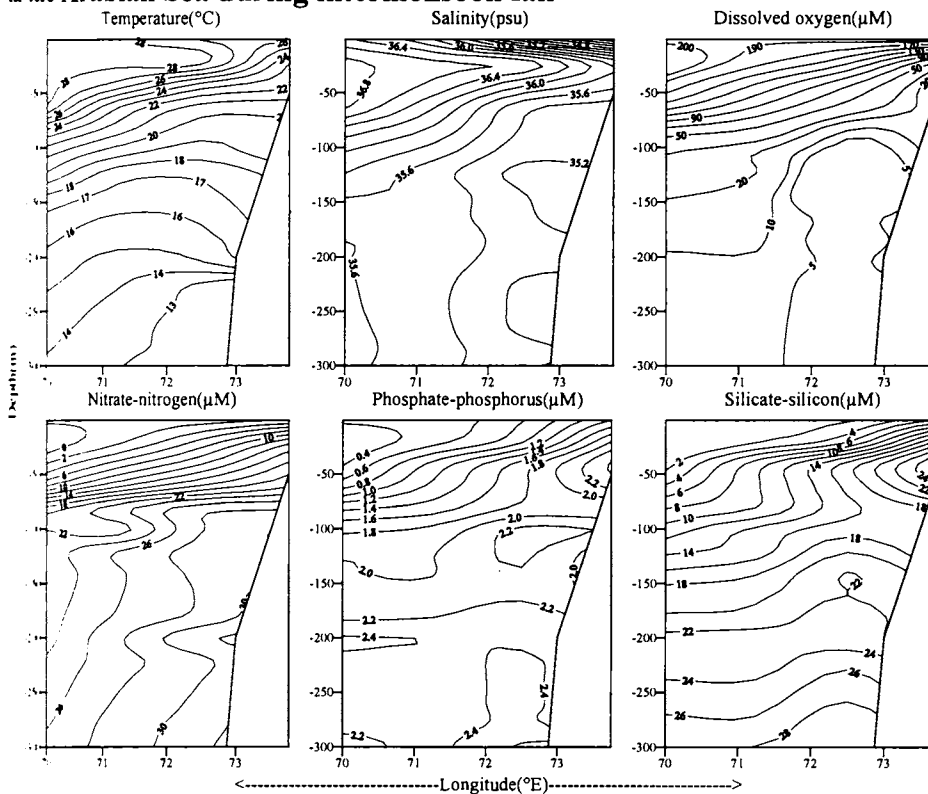
Figure.9. Vertical section of physical and chemical parameters along 17° N in the Arabian Sea during intermonsoon fall

Temperature(°C)   Salinity(psu)   Dissolved oxygen(µM)

Nitrate-nitrogen(µM)   Phosphate-phosphorus(µM)   Silicate-silicon(µM)

<------------------------------Longitude(°E)------------------------------>
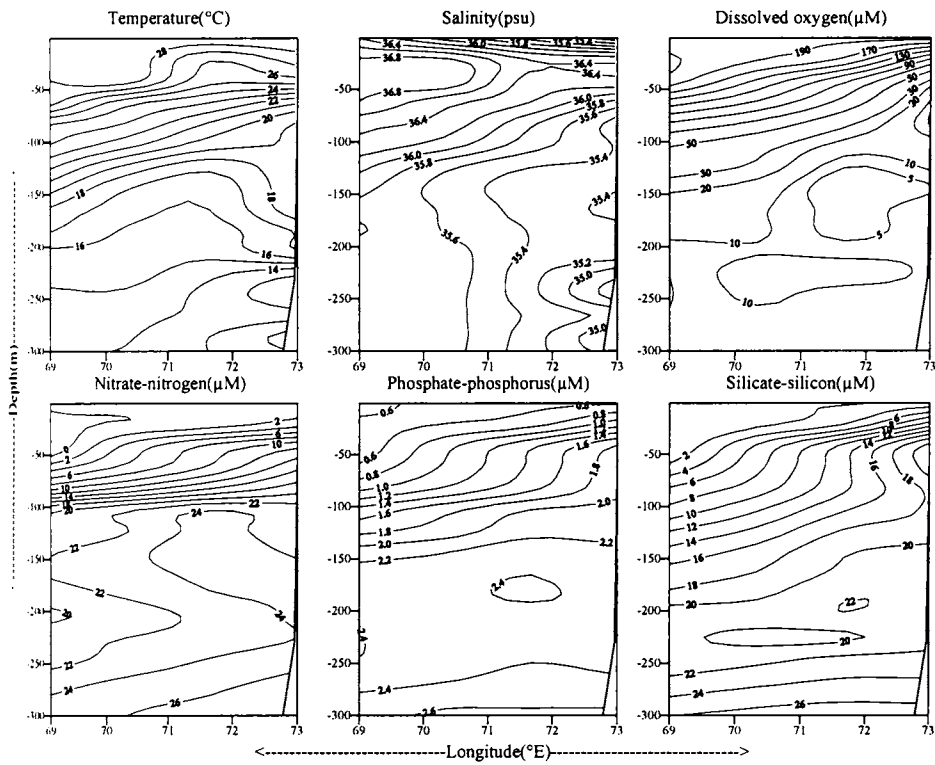
Figure.10. Vertical section of physical and chemical parameters along 19°N in the Arabian Sea during intermonsoon fall

Temperature(°C)   Salinity(psu)   Dissolved oxygen(µM)

Nitrate-nitrogen(µM)   Phosphate-phosphorus(µM)   Silicate-silicon(µM)

<------------------------------Longitude(°E)------------------------------>
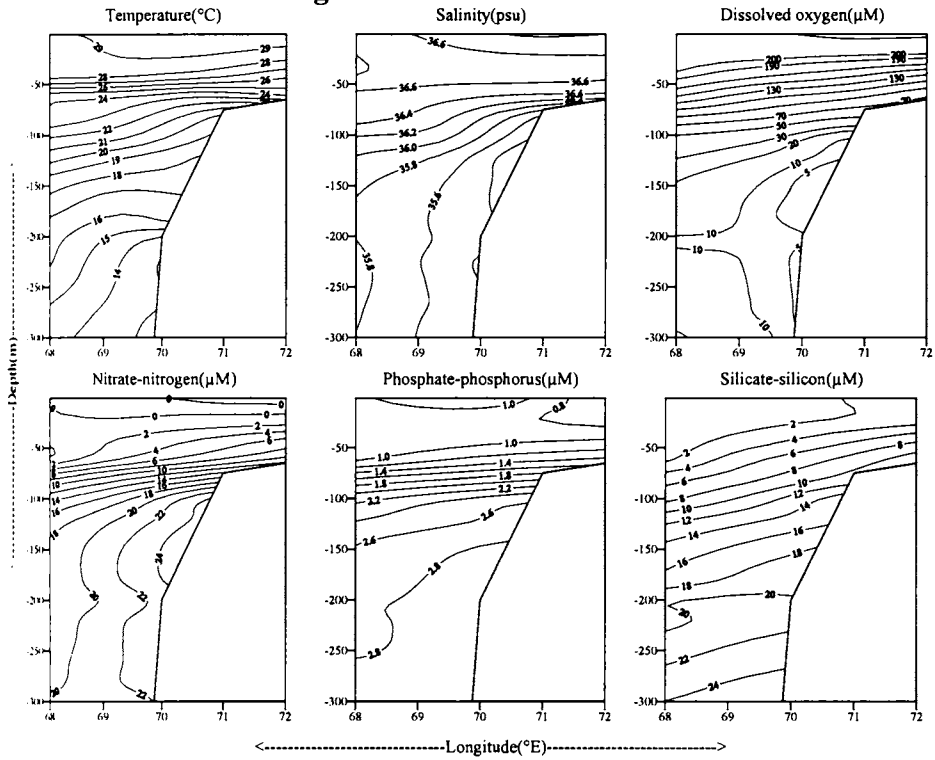
Figure.11. Vertical section of physical and chemical parameters along 21° N in the Arabian Sea during intermonsoon fall

Temperature(°C)   Salinity(psu)   Dissolved oxygen(µM)

Nitrate-nitrogen(µM)   Phosphate-phosphorus(µM)   Silicate-silicon(µM)

<-----------------------------Longitude(°E)----------------------------->
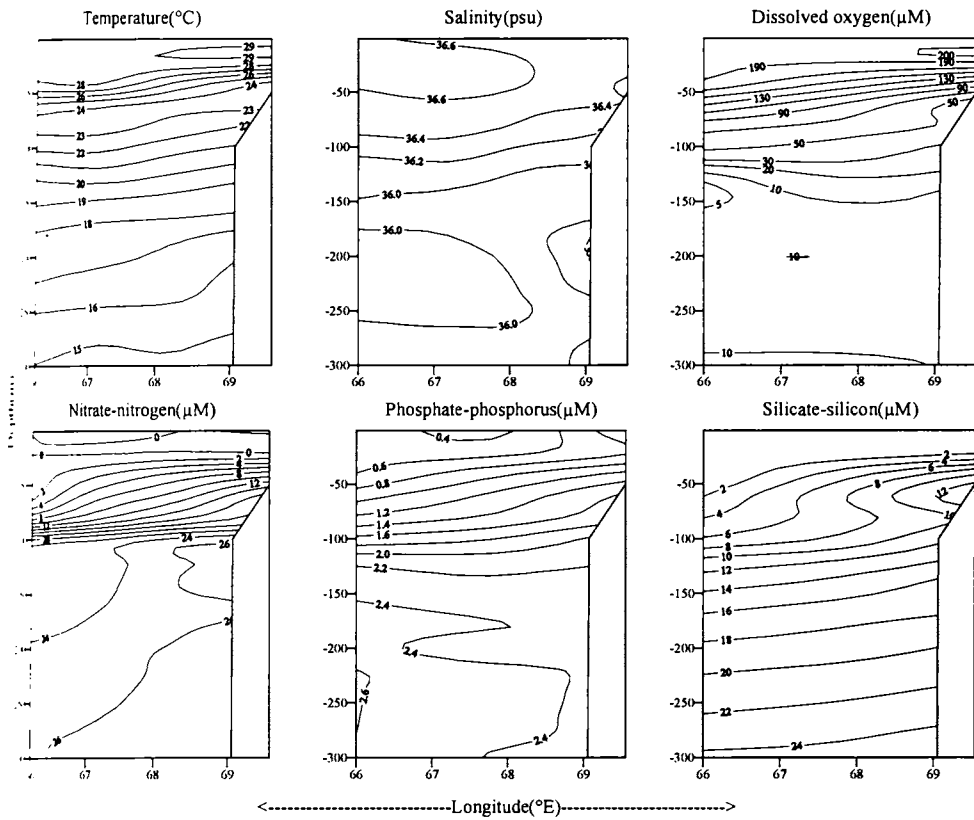
Figure. 12. Horizontal section of nitrite-nitrogen (µM) at different depths in the Arabian Sea during intermonsoon fall

<-----------------------------Longitude(°E)----------------------------->
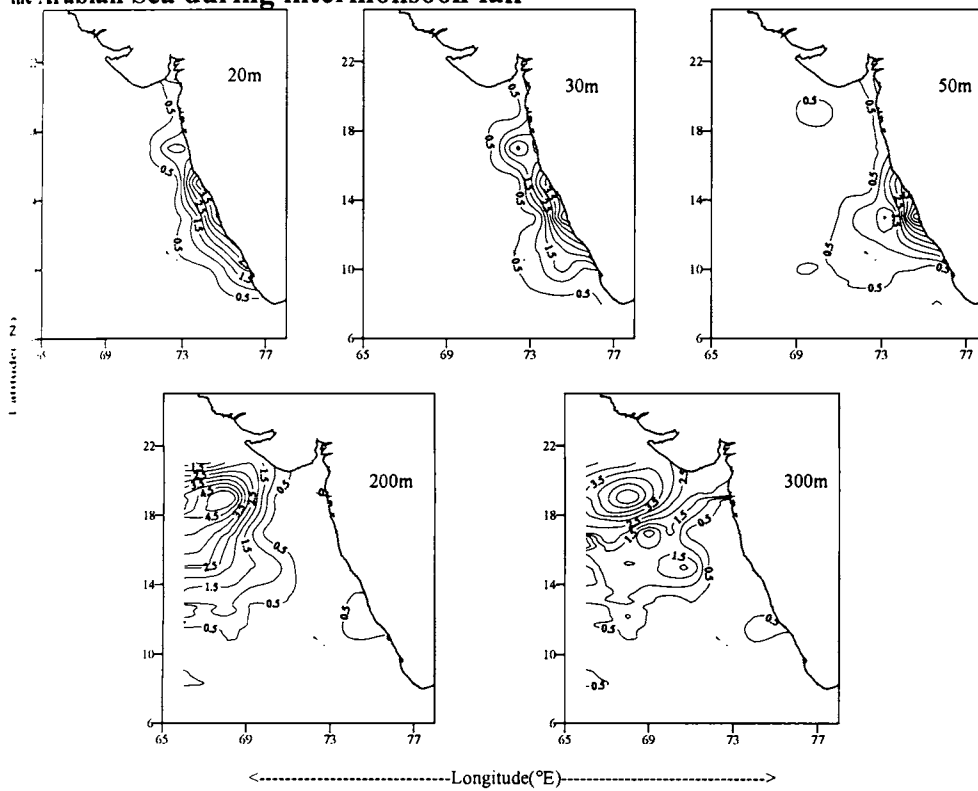
Figure. 13. Horizontal section of dissolved oxygen (μM) at different depths in the Arabian Sea during intermonsoon fall
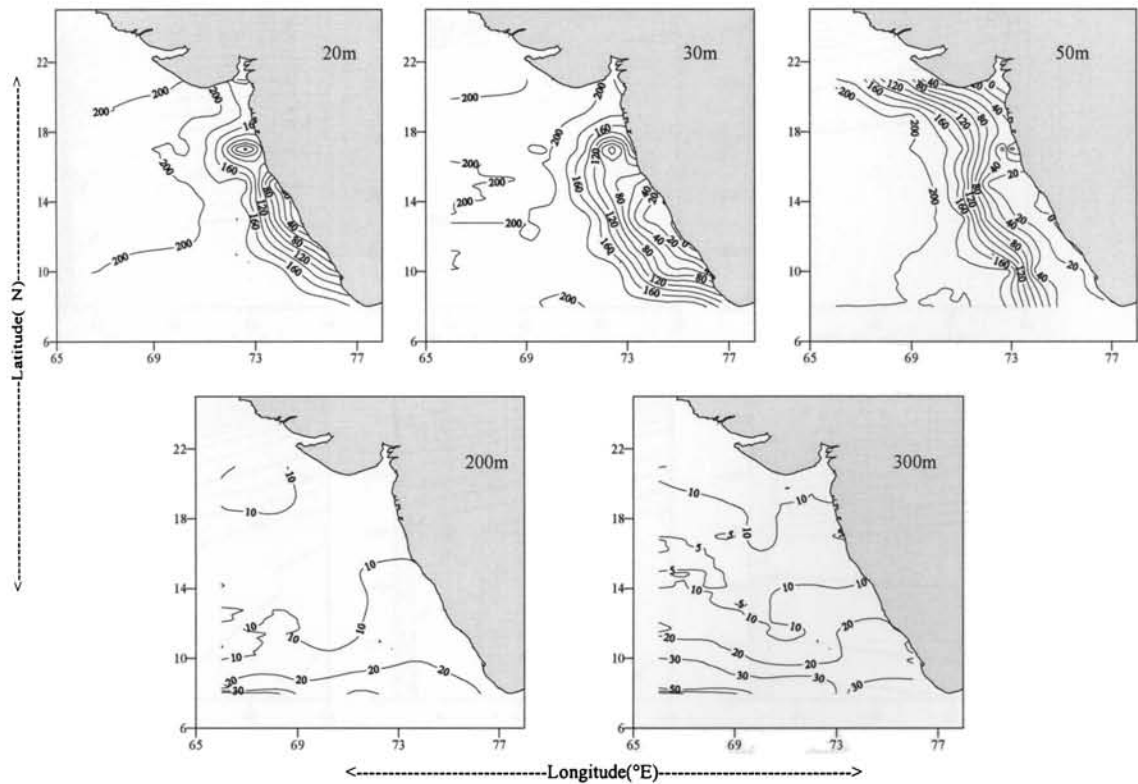
Figure. 14. Vertical section of physical and chemical parameters along 11°N in the Bay of Bengal during winter monsoon
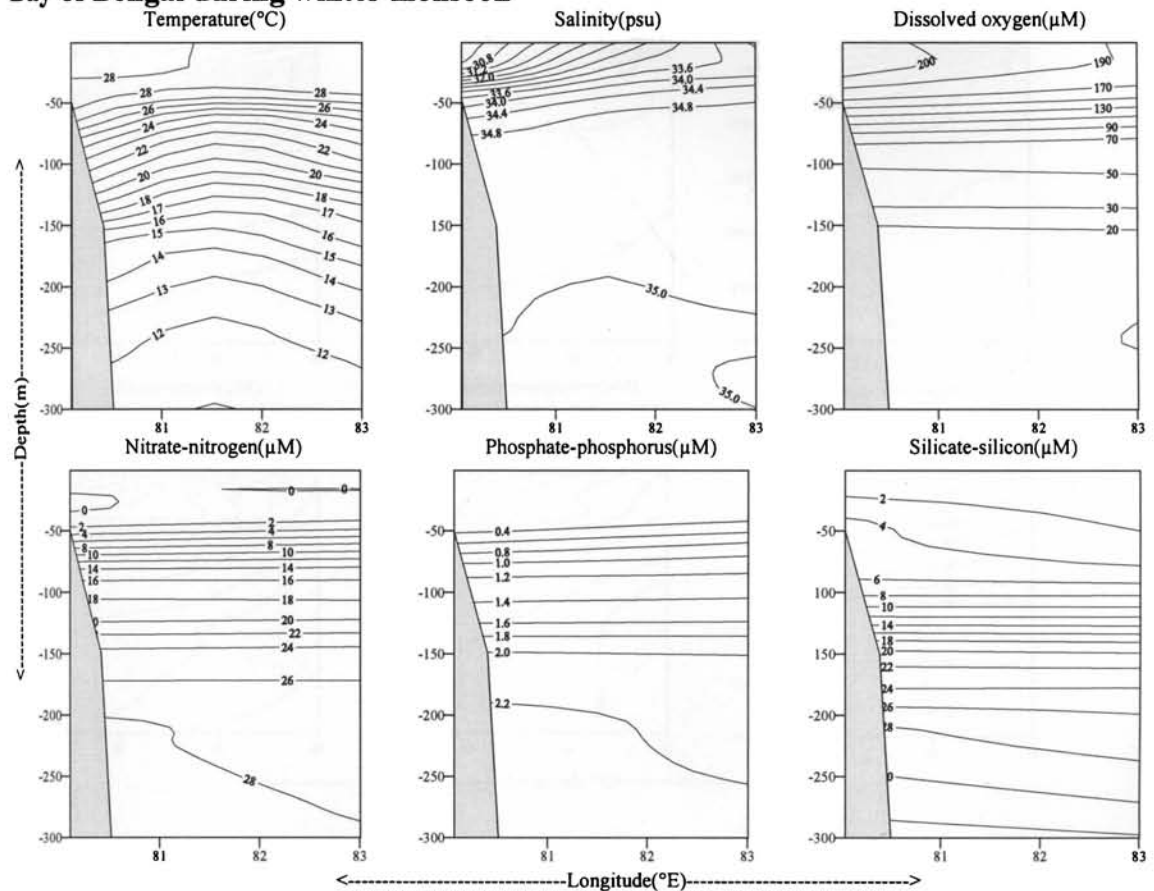
Figure. 15. Vertical section of physical and chemical parameters along 13° N in the Bay of Bengal during winter monsoon

Temperature(°C)   Salinity(psu)   Dissolved oxygen(µM)

Nitrate-nitrogen(µM)   Phosphate-phosphorus(µM)   Silicate-silicon(µM)

<------------------------------------Longitude(°E)------------------------------>
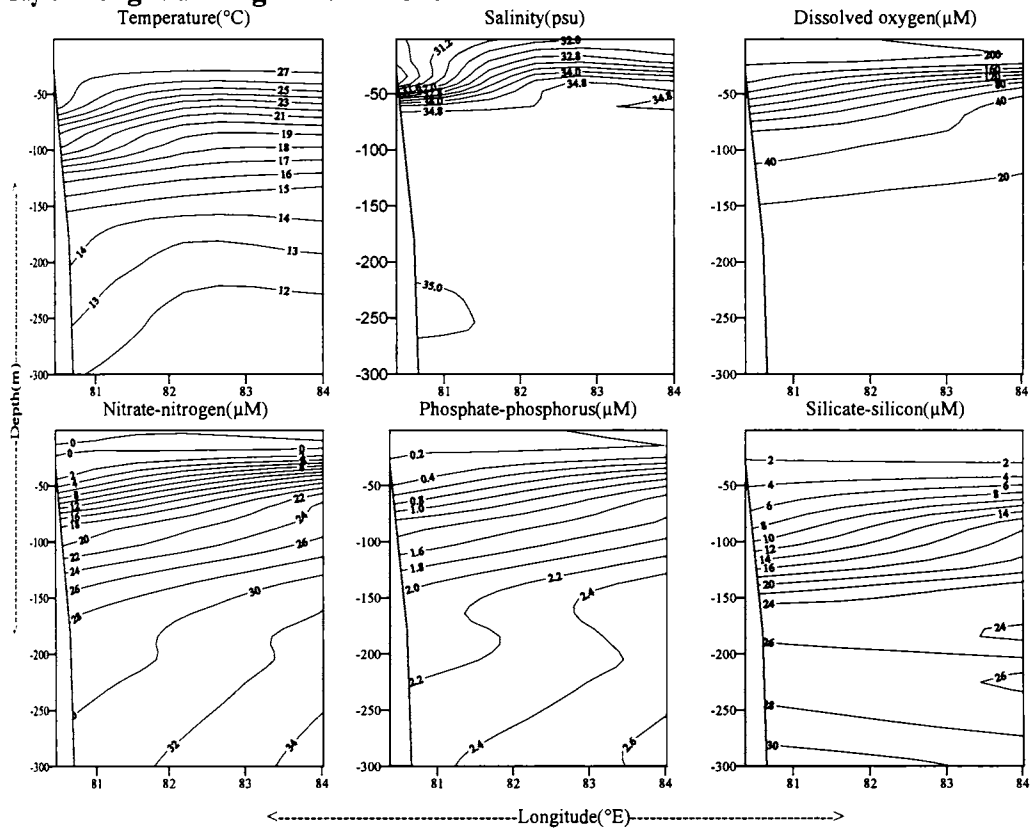
Figure. 16. Vertical section of physical and chemical parameters along 15°N in the Bay of Bengal during winter monsoon

Temperature(°C)   Salinity(psu)   Dissolved oxygen(µM)

Nitrate-nitrgen(µM)   Phosphate-phosphorus(µM)   Silicate-silicon(µM)

<------------------------------------Longitude(°E)------------------------------>

Figure. 17. Vertical section of physical and chemical parameters along 17° N in the Bay of Bengal during winter monsoon

Temperature(°C)   Salinity(psu)   Dissolved oxygen(μM)

Nitrate-nitrogen(μM)   Phosphate-phosphorus(μM)   Silicate-silicon(μM)

<------------------------------Longitude(°E)------------------------------>
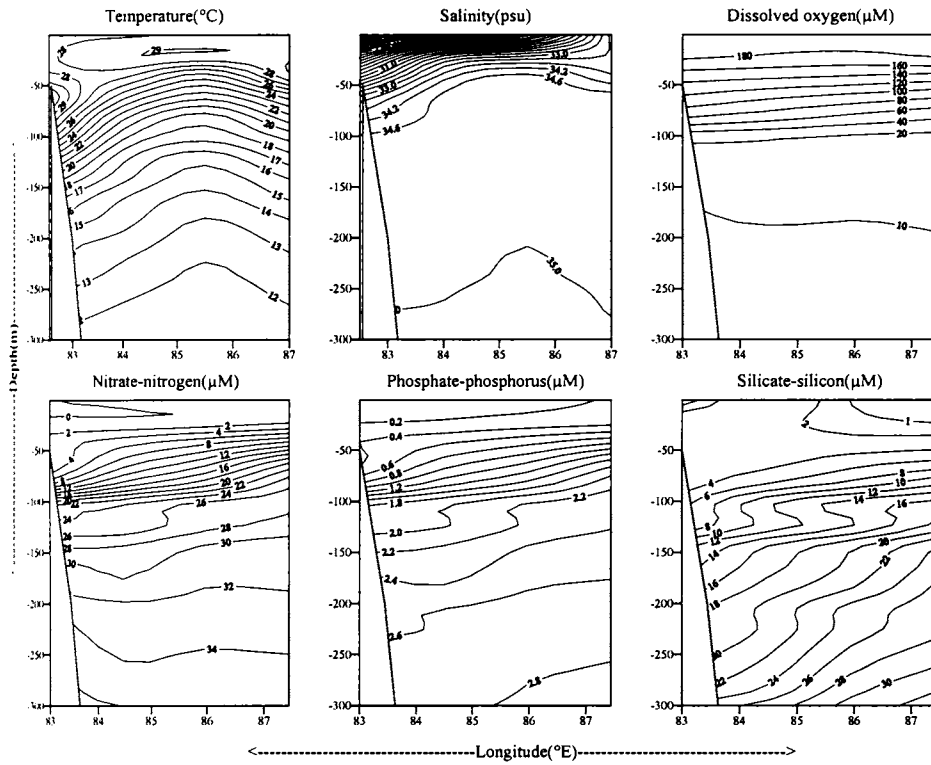
Figure. 18. Vertical section of physical and chemical parameters along 19°N in the Bay of Bengal during winter monsoon

Temperature(°C)   Salinity(psu)   Dissolved oxygen(μM)

Nitrate-nitrogen(μM)   Phosphate-phosphorus(μM)   Silicate-silicon(μM)

<------------------------------Longitude(°E)------------------------------>

Figure. 19. Vertical section of physical and chemical parameters along 20.5°N in the Bay of Bengal during winter monsoon
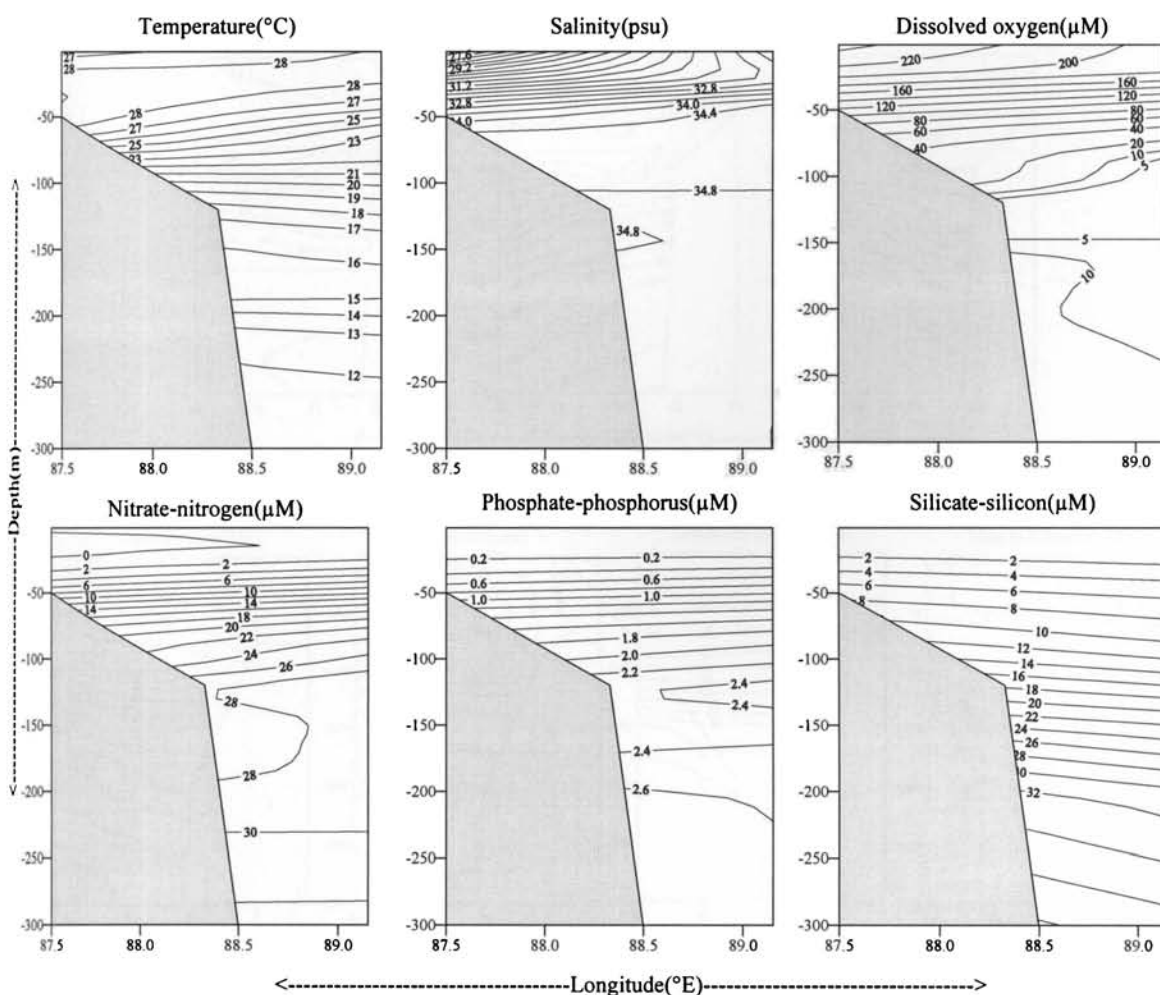
Figure. 20. Vertical section of physical and chemical parameters along 17°N in the Arabian Sea during spring intermonsoon

Temperature(°C)   Salinity(psu)   Dissolved oxygen(µM)   Nitrate-nitrogen(µM)

Phosphate-phosphorus(µM)   Silicate-silicon(µM)   Nitrite-nitrogen(µM)

<----------------------------------Longitude(°E)---------------------------------->

Figure. 21. Vertical section of physical and chemical parameters along 19°N in the Arabian Sea during spring intermonsoon

Temperature(°C)   Salinity(psu)   Dissolved oxygen(µM)   Nitrate-nitrogen(µM)

Phosphate-phosphorus(µM)   Silicate-silicon(µM)   Nitrite-nitrogen(µM)

<----------------------------------Longitude(°E)---------------------------------->

Figure. 22. Vertical section of physical and chemical parameters along 21°N in the Arabian Sea during spring intermonsoon

Temperature(°C)   Salinity(psu)   Dissolved oxygen(μM)   Nitrate-nitrogen(μM)

Phosphate-phosphorus(μM)   Silicate-silicon(μM)   Nitrite-nitrogen(μM)

<---------------------------------Longitude(°E)--------------------------------->

Figure. 23. Vertical section of physical and chemical parameters along 22°N in the Arabian Sea during spring intermonsoon

Temperature(°C)   Salinity(psu)   Dissolved oxygen(μM)   Nitrate-nitrogen(μM)

Phosphate-phosphorus(μM)   Silicate-silicon(μM)   Nitrite-nitrogen(μM)

<---------------------------------Longitude(°E)--------------------------------->

Chapter 4

4. Dissolved and Particulate trace metals in the Eastern Arabian Sea and Western Bay of Bengal

Trace metals are added to the marine environment from both natural sources and as a result of human activity. Runoff from land is a major source of addition of trace elements to the sea. Rivers bring in the trace metals both as dissolved species and as adsorbed onto the suspended matter, concentration of which may vary with the nature of rocks in catchement areas. Geologic weathering of rocks ultimately produce the clay and other minerals that make up the bulk of detrital sediments as well as dissolved metals in seawater. Volcanic activity either on land or in the sea is a natural source of metals, as is diagenetic remobilization from sediment. Many different human activities can add metals to the marine environment, like mining, metal processing manufacturing, transportation, waste disposal etc. From, the numerous sources of trace metals to the marine environment, it is difficult to determine which possible source is most important.

It is important to identify the source of trace metals but the environmental impact of a metal depends on its behavior rather than its source. The behaviors including mobility, transport, transfer and biological uptake, depend on the chemical and physical form of the metal. The size of the metal species or the particle with which it is associated is critical, as this will control its transport and settling. A given metal will behave different as physically, chemically and biologically in each of its forms and it will partition itself among the various possible forms in response to environmental conditions. In this respect, it is important to note that many trace metals are reactive and will quickly associate with particles if added to the marine environment in a dissolved form.

The distribution of trace metals in the ocean, in particular the surface waters, is of importance in understanding their role in various biochemical and geochemical systems. A number of elements are controlled or dominated by their involvement in one or more of the biogeochemical cycles in the oceans. Trace metal removal and

regeneration has been inferred to be a function of chemical behavior and settling characteristics of a solid carrier phase. Organic tissue, and the associated elements such as carbon, nitrogen and phosphorus are fixed by plankton in the upper ocean and are regenerated via oxidative processes. Other biogenic components, such as calcium carbonate and opal, have deeper regenerative cycles, governed by the chemistry and circulation within the deep ocean. Reactive trace metals can be involved to varying degrees in these cycles either actively as micro nutrients and skeletal materials, or passively by adsorption onto particle surfaces or co-precipitation with various solid phases. The interaction of dissolved trace metals with particles suspended in seawater is a major control on the concentrations and distribution of trace metals in oceans (Goldberg, 1954; Turekian, 1977; Whitfield and Turner, 1987; Clegg and Whitfield, 1990). The net flux of riverine trace elements to the oceans depends on the weathering features of the drainage basin. An understanding of trace metal behaviour requires a quantitative description of water / particle interactions. SPM generated at the surface layers is transported downwards in the water column. The coastal waters are good locations for studying water/particle interaction processes because physico-chemical properties change during mixing of river water with seawater at the surface, whereas bottom layers are affected by mixing with subsurface oceanic waters thereby causing a redistribution of metals between solution and suspended solids. However, data on partitioning between dissolved and suspended particulate phases are scarce because only a few such measurements have been made in oceanic environments.

Regarding dissolved trace metals, for instance in the North Pacific and North Atlantic Oceans the vertical distributions of dissolved Cd, Ni, Zn and Cu in seawater have been shown to be more or less related to the major nutrients such as nitrate, phosphate and silicate (Bruland, 1983). In the (northwest) Indian Ocean, Danielson (1980) found a good relationship only with silicate. Zn and Cu are essential to phytoplankton growth, and such biochemical functionality would provide an elegant explanation of the relations with major nutrients in seawater (Redfield *et al.*, 1963; Morel and Hudson, 1985). However the observed correlations between metals (Cd, Zn, Ni, Cu) and nutrients have been explained by the adsorptive or scavenging

removal of trace metals from surface waters along with settling biogenic particles (Goldberg, 1954; Craig, 1974; Turekian, 1977; Balistrieri *et al.*, 1981; Honeyman *et al.*, 1988). When assuming major controls by such adsorptive mechanism, the ensuing metal–nutrient relations, like Cd/PO_4, appear rather fortuitous. Price and Morel (1990) reported that in Zn-depleted surface waters Cd might be utilized instead of Zn by phytoplankton, the first evidence towards a biochemical functionality of Cd as explained by the Cd/PO_4 relation in seawater. The relationship between the metals and nutrients usually break down in shallow marginal seas and semi-enclosed basins such as the Mediterranean (Boyle *et al.*, 1985). Under anoxic conditions, the concentrations of dissolved Cu, Cd and Zn decrease dramatically as a result of sulphide co-precipitation, with major shifts in inorganic complexation (Bryne *et al.*, 1988), except in the case of Ni, which even in anoxic waters is not affected by redox processes (Haraldsson and Westerlund, 1988; Jacobs *et al.*, 1985).

In coastal waters, trace metal concentrations tend to differ with nutrients, reflecting the minor importance of biological processes in comparison with the strong influence of terrestrial and sedimentary inputs, anthropogenic sources, and the local hydrography (Hydes and Kremling, 1993; Laslett, 1995; Tappin *et al.*, 1995). The continental edge represents a transition zone between the oceanic and shelf regimes where the gradients are controlled by dynamic physical, chemical and biological processes. Transport of material across the shelf break is influenced by both mixing and movement of water masses (Huthnance, 1995), for which little quantitative information is available.

Although most of the dissolved trace metals in coastal and shelf waters do not differ from average open ocean waters (Martin and Thomas, 1994) local inputs are found to enrich them with trace metals in ocean margin surface waters (Bruland and Franks, 1983; Kremling, 1985; Kremling and Hydes, 1988; Kremling and Pohl, 1989; Muller *et al.*, 1994; Le Gall *et al.*, 1999). Various sources have been considered to explain these trace metal enrichments such as, coastal inputs, atmospheric deposition and sediment diagenesis. In the past decade, it was reported that upwelling could also

bring trace metals to surface layers (van Geen *et al.*, 1990), but there is no clear evidence to prove this.

In general, the above relationships on trace metal – nutrients are based largely on observations in the North Pacific and North Atlantic basins. Data on dissolved and particulate trace metals are very scanty for the entire Indian EEZ. The present work is hence the first of its kind focussing on the processes affecting the temporal and spatial distributions of trace metals from this region. The significance of this study is in describing the dissolved and particulate trace metal profiles in the water column from the inner shelf, outer shelf and offshore areas. Moreover, it also explains the partitioning of metals between the dissolved and particulate phases.

4. 1. Suspended Particulate Matter

The distribution of suspended particulate matter in the eastern Arabian Sea during intermonsoon fall ranged from 2.30 to 9.45 mg/l, 2.71 to 9.85 mg/l and 1.70 to 6.24 mg/l in the inner shelf, outer shelf and offshore transects respectively. The average values were 6.05 mg/l, 5.83 mg/l and 3.67 mg/l in the inner shelf, outer shelf and offshore transects respectively.

During intermonsoon fall the suspended particulate matter in the south eastern Arabian Sea during intermonsoon fall ranged from 3.68 to 9.45 mg/l, 3.68 to 9.85 mg/l and 1.70 to 5.15 mg/l (values average to 6.18 mg/l, 6.80 mg/l and 3.45 mg/l) in the inner shelf, outer shelf and offshore transects respectively. However, in the northern eastern Arabian Sea, during intermonsoon fall, the ranges were from 2.30 to 8.89 mg/l, 2.71 to 7.35 mg/l and 2.40 to 6.24 mg/l (average to 5.92 mg/l, 4.53 mg/l and 3.95 mg/l) in the inner shelf, outer shelf and offshore transects respectively.

During intermonsoon spring, the suspended particulate matter in the water column of the northeastern Arabian Sea ranged from 2.52 to 5.33 mg/l, 2.24 to 5.33 mg/l and 1.4 to 3.94 mg/l (average to 3.26 mg/l, 3.20 mg/l and 2.89 mg/l) in the inner shelf, outer shelf and offshore transects respectively.

The suspended particulate matter in the Bay of Bengal during winter monsoon ranged from 1.04 to 6.83 mg/l, 1.34 to 7.23 mg/l and 1.08 to 8.4 mg/l (average to 2.96

mg/l, 2.88 mg/l and 2.56 mg/l) in the inner shelf, outer shelf and offshore transects respectively.

In general, the average suspended particulate matter in the Arabian Sea and Bay of Bengal increased towards the inner shelf. However, the average suspended particulate matter in the shelf waters of the southeastern Arabian Sea during intermonsoon fall was relatively higher than in the northeastern Arabian Sea. Similarly, the suspended particulate matter levels in water column of the coastal and offshore waters of the Arabian Sea during intermonsoon fall were also higher than that in the intermonsoon spring and in the Bay of Bengal during winter monsoon.

The vertical sections of suspended particulate matter in the inner shelf, outer shelf and offshore transects of the Arabian Sea during intermonsoon fall (Fig. 24, Fig. 27, Fig. 30 & Fig. 36) and intermonsoon spring (Fig. 42, Fig. 45, & Fig. 48) and Bay of Bengal (Fig. 54, Fig. 57, Fig. 60 & Fig. 66) during winter monsoon are shown.

The suspended particulate matter in the outer shelf of the Arabian Sea during intermonsoon fall south of 17°N, shoaled towards the surface, possibly as a result of upwelling. On the otherhand, a similar shoaling of suspended particulate matter was seen in the outer shelf of the northern Arabian Sea during intermonsoon spring north of 19°N, could be due to the receding winter cooling processes in the area. While considering the Arabian Sea and Bay of Bengal, the suspended particulate matter in the bottom had shown an apparent streaming up towards intermediate depths. The vertical profiles in the inner shelf and outer shelf of the Arabian Sea and Bay of Bengal showed an increasing trend from surface to bottom. However in the offshore transects, there was a decreasing trend towards intermediate layers (100-200m), and this was followed by a near constancy or a slight increase with depth.

The main sources of suspended particulate matter in the oceans are river runoff, biological productivity and aeolian dust. The contribution of aeolian dust in the Bay of Bengal is negligible when compared with that in the Arabian Sea (Rao, 1985). Higher surface values of both basins can be attributed to the river runoff or increased plankton production. Further, the contribution of organic matter to suspended particulate matter as derived from POC fluxes is expected to be higher in the Arabian

Sea than in the Bay of Bengal. It can be therefore presumed that a major part of SPM comprises of inorganic matter derived from either river runoff, aeolian or POC fluxes or from sediment resuspension for both basins. The apparent increase of suspended particles in bottom layers of the shelf areas of both basins can also be attributed to resuspension of sediments. Significant positive correlations observed in the present study between particulate trace metals (Table 13 to 30) and SPM, and among themselves; are evidence for their occurrence with clays and silicate minerals. Rao (1985) observed near bottom enrichment of suspended particulate matter in the eastern continental margin of India, which was attributed to the resuspension of sediments by bottom currents. He has observed the occurrence of fine-grained sediments in association with high SPM containing high terrigenous material in the shelf/slope regions of the Bay of Bengal. Satyanarayana et al., (1985a) has also reported a similar increase in suspended particulate matter with depth in the coastal waters of Vishakhapatnam.

4. 2. Iron

Iron is the fourth most abundant element in the Earth's crust (5.6 %), exceeded only by oxygen, silicon and aluminium (Taylor, 1964). This can be attributed to the highly stable ^{56}Fe nucleus. Iron (Fe) is an essential element required by all eukaryotes and most prokaryotes because it is involved in fundamental enzymatic reactions such as oxygen metabolism, electron transfer processes, and DNA and RNA synthesis (Shanzer et al., 1996). In marine system, Fe is found to limit phytoplankton growth (Martin and Fitzwater, 1988; Martin et al., 1991; Timmermans et al., 1998). High-nutrient low chlorophyll (HNLC) areas represent the lower limit of the Fe required by phytoplankton. In general, Fe concentrations in these areas are low relative to other nutrients because there is little or no atmospheric or riverine input, no upwelled water, and no contribution from resuspended shelf sediments.

In dissolved form it exists mainly as $Fe(OH)_3$ and $Fe(OH)^{2+}$, but there is evidence for the formation of some soluble organic iron compounds in seawater. The concentration of particulate Fe is variable, high in inshore waters and near river mouths. The particulate Fe probably is in association with aluminosilicates (clays),

ferric hydroxide flocs, and organic detritus or living organisms. In anaerobic waters, it exists predominantly as Fe^{2+} either in the form of free ion or as $FeCl^+$.

In HNLC areas, phytoplankton develop strategies for acquiring Fe, which is low (e.g. <1.0 nM). In contrast, Fe-replete areas (e.g.>1.0 nM), phytoplankton is not Fe-limited, as it exceeds biological demand. The Arabian Sea is one such Fe-replete area due to a high input of atmospheric dust and seasonally upwelled waters that are rich in nutrients (Smith and Codispoti, 1980; Swallow, 1984; Madhupratap et al., 1996). The southwest trade winds are known to generate dust storms in the desert regions of Africa and the Arabian Peninsula that advects this lofted material into the Arabian Sea (Husar et al., 1997).

Iron is transported to the ocean via three major pathways: fluvial (riverine) input, atmospheric deposition, and processes occurring on the sea floor such as hydrothermal vents, sediment resuspension, and diagenesis. Iron is initially mobilized from the lithosphere by either mechanical action (i.e. erosion) or by thermal and chemical reactions (i.e. leaching, anoxia, or geothermal activity). Once mobilized, several physicochemical processes occur, altering its solubility and chemical speciation, between the source and ocean interfaces. The iron cycling can be studied by determining fluxes of iron in the different phases of the water column and its export from the sea.

Fluvial inputs transport iron to the coastal zone, following mobilization from soils and rocks. Particulate and dissolved iron concentrations in rivers are typically in the order of 1 mM and 1 μM respectively. On mixing with seawater, the dissolved and particulate iron is scavenged by flocculation occurs within the salinity/pH gradient (Sholkovitz, 1976; Moore et al., 1979; Turner and Millward, 1994;Sanudo-Wilhelmy et al., 1996). Estuarine mixing is found to reduce the global dissolved iron flux to the ocean by about 70-95%. Rivers and land run-off are estimated to deliver approximately half of the surface global iron input to the oceans, despite a high percentage of mobilized iron being lost in estuaries. Riverine inputs of iron to the oceans are extremely variable and dominated by occasional flood events. Although this pathway is likely to provide the main source of bioavailable iron to many coastal

and shelf waters, it remains unknown what proportion of suspended/ soluble iron originating from land run-off is transported by open ocean gyres.

The importance of the atmospheric deposition of iron to the ocean surface is high. Firstly, because it accounts for a major portion of the global iron input to the World Ocean but also because this pathway is considered the principal source of soluble and bioavailable iron to remote open ocean surface waters, often thousands of miles from the aerosol origin. The majority of aeolian iron received by the ocean arrives via wind transported dust originating from arid and semi-arid landmasses, important areas being North Africa, the Asian deserts, and the Middle East. Due to their dependence on meteorological events, rates of dust production and wet/dry deposition to the ocean are sporadic.

Within marine sediments, iron is generally found to have an abundance of 1-20% (by weight) with the highest enrichment found near hydrothermal areas and ferromanganese nodules. The surface layer of sediments are found to be areas of high chemical activity where early diagenesis occurs, causing the oxidation of organic matter. The resulting chemical and biologically mediated conditions mean that most particulate iron species are potentially reducible and can be reintroduced into the overlying waters in a more bioavailable form.

As a result of these redox reactions, solubilised Fe (11) is found to accumulate in marine sediments and pore waters under anoxic conditions, at micro molar concentrations. However, on account of the rapid oxidation of iron (111) in oxic seawater, it is unlikely to be released into the overlying waters in an inorganic form unless the bottom water is anoxic or oxygen penetration depth is small. Hence dissolved Fe (11) and (111) inputs from sediments are only expected to be important in anoxic areas, in areas where there is a significant degree of turbidity, or if there is a gradual release of iron in a chemically stabilized form (e.g. organically complexed).

The dissolved iron (dFe) concentration in the water column of the eastern Arabian Sea during intermonsoon fall (Table 7) ranged from 0.57 to 8.21μg/l, 0.43 to 6.22μg/l and 0.45 to 3.52 μg/l (average 3.45μg/l, 2.15μg/l and 1.73μg/l) in the inner shelf, outer shelf and offshore transects respectively. The particulate iron (pFe)

concentration in the water column of the eastern Arabian Sea during intermonsoon fall (Table 7) ranged from 8.5 to 100.5µg/l, 6.39 to 96.8µg/l and 5.8 to 48.96µg/l (averages to 51.53µg/l, 32.33µg/l and 23.63µg/l) in the inner shelf, outer shelf and offshore transects respectively.

However, the dissolved iron (dFe) concentration in the water column of the southeastern Arabian Sea (Table 8) during intermonsoon fall ranged from 1.27 to 8.21µg/l, 1.21 to 6.22µg/l and 0.83 to 3.20µg/l (averages to 4.16µg/l, 2.90µg/l and 1.97µg/l) in the inner shelf, outer shelf and offshore transects respectively. The particulate iron (pFe) concentration in the whole water column of the southeastern Arabian Sea (Table 8) during intermonsoon fall ranged from 18.8 to 121.5µg/l, 17.91 to 96.81µg/l and 10.61 to 48.96µg/l (averages to 62.59µg/l, 43.76µg/l and 26.69µg/l) in the inner shelf, outer shelf and offshore transects respectively.

Similarly, the dissolved iron (dFe) concentration in the water column of the northeastern Arabian Sea (Table 9) during intermonsoon fall ranged from 0.57 to 6.22µg/l, 0.43 to 2.29µg/l and 0.45 to 3.52µg/l (averages to 2.80µg/l, 1.15µg/l and 1.41µg/l) in the inner shelf, outer shelf and offshore transects respectively. The particulate iron (pFe) concentration in the water column of the northeastern Arabian Sea (Table 9) during intermonsoon fall ranged from 8.47 to 92.06µg/l, 6.39 to 33.89µg/l and 5.80 to 47.89µg/l (averages to 41.47µg/l, 17.10µg/l and 19.55µg/l) in the inner shelf, outer shelf and offshore transects respectively.

The dissolved iron (dFe) concentration in the water column of the northeastern Arabian Sea (Table 10) during intermonsoon spring ranged from 1.18 to 5.42µg/l, 1.01 to 5.42µg/l and 1.09 to 5.53µg/l (averages to 2.89µg/l, 2.26µg/l and 2.28µg/l) in the inner shelf, outer shelf and offshore transects respectively. The particulate iron (pFe) concentration in the water column of the northeastern Arabian Sea (Table 10) during intermonsoon spring ranged from 16.79 to 80.12µg/l, 14.39 to 78.96µg/l and 15.04 to 78.72µg/l (averages to 42.72µg/l, 33.30µg/l and 33.85µg/l) in the inner shelf, outer shelf and offshore transects respectively.

The dissolved iron (dFe) concentration in the water column of the Bay of Bengal during winter monsoon (Table 11) ranged from 0.73 to 3.01µg/l, 0.73 to 3.98µg/l and

0.87 to 3.64µg/l (averages to 2.35µg/l, 2.33µg/l and 2.13µg/l) in the inner shelf, outer shelf and offshore transects respectively. The particulate iron (pFe) concentration in the water column of the Bay of Bengal during winter monsoon (Table 11) ranged from 12.56 to 44.21µg/l, 6.72 to 47.76µg/l and 12.10 to 39.80µg/l (averages to 29.53µg/l, 28.58µg/l and 27.10µg/l) in the inner shelf, outer shelf and offshore transects respectively.

The average dissolved and particulate iron in inner shelf is relatively higher than the offshore transect in the Arabian Sea (during intermonsoon fall and intermonsoon spring) and Bay of Bengal (winter monsoon). The relative enrichment of dissolved and particulate iron towards the inner shelf when compared with the offshore regions of both basins can be attributed to the influence of land run-off and freshwater inputs into the coastal regions. Another potential source appears to be was the remobilization of iron from the shelf sediments.

Simultaneously physical processes affecting the concentration of iron in the Arabian Sea were the upwelling (intermonsoon fall) and winter cooling (spring inter monsoon). Thus a comparison of average concentrations of dissolved and particulate iron (Table 9 & 10) in the water column of the northeastern Arabian Sea during intermonsoon fall and spring intermonsoon showed that iron was relatively high in the outer shelf and offshore transects during spring intermonsoon due to the effect of winter cooling processes. Further a comparison of average concentrations of dissolved and particulate iron (Table 8 & 9) in the water column of the southeastern Arabian Sea and northeastern Arabian Sea during intermonsoon fall showed that iron was relatively high in the southeastern Arabian Sea due to the effect of upwelling. Moreover a comparison of average concentrations of dissolved and particulate iron in the whole water column of the eastern Arabian Sea during intermonsoon fall and western Bay of Bengal during winter monsoon (Table 12) showed that iron was slightly higher in the Arabian Sea. The observed differences for Fe indicating a biologic demand for Fe in the Bay of Bengal because its lack of effective supply. The slight enrichment of iron in the Arabian Sea may be the due to the effective upwelling

of subsurface waters, strong aeolian sources and presence of large quantities of soluble organic matter.

The vertical sections of dissolved and particulate iron in the inner shelf, outer shelf and offshore transects of the Arabian Sea during intermonsoon fall (Fig. 25, Fig. 28, Fig. 32 & Fig. 38) and intermonsoon spring (Fig. 43, Fig. 46 & Fig. 50) and Bay of Bengal (Fig. 55, Fig. 58, Fig. 62 & Fig. 68) during winter monsoon are shown as contoured plots. The vertical section of dissolved and particulate Fe in the inner shelf, outer shelf and offshore transects of both basins showed a surface enrichment, subsurface minima at intermediate depths and followed by a slight increase at the bottom layers. The surface enrichment of Fe may be due to influx of river waters or aeolian inputs. The distribution of iron in the shelf areas of both the Arabian Sea and Bay of Bengal was erratic. This may be partly due to the influence of rivers and local regenerative activity. Eventhough there was heavy river run off in the Bay of Bengal, the iron in the surface layers are less concentrated than in the Arabian Sea. This can be due to the effect of high flocculation and precipitation at the low salinity as well as low pH of seawater in the Bay of Bengal when compared with Arabian Sea. Higher concentrations of iron in the bottom layers of the shelf regions of both basins can be attributed to the release of iron from the bottom deposits due to turbulence. Satyanarayana et al., (1985a) also observed similar enrichment of dissolved iron in harbor and coastal waters of Vishakapatnam, which they believed as its release from sediments.

Surface depletion and bottom enrichment of dissolved iron may partially be due to in situ mechanisms such as biological removal at the surface and regeneration in the bottom waters. However the presence of detectable levels of dissolved iron in the surface layers of the both basins and absence of significant enrichment at bottom in the offshore transects revealed that processes other than biological removal are also operating, such as precipitation and/or adsorption. Iron released from the breakdown of planktonic matter may be quickly converted into colloidal hydrous oxide at the pH (7.6-8.4), and may be readily adsorbed on the descending particles, which in turn, get transported to the sediments. This is supported by the fact that the dissolved iron

contributes only ~ 5% of the total iron in the study region. Murray and Gill (1978) while studying the distribution of acid-soluble iron (unfiltered sample) in the Puget Sound observed relatively low concentration at mid depth and slight increase towards air-water (surface) and sediment-water interface (bottom), which they explained in terms of riverine input and regeneration from sediments respectively. Danielson (1980) while studying the depth profiles of dissolved iron in the Indian Ocean, observed large scatter which he attributed to the chemical behavior of iron in oxygenated seawater where it exists mainly as hydroxy species with low solubility which tend to adsorb onto available surface and form colloidal suspensions which can conceivably give rise to inhomogeneous distribution.

The particulate fraction of iron dominates over the dissolved fraction since it comprises of 92-95 % of total iron in the entire study region of both basins. This may probably be due to the precipitation of iron in the form of colloidal hydrous oxide or the ferric hydroxide coating on pre-existing particles under the pH and redox conditions prevailing in the coastal and offshore waters. Relatively high concentration of particulate iron in bottom waters at shelf areas can be attributed to the diffusion from the sediments across the sediment-water interface and its subsequent precipitation as hydrous iron oxide or as iron oxide coatings on the preexisting particles. Adsorption of dissolved iron on the pre-existing solids on both organic and inorganic surfaces may be responsible for relatively higher concentrations of particulate iron in bottom waters (Krishnaswami and Sarin, 1976). Gluck and Lieser (1982) have shown, using auto radiographic technique that iron can be adsorbed onto organic and inorganic surfaces from seawater. Particulate iron showed significant positive correlations (Table 14 & 20) with SPM in the coastal areas of the Arabian Sea during intermonsoon fall & spring (r = 0.50, at p<0.001). Similarly particulate iron showed significant positive correlations (Table 26) with SPM in the coastal areas of the Bay of Bengal (r = 0.42, at p<0.001), during winter monsoon. A significant positive correlation of particulate iron with SPM (Table 14, 17, 20, 23, 26 & 29) and other particulate trace metals (Co, Ni, Cu, Zn & Pb) for both basins suggest its key

association with the suspended particles probably along with alumino silicate minerals.

The distribution of iron in offshore areas was not completely nutrient-like or scavenged type, even though it exhibited a slight increase at higher depths. The deepwater concentration has provided a picture of the geochemistry of dissolved Fe in the offshore waters of both Arabian Sea and Bay of Bengal. The slight increasing concentration of iron with depth suggests that it had feebly undergone a particle remineralization cycle similar to nutrients such as nitrate (Martin and Gordon, 1988; Sunda and Huntsman, 1995). Iron will differ from nitrate, because of its tendency to be scavenged from the dissolved phase by sinking particles. The subsurface minimum in the offshore showed the scavenging efficiency of dissolved Fe to suspended particles in the both basins. The term "scavenging" is used in a broad sense to denote the many geochemical and biologically mediated reactions, which result in the change in the state of a metal from the dissolved to the particulate form. Whitfield and Turner (1987) developed a scavenging index to classify the behavior of elements in the ocean with respect to removal by adsorption onto sinking particles. This scavenging could act to minimize the increase of iron concentrations in deep-water due to remineralisation of settling biogenic particles. Remineralisation of biogenic particles must release iron, and this process must be responsible for the similarity in vertical distributions of nitrate and iron (Martin et al., 1989). However, remineralisation of iron from biogenic particles was not sufficient in the deep-sea to maintain the observed iron concentrations against a scavenging rate equivalent to that found for metals with a similar scavenging index. At deeper levels below 500m, dissolved iron showed a maxima in its concentration and was roughly constant in both basins. Thus dissolved Fe in both the Arabian Sea and Bay of Bengal reflects scavenging, coupled with regeneration from settling particles. A constant deep-water iron concentration is maintained by a balance of iron to bind by organic ligands (Rue and Bruland, 1995; Wu and Luther, 1995), together with equilibrium between dissolved and particulate iron. This equilibrium could involve iron oxide phases or surface exchange reactions on marine particles. Concentrations of iron greater than the solubility limit or

chelation capacity of seawater would be removed rapidly, while concentrations at or below these values might remain in solution for much longer periods of time. Iron transport in the upper water column is far more dynamic due to intense biological activity and mixing (Hutchins *et al.*, 1993) and is evident from the estimated residence time for iron. Johnson *et al.*, (1997) have argued that Fe may be stabilized in deep waters by organic ligands that inhibit precipitation and scavenging. This is supported by direct evidence for metal complexation of Fe in deep waters of the Atlantic (Wu and Luther, 1995) and Pacific (Rue and Bruland, 1995).

The recent global model of Moore *et al.*, (2002) indicates that the main processes exporting dissolved iron from the mixed layer in the open ocean to be detrainment and sinking detritus, whereas the main inputs are entrainment and atmospheric deposition, although it should be noted that regional processes such as upwelling are highly significant in certain areas. Within the euphotic zone, iron is also cycled within the biological pool. This has a significant effect on iron transport through the upper water column, and rates of iron uptake by marine organisms and remineralisation are estimated to be of the same order as the input and export fluxes, where the global fluxes at mixed layer is 10^{12} g (Fe) yr^{-1} (Moore *et al.*, (2002)).

Oligotropic systems have stratified euphotic zones, based on studies on thorium scavenging (Coale and Bruland, 1987). Primary production in the upper layers is almost based on recycled nutrients and there is little carbon export or metal removal. Iron may have longer residence time at the surface in these systems, where it does not limit primary production. The major portion of the new production, carbon export and metal scavenging in oligotropic system is limited to a lower layer of the euphotic zone near the nitracline (Coale and Bruland, 1987). Although nitrate is increasing to high concentrations in the lower layer, dissolved iron concentrations are a minimum at this layer (Bruland *et al.*, 1994) due to biological uptake and scavenging. Thus iron may regulate export production even in oligotropic regions of the ocean.

Contours of dissolved iron and particulate iron (Fig. 28), chlorophyll *a* and primary production (Table 4, shown at the end of Chapter 3) illustrate the following differences between surface waters of the southern and northern transects along the

outer shelf of the Arabian Sea during intermonsoon fall. The dissolved iron and particulate iron distribution in the outer shelf showed that the isolines of iron shoaled south of 17°N due to upwelling resulting in a rapid increase of surface iron (dissolved Fe from 0.55 µg/l to 2.2 µg/l and particulate Fe from 10µg/l to 30µg/l). Thus in the present study elevated levels of both dissolved and particulate iron were found along the southern transect in the outer shelf. That is surface (0-30 m) concentrations of dissolved and particulate iron were approximately 2 and 3 times higher along the outer shelf of southern transect relative to the northern transect. Consistent with the iron distribution, chlorophyll *a* and primary productivity were higher than that at the northwest coast.

Similarly during inter monsoon spring, the contours of dissolved and particulate iron (Fig. 46), in the outer shelf transect of the northeastern Arabian Sea shows a relative enrichment of iron in the northwest coast. The dissolved and particulate iron distribution in the outer shelf transect showed that the isolines of iron shoaled north of 19°N due to the receding winter mixing resulting in a rapid increase of surface iron (dissolved Fe from 1.10 µg/l to 2.20 µg/l and particulate Fe from 10µg/l to 30µg/l). Thus in the present study elevated levels of both dissolved and particulate iron were found along the outer shelf north of 19°N transect. Consistent with the iron distribution, chlorophyll *a* and primary productivity were higher in the outer shelf transect than that at the open ocean transect (Table 5, shown at the end of Chapter 3). These can be attributed due to differences to the availability of iron. However the source of iron in the Arabian Sea is not known.

The main processes affecting mixed layer concentrations of Fe in the Arabian Sea are the deposition, partial dissolution of eolian material in the surface waters, and the upwelling of sub-surface water during the southwest monsoon (Measures and Vink (1999). However in the present study resuspended particulate Fe together with upwelling of subsurface waters appears to be a major source of iron along the southern transects of the southeastern Arabian Sea during intermonsoon fall. During intermonsoon fall, the concentrations of dissolved and particulate iron are low along the northern outer shelf transect, which may limit the nutrient consumption and

biomass production, and this must lead to retention of iron within the euphotic zone. High surface nitrate concentrations along the southern transect coincides with high dissolved and particulate iron values. This suggests that iron has been mobilized from resuspended sediment, incorporated into biomass, and then exported from the system. As a result, the large supply of resuspended shelf sediment containing particulate iron along the southern transect may enable bloom conditions to occur in the southwest coast of India. Johnson *et al.* (1999) found elevated levels of Fe derived from resuspended material to extend as far as 200km seaward from the California coast and to co-occur with elevated levels of chlorophyll.

Significant phytoplankton blooms and nutrient depletion were found along the southwest coast of India. These blooms may correspond to elevated levels of total Fe. Particulate iron, possibly from resuspended shelf material appears to be a significant source of these elevated levels of iron in this region. During the present study the elevated Fe concentrations coincided with areas of increased productivity, chlorophyll *a* and high nutrients, indicating that Fe may be an important factor controlling the location of phytoplankton blooms in the Arabian Sea.

Although the spring intermonsoon is considered a period of low productivity, recent evidence suggests that sea-surface cooling drives convective processes that lead to high nutrient concentrations in northeastern Arabian Sea surface waters in winter. As a result, the mesozooplankton biomass remains constant throughout the year, although their food source may switch over from phytoplankton during periods of high productivity to the microbial loop during the spring intermonsoon period (Madhupratap *et al.*, 1996). This suggests that even during intermonsoon periods, productivity may remain high and account for increased iron concentrations measured at these sites during spring intermonsoon.

Although the Arabian Sea is not an Fe-limited ocean, the removal of Fe from the dissolved into the particulate pool during the growth of the monsoon-induced blooms, and its subsequent removal from the euphotic zone as a result of the export of organic matter, is expected to play a significant role in the Fe budget of the upper waters of the Arabian Sea.

The separation of nitrogen and phosphorus from iron during remineralisation of organic carbon in the oxic ocean is probably responsible for development of Fe limitation in the high-nutrient, low-chlorophyll a regions. In contrast, in regions where the primary site of organic matter diagenesis is poorly ventilated and Fe solubility is much higher, this separation is less pronounced and the stoichiometric relationship between Fe and the major nutrients can be maintained. However, unless suboxic water with its high levels of Fe is upwelled, an external input of Fe is always required to balance upwelled sources of nutrients. While this Fe may be supplied by river runoff and sedimentary sources in shallow coastal regions, in the open ocean only aeolian deposition and winter mixing can supply the required Fe.

The observed distributions of dissolved Fe and the changes between the southeastern Arabian Sea and northeastern Arabian Sea during intermonsoon fall can be interpreted as a dynamic balance between the addition and removal processes that are occurring seasonally. On the input side, the main processes affecting mixed layer concentrations of Fe in the Arabian Sea are the deposition and partial dissolution of eolian material in the surface waters during winter mixing, and the upwelling of sub-surface water during the southwest monsoon. On the removal side is the incorporation of dissolved material into the particulate phase (primarily biological material associated with the development of phytoplankton blooms during the southwest monsoon), and its net removal by vertical transport. Entrainment of water during mixed layer deepening can also affect concentrations. Estimates of the relative role that each of these processes play in controlling the observed distributions are examined in light of existing knowledge of the Arabian Sea system and the observations of these processes in other parts of the World's ocean.

4.3. Cobalt

Cobalt is an important micronutrient for marine phytoplankton, (Morel *et al.*, 1994), in particular the photosynthetic *Cyanobacteria* (Sunda and Huntsman, 1995), yet its surface-water concentrations are very low based on limited available data. Cobalt is of oceanographic interest both in its biological context of association with vitamin B_{12}, and through its accumulation in manganese nodules. It exists in seawater

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as the Co^{2+} ion and as chloro and carbonato-complexes. The factors controlling the distribution of cobalt in seawater are not well understood. Furthermore, the potential for these low concentrations of cobalt to influence species composition in the oceans is unknown. An understanding of the processes that control the temporal and spatial variability of cobalt in the ocean surface waters are paramount to surmising its potential biologic importance.

The dissolved cobalt (dCo) concentration in the water column of the eastern Arabian Sea during intermonsoon fall ranged from 0.136 to 0.984nM, 0.102 to 3.563nM and 0.093 to 1.374nM (averages to 0.342nM, 0.507nM and 0.427nM) in the inner shelf, outer shelf and offshore transects respectively. The particulate cobalt (pCo) concentration in the water column of the eastern Arabian Sea during intermonsoon fall ranged from 0.228 to 1.867nM, 0.171 to 6.787nM and 0.141 to 2.511nM (averages to 0.601nM, 0.898nM and 0.691nM) in the inner shelf, outer shelf and offshore transects respectively.

Similarly, the dissolved cobalt (dCo) concentration in the water column of the southeastern Arabian Sea during intermonsoon fall ranged from 0.221 to 0.984nM, 0.231 to 1.035nM and 0.204 to 1.374nM (averages to 0.459nM, 0.584nM and 0.533nM) in the inner shelf, outer shelf and offshore transects respectively. The particulate cobalt (pCo) concentration in the water column of the southeastern Arabian Sea during intermonsoon fall ranged from 0.371 to 1.867nM, 0.388 to 1.731nM and 0.307 to 2.511nM (averages to 0.802nM, 1.005nM and 0.858 nM) in the inner shelf, outer shelf and offshore transects respectively.

The dissolved cobalt (dCo) concentration in the water column of the northeastern Arabian Sea during intermonsoon fall ranged from 0.136 to 0.679nM, 0.102 to 3.563nM and 0.093 to 0.950nM (averages to 0.236nM, 0.404nM and 0.285 nM) in the inner shelf, outer shelf and offshore transects respectively. The particulate cobalt (pCo) concentration in the water column of the northeastern Arabian Sea during intermonsoon fall ranged from 0.222 to 1.324nM, 0.171 to 6.787nM and 0.141 to 1.663nM (averages to 0.418nM, 0.756nM and 0.469 nM) in the inner shelf, outer shelf and offshore transects respectively.

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The dissolved cobalt (dCo) concentration in the water column of the northeastern Arabian Sea during intermonsoon spring ranged from 0.339 to 5.091nM, 0.053 to 2.226nM and 0.136 to 0.743nM (averages to 0.741nM, 0.544nM and 0.368 nM) in the inner shelf, outer shelf and offshore transects respectively. The particulate cobalt (pCo) concentration in the water column of the northeastern Arabian Sea during intermonsoon spring ranged from 0.546 to 8.196nM, 0.096 to 1.205nM and 0.246 to 1.345nM (averages to 1.223nM, 0.931nM and 0.652 nM) in the inner shelf, outer shelf and offshore transects respectively.

The dissolved cobalt (dCo) concentration in the water column of the Bay of Bengal during winter monsoon ranged from 0.170 to 2.223nM, 0.212 to 2.732nM and 0.130 to 5.447nM (averages to 1.136nM, 1.055nM and 1.350 nM) in the inner shelf, outer shelf and offshore transects respectively. The particulate cobalt (pCo) concentration in the water column of the Bay of Bengal during winter monsoon ranged from 0.299 to 3.882nM, 0.373 to 4.751nM and 0.206 to 8.824nM (averages to 2.055nM, 1.909nM and 2.274nM) in the inner shelf, outer shelf and offshore transects respectively.

The average concentration levels of dissolved and particulate cobalt in the water column of the inner shelf were relatively higher than the offshore transect in the Arabian Sea during intermonsoon spring. Similarly the average concentration levels of dissolved and particulate cobalt in the water column of the inner shelf were relatively higher than the outer shelf in the Bay of Bengal during winter monsoon. Moreover the average concentration levels of dissolved and particulate cobalt in the water column of the southeastern Arabian Sea and northeastern Arabian Sea during intermonsoon fall showed that cobalt was relatively getting enriched in the outer shelf. The relative enrichment of dissolved and particulate cobalt in the shelf regions of both basins can be attributed to the influence of land run-off and freshwater inputs into the coastal regions. The higher concentrations of cobalt in the bottom layers of the shelf regions in both basins can be due to the remobilization of cobalt into the overlying water column from the shelf sediments.

Apart from river runoff and sedimentary inputs the cobalt in the surface layers of the Arabian Sea were affected by upwelling during intermonsoon fall and winter cooling during spring intermonsoon. A comparison of average concentrations of dissolved and particulate cobalt (Table 9 & 10) in the whole water column of the northeastern Arabian Sea during intermonsoon fall and spring intermonsoon showed that cobalt is relatively high in the shelf regions than offshore due to the effect of winter mixing. Further a comparison of average concentrations of dissolved and particulate cobalt (Table 8 & 9) in the whole water column of the southeastern Arabian Sea and northeastern Arabian Sea during intermonsoon fall showed that cobalt was relatively high in the outer shelf and offshore transects of the southeastern Arabian Sea due to the effect of upwelled waters. Moreover a comparison of average concentrations of dissolved and particulate cobalt in the whole water column of the eastern Arabian Sea during intermonsoon fall and entire Bay of Bengal during winter monsoon (Table 12) showed that cobalt was 2.7 times higher in the Bay of Bengal. The higher amount of freshwater brought by river runoff may partly explain the high concentrations of cobalt in the dissolved and particulate forms in the Bay of Bengal. In the Arabian Sea as evidenced by the low cobalt concentrations, it can be speculated that the biologic demand for cobalt might be more intense relative to that of the Bay of Bengal because of lower supply of Co from intermediate waters by advective processes and winter mixing.

The vertical sections of dissolved and particulate cobalt in the inner shelf, outer shelf and offshore transects of the Arabian Sea during intermonsoon fall (Fig. 26, Fig. 29, Fig. 35 & Fig. 41) and intermonsoon spring (Fig. 44, Fig. 47 & Fig. 53) and in the Bay of Bengal (Fig. 56, Fig. 59, Fig. 65 & Fig. 71) during winter monsoon are shown as contoured plots. The vertical sections of dissolved and particulate cobalt in the inner shelf, outer shelf and offshore transects of both basins showed a slight surface enrichment, subsurface minima at intermediate depths and followed by an increase at the bottom layers. The slight enrichment of cobalt in the surface layer of both basins can be due to river runoff or aeolian inputs. The subsurface minima observed can be due to scavenging of dissolved cobalt by suspended particles from seawater. The

enrichment of dissolved cobalt at both basins towards bottom layers at the offshore areas can be attributed to the regeneration of cobalt from settling particles. The percentage contribution of particulate cobalt to the total varied between 62-68% indicating its dominance over dissolved form in both basins. This can be due to the partial removal of dissolved Co by adsorption onto suspended particles since dissolved Co has the same distribution as that of the particulate Co. Relative enrichment of particulate cobalt in the bottom waters can be attributed to the scavenging of dissolved cobalt from seawater by hydrous manganese oxide. Particulate cobalt showed significant positive correlations (Table 14) with SPM in the coastal areas of the Arabian Sea during intermonsoon fall (r = 0.38, at p<0.001). Similarly particulate cobalt showed significant positive correlations (Table 29) with SPM in the offshore areas of the Bay of Bengal (r = 0.54, at p<0.001), during winter monsoon. The significant positive correlation of particulate cobalt with SPM and other particulate trace metals (Zn, Cu, Ni & Fe) in both basins suggests their association with alumino silicate minerals. Takematsu *et al*; (1981) reported the adsorption of cobalt on to manganese dioxide in regions of low precipitation of manganese. Satyanarayana *et al*., (1985a) observed slight enrichment of cobalt in the bottom in harbor and coastal waters of Visakhapatnam.

Cobalt has been generally thought of as a scavenged-type trace element in seawater. The deep-water concentrations of dissolved Co provide an important insight into its geochemistry. Even though Co exhibits a scavenging tendency, at intermediate depths in the offshore transects of both Arabian Sea and Bay of Bengal, below 500m the concentrations increases towards bottom so that Co has a unique geochemistry, which means that it is neither a typical nutrient-like nor a scavenged-type element. Saito and Moffett (2001) have shown that Co is organically complexed in deep sea and argued that such complexation may inhibit the scavenging of Co as well. Such organic complexation of Co in seawater could serve to stabilize dissolved Co, preventing its microbial co-oxidation with Mn. The oxidation state of Co (II) to Co (III) can be accomplished by co-precipitation with Mn oxides by Mn-oxidizing bacteria (Tebo *et al*., 1984; Tebo, 1998) and is thought to be an important mechanism

for cobalt removal in coastal waters (Moffett and Ho, 1996). In addition, organic complexation would stabilize the Co (111) state because $Co^{3+}_{(aq)}$ is unstable in seawater.

4. 4. Nickel

Various metabolic functions for Ni (Price and Morel, 1991) have been identified. Ni is essential for phytoplankton growth in waters where urea is a nitrogen source but is not required where ammonia is the main nitrogen source (Price and Morel, 1991). Nickel exists in seawater primarily as the free Ni^{2+} ion and chloro and carbonato-complexes. Nickel is known to possess a nutritional requirement for many eukaryotic and prokaryotic organisms and is a component of the proteinaceous metalloenzyme urease, which is necessary for plants to metabolise urea (Thomson, 1982). Urea is an excellent source of nitrogen for phytoplankton (Oliveria and Antia, 1986) and is a common waste product of zooplankton (Carpenter and Capone, 1983).

The dissolved nickel (dNi) concentration in the water column of the eastern Arabian Sea during intermonsoon fall ranged from 0.392 to 3.084nM, 0.477 to 5.129nM and 0.392 to 6.287nM (averages to 1.600nM, 2.541nM and 2.898 nM) in the inner shelf, outer shelf and offshore transects respectively. The particulate nickel (pNi) concentration in the water column of the eastern Arabian Sea during intermonsoon fall ranged from 0.239 to 2.045nM, 0.307 to 3.203nM and 0.239 to 3.425nM (averages to 0.989nM, 1.554nM and 1.626nM) in the inner shelf, outer shelf and offshore transects respectively.

The dissolved nickel (dNi) concentration in the water column of the southeastern Arabian Sea during intermonsoon fall ranged from 0.647 to 3.425nM, 0.494 to 5.129nM and 0.392 to 6.287nM (averages to 1.972nM, 2.711nM and 2.971nM) in the inner shelf, outer shelf and offshore transects respectively. The particulate nickel (pNi) concentration in the water column of the southeastern Arabian Sea during intermonsoon fall ranged from 0.426 to 2.045nM, 0.307 to 3.203nM and 0.239 to 3.425nM(averages to 1.210nM, 1.633nM and 1.669nM) in the inner shelf, outer shelf and offshore transects respectively.

The dissolved nickel (dNi) concentration in the water column of the northeastern Arabian Sea during intermonsoon fall ranged from 0.392 to 2.743nM, 0.477 to 4.498nM and 0.545 to 5.878nM (averages to 1.261nM, 2.315nM and 2.801nM) in the inner shelf, outer shelf and offshore transects respectively. The particulate nickel (pNi) concentration in the water column of the northeastern Arabian Sea during intermonsoon fall ranged from 0.239 to 1.738nM, 0.307 to 2.862nM and 0.333 to 3.220nM (averages to 0.788nM, 1.448nM and 1.568nM) in the inner shelf, outer shelf and offshore transects respectively.

The dissolved nickel (dNi) concentration in the water column of the northeastern Arabian Sea during intermonsoon spring ranged from 1.193 to 3.621nM, 1.070 to 5.026nM and 0.910 to 10.070nM (averages to 1.692nM, 1.936nM and 3.470nM) in the inner shelf, outer shelf and offshore transects respectively. The particulate nickel (pNi) concentration in the water column of the northeastern Arabian Sea during intermonsoon spring ranged from 0.739 to 1.687nM, 0.663 to 2.709nM and 0.564 to 5.640nM (averages to 1.014nM, 1.097nM and 1.970nM) in the inner shelf, outer shelf and offshore transects respectively.

The dissolved nickel (dNi) concentration in the water column of the Bay of Bengal during winter monsoon ranged from 0.341 to 1.687nM, 0.290 to 4.907nM and 0.204 to 6.679nM (averages to 0.764nM, 1.707nM and 3.598nM) in the inner shelf, outer shelf and offshore transects respectively. The particulate nickel (pNi) concentration in the water column of the Bay of Bengal during winter monsoon ranged from 0.204 to 1.056nM, 0.170 to 2.914nM and 0.136 to 3.731nM (averages to 0.458nM, 0.994nM and 1.919nM) in the inner shelf, outer shelf and offshore transects respectively.

The average concentration levels of dissolved and particulate nickel in the water column of the offshore waters are relatively higher than the inner shelf of the Arabian Sea during intermonsoon fall and intermonsoon spring. Similarly they are higher in the offshore waters of the Bay of Bengal during winter monsoon. Thus in both basins dissolved and particulate Ni showed relative enrichment towards offshore regions.

Simultaneously, the physical processes affecting the nickel distribution in the Arabian Sea at the surface layers were the upwelling & eddy formation during intermonsoon fall and winter cooling during spring intermonsoon. In the Bay of Bengal, eddy mixing was found to supply nickel to surface layers during winter monsoon. Another potential source appears to be remobilization of nickel into the overlying water from the shelf sediments. Thus a comparison of average concentrations of dissolved and particulate nickel (Table 9 & 10) in the northeastern Arabian Sea during intermonsoon fall and spring intermonsoon showed that nickel was relatively high in the offshore transect during spring intermonsoon due to the effect of winter cooling. Similarly, a comparison of average concentrations of dissolved and particulate nickel (Table 8 & 9) in the water column of the southeastern Arabian Sea and northeastern Arabian Sea during intermonsoon fall showed that nickel was relatively high in the inner shelf, outer shelf and offshore transects of the southeastern Arabian Sea due to the effect of upwelled waters.

Moreover a comparison of average concentrations of dissolved and particulate nickel in the water column of the eastern Arabian Sea during intermonsoon fall and western Bay of Bengal during winter monsoon (Table 12) showed that nickel concentration was 1.2 times higher in the Arabian Sea. The observed differences for Ni showed a biologic demand for Ni in the Bay of Bengal because of lack of effective supply of Ni from subsurface levels probably due to failure of vertical mixing, even though river runoff was high. On the otherhand, its abundance in the Arabian Sea may be due to the effective upwelling of subsurface waters during the southwest monsoon.

The vertical sections of dissolved and particulate nickel in the inner shelf, outer shelf and offshore transects of the Arabian Sea during intermonsoon fall (Fig. 26, Fig. 29, Fig. 34 & Fig. 40) and intermonsoon spring (Fig. 44, Fig. 47 & Fig. 52) and in the Bay of Bengal (Fig. 56, Fig. 59, Fig. 64 & Fig. 70) during winter monsoon are shown as contoured plots. Vertical sections of dissolved nickel in the offshore transects of both the Arabian Sea and Bay of Bengal showed low concentration at the surface followed by an increase in the intermediate layer-reaching a maximum at 600m

depth. They showed a slight but steady increase in the bottom layer. Thus the vertical distribution of dissolved nickel resembles to that of phosphate in the upper 600m, and that of silicate in the bottom layer. The similarity of its distribution to nutrients indicate that nickel was involved in the biogeochemical cycle and gets regenerated both at shallow depths like phosphate, and in the deepwater, like silicate. Bruland (1980) observed evidence for surface depletion and deep-water maxima for the distribution of dissolved nickel in the north Pacific. According to him, vertical profiles of nickel in the top 800m appear similar to phosphate and below this depth nickel exhibits a deep maxima similar to silicate. Yeats and Campbell (1983) while studying the distribution of nickel in the northwest Atlantic Ocean, observed lowest concentrations at surface, increasing rapidly in the top 100-200m and more gradually between 200-700m, followed by a constancy from 700m to the bottom. Surface depletion and bottom enrichment of nickel can be attributed to its involvement in the biogeochemical cycling resulting in its removal from surface waters by plankton and biologically produced particulate matter, and subsequent regeneration into the water column at bottom where the biological debris while sinking undergoes either oxidation or resolubilisation. Sclater et al., (1976) reported the removal of nickel from surface waters through its incorporation in both the soft and hard parts of organisms, and its regeneration in the water column by biological degradation of the dead organisms and their decay.

Vertical sections of dissolved nickel in the inner shelf, outer shelf and offshore transect of the Arabian Sea and Bay of Bengal showed an increasing trend in its concentration with depth resembling those of nutrients. This was supported by significant positive correlations obtained in the present study between dissolved nickel and nitrate, phosphate, and silicate in the coastal and offshore waters of the Arabian Sea during intermonsoon fall and the Bay of Bengal during winter monsoon. The positive correlations observed in the Bay of Bengal were significant (at $p<0.001$) and for coastal waters the correlation are (r = 0.91, 0.91, 0.81 for nitrate, phosphate and silicate respectively), while for offshore waters (r = 0.98, 0.98, 0.87 for nitrate, phosphate and silicate respectively) during winter monsoon. Similarly, the positive

correlations observed in the Arabian Sea were significant (at p<0.001) for coastal waters and the correlation were (r = 0.90, 0.87, 0.79 for nitrate, phosphate and silicate respectively), while for offshore waters (r = 0.93, 0.90, 0.82 for nitrate, phosphate and silicate respectively) during inter monsoon fall.

The effects of the similarities and differences of dissolved Ni with nutrients were evident in the plots of Ni versus phosphate and Ni versus silicate. The Ni versus phosphate and Ni versus silicate relationship for the coastal and offshore waters of both basins are linear with a high degree of correlation, despite the fact that samples from different stations and from different water masses were included in the regression. The regression of nickel with phosphate from the coastal and offshore waters (Fig. 84 & 85) of the Bay of Bengal yields the following equations.

Ni (nM) = 0.36 + 1.54 P (μM), n = 85, r = 0.91 (Coastal waters)

Ni (nM) = 0.40 + 1.93 P (μM), n = 159, r = 0.98 (Offshore waters)

Similarly the regression of nickel with phosphate from the coastal and offshore waters (Fig. 72 & 73) of the Arabian Sea yields the following equations.

Ni (nM) = 0.11 + 1.57 P (μM), n = 106, r = 0.87 (Coastal waters)

Ni (nM) = 0.12 + 1.51 P (μM), n = 182, r = 0.90 (Offshore waters)

Thus the contributions of both Ni and P to this regression were significant (p < 0.001) in both the Arabian Sea and Bay of Bengal.

The Ni/P slopes obtained for the offshore waters of the Bay of Bengal is relatively higher (1.2 times) than the value obtained for the offshore waters of the Arabian Sea, but the Ni/P slopes for the offshore waters of the Arabian Sea (1.51×10^{-3}) is quite comparable with the values for the Pacific (0.95×10^{-3}) (Bruland, 1980) and Atlantic oceans (1.44×10^{-3} & 1.20×10^{-3}) (Yeats and Campbell, 1983;Danielson et al., 1985).

The regression of nickel with silicate from the coastal and offshore waters (Fig. 86 & 87) of the Bay of Bengal yields the following equations.

Ni (nM) = 0.32 + 0.167 Si (μM), n = 85, r = 0.81 (Coastal waters)

Ni (nM) = 1.62 + 0.081 Si (μM), n = 159, r = 0.87 (Offshore waters)

Similarly the regression of nickel with silicate from the coastal and offshore waters (Fig. 74 & 75) of the Arabian Sea yields the following equations.

Ni (nM) = 0.89 + 0.117 Si (μM), n = 106, r = 0.79 (Coastal waters)

Ni (nM) = 1.48 + 0.061 Si (μM), n = 182, r = 0.81 (Offshore waters)

Thus the contributions of both Ni and Si to this regression remained significant (p < 0.001) in both the Arabian Sea and Bay of Bengal.

These relationships imply significant downward transport of Ni in association with the carrier phases that undergo dissolution in a shallow cycle and also those dissolving in deep water. The Ni/Si slopes were found to decrease from coastal to offshore regions in the both basins as a result of strongly increasing silicate concentration towards depth in the offshore regions. The presence of a relationship between Ni and Si, which was more evident in the offshore data sets of the Arabian Sea and Bay of Bengal, reflects the fact that silicate and Ni appear to be associated with the hard parts of the phytoplankton and got regenerated slowly, and deeper older waters with a larger regenerated signal. This relationship, although still present in the coastal data sets of the Arabian Sea and Bay of Bengal, was partially masked in relatively shallow shelf waters as other processes controlling Si and Ni concentrations were significant.

The Ni/Si slopes for the coastal and offshore waters of the Bay of Bengal was relatively higher (1.3 times) than that in the coastal and offshore waters of the Arabian Sea. The Ni/Si slopes obtained for coastal waters were higher than the offshore waters for both basins. The Ni/Si slopes obtained for the offshore waters of the Arabian Sea (0.061×10^{-3}) was quite comparable with the reported values for the Pacific (3.3×10^{-5}) (Bruland, 1980) and Atlantic oceans (1.9×10^{-5}) (Yeats and Campbell, 1983). Slightly higher Ni/P and Ni/Si slopes were obtained in the present study and can be attributed to higher intercepts (concentrations) when compared with the earlier reports for Pacific and Atlantic oceans. So the concept of the above-mentioned correlations may not globally valid since the regional forcing such as upwelling, winter mixing or eddy mixing where siliceous organisms may dominate in

phytoplankton species composition and benthic fluxes probably largely determine to what extent Ni is correlated with either phosphate or silicate.

Vertical sections of particulate nickel in the inner shelf, outer shelf and offshore transect of both basins showed an increasing trend in its concentration with depth. Its enrichment at the bottom layers can be attributed to its scavenging by hydrous iron and manganese oxide phases. Takematsu et al., (1981) are of the opinion that MnO_2 surfaces accumulate nickel especially in regions where manganese precipitation rates are low. Similar enrichment of particulate nickel in the bottom was reported earlier in the Western Bay of Bengal (Rajendran et al., 1982). Considerable enrichment of nickel in the bottom nepheloid layer in Puget Sound was attributed to its scavenging by the newly formed hydrous oxide of iron and manganese (Feely et al., 1986). The percentage contribution of particulate nickel in the study area of both basins lies in the range 30-40% of total nickel, indicating that a major portion of nickel exists in dissolved fraction. Particulate nickel showed significant positive correlations (Table 14) with SPM in the coastal areas of the Arabian Sea during intermonsoon fall (r = 0.47, at p<0.001). Similarly particulate nickel showed significant positive correlations (Table 29) with SPM in the offshore areas of the Bay of Bengal (r = 0.54, at p<0.001), during winter monsoon. Significant positive correlation of particulate Ni with SPM and other particulate trace metals (Fe, Co, Cu, Zn & Pb) for both basins suggests a fractional association with suspended particles probably in the form of fine-grained terrigenous matter also.

4. 5. Copper

Copper is an essential micronutrient in living system. The principal species of Cu (11) in seawater are hydrated Cu^{2+} ion, $CuCO_3$ and Cu $(OH)^+$. A significant fraction of Cu (11) may also exist as complexes with dissolved organic matter (Riley et al., 1975). Due to its ability to change valency, copper is typically involved as an electron donor or acceptor in enzymatic reactions. There have been a few experiments, demonstrating copper limitation due to deficiency in nature. Manahan and Smith (1973) found the copper requirements of two freshwater algae to be satisfied at cupric

ion activities of 10^{-6} M, whereas Schenck (1984) found the dinoflagellate *Gonyaulax tamarensis* to be limited at cupric ion activities less than 10^{-13} M.

In contrast to the role of copper as a micronutrient, the cupric ion is potentially toxic to phytoplankton at sub-nanomolar concentrations. The mechanism of toxicity often involves competition by copper for active sites occupied by essential metals (Sunda and Guillard, 1976a,b). Due to its placement on the Irving-Williams order, copper has a strong tendency to form complexes with proteins and nucleic acids and, can render these macromolecules non-functional through complex formation. Reduced growth rates have been observed in many marine phytoplankton at cupric ion concentrations above 10^{-11} M (Gavis *et al.*, 1981; Schenck, 1984; Brand *et al.*, 1986; Sunda, 1987). Copper, therefore, can play a dual role in limiting plankton growth through nutritional deficiency or toxicity.

The dissolved copper (dCu) concentration in the water column of the eastern Arabian Sea during intermonsoon fall ranged from 0.01 to 1.88µg/l, 0.02 to 2.64µg/l and 0.08 to 1.89µg/l (averages to 1.00µg/l, 0.99µg/l and 0.81µg/l) in the inner shelf, outer shelf and offshore transects respectively. The particulate copper (pCu) concentration in the water column of the eastern Arabian Sea during intermonsoon fall ranged from 0.02 to 2.23µg/l, 0.02 to 2.90µg/l and 0.09 to 2.41µg/l (averages to 1.11µg/l, 1.10µg/l and 0.95µg/l) in the inner shelf, outer shelf and offshore transects respectively.

The dissolved copper (dCu) concentration in the water column of the southeastern Arabian Sea during intermonsoon fall ranged from 1.01 to 1.98µg/l, 0.32 to 2.64µg/l and 0.41 to 1.89µg/l (averages to 1.43µg/l, 1.35µg/l and 0.89µg/l) in the inner shelf, outer shelf and offshore transects respectively. The particulate copper (pCu) concentration in the water column of the southeastern Arabian Sea during intermonsoon fall ranged from 1.11 to 2.23µg/l, 0.35 to 2.90µg/l and 0.47 to 2.41µg/l (averages to 1.60µg/l, 1.50µg/l and 1.03µg/l) in the inner shelf, outer shelf and offshore transects respectively.

The dissolved copper (dCu) concentration in the water column of the northeastern Arabian Sea during intermonsoon fall ranged from 0.05 to 1.21µg/l, 0.04 to 1.21µg/l

and 0.06 to 1.84μg/l (averages to 0.61μg/l, 0.51μg/l and 0.71μg/l) in the inner shelf, outer shelf and offshore transects respectively. The particulate copper (pCu) concentration in the water column of the northeastern Arabian Sea during intermonsoon fall ranged from 0.06 to 1.33μg/l, 0.05 to 1.33μg/l and 0.07 to 2.22μg/l (averages to 0.67μg/l, 0.56μg/l and 0.84μg/l) in the inner shelf, outer shelf and offshore transects respectively.

Similarly the dissolved copper (dCu) concentration in the water column of the northeastern Arabian Sea during intermonsoon spring ranged from 0.26 to 1.49μg/l, 0.28 to 1.40μg/l and 0.30 to 2.68μg/l (averages to 0.65μg/l, 0.64μg/l and 0.88μg/l) in the inner shelf, outer shelf and offshore transects respectively. The particulate copper (pCu) concentration in the water column of the northeastern Arabian Sea during intermonsoon spring ranged from 0.29 to 1.74μg/l, 0.31 to 1.64μg/l and 0.32 to 2.98μg/l (averages to 0.73μg/l, 0.73μg/l and 1.00μg/l) in the inner shelf, outer shelf and offshore transects respectively.

The dissolved copper (dCu) concentration in the water column of the Bay of Bengal during winter monsoon ranged from 0.46 to 3.89μg/l, 0.41 to 2.65μg/l and 0.21 to 4.51μg/l (averages to 1.27μg/l, 1.46μg/l and 0.86μg/l) in the inner shelf, outer shelf and offshore transects respectively. The particulate copper (pCu) concentration in the water column of the Bay of Bengal during winter monsoon ranged from 0.548 to 4.20μg/l, 0.445 to 2.91μg/l and 0.24 to 4.87μg/l (averages to 1.39μg/l, 1.58μg/l and 0.94μg/l) in the inner shelf, outer shelf and offshore transects respectively.

The average concentration levels of dissolved and particulate copper in the water column of the inner shelf and outer shelf were relatively higher than the offshore transect in the Arabian Sea during intermonsoon fall while in intermonsoon spring an opposite trend was observed. Similarly the average concentration levels of dissolved and particulate iron in the water column of the inner shelf and outer shelf were relatively higher than the offshore transect in the Bay of Bengal during winter monsoon. The relative enrichment of dissolved and particulate copper towards the inner shelf when compared with the offshore regions of both basins can be attributed to the influence of land run-off and freshwater inputs into the coastal regions.

The physical processes that influence the concentration levels of copper in the Arabian Sea at the surface layers were the upwelling during intermonsoon fall and winter cooling during spring intermonsoon. Thus a comparison of average concentrations of dissolved and particulate copper (Table 9 & 10) in the whole water column of the northeastern Arabian Sea during intermonsoon fall and spring intermonsoon showed that copper was relatively high in the offshore transect during spring intermonsoon due to the effect of winter cooling processes. Further a comparison of average concentrations of dissolved and particulate copper (Table 8 & 9) in the whole water column of the southeastern Arabian Sea and northeastern Arabian Sea during intermonsoon fall showed that copper was relatively high in the inner shelf and outer shelf of the southeastern Arabian Sea due to the effect of upwelled waters. Moreover a comparison of average concentrations of dissolved and particulate copper in the whole water column of the eastern Arabian Sea during intermonsoon fall and western Bay of Bengal during winter monsoon (Table 12) showed that copper was slightly higher in the Bay of Bengal. The observed differences for Cu showed a biologic demand for Cu in the Arabian Sea when compared with the Bay of Bengal. The slight enrichment of copper in the Bay of Bengal may be the due to the large river runoff.

The vertical sections of dissolved and particulate copper in the inner shelf, outer shelf and offshore transects of the Arabian Sea during intermonsoon fall (Fig. 25, Fig. 28, Fig. 32 & Fig. 38) and intermonsoon spring (Fig. 43, Fig. 46 & Fig. 50) and Bay of Bengal (Fig. 55, Fig. 58, Fig. 62 & Fig. 68) during winter monsoon are shown as contoured plots. The vertical sections of dissolved copper in the inner shelf, outer shelf and offshore transect of both basins showed a surface enrichment, subsurface minima, followed by an increase at the bottom layers. The surface enrichment of copper can be due to river runoff or aeolian sources. Plausible explanations for the increase of copper towards bottom waters in shelf regions are (1) remobilization of copper from shelf sediments, and (2) release from organism during their degradation.

The vertical section of dissolved copper in the offshore transect of both basins exhibit a minima in the depth layer 75-300m followed by an increase up to the

bottom. Thus it showed least surface depletion unlike nutrients. Below the surface, the concentrations decreased sharply, most likely as a result of *in situ* particle scavenging at subsurface levels in the water column towards considerable depths. Below it copper concentration further increased more or less parallel towards bottom layers. Enrichment of copper in bottom waters may partly be due to its regeneration. Earlier studies in coastal and offshore regions of the Bay of Bengal (Braganca and Sanzgiri, 1980) revealed enrichment of dissolved copper in bottom waters. Satyanarayana *et al.*, (1985a) reported enrichment of both dissolved and particulate copper at bottom in harbor and coastal waters of Vishakapatnam, due to its release during the decomposition of organism.

In near bottom waters, copper may be remobilized by interactions with sediments (Kramer, 1982). Decomposition of partly reduced organic-rich sediments release copper into the water column (Kremling, 1983). Enrichment of copper in bottom waters of shelf regions in the present study may partly be due to its release from the organic-rich sediments and partly due to its regeneration from the organism. Boyle *et al.*, (1977) while studying the distribution of dissolved copper in the Pacific observed a decrease from surface maxima to top of the thermocline, followed by an increase in bottom waters. According to them, this unique distribution was maintained by aeolian input to the surface waters comparable in magnitude to the fluvial component, ubiquitous scavenging in the surface and deep waters, and a strong bottom source. On the other hand, Bruland (1980) observed a continuous increase in the concentration of copper from surface to 600m depth, uniform distribution between 600-1500m followed by a gradual increase up to the bottom in the north Pacific. Though the distribution of copper in intermediate and deep waters in both the reports were attributed to its scavenging coupled with strong bottom source, its enrichment in surface contrary to depletion reported in the latter was presumed to be a transient feature resulting from the advection of copper-rich near shore surface waters into the central regions of the Pacific Ocean. Danielson (1980) while studying the depth profile of dissolved copper in the Indian Ocean, observed a subsurface minimum at

about 200m, followed by a steady increase upto the bottom resembling the distribution of silicate.

The deep-water copper profiles in the offshore regions provide an insight into its geochemistry. Surface enrichment and mid-depth minima observed in the distribution of copper was similar to that of lead indicating that it remained intermediate between that of nutrient type elements (nickel, cadmium and zinc) and others, particularly lead. However Cu exhibited significant positive correlations with silicate in the coastal and offshore waters of the Arabian Sea and Bay of Bengal. The positive correlations observed for silicate in the Bay of Bengal was significant at $p<0.001$, for coastal waters ($r = 0.43$), and for offshore waters ($r = 0.63$) during winter monsoon. Similarly, the positive correlations observed for the same in the Arabian Sea was significant at $p<0.001$, for coastal waters ($r = 0.40$), while for offshore waters ($r = 0.43$) during inter monsoon fall.

The co-variation between copper and silica, was explicit than with any other nutrient in both basins. The regression of copper with silicate from the coastal and offshore waters (Fig. 88 & 89) of the Bay of Bengal yields the following equations;

Cu (nM) = 17.1 + 0.77 Si (μM), n = 85, r = 0.43 (Coastal waters)

Cu (nM) = 6.43 + 0.29 Si (μM), n = 159, r = 0.63 (Offshore waters)

Similarly the regression equation of copper with silicate from the coastal and offshore waters (Fig. 76 & 77) of the Arabian Sea is as follows;

Cu (nM) = 11.1 + 0.41 Si (μM), n = 106, r = 0.40 (Coastal waters)

Cu (nM) = 10.2 + 0.11 Si (μM), n = 182, r = 0.43 (Offshore waters)

Thus the role of both Cu and Si to this regression were significant ($p < 0.001$) in both the Arabian Sea and Bay of Bengal.

These relationships imply significant transport of Cu in association with the carrier phases that undergo dissolution in the water column. This also suggests an involvement of Cu in silicate regeneration cycles. The particulate copper formed at the surface seems to be more or less inert and settles in the water column. The Cu/Si slopes tend to decrease from coastal to offshore regions in both the basins as a result of strongly increasing silicate concentration towards depth in the offshore regions.

This relationship, although still present in the coastal data sets of the Arabian Sea and Bay of Bengal, is partially masked as other processes are also dominantly controlling Si and Cu concentrations which were significant relatively in shallow shelf waters. The low Cu/Si ratio found in the Arabian Sea when compared with the Bay of Bengal fits with the hypothesis that a higher Cu/Si ratio is found in areas with inputs of riverine copper (Bruland and Franks, 1983).

In the shallow waters, Cu concentrations are controlled by processes other than remineralisation such as adsorption onto particles or sedimentary inputs predominating in both basins. However in the offshore areas of both basins at bottom layers, remineralisation processes were controlling Cu concentrations. The Cu/Si slope observed in the offshore waters of Arabian Sea data set (0.11×10^{-3}) broadly agree with the Cu/Si slope reported by Pohl *et al.*, (1993) for the NE Atlantic Ocean (0.028×10^{-3}).

The vertical sections of particulate copper in the inner shelf, outer shelf and offshore transects showed a surface enrichment, subsurface minima and followed by an increase towards the bottom layers. The low values at surface and enrichment in bottom of particulate copper in shelf areas may be due to its utilization by phytoplankton, and regeneration through bacterial decomposition respectively. Moreover the exchange of dissolved and particulate fractions of copper in the water column and scavenging of dissolved copper by iron and manganese hydrous oxides are also responsible for the enrichment of particulate copper in bottom waters. Particulate matter plays an important role in the removal of copper from seawater. Landing and Feely (1981) correlated removal of particulate copper to biological activity and its regeneration in the bottom to remineralisation after bacterial decomposition of the organic carrier in the Gulf of Alaska. Satyanarayana *et al.*, (1985a) observed higher values of particulate copper at bottom in harbor and coastal waters of Vishakapatnam.

Vertical section of particulate copper in the offshore transect indicate an enrichment in the surface, a minima in the depth layer 75-300m followed by an increase up to the bottom. Surface enrichment of particulate copper may be due to the

combined effects of river runoff and high primary production. Its mid-depth minima can be due to removal of copper from total suspended matter by desorption in the water column (Bruland, 1983). Sanzgiri and Moraes (1979) while studying the distribution of trace metals in Laccadive Sea observed high concentrations of particulate copper in deeper layers when compared with surface waters. Particulate copper showed significant positive correlations (Table 14 & 20) with SPM in the coastal areas of the Arabian Sea during intermonsoon fall (r = 0.48, at p<0.001) and spring intermonsoon(r = 0.51, at p<0.001). Similarly particulate copper showed significant positive correlations (Table 26) with SPM in the coastal areas of the Bay of Bengal (r = 0.40, at p<0.001), during winter monsoon. Significant positive correlation of particulate Cu with SPM and other particulate metals (Fe & Zn) for both basins suggests a possible association with suspended particles probably occur in the form of fine-grained hydrogenous matter. Thus the gradients in concentrations from surface to bottom were a consequence of a balance between biological removal, remineralisation and adsorption onto particles, whereas below 500m the preponderance of remineralisation relative to adsorption causes the copper concentration to increase. The contribution of particulate copper to the total varied between 52-55% indicating its dominance over dissolved form in both the basins. This may be due to scavenging of dissolved copper by hydrous iron and manganese oxide phases from the seawater in the form of colloidal suspension.

4. 6. Zinc

Zn is known to be incorporated into diatom frustules (Ellwood and Hunter, 1999) and hence covaries with Si (Bruland, 1980). Zn is also essential for various metabolic functions including carbon fixation via carbonic anhydrase (Sunda and Huntsman, 1992, 1995; Morel et al., 1994). The speciation of Zn is very sensitive to pH changes. At pH 8.2, the principal species were Zn $(OH)^+$, hydrated Zn^{2+}ion and $ZnCO_3$.

The dissolved zinc (dZn) concentration in the water column of the eastern Arabian Sea during intermonsoon fall ranged from 0.40 to 3.14µg/l, 0.30 to 2.87µg/l and 0.33 to 9.84µg/l (averages to 1.46µg/l, 1.55µg/l and 2.81µg/l) in the inner shelf, outer shelf and offshore transects respectively. The particulate zinc (pZn)

concentration in the water column of the eastern Arabian Sea during intermonsoon fall ranged from 0.81 to 5.09μg/l, 0.65 to 4.65μg/l and 0.58 to 15.94μg/l (averages to 2.55μg/l, 2.63μg/l and 4.59μg/l) in the inner shelf, outer shelf and offshore transects respectively.

Similarly, the dissolved zinc (dZn) concentration in the water column of the southeastern Arabian Sea during intermonsoon fall ranged from 0.40 to 3.14μg/l, 0.40 to 2.87μg/l and 0.56 to 9.84μg/l (averages to 1.56μg/l, 1.66μg/l and 3.21μg/l) in the inner shelf, outer shelf and offshore transects respectively. The particulate zinc (pZn) concentration in the water column of the southeastern Arabian Sea during intermonsoon fall ranged from 0.81 to 5.09μg/l, 0.86 to 4.65μg/l and 1.02 to 15.94μg/l (averages to 2.67μg/l, 2.81μg/l and 5.25μg/l) in the inner shelf, outer shelf and offshore transects respectively.

The dissolved zinc (dZn) concentration in the water column of the northeastern Arabian Sea during intermonsoon fall ranged from 0.62 to 2.51μg/l, 0.30 to 2.15μg/l and 0.33 to 6.99μg/l (averages to 1.37μg/l, 1.40μg/l and 2.27μg/l) in the inner shelf, outer shelf and offshore transects respectively. The particulate zinc (pZn) concentration in the water column of the northeastern Arabian Sea during intermonsoon fall ranged from 1.00 to 4.07μg/l, 0.65 to 3.48μg/l and 0.58 to 11.32μg/l (averages to 2.45μg/l, 2.40μg/l and 3.70μg/l) in the inner shelf, outer shelf and offshore transects respectively.

The dissolved zinc (dZn) concentration in the water column of the northeastern Arabian Sea during intermonsoon spring ranged from 0.98 to 3.18μg/l, 0.91 to 4.11μg/l and 0.97 to 9.84μg/l (averages to 1.62μg/l, 1.81μg/l and 3.37μg/l) in the inner shelf, outer shelf and offshore transects respectively. The particulate zinc (pZn) concentration in the water column of the northeastern Arabian Sea during intermonsoon spring ranged from 1.70 to 5.47μg/l, 1.71 to 7.11μg/l and 1.83 to 17.5μg/l (averages to 2.82μg/l, 3.15μg/l and 5.82μg/l) in the inner shelf, outer shelf and offshore transects respectively.

The dissolved zinc (dZn) concentration in the water column of the Bay of Bengal during winter monsoon ranged from 0.92 to 10.10μg/l, 0.94 to 10.7μg/l and 0.88 to

10.7μg/l (averages to 3.26μg/l, 3.45μg/l and 3.03μg/l) in the inner shelf, outer shelf and offshore transects respectively. The particulate zinc (pZn) concentration in the water column of the Bay of Bengal during winter monsoon ranged from 2.00 to 16.23μg/l, 2.1 to 18.6μg/l and 1.61 to 16.8μg/l (averages to 6.33μg/l, 6.49μg/l and 5.12μg/l) in the inner shelf, outer shelf and offshore transects respectively.

The average concentration levels of dissolved and particulate zinc in the water column of the offshore waters were relatively higher than the inner shelf of the Arabian Sea during intermonsoon fall and intermonsoon spring. Similarly the average concentration levels of dissolved and particulate zinc in the water column of the offshore waters were relatively higher than the inner shelf of the Bay of Bengal during winter monsoon. Thus in both basins dissolved and particulate Zn showed relative enrichment towards offshore regions.

The main physical processes that may be affecting the concentration levels of zinc in the Arabian Sea at the surface layers are the upwelled & eddy mixed waters during intermonsoon fall and winter cooled waters during spring intermonsoon. In the offshore transects of the Bay of Bengal during winter monsoon, eddy-mixing plays a role in the supplying zinc to surface layers. Thus a comparison of average concentrations of dissolved and particulate zinc (Table 9 & 10) in the water column of the northeastern Arabian Sea during intermonsoon fall and spring intermonsoon showed that zinc was relatively high in the offshore transect during spring intermonsoon due to the effect of winter cooling processes. Further a similar comparison of average concentrations of dissolved and particulate zinc (Table 8 & 9) in the water column of the southeastern and northeastern Arabian Sea during intermonsoon fall showed that zinc was relatively high in the inner shelf, outer shelf and offshore transects of the southeastern Arabian Sea due to the effect of upwelled waters.

Moreover a comparison of average concentrations of dissolved and particulate zinc in the water column of the Arabian Sea during intermonsoon fall and Bay of Bengal during winter monsoon (Table 12) showed that zinc was 1.8 times higher in the Indian EEZ of the Bay of Bengal. The observed differences for Zn showed a

biological demand for Zn in the Arabian Sea even though upwelling brings up rich subsurface zinc waters to the surface.

Vertical sections of dissolved zinc in the inner shelf, outer shelf and offshore transect showed low values at the surface, followed by an increasing trend with depth, which may be due to its regeneration from sinking biological matter. Surface depletion and bottom enrichment of dissolved Zn observed in the present study lend evidence to its involvement in biogeochemical cycling. Sanzgiri and Moraes (1979) observed significant enrichment of dissolved Zn in deeper waters of Laccadive Sea. Stoffyn (1981) reported concentration maxima near the surface (above 30m) followed by an increase with depth within the surface water mass, in the vertical profiles of iron and zinc off Nova Scotia waters. This phenomenon was explained on the basis of *in situ* mechanisms wherein an increase in trace metal concentrations with depth was caused by their regeneration from sinking biological matter which remove the dissolved trace metals from water column in the photic zone. Relatively higher concentrations of dissolved zinc in bottom compared to surface waters reported in the coastal waters of Vishakapatnam (Satyanarayana *et al.*, 1985a) were explained on the basis of its involvement in the biogeochemical cycling.

The vertical section of dissolved zinc in the offshore transects showed relatively low concentrations at surface and rapid increase in the intermediate layer reaching maximum at about 500m depth followed by a steady increase towards the bottom layer. Thus the vertical distribution of dissolved zinc resembles those of nutrients (nitrate and phosphate) in the surface and intermediate layers, and that of silicate in the bottom layer. This was supported by significant positive correlations obtained in the present study between dissolved zinc and nitrate, phosphate, and silicate in the coastal and offshore waters of the Arabian Sea during intermonsoon fall and Bay of Bengal during winter monsoon. The positive correlations observed in the Bay of Bengal which was significant at p<0.001, for coastal waters were (r = 0.65, 0.68, 0.61 for nitrate, phosphate and silicate respectively), while for offshore waters (r = 0.80, 0.82, 0.97 for nitrate, phosphate and silicate respectively) during winter monsoon. Similarly, the positive correlations observed in the Arabian Sea significant at

p<0.001, for coastal waters were (r = 0.77, 0.79, 0.89 for nitrate, phosphate and silicate respectively), while for offshore waters (r = 0.74, 0.74, 0.98 for nitrate, phosphate and silicate respectively) during inter monsoon fall.

The co-variation between zinc and silica, which was the best fit than with any other nutrient in both basins. The regression of zinc with silicate from the coastal and offshore waters (Fig. 90 & 91) of the Bay of Bengal yields the following equations.

Zn (nM) = 28.6 + 3.70 Si (μM), n = 85, r = 0. 61 (Coastal waters)

Zn (nM) = 10.2 + 1.48 Si (μM), n = 159, r = 0. 97 (Offshore waters)

Similarly the regression equation of zinc with silicate from the coastal and offshore waters (Fig. 78 & 79) of the Arabian Sea is as follows;

Zn (nM) = 12.1+ 1.01 Si (μM), n = 106, r = 0. 89 (Coastal waters)

Zn (nM) = 10.9 + 1.38 Si (μM), n = 182, r = 0. 98 (Offshore waters)

Thus the contributions of both Zn and Si to this regression are significant (p < 0.001) in both the Arabian Sea and Bay of Bengal.

The Zn/Si slopes tend to decrease from coastal to offshore regions in the Bay of Bengal and vice versa in the Arabian Sea. This relationship, present in the coastal data sets of the Bay of Bengal, was relatively higher than Arabian Sea data sets. This was due to masking of Zn/Si slope as processes other than biogeochemical were also important in controlling Si and Zn concentrations in relatively shallow shelf waters. The high scatter in the linear plot coastal data sets for Bay of Bengal showed riverine influences. The low Zn/Si slope obtained for the Arabian Sea was a result of low zinc concentrations in the Arabian Sea when compared to the Bay of Bengal data.

Further, the correlation between zinc and silicate suggests its removal from the surface waters and transportation to bottom as a trace constituent of some biological carrier phase. Since phytoplankton was known to concentrate large amounts of zinc, it may be probable that diatoms play an important role in its biogeochemical cycling. Braganca and Sanzgiri (1980) while studying the trace metal distribution in the coastal and offshore regions of the Bay of Bengal reported similar enrichment of zinc in bottom waters, which they attributed to its regeneration by organisms. Bruland (1980) observed a linear relationship between zinc and silicate in the north Pacific

that was attributed to its removal from the surface waters and transport down to the water column as a trace constituent of some biological carrier phase. He believed that zinc was involved in a deep regeneration cycle analogous to opal and calcium carbonate.

Vertical sections of particulate zinc in the inner shelf, outer shelf and offshore transect of both basins showed low values at the surface, followed by an increasing trend with depth. Increase of particulate zinc in the intermediate and bottom waters of the shelf and offshore regions may be due to its scavenging by the hydrous oxides of iron and manganese. Several workers (Li, 1981; Balistrieri and Murray, 1982) conclusively proved the ability of iron and manganese oxide coatings in scavenging trace metals like cobalt, copper, cadmium and zinc from seawater. The percentage contribution of particulate zinc in the study area lies in the range 60-68% of total zinc indicating that a major portion of it exists in particulate form. Particulate zinc showed significant positive correlations (Table 14 & 20) with SPM in the coastal areas of the Arabian Sea during intermonsoon fall and intermonsoon spring($r = 0.46$, at $p<0.001$). Similarly particulate zinc showed significant positive correlations (Table 26) with SPM in the coastal areas of the Bay of Bengal ($r = 0.38$, at $p<0.001$), during winter monsoon. Significant positive correlations of particulate Zn with SPM and other particulate trace metals (Fe, Co & Ni) for both basins suggest a portion of its association with suspended particles probably of terrigenous origin and occur in association with alumino silicates.

4.7. Cadmium

The dissolved cadmium (dCd) concentration in the water column of the eastern Arabian Sea during intermonsoon fall ranged from 0.302 to 2.349nM, 0.258 to 2.562nM and 0.214 to 2.340nM (averages to 1.059nM, 1.369nM and 1.120nM) in the inner shelf, outer shelf and offshore transects respectively. The particulate cadmium (pCd) concentration in the whole water column of the eastern Arabian Sea during intermonsoon fall ranged from 0.064 to 0.276nM, 0.092 to 0.276nM and 0.065 to 0.205nM (averages to 0.173nM, 0.194nM and 0.135nM) in the inner shelf, outer shelf and offshore transects respectively.

The dissolved cadmium (dCd) concentration in the water column of the southeastern Arabian Sea during intermonsoon fall ranged from 0.302 to 2.349nM, 0.258 to 2.331nM and 0.214 to 2.340nM (averages to 1.216nM, 1.393nM and 1.168nM) in the inner shelf, outer shelf and offshore transects respectively. The particulate cadmium (pCd) concentration in the water column of the southeastern Arabian Sea during intermonsoon fall ranged from 0.064 to 0.276nM, 0.054 to 0.355nM and 0.045 to 0.205nM (averages to 0.190nM, 0.206nM and 0.141nM) in the inner shelf, outer shelf and offshore transects respectively.

The dissolved cadmium (dCd) concentration in the water column of the northeastern Arabian Sea during intermonsoon fall ranged from 0.525 to 1.966nM, 0.347 to 2.562nM and 0.338 to 1.939nM (averages to 0.917nM, 1.337nM and 1.056nM) in the inner shelf, outer shelf and offshore transects respectively. The particulate cadmium (pCd) concentration in the water column of the northeastern Arabian Sea during intermonsoon fall ranged from 0.110 to 0.187nM, 0.073 to 0.224nM and 0.071 to 0.164nM (averages to 0.158nM, 0.178nM and 0.127nM) in the inner shelf, outer shelf and offshore transects respectively.

The dissolved cadmium (dCd) concentration in the water column of the northeastern Arabian Sea during intermonsoon spring ranged from 0.578 to 1.886nM, 0.365 to 2.322nM and 0.365 to 2.206nM (averages to 0.842nM, 1.014nM and 1.280nM) in the inner shelf, outer shelf and offshore transects respectively. The particulate cadmium (pCd) concentration in the water column of the northeastern Arabian Sea during intermonsoon spring ranged from 0.118 to 0.245nM, 0.077 to 0.418nM and 0.077 to 0.327nM (averages to 0.162nM, 0.166nM and 0.187nM) in the inner shelf, outer shelf and offshore transects respectively.

The dissolved cadmium (dCd) concentration in the water column of the Bay of Bengal during winter monsoon ranged from 0.107 to 0.845nM, 0.089 to 1.432nM and 0.107 to 2.224nM (averages to 0.297nM, 0.599nM and 0.931nM) in the inner shelf, outer shelf and offshore transects respectively. The particulate cadmium (pCd) concentration in the water column of the Bay of Bengal during winter monsoon ranged from 0.018 to 0.125nM, 0.018 to 0.151nM and 0.022 to 0.214nM (averages to

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0.046nM, 0.071nM and 0.107nM) in the inner shelf, outer shelf and offshore transects respectively.

However, physical processes that may also be affecting the concentration levels of cadmium in the Arabian Sea at the surface layers are the upwelled & eddy mixed waters during intermonsoon fall and winter cooled waters during spring inter monsoon. In the offshore transects of the Bay of Bengal during winter monsoon eddy mixing plays a role in the supplying cadmium to surface layers. Thus a comparison of average concentrations of dissolved and particulate cadmium (Table 9 & 10) in the whole water column of the northeastern Arabian Sea during intermonsoon fall and spring intermonsoon showed that cadmium is relatively high in the offshore transect during spring intermonsoon due to the effect of winter cooling processes. Further a comparison of average concentrations of dissolved and particulate cadmium (Table 8 & 9) in the whole water column of the southeastern Arabian Sea and northeastern Arabian Sea during intermonsoon fall showed that cadmium was relatively high in the inner shelf, outer shelf and offshore transects of the southeastern Arabian Sea due to the effect of upwelled and eddy mixed waters.

Surface water characteristics may also be modified by mixing with deep-water masses brought to the surface by upwelling. This can influence trace metal distributions if there was a significant difference between deep and surface concentrations. This may be the case for cadmium along the southwest coast of India. The occurrence of upwelling in the area may partially explain why the cadmium concentrations reported in this study were higher in the southeastern Arabian Sea.

Moreover a comparison of average concentrations of dissolved and particulate cadmium in the water column of the eastern Arabian Sea during intermonsoon fall and western Bay of Bengal during winter monsoon (Table 12) showed that cadmium was 1.94 times higher in the Arabian Sea. The observed differences for Cd showed a biological demand for Cd in the Bay of Bengal even though river runoff brings cadmium to surface waters.

Vertical sections of dissolved cadmium in the inner shelf, outer shelf and offshore transect of both basins showed an increasing trend with depth resembling those of

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other trace metals (nickel and zinc) and nutrients. In general, dissolved cadmium showed relatively higher values in bottom when compared with surface waters. The mean concentration for surface and deep waters in the inner shelf of the Bay of Bengal during winter monsoon and Arabian Sea during intermonsoon fall showed enrichment in deep waters by a factor of 5. The mean concentration for surface and deep waters in the outer shelf of the Bay of Bengal during winter monsoon and Arabian Sea during intermonsoon fall showed enrichment in deep waters by a factor of 6 and 9 respectively. However the mean concentration for surface and deep waters in the offshore regions of the Bay of Bengal during winter monsoon and Arabian Sea during intermonsoon fall showed an enrichment in deep waters by a factor of 7 and 4.5 respectively. Similar enrichment factors of about 5 (Bender and Gagner, 1976) and 4 (Danielson, 1980) were reported for the Sargassso Sea and the Indian Ocean respectively. However, Boyle *et al.*, (1976) observed somewhat higher (10) enrichment factor for the Pacific Ocean. These trends are apparently a reflection of the general pattern of bottom water circulation with sinking of water masses and their subsequent movements.

Vertical sections of dissolved cadmium in the offshore waters of both basins showed relatively lower concentrations at surface followed by a rapid increase in the intermediate layer-reaching maximum in the depth layer 300-600m. In the bottom layer (below 750m) the concentration of cadmium remained almost constant. Thus the distribution of cadmium was often dominated by its involvement in a shallow regeneration cycle similar to those of phosphate and nitrate. Such a distribution indicates uptake of cadmium by organism at the surface, and its regeneration from sinking biological debris in the deeper water column by oxidative processes (Stoffyn, 1981). Since cadmium has no physiological role, it is probably adsorbed on the surface of plankton debris or faecal pellets during its transport to bottom waters (Kremling *et al.*, 1978). It is clear from the close relationship with macronutrients that Cd is closely involved in organic-matter formation through photosynthesis and subsequent remineralisation of the plankton (Sunda, 1994). The exact mechanism by which Cd is taken up by phytoplankton was not well understood at present.

Replacement of Zn by Cd within phytoplankton has been reported (Price and Morel, 1990; Lee et al., 1995). Recently, Cd in the form of carbonic anhydrase has been detected in Zn-stressed diatoms (Cullen et al., 1999). However in the Arabian Sea, upwelling and winter mixing would bring waters with high concentrations of Zn to the surface waters, so that Cd substitution for Zn may be relatively unimportant at this site.

Dissolved cadmium showed a high degree of covariance with nutrients, as evident from the vertical sections of the inner, outer and offshore transects of both Arabian Sea and Bay of Bengal. This was supported by significant positive correlations obtained in the present study between dissolved nickel and nitrate, phosphate, and silicate in the coastal and offshore waters of the Arabian Sea during intermonsoon fall and Bay of Bengal during winter monsoon. The positive correlations observed in the Bay of Bengal was significant at $p<0.001$ and for coastal waters the correlations were ($r = 0.90$, 0.90, 0.75 for nitrate, phosphate and silicate), while for offshore waters ($r = 0.95$, 0.96, 0.86 for nitrate, phosphate and silicate respectively) during winter monsoon. Similarly, the positive correlations observed in the Arabian Sea significant at $p<0.001$, for coastal waters are ($r = 0.83$, 0.89, 0.85 for nitrate, phosphate and silicate respectively), while for offshore waters ($r = 0.88$, 0.96, 0.87 for nitrate, phosphate and silicate respectively) during inter monsoon fall.

The co-variation between cadmium and phosphate showed one of the best co-variations of nutrients in both basins. Throughout the water-column, a remarkable correlation with nutrients phosphate or nitrate was found, indicative of an involvement of Cd in the marine biological cycle. The regression of cadmium with phosphate from the coastal and offshore waters (Fig. 94 & 95) of the Bay of Bengal gives the following equations.

Cd (nM) = 0.20 + 0.43 P (μM), n = 85, r = 0.90 (Coastal waters)

Cd (nM) = 0.11 + 0.49 P (μM), n = 159, r = 0.96 (Offshore waters)

Similarly the regression of cadmium with phosphate from the coastal and offshore waters (Fig. 82 & 83) of the Arabian Sea yields the following equations;

Cd (nM) = 0.20 + 0.70 P (μM), n = 106, r = 0.89 (Coastal waters)

Cd (nM) = 0.26 + 0.46 P (μM), n = 182, r = 0.96 (Offshore waters)

Thus the contributions of both Cd and P to this regression were significant (p < 0.001) in both the Arabian Sea and Bay of Bengal. The Cd/P slopes obtained in the shelf waters were higher in the Arabian Sea than offshore waters due to a consequence of upwelling observed during this period.

The Cd/P slopes obtained for the offshore waters of the Bay of Bengal was relatively higher than the value obtained for the offshore waters of the Arabian Sea. The Cd/P slopes obtained for the offshore waters of the Arabian Sea (0.46×10^{-3}) was slightly higher compared with the reported values for the Pacific (3.47×10^{-4}) (Bruland, 1980), and Atlantic oceans (1.9×10^{-4}) (Yeats and Campbell, 1983) respectively.

The regression of cadmium with nitrate from the coastal and offshore waters (Fig. 92 & 93) of the Bay of Bengal yields the following equations;

Cd (nM) = 0.27 + 0.031 N (μM), n = 85, r = 0.90 (Coastal waters)

Cd (nM) = 0.18 + 0.037 N (μM), n = 159, r = 0.95 (Offshore waters)

Similarly the regression of cadmium with nitrate from the coastal and offshore waters (Fig. 80 & 81) of the Arabian Sea yields the following equations.

Cd (nM) = 0.73 + 0.045 N (μM), n = 106, r = 0.83 (Coastal waters)

Cd (nM) = 0.57 + 0.035 N (μM), n = 182, r = 0.88 (Offshore waters)

Thus the contributions of both Cd and N to this regression were significant (p < 0.001) in both the Arabian Sea and Bay of Bengal. The Cd/N slopes obtained in the shelf waters were higher in the Arabian Sea than offshore waters due to a consequence of upwelling observed during this period.

The Cd/N slopes obtained for the offshore waters of the Bay of Bengal were slightly higher than the Arabian Sea offshore waters. The Cd/N slopes obtained for the offshore waters of the Arabian Sea (0.035×10^{-3}) was almost same with the reported values for the Pacific ocean (3.47×10^{-4}) (Bruland, 1980) respectively.

In all the observed correlating properties, there was substantial differences in the metal-nutrient slopes for the coastal and offshore waters of the Arabian Sea and Bay of Bengal. Correlating properties throughout the vertical water column was in fact a

violation of a basic principle of the water exchange in the ocean, proceeding predominantly along isopycnals, i.e. horizontally. Since surface and deep waters were separated by a strong density gradient and had totally different renewal time scales, it may not be surprising if one observes different slopes in both water masses of the Arabian Sea and Bay of Bengal. This was because of the deep water Cd/P ratio, probably a function of performed concentrations, regeneration of both elements during decomposition of organic matter and the general deep-water circulation. Currently, the global distribution of Cd/P slope in surface, thermocline and deep waters is consistent with preferential biogeochemical removal of Cd versus phosphate from surface waters (de Baar *et al.*, 1994).

Vertical sections of particulate cadmium in the inner shelf, outer shelf and offshore transect of both basins showed a slight increasing trend with depth. In the offshore transects, the profiles of particulate cadmium reveal an increasing trend with depth to 200m, followed by near constancy in the intermediate and bottom layers. This may be due to the scavenging of dissolved cadmium from seawater by hydrous oxides of iron and manganese. The suspended cadmium level found in the euphotic surface layer of both basins, which was also rather patchy, was most probably generated by biota, which actively accumulates cadmium. The plankton in these cold waters probably dissolves more slowly, owing to its high fat content, and consequently stays in the water column longer.

The percentage contribution of particulate cadmium in the study area of both basins remained in the range 8-17% of total cadmium indicating that a major portion of it exists in dissolved fraction. This may be due to its inertness to adsorption onto solid surfaces, and poor scavenging efficiency of cadmium by hydrous iron and manganese oxides. Oakley *et al.*, (1981) were of the opinion that cadmium has very low affinity for adsorption onto solid surfaces. While studying the distribution of copper, lead and cadmium, Balls (1985) reported occurrence of dominant fraction (> 95%) of dissolved cadmium in the coastal waters of the western North Sea. Villa and Pucci (1987) reported the occurrence of 74% of cadmium in dissolved fraction in the Blanca Bay.

4. 8. Lead

Dissolved lead distribution in ocean waters is substantially influenced by human activities. The principal dissolved lead species are probably $Pb(OH)^+$ and $PbCO_3$ with lesser proportions of $PbCl^+$ and $PbCl_2$. Lead showed substantial enrichment in surface relative to bottom waters due to its anthropogenic atmospheric input (Schaule and Patterson, 1981). It is probably associated with both organic and inorganic phases of marine particulates. On an average, particulate lead comprises of 50-80% of the total in inshore waters (Preston et al., 1972).

The dissolved lead (dPb) concentration in the water column of the eastern Arabian Sea during intermonsoon fall ranged from 0.050 to 1.335µg/l, 0.021 to 1.335µg/l and 0.030 to 1.900µg/l (averages to 0.468µg/l, 0.344µg/l and 0.285µg/l) in the inner shelf, outer shelf and offshore transects respectively. The particulate lead (pPb) concentration in the water column of the eastern Arabian Sea during intermonsoon fall ranged from 0.070 to 2.410µg/l, 0.031 to 2.340µg/l and 0.041 to 1.860µg/l (averages to 0.793µg/l, 0.576µg/l and 0.485µg/l) in the inner shelf, outer shelf and offshore transects respectively.

The dissolved lead (dPb) concentration in the water column of the southeastern Arabian Sea during intermonsoon fall ranged from 0.102 to 1.335µg/l, 0.100 to 1.335µg/l and 0.092 to 1.900µg/l (averages to 0.576µg/l, 0.496µg/l and 0.366µg/l) in the inner shelf, outer shelf and offshore transects respectively. The particulate lead (pPb) concentration in the water column of the southeastern Arabian Sea during intermonsoon fall ranged from 0.154 to 2.410µg/l, 0.150 to 2.340µg/l and 0.141 to 3.100µg/l (averages to 0.991µg/l, 0.830µg/l and 0.621µg/l) in the inner shelf, outer shelf and offshore transects respectively.

The dissolved lead (dPb) concentration in the water column of the northeastern Arabian Sea during intermonsoon fall ranged from 0.050 to 1.300µg/l, 0.021 to 0.328µg/l and 0.030 to 0.640µg/l (averages to 0.371µg/l, 0.142µg/l and 0.177µg/l) in the inner shelf, outer shelf and offshore transects respectively. The particulate lead

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(pPb) concentration in the water column of the northeastern Arabian Sea during intermonsoon fall ranged from 0.070 to 2.210μg/l, 0.031 to 0.600μg/l and 0.041 to 1.120μg/l (averages to 0.613μg/l, 0.238μg/l and 0.303μg/l) in the inner shelf, outer shelf and offshore transects respectively.

The dissolved lead (dPb) concentration in the water column of the northeastern Arabian Sea during intermonsoon spring ranged from 0.003 to 0.241μg/l, 0.006 to 0.275μg/l and 0.003 to 1.520μg/l (averages to 0.077μg/l, 0.068μg/l and 0.172μg/l) in the inner shelf, outer shelf and offshore transects respectively. The particulate lead (pPb) concentration in the water column of the northeastern Arabian Sea during intermonsoon spring ranged from 0.005 to 0.410μg/l, 0.010 to 0.542μg/l and 0.005 to 2.580μg/l (averages to 0.130μg/l, 0.117μg/l and 0.289μg/l) in the inner shelf, outer shelf and offshore transects respectively.

The dissolved lead (dPb) concentration in the water column of the Bay of Bengal during winter monsoon ranged from 0.061 to 0.485μg/l, 0.035 to 0.873μg/l and 0.048 to 0.511μg/l (averages to 0.153μg/l, 0.152μg/l and 0.150μg/l) in the inner shelf, outer shelf and offshore transects respectively. The particulate lead (pPb) concentration in the water column of the Bay of Bengal during winter monsoon ranged from 0.070 to 0.650μg/l, 0.050 to 1.420μg/l and 0.080 to 1.100μg/l (averages to 0.259μg/l, 0.246μg/l and 0.250μg/l) in the inner shelf, outer shelf and offshore transects respectively.

The vertical sections of dissolved lead in the inner shelf, outer shelf and offshore transects of both basins showed a surface enrichment, subsurface minima and followed by a near constancy at intermediate and bottom waters. A comparison of the average concentration of dissolved and particulate Pb in the water column of the eastern Arabian Sea during intermonsoon fall and western Bay of Bengal during winter monsoon showed that Pb was 2.4 times higher in the Arabian Sea and may be due to the existence of higher anthropogenic sources from the West coast of India than East coast. Surface enrichment of lead in the inner, outer and offshore transects of both basins indicated that its distribution was controlled primarily through atmosphere. This maximum was thought to be caused by an input of atmospheric

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deposition of anthropogenic particles, which were rich in lead. Enrichment of 15-fold of lead in the upper part of the water column relative to the deep waters in the north Pacific is believed to be due to anthropogenic input and its short residence time ($<$ 100 years) within the water column (Schuale and Patterson, 1981). Sanzgiri and Braganca (1981) observed higher concentrations of lead at surface when compared to bottom waters in the Andaman Sea. Satyanarayana *et al.*, (1985a) also had observed higher values of dissolved lead at surface in coastal waters of Vishakapatnam, which they attributed to anthropogenic input. Relatively low values in subsurface water can be attributed to its uptake by phytoplankton during photosynthesis. Further, a possible exchange between the dissolved and particulate phases of lead may partly be possible for the slight increase in the subsurface waters. The decrease in lead at subsurface waters of both basins was indicative of transfer of dissolved Pb to the particulate phase, either by biological uptake or scavenging or passive adsorption reactions above the seasonal thermocline, and a partial release of Pb to solution in deeper layers (by organic matter remineralisation) above the permanent thermocline. The absence of significant concentration gradients at intermediate depths in the vertical profiles of both basins was in support of this interpretation. Once released in solution, dissolved Pb is removed from the water column by adsorption onto settling inorganic particles, leading to the low, uniform concentration levels observed in the deep waters. This explanation is in agreement with scavenging models of metals (Moran and Moore, 1992) where scavenging is described as a two step process: a reversible association between metals and biogenic particles in surface waters followed by an irreversible adsorption and removal of released metals onto settling particles at depth.

The vertical sections of particulate lead in the inner shelf, outer shelf and offshore transect of both basins showed a surface enrichment, subsurface minima and followed by a near constancy at intermediate and the bottom layers. Surface enrichment of particulate lead can be attributed to the combined effects of river runoff, atmospheric input and high primary production. Its decrease in the subsurface layer (50-200m) may be due to degradation processes. The percentage contribution of particulate lead in the study area lies in the range 60-65% of total lead indicating that a major portion

of it exists in particulate form. Balls (1985) observed a similar dominance of particulate lead over dissolved fraction in the coastal waters of the western North Sea. High concentration of particulate lead was attributed to its adsorption on organic particulates. Particulate lead showed significant positive correlations (Table 17 & 23) with SPM in the offshore areas of the Arabian Sea during intermonsoon fall (r = -0.43, at p<0.001) and intermonsoon spring(r = -0.50, at p<0.001). Similarly particulate lead showed significant positive correlations (Table 29) with SPM in the offshore areas of the Bay of Bengal (r = 0.32, at p<0.001), during winter monsoon. Significant positive correlations of particulate Pb with SPM and other particulate trace metals (Cu & Zn) for both basins suggest its dominant association with fine-grained suspended particles probably of terrigenous origin.

4. 9. Salinity and its relationships with trace metals in the Arabian Sea and Bay of Bengal

Least-squares linear regression is used for an analysis of the metal-salinity correlation, where a linear relationship would indicate conservative behaviour (Officer, 1979). A scatter in the regression is caused by presence of several river water runoff and low and high saline end-members, and by processes including aeolian and sedimentary sources, physical process such as upwelling or convective mixing, water column removal by *in situ* biological processes etc.

There is a considerable difference in the metal versus salinity plots for the Arabian Sea and Bay of Bengal waters suggesting that metal concentrations are salinity dependent. The plots of metal concentrations against salinity in the Bay of Bengal where riverine influences are important showed trends in the data, which in turn reflect the relative magnitude of riverine inputs. The trends of increasing metal concentration with increasing salinity were generally observed for most metals in the Bay of Bengal while an opposite trend of increasing metal concentrations with a decreasing salinity were observed in the Arabian Sea.

The near-conservative behavior of Cu and Ni with salinity has been reported for European shelf waters (Burton *et al.*, 1993; Hydes and Kremling, 1993; Tappin *et al.*, 1995; Achterberg *et al.*, 1999). In the Arabian Sea similar relationships could be

observed in the coastal and offshore waters. However in the Bay of Bengal similar relationships will be observed when data on metals from coastal and offshore waters were plotted against salinity. This was, in part, because only a narrow range of salinity was covered, but also because at depth, the mixing between oceanic water masses dominates over the influence of terrestrial inputs or riverine discharges. For offshore waters, linear relationships were obtained for Cd, Zn and Ni. These relationships showed that surface waters at the Arabian Sea were subjected to increased terrestrial influence than the Bay of Bengal, where metal concentrations were influenced by rivers. This was in agreement with the general hydrography of the Arabian Sea and Bay of Bengal. The Bay of Bengal is influenced by strong freshwater influences whereas Arabian Sea is subjected to excess evaporation over precipitation. The metal concentrations in the surface waters of the Arabian Sea and Bay of Bengal mirror the salinity.

Distribution of dissolved trace metals in the oceans will be interpreted to the extent to which they behave conservatively during mixing of the different water bodies. Major metal fluxes to Bay of Bengal and Arabian Sea come from rivers, land runoff, aeolian sources as well as from the biogenic particles produced in the euphotic zone.

In the coastal and offshore waters (n = 105 & 182 respectively) of the Arabian Sea, during intermonsoon fall (Table 13 & 16 and Fig. 96 & 97), Fe-Salinity relations observed were (r = -0.41, significant at p< 0.001 & -0.18 (not significant), respectively) and during intermonsoon spring (Table 19 & 22 and Fig. 108 & 109), it was (r = -0.06 (not significant) & -0.61 significant at p< 0.001, respectively). Similarly Fe-Salinity relations observed in the coastal and offshore waters of the Bay of Bengal (Table 25 & 28 and Fig. 120 & 121) were (r = 0.12 & -0.14 respectively), during winter monsoon. In the coastal and offshore waters of the Arabian Sea, during intermonsoon fall (Table 13 & 16 and Fig. 98 & 99) Co-Salinity relations observed were (r = -0.39 & -0.56 significant at p< 0.001, respectively) and during inter monsoon spring (Table 19 & 22 and Fig. 110 & 111) it was (r = -0.11 (not significant) & -0.24 significant at p< 0.01, respectively). Similarly Co-Salinity relations (Table 25

& 28 and Fig. 122 & 123) observed in the coastal and offshore waters of the Bay of Bengal were (r = 0.30 significant at p< 0.001, & 0.08(not significant) respectively), during winter monsoon. In the coastal and offshore waters of the Arabian Sea, during intermonsoon fall (Table 13 & 16 and Fig. 102 & 103) Cu-Salinity relations observed were (r = -0.66 significant at p< 0.001, & -0.13 respectively) and during inter monsoon spring (Table 19 & 22 and Fig. 114 & 115) it was (r = -0.01 (not significant) & -0.76 significant at p< 0.001, respectively). Similarly Cu-Salinity relations (Table 25 & 28 and Fig. 126 & 127) observed in the coastal and offshore waters of the Bay of Bengal were (r = 0.30 (significant at p< 0.001) & 0.19 (not significant) respectively), during winter monsoon.

Thus significant correlations observed for Fe, Co & Cu with salinity in the coastal waters of the Arabian Sea during intermonsoon fall can be due to the effect of upwelled waters. A correlation of similar significance was also observed in the northern Arabian Sea of the offshore waters during intermonsoon spring due to receding winter cooling phenomenon. But no significant correlations were observed for Fe, Co & Cu with salinity in the offshore waters of the Bay of Bengal due to the effect of river runoff. The only significant correlation observed in the coastal waters of the Bay of Bengal are for Co and Cu with salinity. However a near conservative behavior with respect to Fe, Co and Cu to salinity is established in the coastal and offshore waters of the both basins.

The scattering of data points in the coastal and offshore waters points to the fact that Fe, Co & Cu distributions cannot be judged completely by upwelling or winter cooling phenomenon in the Arabian Sea. This scattering of data during intermonsoon fall in the offshore waters corresponding to the upper high saline waters was due to aeolian sources or eddy mixing whereas the scattering of data observed at the coastal waters corresponding to the low salinity layer was due to sedimentary sources or mixing of oceanic waters in the shelf areas of the Arabian Sea during intermonsoon fall. Similarly a wide scattering of data observed in offshore waters corresponding to the low salinity layer was observed in the northern Arabian Sea during intermonsoon spring which was due to the mixing of different water masses while the other

scattering of data corresponding to high saline water was due to the strong aeolian sources. The scattering of data in the mid saline waters corresponding to offshore regions of both basins was attributed to the effect of scavenging reactions (often biologically mediated reactions), which were operating in both basins. Adsorption onto suspended particles might be the possible interpretation for the removal of dissolved Fe, Co and Cu at both basins since dissolved Fe, Co and Cu have the same distribution as that of particulate Fe, Co and Cu. As the river water mixes with seawater, the negative charge on suspended colloids is not reversed by adsorption of seawater cations, but remains uniformly negative throughout the salinity range, decreasing sharply in magnitude during the first few per mill salinity (Hunter, 1983). This means that the adsorption of suspended particles may happen continuously across the salinity gradient, although this reaction may be magnified at low salinities by coagulation or precipitation in the Bay of Bengal. Fe, Cu & Co are particle reactive metals, and will therefore be scavenged by SPM in coastal and offshore areas. Furthermore, in a number of aquatic systems such as North Sea and English coastal waters a strong linearity has been observed between the redox-controlled metals like Fe and Co (Burton *et al.*, 1993;Achterberg *et al.*, 1997). These elements are remobilized from sediments upon reduction of the redox-potential at the sediment water interface as a result of mineralization of biogenic material (Burton *et al.*, 1993; Tappin *et al.*, 1995). Therefore, in addition to removal by scavenging, anoxic sediments may result in benthic inputs of dissolved Co, weakening the Co-Salinity relationship.

In the coastal waters of the Bay of Bengal (Table 25 and Fig. 124, 130, 128), metal-salinity relationships were strong Ni, Cd & Zn (r = 0.68, r = 0.67 and 0.57 significant at p< 0.001, respectively) and also in offshore waters (Table 28 and Fig. 125, 131, 129) the metal-salinity relationships were strong Ni, Cd & Zn (r = 0.74, r = 0.73 and 0.52 significant at p< 0.001, respectively) indicating that the salinity accounted for the major part of their variance. Even though there was scattering in the data sets with respect to low salinity layer due to the influence of river waters, this correlation suggests an active cycling of these metals in biologically mediated

reactions in the coastal and offshore waters of the Bay of Bengal. The high accumulation of these metals was seen in the high salinity zone suggesting deeper waters as a source of metals in the Bay of Bengal. However a slight scattering of data sets suggests that other than biologically mediated reactions, sedimentary inputs, benthic sources and mixing of oceanic waters at bottom layers were important for these metals in the coastal waters.

Among the metals studied in the coastal waters of the Arabian Sea during intermonsoon fall (Table 13 and Fig. 100, 106, 104), metal-salinity relationships were strong Ni, Cd & Zn (r = -0.45, r = -0.38 and -0.45 and all significant at p< 0.001, respectively). In offshore waters (Table 16 and Fig. 101, 107, 105) the metal-salinity relationships were strong Ni, Cd & Zn (r = -0.70, r = -0.73 and -0.57 and all significant at p< 0.001,respectively) indicating that salinity accounted for their variance. Similarly, in the coastal waters of the Arabian Sea during intermonsoon spring (Table 19 and Fig. 112, 118, 116), metal-salinity relationships were poor Ni, Cd & Zn (r = -0.05, r = 0.00 and 0.16 respectively (all not significant)) while in offshore waters (Table 22 and Fig. 113, 119, 117), the metal-salinity relationships were strong Ni, Cd & Zn (r = -0.80, r = -0.75 and -0.80 and all significant at p< 0.001,respectively) indicating that salinity accounted for their variance only in the offshore waters.

The Ni, Zn & Cd-Salinity plot suggests that all metals mixed conservatively in the coastal and offshore areas of both basins between the water masses with regards to salinity. Even though there was scattering in the data sets with respect to high salinity layer due to the influence of land runoff or atmospheric sources, this correlation suggests an active cycling of these metals in biologically mediated reactions in the coastal and offshore waters of the Arabian Sea during intermonsoon fall. The high accumulation of these metals was seen in the low salinity zone suggesting that deeper waters were a source for these metals in the coastal and offshore waters of the Arabian Sea during intermonsoon fall. However a slight scattering of data sets with respect to these metals and salinity suggests that other than biologically mediated reactions like sedimentary inputs or benthic sources and mixing of oceanic waters at

bottom layers were important for this metals in the coastal waters during intermonsoon fall. There was a wide scattering in the data sets with respect to these metals and salinity in the coastal waters of the Arabian Sea during intermonsoon spring due to the high mixing of coastal waters with oceanic waters or aeolian sources.

Saager et al., (1997) suggested that Cd and Ni were conservatively mixed in the Eastern North Atlantic and that Cu concentrations were affected by diagenetic inputs. Ni and Zn are reported to show some extent of an oceanic behavior influenced by biologically mediated removal in surface waters with subsequent down-column transport in association with biogenic particles (Bruland and Franks, 1983). However, Burton et al., (1993) and Tappin et al., (1995) observed no clear coupling of dissolved Ni and Zn to the utilization and regeneration of nutrients in the North Sea. These workers explained these observations by the time and space scales occurring in shallow water regimes, with the result that large concentration gradients cannot be maintained.

Trace metal relationships with salinity suggested that, mixing between shelf and oceanic waters was significant for most of the metals. At depth, the effect of mixing decreases, and open ocean processes, such as the mixing of different water masses and remineralisation etc, appeared to be dominant. These observations indicated that processes other than mixing between riverine and saline waters were also important. The other processes may include aeolian and benthic inputs, and removal by particulate matter and uptake by primary producers. Thus trace metal distributions in the water column of both basins reflect a balance between conservative mixing of end-member water masses and non-conservative processes in the water column and sediments.

4. 10. Partitioning of trace metals in the water column of the Arabian Sea and Bay of Bengal

It is well known that trace metals are present in aquatic environments in different forms (species) and the distribution between these species is a critical factor in understanding the role of trace metals in aquatic systems. In this work, discrimination

between dissolved and particulate state was operationally obtained by filtration through 0.45μ pore size filters. Moreover inside of these matrices (dissolved and particulate forms), any metal can assume various chemical forms, being able to form a wide variety of ions, compounds or complexes or being associated with different mineralogical or organic solid phases. The interactions among the dissolved and particulate phases appear to govern the fate of trace metals in the marine environment. Although free metal ions in the dissolved phase are considered to be the most bioavailable species, (Campbell, 1995) trace metals adsorbed and / or complexed to suspended solids are also important, as they become mobilized under changed physico-chemical conditions either in the water column or upon settling as bottom sediment.

4.10. 1Correlations between trace metals in each compartment

To investigate the behavior of trace metals in the Arabian Sea and Bay of Bengal, correlations (Pearson coefficient) between metals are calculated for the compartments such as dissolved phase, particulate phase and total water.

4.10. 1.1 Arabian Sea

4.10. 1.1a Intermonsoon fall

In the dissolved phase, strong correlations existed between seven trace metals Fe, Co, Ni, Cu, Zn, Cd and Pb. In the coastal areas (n = 105) the best correlations (Table 13) were for Cd and metals like Zn & Ni (r = 0.79 to 0.84) significant at p< 0.001, Ni and metals like Zn & Co (r = 0.38 to 0.71) significant at p< 0.001, Fe and metals like Cu & Pb (r = 0.53 to 0.58) significant at p< 0.001, Cu and metals like Pb & Co (r = 0.47 to 0.50) significant at p< 0.001, other correlations observed were for Co and metals like Cd & Pb (r = 0.24) significant at p< 0.02, Cd-Cu (r = 0.23) significant at p< 0.02, Pb and metals like Cd & Ni (r = -0.39 to -0.31) significant at p< 0.001, Ni-Fe (r = 0.19) significant at p< 0.10, Ni-Cu (r = 0.26) significant at p< 0.01, Co-Fe (r = 0.27) significant at p< 0.01, Cu-Zn (r = 0.29) significant at p< 0.01, Pb-Zn (r = -0.33) significant at p< 0.001, Co-Zn (r = 0.20) significant at p< 0.05 were observed for metal pairs. In the offshore areas (n = 182) the best correlations (Table 16) were for Cd and metals like Zn & Ni (r = 0.82 to 0.85) significant at p< 0.001, Zn and metals

like Co & Ni (r = 0.57 to 0.74) significant at p< 0.001, Cu and metals like Zn, Fe & Co (r = 0.45 to 0.61) significant at p< 0.001, Fe and metals like Zn, Cu & Co (r = 0.48 to 0.61) significant at p< 0.001, Cd-Co (r = 0.45) significant at p< 0.001, other correlations were for Pb and metals like Fe & Cu (r = 0.24) significant at p< 0.02, Pb and metals like Ni & Cd (r = -0.50 to -0.39) significant at p< 0.001, Pb-Zn (r = -0.30) significant at p< 0.01 and Cd-Cu (r = 0.20) significant at p< 0.05 were observed suggesting that the cycling of these metals was firmly linked in the water column of coastal and offshore areas.

However in the particulate phase also showed strong inter-metal relationships. At the coastal areas (n = 105) the best correlations (Table 14) were for Fe and metals like Cu & Pb (r = 0.52 to 0.60) significant at p< 0.001, Co and metals like Ni & Cu (r = 0.39 to 0.43) significant at p< 0.001, Cu-Pb (r = 0.48) significant at p< 0.001, Ni-Zn (r = 0.65) significant at p< 0.001, Cu and metals like Cd & Zn (r = 0.25 to 0.30) significant at p< 0.01, Pb and metals like Ni & Zn (r = -0.37 to -0.35) significant at p< 0.01, other correlations were for Fe-Co (r = 0.25) significant at p< 0.01, Zn-Co (r = 0.25) significant at p< 0.05, Pb-Cd (r = -0.27) significant at p< 0.01, Ni-Fe (r = 0.19) significant at p< 0.05, Ni-Cu (r = 0.25) significant at p< 0.01 were observed. In offshore areas the best correlations (Table 17) were for Fe and metals like Cu, Co & Zn (r = 0.60 to 0.68) significant at p< 0.001, Co and Zn (r = 0.66) significant at p< 0.001, Ni and metals like Zn, Co & Cd (r = 0.37 to 0.73) significant at p< 0.001, Cd and metals like Ni & Zn (r = 0.36 to 0.37) significant at p< 0.001, other correlations were for Pb and metals like Ni & Zn (r = -0.54 to -0.32) significant at p< 0.001, Cd-Co (r = 0.24) significant at p< 0.02, Cd-Fe (r = 0.18) significant at p< 0.10, Cu-Pb (r = 0.21) significant at p< 0.05 were observed suggesting the cycling of these particulate metals was firmly linked in the water column of coastal and offshore areas.

However the total metal concentrations showed strong inter-metal relationships much better than the individual phases. At the coastal areas (n = 105) the best correlations (Table 15) were observed for Cd and metals like Zn & Ni (r = 0.75 to 0.83) significant at p< 0.001, Ni and metals like Zn & Co (r = 0.39 to 0.68)

significant at p< 0.001, Fe and metals like Cu & Pb (r = 0.53 to 0.60) significant at p< 0.001, Cu and metals like Pb & Co (r = 0.44 to 0.48) significant at p< 0.001, other correlations were Cd and metals like Cu & Co(r = 0.25) significant at p< 0.01, Cu and metals like Ni & Zn (r = 0.27 to 0.30) significant at p< 0.01, Pb and metals like Cd, Ni & Zn (r = -0.40 to -0.34) significant at p< 0.01, Fe-Co (r = 0.26) significant at p< 0.01, Fe-Ni (r = 0.19) significant at p< 0.05, Co and metals like Pb & Zn (r = 0.19 to 0.20) significant at p< 0.05 were observed. In offshore areas the best correlations (Table 18) were for Cd and metals like Zn & Co (r = 0.49 to 0.81) significant at p< 0.001, Ni and metals like Zn, Cd & Co (r = 0.43 to 0.84) significant at p< 0.001, Co-Zn (r = 0.63) significant at p< 0.001, Fe and metals like Co, Cu & Zn (r = 0.59 to 0.66) significant at p< 0.001, Cu and metals like Co & Zn (r = 0.47 to 0.51) significant at p< 0.001, other correlations were for Pb and metals like Ni & Cd (r = -0.53 to 0.40) significant at p< 0.001, Cd-Fe (r = 0.25) significant at p< 0.01, Cd-Cu (r = 0.20) significant at p< 0.05, Pb-Cu (r = 0.23) significant at p< 0.02, suggesting the cycling of these total metals was firmly linked in the water column of coastal and offshore areas.

4.10. 1.1b Intermonsoon spring

In the dissolved phase of the Arabian Sea during spring intermonsoon (the filtrate passing a 0.45-μm filter), strong correlations between the seven trace metals Fe, Co, Ni, Cu, Zn, Cd and Pb were noticed. At the coastal areas (n = 60) the best correlations (Table 19) were for Cd and metals like Cu, Zn & Ni (r = 0.60 to 0.83) significant at $p< 0.001$, Zn and metals like Cu, Fe & Ni (r = 0.44 to 0.81) significant at $p< 0.001$, Ni and metals like Cu & Fe (r = 0.40 to 0.61) significant at $p< 0.001$, Fe-Cu (r = 0.63) significant at $p< 0.001$, were observed, other correlations were for Pb and metals like Ni & Cu (r = -0.26 to -0.27) significant at $p< 0.05$, Fe-Cd (r = 0.33) significant at $p< 0.01$, Pb-Cd (r = -0.36) significant at $p< 0.01$, Pb-Zn (r = -0.41) significant at $p< 0.001$, were observed. In offshore areas (n=60) the best correlations (Table 22) were for Zn and metals like Ni, Cu, Cd & Fe (r = 0.67 to 0.90) significant at $p< 0.001$, Cd and metals like Ni, Cu & Zn (r = 0.62 to 0.82) significant at $p< 0.001$, Ni and metals like Cu & Fe (r = 0.58 to 0.86) significant at $p< 0.001$, Cu and metals like Co & Fe (r

= 0.51 to 0.78) significant at $p<$ 0.001, the other correlations were for Co-Fe(r = 0.51) significant at $p<$ 0.001, Co-Ni(r = 0.31) significant at $p<$ 0.02, Co-Zn(r = 0.38) significant at $p<$ 0.01, Cd-Fe(r = 0.36) significant at $p<$ 0.01, Co-Pb(r = 0.26) significant at $p<$ 0.05, Zn-Pb(r = -0.22) significant at $p<$ 0.10, Cd-Pb(r = -0.39) significant at $p<$ 0.001 were observed suggesting that the cycling of these dissolved metals was firmly linked in the water column of coastal and offshore areas.

However in the particulate phase showed strong inter-metal relationships. At the coastal areas (n = 60) the best correlations (Table 20) were for Cd and metals like Cu, Ni & Zn(r = 0.51 to 0.69) significant at $p<$ 0.001, Zn and metals like Cu, Ni & Fe(r = 0.47 to 0.77) significant at $p<$ 0.001, Cu and metals like Ni & Fe(r = 0.55 to 0.66) significant at $p<$ 0.001, where as other correlations were for metal pairs such as Fe-Cd(r = 0.32) significant at $p<$ 0.02, Zn-Pb(r = -0.40) significant at $p<$ 0.001, Ni-Fe(r = 0.35) significant at $p<$ 0.01, Ni-Pb(r = -0.23) significant at $p<$ 0.10, and Cu-Pb(r = -0.28) significant at $p<$ 0.05, were observed. In offshore areas the best correlations (Table 23) were for Zn and metals like Cu, Ni, Co & Fe (r = 0.46 to 0.92) significant at $p<$ 0.001, Ni and metals like Cu & Fe (r = 0.66 to 0.86) significant at $p<$ 0.001, Cu and metals like Co & Fe (r = 0.53 to 0.83) significant at $p<$ 0.001, where as other correlations were for Cd and metals like Zn & Ni (r = 0.34 to 0.35) significant at $p<$ 0.01, Fe-Co(r = 0.50) significant at $p<$ 0.001, Ni-Co(r = 0.37) significant at $p<$ 0.01, Pb-Co(r = 0.24) significant at $p<$ 0.10, Cd-Cu(r = 0.23) significant at $p<$ 0.10, Cd-Pb(r = -0.40) significant at $p<$ 0.001 were observed suggesting cycling of these particulate metals was firmly linked in the water column of coastal and offshore areas.

The total metal concentrations showed strong inter-metal relationships than the individual phases. At the coastal areas (n= 60) the best correlations (Table 21) were for Cd and metals like Cu, Zn & Ni (r = 0.60 to 0.83) significant at $p<$ 0.001, Zn and metals like Cu, Fe & Ni (r = 0.47 to 0.80) significant at $p<$ 0.001, Ni and metals like Cu & Fe (r = 0.40 to 0.60) significant at $p<$ 0.001, Fe-Cu (r = 0.66) significant at $p<$ 0.001, were observed, other correlations were for Cd-Fe (r = 0.35) significant at $p<$ 0.01, Cd-Pb (r = -0.35) significant at $p<$ 0.01, Zn-Pb (r = -0.40) significant at $p<$

0.001, Pb and metals like Cu & Ni (r = -0.28 to -0.26) significant at p< 0.001 were observed. In offshore areas (n=60), the best correlations (Table 24) were for Ni and metals like Cu & Fe (r = 0.65 to 0.86) significant at *p*< 0.001, Cu and metals like Co & Fe (r = 0.53 to 0.83) significant at *p*< 0.001, Zn and metals like Ni, Cu, Co & Fe (r = 0.43 to 0.91) significant at *p*< 0.001, Cd and metals like Zn, Ni, Cu & Fe (r = 0.41 to 0.79) significant at *p*< 0.001, Co-Fe (r = 0.50) significant at *p*< 0.001, other correlations were for Cd-Pb(r = -0.40) significant at *p*< 0.001, Zn-Pb(r = -0.21) significant at *p*< 0.10, Co-Ni(r = 0.35) significant at *p*< 0.01, Co-Pb(r = 0.25) significant at *p*< 0.05 were observed suggesting the cycling of these total metals was firmly linked in the water column of coastal and offshore areas.

4.10. 1.2 Bay of Bengal

4.10. 1.2a Winter monsoon

In the dissolved phase, strong correlations between the seven trace metals Fe, Co, Ni, Cu, Zn, Cd and Pb were noticed. At the coastal areas (n = 85) the best correlations (Table 25) significant at p< 0.001, were for Cd and metals such as Zn & Ni (r = 0.70 to 0.89), other correlations significant at p< 0.001 was for Co – Ni (r = 0.40), Co – Cd (r = 0.24) significant at p< 0.02, Fe and metals such as Cd & Zn (r = 0.26 to 0.30) significant at p< 0.01, Fe – Pb (r = 0.20) significant at p< 0.05, Fe – Ni (r = 0.24) significant at p< 0.02, Cu and metals such as Zn, Cd, Ni & Fe (r = 0.44 to 0.60) significant at p< 0.001, Pb and metals such as Zn & Co (r = -0.38 to -0.32) significant at p< 0.001, Pb - Ni (r = -0.28) significant at p< 0.01, Pb - Cd (r = -0.25) significant at p< 0.02 were observed. In the offshore areas (n = 159) the best correlations (Table 28) significant at p< 0.001, were for Cd and metals like Ni, Cu & Zn (r = 0.49 to 0.95), Co-Zn (r = 0.38) significant at p< 0.001, Co-Cd (r = 0.22) significant at p< 0.05, Co-Ni (r = 0.24) significant at p< 0.02, Pb and metals like Zn, Cd & Ni (r = -0.53 to –0.38) significant at p< 0.001, Cu and metals like Ni, Fe & Zn (r = 0.39 to 0.66) significant at p< 0.001 were observed suggesting that the cycling of these metals was firmly linked in the water column of coastal and offshore areas.

However in the particulate phase showed strong inter-metal relationships. At the coastal areas (n = 85) the best correlations (Table 26) were for Cd and metals such as

Ni, Cu & Zn (r = 0.50 to 0.78) significant at p< 0.001, other correlations was for Zn –
Co (r = 0.35) significant at $p<$ 0.001, Ni – Pb (r = -0.32) significant at $p<$ 0.001, Ni
and metals like Zn, Co & Cu (r = 0.38 to 0.67) significant at $p<$ 0.001, Pb and metals
like Zn & Co (r = -0.35 to –0.36) significant at $p<$ 0.001, Pb – Cd (r = -0.24)
significant at $p<$ 0.02, Fe – Pb (r = 0.22) significant at $p<$ 0.05, Fe and metals like Zn,
Cd & Ni (r = 0.26 to 0.31) significant at $p<$ 0.01, Cu and metals like Zn, Cd & Fe (r =
0.43 to 0.63) significant at $p<$ 0.001 were observed. In offshore areas the best
correlations (Table 29) significant at $p<$ 0.001, were for Cd and metals like Ni & Zn
(r = 0.41 to 0.74), Ni and metals like Zn & Cu (r = 0.42 to 0.82) significant at $p<$
0.001, Ni-Co (r = 0.20) significant at $p<$ 0.05, Zn-Co (r = 0.37) significant at $p<$
0.001, Pb and metals like Zn, Cd & Ni (r = -0.52 to -0.39) significant at $p<$ 0.001, Fe-
Zn (r = 0.21) significant at $p<$ 0.05, Fe-Pb (r = 0.18) significant at $p<$ 0.10, Cu and
metals like Zn & Fe (r = 0.34 to 0.65) significant at $p<$ 0.001 were observed
suggesting the cycling of these particulate metals was firmly linked in the water
column of coastal and offshore areas.

The total metal concentrations showed strong inter-metal relationships than in
individual phases. At the coastal areas (n=85) the best correlations (Table 27) were
observed for Cd and metals such as Ni, Zn, Fe & Cu (r = 0.32 to 0.87) significant at
p< 0.001, other correlations for Ni and metals such as Zn, Co & Cu (r = 0.38 to 0.68)
significant at p< 0.001, Co - Zn (r = 0.37) significant at p< 0.001, Co - Cd (r = 0.22)
significant at p< 0.05, Pb and metals such as Co, Zn & Ni (r = -0.36 to –0.31)
significant at p< 0.001, Fe and metals such as Zn & Ni (r = 0.26 to 0.27) significant at
p< 0.01, Fe-Pb (r = 0.23) significant at p< 0.02, Cd-Pb (r = -0.28) significant at p<
0.01, Cu and metals such as Zn, Cd & Fe (r = 0.45 to 0.63) significant at p< 0.001. In
offshore areas the best correlations (Table 30) significant at p< 0.001, were for Cd
and metals like Zn, Ni & Cu (r = 0.46 to 0.81), Cd-Co (r = 0.19) significant at p<
0.10, Ni and metals like Cd, Zn & Cu (r = 0.43 to 0.95) significant at p< 0.001, Ni-Co
(r = 0.21) significant at p< 0.05, Zn-Co (r = 0.37) significant at p< 0.001, Pb and
metals like Cd, Zn & Ni (r = -0.55 to -0.39) significant at p< 0.001, Fe-Zn (r = 0.22)
significant at p< 0.05, Cu and metals like Fe & Zn (r = 0.35 to 0.66) significant at p<

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0.001 were observed suggesting the cycling of these total metals was firmly linked in the water column of coastal and offshore areas.

The vertical section of dissolved and particulate forms of Fe, Co & Cu in offshore waters of both basins showed a constantly high profile at intermediate depths, and slight enrichment at bottom layers, concomitant with the high concentration of total suspended matter. The slight enrichment of particulate forms of these metals in bottom layers of the offshore areas of both study regions can be ascribed to the scavenging of Fe, Co and Cu from the particulate matter, which occurred at intermediate depths in the absence of well-defined stratification of the water column. Similar to an enrichment of particulate forms of Fe, Co and Cu which further coincided with maximum values of dissolved forms of Fe, Co and Cu which were found in the surface and bottom layers of the both study regions showed a highly partitioned dynamic existence for these metals.

Average partition coefficient (K_d) values for the metals in the water column of the Arabian Sea and Bay of Bengal are presented in Table 31 to 35. This coefficient is defined as the ratio of the particulate metal concentration ($\mu g\ l^{-1}$) over the dissolved metal concentration ($\mu g\ l^{-1}$). Kd is the tendency of an element to be associated with the particulate phase and an important factor in geochemical studies. The averaged values from the Arabian Sea (intermonsoon fall), northern Arabian Sea (intermonsoon spring) and Bay of Bengal (winter monsoon), demonstrate a similar ranking Fe> Zn>Co>Pb>Cu>Ni>Cd, for all the metals. The partition co-efficients for the metals like Fe, Cu, Cd and Pb was slightly lower in the coastal areas than offshore areas of the Bay of Bengal due to a dilution effect caused on suspended particulates following the river runoff. However partition co-efficients for the metals like Co, Ni and Zn was slightly higher in the coastal areas than offshore areas of the Bay of Bengal possibly due to the exchange with particulate phase derived from river runoff.

Similarly the average partition co-efficients Fe, Co, Ni, Zn, and Cd was slightly higher in the coastal areas than offshore areas of the southeast Arabian Sea and northern Arabian Sea during intermonsoon fall due to the slight enrichment of suspended particulates following the upwelling and land drainage during this period.

However, the average partition co-efficients of the metal Cu was higher in the offshore areas than in coastal areas of the southeast Arabian Sea during intermonsoon fall due to possible exchange of dissolved to the particulate phase following eddy mixing.

A comparison of average partition coefficient values in the offshore stations for Fe, Co, Ni, Zn and Cd showed slightly higher values in the northern Arabian Sea during intermonsoon spring than during intermonsoon fall, due to enrichment of these metals in particulates following the receding winter cooling processes. Similarly a comparison of average partition coefficient values for metals in the entire water column of the Arabian Sea during intermonsoon fall and Bay of Bengal during winter monsoon showed that the values are slightly higher for metals like Fe, Ni, Cu, Cd and Pb in the Arabian Sea. Of all the metal investigated, cadmium and iron showed the lowest and highest Kd values respectively, in both the Arabian Sea and the Bay of Bengal. Values of Kd for particle-reactive and biologically required Fe are much higher than those organically strong bound trace metals like Ni, Zn & Cu and those for surface-reactive elements such as Pb. This ranking may be due to specific characteristics of each metal. In general variation in Kd values between metals in both areas were more or less related to metal affinity to SPM with Fe (92-95%), Co (63-67%), Zn (62-69%), Pb (60-65%) and Cu (52-54%) demonstrating the highest variation while Ni (34-40%) and Cd (8-15%) showed the least variation. A high value of Kd for iron indicated its strong affinity with the particle. Iron showed strong affinity for the particulate phase; usually greater than 92% of the total load in the water column which was bound to keep the particulate matter suspension in both the basins. The tendency of decreasing partition coefficient of cadmium with depth for both basins indicated a stronger affinity to the dissolved phase, which existed mainly in the dissolved phase (>80%) for both basins. Moreover cadmium concentrations showed that a high proportion of cadmium was remaining in the dissolved phase, irrespective of the values of suspended particulate matter in both basins. Nearly > 50% of the total copper in the deeper layers of the Arabian Sea and the Bay of Bengal was associated with suspended particulate matter, presumably due to formation of

insoluble copper precipitates. The fluctuation in partition coefficient for copper in the surface layers of the Bay of Bengal can be caused by the formation of dissolved copper species such as hydroxy, chloro or organic complexes following the river runoff. Similarly Gerringna et al., (1991), showed that total dissolved copper concentration can also be influenced by dissolved organic matter which contains strong Cu-complexing ligands. Further in the upper layers of the central Pacific Ocean Zn and Cu are present mostly in the form of organic complexes (Bruland, 1989; Bruland et al., 1991). Lead shows a strong affinity to the particle phase. In view of high affinity of lead to particles especially of terrigenic origin (Muller, 1996), it is assumed that lead is adsorbed by organic particulates which is further supported by the (>62%) of the total metal load existing in the particulate form.

When the river water enters the seawater, the trace metals in suspended matter may be displaced by major cations of seawater (Kharkar et al., 1968). The adsorption of metal onto the suspended matter is governed by the pH of the seawater and also by the nature of the suspended particles. Thus K_d can be influenced by pH, changes in salinity and particle concentration, particle size and the nature (Bourg, 1987). SPM may consist of biological, organic and mineral phases that will contain different co-ordination sites to bind metals (Stumm, 1992). Even though pH is assumed to be the most important factor explaining trace metal partitioning, in systems which are highly buffered and relatively stable with respect to pH, such as the Arabian Sea and the Bay of Bengal, the influence of other environmental variables may be more important in explaining the variation in trace metal partitioning. The relatively high Kd values reported for lead are likely to be due to its high affinity for clays, metal oxides and sulphides (Morse et al., 1993), and its intermediate affinity for organic matter (Shafer et al., 1997). For iron and lead, its high particle reactivity may promote association with particulate matter, while, in contrast, low particle reactivity and a stronger potential to form stable complexes allow nickel and cadmium to remain in dissolved phase. For both basins in the offshore waters instead, a slight decreasing trend with SPM concentration was only noticeable for Ni, Zn and Cd, a slight increasing trend with SPM concentration was observed for Co and Cu though the K_d of Fe and Pb

were nearly independent of SPM. Similarly Wen (1996) and Wen *et al.*, (1999 a, b) also observed little dependency of K_d on SPM concentrations for Cd, and Zn, and only small changes for Cu and Ni in Galveston Bay. Spatial and depth wise distribution of K_d values in both the Arabian Sea and the Bay of Bengal will not vary substantially indicating their stability.

In general, K_d for Fe, Ni, Cu, Cd and Pb are consistently higher in the Arabian Sea than in the Bay of Bengal, but for Co and Zn, an opposite trend is observed. Such differences may be related to particle size and/or particle geochemistry of both areas. However in the absence of information on the mineralogy of particles, this remains speculative. It is possible that the changes in mineralogy of the particles, depending on hydrological factors (e.g. river runoff), physical factors and different water masses may be responsible for the K_d and SPM relationship. For instance, the strong positive correlation between SPM and total metal concentrations reflect the role of physical processes such as upwelling or eddy mixing, which can significantly increase SPM, which may play in the chemical cycling of metals in these waters. High K_d values for metals like Fe, Ni, Cu, Cd and Pb observed in the Arabian Sea may be a consequence of the trace metal enrichment of particulates by these processes. This indicated that the nature of particles is important in controlling the metal concentrations in dissolved and particulate phases. Particle size has been demonstrated to exert an important influence on the trace metal composition of SPM (Duinker, 1983). There is little information on the extent to which particle size effects on Kd values, but values were generally greater for smaller particles (Duursma and Eisma, 1973). It is established that higher trace metal contents were associated with finer suspended material (Duinker, 1983; Salomons and Mook, 1987). Even if finer suspended particles are expected to be more in the Bay of Bengal the Kd values are only higher for Zn and Co in the Bay of Bengal as a consequence of trace metal enrichment in particulates from this area. However even if particulate Cu in the Bay of Bengal (Table 12) shows enrichment, the K_d for Cu is lower in the Bay of Bengal than in the Arabian Sea for unknown reasons. In the Arabian Sea and Bay of Bengal sinking is mainly by lithogenic particles of detrital origin and nonlithogenic particles of biogenic origin. In

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the Bay of Bengal the lithogenic component is relatively large primarily due to particles of local riverine origin, although atmospheric transport may also be a source for the Arabian Sea. However in the Arabian Sea the nonlithogenic particles of biogenic origin exceeds lithogenic particles of detrital origin due to high biological production. Another possibility is the high SPM concentration in the Arabian Sea may result in an elevated scavenging from the water column. This together with an effective and fast remineralisation of settling particles may result in an enrichment of trace metals like Fe, Ni, Cd, Cu and Pb in particulates from the Arabian Sea. In addition, uptake by biota and release of metals from benthic sediments may also be potentially important. The difference in water masses between the two regions can induce metals to suspended particles and hence in dissolved and particulate forms. To sum up, the apparent change in partition between dissolved and particulate form of metals may be related to the ocean dynamics i.e. different residence time of waters, different water masses and SPM. Further work is required to identify the sources of suspended particles and elucidate local cycling of metals.

4. 11. Processes controlling trace metal distribution in the Arabian Sea and Bay of Bengal

It is well documented that shelf areas receive increased loads of trace metals from terrestrial sources relative to oceanic waters (Hydes and Kremling, 1993). Both the Arabian Sea and Bay of Bengal are complex systems with extensive coastal zone as well as deep basins with different water masses and receive fresh water inputs from nearby rivers to the coastal zone. While the freshwater drainage from nearby river systems result in lowering the salinity gradient only to ~ 2.0 psu in the Arabian Sea, whereas the salinity gradient drops to > 8.0 psu or more in the Bay of Bengal. The northern shelf of the Bay of Bengal gets affected strongly by the entrainment of increased loads of fresh waters during summer and winter, originating from the Ganges-Brahamaputra and Godavari riverine systems in the north; it is characterized by a permanent salinity-temperature front. Similarly during intermonsoon fall while the shelf waters of the southeastern Arabian Sea is characterized by cold-nutrient rich and low saline waters resulting from local precipitation as well as related upwelling

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whereas northwest shelf is characterized by thermally stable and oligotropic waters. However northern Arabian Sea during spring is characterized by deep mixed layers induced by winter cooling.

The climatic conditions prevailing in the northwestern Bay of Bengal, during winter, favor the formation of dense water in the area. However the surface waters of the Bay of Bengal is an already mixed layer, consisting of cool river waters capped over warm Bay of Bengal waters, causing thermal inversions. Little mixing occurs between this upper layer and intermediate waters of the whole shelf area with a decreasing tendency from inner shelf to far offshore. Simultaneously this low saline layer act as an "insulating lid", thereby inhibiting deep-water mixing in the area.

In order to identify the relative importance of dissolved and particulate trace metals in the shelf areas, of both the Arabian Sea and Bay of Bengal, the data on concentrations of dissolved and particulate trace metals in the whole water column were averaged. The average concentrations of trace metals in the western Bay of Bengal (Table 11) showed an enrichment in Fe, Cu, Zn and Pb in the shelf areas relative to open ocean. Similarly the average concentrations of trace metals in the Arabian Sea (Table 7) during intermonsoon fall showed an enrichment in Fe, Cu, Cd and Pb in the shelf areas relative to open ocean. In order to evaluate the seasonal effect the available data on the northern Arabian Sea during intermonsoon fall and intermonsoon spring were averaged. The average concentration of trace metals in the northern Arabian Sea during intermonsoon fall (Table 9) showed an enrichment of Fe, Co, Cd and Pb in the shelf areas relative to open ocean. Similarly, the average concentration of trace metals in the northern Arabian Sea during intermonsoon spring (Table 10) showed an enrichment of Fe and Co in the shelf areas relative to open ocean. Similarly in the southeastern Arabian Sea in the upwelling zone during inter monsoon fall (Table 8) showed an enrichment for Fe, Co, Cu, Cd and Pb in the shelf areas relative to open ocean.

The surface, subsurface and bottom layers of both basins consist of a mixture of water masses. The water masses observed in both basins were; the low saline BOB water mass probably of riverine origin extending from surface to approximately 30-

50m depth, Arabian Sea High Saline Water Mass (ASHSW) extending from surface to 75m, Persian Gulf Water Mass (PGW) at 200-300m depth, Red Sea Water Mass (RSW) 300-500m depth, and Antarctic bottom waters (1000 to bottom). Relationship of trace metals with salinity showed the extent of mixing on the distribution of metals in shelf areas and how different water masses regulate their distribution in offshore areas.

The relationship between metals and salinity in the Bay of Bengal showed a near conservative behavior for most metals even though the correlation of Fe, Co and Cu with salinity were weaker in offshore areas. The relationships suggest that waters of low salinity and moderate metal concentration mix conservatively with high saline bottom waters, in accordance with the hydrography. The low saline Bay of Bengal waters with moderate metal concentrations is of riverine origin coming from northern portion of the system, probably draining from Ganges-Brahamaputra and off Godavari rivers and mixes with the eddies as it flows southwards by East India Coastal Current (EICC) with a moderately saline and with low metal concentration as observed in the southern tip of the shelf areas. Fresh and new riverine waters with high metal contents, enters the system from the north and mix with the already modified water mass by eddies moving southwards. This results in a possible change of metal to salinity gradient as evidenced by the weakening of salinity gradients from north to south in the inner shelf and outer shelf. It should be noted that loads of fresh water increased in winter and summer to this area from local riverine sources. As a result mixed surface waters with low salinity, which cover almost the entire area of the Bay of Bengal.

Most metals like Zn, Cd and Ni were conservatively mixed between the major water masses of both basins, i.e. there was only little influence from other inputs or processes. Therefore the relationships described were controlled largely by the presence of water masses in the subsurface to bottom of both basins; as such, they show these water masses act as a source of trace metals in the Arabian Sea and Bay of Bengal.

25μg/l, dCo = 0.50 nM & pCo = 0.75 nM, dCu = 1.00 μg/l & pCu = 1.00μg/l) of the Arabian Sea respectively extended to bottom also. Similarly the high concentration of dissolved and particulate metals (Fe, Co & Cu) in the surface at certain areas of inner (dFe = 2.50μg/l & pFe = 30 μg/l, dCo = 1.00 nM & pCo =1.65 nM, dCu = 1.00μg/l & pCu = 1.2μg/l) and outer shelfs (dFe = 2.20 μg/l & pFe = 30μg/l, dCo = 1.25 nM & pCo = 2.20nM, dCu = 1.6μg/l & pCu = 1.80μg/l) of the Bay of Bengal respectively reach to the bottom also. This type of distribution, but of less magnitude can be seen for other metals in the Bay of Bengal since the peaking of metal concentrations contours from bottom was restricted to few meters above the bottom layers.

An alternate explanation for the patchiness of metal distributions within the shelf area of both areas is that there is an additional source of trace elements to the water column through the remobilization of metals from the shelf sediments. It is generally accepted that in anoxic marine sediments manganese oxides are reduced early in the redox sequence after consumption of the oxygen and nitrate. The depth at which this redox reaction takes place depends on the content of organic material and its biologically mediated decomposition, which is the driving force for the reduction processes. In shelf regions with high primary production and particle flux, this can start at shallow depth. Much of the soluble reduced manganese gets remobilized into the overlying water column. This happens when oxygen in sediments, which are rich in organic material (mainly originating from riverborne detritus and quite significant in the shelf areas) is depleted by biological processes, and Mn and Fe oxides are reduced to Mn^{2+} and Fe^{2+}. These ions migrate into the pore waters of the sediment and then diffuse (or become resuspended by turbulent mixing) into the waters overlying the bottom (Landing and Bruland, 1980; Yeats et al., 1979; Kremling et al., 1978; Balzer, 1982; Klinkhammer, 1980). Although there is very little known about the geochemistry of Cd in partly reduced sediments, there is strong evidence supporting the suggestion that copper is probably released during the early diagenesis of organic matter at the sediment surface (Klinkhammer et al., 1982; Heggie, 1982). Shelf sediments in the both basins contain high concentrations of organic matter potentially driving benthic Cu fluxes. The interstitial water chemistry of Cu is

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coupled to the decomposition of organic matter (Elderfield, 1981) with high pore water concentrations in sediments and high organic matter. Several authors (Boyle *et al.* 1981; Bruland and Franks, 1983; Kremling, 1983a; Jones and Murray, 1984; Martin and Knauer, 1985; Martin *et al.,* 1985) have proposed that such processes along with the resuspension of Mn-rich bottom sediments, may be responsible for the pronounced Cd, Cu, Ni and Mn enrichments in continental slope and shelf waters encountered in their studies.

These measurements strongly indicate that detectable seasonal differences in the composition of coastal surface waters in the Arabian Sea actually exist for nutrient-type elements, and that this phenomenon may contribute significantly to the patchiness and scattering of intermonsoon fall and spring data encountered in the relationship of the elements with salinity.

Alternate sources that could produce trace metal enrichments in the surface waters of the inner and outer shelf waters of both basins cannot be ruled out. An aeolian input could produce a peak concentration level for certain metals with distinct boundaries. However unless information is available on local aeolian deposition rates, net fluvial input from the riverine sources or benthic fluxes from shelf sediments, it is not possible to explain the origin of metal enrichment in surface waters. Rivers with significant discharge of metals are present in the near by area of both basins.

It is concluded that the remobilization of trace metals from partly reduced sediments and subsequent mixing into the surface waters by physical processes is a subject of major concern in the shelf waters of both basins. These processes are probably variable in the West and East coast depending on the seasonal changes in the currents and hydrography and perhaps even on temporal variations in the chemistry and biology of the shelf sediments.

In order to evaluate the trace metal transport to the euphotic zone in the Arabian Sea and Bay of Bengal, nutrient and metal concentration profiles above the permanent thermocline of both basins are examined. Most of the trace metal profiles in the outer shelf areas of the Arabian Sea and Bay of Bengal were similar to the metal profiles in the open ocean areas, suggesting that the outer shelf was primarily

influenced by oceanic water. The influences of the distinct shelf processes were confined to the nearshore waters. Surface waters characteristics may also be modified by mixing with deep-water masses brought to the surface by upwelling, eddy mixing and winter mixing. This can influence trace metal distributions if there is a significant difference between deep and surface concentrations. In the southeastern Arabian Sea during intermonsoon fall in the outer shelf due to upwelling, an enrichment of nutrients and nutrient like trace metals, namely (Zn, Cd & Ni of high magnitude, Fe, Co & Cu of low magnitude) was seen, as a result of deepwater outcropping. A similar degree of enrichment for nutrients and nutrient like trace metals can be seen in the open ocean transects of southwest Arabian Sea due to eddy mixing. The metals and nutrients showed approximately two times higher degree of enrichment in the southwest coast than the north west coast above the permanent thermocline during intermonsoon fall. The isolines of these trace metals and nutrients in the outer shelf of the West coast of India during intermonsoon fall shoals up from intermediate depths and surfaces at the southwest coast whereas northwest coast remained oligotropic. This may be the case for Cd along the shelf waters of the West coast of India during intermonsoon fall. At depths greater than 150 m, Cd concentrations were in excess of 2.0 nM, whereas it was only between 0.5 and 1.5 nM above 150 m. The occurrence of upwelling in the area may partially explain why the Cd concentrations reported in this study were high compared to the world average Cd concentrations in surface waters of 0.01 nM (Chester and Murphy, 1990).

Similarly in the northern Arabian Sea during winter monsoon, the top of the thermocline was eroded by vertical mixing and the effect of this process continued even in spring intermonsoon. Even though northern Arabian Sea seems to be oligotropic during intermonsoon fall, it got enriched with trace metals and nutrients and its magnitude was as high as the enrichment by upwelling during spring intermonsoon since northern Arabian Sea was under the grip of receding winter cooling. In the Bay of Bengal during winter monsoon in the offshore transects due to eddy mixing, an enrichment of nutrients and nutrient like trace metals, namely (Zn, Cd & Ni of high magnitude, Fe, Co & Cu of low magnitude) was seen, as a result of

deepwater outcropping. Under the influence of these eddies, the nutrients and nutrient like trace metals in the Bay of Bengal were likely to churn up from subsurface levels but the insulated low saline layer prevent it to reach the surface waters. Thus for these elements, the upwelling zone in southeastern Arabian Sea and the winter cooled waters in the northern Arabian Sea were characterized by some degree of enrichment in the surface waters which gets smoothened due to seasonal stratification.

Thus regenerated sources (i.e., upwelling, eddy mixing and winter mixing) do more significantly influence the distribution of nutrients, and nutrient-like trace metals in the Arabian Sea. The results speculate that upwelling, eddy mixing and winter mixing lead to the redistribution of nutrients and nutrient-like trace metals above the permanent thermocline with out large export of metals to deeper waters.

The data on metals like Fe, Co & Cu are roughly constant in the OMZ of the Arabian Sea with out any significant increase. It therefore appears that the OMZ, low oxygen alone does not make these elements more reactive. This observation contrasts with low-oxygen settings where circulation is restricted, and seawater has more time to interact with reacting sediments (van Geen et $al.$, 1995). The influence of suboxic conditions in the water column is not seen significantly for any metal studied. Since the nitrogen transformations require metalloenzymes, it is possible that low metal availability also limits critical steps in the nitrogen cycle. The low metal availability of Fe and Cu in the OMZ may be the reason for the release of greenhouse gases to the atmosphere from the intermediate waters of the Arabian Sea. For instance, low Cu availability in the OMZ is hypothesized to be responsible for the release of N_2O to the atmosphere as a result of low nitrous oxide reductase activity (Granger and Ward, 2003).

Table 7: Average concentration of trace metals in the water column of inner shelf, outer shelf and offshore transects of the eastern Arabian Sea during intermonsoon fall

Metal concentration	Fe (μg/l)	Co (nM)	Ni (nM)	Cu (μg/l)	Zn (μg/l)	Cd (nM)	Pb (μg/l)
Dissolved (Inner shelf)	3.45	0.342	1.600	1.00	1.46	1.059	0.468
Particulate (Inner shelf)	51.53	0.601	0.989	1.11	2.55	0.173	0.793
Dissolved (Outer shelf)	2.15	0.507	2.541	0.99	1.55	1.369	0.344
Particulate (Outer shelf)	32.33	0.898	1.554	1.10	2.63	0.194	0.576
Dissolved (Offshore)	1.73	0.427	2.898	0.81	2.81	1.120	0.285
Particulate (Offshore)	23.63	0.691	1.626	0.95	4.59	0.135	0.485

Table 8: Average concentration of trace metals in the water column of inner shelf, outer shelf and offshore transects of the southeastern Arabian Sea during intermonsoon fall

Metal concentration	Fe (μg/l)	Co (nM)	Ni (nM)	Cu (μg/l)	Zn (μg/l)	Cd (nM)	Pb (μg/l)
Dissolved (Inner shelf)	4.16	0.459	1.972	1.43	1.56	1.216	0.576
Particulate (Inner shelf)	62.59	0.802	1.210	1.60	2.67	0.190	0.991
Dissolved (Outer shelf)	2.90	0.584	2.711	1.35	1.66	1.393	0.496
Particulate (Outer shelf)	43.76	1.005	1.633	1.50	2.81	0.206	0.830
Dissolved (Offshore)	1.97	0.533	2.971	0.89	3.21	1.168	0.366
Particulate (Offshore)	26.69	0.858	1.669	1.03	5.25	0.141	0.621

Table 9: Average concentration of trace metals in the water column of inner shelf, outer shelf and offshore transects of the northeastern Arabian Sea during intermonsoon fall

Metal concentration	Fe (µg/l)	Co (nM)	Ni (nM)	Cu (µg/l)	Zn (µg/l)	Cd (nM)	Pb (µg/l)
Dissolved (Inner shelf)	2.80	0.236	1.261	0.61	1.37	0.917	0.371
Particulate (Inner shelf)	41.47	0.418	0.788	0.67	2.45	0.158	0.613
Dissolved (Outer shelf)	1.15	0.404	2.315	0.51	1.40	1.337	0.142
Particulate (Outer shelf)	17.10	0.756	1.448	0.56	2.40	0.178	0.238
Dissolved (Offshore)	1.41	0.285	2.801	0.71	2.27	1.056	0.177
Particulate (Offshore)	19.55	0.469	1.568	0.84	3.70	0.127	0.303

Table 10: Average concentration of trace metals in the water column of inner shelf, outer shelf and offshore transects of the northeastern Arabian Sea during intermonsoon spring

Metal concentration	Fe (µg/l)	Co (nM)	Ni (nM)	Cu (µg/l)	Zn (µg/l)	Cd (nM)	Pb (µg/l)
Dissolved (Inner shelf)	2.89	0.741	1.692	0.65	1.62	0.842	0.077
Particulate (Inner shelf)	42.72	1.223	1.014	0.73	2.82	0.162	0.130
Dissolved (Outer shelf)	2.26	0.544	1.936	0.64	1.81	1.014	0.068
Particulate (Outer shelf)	33.30	0.931	1.097	0.73	3.15	0.166	0.117
Dissolved (Offshore)	2.28	0.368	3.470	0.88	3.37	1.280	0.172
Particulate (Offshore)	33.85	0.652	1.970	1.00	5.82	0.187	0.289

Table 11: Average concentration of trace metals in the water column of inner shelf, outer shelf and offshore transects of the western Bay of Bengal during winter monsoon

Metal concentration	Fe (μg/l)	Co (nM)	Ni (nM)	Cu (μg/l)	Zn (μg/l)	Cd (nM)	Pb (μg/l)
Dissolved (Inner shelf)	2.35	1.136	0.764	1.27	3.26	0.297	0.153
Particulate (Inner shelf)	29.53	2.055	0.458	1.39	6.33	0.046	0.259
Dissolved (Outer shelf)	2.33	1.055	1.707	1.46	3.45	0.599	0.152
Particulate (Outer shelf)	28.58	1.909	0.994	1.58	6.49	0.071	0.246
Dissolved (Offshore)	2.13	1.35	3.598	0.86	3.03	0.931	0.150
Particulate (Offshore)	27.10	2.274	1.919	0.94	5.12	0.107	0.250

Table 12: Average concentration of trace metals in the water column of the eastern Arabian Sea during inter monsoon fall and western Bay of Bengal during winter monsoon

Metal concentration	Fe (μg/l)	Co (nM)	Ni (nM)	Cu (μg/l)	Zn (μg/l)	Cd (nM)	Pb (μg/l)
Dissolved (AS)	2.44	0.425	2.346	0.93	1.94	1.182	0.366
Particulate (AS)	35.83	0.730	1.389	1.05	3.26	0.167	0.618
Dissolved (BOB)	2.27	1.180	2.023	1.19	3.25	0.609	0.152
Particulate (BOB)	28.40	2.079	1.123	1.30	5.98	0.075	0.251

Table 13: Pearson product-moment correlation coefficients between dissolved trace metals, SPM & Salinity in the coastal waters of the eastern Arabian Sea during intermonsoon fall (n= 105)

Dissolved metal	Fe	Co	Ni	Cu	Zn	Cd	Pb	SPM	Salinity
Fe	1.00								
Co	0.27	1.00							
Ni	0.19	0.38	1.00						
Cu	0.58	0.47	0.26	1.00					
Zn	0.17	0.20	0.71	0.29	1.00				
Cd	0.12	0.24	0.84	0.23	0.79	1.00			
Pb	0.53	0.24	-0.31	0.50	-0.33	-0.39	1.00		
SPM	0.48	0.38	0.50	0.48	0.49	0.41	0.16	1.00	
Salinity	-0.41	-0.39	-0.45	-0.66	-0.45	-0.38	-0.37	-0.44	1.00

Table 14: Pearson product-moment correlation coefficients between particulate trace metals, SPM & Salinity in the coastal waters of the eastern Arabian Sea during intermonsoon fall (n= 105)

Particulate metal	Fe	Co	Ni	Cu	Zn	Cd	Pb	SPM	Salinity
Fe	1.00								
Co	0.25	1.00							
Ni	0.19	0.39	1.00						
Cu	0.60	0.43	0.25	1.00					
Zn	0.15	0.25	0.65	0.30	1.00				
Cd	0.07	0.12	0.50	0.25	0.50	1.00			
Pb	0.52	0.17	-0.37	0.48	-0.35	-0.27	1.00		
SPM	0.49	0.38	0.47	0.48	0.46	0.30	0.11	1.00	
Salinity	-0.41	-0.37	-0.43	-0.66	-0.44	-0.24	-0.36	-0.44	1.00

Table 15: Pearson product-moment correlation coefficients between total metals, SPM & Salinity in the coastal waters of the eastern Arabian Sea during intermonsoon fall (n= 105)

Total metal	Fe	Co	Ni	Cu	Zn	Cd	Pb	SPM	Salinity
Fe	1.00								
Co	0.26	1.00							
Ni	0.19	0.39	1.00						
Cu	0.60	0.44	0.27	1.00					
Zn	0.16	0.20	0.68	0.30	1.00				
Cd	0.12	0.25	0.83	0.25	0.75	1.00			
Pb	0.53	0.19	-0.34	0.48	-0.34	-0.40	1.00		
SPM	0.49	0.39	0.49	0.48	0.47	0.41	0.13	1.00	
Salinity	-0.41	-0.38	-0.44	-0.66	-0.44	-0.37	-0.37	-0.44	1.00

Table 16: Pearson product-moment correlation coefficients between dissolved trace metals, SPM & Salinity in the offshore waters of the eastern Arabian Sea during intermonsoon fall (n= 182)

Dissolved metal	Fe	Co	Ni	Cu	Zn	Cd	Pb	SPM	Salinity
Fe	1.00								
Co	0.55	1.00							
Ni	0.03	0.39	1.00						
Cu	0.61	0.45	0.10	1.00					
Zn	0.48	0.57	0.74	0.51	1.00				
Cd	0.15	0.45	0.85	0.20	0.82	1.00			
Pb	0.24	0.10	-0.50	0.24	-0.30	-0.39	1.00		
SPM	-0.02	0.22	0.55	-0.06	0.49	0.60	-0.41	1.00	
Salinity	-0.18	-0.56	-0.70	-0.13	-0.57	-0.73	-0.04	-0.39	1.00

Table 17: Pearson product-moment correlation coefficients between particulate trace metals, SPM & Salinity in the offshore waters of the eastern Arabian Sea during intermonsoon fall (n= 182)

Particulate metal	Fe	Co	Ni	Cu	Zn	Cd	Pb	SPM	Salinity
Fe	1.00								
Co	0.66	1.00							
Ni	0.16	0.44	1.00						
Cu	0.68	0.50	0.14	1.00					
Zn	0.60	0.66	0.73	0.55	1.00				
Cd	0.18	0.24	0.37	0.06	0.36	1.00			
Pb	0.16	0.04	-0.54	0.21	-0.32	-0.08	1.00		
SPM	0.07	0.28	0.54	-0.02	0.48	0.25	-0.43	1.00	
Salinity	-0.24	-0.57	-0.69	-0.15	-0.57	-0.49	-0.01	-0.39	1.00

Table 18: Pearson product-moment correlation coefficients between total metals, SPM & Salinity in the offshore waters of the eastern Arabian Sea during intermonsoon fall (n= 182)

Total metal	Fe	Co	Ni	Cu	Zn	Cd	Pb	SPM	Salinity
Fe	1.00								
Co	0.64	1.00							
Ni	0.14	0.42	1.00						
Cu	0.66	0.47	0.11	1.00					
Zn	0.59	0.63	0.73	0.51	1.00				
Cd	0.25	0.49	0.84	0.20	0.81	1.00			
Pb	0.17	0.06	-0.53	0.23	-0.31	-0.41	1.00		
SPM	0.07	0.26	0.55	-0.04	0.48	0.59	-0.42	1.00	
Salinity	-0.24	-0.56	-0.70	-0.13	-0.57	-0.74	-0.02	-0.39	1.00

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Table 19: Pearson product-moment correlation coefficients between dissolved trace metals, SPM & Salinity in the coastal waters of the northeastern Arabian Sea during intermonsoon spring (n= 60)

Dissolved metal	Fe	Co	Ni	Cu	Zn	Cd	Pb	SPM	Salinity
Fe	1.00								
Co	0.33	1.00							
Ni	0.44	-0.08	1.00						
Cu	0.63	0.08	0.61	1.00					
Zn	0.44	-0.12	0.81	0.61	1.00				
Cd	0.33	-0.10	0.83	0.60	0.80	1.00			
Pb	0.08	-0.03	-0.27	-0.26	-0.41	-0.36	1.00		
SPM	0.50	-0.10	0.26	0.54	0.47	0.38	-0.31	1.00	
Salinity	-0.06	-0.11	-0.05	-0.01	0.16	0.00	-0.28	0.30	1.00

Table 20: Pearson product-moment correlation coefficients between particulate trace metals, SPM & Salinity in the coastal waters of the northeastern Arabian Sea during intermonsoon spring (n= 60)

Particulate metal	Fe	Co	Ni	Cu	Zn	Cd	Pb	SPM	Salinity
Fe	1.00								
Co	0.06	1.00							
Ni	0.35	-0.09	1.00						
Cu	0.66	0.17	0.55	1.00					
Zn	0.47	-0.09	0.77	0.62	1.00				
Cd	0.32	-0.01	0.69	0.51	0.69	1.00			
Pb	0.03	-0.05	-0.23	-0.28	-0.40	-0.19	1.00		
SPM	0.50	-0.08	0.19	0.51	0.46	0.25	-0.31	1.00	
Salinity	-0.08	-0.11	-0.06	-0.02	0.16	0.04	-0.29	0.30	1.00

Table 21: Pearson product-moment correlation coefficients between total metals, SPM & Salinity in the coastal waters of the northeastern Arabian Sea during intermonsoon spring (n= 60)

Total metal	Fe	Co	Ni	Cu	Zn	Cd	Pb	SPM	Salinity
Fe	1.00								
Co	0.05	1.00							
Ni	0.40	-0.07	1.00						
Cu	0.66	0.13	0.60	1.00					
Zn	0.47	-0.10	0.80	0.61	1.00				
Cd	0.35	-0.08	0.83	0.60	0.80	1.00			
Pb	0.03	-0.04	-0.26	-0.28	-0.40	-0.35	1.00		
SPM	0.50	-0.09	0.24	0.53	0.46	0.37	-0.31	1.00	
Salinity	-0.08	-0.11	-0.05	-0.01	0.16	0.01	-0.28	0.30	1.00

Table 22: Pearson product-moment correlation coefficients between dissolved trace metals, SPM & Salinity in the offshore waters of the northeastern Arabian Sea during intermonsoon spring (n= 60)

Dissolved metal	Fe	Co	Ni	Cu	Zn	Cd	Pb	SPM	Salinity
Fe	1.00								
Co	0.51	1.00							
Ni	0.58	0.31	1.00						
Cu	0.78	0.51	0.86	1.00					
Zn	0.67	0.38	0.90	0.90	1.00				
Cd	0.36	0.11	0.79	0.62	0.82	1.00			
Pb	0.15	0.26	-0.20	0.01	-0.22	-0.39	1.00		
SPM	0.20	0.19	0.54	0.39	0.54	0.64	-0.51	1.00	
Salinity	-0.61	-0.24	-0.80	-0.76	-0.80	-0.75	-0.10	-0.41	1.00

Table 23: Pearson product-moment correlation coefficients between particulate trace metals, SPM & Salinity in the offshore waters of the northeastern Arabian Sea during intermonsoon spring (n= 60)

Particulate metal	Fe	Co	Ni	Cu	Zn	Cd	Pb	SPM	Salinity
Fe	1.00								
Co	0.50	1.00							
Ni	0.66	0.37	1.00						
Cu	0.83	0.53	0.86	1.00					
Zn	0.75	0.46	0.90	0.92	1.00				
Cd	0.08	0.00	0.34	0.23	0.35	1.00			
Pb	0.11	0.24	-0.18	-0.01	-0.20	-0.40	1.00		
SPM	0.26	0.22	0.52	0.41	0.52	0.54	-0.50	1.00	
Salinity	-0.67	-0.28	-0.79	-0.76	-0.80	-0.31	-0.10	-0.41	1.00

Table 24: Pearson product-moment correlation coefficients between total metals, SPM & Salinity in the offshore waters of the northeastern Arabian Sea during intermonsoon spring (n= 60)

Total metal	Fe	Co	Ni	Cu	Zn	Cd	Pb	SPM	Salinity
Fe	1.00								
Co	0.50	1.00							
Ni	0.65	0.35	1.00						
Cu	0.83	0.53	0.86	1.00					
Zn	0.74	0.43	0.90	0.91	1.00				
Cd	0.41	0.15	0.76	0.60	0.79	1.00			
Pb	0.11	0.25	-0.19	0.00	-0.21	-0.40	1.00		
SPM	0.26	0.21	0.53	0.40	0.53	0.65	-0.51	1.00	
Salinity	-0.66	-0.27	-0.80	-0.76	-0.80	-0.73	-0.10	-0.41	1.00

Table 25: Pearson product-moment correlation coefficients between dissolved trace metals, SPM & Salinity in the coastal waters of the western Bay of Bengal during winter monsoon (n= 85)

Dissolved metal	Fe	Co	Ni	Cu	Zn	Cd	Pb	SPM	Salinity
Fe	1.00								
Co	-0.13	1.00							
Ni	0.24	0.40	1.00						
Cu	0.60	0.06	0.44	1.00					
Zn	0.26	0.40	0.70	0.48	1.00				
Cd	0.30	0.24	0.89	0.54	0.70	1.00			
Pb	0.20	-0.38	-0.28	-0.05	-0.32	-0.25	1.00		
SPM	0.48	0.04	0.22	0.41	0.33	0.26	-0.09	1.00	
Salinity	0.12	0.30	0.68	0.30	0.57	0.67	-0.49	0.27	1.00

Table 26: Pearson product-moment correlation coefficients between particulate trace metals, SPM & Salinity in the coastal waters of the western Bay of Bengal during winter monsoon (n= 85)

Particulate metal	Fe	Co	Ni	Cu	Zn	Cd	Pb	SPM	Salinity
Fe	1.00								
Co	-0.09	1.00							
Ni	0.26	0.38	1.00						
Cu	0.63	0.04	0.40	1.00					
Zn	0.27	0.35	0.67	0.43	1.00				
Cd	0.31	0.12	0.78	0.50	0.64	1.00			
Pb	0.22	-0.35	-0.32	-0.04	-0.36	-0.24	1.00		
SPM	0.42	0.03	0.23	0.40	0.38	0.18	-0.12	1.00	
Salinity	0.07	0.26	0.67	0.28	0.53	0.54	-0.54	0.27	1.00

Table 27: Pearson product-moment correlation coefficients between total metals, SPM & Salinity in the coastal waters of the western Bay of Bengal during winter monsoon (n= 85)

Total metal	Fe	Co	Ni	Cu	Zn	Cd	Pb	SPM	Salinity
Fe	1.00								
Co	-0.10	1.00							
Ni	0.26	0.38	1.00						
Cu	0.63	0.05	0.42	1.00					
Zn	0.27	0.37	0.68	0.45	1.00				
Cd	0.32	0.22	0.87	0.52	0.70	1.00			
Pb	0.23	-0.36	-0.31	-0.05	-0.35	-0.28	1.00		
SPM	0.43	0.03	0.23	0.40	0.36	0.25	-0.11	1.00	
Salinity	0.07	0.28	0.67	0.29	0.55	0.66	-0.52	0.27	1.00

Table 28: Pearson product-moment correlation coefficients between dissolved trace metals, SPM & Salinity in the offshore waters of the western Bay of Bengal during winter monsoon (n= 159)

Dissolved metal	Fe	Co	Ni	Cu	Zn	Cd	Pb	SPM	Salinity
Fe	1.00								
Co	-0.05	1.00							
Ni	0.02	0.24	1.00						
Cu	0.39	0.16	0.44	1.00					
Zn	0.24	0.38	0.83	0.66	1.00				
Cd	0.11	0.22	0.95	0.49	0.84	1.00			
Pb	0.17	-0.03	-0.48	-0.14	-0.38	-0.53	1.00		
SPM	0.28	0.55	0.54	0.41	0.64	0.55	-0.31	1.00	
Salinity	-0.14	0.08	0.74	0.19	0.52	0.73	-0.69	0.22	1.00

Table 29: Pearson product-moment correlation coefficients between particulate trace metals, SPM & Salinity in the offshore waters of the western Bay of Bengal during winter monsoon (n= 159)

Particulate metal	Fe	Co	Ni	Cu	Zn	Cd	Pb	SPM	Salinity
Fe	1.00								
Co	0.00	1.00							
Ni	0.02	0.20	1.00						
Cu	0.34	0.15	0.42	1.00					
Zn	0.21	0.37	0.82	0.65	1.00				
Cd	0.05	0.06	0.74	0.22	0.41	1.00			
Pb	0.18	-0.01	-0.52	-0.13	-0.39	-0.48	1.00		
SPM	0.27	0.54	0.54	0.38	0.63	0.31	-0.31	1.00	
Salinity	-0.15	0.03	0.74	0.16	0.50	0.69	-0.72	0.22	1.00

Table 30: Pearson product-moment correlation coefficients between total metals, SPM & Salinity in the offshore waters of the western Bay of Bengal during winter monsoon (n= 159)

Total metal	Fe	Co	Ni	Cu	Zn	Cd	Pb	SPM	Salinity
Fe	1.00								
Co	-0.01	1.00							
Ni	0.01	0.21	1.00						
Cu	0.35	0.16	0.43	1.00					
Zn	0.22	0.37	0.83	0.66	1.00				
Cd	0.09	0.19	0.95	0.46	0.81	1.00			
Pb	0.18	-0.02	-0.51	-0.13	-0.39	-0.55	1.00		
SPM	0.27	0.54	0.54	0.40	0.63	0.54	-0.33	1.00	
Salinity	-0.15	0.05	0.74	0.17	0.51	0.74	-0.71	0.22	1.00

Table 31: Average partition coefficient (Kd) of trace metals in the coastal and offshore areas of the eastern Arabian Sea during intermonsoon fall

Metal (Kd)	Fe	Co	Ni	Cu	Zn	Cd	Pb
Coastal	14.89	1.744	0.625	1.120	1.780	0.169	1.641
Offshore	13.52	1.583	0.575	1.170	1.670	0.144	1.645
Coastal & Offshore	14.20	1.664	0.600	1.145	1.725	0.157	1.643

Table 32: Average partition coefficient (Kd) of trace metals in the coastal and offshore areas of the western Bay of Bengal during winter monsoon

Metal (Kd)	Fe	Co	Ni	Cu	Zn	Cd	Pb
Coastal	12.47	1.828	0.602	1.099	2.00	0.140	1.615
Offshore	14.00	1.680	0.554	1.100	1.77	0.144	1.630
Coastal & Offshore	13.23	1.754	0.578	1.099	1.89	0.142	1.622

Table 33: Average partition coefficient (Kd) of trace metals in the southeastern Arabian Sea during intermonsoon fall

Metal (Kd)	Fe	Co	Ni	Cu	Zn	Cd	Pb
Coastal	14.97	1.729	0.612	1.130	1.77	0.166	1.657
Offshore	13.39	1.588	0.576	1.160	1.68	0.143	1.655

Table 34: Average partition coefficient (Kd) of trace metals in the northeastern Arabian Sea during intermonsoon fall

Metal (Kd)	Fe	Co	Ni	Cu	Zn	Cd	Pb
Coastal	14.80	1.761	0.641	1.10	1.79	0.171	1.624
Offshore	13.71	1.576	0.575	1.17	1.65	0.145	1.642

Table 35: Average partition coefficient (Kd) of trace metals in the northeastern Arabian Sea during spring intermonsoon

Metal (Kd)	Fe	Co	Ni	Cu	Zn	Cd	Pb
Coastal	14.66	1.773	0.593	1.12	1.75	0.190	1.674
Offshore	15.01	1.772	0.584	1.11	1.79	0.165	1.643

Figure. 24. Vertical section of physical and chemical parameters along the inner shelf of the Arabian Sea during intermonsoon fall
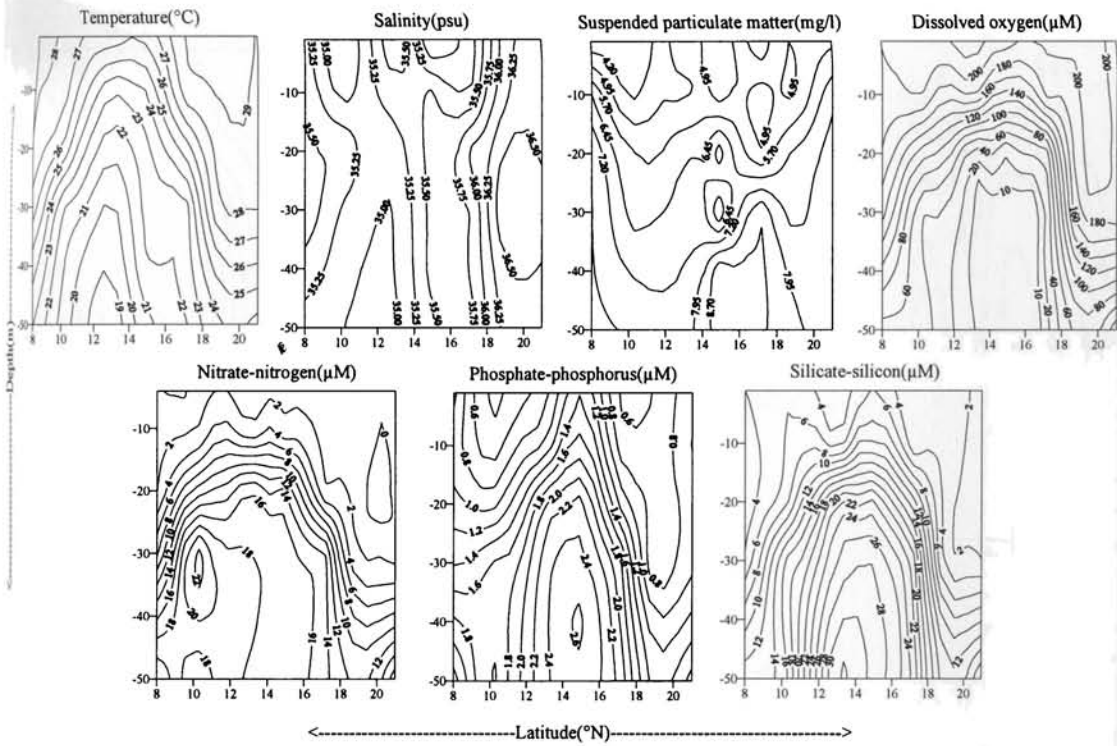
Figure. 25. Vertical section of dissolved and particulate Fe, Cu, Zn & Pb along the inner shelf of the Arabian Sea during intermonsoon fall
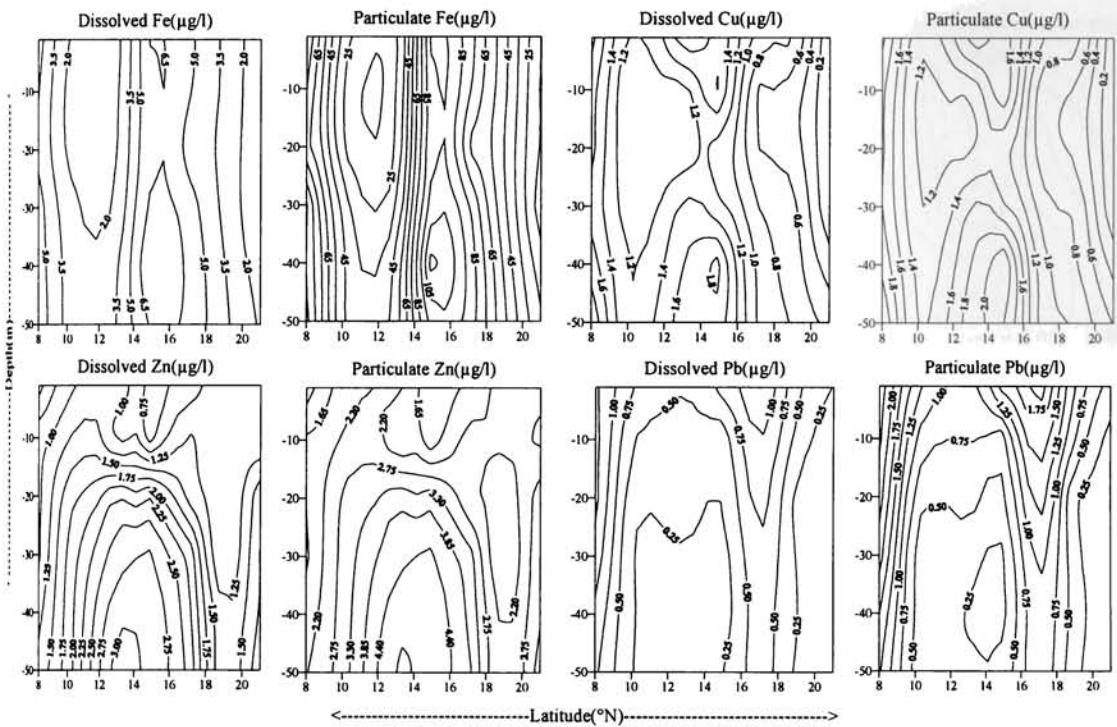
Figure. 26. Vertical section of dissolved and particulate Cd, Ni & Co along the inner shelf of the Arabian Sea during intermonsoon fall
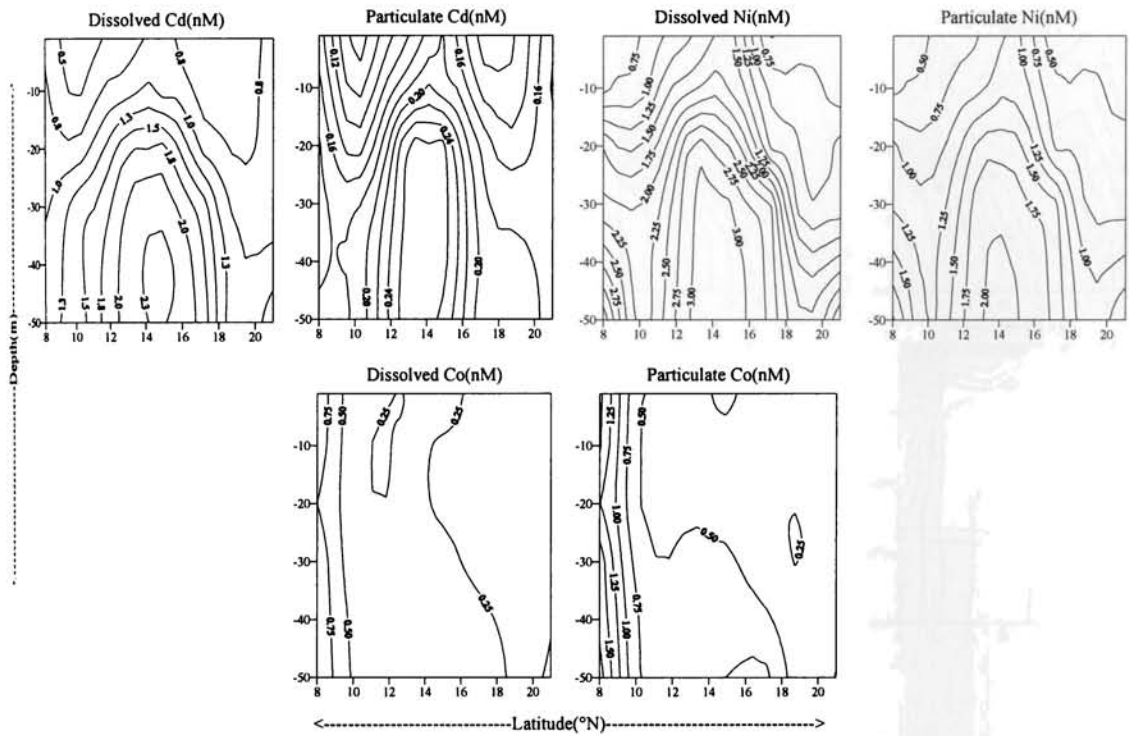
Figure. 27. Vertical section of physical and chemical parameters along the outer shelf of the Arabian Sea during intermonsoon fall
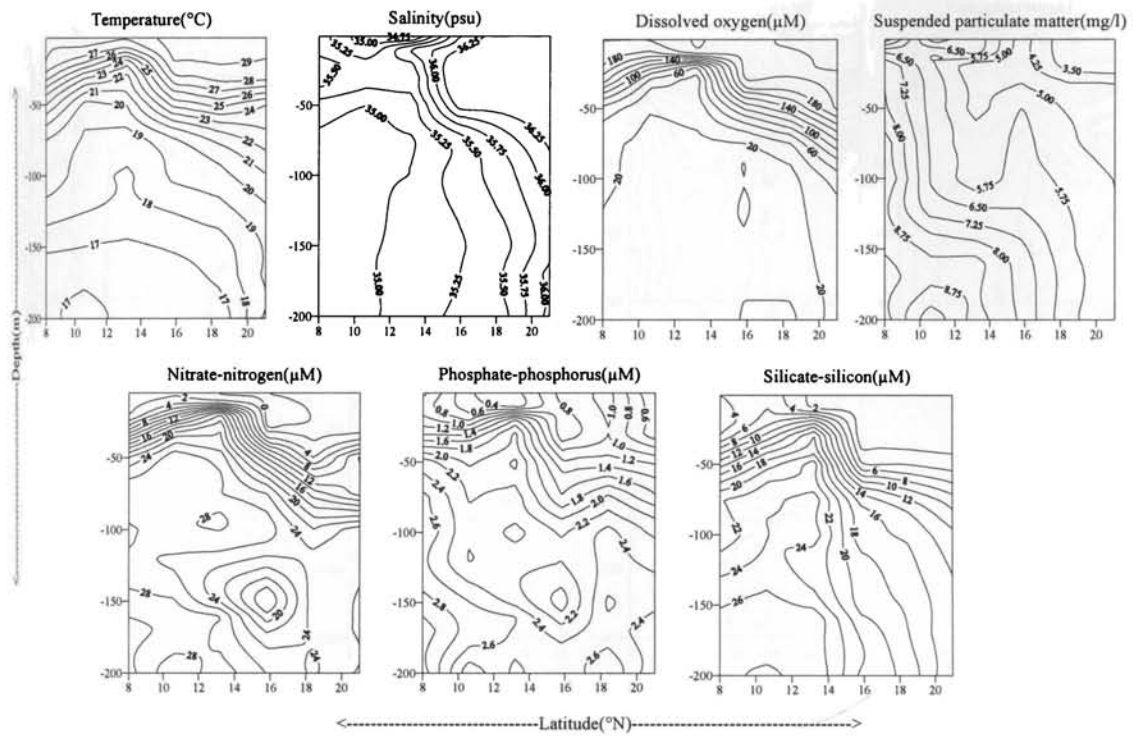
Figure. 28. Vertical section of dissolved and particulate Fe, Cu, Zn & Pb along the outer shelf of the Arabian Sea during intermonsoon fall

Dissolved Fe(μg/l)   Particulate Fe(μg/l)   Dissolved Cu(μg/l)   Particulate Cu(μg/l)

Dissolved Zn(μg/l)   Particulate Zn(μg/l)   Dissolved Pb(μg/l)   Particulate Pb(μg/l)

<------------------------Latitude(°N)------------------------>
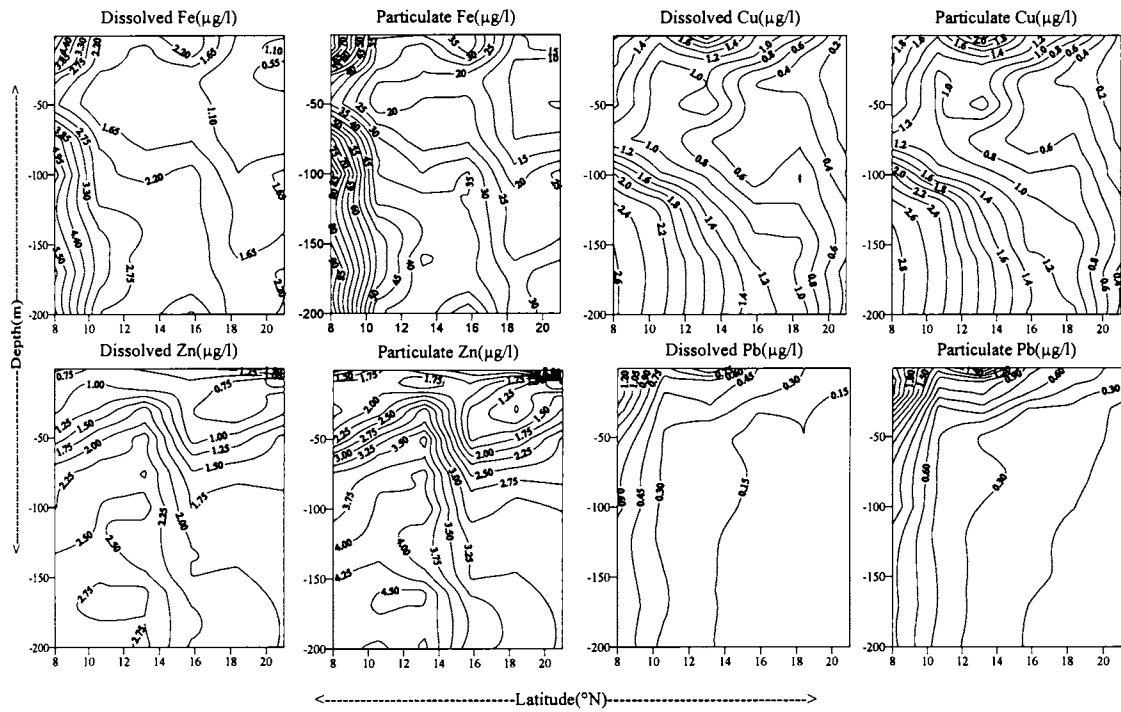
Figure. 29. Vertical section of dissolved and particulate Cd, Ni & Co along the outer shelf of the Arabian Sea during intermonsoon fall

Dissolved Cd(nM)   Particulate Cd(nM)   Dissolved Ni(nM)   Particulate Ni(nM)

Dissolved Co(nM)   Particulate Co(nM)

<------------------------Latitude(°N)------------------------>
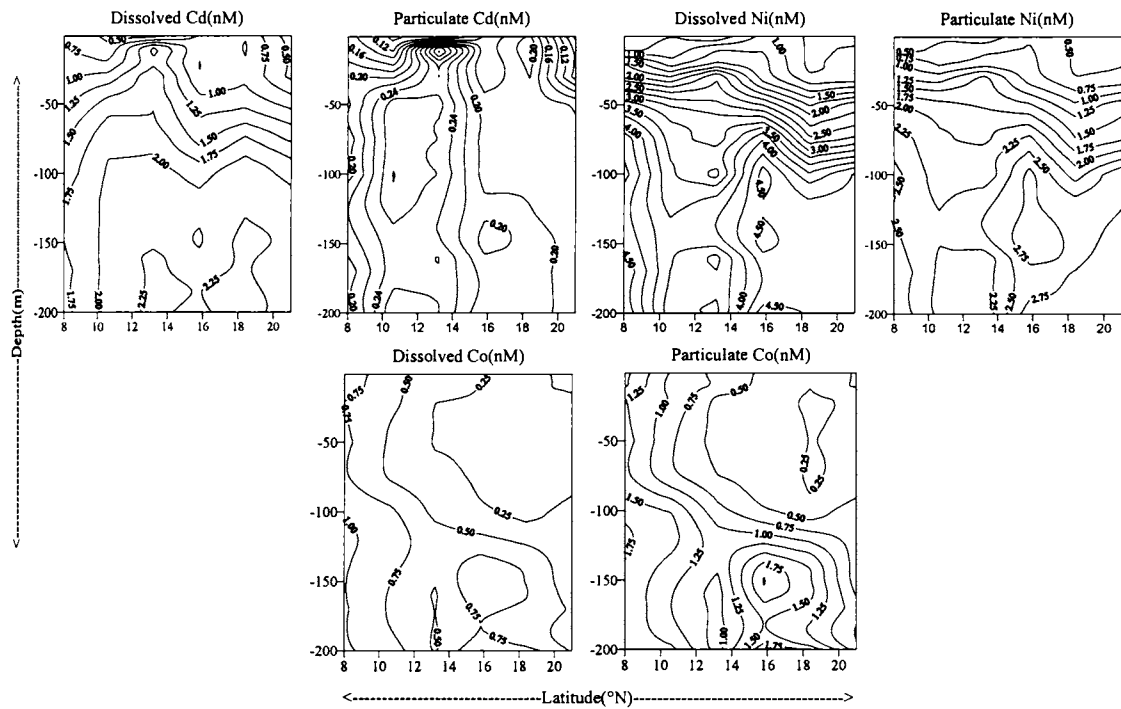
Figure. 30. Vertical section of physical and chemical parameters along the offshore transect (T1) of the Arabian Sea during intermonsoon fall

Temperature(°C)   Salinity(psu)   Suspended particulate matter(mg/l)   Dissolved oxygen(µM)

<-----------------------------Latitude(°N)----------------------------->
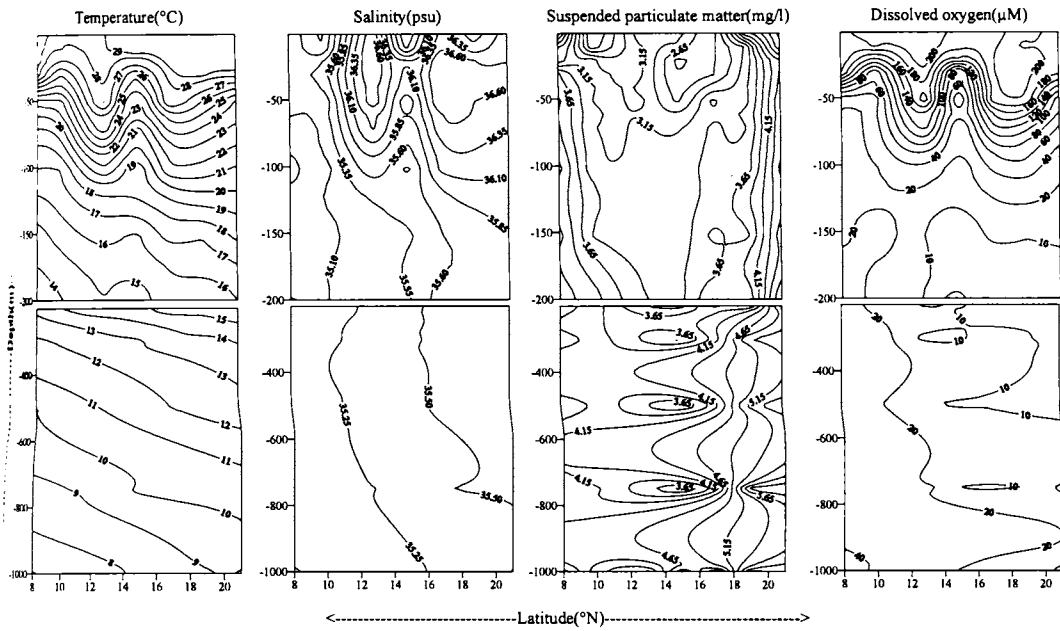
Figure. 31. Vertical section of chemical parameters along the offshore transect (T1) of the Arabian Sea during intermonsoon fall

Nitrate-nitrogen(µM)   Phosphate-phosphorus(µM)   Silicate-silicon(µM)

<-----------------------------Latitude(°N)----------------------------->
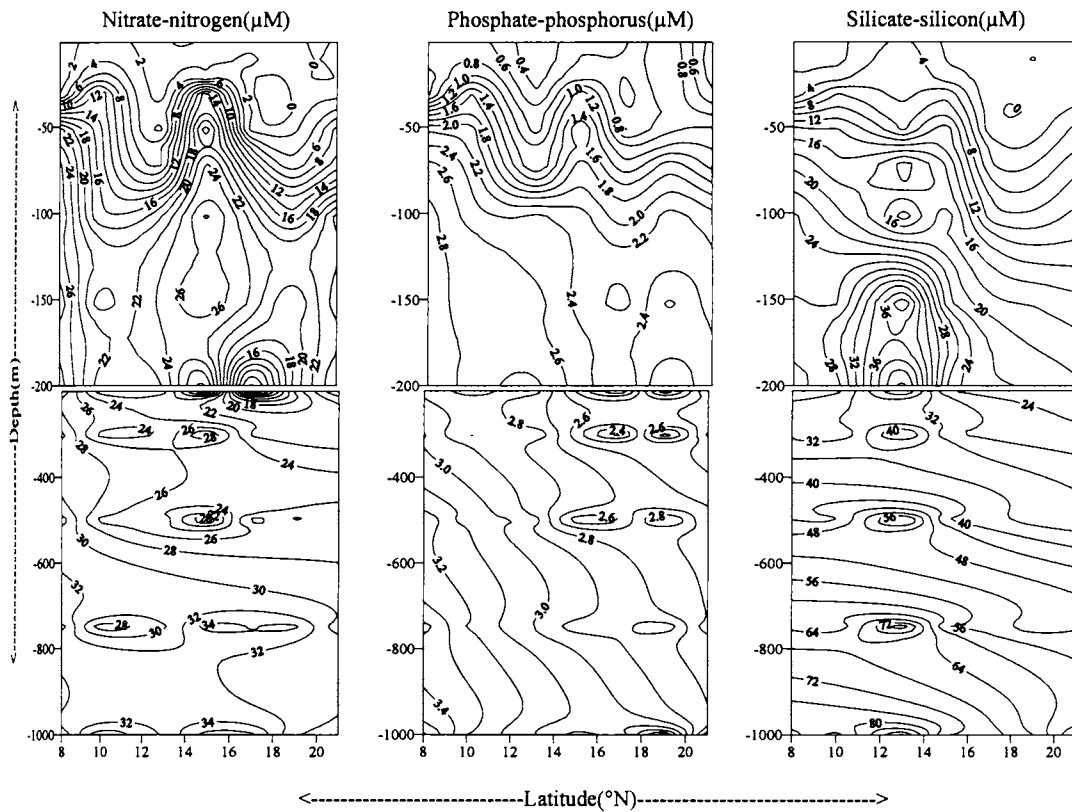
Figure. 32. Vertical section of dissolved and particulate Fe & Cu along the offshore transect (T1) of the Arabian Sea during intermonsoon fall

Dissolved Fe(µg/l) Particulate Fe(µg/l) Dissolved Cu(µg/l) Particulate Cu(µg/l)

<------------------------------Latitude(°N)------------------------------>
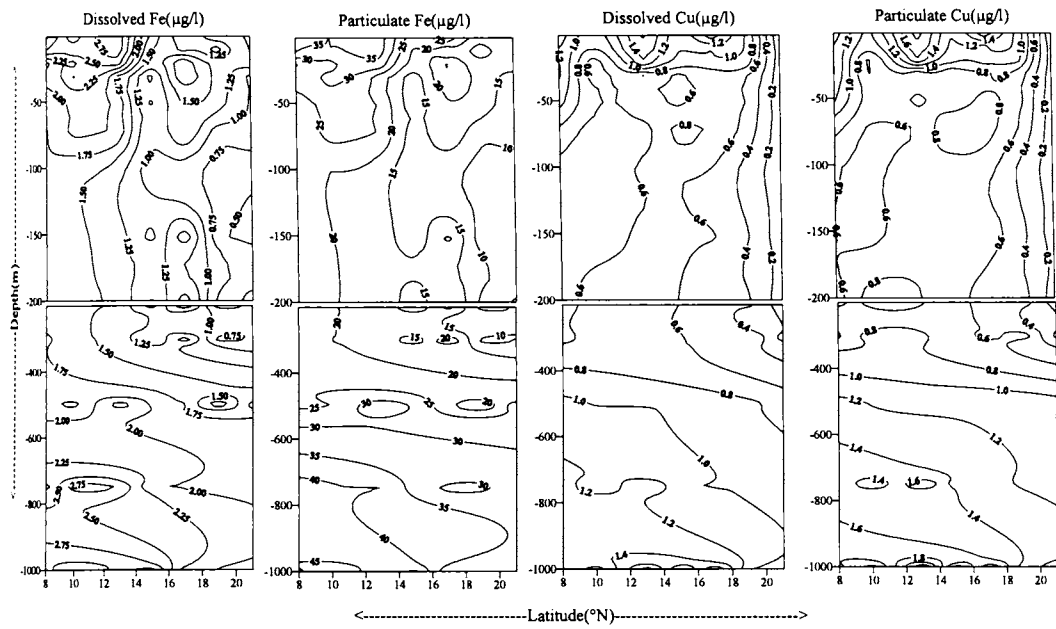
Figure. 33. Vertical section of dissolved and particulate Zn & Pb along the offshore transect (T1) of the Arabian Sea during intermonsoon fall

Dissolved Zn(µg/l) Particulate Zn(µg/l) Dissolved Pb(µg/l) Particulate Pb(µg/l)

<------------------------------Latitude(°N)------------------------------>
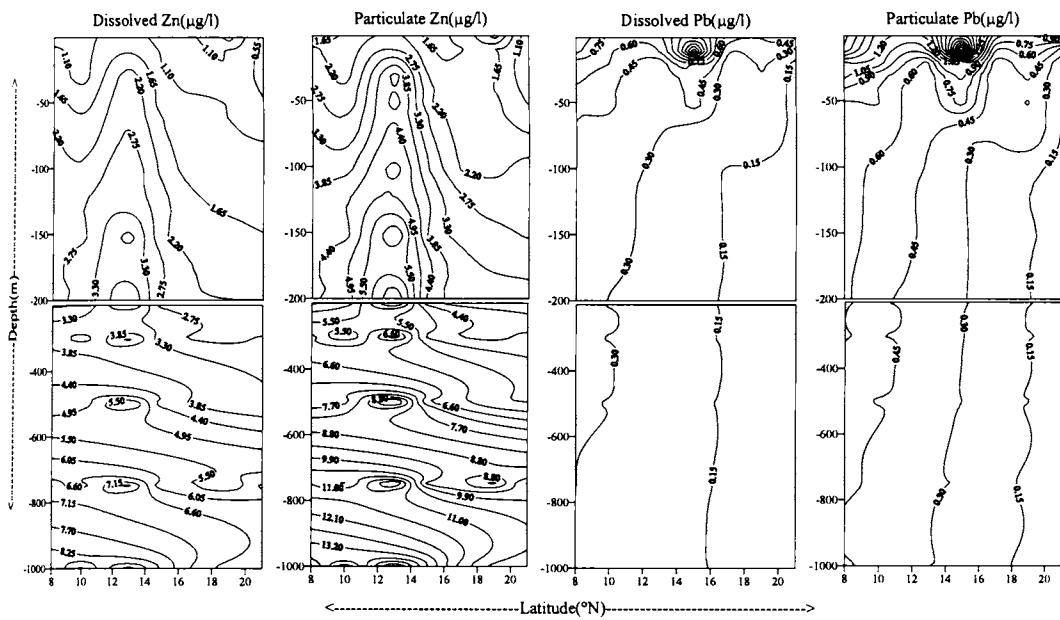
Figure. 34. Vertical section of dissolved and particulate Cd & Ni along the offshore transect (T1) of the Arabian Sea during intermonsoon fall

Dissolved Cd(nM)   Particulate Cd(nM)   Dissolved Ni(nM)   Particulate Ni(nM)

<-------------------------------Latitude(°N)------------------------------->
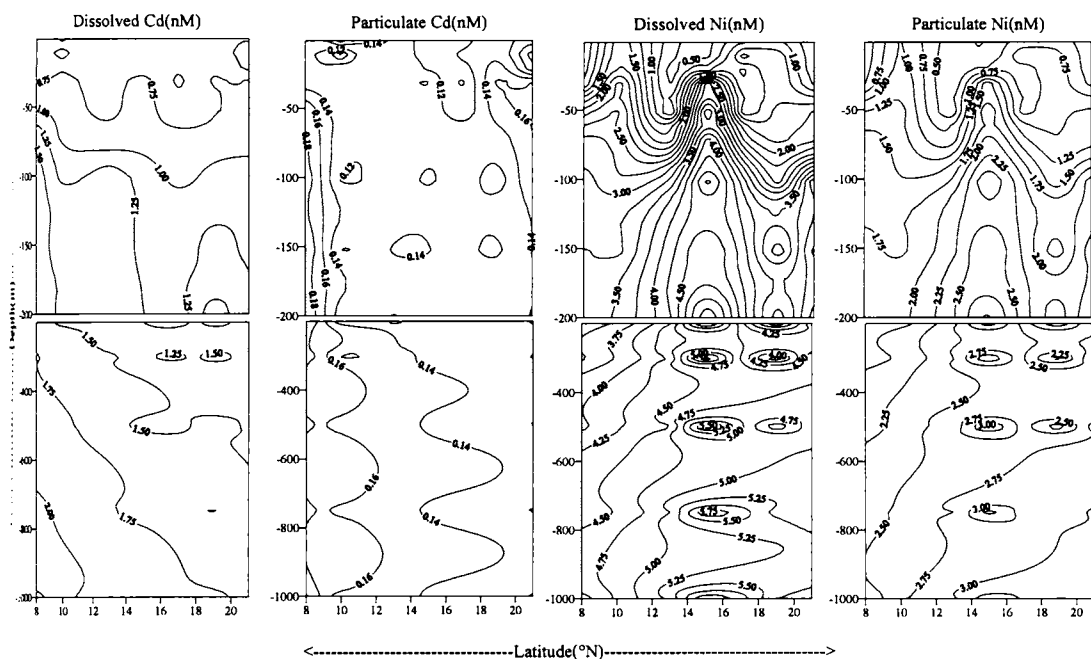
Figure. 35. Vertical section of dissolved and particulate Co along the offshore transect (T1) of the Arabian Sea during intermonsoon fall

Dissolved Co(nM)   Particulate Co(nM)

<---------------------------------Latitude(°N)--------------------------------->
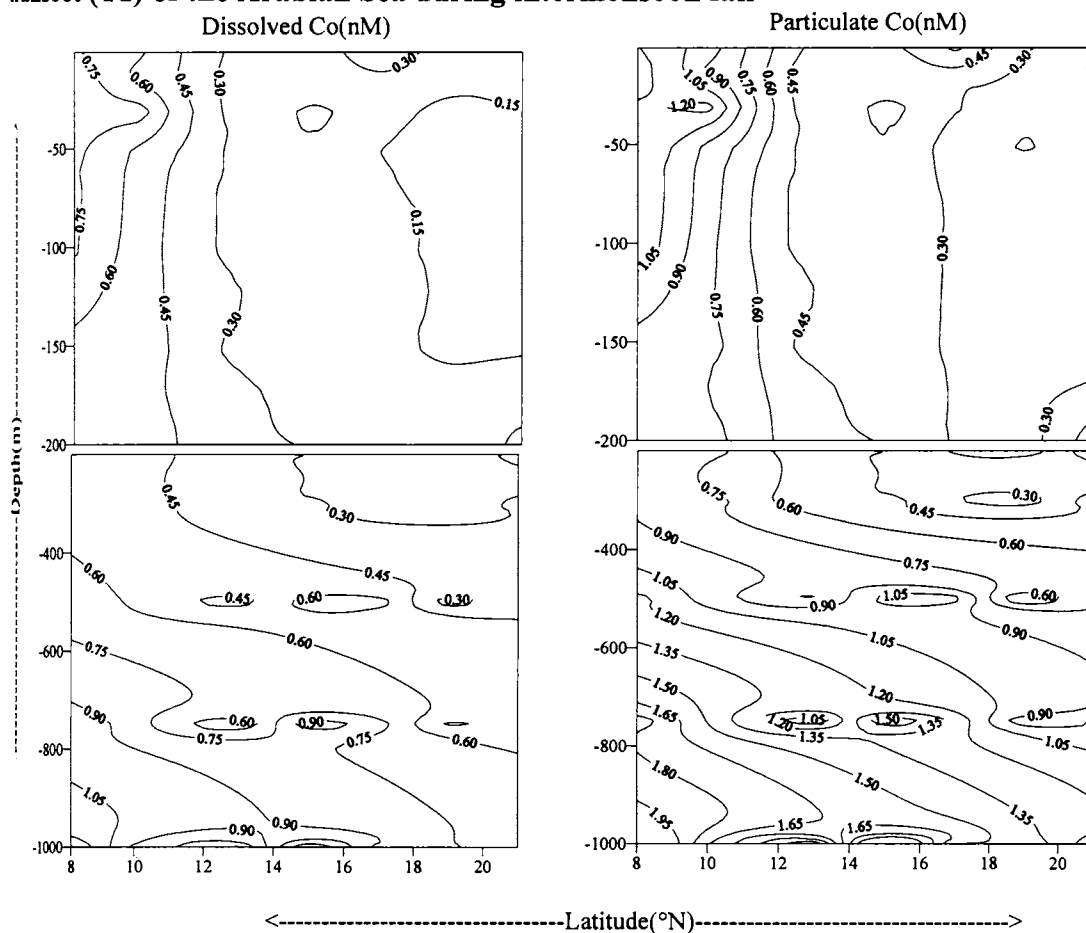
Figure. 36. Vertical section of physical and chemical parameters along the offshore transect (T2) of the Arabian Sea during intermonsoon fall

Temperature(°C)　　　Salinity(psu)　　　Suspended particulate matter(mg/l)　　　Dissolved oxygen(µM)

<-------------------------------Latitude(°N)------------------------------->
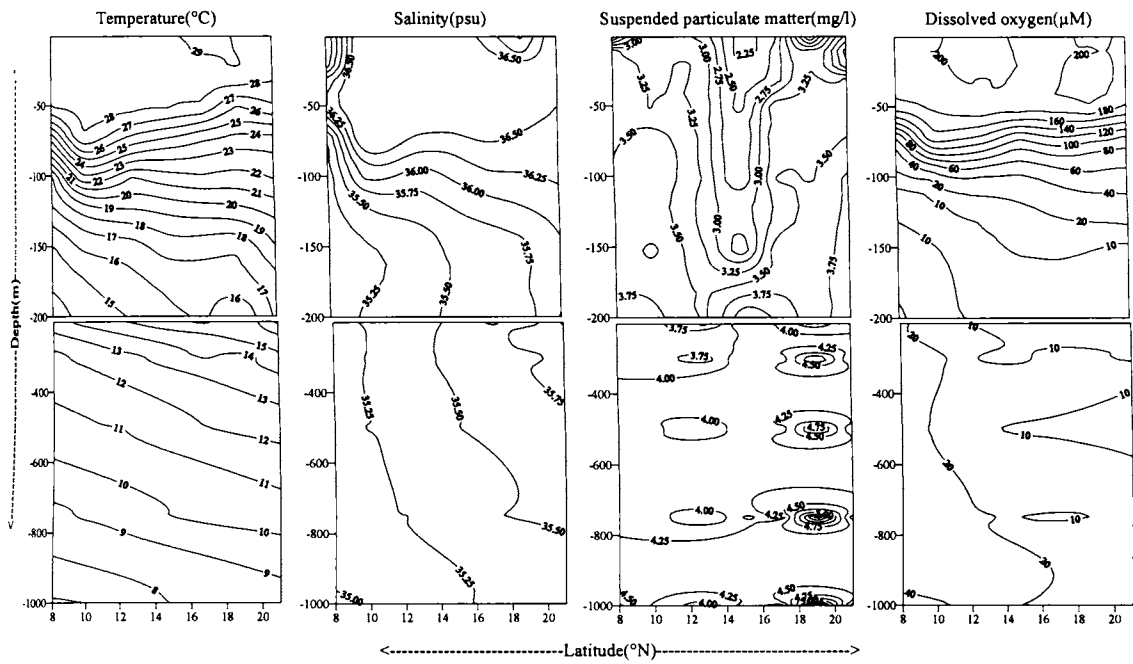
Figure. 37. Vertical section of chemical parameters along the offshore transect (T2) of the Arabian Sea during intermonsoon fall

Nitrate-nitrogen(µM)　　　Phosphate-phosphorus(µM)　　　Silicate-silicon(µM)

<-------------------------------Latitude(°N)------------------------------->
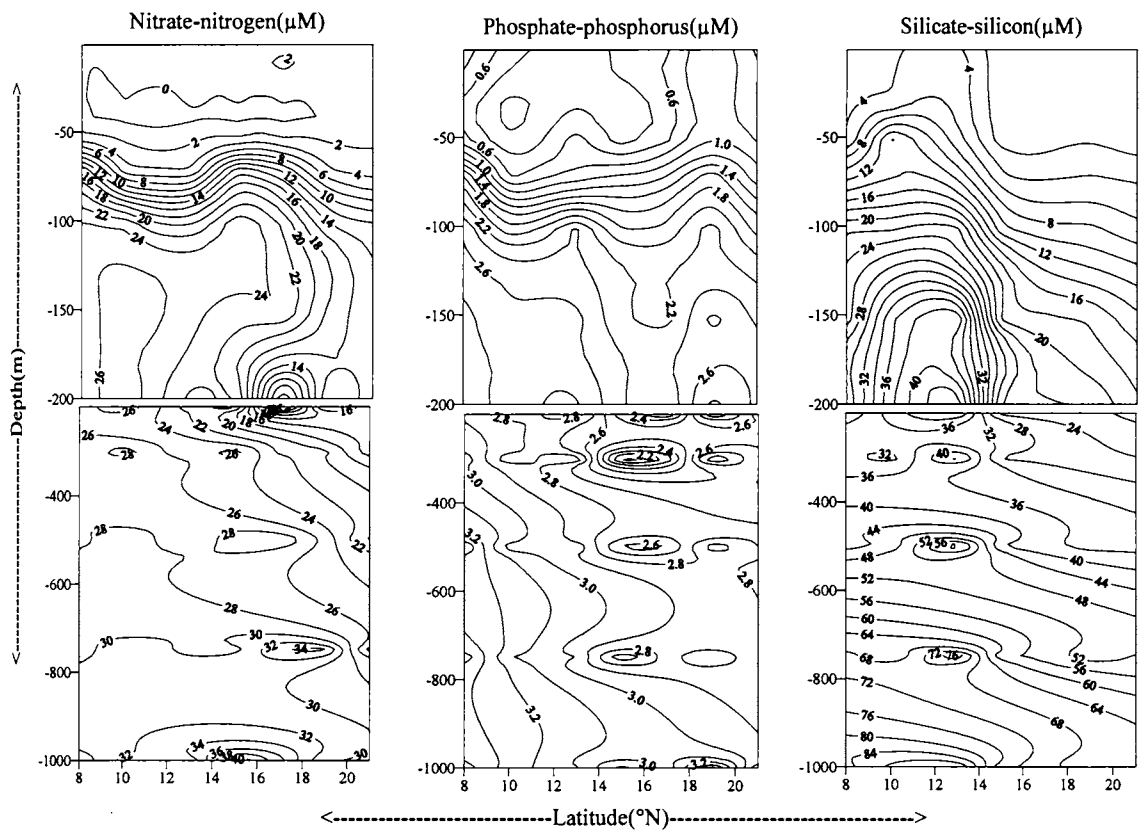
Figure. 38. Vertical section of dissolved and particulate Fe & Cu along the offshore transect (T2) of the Arabian Sea during intermonsoon fall

Dissolved Fe(µg/l)　　Particulate Fe(µg/l)　　Dissolved Cu(µg/l)　　Particulate Cu(µg/l)

Depth(m)

<-------------------------------Latitude(°N)------------------------------->
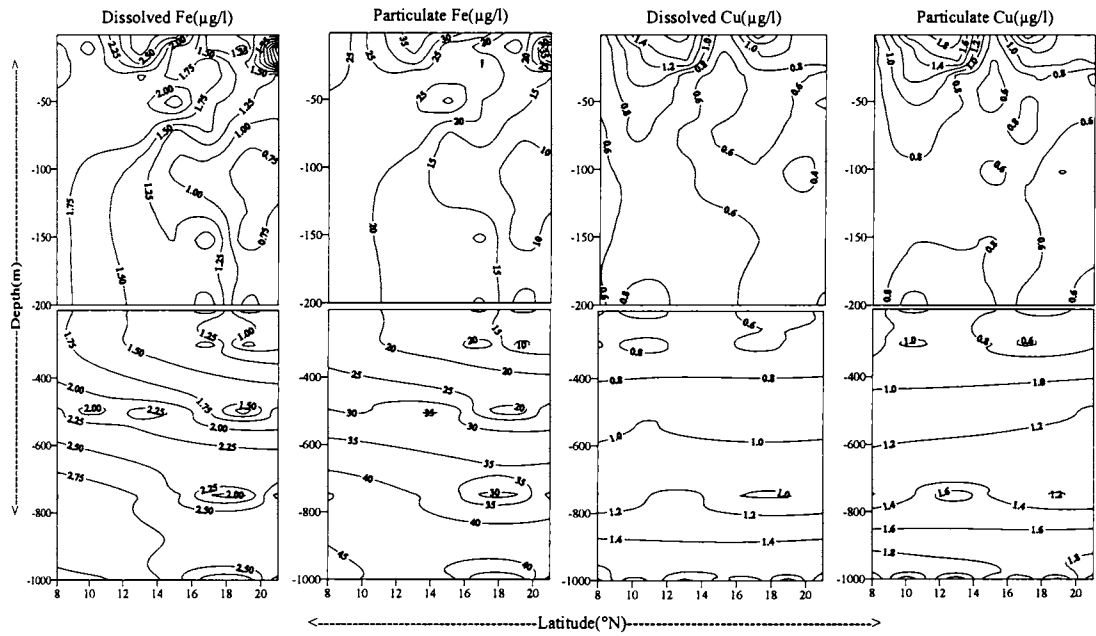
Figure. 39. Vertical section of dissolved and particulate Zn & Pb along the offshore transect (T2) of the Arabian Sea during intermonsoon fall

Dissolved Zn(µg/l)　　Particulate Zn(µg/l)　　Dissolved Pb(µg/l)　　Particulate Pb(µg/l)

Depth(m)

<-------------------------------Latitude(°N)------------------------------->
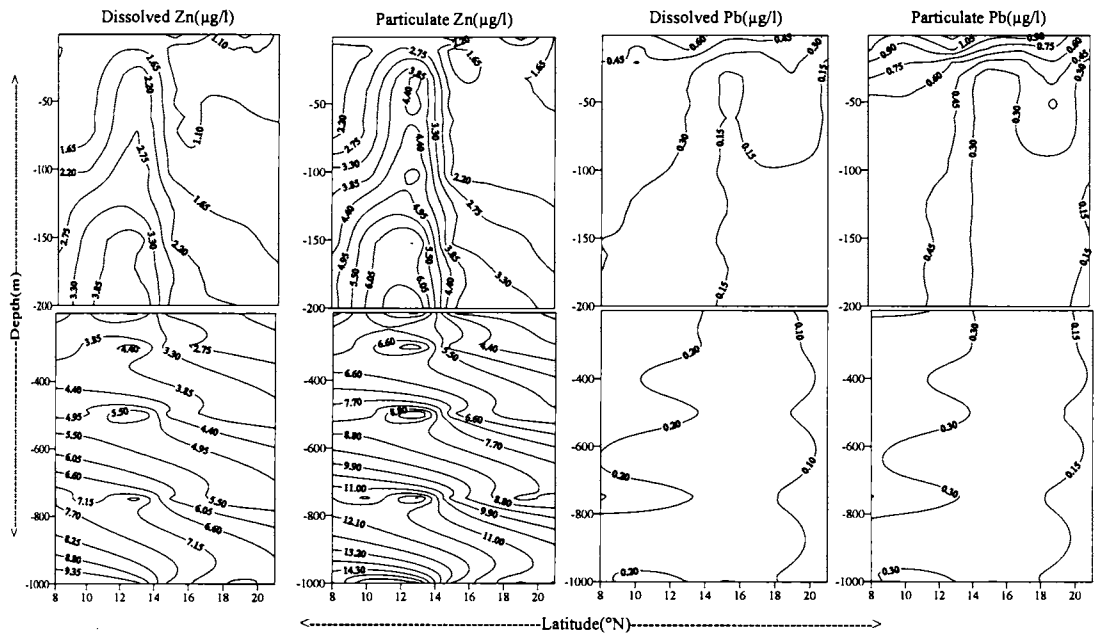
Figure. 40. Vertical section of dissolved and particulate Cd & Ni along the offshore transect (T2) of the Arabian Sea during intermonsoon fall

Dissolved Cd(nM)   Particulate Cd(nM)   Dissolved Ni(nM)   Particulate Ni(nM)

<--Latitude(°N)-->
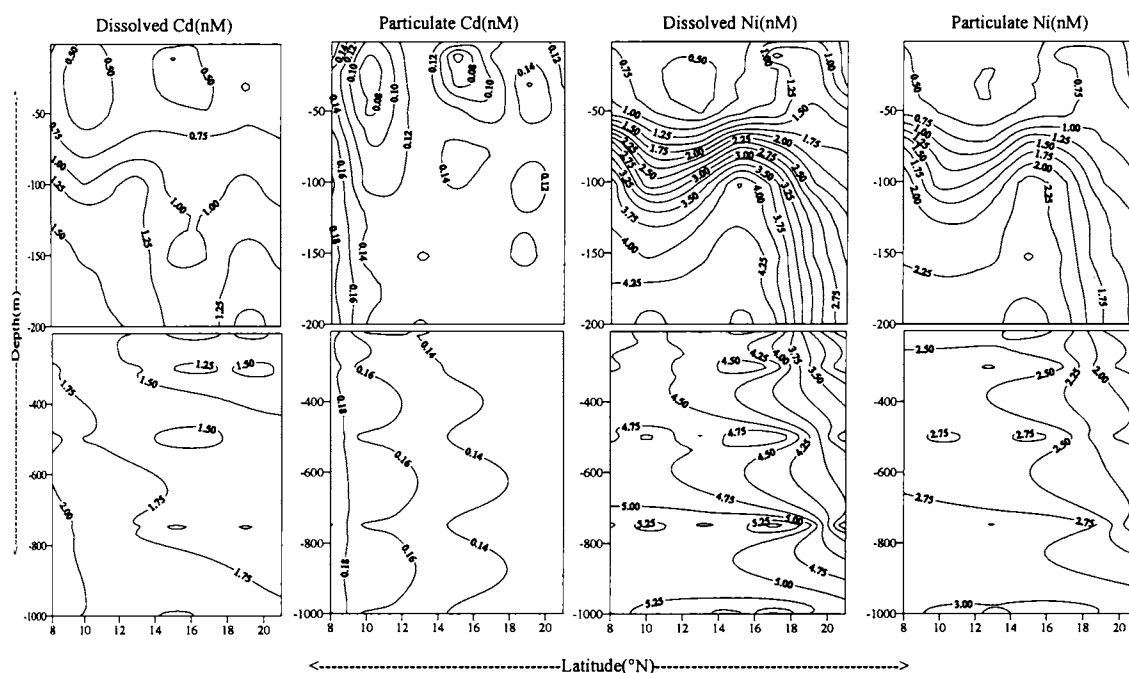
Figure. 41. Vertical section of dissolved and particulate Co along the offshore transect (T2) of the Arabian Sea during intermonsoon fall

Dissolved Co(nM)   Particulate Co(nM)

<---Latitude(°N)--->
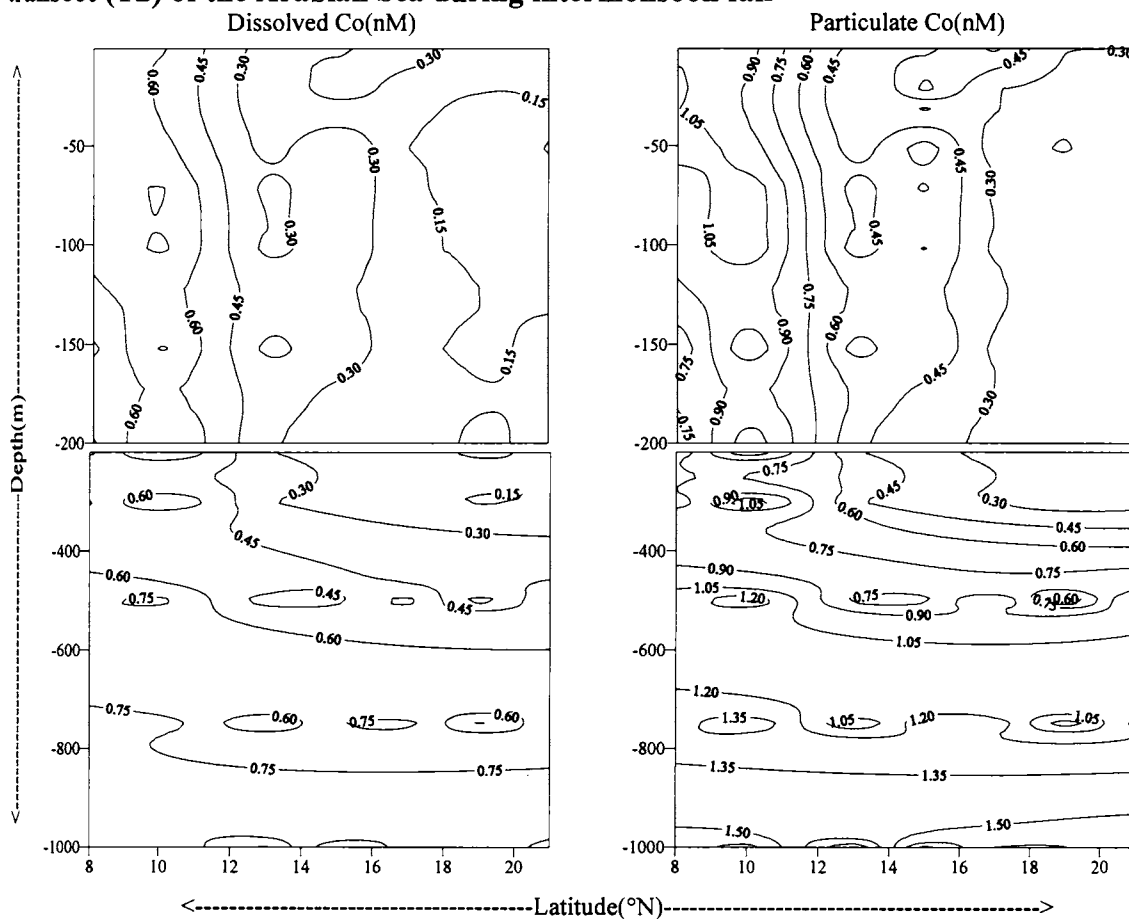
Figure. 42. Vertical section of physical and chemical parameters along the inner shelf of the Arabian Sea during spring intermonsoon
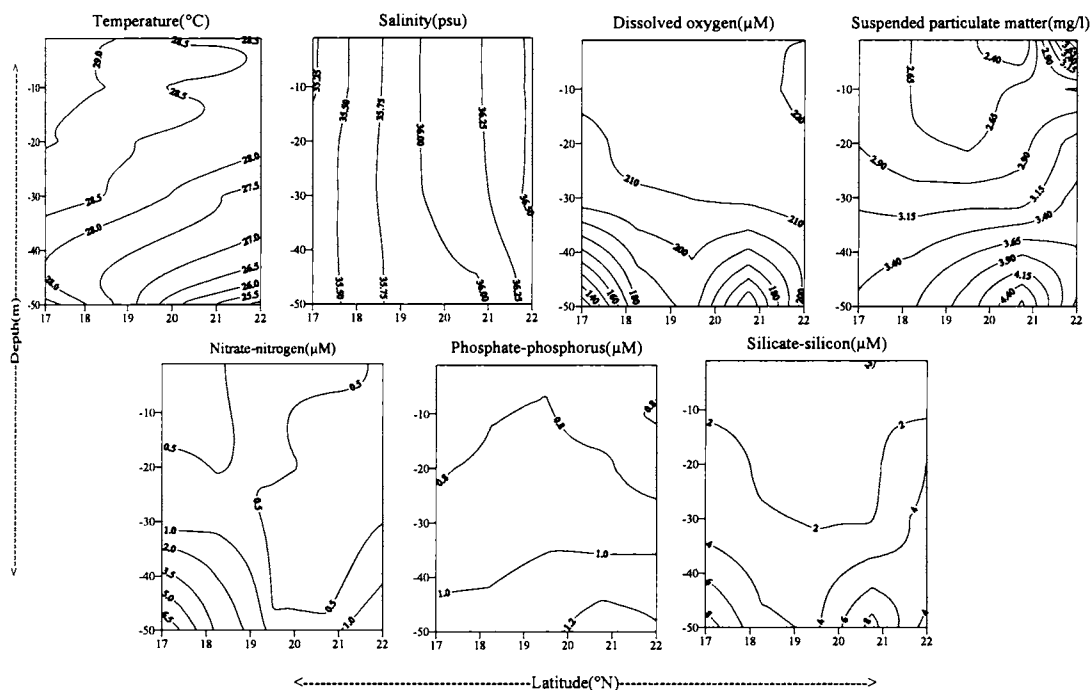
Figure. 43. Vertical section of dissolved and particulate Fe, Cu, Zn & Pb along the inner shelf of the Arabian Sea during spring intermonsoon
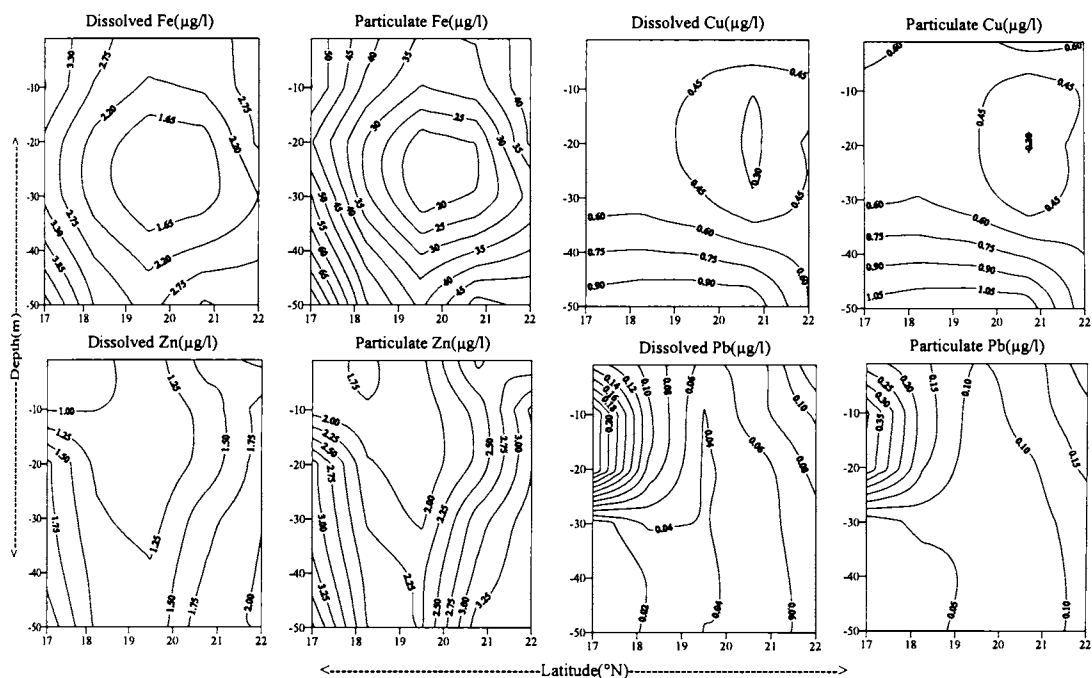
Figure. 44. Vertical section of dissolved and particulate Cd, Ni & Co along the inner shelf of the Arabian Sea during spring intermonsoon
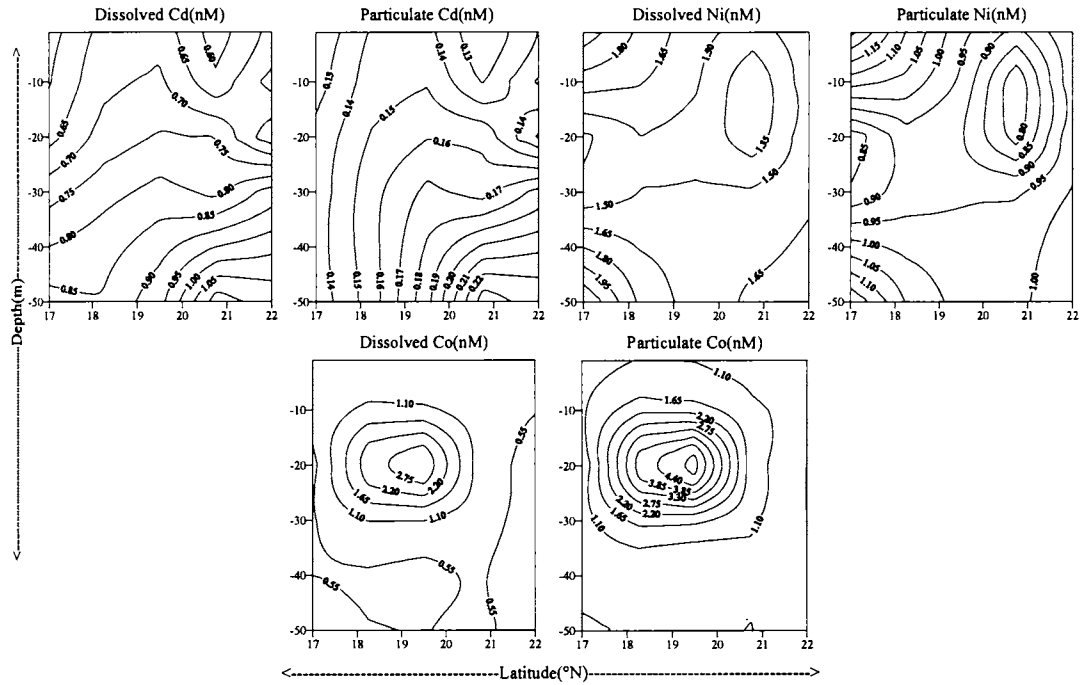
Figure. 45. Vertical section of physical and chemical parameters along the outer shelf of the Arabian Sea during spring intermonsoon
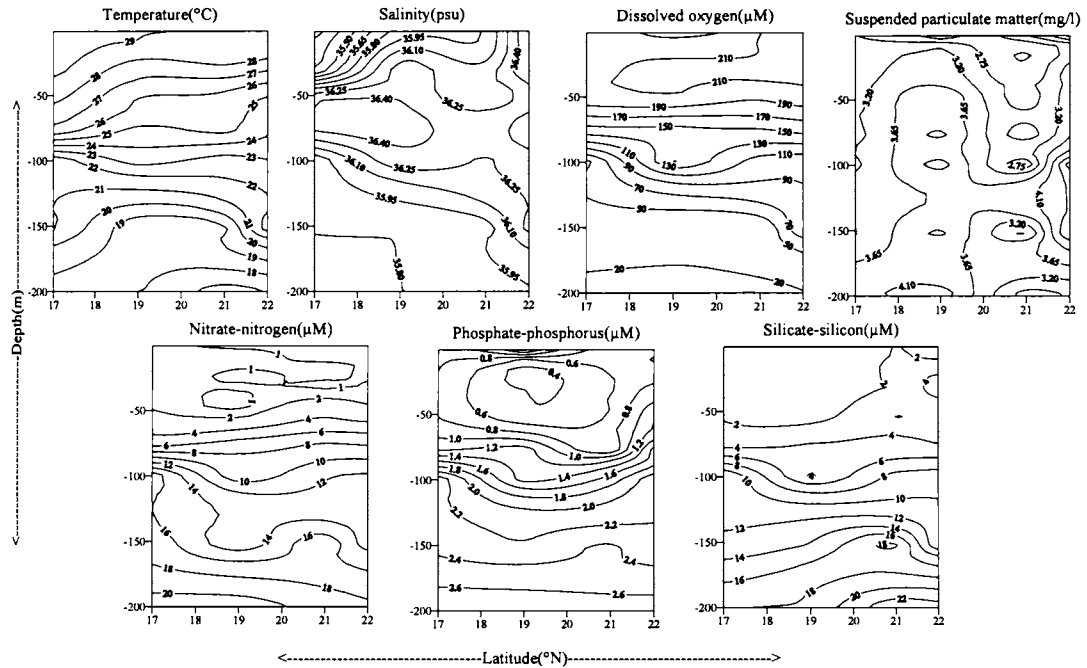
Figure. 46. Vertical section of dissolved and particulate Fe, Cu, Zn & Pb along the outer shelf of the Arabian Sea during spring intermonsoon
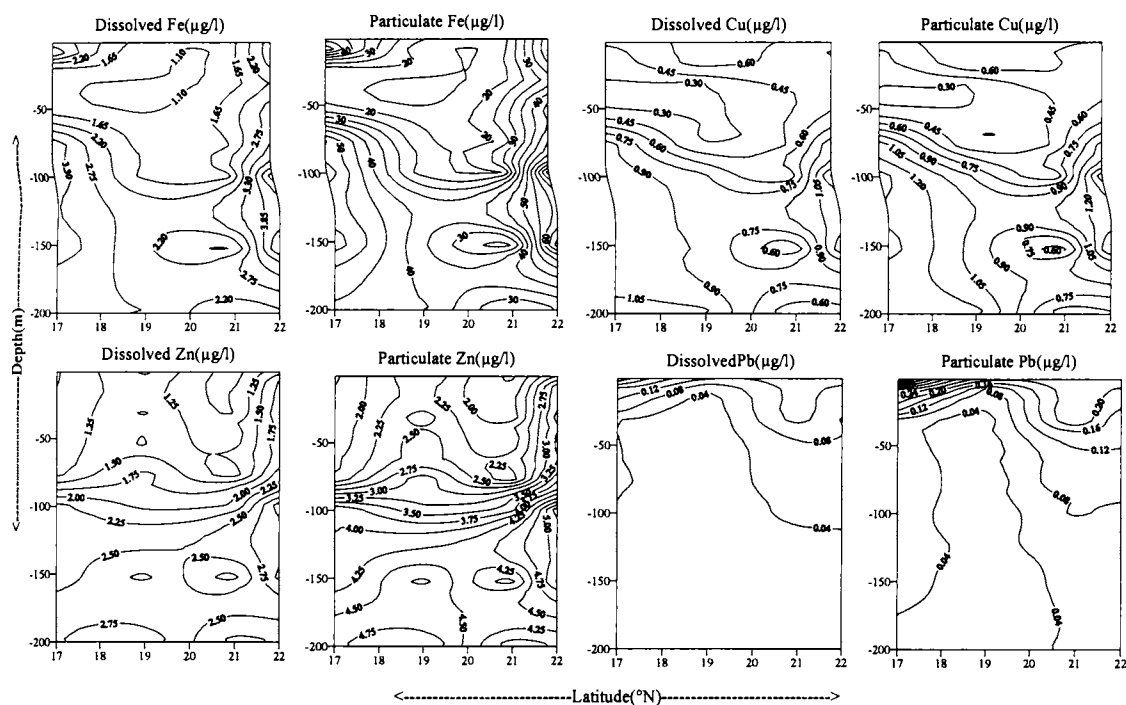
Figure. 47. Vertical section of dissolved and particulate Cd, Ni & Co along the outer shelf of the Arabian Sea during spring intermonsoon
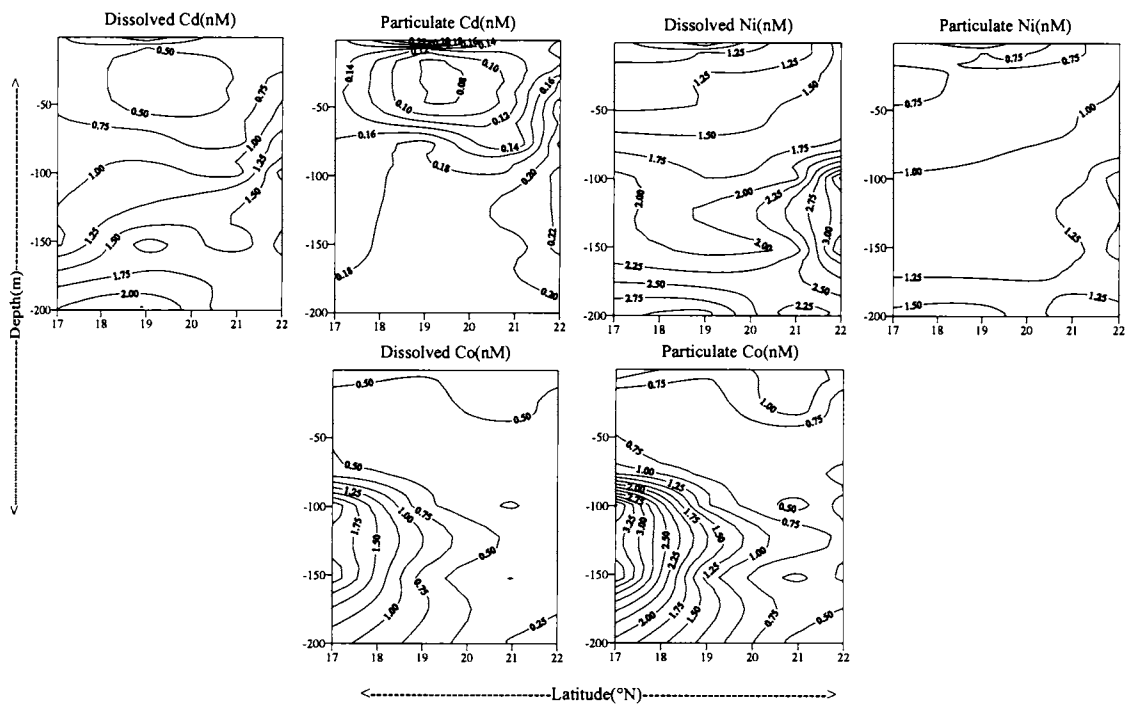
Figure. 48. Vertical section of physical and chemical parameters along the offshore transect (T1) of the Arabian Sea during spring intermonsoon

Temperature(°C)   Salinity(psu)   Dissolved oxygen(μM)   Suspended particulate matter(mg/l)

Depth(m)

<-------------------------------Latitude(°N)------------------------------->
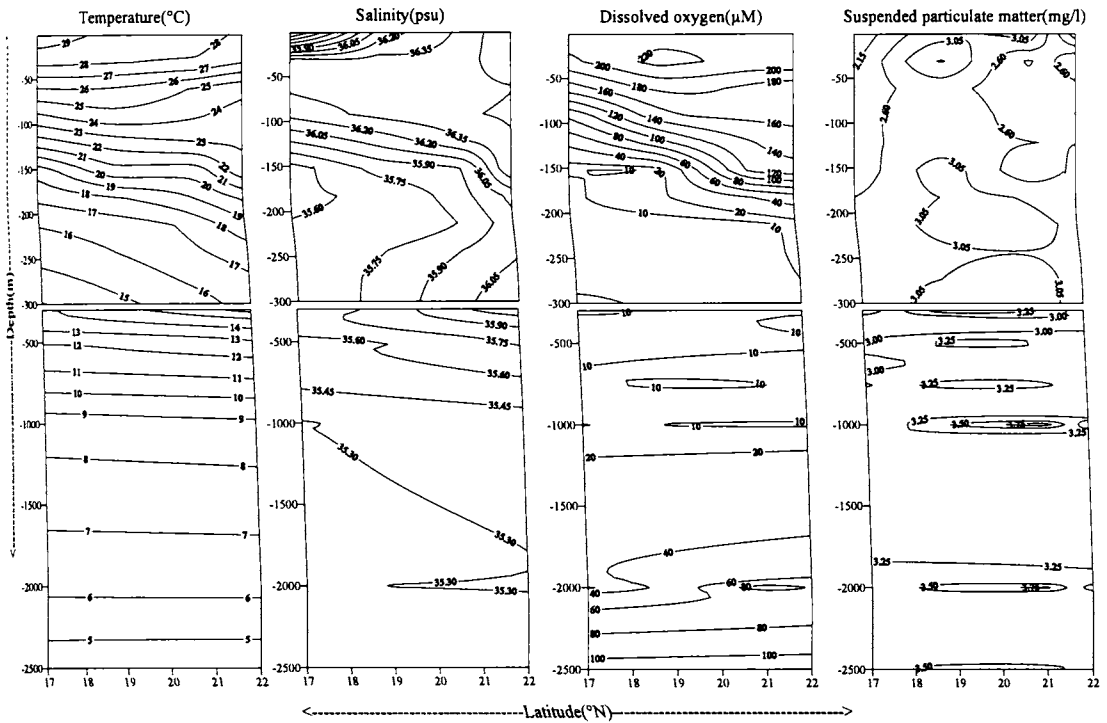
Figure. 49. Vertical section of chemical parameters along the offshore transect (T1) of the Arabian Sea during intermonsoon spring

Nitrate-nitrogen(μM)   Phosphate-phosphorus(μM)   Silicate-silicon(μM)

Depth(m)

<-------------------------------Latitude(°N)------------------------------->
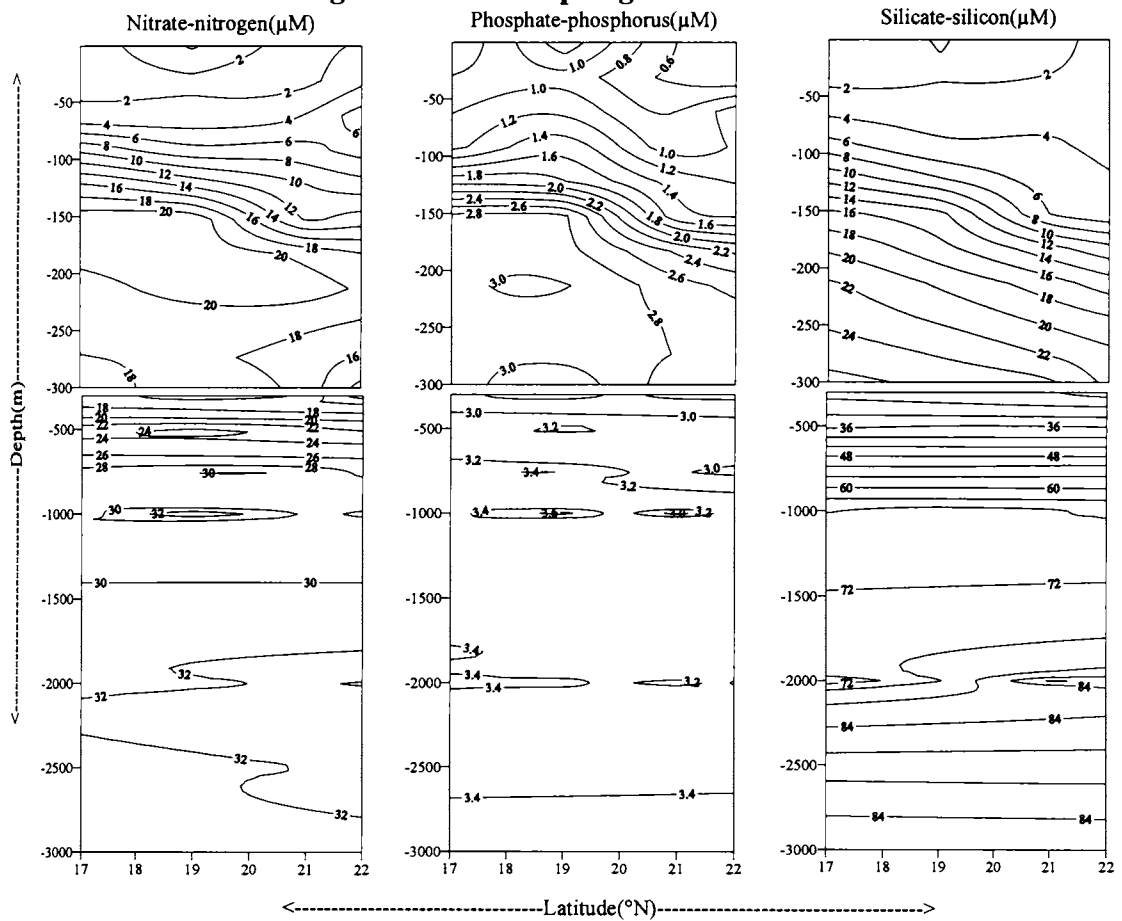
Figure. 50. Vertical section of dissolved and particulate Fe & Cu along the offshore transect (T1) of the Arabian Sea during spring intermonsoon
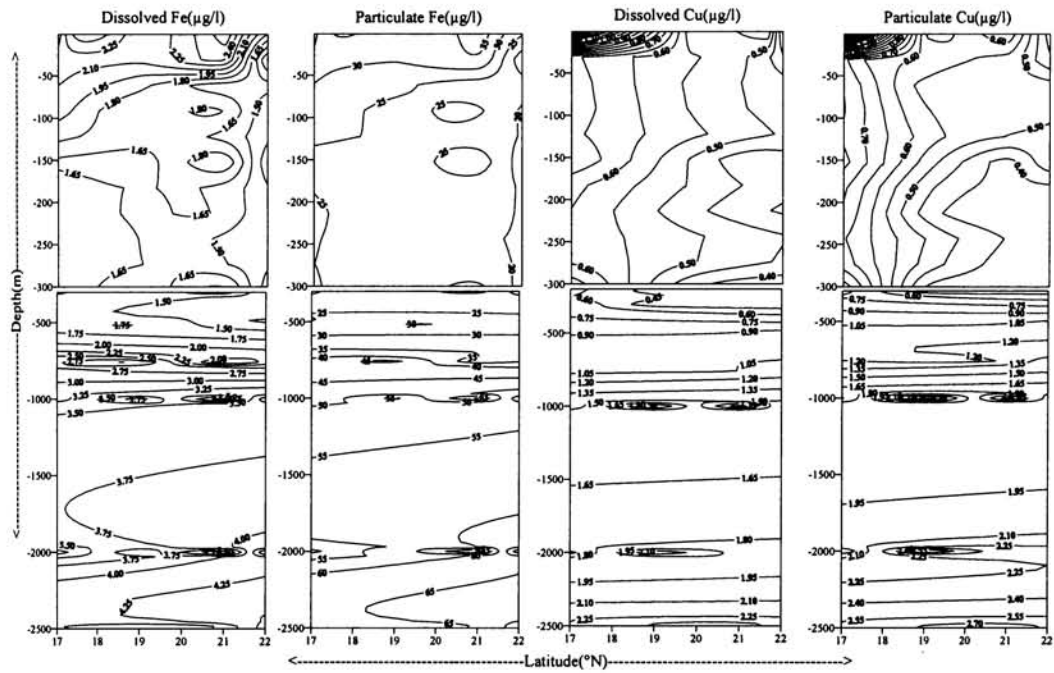
Figure. 51. Vertical section of dissolved and particulate Zn & Pb along the offshore transect (T1) of the Arabian Sea during spring intermonsoon
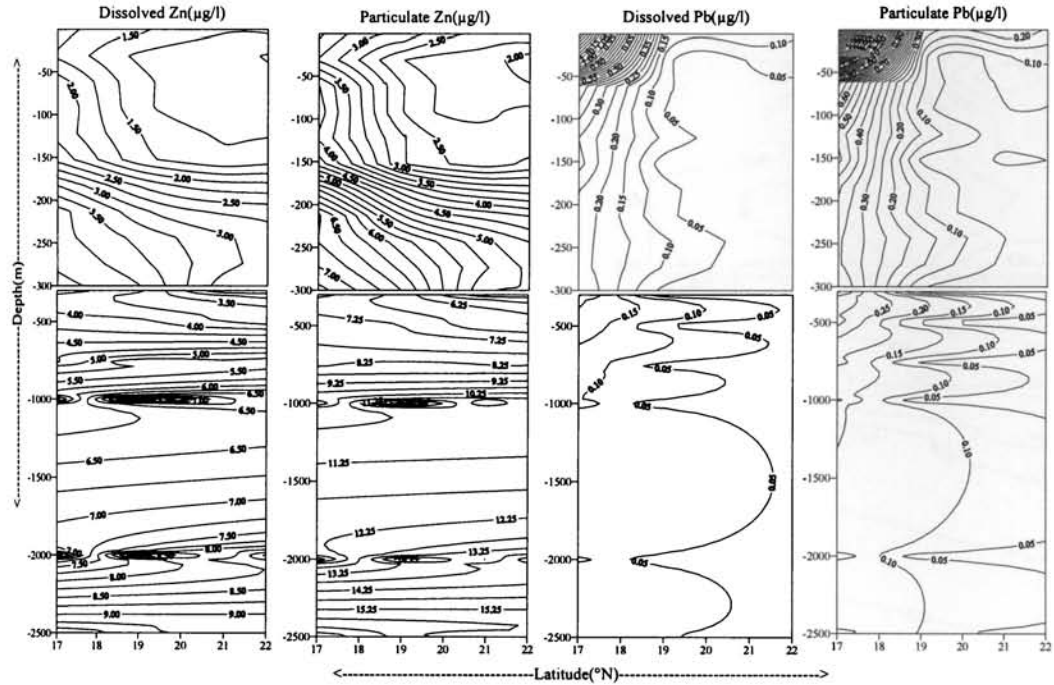
Figure. 52. Vertical section of dissolved and particulate Cd & Ni along the offshore transect (T1) of the Arabian Sea during spring intermonsoon

Dissolved Cd(nM)   Particulate Cd(nM)   Dissolved Ni(nM)   Particulate Ni(nM)

<-------------------------------Latitude(°N)------------------------------->
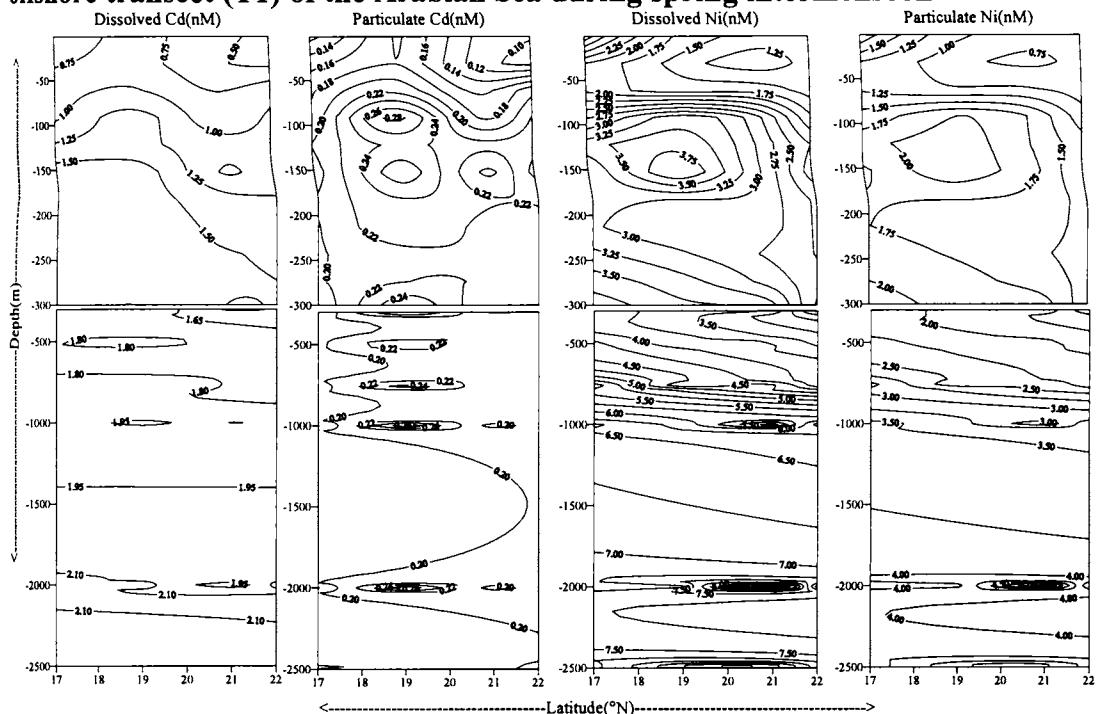
Figure. 53. Vertical section of dissolved and particulate Co along the offshore transect (T1) of the Arabian Sea during spring intermonsoon

Dissolved Co(nM)   Particulate Co(nM)

<-------------------------------Latitude(°N)------------------------------->
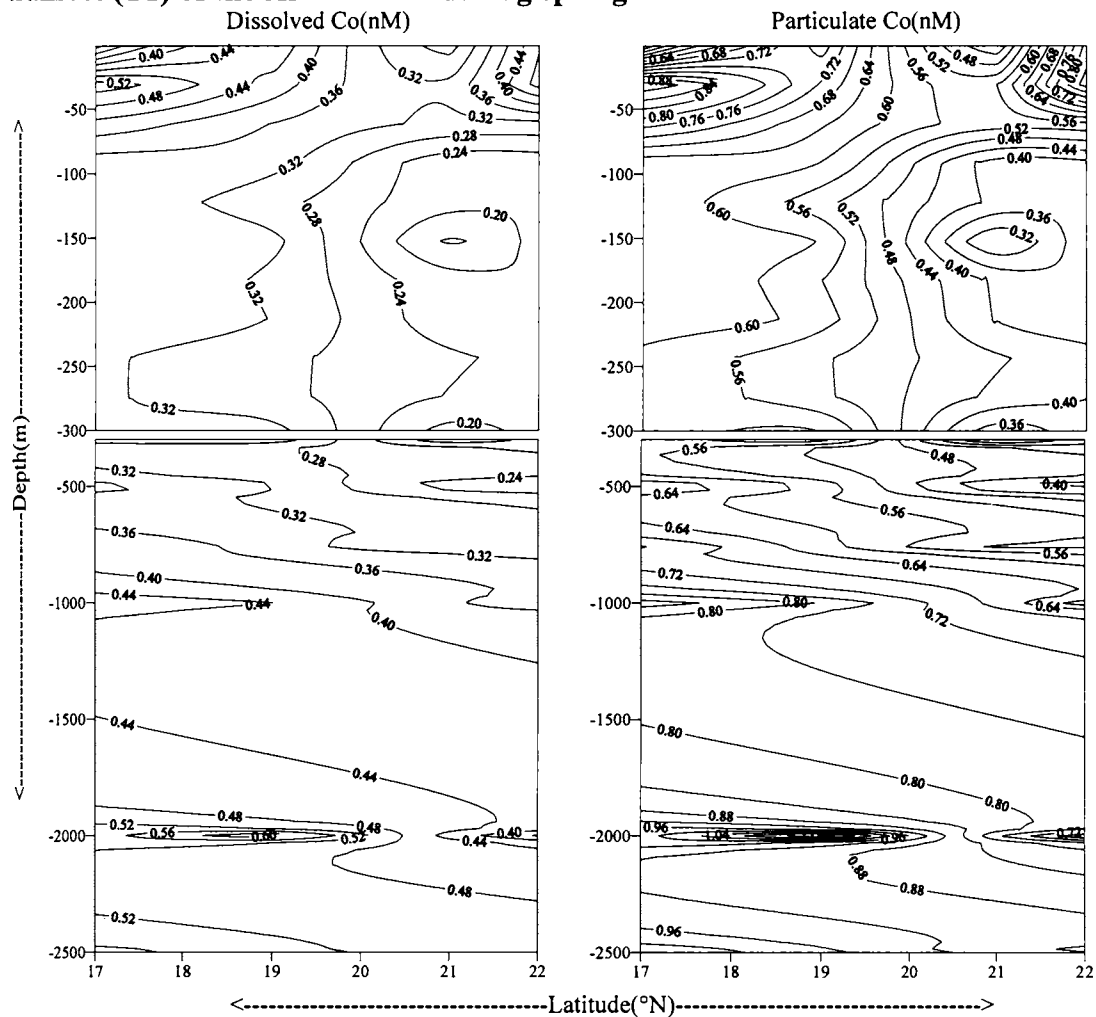
Figure. 54. Vertical section of physical and chemical parameters along the inner shelf of the Bay of Bengal during winter monsoon

Temperature(°C) Salinity(psu) Dissolved oxygen(μM) Suspended particulate matter(mg/l)

Nitrate-nitrogen(μM) Phosphate-phosphorus(μM) Silicate-silicon(μM)

<------------------------------Latitude(°N)------------------------------->
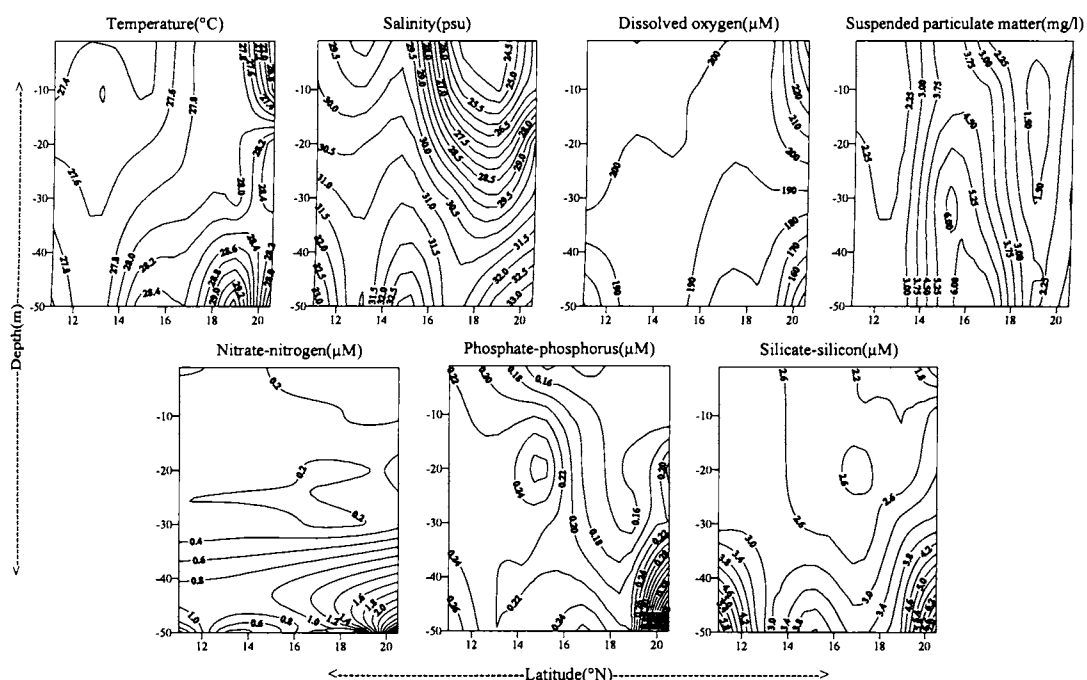
Figure. 55. Vertical section of dissolved and particulate Fe, Cu, Zn & Pb along the inner shelf of the Bay of Bengal during winter monsoon

Dissolved Fe(μg/l) Particulate Fe(μg/l) Dissolved Cu(μg/l) Particulate Cu(μg/l)

Dissolved Zn(μg/l) Particulate Zn(μg/l) Dissolved Pb(μg/l) Particulate Pb(μg/l)

<------------------------------Latitude(°N)------------------------------->
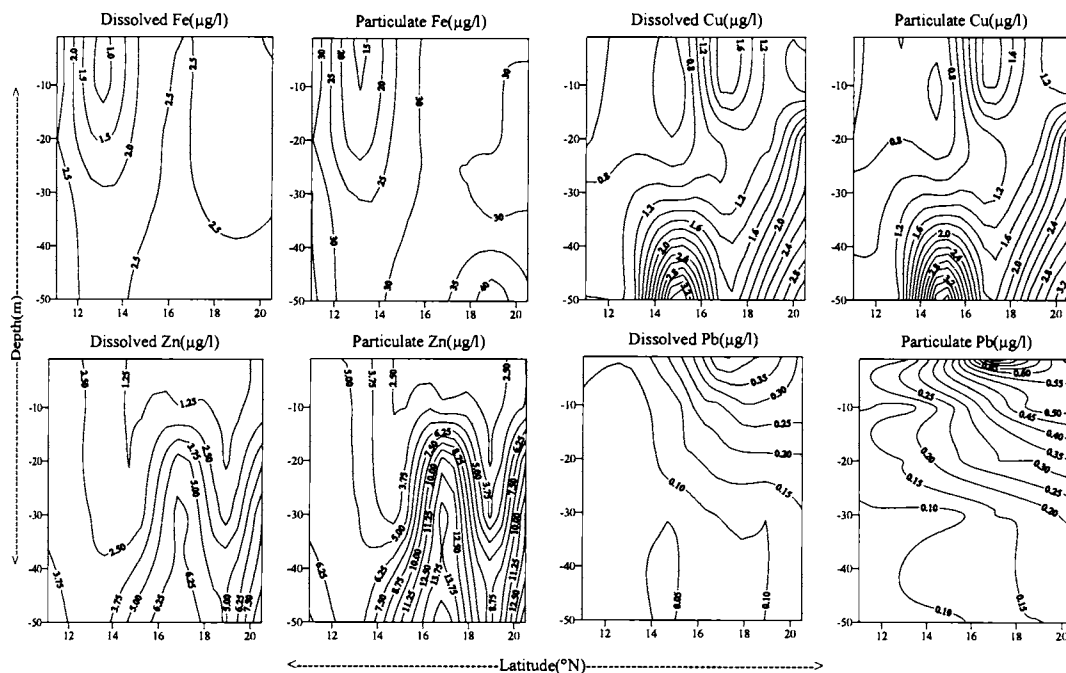
Figure. 56. Vertical section of dissolved and particulate Cd, Co & Ni along the inner shelf of the Bay of Bengal during winter monsoon

Figure. 57. Vertical section of physical and chemical parameters along the outer shelf of the Bay of Bengal during winter monsoon
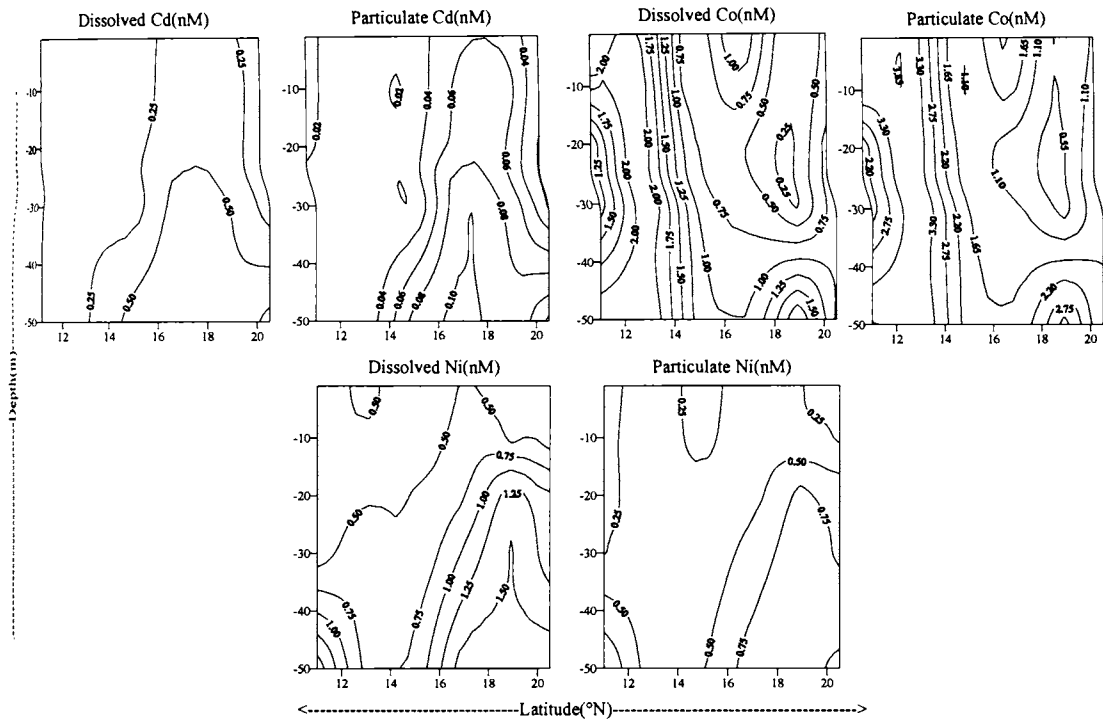
Figure. 58. Vertical section of dissolved and particulate Fe, Cu, Zn & Pb along the outer shelf of the Bay of Bengal during winter monsoon
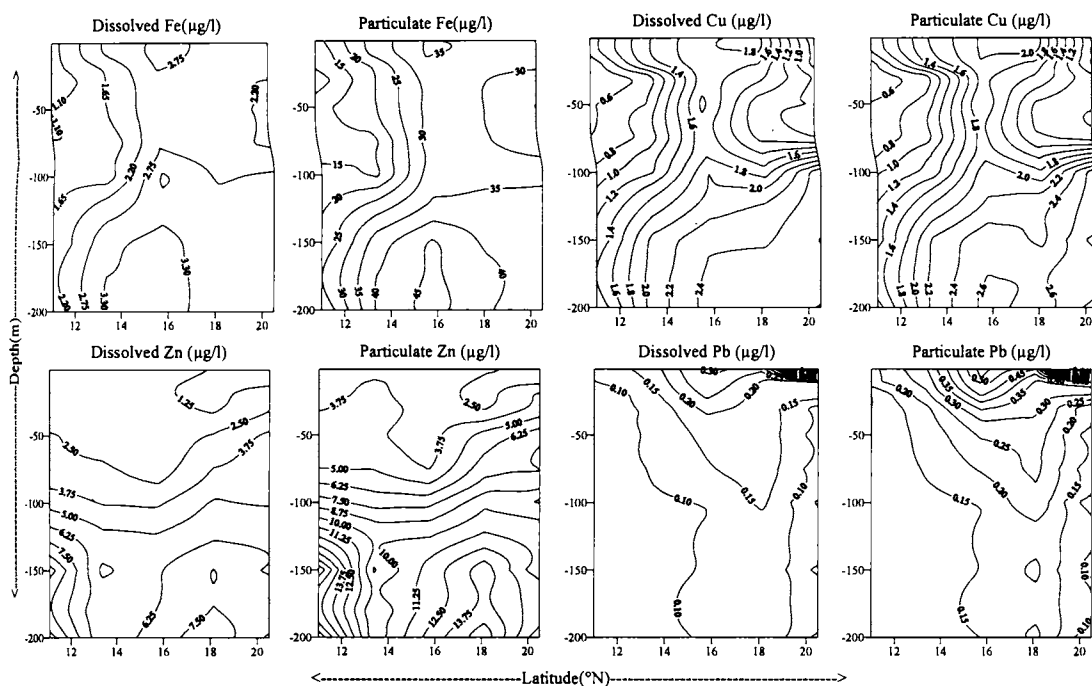
Figure. 59. Vertical section of dissolved and particulate Cd, Co & Ni along the outer shelf of the Bay of Bengal during winter monsoon
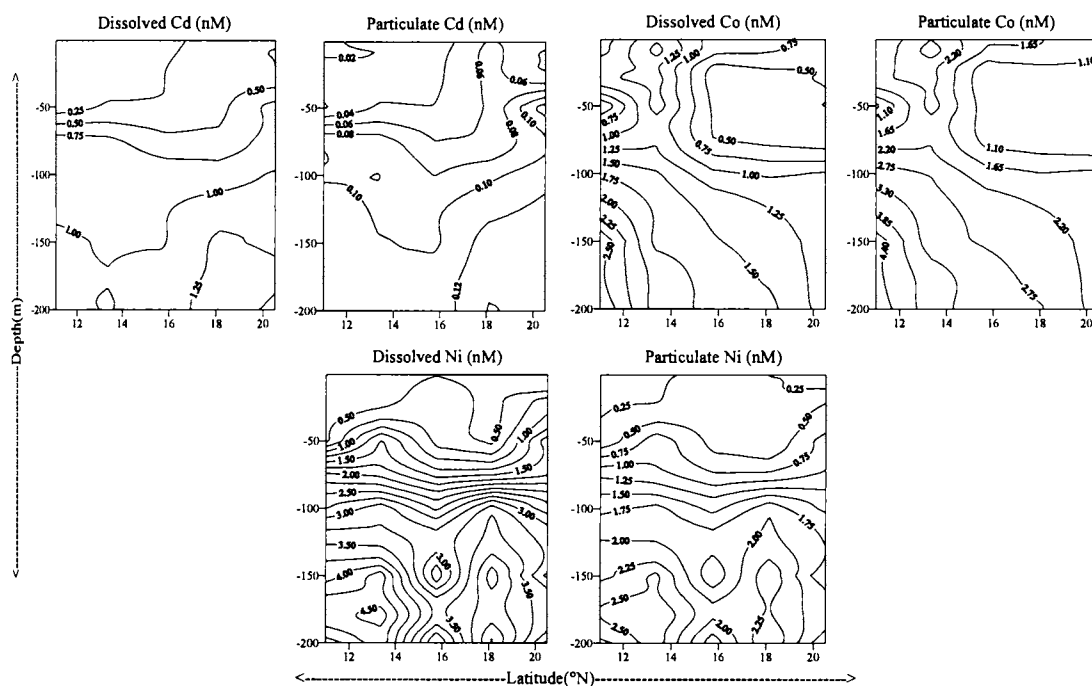
Figure. 60. Vertical section of physical and chemical parameters along the offshore transect (T1) of the Bay of Bengal during winter monsoon
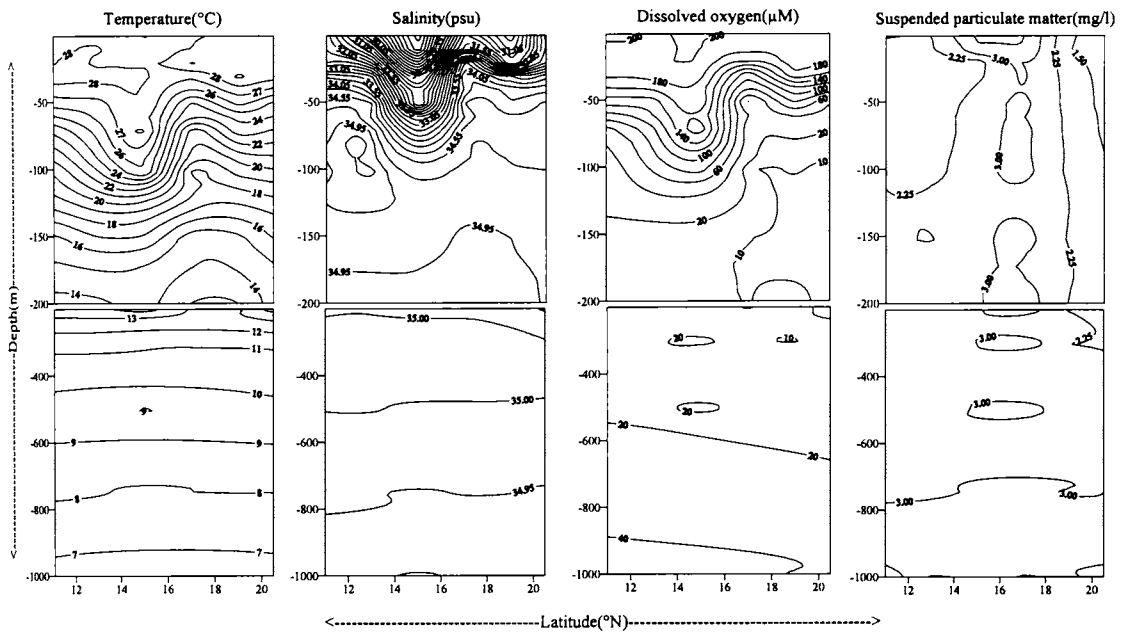
Figure. 61. Vertical section of chemical parameters along the offshore transect (T1) of the Bay of Bengal during winter monsoon
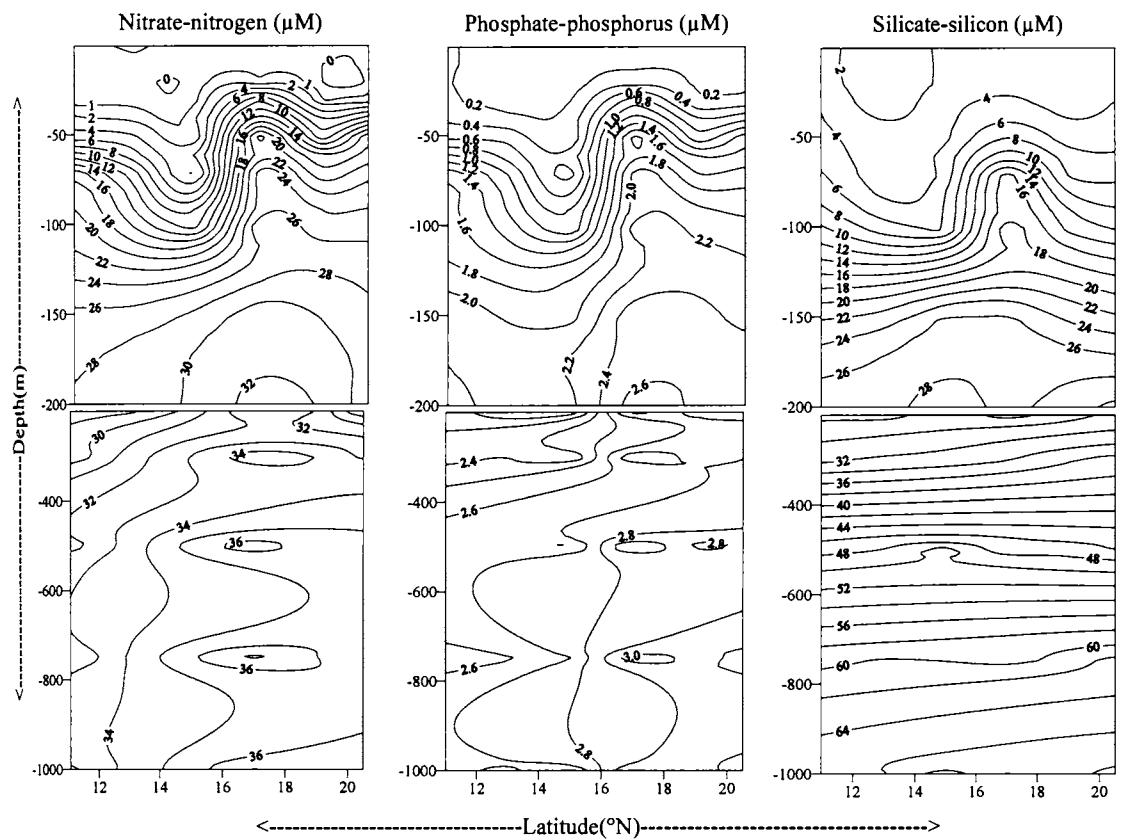
Figure. 62. Vertical section of dissolved and particulate Fe & Cu along the offshore transect (T1) of the Bay of Bengal during winter monsoon

Dissolved Fe (µg/l)   Particulate Fe (µg/l)   Dissolved Cu (µg/l)   Particulate Cu (µg/l)

<------------------------------Latitude(°N)------------------------------>
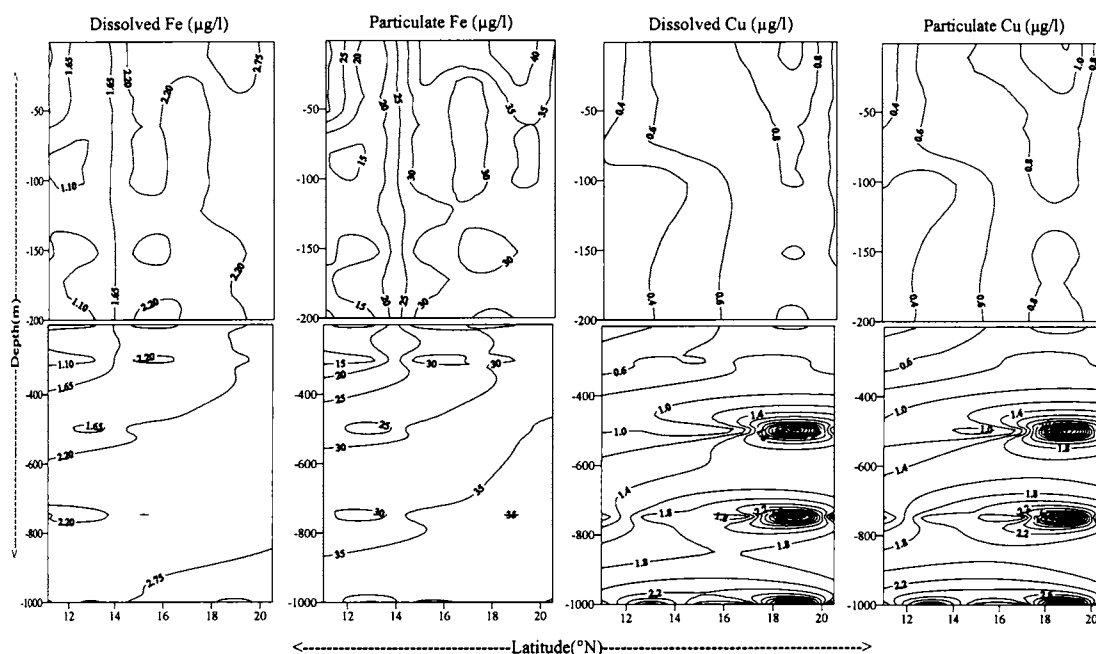
Figure. 63. Vertical section of dissolved and particulate Zn & Pb along the offshore transect (T1) of the Bay of Bengal during winter monsoon

Dissolved Zn (µg/l)   Particulate Zn (µg/l)   Dissolved Pb (µg/l)   Particulate Pb (µg/l)

<------------------------------Latitude(°N)------------------------------>
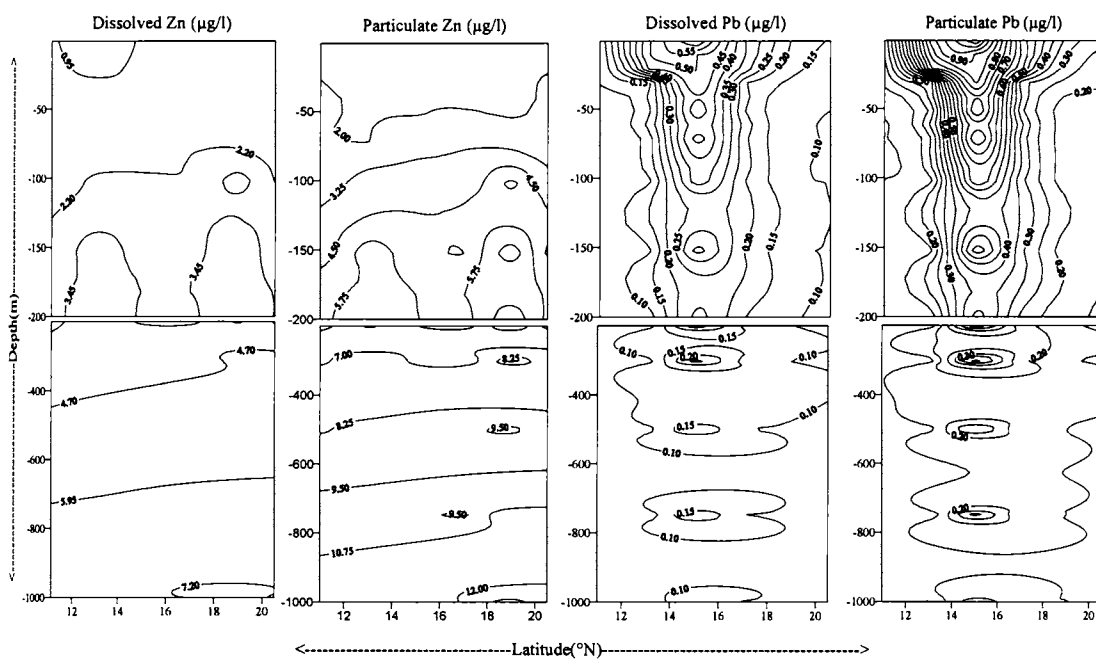
Figure. 64. Vertical section of dissolved and particulate Cd & Ni along the offshore transect (T1) of the Bay of Bengal during winter monsoon

Dissolved Cd (nM) Particulate Cd (nM) Dissolved Ni (nM) Particulate Ni (nM)

<--Latitude(°N)-->
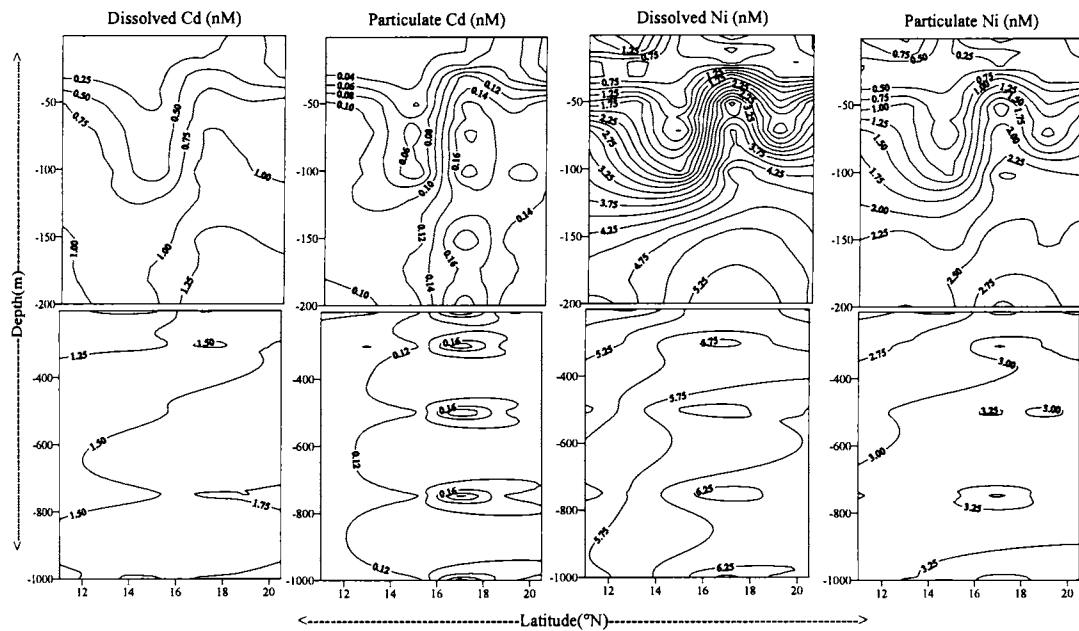
Figure. 65. Vertical section of dissolved and particulate Co along the offshore transect (T1) of the Bay of Bengal during winter monsoon

Dissolved Co (nM) Particulate Co (nM)

<-------------------------------------Latitude(°N)--->
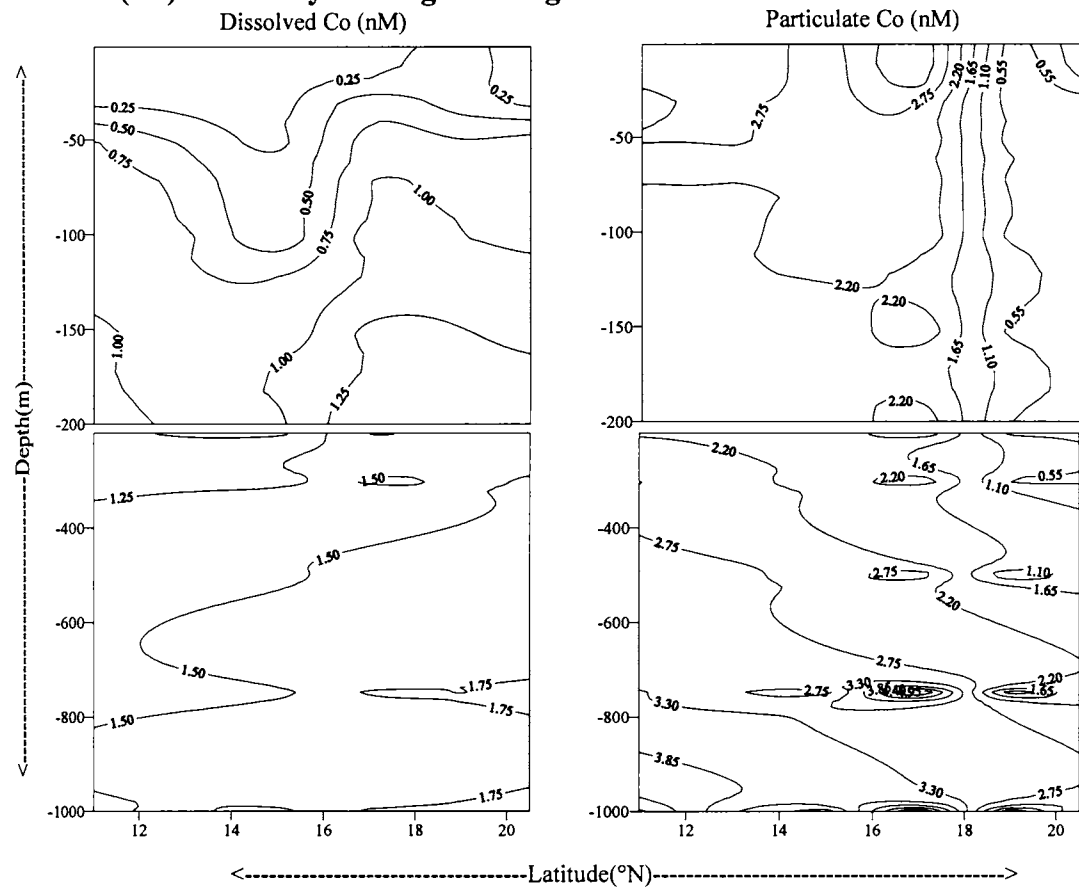
Figure. 66. Vertical section of physical and chemical parameters along the offshore transect (T2) of the Bay of Bengal during winter monsoon

Temperature(°C) Salinity(psu) Dissolved oxygen(μM) Suspended particulate matter(mg/l)

Latitude(°N)
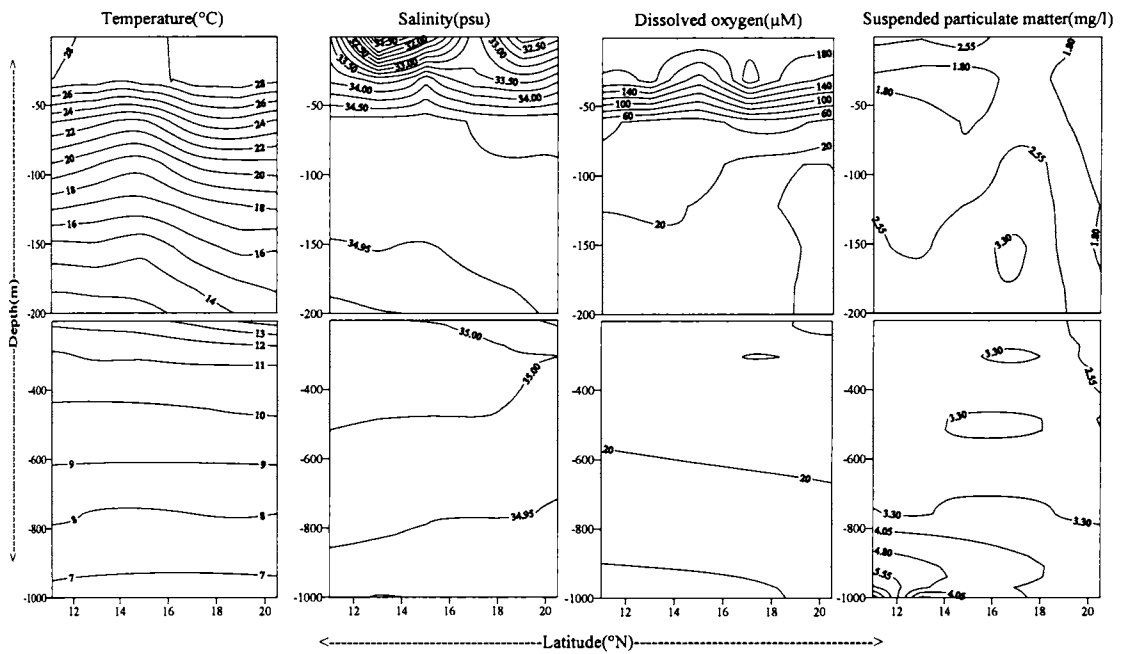
Figure. 67. Vertical section of chemical parameters along the offshore transect (T2) of the Bay of Bengal during winter monsoon

Nitrate-nitrogen(μM) Phosphate-phosphorus(μM) Silicate-silicon(μM)

Latitude(°N)
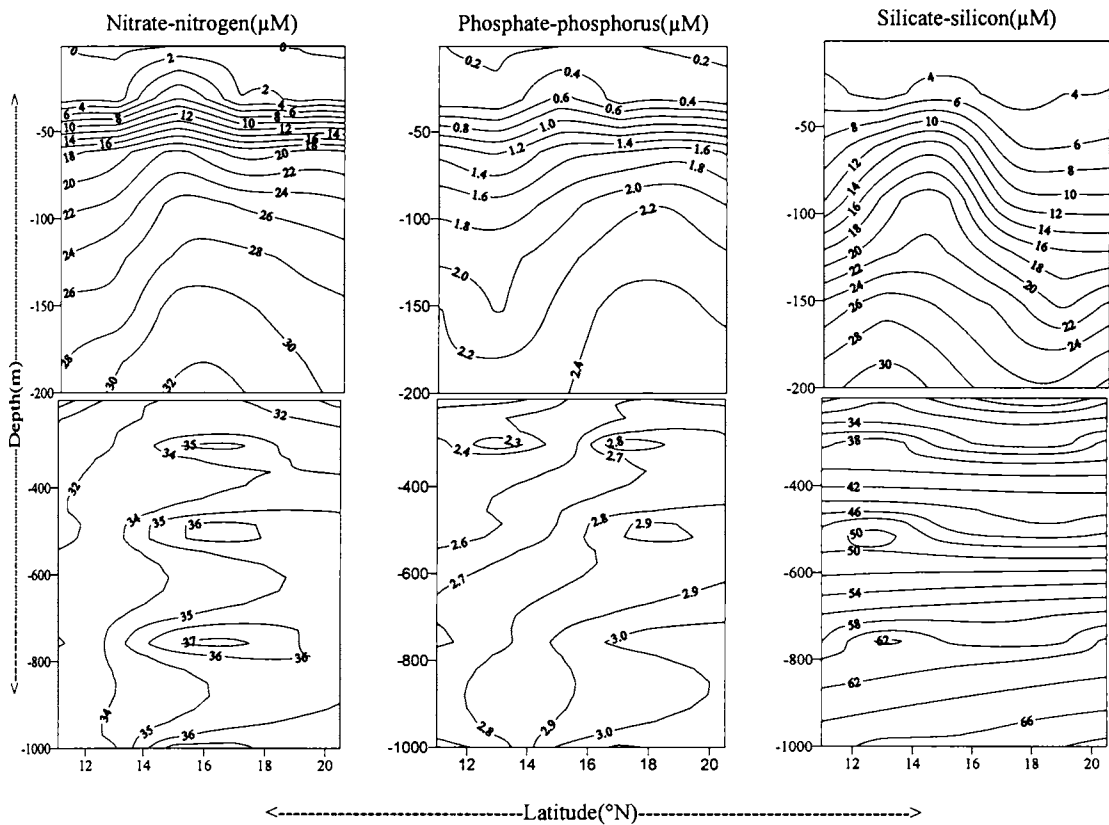
Figure. 68. Vertical section of dissolved and particulate Fe & Cu along the offshore transect (T2) of the Bay of Bengal during winter monsoon

Dissolved Fe(µg/l) Particulate Fe(µg/l) Dissolved Cu(µg/l) Particulate Cu(µg/l)

<----------------------------------Latitude(°N)---------------------------------->
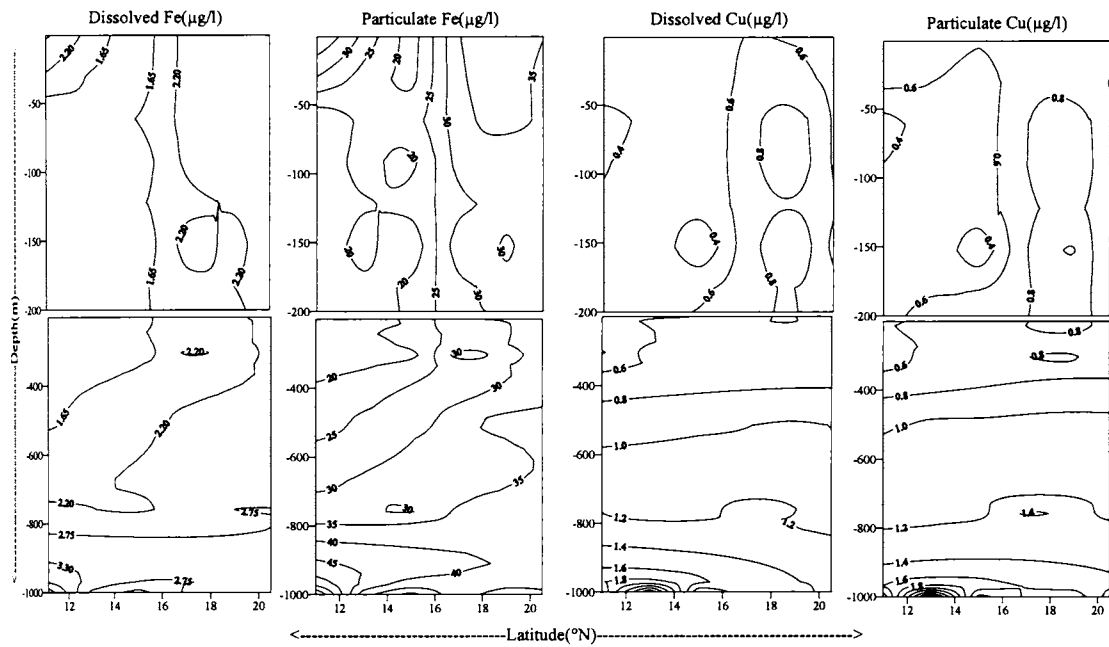
Figure. 69. Vertical section of dissolved and particulate Zn & Pb along the offshore transect (T2) of the Bay of Bengal during winter monsoon

Dissolved Zn(µg/l) Particulate Zn(µg/l) Dissolved Pb(µg/l) Particulate Pb(µg/l)

<----------------------------------Latitude(°N)---------------------------------->
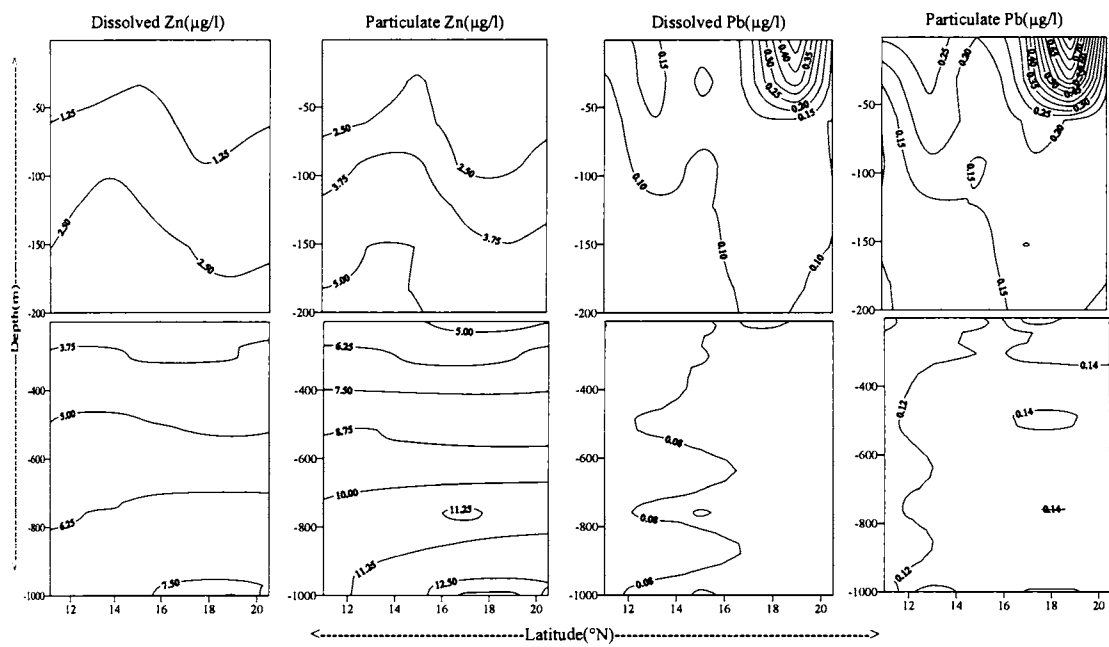
Figure. 70. Vertical section of dissolved and particulate Cd and Ni along the offshore transect (T2) of the Bay of Bengal during winter monsoon

Dissolved Cd(nM)   Particulate Cd(nM)   Dissolved Ni(nM)   Particulate Ni(nM)

<----------------------------Latitude(°N)---------------------------->
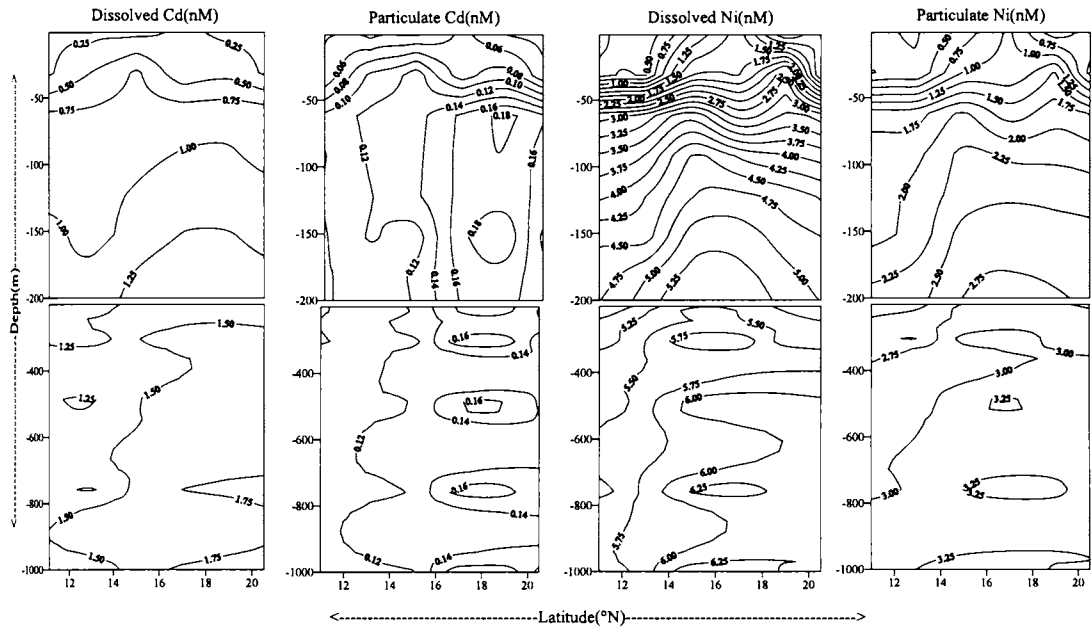
Figure. 71. Vertical section of dissolved and particulate Co along the offshore transect (T2) of the Bay of Bengal during winter monsoon

Dissolved Co(nM)   Particulate Co(nM)

<---------------------------------Latitude(°N)--------------------------------->
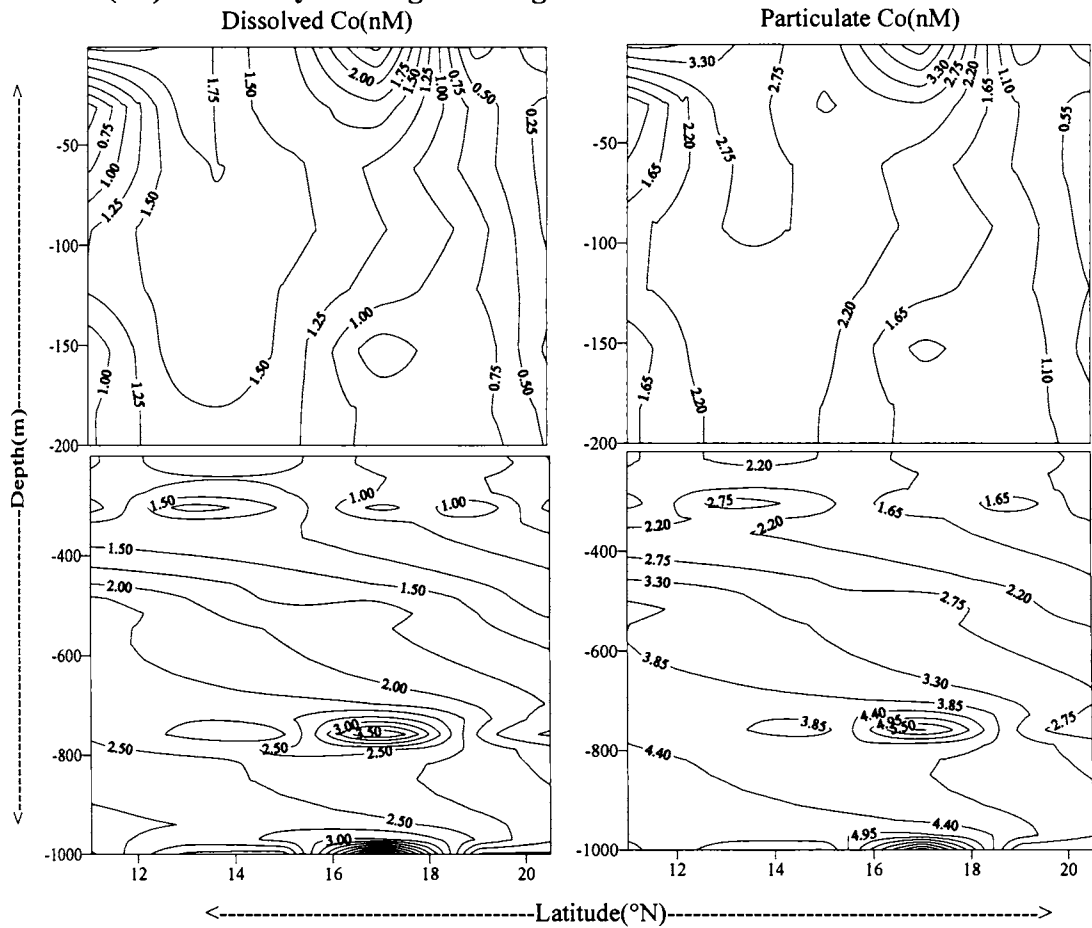
Figure. 72 to 75. Nickel-phosphate and nickel-silicate relationships in the coastal & offshore waters of the eastern Arabian Sea

Figure. 72

Figure. 73
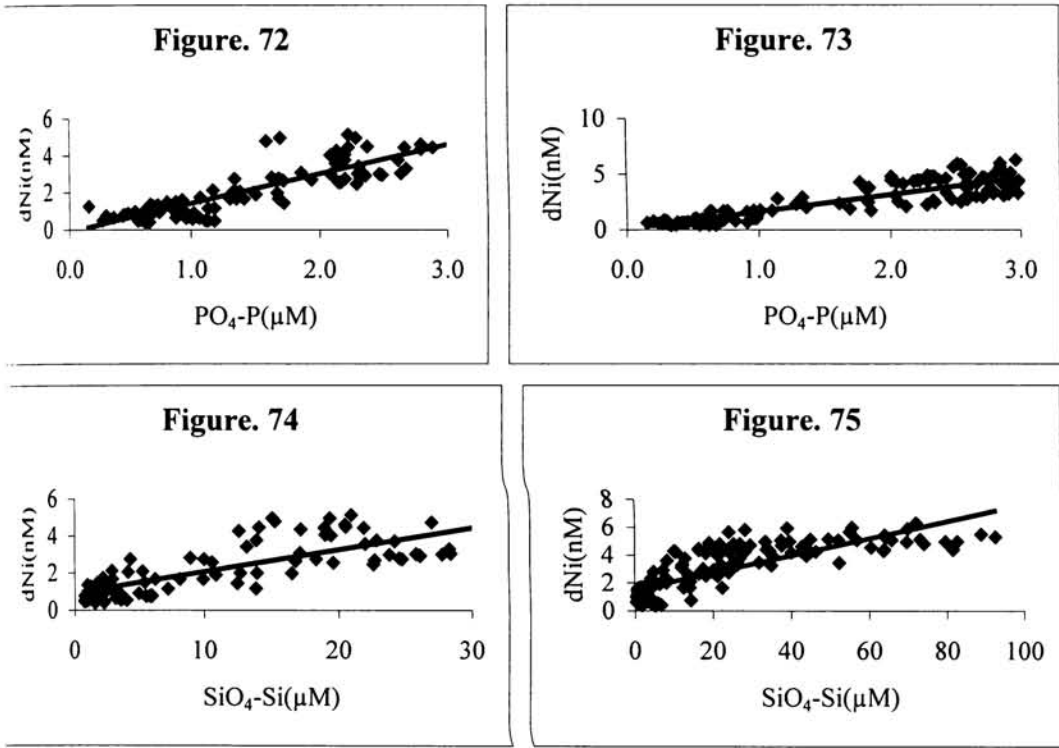
Figure. 74

Figure. 75

Figure. 76 to 77. Copper-silicate relationships in the coastal & offshore waters of the eastern Arabian Sea
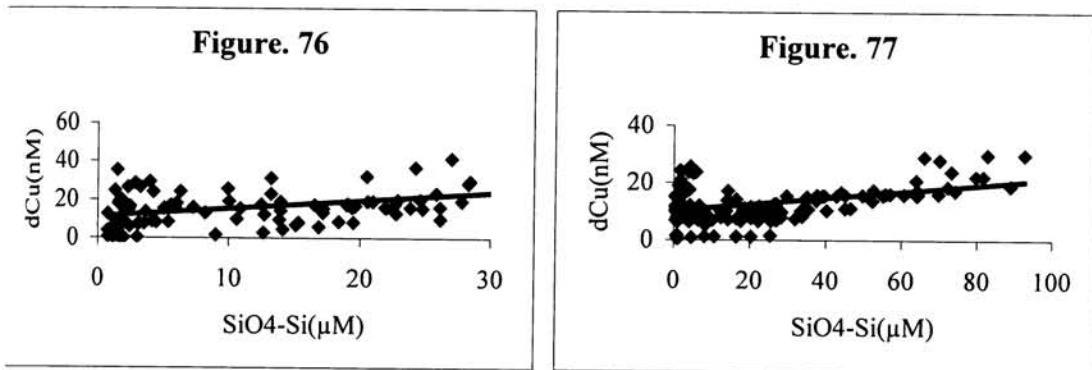
Figure. 76

Figure. 77

Figure. 78 to 79. Zinc-silicate relationships in the coastal & offshore waters of the eastern Arabian Sea
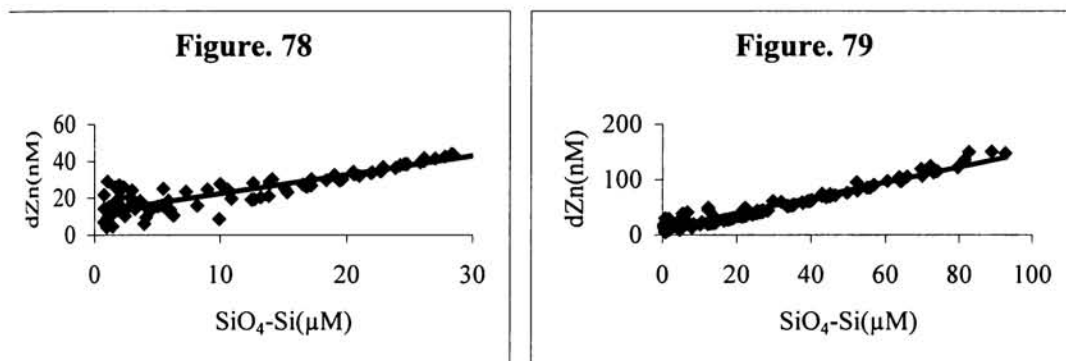
Figure. 78

Figure. 79

Figure. 80 to 83. Cadmium-nitrate and cadmium-phosphate relationships in the coastal & offshore waters of the eastern Arabian Sea

Figure. 80

Figure. 81
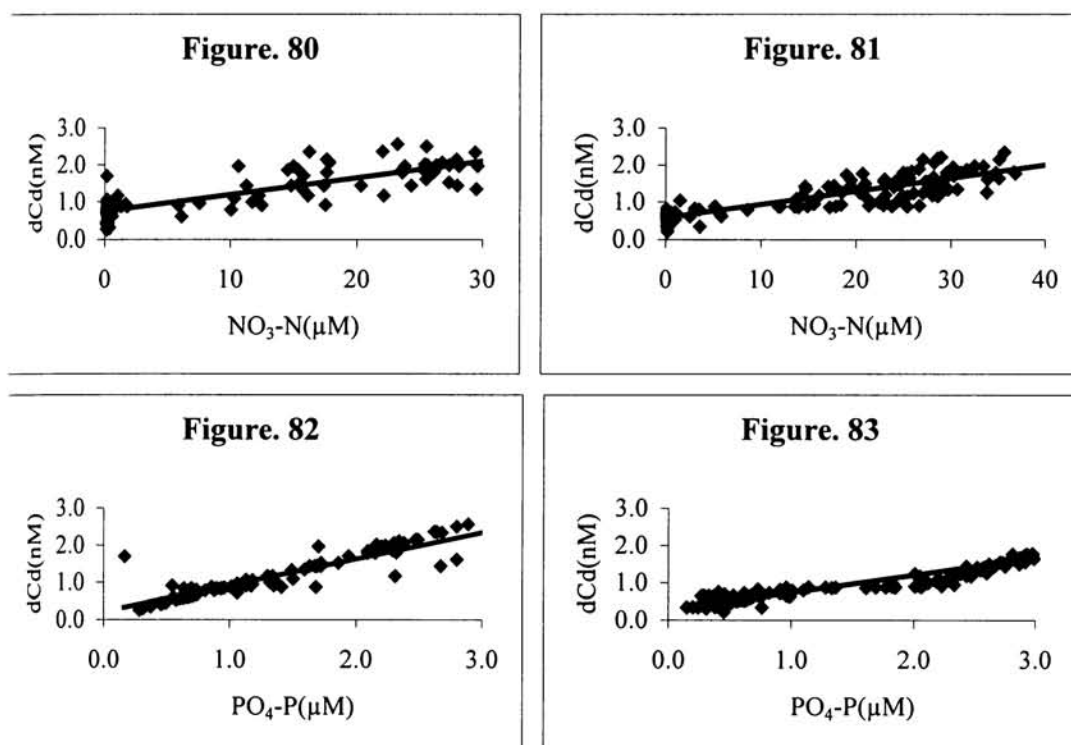
Figure. 82

Figure. 83

Figure. 84 to 87. Nickel-phosphate and nickel-silicate relationships in the coastal & offshore waters of the western Bay of Bengal

Figure. 84

Figure. 85
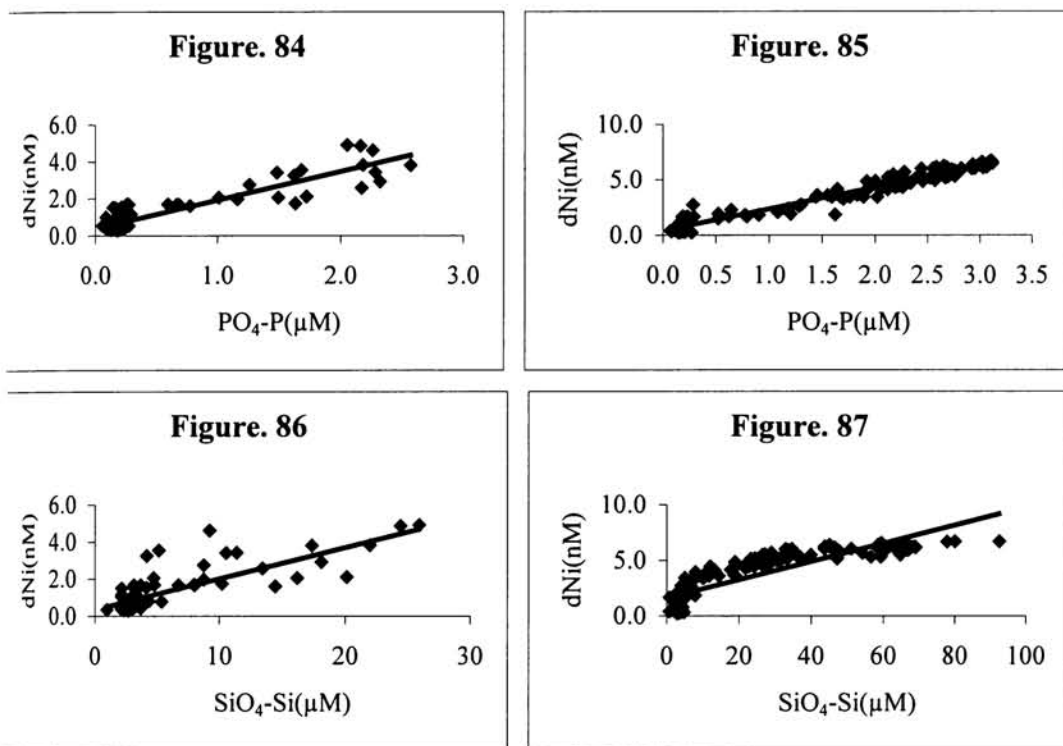
Figure. 86

Figure. 87

Figure. 88 to 89. Copper-silicate relationships in the coastal & offshore waters of the western Bay of Bengal
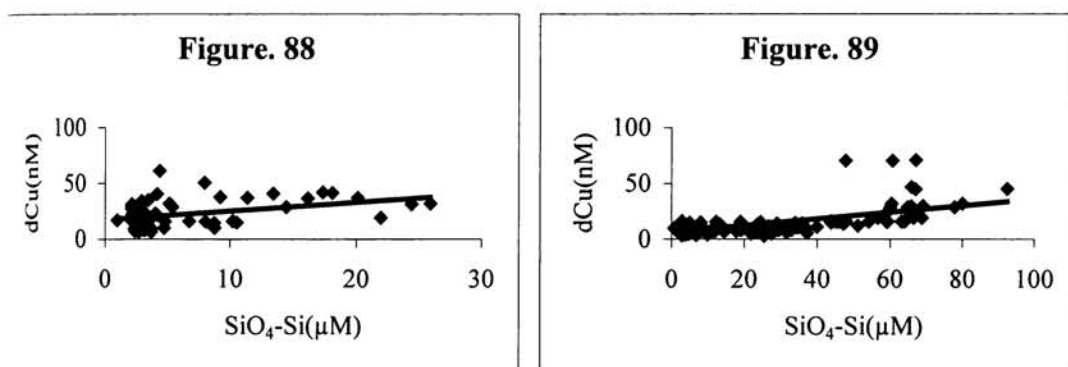
Figure. 88

Figure. 89

Figure. 90 to 91. Zinc-silicate relationships in the coastal & offshore waters of the western Bay of Bengal
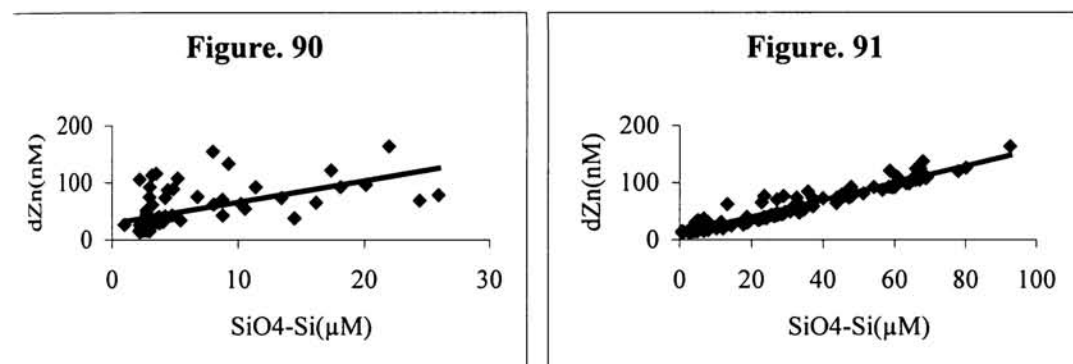
Figure. 92 to 95. Cadmium-nitrate and cadmium-phosphate relationships in the coastal & offshore waters of the western Bay of Bengal

Figure. 96

Figure. 97

Figure. 98

Figure. 99

Figure. 100

Figure. 101

Figure. 102 to 107. Dissolved Cu, Zn and Cd versus salinity in the coastal and offshore waters of the eastern Arabian Sea during intermonsoon fall
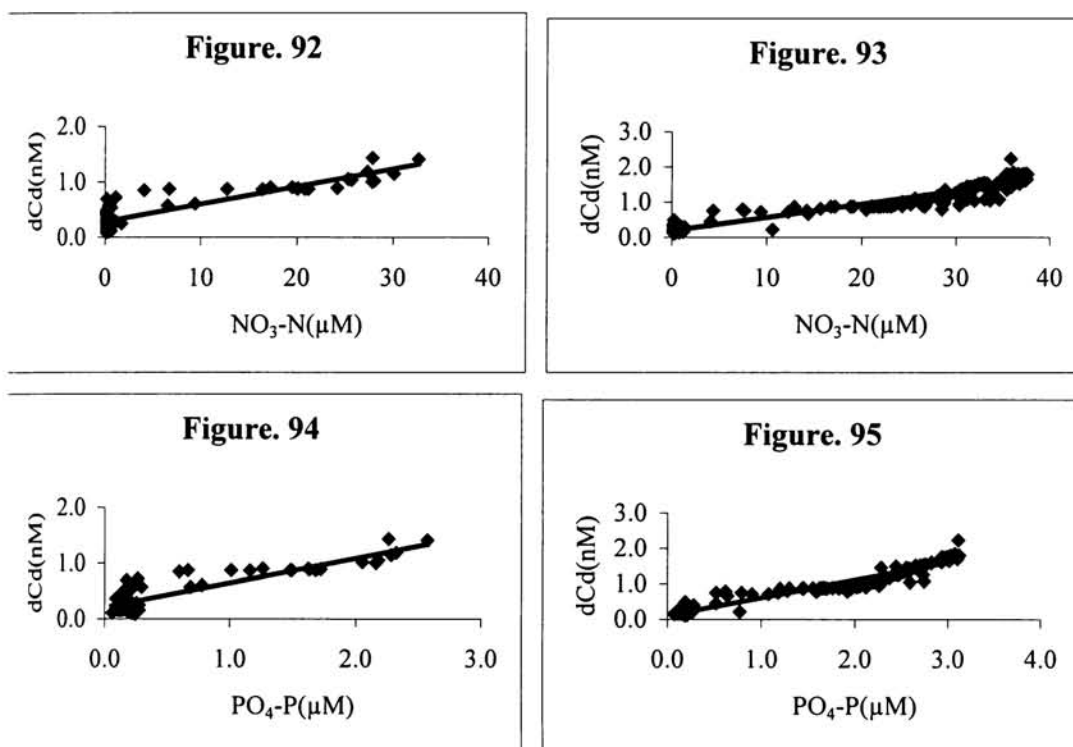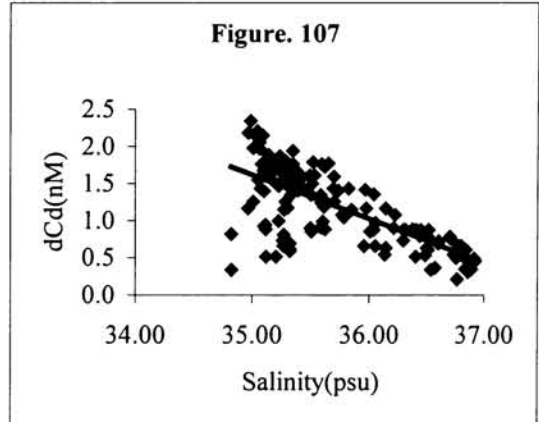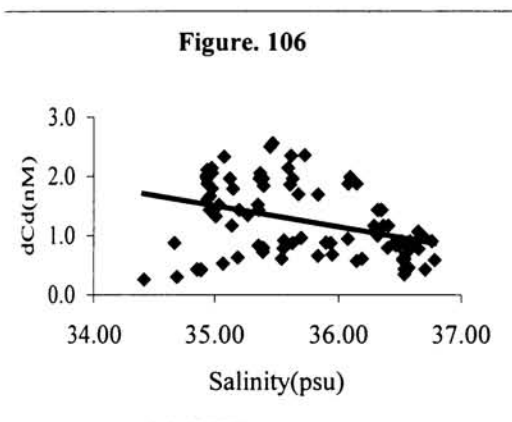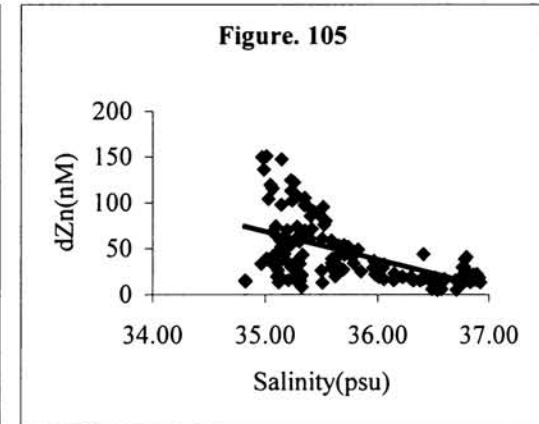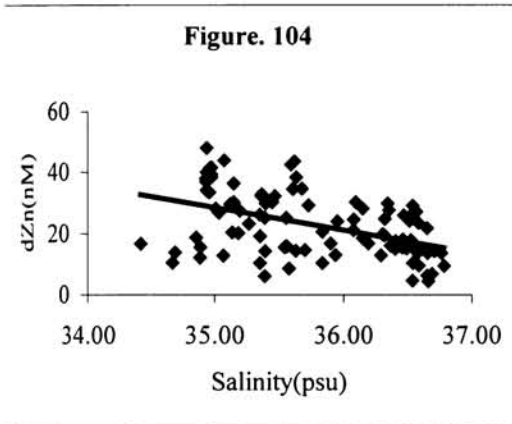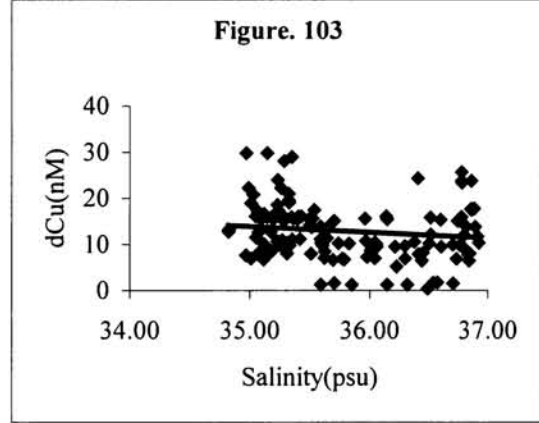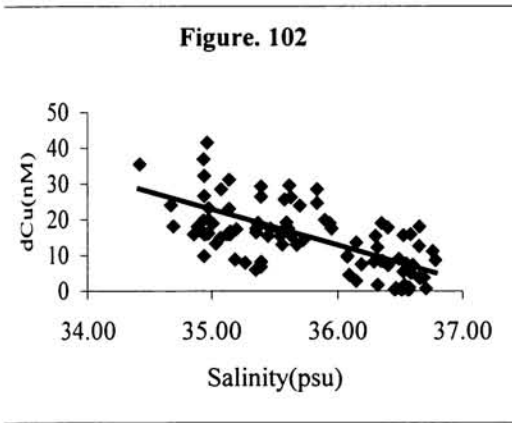
Figure. 108 to 113. Dissolved Fe, Co and Ni versus salinity in the coastal and offshore waters of the northeastern Arabian Sea during intermonsoon spring

Figure. 108

Figure. 109

Figure. 110

Figure. 111

Figure. 112

Figure. 113

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Figure. 115

Figure. 116

Figure. 117

Figure. 118

Figure. 119

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Figure. 124
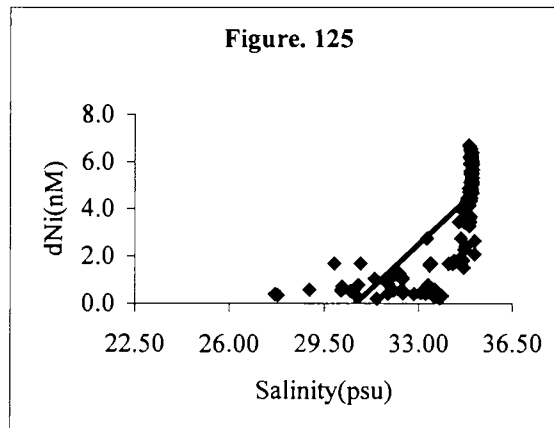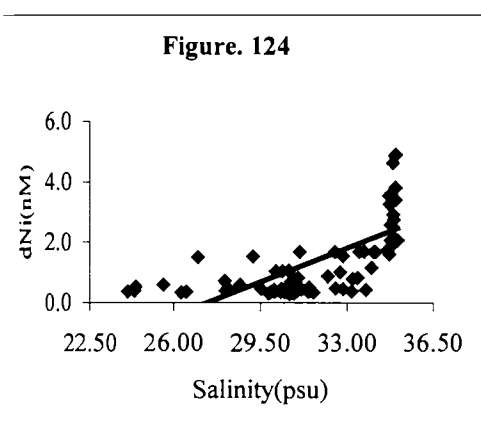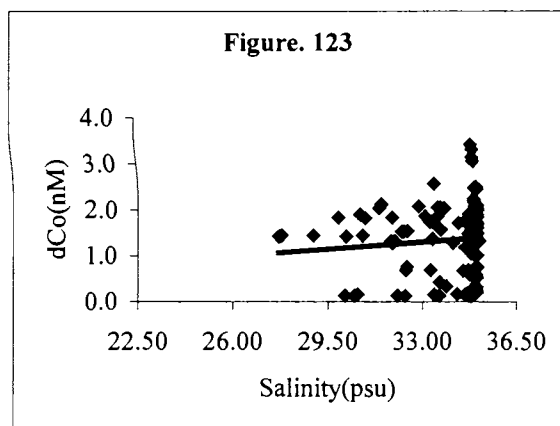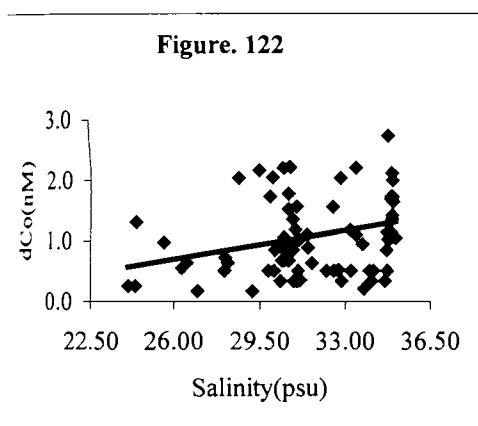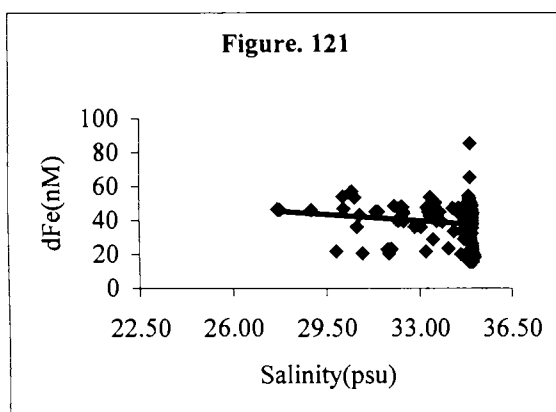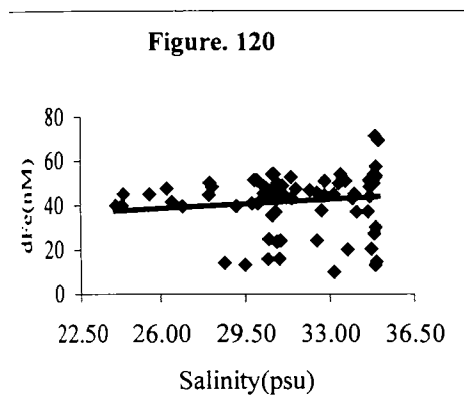
Figure. 125

Figure. 126 to 131. Dissolved Cu, Zn and Cd versus salinity in the coastal and offshore waters of the western Bay of Bengal during winter monsoon
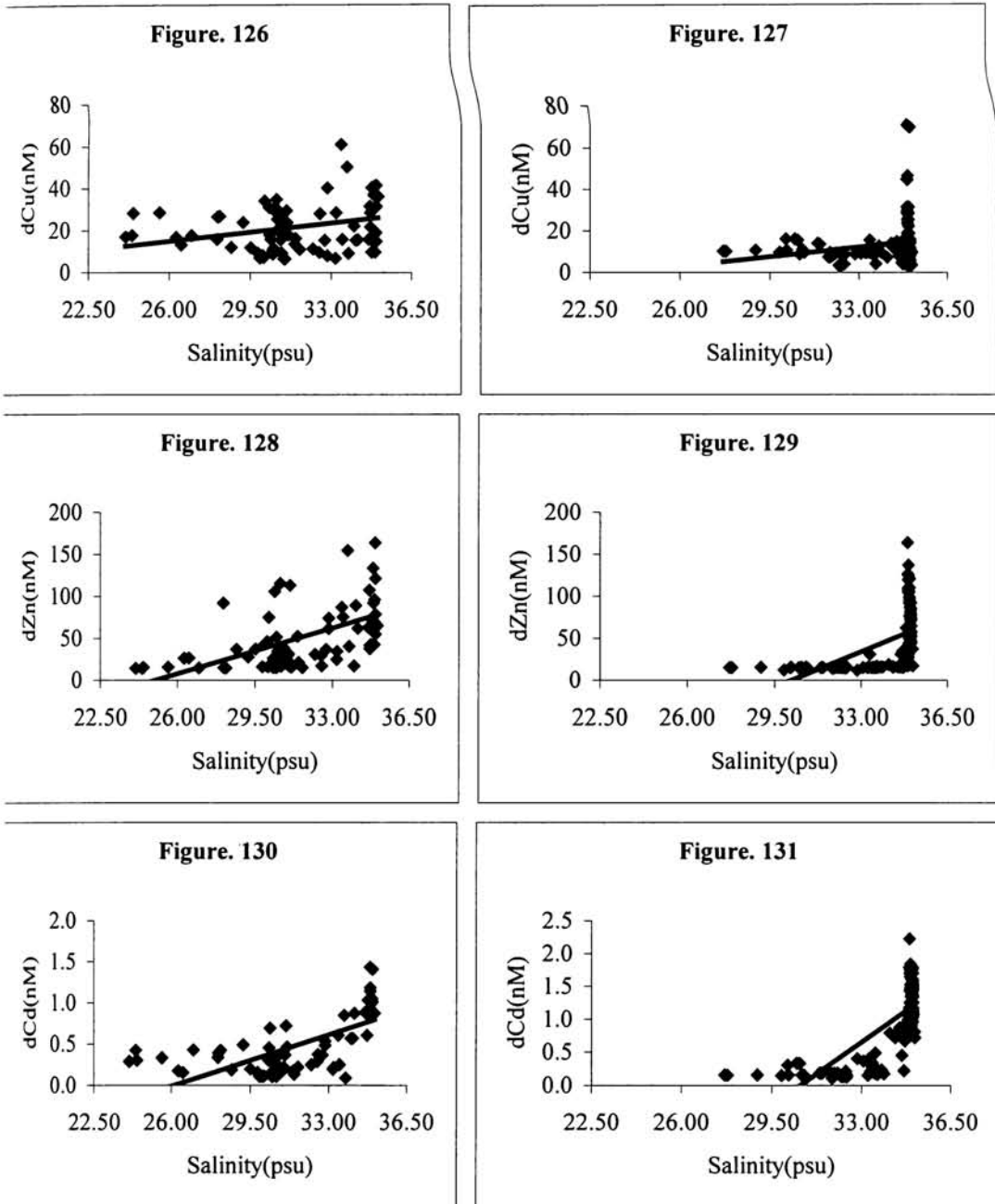
Chapter 5

5.Bioaccumulation of trace metals in zooplankton from the Eastern Arabian Sea and Western Bay of Bengal

Trace metals in aquatic systems are distributed over different compartments such as the dissolved state, colloidal state, particulate matter (abiotic or biotic), in planktonic and higher organisms. Studies on trace metal distributions and its recycling processes within zooplankton from the Arabian Sea and Bay of Bengal are not much explored other than the random reports by (George and Kureishy, 1979; Gajbhiye *et al.*, 1985). Zooplankton forms one of the most significant consumers of phytoplankton biomass; in particular diatoms (Kleppel, 1993). The manner and rate of metal recycling by zooplankton may thus affect its availability to higher organisms. Both phytoplankton and zooplankton may play a role in the biogeochemical cycles of trace metals either by bioaccumulation and later transfer to higher levels or by redistribution (Martin and Knauer, 1973). Zooplankton accumulates metals by direct absorption from water and also by assimilation through food substances. Due to their vital role in the food chain of the life in the sea and their relative abundance, they are interesting groups for bioaccumulation studies. Even though investigations about the trace metal behaviour in the Arabian Sea and Bay of Bengal started in the early nineties, they are mainly focussed on metals in sediments, including their speciation, distribution and transformation. Information about trace metal partitioning and distribution in marine organisms has important implications in understanding both elemental bioavailability and the time scales of cycling (Hutchins *et al.* 1995). Unfortunately, a general picture of metal distribution in and between the various compartments of the surface layer in the Arabian Sea and Bay of Bengal and their bioavailability are not or only to a limited extent available. Despite the obvious importance of marine food web to trace metal cycling, it is remarkable that there is so little information in the literature on the trace metal composition of zooplankton in general from the Arabian Sea and Bay of Bengal. In view of this, zooplankton samples are collected from two geographically close but biogeochemically distinct water masses in which particular attention has been paid to avoiding possible contamination artefacts. This chapter focuses on inter-metal correlations in the three major compartments of the

surface seawater namely dissolved, particulate and zooplankton as well as on inter-phases relationships.

To investigate the common characteristics (behaviour) of trace metals in ocean, correlation coefficients between metals are calculated for the following phases such as dissolved, particulate, total water and zooplankton in the Arabian Sea and the Bay of Bengal. Relations between dissolved, particulate and zooplankton phases are discussed along with corresponding partitioning coefficients or bioaccumulation factors (baf). Biomagnification, the enrichment (positive value) or depletion (negative value) of a higher tropic level versus its availability of food in the medium is also calculated. The transfer of trace metals through the food chain can be assessed by the biomagnification factor (bmf). Inside an environmental compartment (dissolved phase, SPM, biota) relations between the various metals can be established through correlations. Correlations are based on Pearson product moment coefficients and are presented in correlation matrices.

Bioaccumulation and biomagnification factors are metal and organism-dependent. Bioaccumulation factor (baf) represents the metal accumulation into an organism from its surrounding water. It helps to assess the potential of organisms for bioaccumulation. Biomagnification factor (bmf) describes the metal accumulation in an organism at a higher tropic level from its food source. Bioaccumulation and biomagnification factors were calculated for each metal and organism as the ratio of the metal concentration in the organism's body and its concentration in the dissolved and particulate phase respectively.

5.1. Spatial distribution of trace metals in the surface zooplankton samples

The biological composition of zooplankton samples from all the stations of both the Arabian Sea (Intermonsoon fall and Spring intermonsoon) and Western Bay of Bengal (Winter monsoon) showed that copepods were most dominant in all the samples. Chaetognaths were the next in abundance and this was followed by ostracods and euphausids. The concentration of trace metals in water (dissolved and particulate forms) and zooplankton samples from the western Bay of Bengal (winter monsoon) are presented in Fig. 160 to 180. In the Bay of Bengal (winter monsoon) low trace metal concentrations were found in water and zooplankton from the coastal stations, except

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those samples from off Vishakapatnam (Station Positions: B13 & B14) and followed by off Madras transect (Station Positions: B5 & B6) where the levels were high. Further, an offshore enrichment of trace metals in zooplankton from the open ocean stations off Gopalpur (Station Position: B20), followed by open ocean stations off Vishakapatnam (Station Position: B16) and open ocean stations off Nagapatnam transect (Station Position: B4) where the levels were high.

The concentrations of trace metals in water (dissolved and particulate forms) and zooplankton from the eastern Arabian Sea during intermonsoon fall and spring intermonsoon are presented in Fig. 132 to 152 & 188 to 208. During intermonsoon fall, low trace metal concentrations were found in water (dissolved and particulate forms) and zooplankton from the open ocean stations whereas coastal samples taken from off Goa (Station Positions: A13 & A14) showed higher concentrations followed by samples taken from off Kanyakumari (Station Positions: A1 & A2). However, during intermonsoon spring, low trace metal concentrations were found in water (dissolved and particulate forms) and zooplankton from the coastal stations whereas the offshore samples collected off Kandala (Station Positions: C15 & C16) and off Veraval (Station Positions: C11 & C12) exhibited higher concentrations. The higher concentrations of trace metals observed in zooplankton samples from the coastal and offshore samples of the Bay of Bengal and the Arabian Sea might be due to their higher concentrations existing in the ambient medium.

Iron content (50980 ppm) in zooplankton and seawater (dissolved; 3.03 ppb & particulate; 44.16 ppb) off Vishakapatnam coast showed a two-fold increase in its concentration when compared to coastal stations of other transects in the Bay of Bengal. This might me due to extensive iron ore handling in the outer Vishakapatnam harbour and its gradual dissipation into the coastal regions. Relatively high concentration of iron (22864 ppm) in zooplankton and seawater (dissolved; 2.88 ppb & particulate; 38.85 ppb) respectively of coastal samples off Madras coast obtained in the present investigations compared to oceanic data also might be due to iron ore handling in the port and the subsequent input of this terrigenous material towards the coastal areas by land drainage and currents.

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During intermonsoon fall, iron content (14166 ppm) in zooplankton and sea water (dissolved; 6.77 ppb & particulate; 99.16 ppb) off Goa coast showed a two-fold increase in its concentration when compared to other coastal stations in the Arabian Sea. However during spring intermonsoon in the northern Arabian Sea in the offshore stations off Kandala, iron content (15276 ppm) in zooplankton and seawater (dissolved; 3.78 ppb & particulate; 53.79) showed a two-fold increase in its concentration when compared to other coastal stations. This was followed by offshore stations off Veraval coast where the iron content in water (dissolved; 2.99 ppb & particulate; 42.66 ppb) and zooplankton (12221ppm) were higher. During intermonsoon fall, an increased metal levels in water and zooplankton off Goa, might be due to extensive iron ore handling in and around the Goa port and its subsequent dissipation into coastal regions by runoff from Mandovi and Zuari estuaries. The observed high concentration of iron in zooplankton (9338ppm) and sea water (dissolved; 5.70ppb & particulate; 84.3 ppb) off Kanyakumari coast during intermonsoon fall might be related to surface and river runoff from Kerala coast and upwelling of the area.

Cobalt in seawater (dissolved and particulate forms) and zooplankton of the coastal stations off Vishakapatnam (0.149 ppb, 0.265 ppb & 41 ppm) and off Madras (0.121 ppb, 0.228 ppb & 38 ppm) showed higher values than the other coastal stations in the Bay of Bengal. During intermonsoon fall, in the Arabian Sea, cobalt in seawater (dissolved and particulate forms) and zooplankton of the coastal stations off Goa (0.055 ppb, 0.091 ppb & 39.7 ppm) and off Kanyakumari (0.044 ppb, 0.069 ppb & 34.95 ppm) showed higher values than the other coastal stations in the Arabian Sea. During spring intermonsoon in the northern Arabian Sea, at the offshore stations off Kandala coast, cobalt content in seawater (dissolved; 0.044ppb & particulate; 0.071ppb) and zooplankton (22.2 ppm) were higher than other coastal stations. Similarly during spring intermonsoon, at the offshore stations off Veraval, the cobalt content in seawater (dissolved; 0.042 ppb & particulate; 0.062 ppb) and zooplankton (18.2 ppm) were higher. This might be due to land drainage in these coastal stations of the Arabian sea (inter monsoon fall) and Bay of Bengal.

It was evident from the data of the Bay of Bengal that coastal stations off Vishakapatnam transect recorded higher values for nickel in seawater (dissolved& particulate) and zooplankton (0.097 ppb, 0.069 ppb & 49 ppm) followed by off Madras transect (0.08 ppb, 0.061 ppb & 44 ppm). It is also evident from the data of the Arabian Sea during intermonsoon fall that coastal stations off Goa transect recorded higher values for nickel in seawater (dissolved& particulate) and zooplankton (0.098 ppb, 0.098 ppb & 64 ppm) followed by off Kanyakumari transect (0.077 ppb, 0.048 ppb & 46.6ppm). During spring intermonsoon in the northern Arabian Sea at the offshore stations off Kandala, the nickel content in water (dissolved & particulate) and zooplankton (0.188 ppb, 0.116 ppb & 27.8 ppm), followed by offshore stations off Veraval (0.116 ppb, 0.074 ppb & 27.7 ppm) were higher than other coastal stations. Higher concentration at the Vishakapatnam transect may be due to discharge of industrial effluents and domestic sewage, and its gradual dispersion towards the nearby coastal region. Relatively higher concentration of nickel in coastal zooplankton samples off Madras might be due to land drainage. During intermonsoon fall, the observed relatively higher concentrations of nickel in zooplankton from off Goa transect might be related to ore bearing land mass of the area, whereas the high concentration observed off Kanyakumari transect is related to upwelling and river runoff from Kerala coast.

The coastal stations off Vishakapatnam in the Bay of Bengal had higher values for copper in water (dissolved and particulate forms) and zooplankton (1.89 ppb, 2.07ppb & 78ppm) followed by Madras transect (1.28 ppb, 1.49ppb & 74ppm). During intermonsoon fall, the coastal stations off Goa had higher values for copper in water (dissolved and particulate forms) and zooplankton (2.25 ppb, 2.43 ppb & 64ppm) followed by Kanyakumari transect (1.86 ppb, 2.05ppb & 44 ppm) in the Arabian Sea. During intermonsoon spring in the northern Arabian Sea, at the offshore stations off Kandala, copper content in water (dissolved & particulate) and zooplankton (1.42ppb, 1.53ppb and 46 ppm), followed by offshore stations off Veraval (0.95 ppb, 0.94ppb & 38.1ppm) have metal levels higher than other coastal stations. The observed high concentrations in Vishakapatnam transect can be attributed to pollution in Vishakapatnam harbour by industrial effluents and domestic sewage. Another possibility for higher

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concentration of copper in zooplankton of the coastal stations might be the flooding associated with heavy rainfall of the period. The high concentrations of copper in zooplankton samples off Goa and off Kanyakumari transect might be related to surface run off in these coastal areas during intermonsoon fall. Moreover, in the presence of high organic matter, copper forms soluble and chelating of insoluble metal also favours higher concentration in the coastal and offshore zooplankton samples of both the Arabian Sea and Bay of Bengal (Raman and Ganapati, 1983).

Concentration of zinc in seawater (dissolved & particulate forms) and zooplankton of the coastal stations off Vishakapatnam (2.82 ppb, 5.01 ppb & 7114 ppm) and off Madras (2.36 ppb, 3.84 ppb & 4944ppm) were higher than that of the other coastal stations of the Bay of Bengal. Concentration of zinc in seawater (dissolved & particulate forms) and zooplankton of the coastal stations off Goa (2.65 ppb, 3.83 ppb & 1845 ppm) and off Kanyakumari (2.40 ppb, 3.55 ppb & 1592 ppm) were also higher than that of the other coastal stations. During intermonsoon spring, in the northern Arabian Sea, the concentration of zinc in seawater (dissolved & particulate forms) and zooplankton of the offshore stations off Kandala (1.89 ppb, 3.57 ppb & 5653 ppm) and off Veraval (1.75ppb, 3.02ppb & 2156ppm) were higher than that of the other coastal stations. The high concentration of zinc observed in seawater and in the zooplankton samples of the coastal stations of Vishakapatnam transect may be due to the drainage of domestic sewage and industrial effluents into the inner harbour and their dissipation into the coastal regions. The effluents from the zinc smelter may also find its way into the coastal region through the Vishakapatnam Harbour.This is further supported by high concentrations of zinc (276-480 ppm) in the effluents of Hindustan Zinc Ltd (Someswara Rao and Venkateswara Rao, 1989). However the high concentrations observed in the coastal stations off Madras could be the result of land runoff from the port areas. The high concentration of zinc observed during intermonsoon fall in seawater and zooplankton samples from off Goa coastal stations is related to the ore bearing land mass of the area and associated land drainage in the coastal areas whereas the high concentration of zinc observed in off Kanyakumari transect is associated with surface and riverine runoff of industrial effluents from Kerala coast.

Cadmium values in sea water (dissolved & particulate forms) and in surface ooplankton of the coastal stations off Vishakapatnam (0.047 ppb, 0.009 ppb & 41 ppm) id off Madras (0.041ppb, 0.007 ppb & 29 ppm) showed higher values than offshore mples in the respective transects of the Bay of Bengal. During intermonsoon fall in the rabian Sea, cadmium values in sea water (dissolved & particulate forms) and in surface ooplankton of the coastal stations off Goa (0.098 ppb, 0.031ppb & 29 ppm) and off anyakumari (0.091 ppb, 0.021 ppb & 25 ppm) showed higher values than offshore imples in the respective transects of the Arabian Sea. During spring intermonsoon, in e northern Arabian Sea, cadmium values in sea water (dissolved & particulate forms) id in surface zooplankton of the offshore stations off Kandala (0.141ppb, 0.03ppb & 8.5 ppm) and off Veraval (0.098ppb, 0.024ppb & 27.4ppm) showed higher values than oastal samples in the respective transects of the Arabian Sea. The high value off 'ishakapatnam may be due to industrial effluents from zinc smelter into the harbour and s passage to the coastal areas and the high value in coastal area off Madras transect light be attributed to land drainage. The high value observed during intermonsoon fall, ff Goa may be due to rich ore bearing landmass of the area and associated surface runoff o the coastal areas and the high value in coastal area off Kanyakumari transect might be ttributed to surface runoff of industrial effluents from the Kerala coast to adjacent oastal areas together with upwelling.

In the Bay of Bengal a high concentration of lead (20 ppm) in coastal zooplankton ind seawater (dissolved & particulate forms) (0.69 & 1.16 ppb) samples off /ishakapatnam was observed and the same trend was observed in stations off Madras for ooplankton (14 ppm) and seawater (0.516 & 0.98 ppb). In the Arabian Sea during ntermonsoon fall, a high concentration of lead (22 ppm) in coastal zooplankton and vater (dissolved & particulate forms) - 1.54 & 2.75ppb respectively samples off Goa vere found, followed off Kanyakumari area (zooplankton -14 ppm) and sea water (1.3 & !.01ppb). During intermonsoon spring, a high concentration of lead (28.9ppm) in offshore zooplankton and water (dissolved & particulate forms) (1.52 & 2.58ppb) samples off Kandala were observed and off Veraval the concentration for offshore zooplankton was 16.5ppm and for seawater it was 0.97& 1.28ppb. The observed high

metal levels in seawater and zooplankton in the Bay of Bengal might be attributed to high influxes of lead in the Vishakapatnam and Madras region, primarily from automotive exhausts /or due to loading and unloading of large quantities of general and bulk cargo at these localities. The lead is transported principally through the atmosphere and accommodated in the seawater following wet and dry fallout. The subsequent uptake of the metal by the zooplankton is evidenced its high concentration within these whole bodies. Lead is known to form colloids in seawater, and such colloids would have adsorbed onto planktonic debris, which consequently might have resulted in higher concentration of this element in zooplankton from the coastal waters off Goa and off Kanyakumari respectively during intermonsoon fall.

From the data it is clear that trace metal concentration in zooplankton can lead to identify "hot spots". The spatial variation in the metal content was evident in the eastern Arabian Sea and western Bay of Bengal from the extensive area investigated. In general coastal zooplankton samples showed higher values for all the metals than offshore samples in both the Arabian Sea (intermonsoon fall) and Bay of Bengal (winter monsoon). Zooplankton in coastal areas has high concentration of trace metals than those in the open ocean because they get influenced by local sources such as river runoff, sewage discharge, industrial effluents and also from enriched bottom waters. Port activities such as shipping, loading of Ferro-manganese ore and unloading of zinc-lead ore concentrates and other bulk cargo also partly contribute to the enhanced levels of some of these trace metals in seawater and zooplankton of the coastal areas of both the Arabian Sea and Bay of Bengal. Moreover a large quantity of sediments impregnated with heavy metals are supplied by major rivers along the east coast and were constantly moved by waves either towards north or south depending on the direction and angle of wave approach with respect to the coast. The offshore enrichment of trace metals in zooplankton from the open ocean stations off Gopalpur (Station Position: B20), followed by open ocean stations off Vishakapatnam (Station Position: B16) and open ocean stations off Nagapatnam transect (Station Position: B4) seems to be related to the southerly flowing East India Coastal Current (EICC) from the head of the Bay of Bengal and the peculiar gyral circulation of the Bay of Bengal. Under the influence of these

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gyres and as a consequence of the geometry of the East Coast of India (U-shaped basin), the low saline waters, probably of riverine origin, is drifted offshore by the simultaneous prevalence of anticlockwise surface currents, thereby favouring significant accumulation of heavy metals in zooplankton. The slight increase of metals in water and zooplankton towards northern latitudes can be indicative of slight riverine influences in the metal concentrations. In winter this southward flowing East India Coastal Current (EICC) carry warm and low salinity Bay of Bengal waters from the northern Bay (probably carrying riverine waters off Ganges-Brahmaputra, Godavari, Krishna and Cauveri origin) to the southern part of the peninsular India and feeds the northward flowing West India Coastal Current (WICC) in the Arabian Sea. The intrusion of this Bay of Bengal water into the Arabian Sea during winter monsoon and associated chemical and biological response has been reported (Prasanna Kumar *et al.*, 2004).

In the Arabian Sea during intermonsoon fall the enrichment of trace metals in water and zooplankton from the coastal samples off Goa is possibly related to the ore bearing land mass and associated surface run off from the near by Madovi and Zuari estuaries to the coastal waters off Goa transect. However the similar enrichment of trace metals in water and zooplankton at the coastal waters off Kanyakumari transect is coupled with the upwelling of subsurface waters and surface run off from the Kerala coast rivers. These factors in turn lead to enrichment of metals in zooplankton from the coastal waters of the south west coast of India.

However in the northern Arabian Sea during spring intermonsoon, the offshore enrichment of trace metals in water and zooplankton from off Kandala and off Veraval were probably originated as a consequence of continental influence from the northeastern part of the basin. In the northeastern part of the Arabian Sea, Rajastan and Gujarat share the deserts by 61% and 20% respectively. Rajasthan's Thar desert occupies an area of approximately 4,46,500 square kilometers. Induced by favourable northeasterly trade winds, a considerable amount of dust is brought to the atmosphere from the northeastern side of the Arabian Sea and is transported principally through the wet and dry wind fall out, which in turn gets accommodated at the surface layers in the offshore regions the

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northern Arabian Sea as evidenced by the subsequent enhancement of metals in zooplankton from this region.

5.2. Correlations between trace metals in each compartment

For correlation studies at the surface layer data obtained during intermonsoon fall in the Arabian Sea and winter monsoon in the Bay of Bengal are alone used.

5.2.1 Arabian Sea

5.2.1.1 Water column

In the dissolved phase at the surface layer (n = 29) of the Arabian Sea (Table 39), the best correlations significant at $p < 0.001$, were observed for the Pb-Cu (r = 0.55) and for Pb-Zn (r = -0.54). Other correlations significant at $p < 0.01$, were observed for Cd-Ni (r = 0.46), Pb-Co (r = 0.47) and for Fe-Zn (r = -0.47) pairs. Another set of correlations significant at $p < 0.02$, were for Co and metals like Fe & Cu (r = 0.42 to 0.43), Fe and metals like Pb & Co (r = 0.42 to 0.43), and for Co-Zn (r = -0.42) pairs. Significant correlations at $p < 0.05$, were also observed for Fe and metals like Cd & Cu (r = 0.34 to 0.38) pairs.

In the particulate phase at the surface layer (n = 29) of the Arabian Sea (Table 40), the best correlations significant at $p < 0.001$, were observed for Pb and metals like Fe, Cu & Co (r = 0.56 to 0.67), and for Pb-Zn (r = -0.62) pairs. Other correlations significant at $p < 0.01$, were observed for Cd-Ni (r = 0.46) and Co-Fe (r = 0.49) pairs. Another set of correlations significant at $p < 0.02$, were for Cu and metals like Fe & Co (r = 0.40 to 0.43), Zn and metals like Fe & Co (r = -0.44 to -0.41) were observed. A weak correlation significant at $p < 0.1$, were observed for Cd-Fe (r = 0.32) pairs.

Considering total metal concentrations (Table 41) in the water column (n = 29) as the sum of the dissolved and particulate metal concentrations (both expressed in volumetric units, $\mu g l^{-1}$), correlations between these metals were almost same like that in individual phases. Again a strong correlation significant at $p < 0.001$, were observed for Pb and metals like Fe, Cu & Co (r = 0.53 to 0.62). Similar significant correlations at $p < 0.01$, were observed for Cd-Ni (r = 0.46), Fe-Zn (r = -0.46), and Co-Fe (r = 0.47) pairs. Other correlations significant at $p < 0.02$ is for Cu and metals like Fe & Co (r = 0.41 to 0.43)

and for Co-Zn (r = -0.42) pairs are observed. A correlation significant at $p < 0.1$, were observed for Cd-Fe (r = 0.33) pairs.

5.2.1.2 Zooplankton

In zooplankton highly significant correlations (n = 29) were observed for certain metals (Table 42) in the Arabian Sea. In zooplankton the strongest correlation significant at $p < 0.001$ was found between Fe and Ni (r = 0.76) and a few other high correlations significant at $p < 0.001$ were observed between Fe and other metals such as Pb & Zn (r = 0.53–0.64), suggesting that these metals share a common accumulation process in the zooplankton from the Arabian Sea. Another strong correlation significant at $p < 0.001$ was between Cu-Ni (r = 0.71). Other correlations observed for Zn and metals such as Ni & Pb (r = 0.57–0.61) significant at $p < 0.001$ were observed. Correlations significant at $p < 0.01$, were also observed for Fe-Cu (r = 0.49), Zn-Cu (r = 0.47) pairs. Another set of weak correlations for Fe-Cd (r = -0.43) significant at $p < 0.02$, Ni-Cd (r = -0.34) significant at $p < 0.05$, Zn-Cd (r = -0.33) significant at $p < 0.1$, were also observed.

Some metal pairs showed significant correlations in dissolved, particulate, and total phases in the surface layer of the Arabian Sea. The best correlations significant at $p < 0.001$, observed were for Cu-Pb pairs, in the dissolved, particulate and total phases(r = 0.55, r = 0.57 & r = 0.58 respectively) in the surface layer of the Arabian Sea. Other correlations significant at $p < 0.01$, observed were for Ni-Cd pairs, in the dissolved, particulate and total phases(r = 0.46 for all phases respectively) in the surface layer of the Arabian Sea. Also Co-Cu pairs show significant correlations at $p < 0.02$, in the dissolved, particulate and total phases (r = 0.42, r = 0.43 & r = 0.43) in the surface layer of the Arabian Sea. However these correlations were not immediately reflected in zooplankton at surface layer of the Arabian Sea. The only correlation observed in zooplankton significant at $p < 0.05$, was for Cd-Ni (-0.34) pairs.

5.2.2 Bay of Bengal

5.2.2.1 Water column

In the dissolved phase at the surface layer (n = 24) of the Bay of Bengal, no strong correlations (Table 43) between the seven trace metals Fe, Co, Ni, Cu, Zn, Cd and Pb were noticeable. The best correlations observed at surface significant at $p < 0.01$, were

observed for the Cd-Cu (r = 0.53) and correlations significant at $p< 0.02$, were observed for the Co-Ni (r = 0.46) suggesting that cycling of dissolved Cd and Cu was to some extent linked. Other correlations significant at $p< 0.05$, were observed for Ni-Cu (r = -0.38) pairs. Another set of weak correlations significant at $p< 0.10$, were between Ni-Zn (r = -0.35) and Cd-Zn (r = -0.33) pairs.

In the particulate phase at the surface layer of the Bay of Bengal (Table 44), no strong inter-metal correlations between the seven trace metals Fe, Co, Ni, Cu, Zn, Cd and Pb were noticeable. Correlations significant at $p< 0.02$, were observed for Zn and metals such as Cd & Ni (-0.51 to –0.43) and Cd-Fe (r = 0.46) pairs. Again correlations significant at $p< 0.05$, were observed for the Co-Ni (r = 0.40) and Ni-Cu (r = -0.38) pairs. A weak correlation significant at $p< 0.10$, were observed for the Cd-Cu (r = 0.33).

For total metal concentrations (Table 45) in the surface water column a correlation significant at $p< 0.01$, were observed for the Cd-Cu (r = 0.50), suggesting that cycling of Cd and Cu was to some extent linked. Another correlations significant at $p< 0.05$, were observed for the Co-Ni (r = 0.42), Ni-Cu (r = -0.39) pairs. Yet another weak correlation significant at $p< 0.10$, were observed for Zn-Cd (r = -0.35) and Cd-Fe (r = 0.36) pairs.

5.2.2.2 Zooplankton

In zooplankton highly significant correlations (Table 46) were observed for certain metals. In zooplankton the strongest correlation significant at $p< 0.001$ was found between Fe and Pb (r = 0.93) and a few other high correlations significant at $p< 0.001$ were observed between Fe and other metals such as Zn and Ni (r = 0.92 – 0.80), suggesting that these metals share a common accumulation process in the zooplankton in the Bay of Bengal. Other correlation significant at $p< 0.001$ was observed for Fe and metals such as Co and Pb (r = 0.74 – 0.76). A considerable number of significant correlations being significant at $p<0.001$ in the zooplankton were also observed between Cu and metals such as Fe, Zn, Co, Ni & Pb (r = 0.65 – 0.76), Zn and metals such as Cd, Ni, Co & Pb (r = 0.68 – 0.74), Ni and metals such as Co, Pb & Cd (r = 0.68 – 0.74). A correlation significant at $p< 0.01$ were observed between Fe and Cd (r = 0.53). Another set of weak correlations but significant at $p< 0.02$, between Cd and metals such as Co & Pb (r = 0.45 – 0.47) were also observed.

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Thus Ni-Cu pairs showed significant correlations at $p < 0.05$ and were observed in the dissolved, particulate and total phases ($r = -0.38$, -0.38 & -0.39) respectively in the surface layer of the Bay of Bengal. This was also reflected in the zooplankton phase with a strong correlation significant at $p < 0.001$, for Cu-Ni pairs($r = 0.67$).

To explain the differences in correlations between trace metals in each of the compartments, one should consider physical, chemical and biological processes occurring in the aquatic environment (internal processes) as well as influence of pollutants and other anthropogenic activities (external processes) and their effects on the partitioning and behaviour of heavy metals in that aquatic system (Baeyens *et al.*, 1998a). In the Bay of Bengal, having such a shallow shelf, the dissolved phase is the most sensitive compartment than particulate phase to the changes in water conditions. Even though the buffering capacity is moderate relative to discharges from the huge rivers and turbidity arising as a result of sediment influxes, vertical and horizontal mixing is weak due to fresh water induced stratification, which in turn leads to low biological production. These factors can prompt variation in the different phases of metals in seawater, as evidenced by the weakening of inter-element correlations in the dissolved and particulate compartment of the surface layer of the Bay of Bengal.

In contrast the Arabian Sea, has a wide shelf and relatively high buffering capacity as a result of excessive evaporation over precipitation. Moreover, vertical and horizontal mixing was relatively high due to weak thermohaline stratification and progressive summer cooling due to favourable wind effect which in turn leads to high biological production. These factors might arise in a strong inter-element correlation in the dissolved and particulate compartment of the surface layer of the Arabian Sea.

Inter-element correlations were different in each compartment of the surface layer of the Arabian Sea and Bay of Bengal. The number of strong and significant correlations increased from dissolved<suspended particulate matter<zooplankton in both areas. Strong correlations between Cu-Pb and Co-Cu metal pairs in all compartments except zooplankton, suggest similar partitioning mechanisms in the surface layer of the Arabian Sea. But the Ni-Cd metal pairs in the three compartments of the Arabian Sea showed strong correlations suggesting a similar dynamic partition exists in the surface layer.

However, in the Bay of Bengal, at the surface layer, only Ni-Cu pairs showed a common partition mechanism with significant correlation in all the three compartments. When total metal concentrations in the surface water column of both areas were considered, most of the metals appear to be not well correlated either in dissolved or particulate phase. In addition, no significant correlation with the suspended particulate matter supports the lesser influence of the latter compartment in the total metal concentration.

5.3. Bioaccumulation of trace metals in zooplankton samples from the Arabian Sea and Bay of Bengal

The average concentration of trace metals in zooplankton from the Arabian Sea during intermonsoon fall (Table 36) followed the order Fe > Zn > Cu > Ni > Cd > Co > Pb whereas during spring intermonsoon (Table 38) it followed the order Fe > Zn > Cu > Cd > Ni > Co > Pb and from the Bay of Bengal during winter monsoon (Table 37) followed the order Fe > Zn > Cu > Ni > Co > Cd > Pb. The sequence of metal levels in zooplankton from both the Arabian Sea (intermonsoon fall) and Bay of Bengal (winter monsoon) followed the same order for Fe, Zn, Cu, Ni and Pb except for Cd and Co. Similarly the sequence of metal levels in zooplankton from the Arabian Sea during spring intermonsoon and fall intermonsoon followed the same order for all elements except Cd and Ni. Even though elements like iron, zinc, copper, cadmium and lead are slightly enriched in zooplankton from the Arabian Sea, the elements like cobalt did not exhibit appreciable enrichment during spring intermonsoon when compared with intermonsoon fall. All the elements showed relative enrichment in zooplankton from the Bay of Bengal (winter monsoon) except for Cd from the Arabian Sea, which showed enrichment during spring intermonsoon only. The element iron and zinc in zooplankton showed a four-fold increase in its concentration from the Bay of Bengal (winter monsoon) when compared to the concentration of iron and zinc in zooplankton from the Arabian Sea (intermonsoon fall). The element copper in zooplankton showed a two-fold increase in its concentration from the Bay of Bengal (winter monsoon) when compared to the concentration of copper in zooplankton from the Arabian Sea (inter monsoon fall). Similarly the elements Co, Ni, Cd and Pb were slightly enriched in zooplankton from the Bay of Bengal (winter

monsoon) when compared to zooplankton samples taken from the Arabian Sea (intermonsoon fall).

Since bioaccumulation factors represent the potential of organisms to bioaccumulate metals, a comparative ranking of bioaccumulation factors is of great interest. The bioaccumulation factor is evaluated in relation to the concentration of the soluble metal ion in which the zooplankton inhabits. The average bioaccumulation factor of elements in zooplankton from the Arabian Sea (intermonsoon fall - Table 36) followed an order: Fe > Co > Ni > Zn > Cd > Cu > Pb and during spring intermonsoon followed the order: Fe > Zn > Co > Cd > Ni > Cu > Pb, whereas the average bioaccumulation factor of elements in zooplankton from the Bay of Bengal (winter monsoon - Table 37) followed the order Fe > Zn > Cd > Ni > Co > Cu > Pb. The sequence of bioaccumulation factors for all elements except Fe, Cu and Pb varied for both the Arabian Sea (intermonsoon fall & inter monsoon spring) and Bay of Bengal (winter monsoon) zooplankton. The bioaccumulation factor for iron and zinc in zooplankton from the Bay of Bengal (winter monsoon) revealed that it was four-fold higher than the Arabian Sea (intermonsoon fall) zooplankton even though both areas had same range of dissolved iron and zinc. Similarly the bioaccumulation factor for lead and cadmium in zooplankton from the Bay of Bengal (winter monsoon) revealed that it was three-fold higher than in the Arabian Sea (inter monsoon fall) zooplankton even though dissolved lead and cadmium was 2.5 times lower than in the Arabian Sea (inter monsoon fall). Moreover the bioaccumulation factor for nickel and copper in zooplankton from the Bay of Bengal (winter monsoon) showed that it was 1.7 times higher than the Arabian Sea zooplankton (inter monsoon fall) even though dissolved nickel remained in the same range in both areas and dissolved copper was 1.3 times lower than that of the Arabian Sea (inter monsoon fall). However the bioaccumulation factor of cobalt in zooplankton did not change appreciably in both areas even though dissolved cobalt in Arabian Sea (inter monsoon fall) was 3.5 times lower than that in the Bay of Bengal (winter monsoon).

Earlier study by George and Kureishy, (1979) on bioaccumulation factor of the Bay of Bengal zooplankton from a limited area showed an order of Fe (15638)>Co (1955)>Zn (1042)>Ni (442)>Mn (358) and Cu (228). A comparison of bioaccumulation factors for

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the Bay of Bengal (winter monsoon) zooplankton during the present study with the earlier report mentioned above showed a magnitude of 2.7, 3.2 and 3.8 times low values for iron, cobalt and copper respectively. However the bioaccumulation factor for elements like zinc and nickel were 1.32 & 1.72 times higher than the earlier report. Thus bioaccumulation factors during the present study for the elements like iron, cobalt and copper appear to be considerably lower while for elements like zinc and nickel it was higher than the earlier report since the potential of organisms to bioaccumulate metals varies for all the other elements except iron and copper.

A comparison of bioaccumulation factors for iron and zinc in zooplankton from the Arabian Sea during inter monsoon spring was 1.2 & 3.6 times higher than during intermonsoon fall. Further, a comparison of bioaccumulation factor for iron & zinc in zooplankton from the Bay of Bengal (winter monsoon) and Arabian Sea (intermonsoon fall) showed that iron & zinc is bioaccumulated four fold in the Bay of Bengal zooplankton than in the Arabian Sea zooplankton. Interestingly both areas have almost the same range of dissolved iron and zinc concentrations. Also a comparison of bioaccumulation factor for iron & zinc during the present study in Bay of Bengal zooplankton (winter monsoon) with an earlier report mentioned above was 2.7 & 3.2 times lower. The four-fold enrichment of iron & zinc concentrations in zooplankton from the Bay of Bengal when compared with the Arabian Sea zooplankton and the 1.3 & 2.6 times enrichment of iron & zinc concentrations in the Arabian Sea zooplankton during spring when compared to fall intermonsoon might be due to high bioaccumulation factor rather than a higher degree of bioavailable iron and zinc in seawater.

The bioaccumulation factors for lead in zooplankton from the Arabian Sea during intermonsoon spring was 2.6 times higher than during intermonsoon fall while for cadmium it was slightly higher in intermonsoon fall. The slight enrichment of cadmium concentration in zooplankton from the Arabian Sea during spring intermonsoon can be due to the presence of a slightly higher availability of bioavailable cadmium in the surface layers during intermonsoon spring when compared to intermonsoon fall. A comparison of bioaccumulation factors for lead and cadmium in zooplankton from the Bay of Bengal (winter monsoon) has revealed that it is three fold higher than the Arabian

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Sea (intermonsoon fall) zooplankton even though dissolved lead and cadmium was 2.5 times lower than in the Arabian Sea during intermonsoon fall. Even though the dissolved lead in both Arabian Sea and Bay of Bengal fluctuates appreciably the lead enrichment in zooplankton remains almost the same in both areas. The slight enrichment of cadmium concentration in zooplankton from the Bay of Bengal (winter monsoon) when compared to its metal enrichment in zooplankton from the Arabian Sea (inter monsoon fall) may be due to high bioaccumulation factor of this element existing in the Bay of Bengal zooplankton.

A comparison of bioaccumulation factors for copper in zooplankton from the Arabian Sea during intermonsoon spring was slightly higher than during intermonsoon fall while for zinc it was 2.2 times higher in spring intermonsoon than intermonsoon fall. The slight enrichment of copper in zooplankton from the Arabian Sea during spring intermonsoon was likely to be due to the slight enrichment of bioaccumulation factor of copper observed in zooplankton from the Arabian Sea during this season when compared with intermonsoon fall. Also a comparison of bioaccumulation factor for nickel and copper during the present study in the Bay of Bengal zooplankton (winter monsoon) with an earlier report mentioned above was 1.72 higher for nickel and 3.85 times lower for copper. Moreover the bioaccumulation factor for nickel and copper in zooplankton from the Bay of Bengal (winter monsoon) showed that it was 1.7 times higher than the Arabian Sea zooplankton even though dissolved nickel lies within the same range in both areas and dissolved copper was 1.3 times lower than the Arabian Sea zooplankton. Thus 1.4 times enrichment of nickel concentration, 2.2 times enrichment of copper concentration in zooplankton from the Bay of Bengal are likely to be due to high bioaccumulation factor of these elements in the Bay of Bengal zooplankton.

A comparison of bioaccumulation factors for cobalt in zooplankton from the Arabian Sea during intermonsoon spring is 1.25 times higher than during intermonsoon fall. Although the cobalt concentration in zooplankton for the two seasons remained the same eventhough the dissolved cobalt was slightly higher in intermonsoon spring. However the bioaccumulation factor of cobalt in zooplankton did not change appreciably in both areas eventhough the dissolved cobalt in Arabian Sea was 3.5 times lower than the Bay of

Bengal. Also a comparison of bioaccumulation factor for cobalt during the present study in the Bay of Bengal zooplankton (winter monsoon) with the earlier report mentioned above was 3.2 times higher. The 1.7 times higher enrichment of cobalt concentrations in zooplankton from the Bay of Bengal when compared with the Arabian Sea may be due to bioavailability of cobalt in the surface layers of the Bay of Bengal.

From this study it is clear that the sequence of average metal levels in zooplankton from both the Arabian Sea (inter monsoon fall) and Bay of Bengal (winter monsoon) follows the same order for Fe, Zn, Cu, Ni and Pb except for Cd and Co. Further the average metal levels in zooplankton from the Bay of Bengal (winter monsoon) showed relative enrichment when compared with Arabian Sea (intermonsoon fall) zooplankton. However the sequence of bioaccumulation factors for all elements except Fe, Cu and Pb varied for both the Arabian Sea (intermonsoon fall & intermonsoon spring) and Bay of Bengal (winter monsoon) zooplankton. The bioaccumulation factors for all the elements except cobalt are lower in the Arabian Sea zooplankton (inter monsoon fall) when compared to Bay of Bengal zooplankton (winter monsoon). The metal content in zooplankton and bioaccumulation factors will not vary appreciably with elements in the Arabian Sea during intermonsoon fall but the element cobalt and copper showed variations during intermonsoon spring. However the metal content in zooplankton and bioaccumulation factors will vary with elements like Cd and Cu in the Bay of Bengal. This points to the importance of bioavailability of metals in seawater as well as differences in the potential of heavy metal accumulation in zooplankton organisms from the Arabian Sea and Bay of Bengal. The trace metal enrichment of Fe, Zn, Cd, Ni, and Cu in zooplankton are likely to be due to high bioaccumulation factor of these elements in the Bay of Bengal zooplankton whereas the slight cobalt enrichment is due to the bioavailability of cobalt in the seawater.

Thus significant variations in the metal concentrations observed for some metals during the sampling period in the Arabian Sea (intermonsoon fall & spring intermonsoon) might result from variations caused by the annual cycle of metal bioavailability. A comparison of bioaccumulation of metals in zooplankton from the Arabian Sea (intermonsoon spring) and the Bay of Bengal (winter monsoon) reveals that iron is

bioaccumulated more than any other metal; zinc and cadmium showed a similar enrichment and least for lead.

In general, the non-essential element cadmium was usually taken up at a higher rate than the essential element copper under study in the Arabian Sea and Bay of Bengal. The occurrence of zinc in marine environment is immediately reflected on the zinc levels in zooplankton, which in fact is concentrated more effectively than copper. High accumulation of zinc in zooplankton may be due to co-precipitation of zinc with calcium carbonate. It is, however, apparent that the trace metal accumulation by zooplankton does not depend only on the soluble fraction in water. The accumulation of non-essential elements to such high levels in zooplankton inhabiting the aquatic system is yet to be fully understood. It is likely that for essential elements like iron, the endogenous or exogenous ligands or chelating agents combine with the metal ions to form soluble complexes and are probably transferred into the cell (Saltman, 1965).

5.4. Biomagnification of trace metals in zooplankton samples from the Arabian Sea and Bay of Bengal

The spatial variation of the logarithm of biomagnification factors (log (bmf)) for trace metals in zooplankton from the Arabian Sea during intermonsoon fall and spring intermonsoon are shown in Fig. 153 to 159 & 209 to 215, whereas for the Bay of Bengal during winter monsoon are illustrated in Fig. 181 to 187.

For the metal iron in the zooplankton from the Arabian Sea during intermonsoon fall and intermonsoon spring the log (bmf) of Fe (Fig. 153 & Fig.209) was largely negative with locations. For the iron in zooplankton from the Bay of Bengal (winter monsoon), the log (bmf) of Fe (Fig. 181) had slightly positive values (Station Positions: B4, B5, B6, B13, B14 and B19), which varied with locations. This was found to coincide with high concentration of iron obtained for zooplankton from coastal stations off Vishakapatnam and Madras. The slightly high positive value for log (bmf) of Fe in zooplankton for some locations revealed a minor biomagnification of Fe in zooplankton from the Bay of Bengal even though the average value was negative.

For the element cobalt, the log (bmf) values with locations in the Arabian Sea (intermonsoon fall) showed some alternate positive and negative values eventhough the

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majority of values were positive. However during spring intermonsoon, in the Arabian Sea the log (bmf) values of Co was almost negative with locations in majority of stations even though there was slight positive values at certain positions. Consequently in the Arabian Sea during spring intermonsoon, the zooplankton samples at the offshore locations off Kandala and off Veraval showed slightly positive log (bmf) values for Co and thereby coincided with elevated cobalt concentrations in zooplankton. Similarly in the Arabian Sea during intermonsoon fall, the positive log (bmf) values for Co, at the coastal stations off Kanyakumari and off Goa, coincided with higher cobalt concentrations. However, in the Bay of Bengal the log (bmf) values for Co in zooplankton was negative in a majority of stations except at the offshore stations off Gopalpur transect where a slightly positive value was obtained.

For the element Ni, in the Arabian Sea during intermonsoon fall, all log (bmf) values for Ni in zooplankton were positive with locations whereas during intermonsoon spring most of the values with locations were almost negative, there by showing a seasonal effect on biomagnification of Ni in zooplankton. However, in the Bay of Bengal during winter monsoon, almost all the log (bmf) values of Ni in zooplankton were positive with locations. The coastal waters off Vishakapatnam & off Madras with high concentrations of nickel in zooplankton from the Bay of Bengal and the coastal waters off Kanyakumari & off Goa with high concentrations of nickel in zooplankton from the Arabian Sea (intermonsoon fall) coincided with moderate positive values of log (bmf) of Ni in zooplankton from these areas.

For the element Cu, in the Arabian Sea (during intermonsoon fall and intermonsoon spring), the log (bmf) for Cu in zooplankton was largely negative in almost all locations. Similarly, in the Bay of Bengal during winter monsoon, the log (bmf) values for Cu in zooplankton was largely negative for all locations.

The log (bmf) for the element zinc in zooplankton during intermonsoon fall & spring intermonsoon from the Arabian Sea and Bay of Bengal during winter monsoon with locations, showed that most of the values were negative, but with some alternate positive values. The alternate positive value for the biomagnification factor for zinc in zooplankton from the Arabian Sea during intermonsoon fall coincided with higher zinc

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concentrations in zooplankton from the coastal stations off Kanyakumari and off Goa transect. Similarly the alternate positive value for the biomagnification factor for zinc in zooplankton from the Arabian Sea during intermonsoon spring coincided with higher zinc concentrations in zooplankton from the offshore stations off Kandala and off Veraval transect. In the Bay of Bengal, the alternate positive log (bmf) values for zinc in zooplankton also coincided with higher concentrations of zinc in zooplankton from coastal stations off Vishakapatnam and off Madras.

For the element Cd, in the Arabian Sea during intermonsoon fall and spring intermonsoon, the log (bmf) for Cd in zooplankton was largely positive with almost all locations. In the Bay of Bengal during winter monsoon, the log (bmf) values for cadmium in zooplankton was also largely positive with locations.

The log (bmf) values for Pb in zooplankton, from the Arabian Sea during intermonsoon fall & spring intermonsoon and Bay of Bengal during winter monsoon showed that all the values with locations were largely negative.

The average absolute log (bmf) values of trace metals in zooplankton from the Bay of Bengal during winter monsoon (Table 37) can be ranked in the following order: Cd <Ni < Zn <Fe < Co < Cu < Pb and Arabian Sea during intermonsoon fall (Table 36) can be ranked in the order: Cd < Ni < Co < Zn < Fe < Cu < Pb respectively where as during spring inter monsoon (Table 38) it follows the order: Cd < Zn < Co < Ni < Fe < Cu < Pb. The absolute log (bmf) values of trace metals in zooplankton from the Arabian Sea during intermonsoon fall and spring intermonsoon vary with all elements except Cd, Cu and Pb. A comparison of the absolute log (bmf) values of trace metals in zooplankton from the Arabian Sea during intermonsoon fall and the Bay of Bengal during winter monsoon vary with all elements except Cd, Ni, Cu and Pb.

A comparison of average log (bmf) values of iron in zooplankton from the Arabian Sea during intermonsoon fall & spring inter monsoon showed that the value was highly negative for intermonsoon fall. Moreover a comparison of average log (bmf) value of iron in zooplankton from the Arabian Sea during intermonsoon fall (log (bmf) of Fe = - 0.62) and Bay of Bengal during winter monsoon (log (bmf) of Fe = -0.24) showed that the value was highly negative for Arabian Sea zooplankton, even though there existed a

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small positive value in the coastal locations off Vishakapatnam and off Madras. The highly negative value for the average log (bmf) for Fe in zooplankton from the Arabian Sea during intermonsoon fall and spring intermonsoon when compared to the average log (bmf) for Fe in zooplankton from the Bay of Bengal during winter monsoon is a consequence of enrichment of Fe in particulates from the Arabian Sea than the Bay of Bengal.

A comparison of average log (bmf) values of cobalt in zooplankton from the Arabian Sea during intermonsoon fall & spring inter monsoon showed that the value was negative for spring intermonsoon and positive for intermonsoon fall. Moreover a comparison of average log (bmf) value of cobalt in zooplankton from the Arabian Sea during intermonsoon fall (log (bmf) of Co = 0.13) was positive and for Bay of Bengal zooplankton during winter the value was highly negative (log (bmf) of Co = -0.34). The high average negative value for log (bmf) of Co in zooplankton from the Bay of Bengal and the positive value for log (bmf) of Co in zooplankton from the Arabian Sea during intermonsoon fall have resulted from the relative enrichment of Co in particulates from the Bay of Bengal when compared with the Arabian Sea particulates.

A comparison of average log (bmf) values of nickel in zooplankton from the Arabian Sea during intermonsoon fall & spring intermonsoon showed that the value was negative for spring intermonsoon and positive for intermonsoon fall. But a comparison of average log (bmf) values of nickel in zooplankton from the Arabian Sea during intermonsoon fall (log (bmf) of Ni = 0.36) was positive and Bay of Bengal during winter monsoon showed that the value was slightly more positive (log (bmf) of Ni = 0.38) for Bay of Bengal zooplankton. Interestingly both areas have same range of Ni enrichment in particulates. So the slight higher positive value for log (bmf) for Ni in Bay of Bengal zooplankton remains yet to be answered.

Similarly a comparison of average log (bmf) values of copper in zooplankton from the Arabian Sea during intermonsoon fall & spring intermonsoon showed that the value was largely negative for the former season. But a comparison of average log (bmf) values of copper in zooplankton from the Arabian Sea during intermonsoon fall (log (bmf) of Cu = -1.24) and Bay of Bengal during winter monsoon (log (bmf) of Cu = -0.99) showed that

the value was largely negative for Arabian Sea zooplankton. The largely negative value for log (bmf) of Cu in zooplankton from the Arabian Sea during intermonsoon fall and spring inter monsoon when compared with the value of log (bmf) of Cu in zooplankton from the Bay of Bengal during winter monsoon was a consequence of relative enrichment of copper in the particulates from the Arabian Sea than in the Bay of Bengal.

A comparison of average log (bmf) value of zinc in zooplankton from the Arabian Sea during intermonsoon fall & spring inter monsoon showed that the value was slightly more negative for spring intermonsoon. But a comparison of average log (bmf) values of zinc in zooplankton from the Arabian Sea during intermonsoon fall (log (bmf) of Zn = -0.34) and Bay of Bengal during winter monsoon (log (bmf) of Zn = -0.02) showed that the value was highly negative for Arabian Sea zooplankton. The high negative value for log (bmf) of Zn in zooplankton from the Arabian Sea during intermonsoon fall and spring intermonsoon was attributed to the relative enrichment of Zn in particulates from the Arabian Sea than in the Bay of Bengal.

A comparison of average log (bmf) values of cadmium in zooplankton from the Arabian Sea during intermonsoon fall & spring inter monsoon showed that the value was highly positive for intermonsoon fall. But a comparison of average log (bmf) values of cadmium in zooplankton from the Arabian Sea during intermonsoon fall (log (bmf) of Cd = 0.601) and Bay of Bengal during winter monsoon (log (bmf) of Cd = 0.92) showed that the value was largely positive for Bay of Bengal zooplankton. The highly positive value for log (bmf) of Cd in zooplankton from the Bay of Bengal during winter monsoon was attributed to the low enrichment of Cd in particulates from the Bay of Bengal than the Arabian Sea particulates during intermonsoon fall and spring intermonsoon.

A comparison of average log (bmf) values of lead in zooplankton from the Arabian Sea during intermonsoon fall & spring intermonsoon showed that the value was slightly more negative for intermonsoon fall. But a comparison of average log (bmf) values of lead in zooplankton from the Arabian Sea during intermonsoon fall (log (bmf) of Pb = -2.0) and Bay of Bengal during winter monsoon (log (bmf) of Pb = -1.6) showed that the value was largely negative for Arabian Sea zooplankton. The slightly high negative value for log (bmf) of Pb in zooplankton from the Arabian Sea during intermonsoon fall and

spring intermonsoon could be attributed to the relative enrichment of Pb in particulates from the Arabian Sea than in the Bay of Bengal.

Thus a comparison of average log (bmf) of metals in zooplankton from the Arabian Sea during intermonsoon fall with metals in zooplankton from the Bay of Bengal during winter monsoon showed that the values were highly negative for metals like Fe, Cu, Zn and Pb. This might have been resulted as a consequence of enrichment of these metals in the particulates from the Arabian Sea relative to their enrichment in the Bay of Bengal. However the log (bmf) for Co in zooplankton was negative for the Bay of Bengal during winter monsoon and positive for the Arabian Sea during intermonsoon fall due to the enrichment of Co in particulates from the Bay of Bengal relative to that in the Arabian Sea. However the log (bmf) values of Cd and Ni in both the Arabian Sea during intermonsoon fall and Bay of Bengal during winter monsoon were positive. The high positive value for log (bmf) of Cd in zooplankton from the Bay of Bengal may be attributed to the low enrichment of cadmium in particulates from this area rather than the high enrichment of cadmium in particulates from the Arabian Sea during intermonsoon fall and intermonsoon spring. Even though log (bmf) of Ni in zooplankton, from the Bay of Bengal (winter monsoon) was slightly positive than the log (bmf) of Ni in zooplankton from the Arabian Sea (intermonsoon fall) and both areas showed a similar enrichment of Ni in particulates.

Table 36 to 38 illustrates the average of the log (bmf) values of various metals in zooplankton from the Arabian Sea and the Bay of Bengal. For some metals in the Bay of Bengal the mean log (bmf) was found to be positive with very low value for nickel (0.38), revealing a small biomagnification of this metal in zooplankton. However for cadmium (0.92) a high positive value was found, revealing a high biomagnification of this metal in zooplankton from the Bay of Bengal. For the metals studied in the Arabian Sea during intermonsoon fall the mean log (bmf) was found to be positive for some metals with very low value for Co (0.13) and Ni (0.361), revealing a small biomagnification of these metals in zooplankton. For the metals studied in the Arabian Sea during intermonsoon spring the mean log (bmf) was found to be negative for some metals but very low positive value exist for Cd (0.448), revealing a small

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biomagnification of these metals in zooplankton. However, for cadmium (0.601) a high positive value was found there by revealing a high biomagnification of this metal in zooplankton from the Arabian Sea during intermonsoon fall. Almost all log-transformed biomagnification values in both the areas were negative which means that the metal concentration was larger in suspended matter than in zooplankton. The sequence of the absolute log (bmf) values of trace metals in zooplankton from the Arabian Sea and the Bay of Bengal indicated that metals such as copper and lead were biodiminishing from suspended matter particles to zooplankton in both areas. No considerable biomagnification from water to zooplankton was recognized; instead biodiminishion was the prevailing process. The exception was the slight enrichment of cadmium and nickel from suspended particulate matter to zooplankton, which was identified for both the areas.

Table 36: Average concentration of trace metals in different compartments and average bioaccumulation (baf) & biomagnification (bmf) factors for trace metals in zooplankton samples from the eastern Arabian Sea during inter monsoon fall

Metal	Fe	Co	Ni	Cu	Zn	Cd	Pb
Dissolved (ppb)	2.59	0.023	0.049	1.16	1.38	0.067	0.73
Particulate (ppb)	37.9	0.037	0.031	1.30	2.36	0.015	1.31
Zooplankton (ppm)	3467	14.2	20.7	21	443	16	5
Bioaccumulation factors (baf)	1470	629	425	34	322	266	6.4
log (baf)	2.97	2.75	2.58	1.21	2.33	2.37	0.58
Biomagnification factors (bmf)	0.426	1.77	2.76	0.16	0.846	4.99	0.02
log (bmf)	-0.621	0.130	0.361	-1.24	-0.34	0.601	-2.0

Table 37: Average concentration of trace metals in different compartments and average bioaccumulation (baf) & biomagnification (bmf) factors for trace metals in zooplankton samples from the western Bay of Bengal during winter monsoon

Metal	Fe	Co	Ni	Cu	Zn	Cd	Pb
Dissolved (ppb)	2.34	0.08	0.046	0.89	1.38	0.026	0.31
Particulate (ppb)	32.94	0.14	0.031	1.04	2.63	0.005	0.55
Zooplankton (ppm)	14073	24	30	46	2001	19	6.5
Bioaccumulation factors (baf)	5709	614	761	59	1357	775	24
log (baf)	3.57	2.59	2.84	1.72	2.92	2.84	1.22
Biomagnification factors (bmf)	0.89	0.64	2.88	0.12	1.54	10	0.03
log (bmf)	-0.24	-0.34	0.38	-0.99	-0.02	0.92	-1.6

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Table 38: Average concentration of trace metals in different compartments and average bioaccumulation (baf) & biomagnification (bmf) factors for trace metals in zooplankton samples from the northeastern Arabian Sea during spring intermonsoon

Metal	Fe	Co	Ni	Cu	Zn	Cd	Pb
Dissolved (ppb)	2.34	0.031	0.101	0.69	1.41	0.079	0.41
Particulate (ppb)	32.37	0.049	0.065	0.75	2.46	0.017	0.66
Zooplankton (ppm)	4622	14.7	18.2	25.2	1177	21.7	6.6
Bioaccumulation factors (baf)	1758	500	187	38	736	259	17.1
log (baf)	3.10	2.69	2.27	1.52	2.49	2.38	1.1
Biomagnification factors (bmf)	0.362	0.83	0.767	0.09	1.156	3.17	0.03
log (bmf)	-0.64	-0.11	-0.144	-1.11	-0.352	0.448	-1.71

Table 39: Pearson product-moment correlation coefficients between dissolved trace metals in the surface layer of the eastern Arabian Sea (n=29)

Dissolved metal	Fe	Co	Ni	Cu	Zn	Cd	Pb	SPM
Fe	1.00							
Co	0.43	1.00						
Ni	0.09	0.05	1.00					
Cu	0.38	0.42	0.14	1.00				
Zn	-0.47	-0.42	0.11	-0.12	1.00			
Cd	0.34	0.12	0.46	-0.04	-0.03	1.00		
Pb	0.42	0.47	-0.08	0.55	-0.54	-0.15	1.00	
SPM	-0.07	0.17	0.21	-0.01	-0.08	-0.04	-0.26	1.00

Table 40: Pearson product-moment correlation coefficients between particulate trace metals in the surface layer of the eastern Arabian Sea (n=29)

Particulate metal	Fe	Co	Ni	Cu	Zn	Cd	Pb	SPM
Fe	1.00							
Co	0.49	1.00						
Ni	0.20	0.06	1.00					
Cu	0.40	0.43	0.13	1.00				
Zn	-0.44	-0.41	0.09	-0.09	1.00			
Cd	0.32	0.13	0.46	-0.05	-0.05	1.00		
Pb	0.67	0.56	-0.12	0.57	-0.62	-0.09	1.00	
SPM	-0.08	-0.13	0.21	-0.04	0.00	-0.05	-0.20	1.00

Table 41: Pearson product-moment correlation coefficients between total metals in the surface layer of the eastern Arabian Sea (n=29)

Total metal	Fe	Co	Ni	Cu	Zn	Cd	Pb	SPM
Fe	1.00							
Co	0.47	1.00						
Ni	0.16	0.05	1.00					
Cu	0.41	0.43	0.14	1.00				
Zn	-0.46	-0.42	0.10	-0.10	1.00			
Cd	0.33	0.12	0.46	-0.04	-0.04	1.00		
Pb	0.62	0.53	-0.11	0.58	-0.60	-0.12	1.00	
SPM	-0.08	-0.15	0.21	-0.03	-0.03	-0.04	-0.22	1.00

Table 42: Pearson product-moment correlation coefficients between zooplankton trace metals in the eastern Arabian Sea (n=29)

Zooplankton metal	Fe	Co	Ni	Cu	Zn	Cd	Pb	SPM
Fe	1.00							
Co	-0.07	1.00						
Ni	0.76	-0.01	1.00					
Cu	0.49	-0.12	0.71	1.00				
Zn	0.64	0.13	0.61	0.47	1.00			
Cd	-0.43	0.12	-0.34	-0.12	-0.33	1.00		
Pb	0.53	-0.08	0.26	0.28	0.57	-0.27	1.00	
SPM	0.19	-0.03	0.15	-0.04	0.21	-0.28	0.12	1.00

Table 43: Pearson product-moment correlation coefficients between dissolved trace metals in the western Bay of Bengal (n=24)

Dissolved metal	Fe	Co	Ni	Cu	Zn	Cd	Pb	SPM
Fe	1.00							
Co	-0.31	1.00						
Ni	-0.25	0.46	1.00					
Cu	0.27	-0.24	-0.38	1.00				
Zn	-0.12	0.11	-0.35	0.12	1.00			
Cd	0.29	-0.19	-0.07	0.53	-0.33	1.00		
Pb	0.26	-0.25	-0.14	0.15	-0.31	0.27	1.00	
SPM	0.01	0.11	-0.17	0.22	0.04	-0.24	0.06	1.00

Table 44: Pearson product-moment correlation coefficients between particulate trace metals in the western Bay of Bengal (n=24)

Particulate metal	Fe	Co	Ni	Cu	Zn	Cd	Pb	SPM
Fe	1.00							
Co	-0.22	1.00						
Ni	-0.08	0.40	1.00					
Cu	0.17	-0.24	-0.38	1.00				
Zn	-0.27	0.11	-0.43	0.22	1.00			
Cd	0.46	-0.16	0.18	0.33	-0.51	1.00		
Pb	0.24	-0.27	-0.10	0.16	-0.28	0.18	1.00	
SPM	-0.06	0.11	-0.19	0.22	0.08	-0.29	0.07	1.00

Table 45: Pearson product-moment correlation coefficients between total metals in the western Bay of Bengal (n=24)

Total metal	Fe	Co	Ni	Cu	Zn	Cd	Pb	SPM
Fe	1.00							
Co	-0.23	1.00						
Ni	-0.09	0.42	1.00					
Cu	0.17	-0.24	-0.39	1.00				
Zn	-0.26	0.11	-0.41	0.19	1.00			
Cd	0.36	-0.18	-0.01	0.50	-0.35	1.00		
Pb	0.24	-0.26	-0.11	0.16	-0.29	0.25	1.00	
SPM	-0.05	0.11	-0.18	0.22	0.06	-0.26	0.06	1.00

Table 46: Pearson product-moment correlation coefficients between zooplankton trace metals in the western Bay of Bengal (n=24)

Zooplankton metal	Fe	Co	Ni	Cu	Zn	Cd	Pb	SPM
Fe	1.00							
Co	0.76	1.00						
Ni	0.80	0.69	1.00					
Cu	0.76	0.72	0.67	1.00				
Zn	0.92	0.68	0.77	0.71	1.00			
Cd	0.53	0.47	0.68	0.40	0.72	1.00	.	
Pb	0.93	0.74	0.74	0.65	0.78	0.45	1.00	
SPM	-0.09	-0.08	-0.05	-0.26	-0.07	-0.11	0.00	1.00

Figure.132 to 134. Spatial variation of Fe in different phases from the eastern Arabian Sea during intermonsoon fall

Figure. 132

Figure. 133
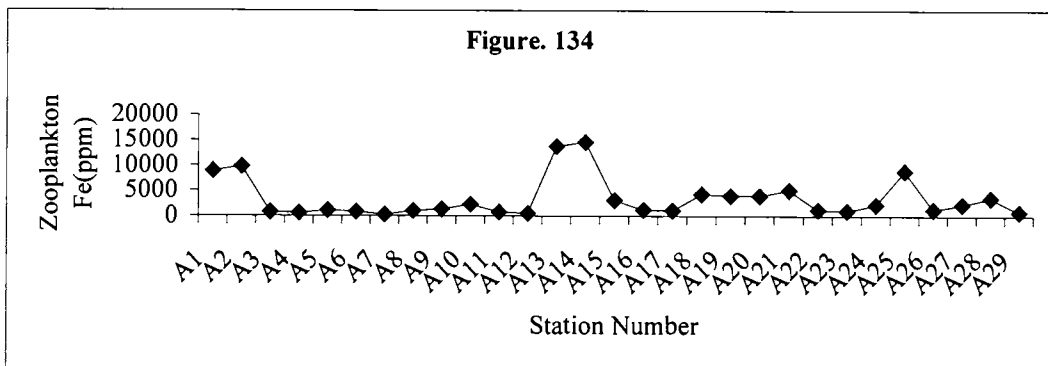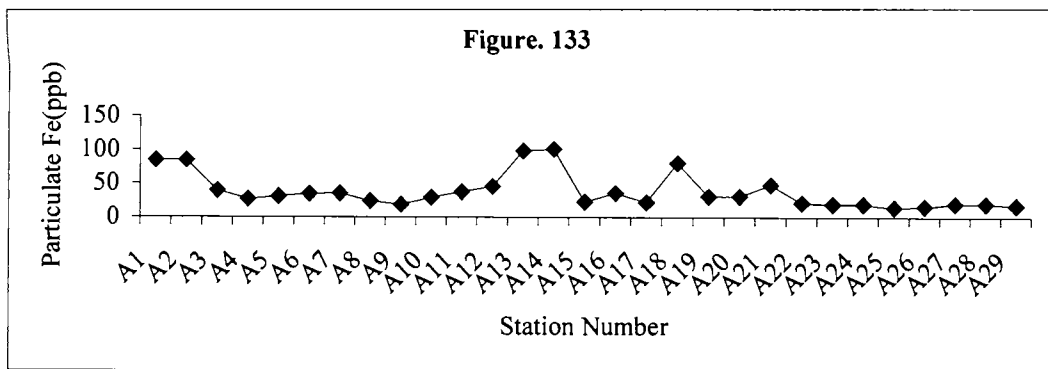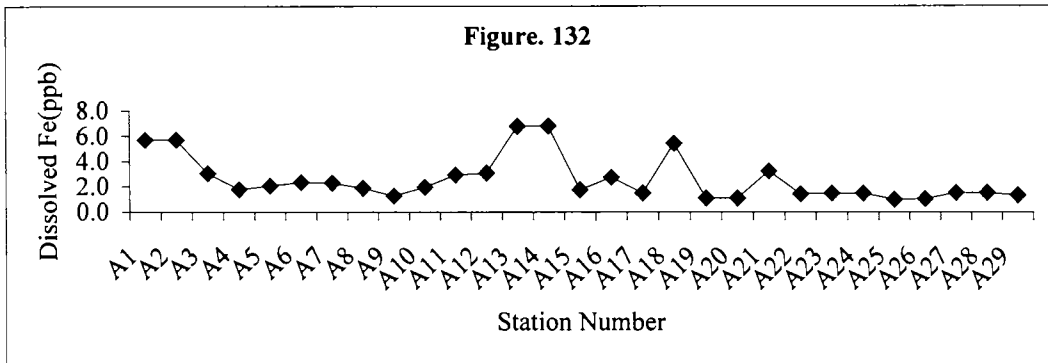
Figure. 134

Figure.135 to 137. Spatial variation of Co in different phases from the eastern Arabian Sea during intermonsoon fall

Figure. 135

Figure. 136
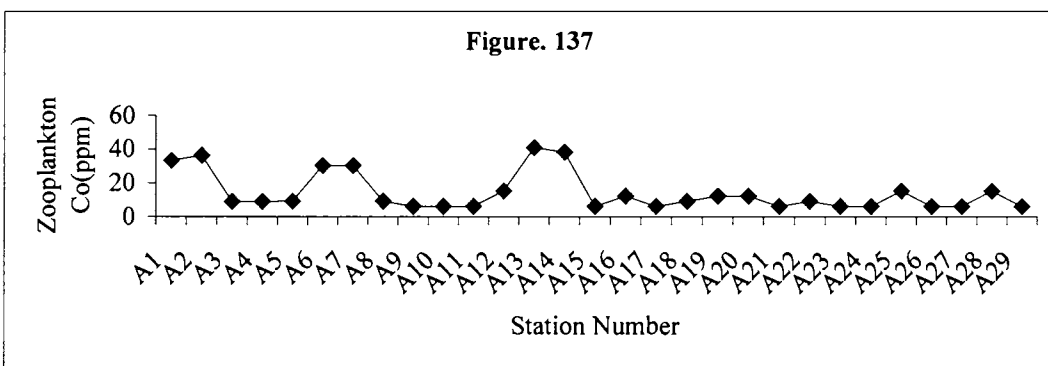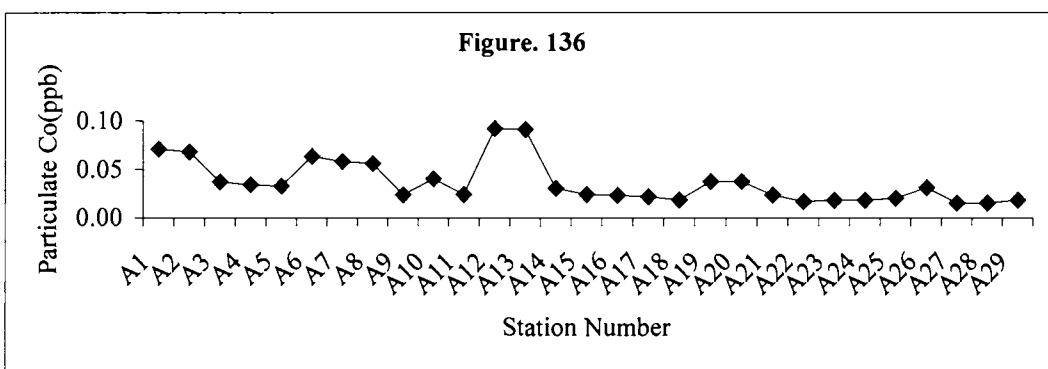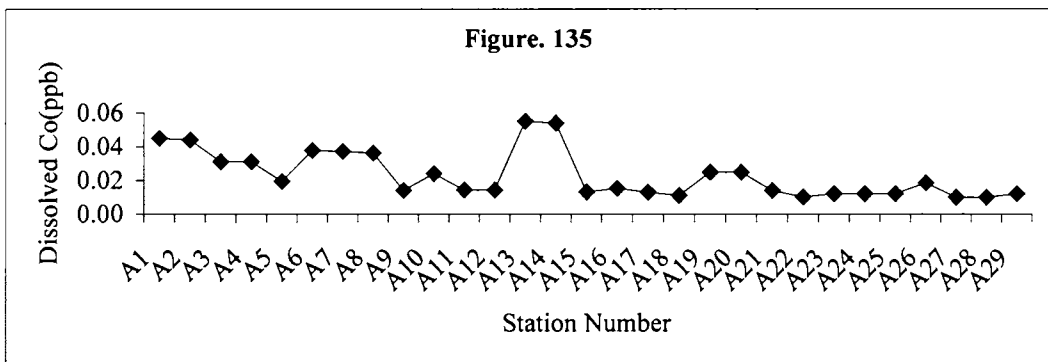
Figure. 137

Figure.138 to 140. Spatial variation of Ni in different phases from the eastern Arabian Sea during intermonsoon fall

Figure. 138

Figure. 139
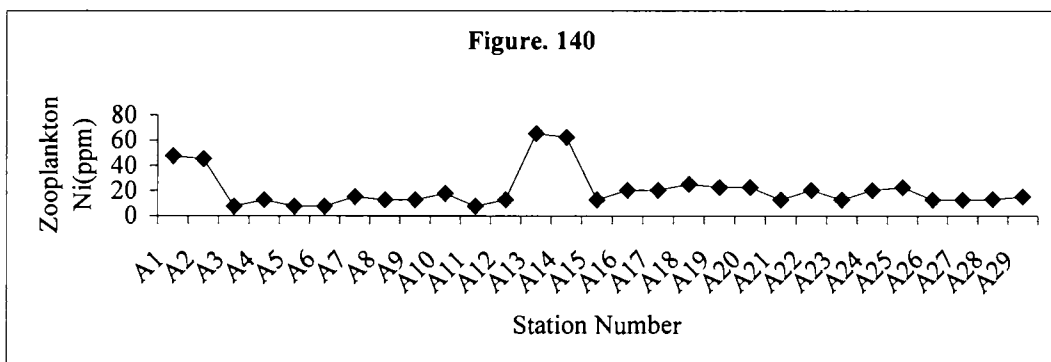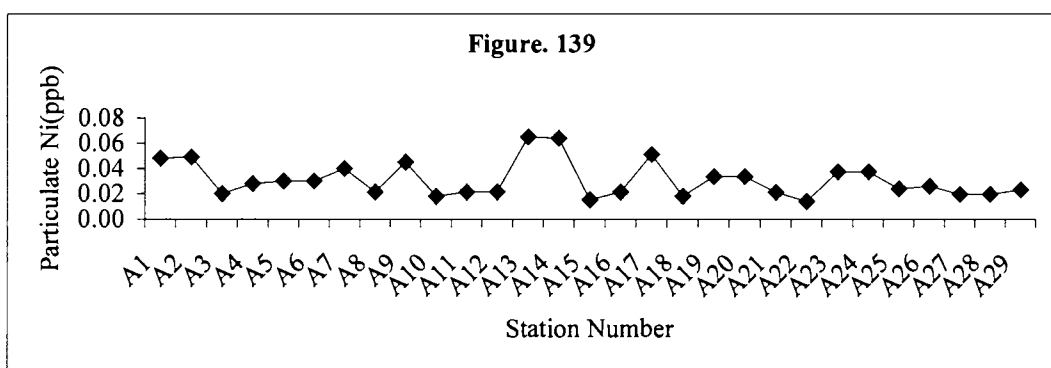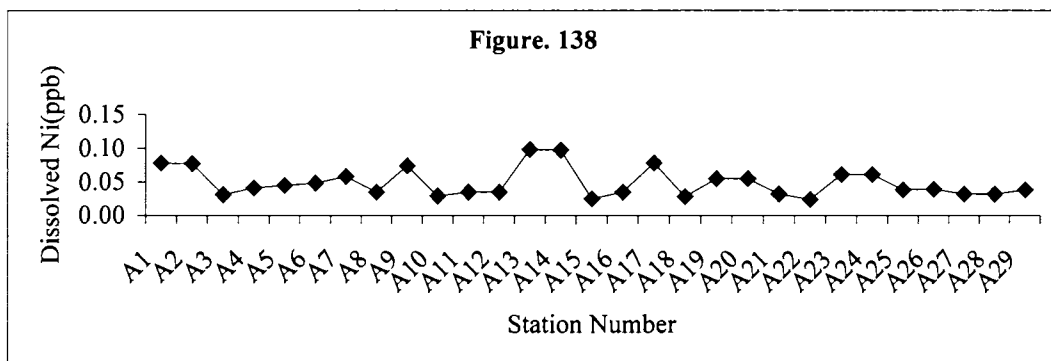
Figure. 140

Figure.141 to 143. Spatial variation of Cu in different phases from the eastern Arabian Sea during intermonsoon fall

Figure. 141

Figure. 142
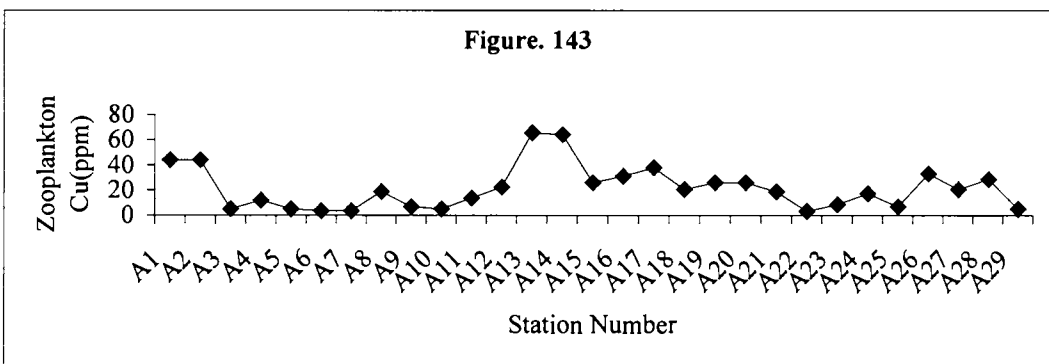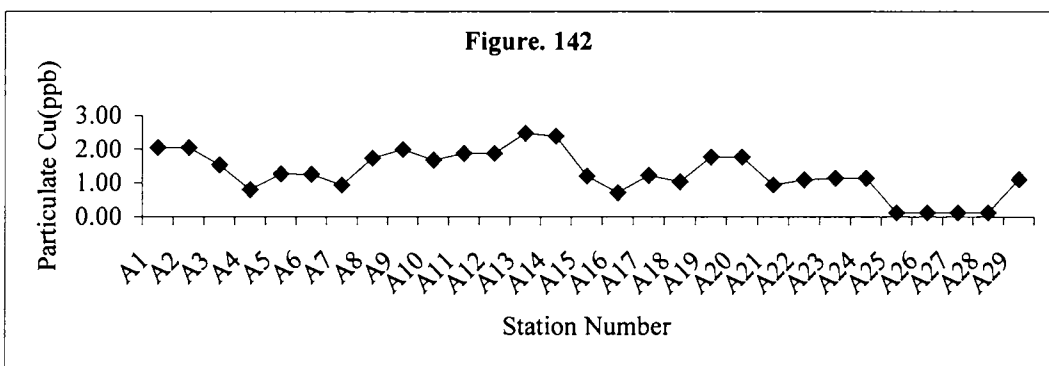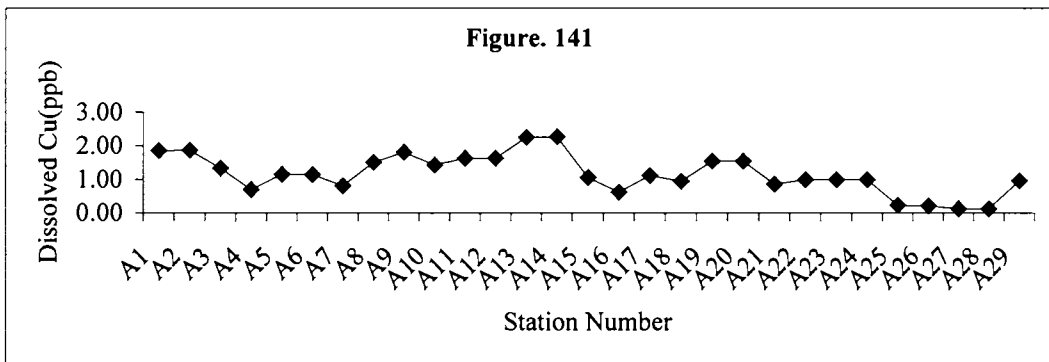
Figure. 143

Figure.144 to 146. Spatial variation of Zn in different phases from the eastern Arabian Sea during intermonsoon fall

Figure. 144

Figure. 145
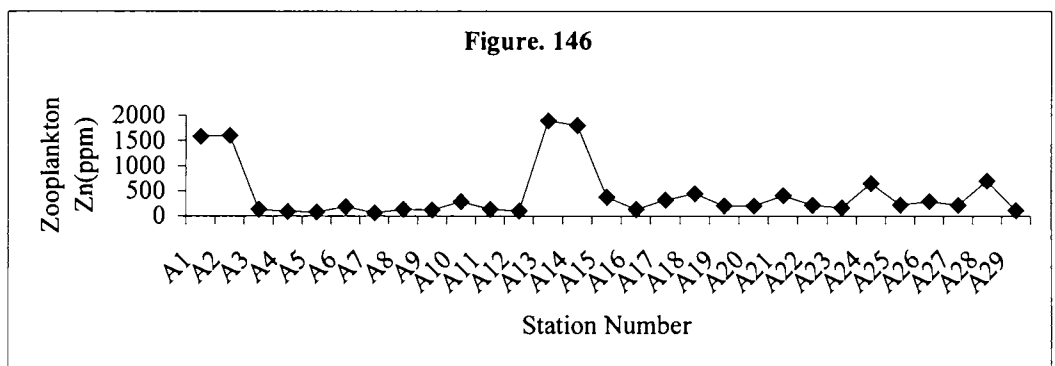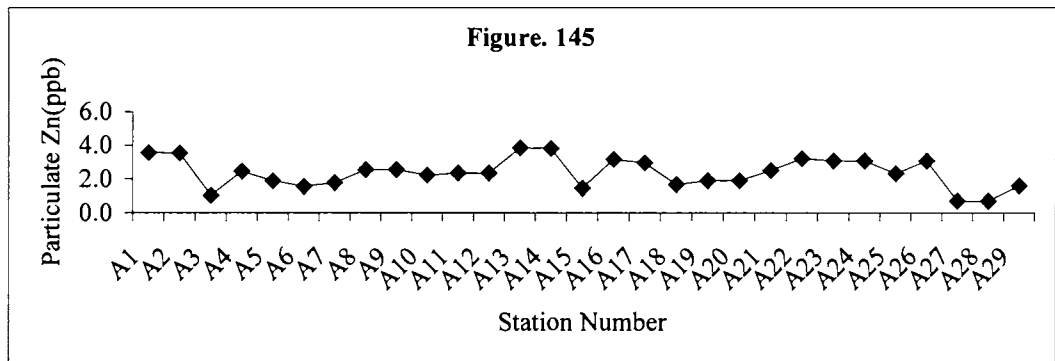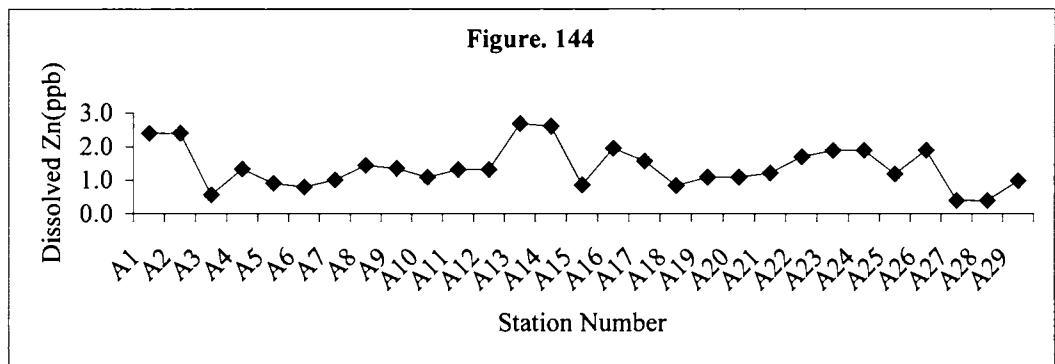
Figure. 146

Figure.147 to 149. Spatial variation of Cd in different phases from the eastern Arabian Sea during intermonsoon fall

Figure. 147

Figure. 148
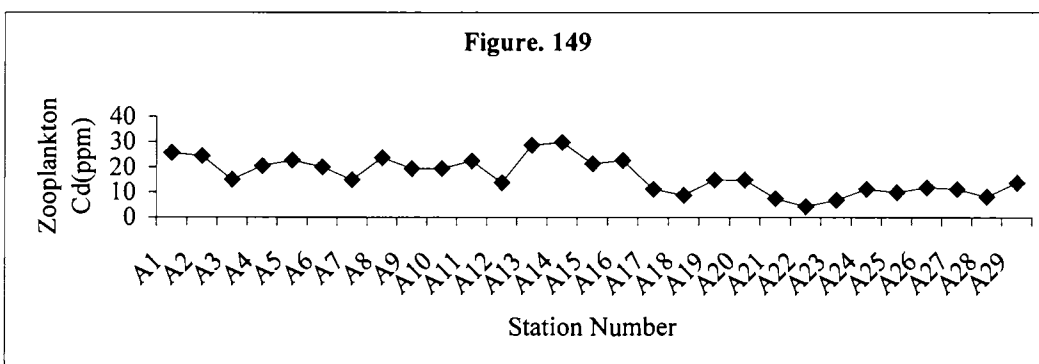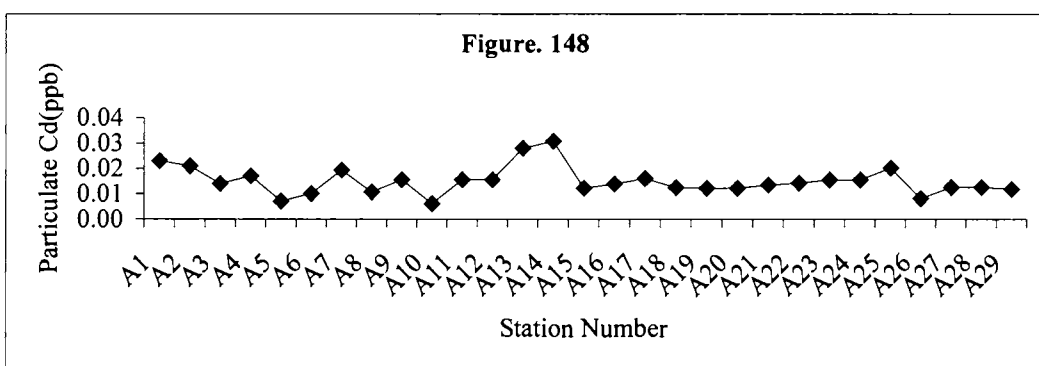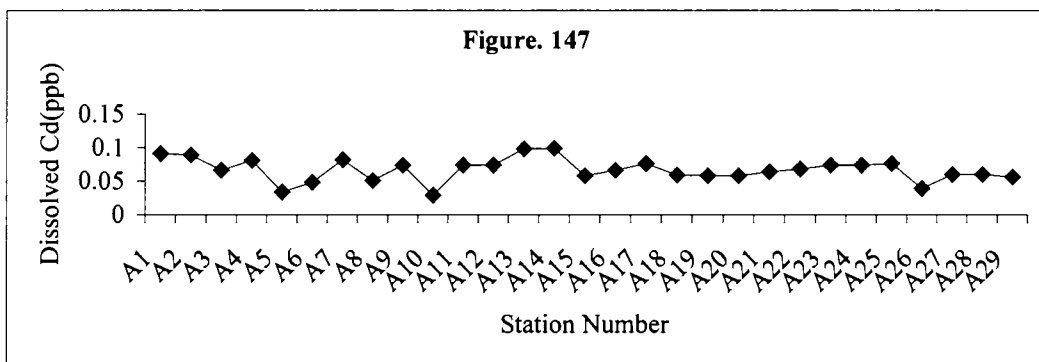
Figure. 149

**Figure.150 to 152. Spatial variation of Pb in different phases from the eastern Arabian Sea during intermonsoon fall**

Figure. 150

Figure. 151
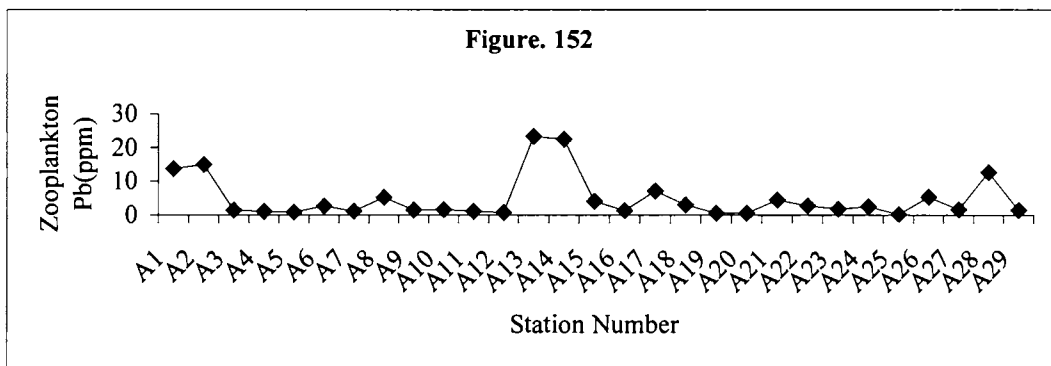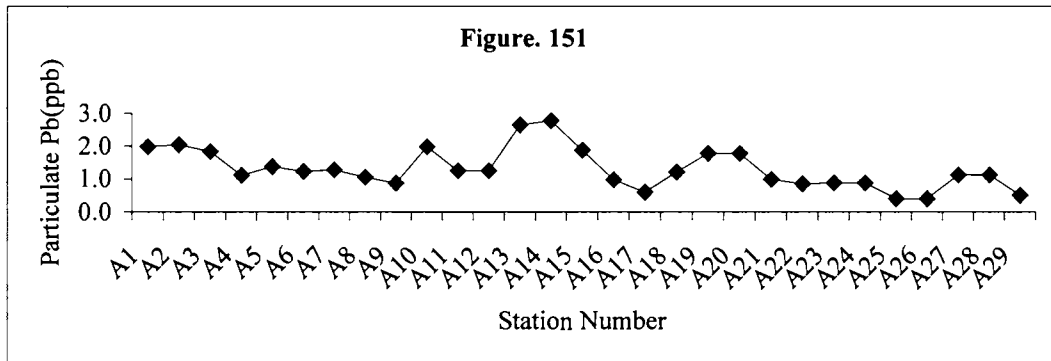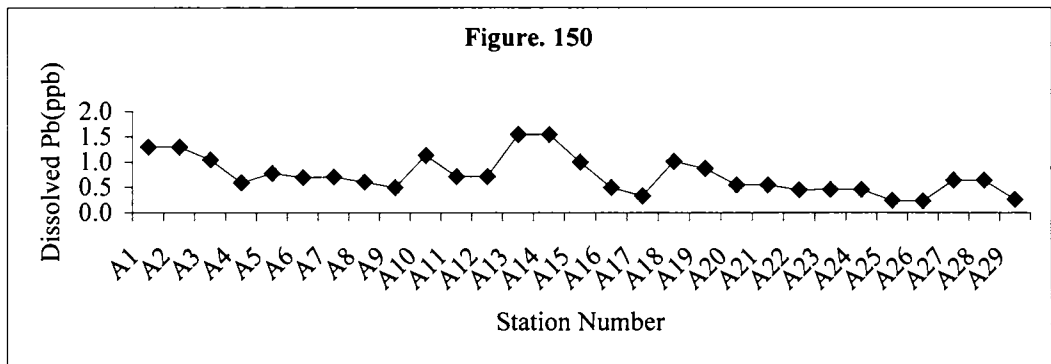
Figure. 152

Figure.153 to 156. Spatial variation of biomagnification factors for Fe, Co, Ni and Cu in zooplankton from the eastern Arabian Sea during intermonsoon fall

Figure. 153

Figure. 154

Figure. 155
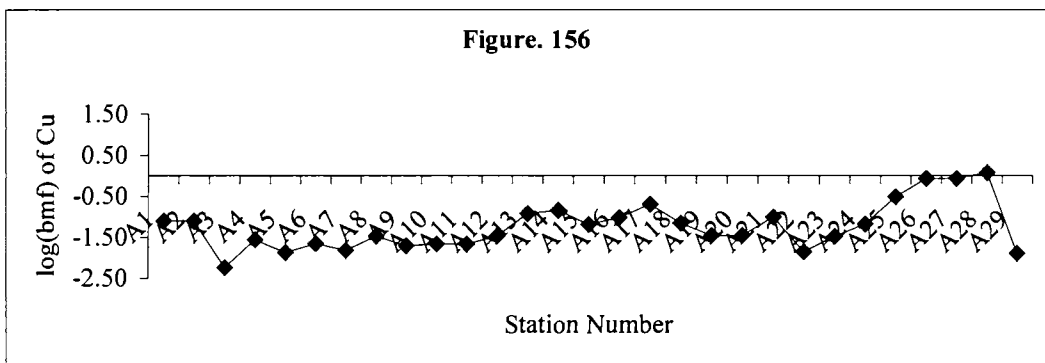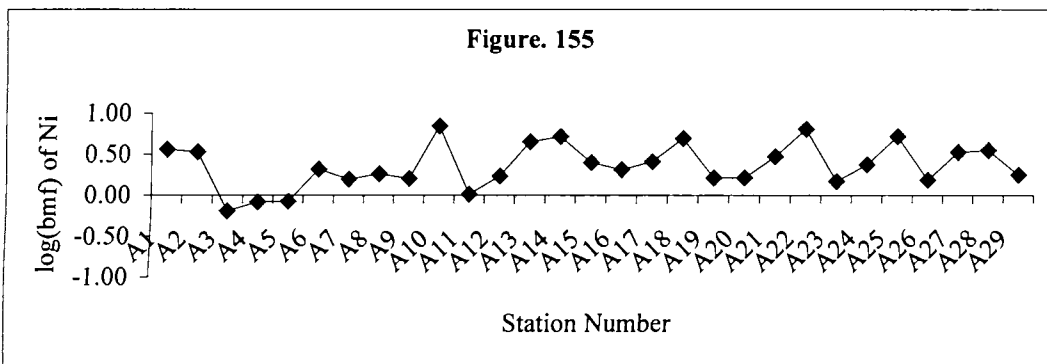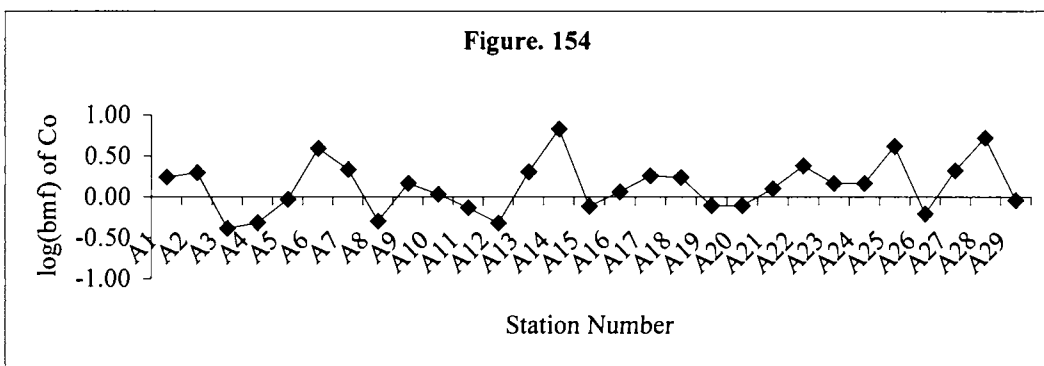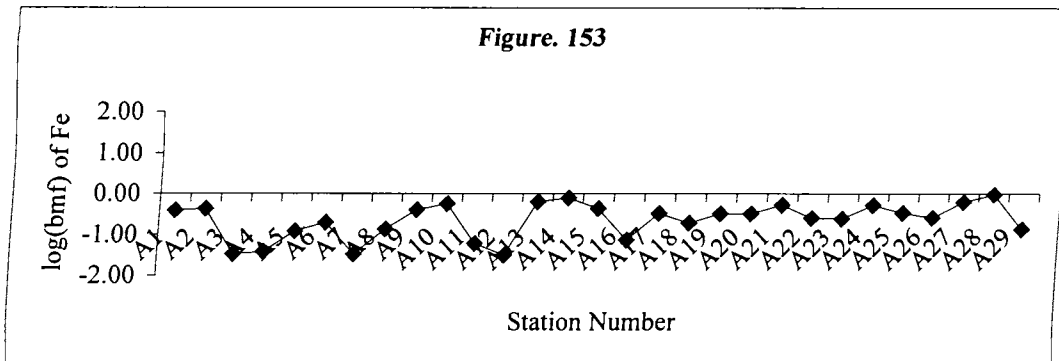
Figure. 156

Figure.157 to 159. Spatial variation of biomagnification factors for Zn, Cd and Pb in zooplankton from the eastern Arabian Sea during intermonsoon fall
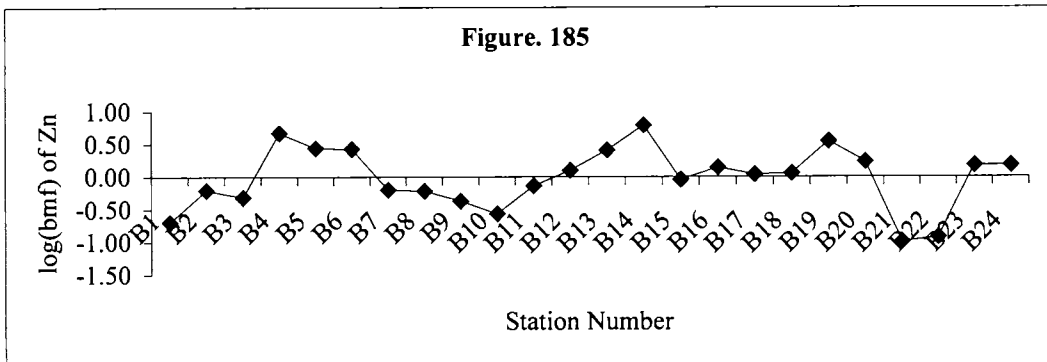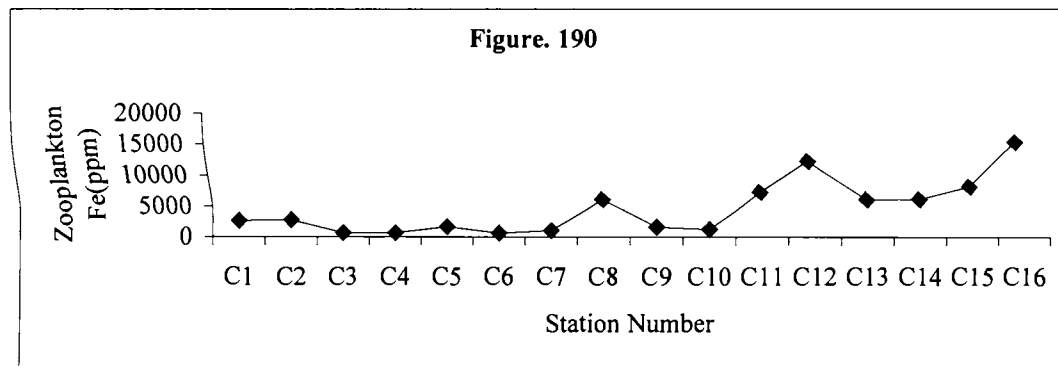

Figure. 157

Y-axis: log(bmf) of Zn

X-axis: Station Number

Figure. 158

Y-axis: log(bmf) of Cd

X-axis: Station Number

Figure. 159

Y-axis: log(bmf) of Pb

X-axis: Station Number
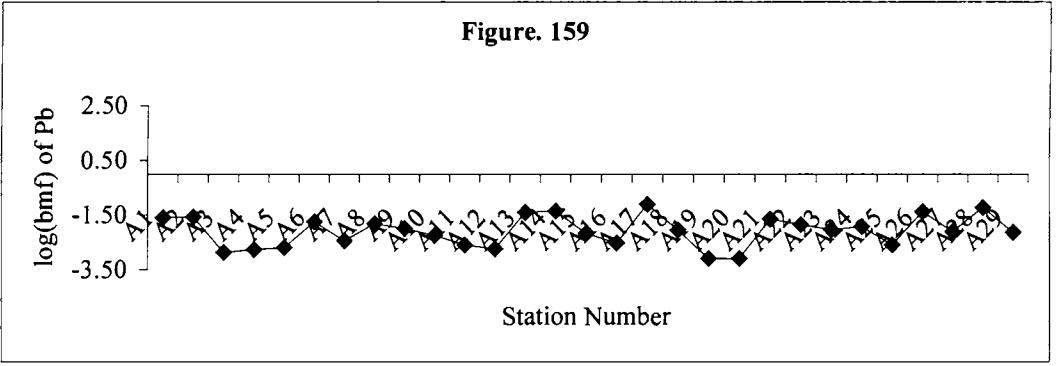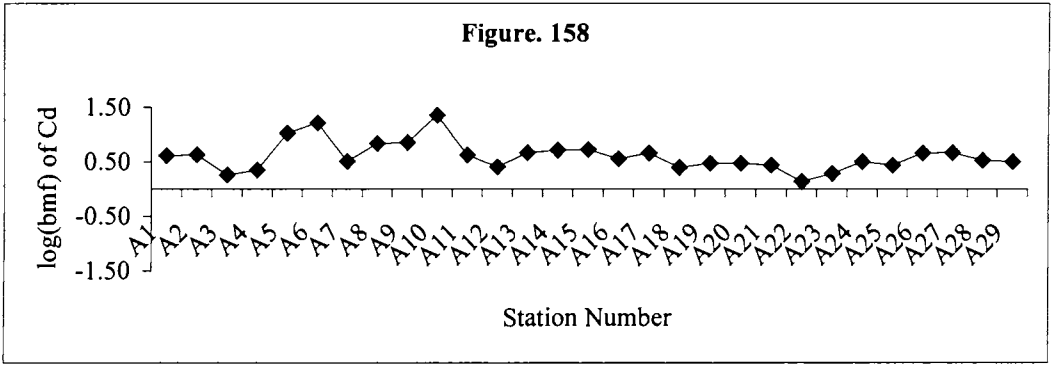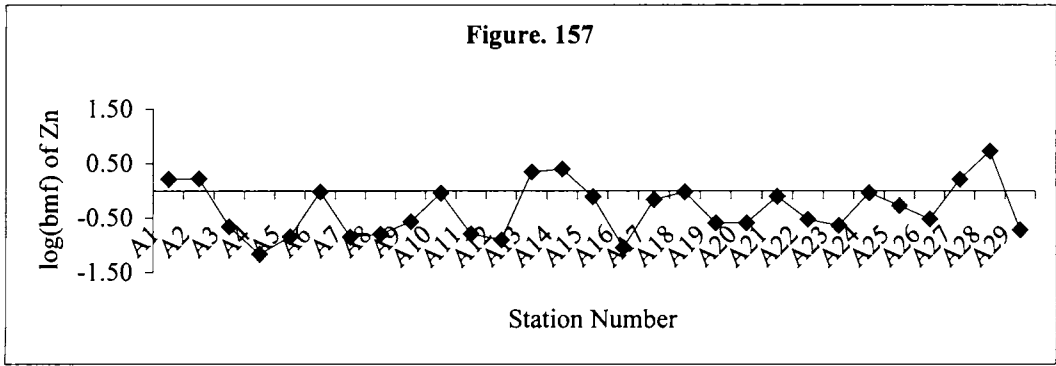
Figure.160 to 162. Spatial variation of Fe in different phases from the western Bay of Bengal during winter monsoon

Figure. 160

Dissolved Fe(ppb) vs Station Number (B1–B24)

Figure. 161

Particulate Fe(ppb) vs Station Number (B1–B24)

Figure. 162

Zooplankton Fe(ppm) vs Station Number (B1–B24)
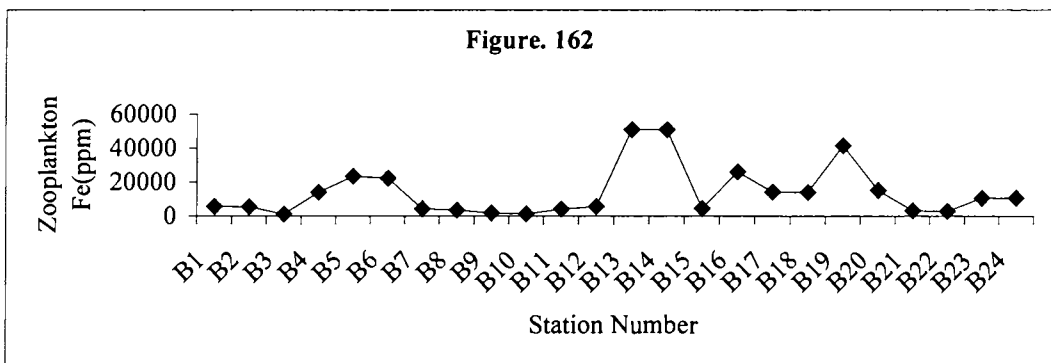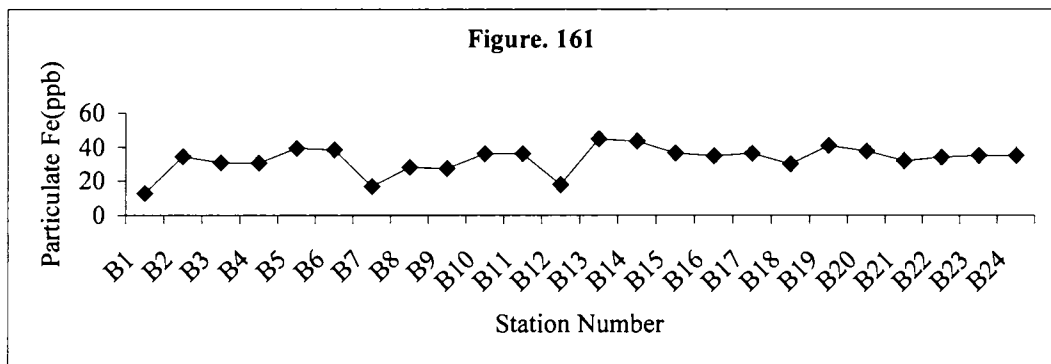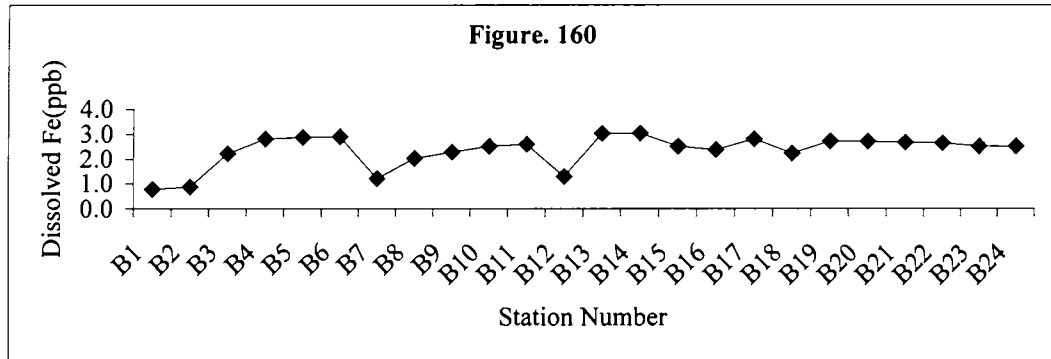
Figure.163 to 165. Spatial variation of Co in different phases from the western Bay of Bengal during winter monsoon

Figure. 163

Dissolved Co(ppb) vs Station Number (B1 to B24)

Figure. 164

Particulate Co(ppb) vs Station Number (B1 to B24)

Figure. 165
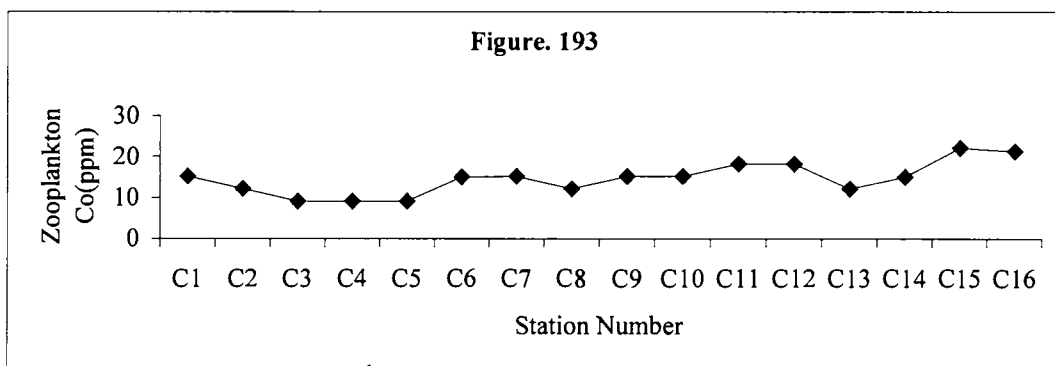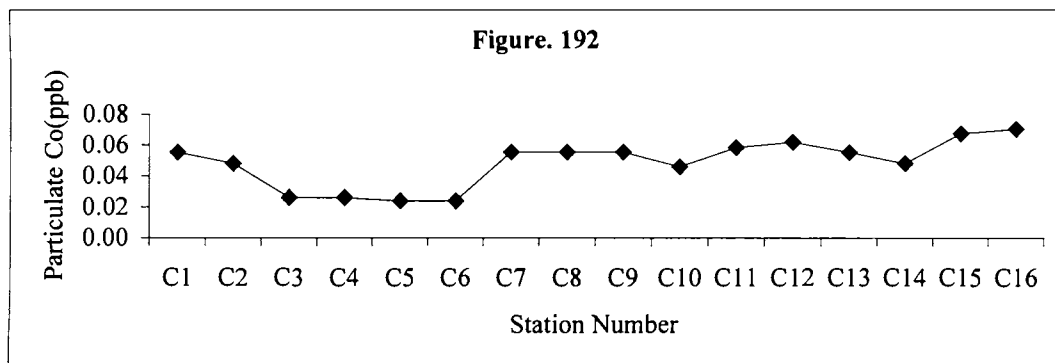
Zooplankton Co(ppm) vs Station Number (B1 to B24)
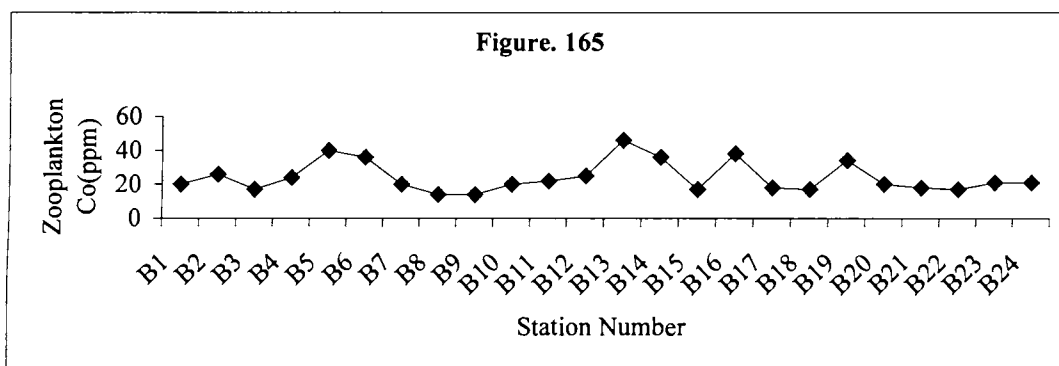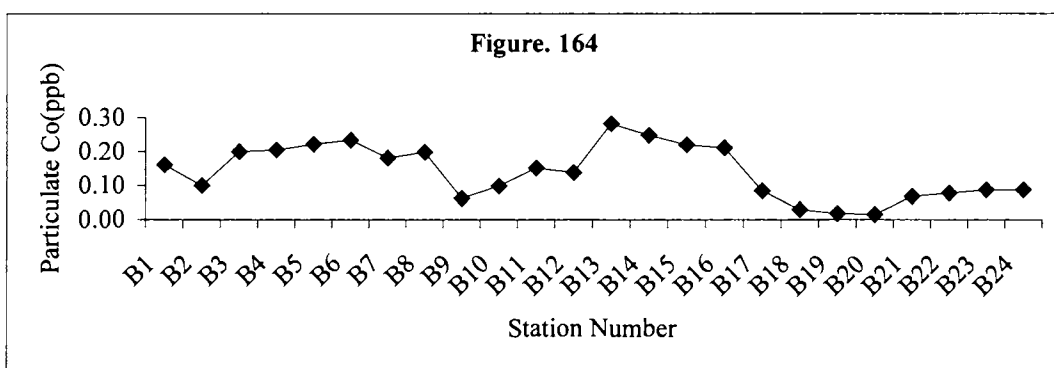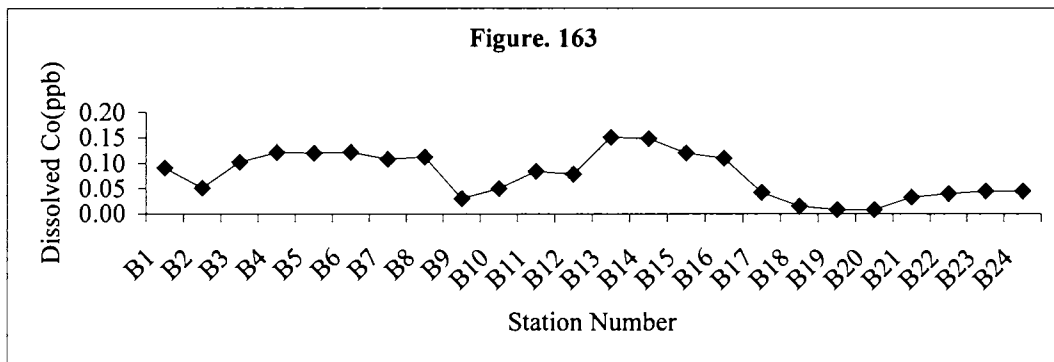
Figure.166 to 168. Spatial variation of Ni in different phases from the western Bay of Bengal during winter monsoon

Figure. 166

Figure. 167
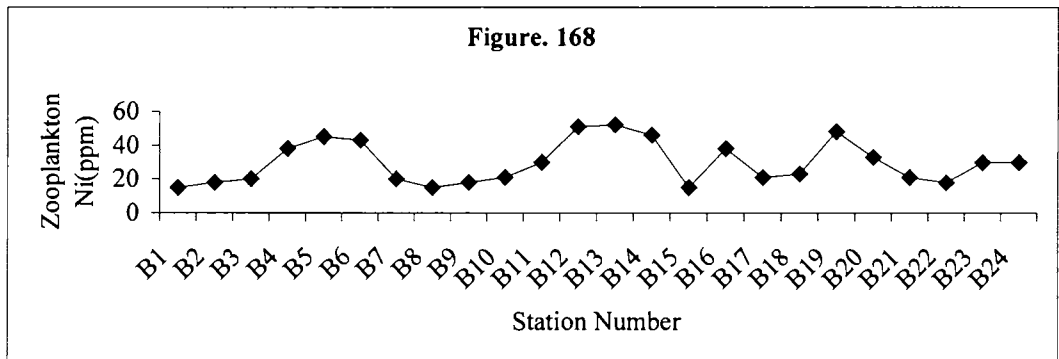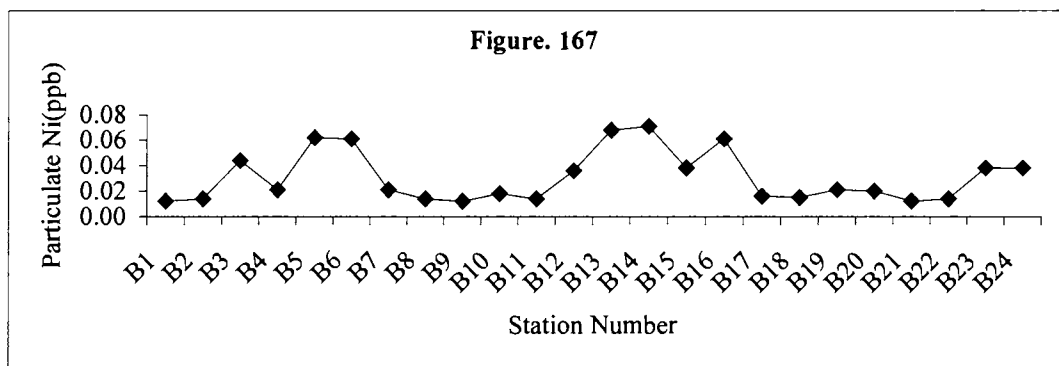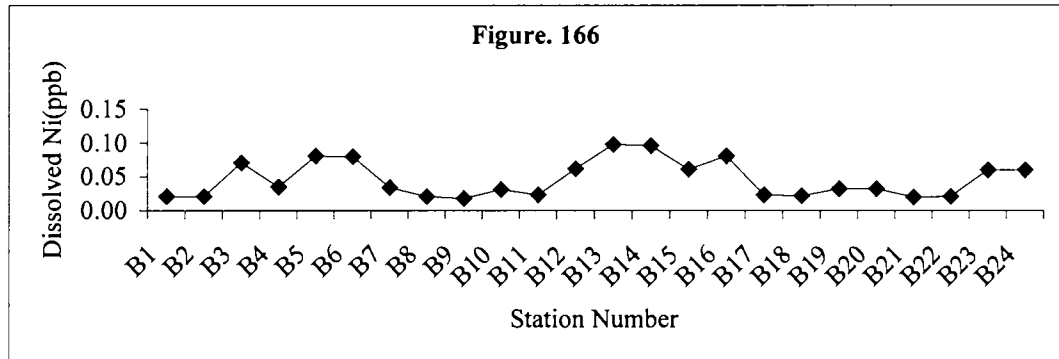
Figure. 168

Figure.169 to 171. Spatial variation of Cu in different phases from the western Bay of Bengal during winter monsoon

Figure. 169

Figure. 170
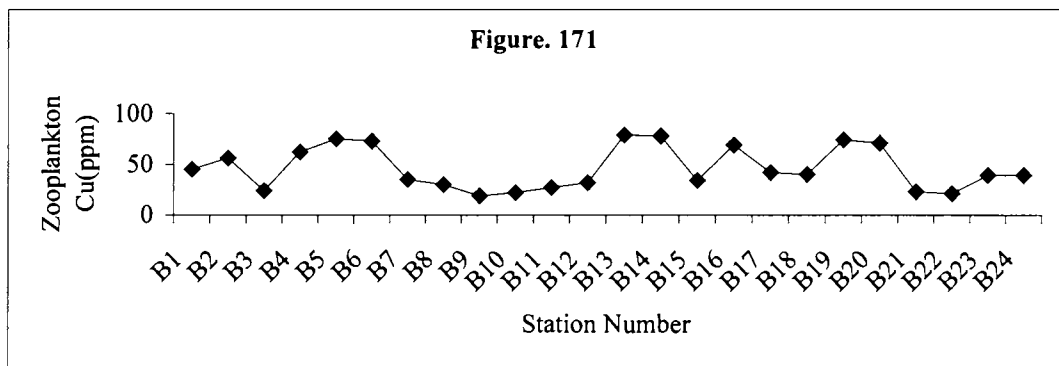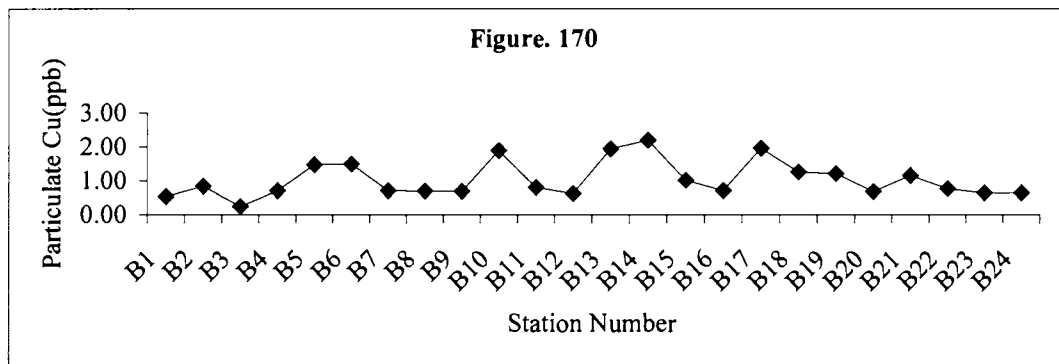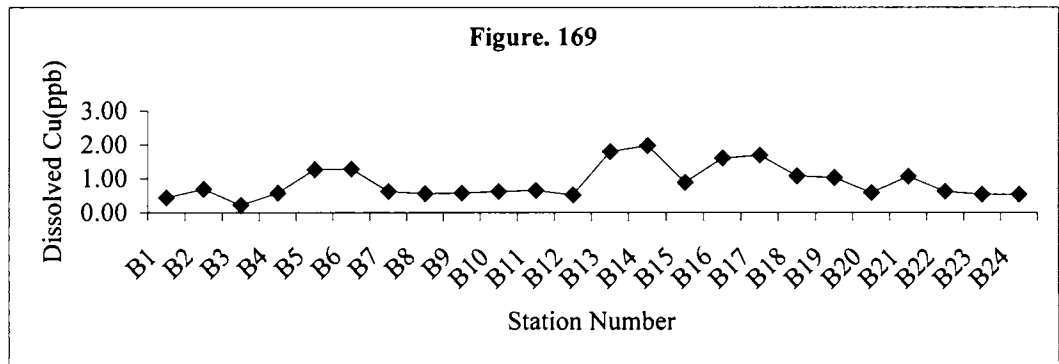
Figure. 171

Figure.172 to 174. Spatial variation of Zn in different phases from the western Bay of Bengal during winter monsoon

Figure. 172

Figure. 173
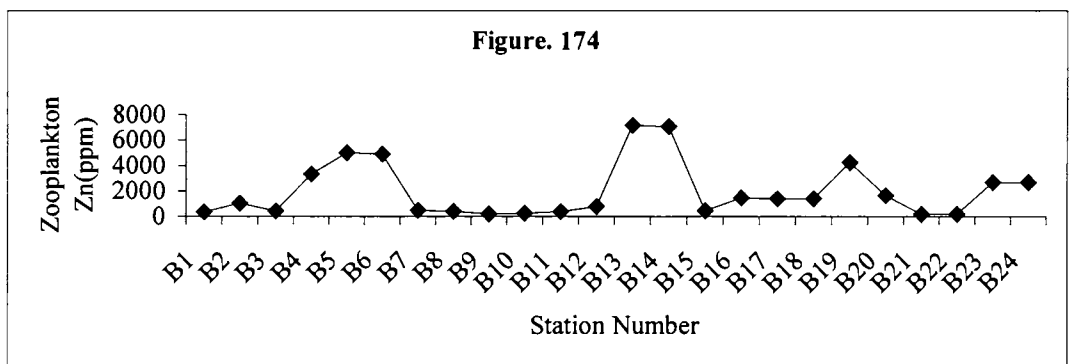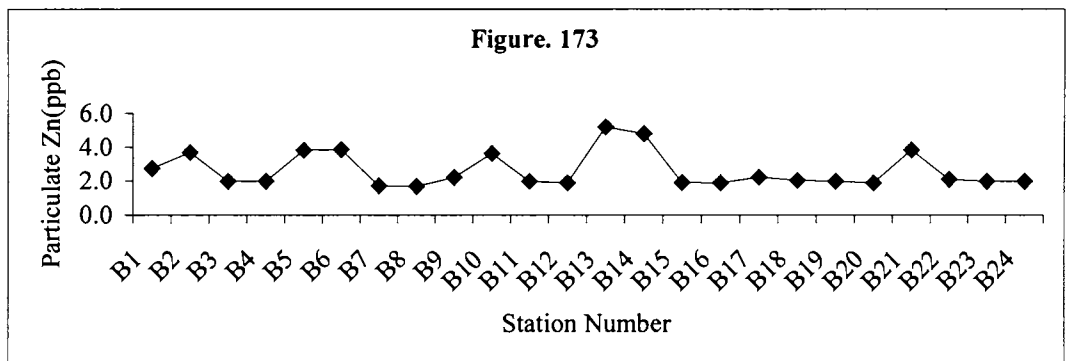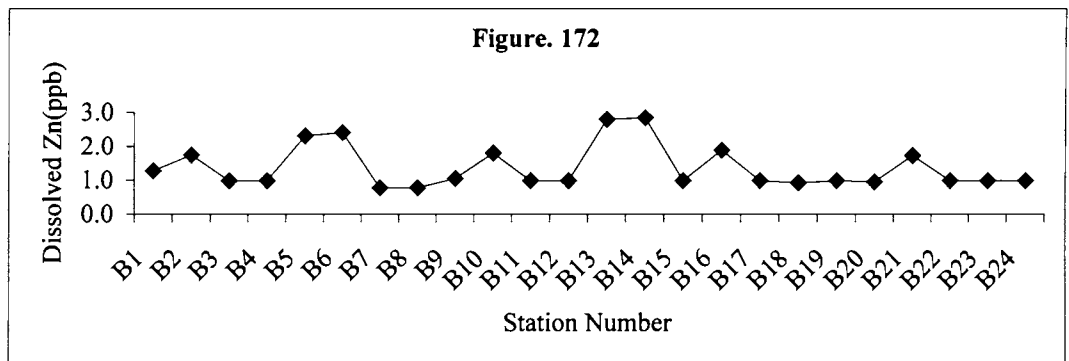
Figure. 174

Figure.175 to 177. Spatial variation of Cd in different phases from the western Bay of Bengal during winter monsoon

Figure. 175

Figure. 176
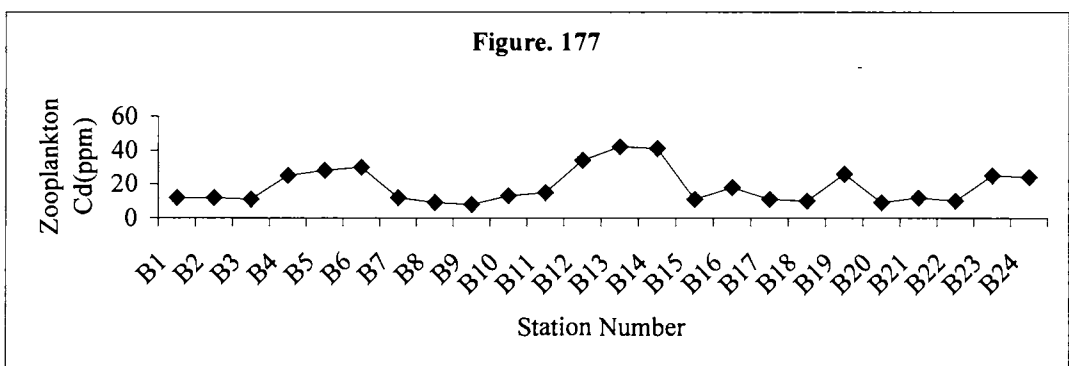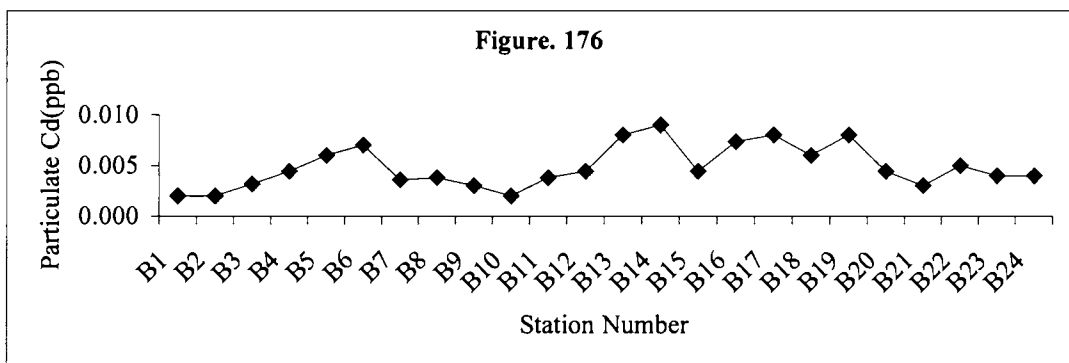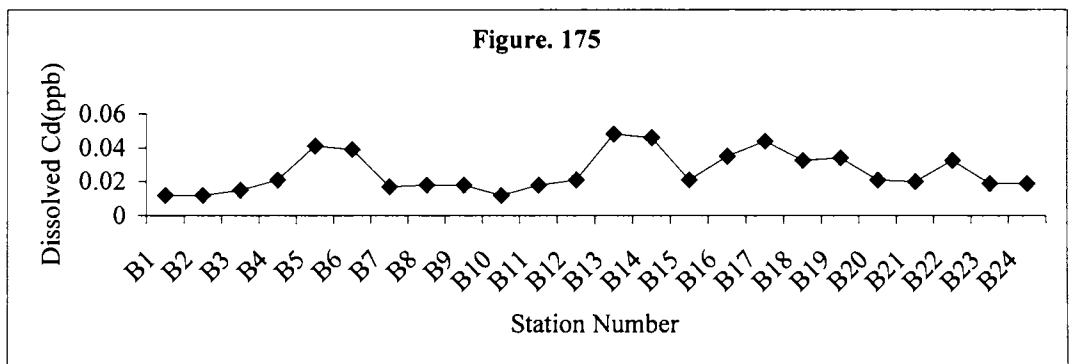
Figure. 177

Figure.178 to 180. Spatial variation of Pb in different phases from the western Bay of Bengal during winter monsoon

Figure. 178

Figure. 179
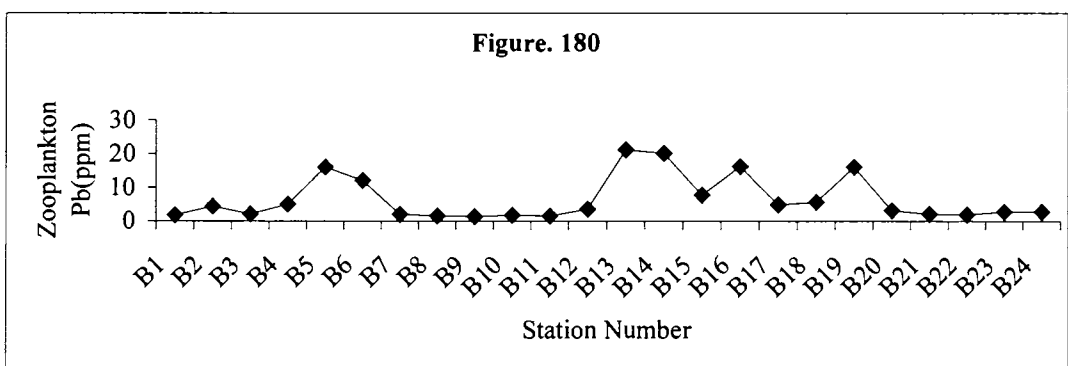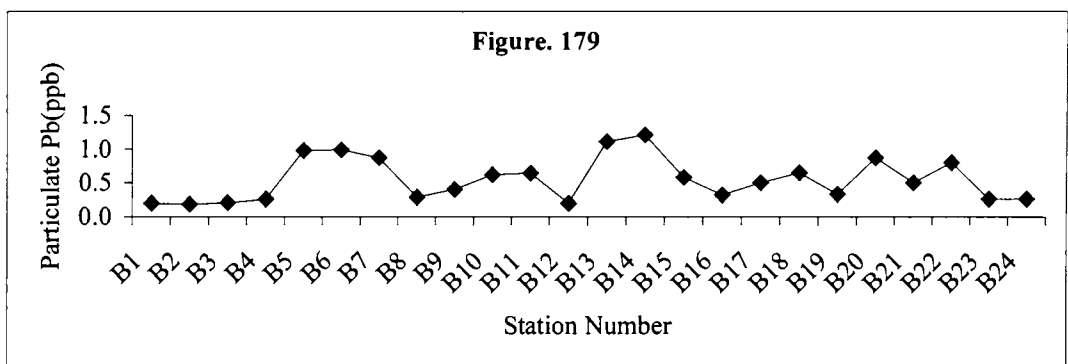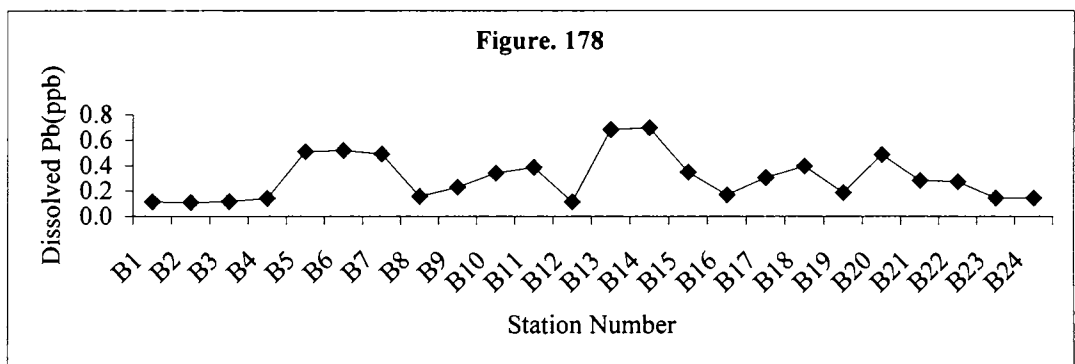
Figure. 180

Figure.181 to 184. Spatial variation of biomagnification factors for Fe, Co, Ni and Cu in zooplankton from the western Bay of Bengal during winter monsoon

Figure. 181

Figure. 182

Figure. 183
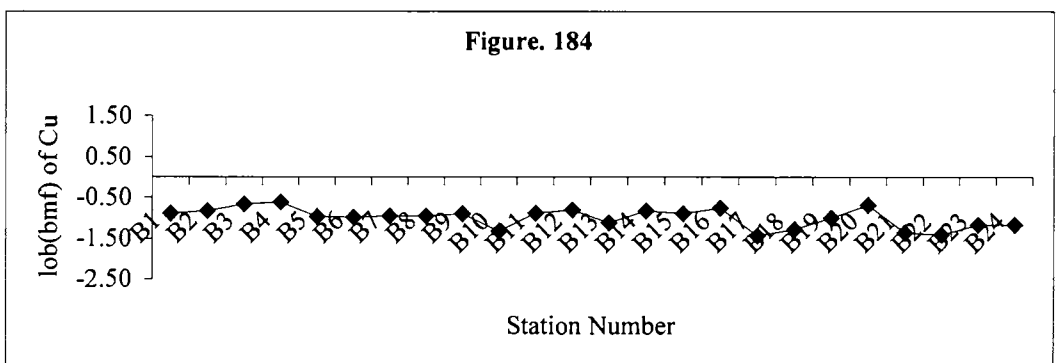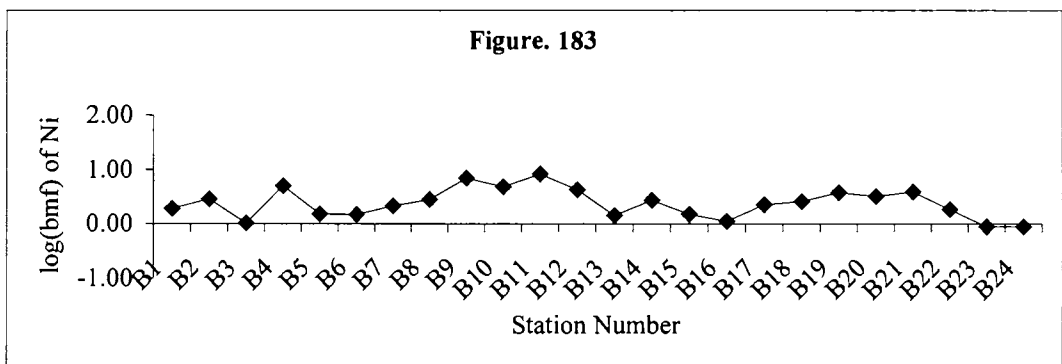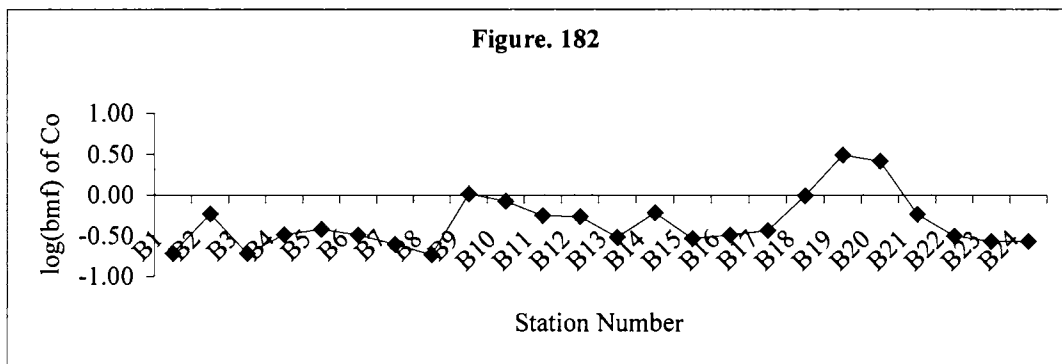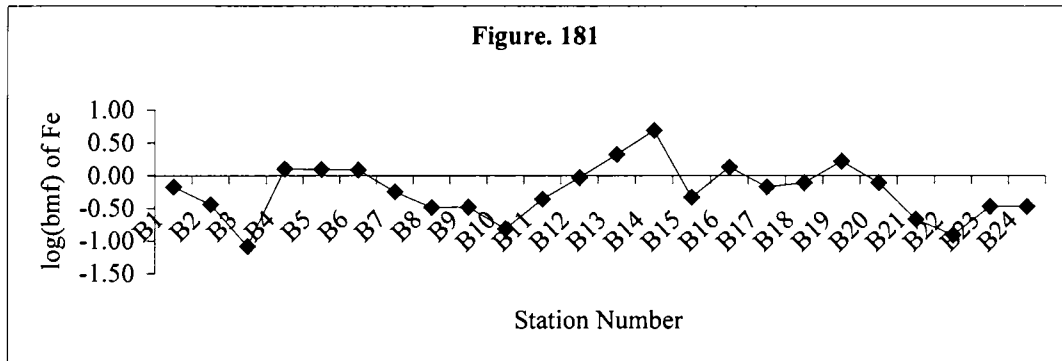
Figure. 184

Figure.185 to 187. Spatial variation of biomagnification factors for Zn, Cd and Pb in zooplankton from the western Bay of Bengal during winter monsoon

Figure. 185

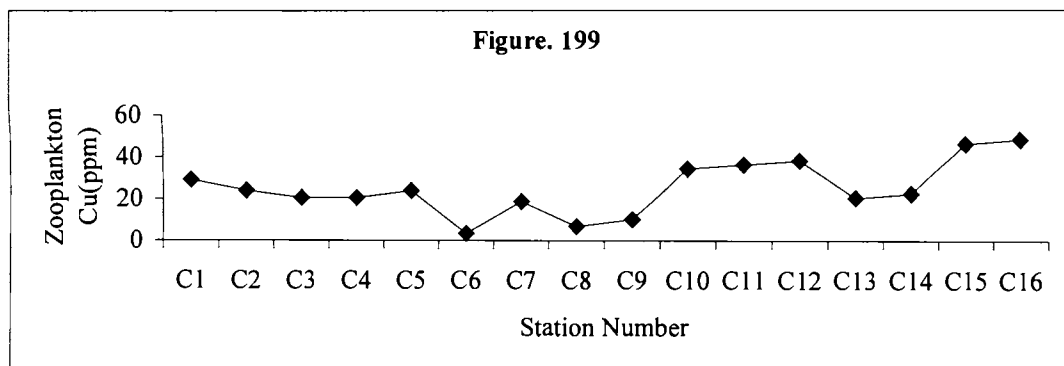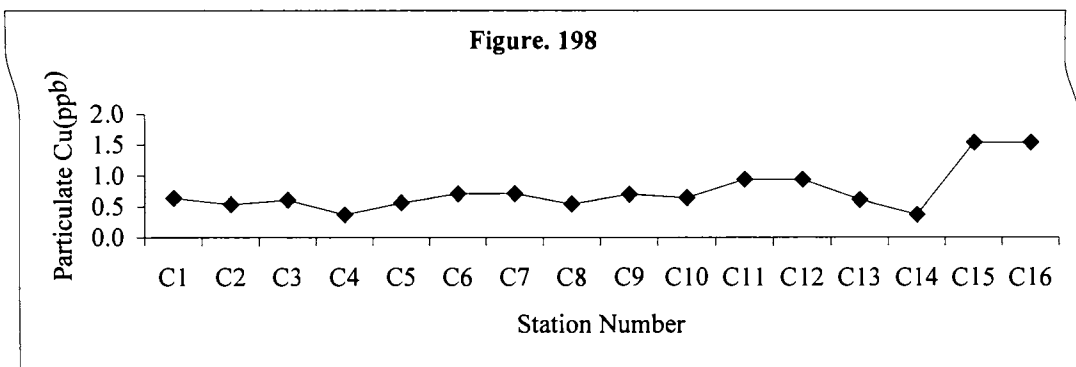

Figure. 186
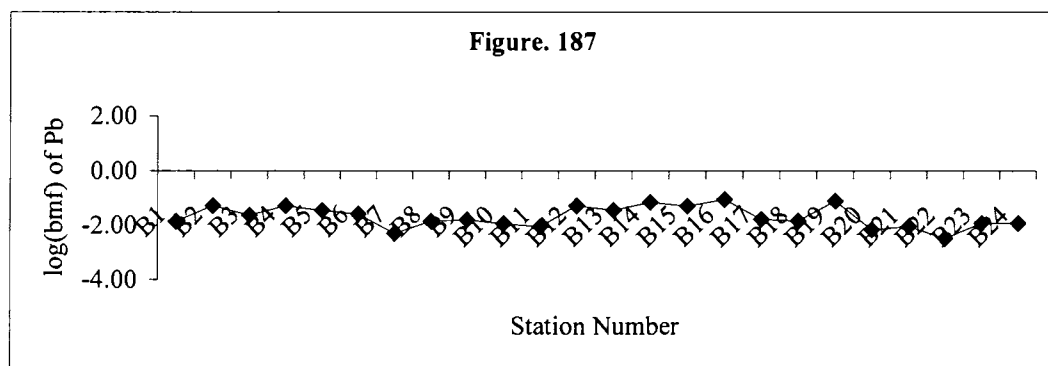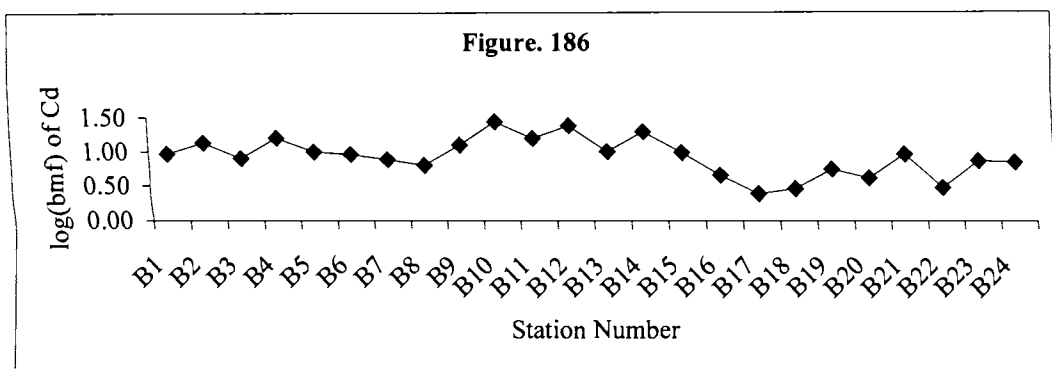
Figure. 187

Figure.188 to 190. Spatial variation of Fe in different phases from the northeastern Arabian Sea during intermonsoon spring

Figure. 188

Dissolved Fe(ppb) vs Station Number (C1–C16)

Figure. 189

Particulate Fe(ppb) vs Station Number (C1–C16)

Figure. 190

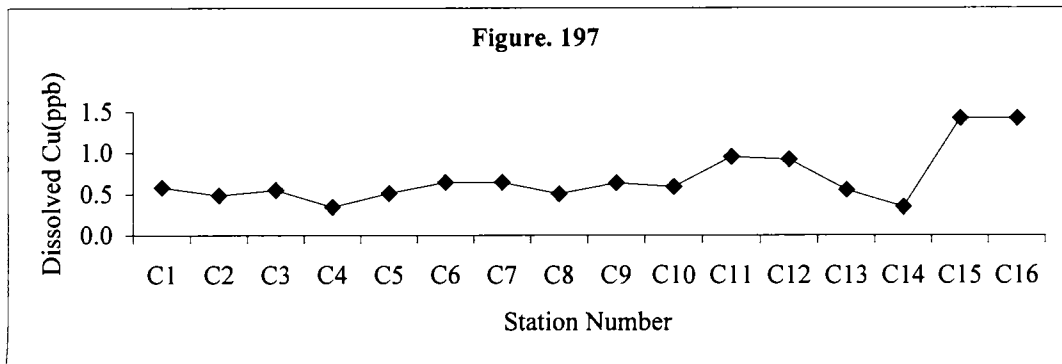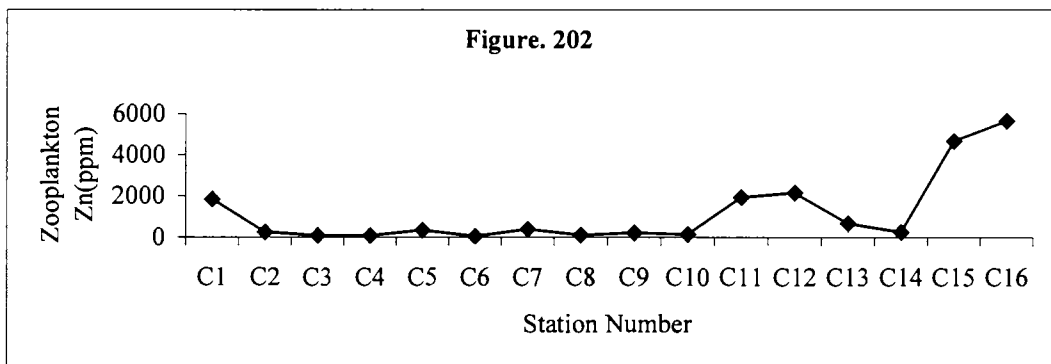Zooplankton Fe(ppm) vs Station Number (C1–C16)
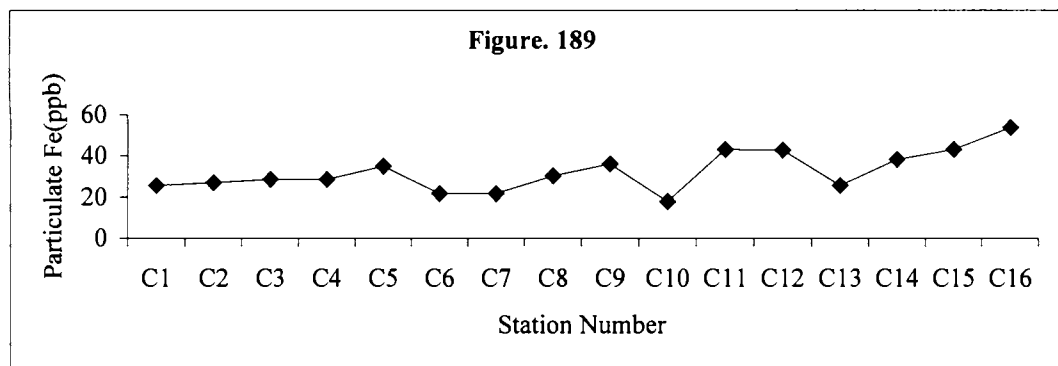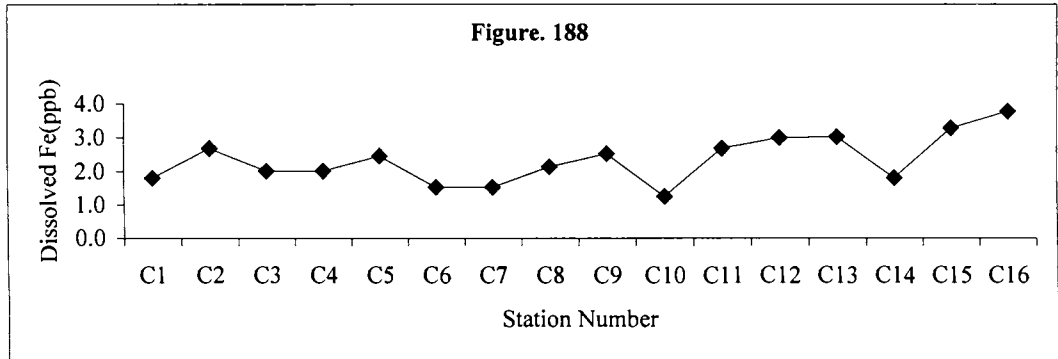
Figure.191 to 193. Spatial variation of Co in different phases from the northeastern Arabian Sea during intermonsoon spring

Figure. 191

Dissolved Co(ppb) vs Station Number (C1–C16)

Figure. 192

Particulate Co(ppb) vs Station Number (C1–C16)

Figure. 193

Zooplankton Co(ppm) vs Station Number (C1–C16)
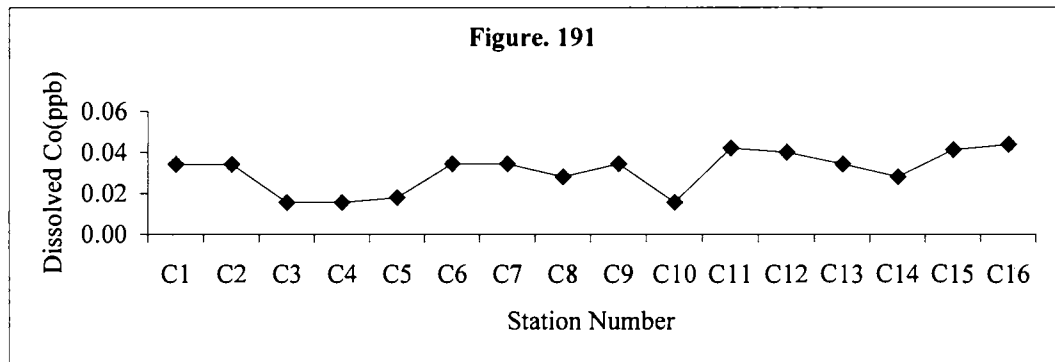
Figure.194 to 196. Spatial variation of Ni in different phases from the northeastern Arabian Sea during intermonsoon spring

Figure. 194

Figure. 195
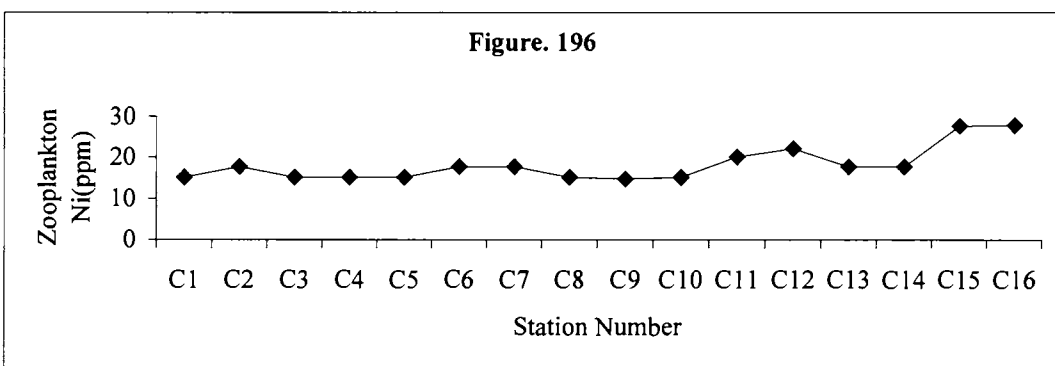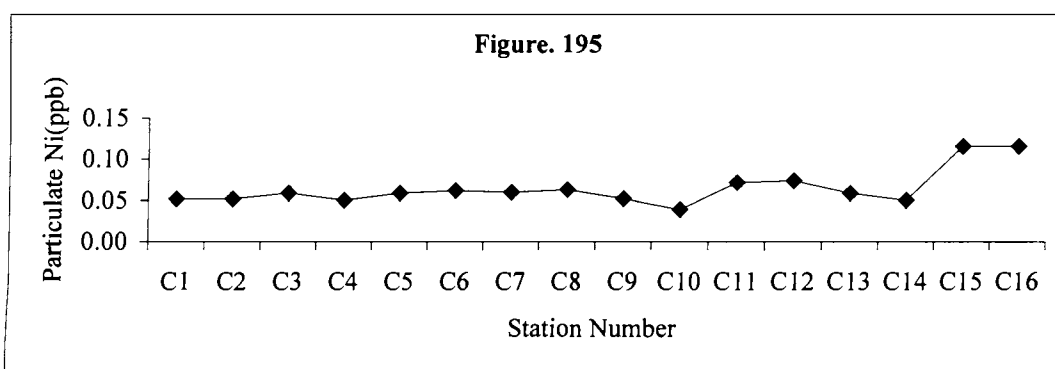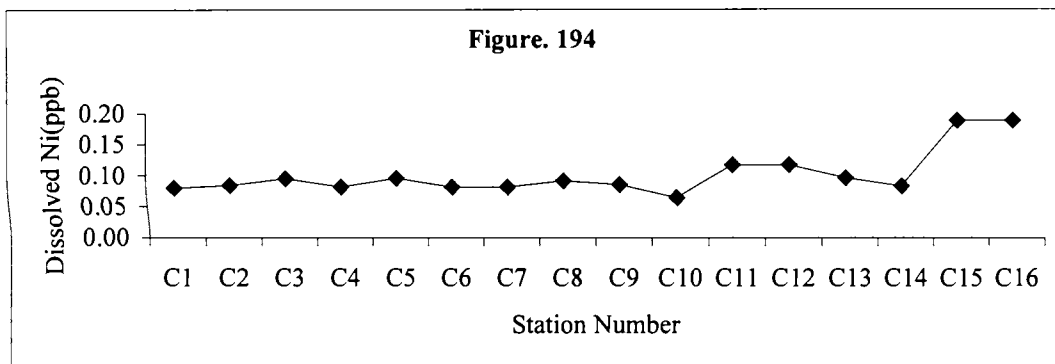
Figure. 196

Figure.197 to 199. Spatial variation of Cu in different phases from the northeastern Arabian Sea during intermonsoon spring
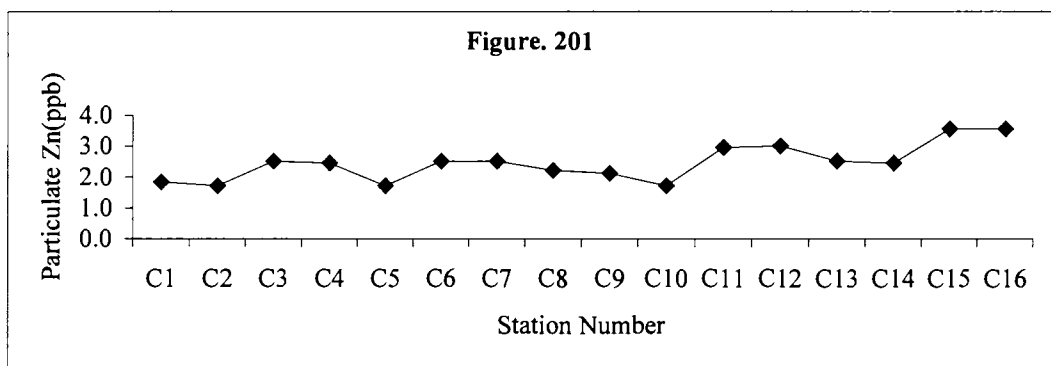

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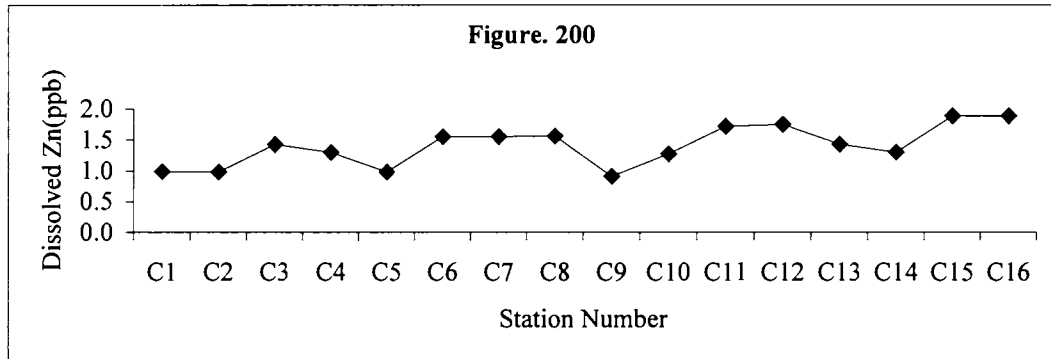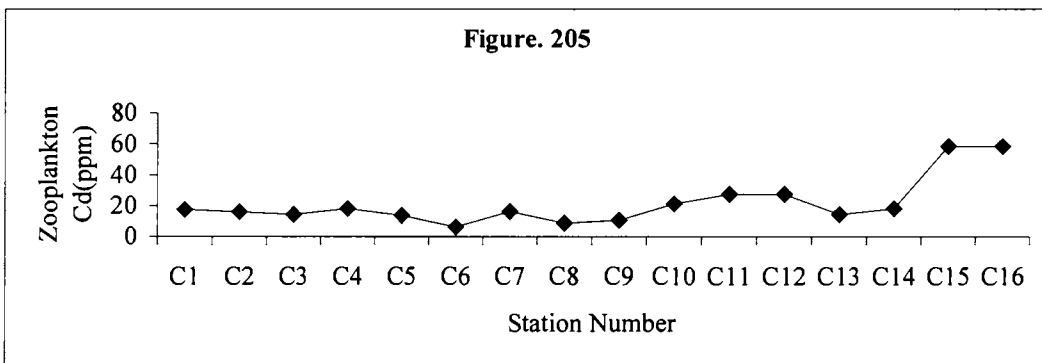

Figure. 198

Figure. 199

Figure.200 to 202. Spatial variation of Zn in different phases from the northeastern Arabian Sea during intermonsoon spring

Figure. 200

Y-axis: Dissolved Zn(ppb); X-axis: Station Number (C1–C16)

Figure. 201

Y-axis: Particulate Zn(ppb); X-axis: Station Number (C1–C16)

Figure. 202

Y-axis: Zooplankton Zn(ppm); X-axis: Station Number (C1–C16)

Figure.203 to 205. Spatial variation of Cd in different phases from the northeastern Arabian Sea during intermonsoon spring

Figure. 203
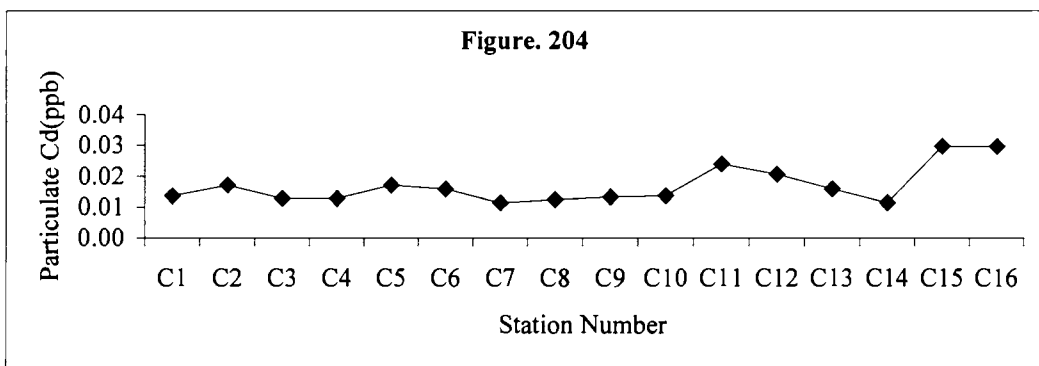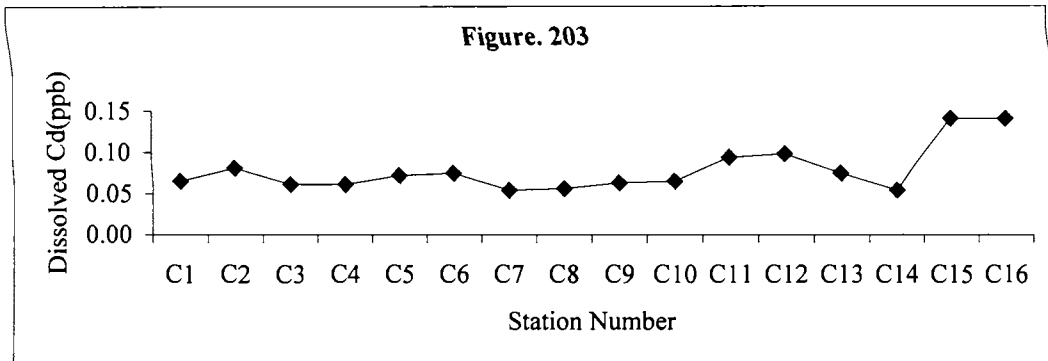

Figure. 204

Figure. 205

Figure.206 to 208. Spatial variation of Pb in different phases from the northeastern Arabian Sea during intermonsoon spring

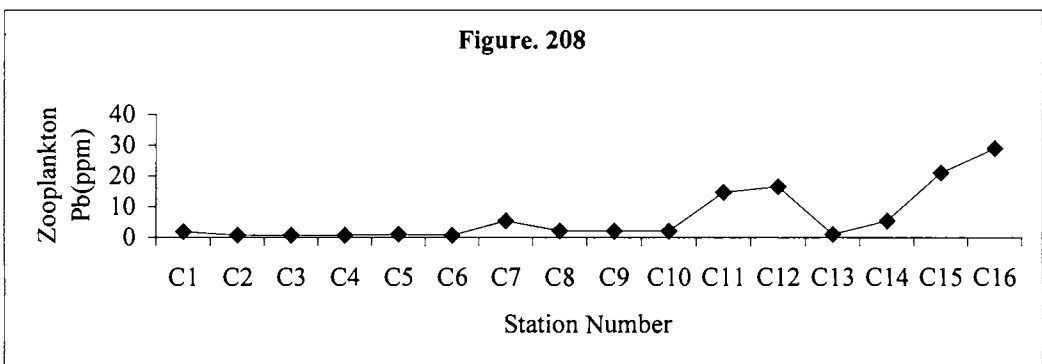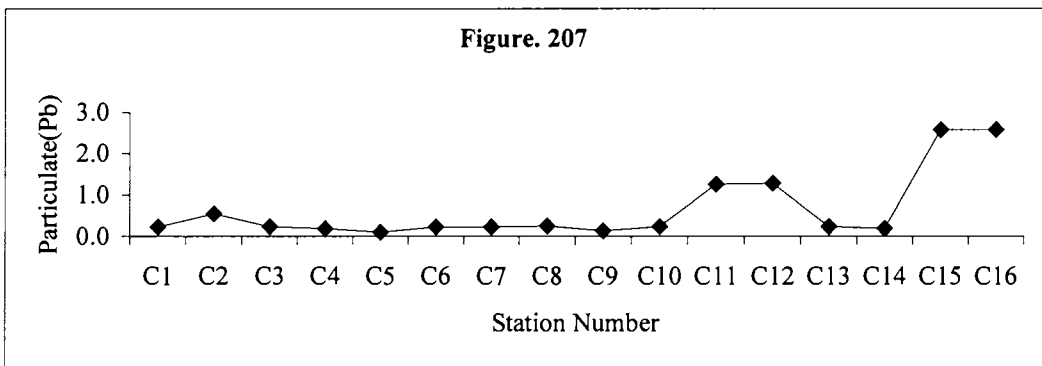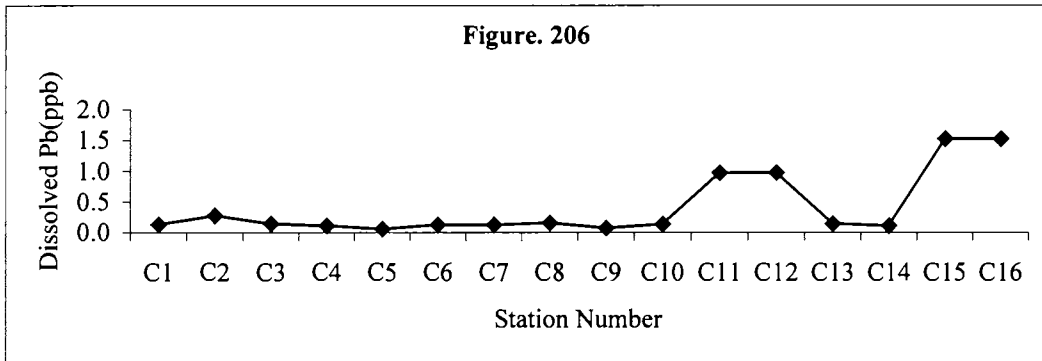Figure. 206

Figure. 207

Figure. 208

Figure.209 to 212. Spatial variation of biomagnification factors for Fe, Co, Ni and Cu in zooplankton from the northeastern Arabian Sea during intermonsoon spring

Figure. 209

Figure. 210

Figure. 211

Figure. 212

Figure.213 to 215. Spatial variation of biomagnification factors for Zn, Cd and Pb in zooplankton from the northeastern Arabian Sea during intermonsoon spring

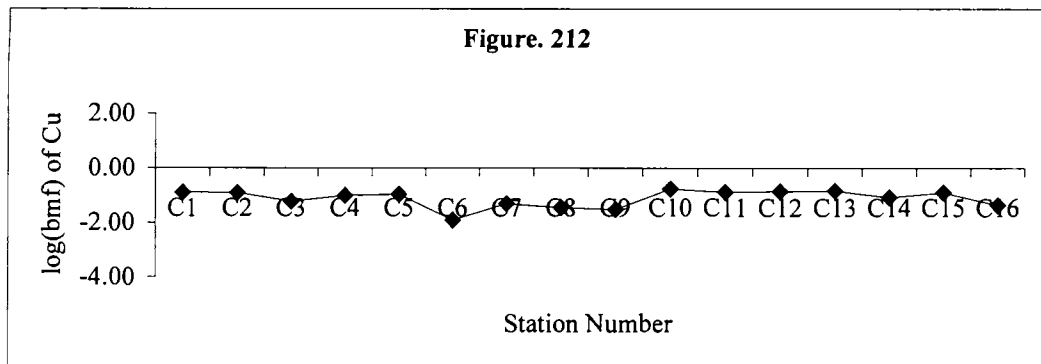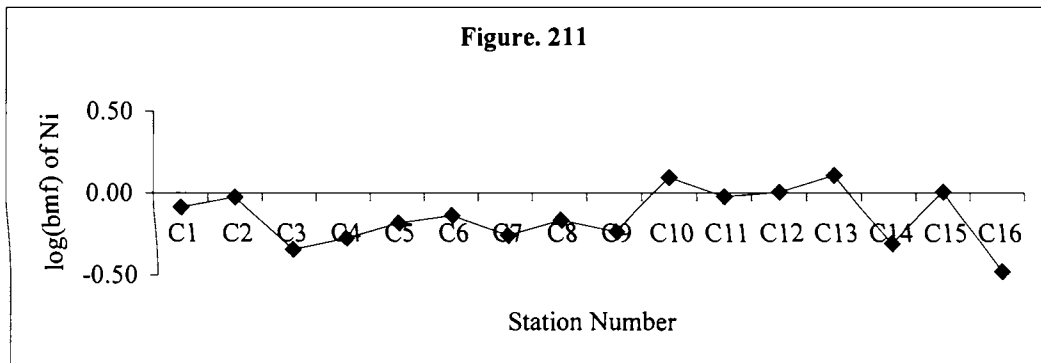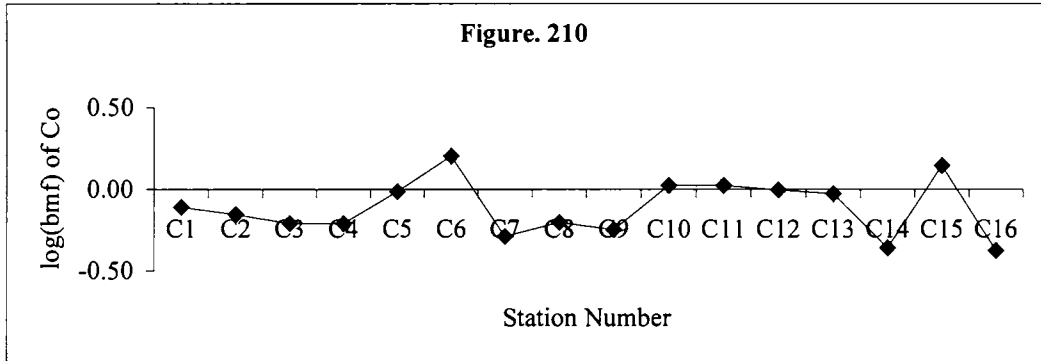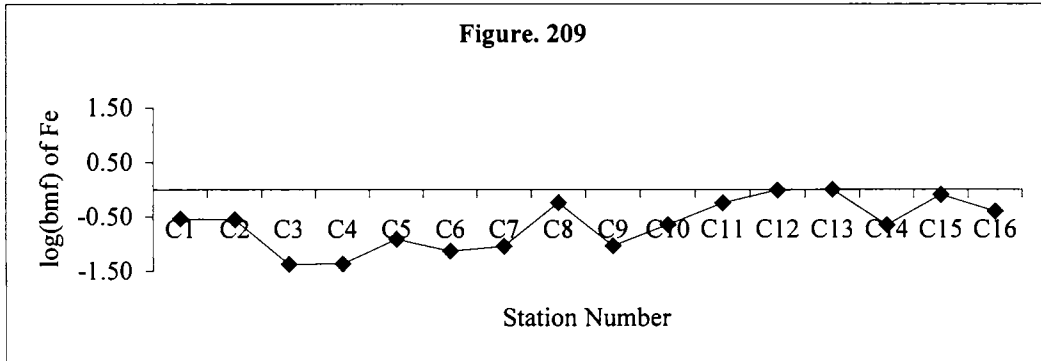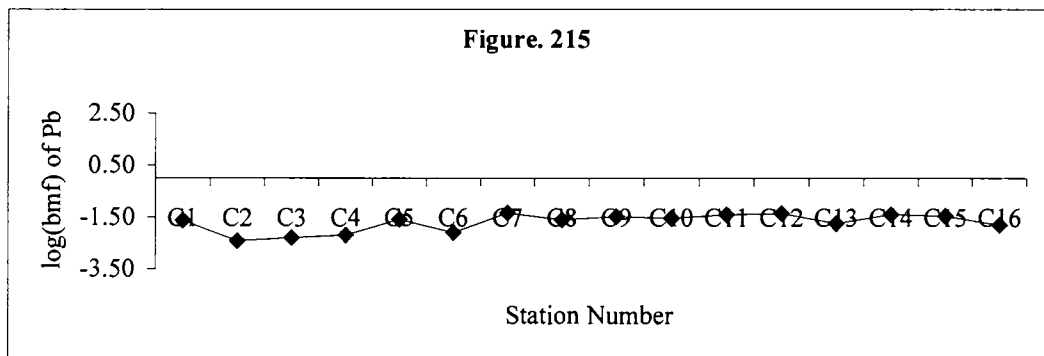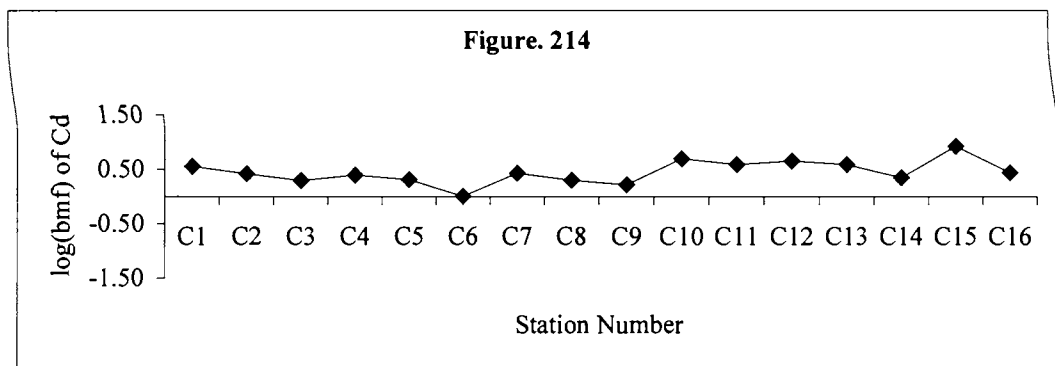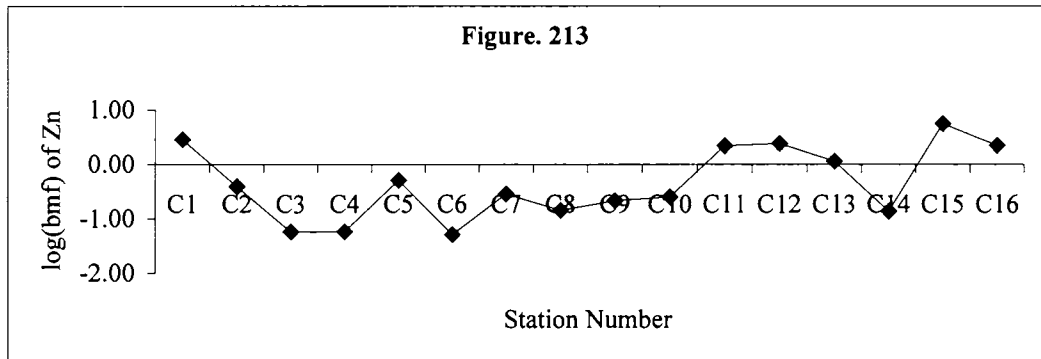
Figure. 213

Figure. 214

Figure. 215

Chapter 6

Summary and conclusion

The thesis is an outcome of the environmental study with special emphasis to hydrography, nutrients, biological characteristics and trace metals in the water column as well as zooplankton covering the EEZ of the eastern Arabian Sea during intermonsoon fall, northern Arabian Sea during spring intermonsoon and western Bay of Bengal during winter monsoon. The data used for this study was collected during 2002-2004 from the oceanographic cruises of FORV Sagar Sampada from the Arabian Sea and Bay of Bengal. The physical oceanographic data was collected using a Conductivity-Temperature-Depth (CTD) profiler (at 1m-depth interval) and the chemical oceanographic parameters (nutrients, dissolved oxygen and trace metals) were estimated from standard depths.

The analytical methods used in this study are given in Chapter 2 adopting the latest techniques for the generation of precise and accurate data. Sampling was done from various pre-determined stations in the EEZ, from standard depths upto 1000m or more wherever depth permitted. Sampling was performed at 1-degree longitudinal grid and 2-degree latitudinal grid and the sampling depths chosen (0, 10, 20, 30, 50, 75, 100, 150, 200, 300, 500, 750 and 1000m or more) were representative of the entire water column. A closer sampling in the first 200m was done since this was the layer where seasonal changes were predominant. Physical oceanographic parameters like temperature and salinity were obtained from the CTD. The concentrations of the essential micronutrients like nitrate, nitrite, silicate, phosphate, dissolved oxygen and trace metals were measured using standard analytical techniques. The analysis was carried out using Segmented Flow Auto Analyzer (SKALAR) fitted on board FORV Sagar Sampada. The titrimetric Winkler method was used for the measurement of dissolved oxygen. Dissolved trace metals were analysed using Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS, ZL-4110) whereas trace metals in particulate matter & zooplankton were analysed using Flame Atomic Absorption Spectrophotometer (FAAS, *PE AAanalyst 100*).

The hydrographic features are discussed in Chapter 3 on the West coast of India during intermonsoon fall which showed that the south-east Arabian Sea (10°N – 15°N) continued to exhibit upwelling with colder (< 28°C), nutrient rich (NO3⁻ > 2.0μM; $PO4^{3-}$>0.8μM; $SiO4^{4-}$>4.0μM) and relatively low oxygenated waters (~180μM) in the shelf regions, whereas along the northern transects (north of 17°N) the surface waters were characterized by thermally stable oligotropic waters. The high chlorophyll concentration and primary productivity in the southwest coast was associated with nitrate injected to the upper layers due to upwelling.

Similarly the hydrographic features of northern Arabian Sea during intermonsoon spring, showed that northwestern part of the Indian ocean were still under the grip of winter cooling. The open ocean waters of the northern transects (19°N, 21°N and 22°N) registered comparatively low temperatures (< 28°C). During intermonsoon spring, the rich nutrients (NO3⁻ > 1.0μM; $PO4^{3-}$>0.8μM; $SiO4^{4-}$>2.0μM) in the upper 50m of the northern Arabian Sea, north of 17°N were found to be due to the receding winter cooling processes in the area. Nitrate concentration increased from 1.0μM at 19°N to 2.0μM at 21°N and its intensity increased towards offshore. The high chlorophyll concentration and primary productivity in the northern Arabian Sea was associated with the availability of nitrate in the upper layers due to the existence of receding winter cooling.

In the Bay of Bengal, during winter monsoon, a significant feature observed from the thermal structure along the open ocean and outer shelf regions was the presence of thermocline oscillations and cold core eddy signatures. A similar feature was also observed in the open ocean regions of the southeastern Arabian Sea during intermonsoon fall. Under the influence of these eddies, the nutrients were pumped into subsurface layers of the both basins as evidenced by the shoaling of nitracline consistent with isotherms. Thus, consistent with the southward shoaling of isotherms and isohalines, nitracline also shoaled and there by induced by favorable winds lead to surfacing of nutrients in the Arabian Sea. However in the Bay of Bengal the upper low-salinity layer formed due to fresh water runoff caused distinct stratification resulting in thermal inversion and shallow mixed layer. Consistent with thermal

inversion and low saline surface waters brought by river-runoff, the nutrient characteristic of the area was remarkable. The inner shelf area was found to have (north of 17°N), low salinity (24.5 to 30.5 psu), with saturated dissolved oxygen (200-220μM) and low nutrients (NO_3^- ~ 0.2μM, PO_4^{3-} ~ 0.2μM). The low salinity layer in the inner shelf of the Bay of Bengal coincided with 2.6μM silicate-indicated influence of fresh water in the northern transects. However the strong stratification restricted nitrate and phosphate rich waters rising from depths. Thus, eddies were capped by fresh water which prevented nutrients reaching the upper layers or restricted the chances of sinking of surface water by densification. To sum up, neither the river plume, nor the eddies brought appreciable nutrients to the surface in the Bay of Bengal. This was confirmed by the undetectable level of nitrate in the surface layers of the Bay of Bengal that eventually resulted in the low biological production.

The fourth chapter deals with the dissolved and particulate trace metals in the eastern Arabian Sea and western Bay of Bengal. Based on the concentration profiles, geochemical behavior of the metals in the water column has been discussed. Dissolved and particulate forms of Ni, Cd and Zn in both basins showed nutrient - type profiles exhibiting very low surface values due to their removal from surface waters by biogenic particles and relative enrichment at intermediate/bottom layer as a result of remineralisation indicative of biogeochemical cycling. However, dissolved and particulate Fe, Co and Cu in both basins exhibited surface enrichment, mid-depth minima and slight increase at the bottom. This can be explained in terms of adsorption of dissolved Fe, Co and Cu onto suspended particles, scavenging in the water column at the intermediate layers followed by its regeneration at higher depths and, that their behavior is intermediate between nutrient-type elements (Ni, Cd & Zn) and Pb. But dissolved and particulate Pb in both basins showed a surface enrichment of a higher magnitude in the Arabian Sea compared to the Bay of Bengal due to higher anthropogenic particles derived from atmospheric fluxes in the West coast than the East coast of India. The subsurface minima of dissolved Pb in both basins are possibly due to biological uptake or scavenging and followed by a near constancy at

intermediate and bottom layers, which may be due to adsorption onto settling particles.

Based on the interrelationships between Ni, Zn, Cd, Cu and nutrients, the metal-nutrient atomic slopes of Ni/P, Ni/Si, Zn/Si, Cu/Si were computed from their regression equations. The Ni/P and Ni/Si slopes obtained for the offshore waters of the Bay of Bengal was relatively higher than the value obtained for the offshore waters of the Arabian Sea and was comparable with the values for the Pacific and Atlantic oceans. The Zn/Si slopes tend to decrease from coastal to offshore in the Bay of Bengal and vice versa in the Arabian Sea. The Cu/Si slopes also tend to decrease from coastal to offshore regions in both basins. Similarly Cd/P and Cd/N slopes obtained for the offshore waters of the Bay of Bengal was relatively higher than that of the offshore waters of the Arabian Sea. The Cd/P slopes obtained for the offshore waters of the Arabian Sea was slightly higher than the Pacific and Atlantic oceans. However the Cd/N slopes obtained for the offshore waters of the Arabian Sea was almost same with the reported value for the Pacific ocean. Even though the metal-nutrient relationships imply significant downward transport of metals in association with the carrier phases that undergo dissolution, the substantial difference in the metal-nutrient slopes for the coastal and offshore waters of both basins was due to a significant difference in their biogeochemical behaviors. These differences may be owing to the variation in the biological utilization and regeneration of metals between the Arabian Sea and Bay of Bengal. The slightly higher metal-nutrient slopes obtained in the present study can be attributed to higher intercepts (concentrations) than those for Pacific and Atlantic oceans.

Partition coefficient values for metals showed that in both basins they were more or less related to the metal affinity for suspended particulate matter with Fe (92-95%), Co (63-67%), Zn (62-69%), Pb (60-65%) and Cu (52-54%) demonstrating the most variation while Ni (34-40%) and Cd (8-15%) showed the least variation due to specific chemical characteristics of each metal. For iron and lead, its high affinity to particles may promote association with particulate matter, while, low affinity to

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particles and a stronger potential to form stable complexes allow nickel and cadmium to remain in dissolved phase.

Based on metal-salinity scatter plots, it is evident that the oceanic distributions of trace metals in both basins are affected by a number of geochemical and physical processes of comparable magnitude. These include aeolian input of metals to surface waters, biological uptake and regeneration in the water column, scavenging of metals by particulate matter, releases of metals from bottom sediments, and advection and mixing of oceanic water masses. The relative importance of the various processes for each metal in both basins are predicted based on the extent of scattering observed from the trend line.

In the southeastern Arabian Sea, during intermonsoon fall, the surface waters (0-75m) were impoverished and well stratified with high vertical concentration gradients of nutrients and trace metals as a result of deepwater out cropping, while the northern Arabian Sea remained thermally stable and oligotropic. Similarly, northern Arabian Sea during spring intermonsoon, the upper waters (0-75m) were homogenous with respect to nutrients and trace metals as a consequence of winter vertical mixing. Thus for these elements, the upwelling and winter mixing zones were characterized by some degree of enrichment of the surface waters with these chemical constituents and a certain smoothing of the seasonal stratification. The data from the Arabian Sea and Bay of Bengal were limited in both time and space, and does not allow to infer the trace metal export by settling organic debris through and below the thermocline. Since the export of metals below the thermocline was small relative to the recycling of metals due to seasonal processes above the thermocline. Below the thermocline, metal concentrations were consistent with the occurrence of a different water mass. Thus the results imply that upwelling and winter mixing act as regenerated sources in the Arabian Sea and hence play a significant role in redistribution of nutrients and bioreactive trace metals above the permanent thermocline with a low export of metals to deeper waters.

The fifth chapter deals with bioaccumulation of trace metals in zooplankton from the eastern Arabian Sea and western Bay of Bengal. The bioaccumulation of metals in

zooplankton from the Arabian Sea and Bay of Bengal illustrate that iron was bioaccumulated more than any metal; zinc and cadmium showed a similar enrichment and was least for lead. All the average metal concentrations in zooplankton from the Bay of Bengal during winter monsoon showed relative enrichment when compared with Arabian Sea during intermonsoon fall pointing to the importance of the bioavailability of metals in seawater, as well as the differences in potential of heavy metal accumulation of these organisms from both the basins. Thus, a significant enrichment of trace metals like Fe, Zn, Cd, Ni and Cu in the Bay of Bengal zooplankton when compared to Arabian Sea zooplankton are likely be due to the high bioaccumulation factors of these elements existing in the East coast of India.

Similarly Fe, Cu, Zn, Cd & Pb showed a slight enrichment in zooplankton from the Arabian Sea during spring intermonsoon compared to intermonsoon fall. The relative enrichment of Fe, Cu & Zn in zooplankton from the Arabian Sea during intermonsoon spring than intermonsoon fall was due to favourable bioaccumulation factors of these elements during this season. However, the slight enrichment of Cd in zooplankton from the Arabian Sea during intermonsoon spring was due to availability of bioavailable Cd in the surface layers as a consequence of winter mixing.

The average biomagnification values of Cd & Ni were relatively positive in the zooplankton from the Bay of Bengal during winter monsoon than the Arabian Sea during intermonsoon fall. The high positive values of Cd relative to Ni indicate that the biomagnification was higher than the latter with a considerable extent of its accumulation in zooplankton from the Bay of Bengal than the Arabian Sea. For other metals studied in zooplankton from both the basins a negative biomagnification value was recognized which means that metal concentrations were larger in suspended particles.

Studies involving a fixed station grid during the cruise of a research vessel always have a disadvantage that samples from different locations cannot be collected at the same time. Consequently, the variations cannot be related exclusively to either spatial or temporal effects. Furthermore, due to the surface currents and the monsoon gyres, water was continuously being exchanged in the study area. Thus, even though

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analysis of temporal effects would require repeated sampling in a specific water body, which was not feasible in a scheduled cruise, the Arabian Sea was sampled during intermonsoon fall and spring due to its monsoon driven circulation and large scale seasonal variability. The above withdrawal phase seasons were selected to comprehend the effect of upwelling and winter cooling on the vertical flux of nutrients and trace metals in the EEZ of the Arabian Sea. Likewise the Bay of Bengal was sampled during the withdrawal phase of summer monsoon (beginning of winter) so as to understand the role of river runoff and winter cooling on the vertical flux of nutrients and trace metals. Since food items of zooplankton (phytoplankton), as well as the zooplankton itself are carried by water currents over significant distances, metal concentrations can only be related to spatial variations on a larger geographical scale.

Eventhough the Arabian Sea has been sampled only during intermonsoon fall & spring and the Bay of Bengal during winter this work may assume utmost importance owing to the fact that no comprehensive work hitherto has focused on the EEZ of the Arabian Sea and Bay of Bengal to address the biogeochemistry of trace metals. From this study it can be inferred, that there is a need for a better understanding of background informations on trace metal concentrations with respect to space and time and their fluctuations in the Arabian Sea and Bay of Bengal zooplankton. Without a sound knowledge on spatio-temporal fluctuations, it will be impossible to differentiate anthropogenic metal inputs from natural background concentrations with a routine biomonitoring programme. Nevertheless this study can be looked upon as a starting point for further investigations on these biogeochemically important processes, which are vital in addressing the dynamics of productivity of waters.

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