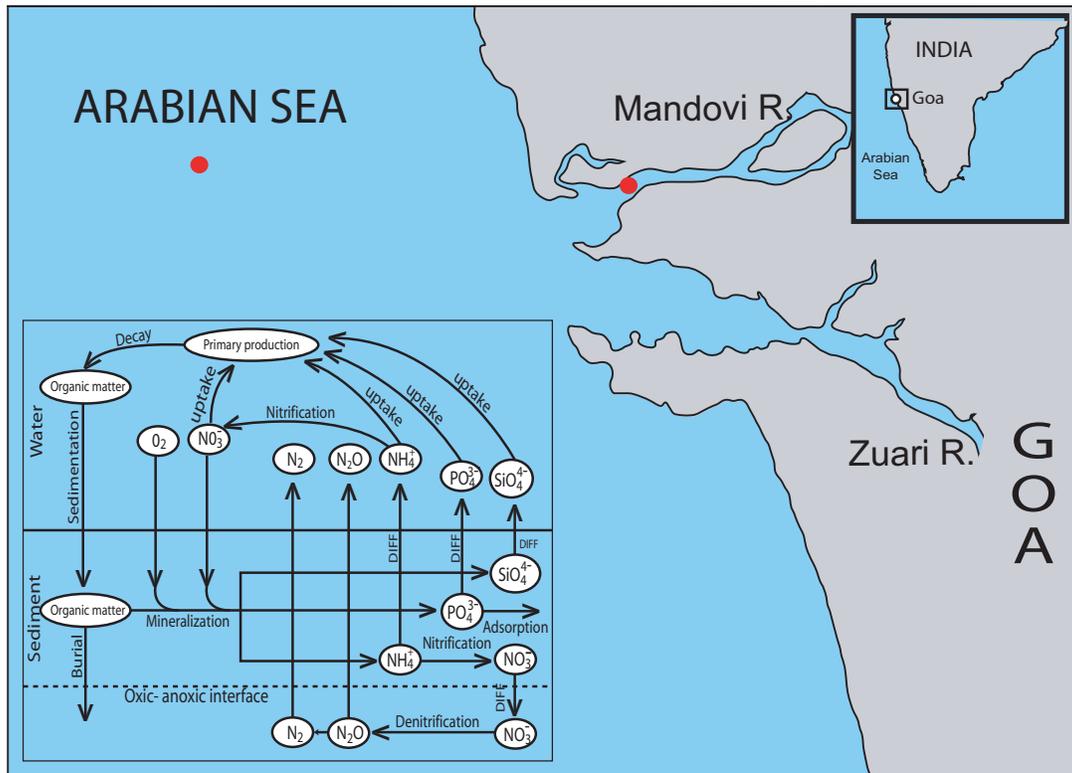


# Benthic Exchange of Biogenic Elements in the Estuarine and Nearshore Waters of Western India



THESIS SUBMITTED TO  
**MANGALORE UNIVERSITY**  
 FOR THE DEGREE OF  
**DOCTOR OF PHILOSOPHY**  
 IN THE  
 FACULTY OF SCIENCE  
 BY  
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### **Abstract of the Thesis**

In order to get a quantitative understanding of coupling between benthic regeneration and fluxes with pelagic nutrient cycles and primary productivity in shallow environments of eastern Arabian sea, biogeochemical studies were carried out at two chosen sites i.e. Mandovi estuary (15.502°N, 73.825°E) and a coastal station (15.509°N, 73.65°E) ~15 Km off Goa coast during 2004 to 2006. Monthly variation of relevant physico-chemical and biological parameters were also recorded at these sites. Benthic flux measurements were undertaken in premonsoon and postmonsoon period following standard methods of *in-situ* and laboratory incubation of sediment. Phosphorus dynamics in relation to its exchange across sediment-water interface were specially studied by a series of laboratory based incubation experiments mimicking the natural physical condition of the estuary. Nutrient enrichment experiments were carried out at these sites to understand the coupling between benthic inputs and ecosystem productivity.

The rate of benthic respiration and nutrient exchange exhibited pronounced seasonality in the estuary. The estuarine sediment behaved as net source of DIN especially in the form  $\text{NH}_4^+$  (70-100%) in the dry season (February-May) but became a net sink for combined N in the monsoon season implying active benthic denitrification. Nutrient fluxes peaked in April coinciding with high pelagic production but attained minimal in August reflecting the variation in temperature and availability of labile organic matter. Benthic supply of DIN, DIP and  $\text{SiO}_4^{4-}$  met 49, 25 and 55% of algal N, P and Si demand respectively in premonsoon season. Shelf sediments were also found to be a significant source of nutrients to the pelagic algal community.

The estuarine sediment showed high adsorbing capacity for DIP presumably due to presence of ferric oxide minerals which was further confirmed by exponential  $\text{PO}_4^{3-}$  release from sediment under anoxic condition. An equilibrium concentration of 0.7-0.9  $\mu\text{M}$  was maintained in the bottom water owing to  $\text{PO}_4^{3-}$  buffering capacity of the sediment. Salinity of the overlying water was found to exert significant control on benthic P release agreeing with the results of *in-situ* measurements in different seasons.

Nutrient uptake in the estuarine water was rapid after a time lag of ~24hours where as coastal phytoplankton took longer time (~48h) to respond to the nutrified ambience though followed by rapid uptake of nutrients which indicates their physiological adaptation to an environment which is nutrified in a typical natural process. Contrary to classical algal N preference, both estuarine and coastal phytoplankton preferred  $\text{NO}_3^-$  rather than  $\text{NH}_4^+$  even in the availability of the latter at a substantial concentration (~4 $\mu\text{M}$ ) indicating species specific N preference. Simultaneous rapid uptake of  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$  and  $\text{SiO}_4^{4-}$  by phytoplankton revealed the tight coupling between benthic fluxes and algal uptake of nutrients and a significant contribution of benthic fluxes to pelagic primary production.

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**NOTIFICATION**

Sub: Award of Ph.D. degree to Mr. Anil Kiran Pratihary.

Ref: Decision of the Syndicate at its meeting held on 06.08.2008,  
vide Agenda No. Evaluation: Saa.Sa.4-46(2008).

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**Department of Marine Geology**

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**Supervisor's Certificate**

I certify that the thesis titled **“Benthic Exchange of Biogenic Elements in the Estuarine and Nearshore Waters of Western India”** is Mr. Anil Kiran Pratihary's genuine research work carried out under my guidance and direct supervision. I further certify that this thesis or a part thereof has not been the basis for the award of any other degree or diploma.

*B.R. Manjunatha*  
1st Aug. 2008  
Dr. B. R. Manjunatha

## Declaration

I, hereby declare that the thesis titled "*Benthic Exchange of Biogenic Elements in the Estuarine and Nearshore Waters of Western India*" embodies the results of bonafide research work carried out by me under the guidance and direct supervision of Dr. B. R. Manjunatha, Reader, Department of Marine Geology, Mangalore University. I further declare that this thesis or a part thereof has not been the basis of the award of any other degree or diploma.

  
01/8/08  
Anil Kiran Pratihary

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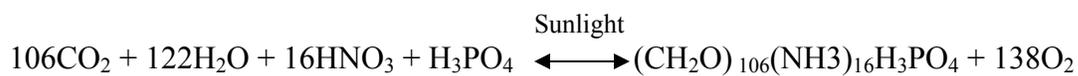
**Dedicated**  
**to**  
**My Parents**

## CHAPTER - I

## INTRODUCTION

## 1.1. Introduction

Life on earth is ultimately dependent on primary producers such as grass, plants, trees, algae and phytoplankton who synthesize organic compounds e.g. lipids, proteins purely from inorganic nutrient elements carbon, hydrogen, oxygen, nitrogen, phosphorous, etc. in the process of photosynthesis, which is the primary food source for all living beings on earth. In the oceans, production/respiration of organic matter can be approximately represented by the following equation (Redfield *et al.*, 1963)



Although oceans cover about 71% of the earth's surface area, a major fraction of global primary production is of terrestrial origin. The ocean contributes nearly 25% of the global primary production out of which > 90% is produced by phytoplankton and benthic macro algae and < 10% is by marshes. The great majority of the plants in the ocean are various types of microscopic, planktonic and unicellular algae, collectively called phytoplankton which along with other minor macroscopic plants like seaweeds, sea grasses and other macroalgae form the bases of marine food chain.

One of the major controlling factors of marine primary production is sunlight. The next major ingredient for photosynthesis is carbon dioxide (CO<sub>2</sub>) which is reduced to organic carbon in presence of sunlight. The total concentration of free dissolved CO<sub>2</sub>, bicarbonate and carbonate ions in seawater remains sufficiently high (>2 mmol L<sup>-1</sup>) not to limit photosynthesis.

Next to sunlight and carbon dioxide, a number of elements in suitable chemical forms are essential for the growth of phytoplankton. Such elements are called either macronutrients or micronutrients depending upon their biological demand. Three elements fall in the first

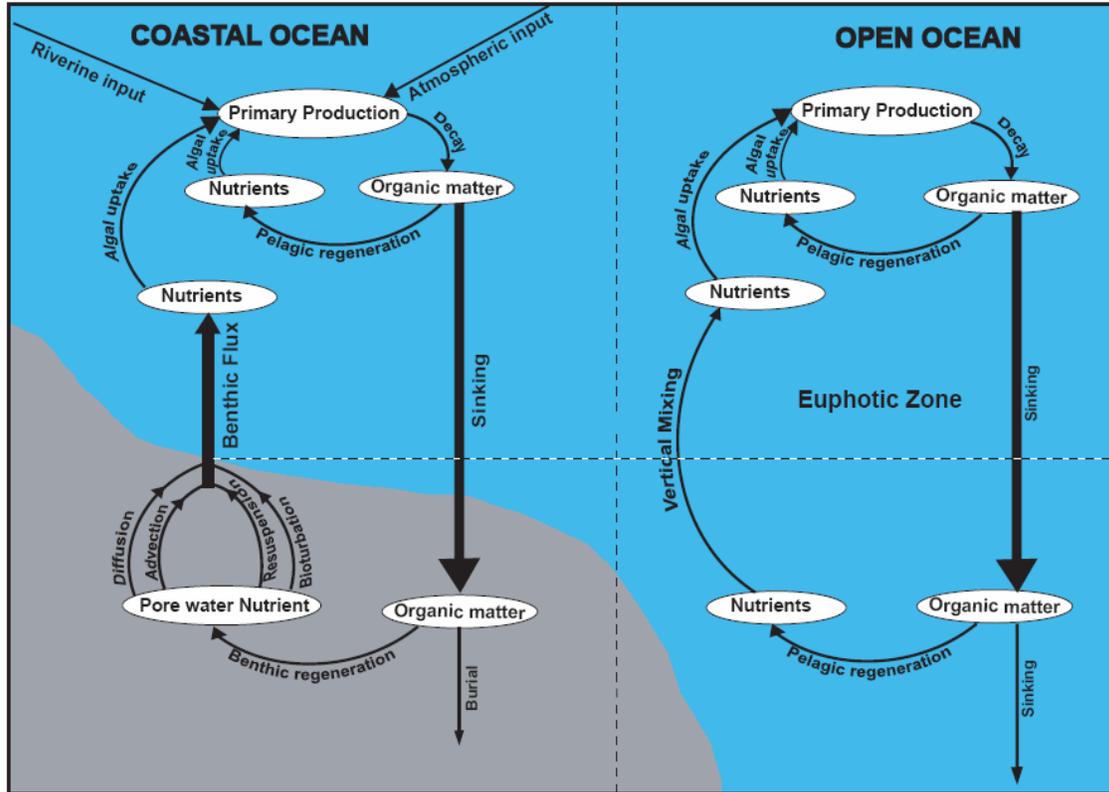
category - N, P and Si - whereas there are numerous micronutrient elements such as Fe, Mn, Zn, Cu, Mo, Co and I, of which Fe is perhaps the most important. Among the macronutrients N and P are utilized by the organisms to build their soft tissue, whereas Si is used for developing the exoskeleton. Although molecular nitrogen ( $N_2$ ) is the most abundant form of N on our planet, only a select group of primary producers (Cyanobacteria) can make use of it. Most phytoplankton require N in the combined (or fixed) forms, the principal species being  $NO_3^-$ ,  $NO_2^-$  and  $NH_4^+$  and some organic forms (such as urea); P is used as  $PO_4^{3-}$  or  $HPO_4^{2-}$ , and Si as  $SiO_4^{4-}$  or  $Si(OH)_4$ . In addition, some vitamins are also required for a complete nourishment of these micro plants.

At higher latitudes adequate quantities of nutrients are supplied to the surface layer by vertical mixing and hence sunlight often controls marine production. In the tropics, on the other hand, solar radiation remains intense throughout the year, with negligible seasonal variation, leading to a permanent thermocline, which prevents vertical mixing and consequent nutrient enrichment of the euphotic zone. Thus, the availability of nutrients becomes a major controlling factor for primary production.

In the world oceans primary production has been observed to be limited mainly by availability of nitrogen (Dugdale & Goering, 1967; Ryther & Dunstan, 1971), phosphorus (Garrels & Mackenzie, 1971; Holland, 1978 & Broecker & Peng, 1982) and iron (Martin *et al.*, 1989; Hutchin & Bruland, 1998).

Unlike the open ocean where nutrients are mainly supplied from subsurface waters, estuarine and coastal systems receive additional nutrient load from river and land run-off, atmospheric deposition and benthic remineralization. This makes coastal systems highly productive as compared to open ocean. Although ocean marginal areas like estuaries, coastal and continental shelves occupy just about 10% of the global oceanic area, between 30% and 50% of the marine primary production occurs in these regions (Romankevich, 1984; Walsh, 1988; 1991) that also sustains ~90% of the fisheries resource.

Unlike the open ocean, in estuarine and coastal environments a major fraction of organic matter fixed by phytoplankton sinks to the seafloor because of shallow depths (Fig. 1.1). Based on the mass balances Walsh *et al.* (1985); Christensen (1989) and Jahnke *et al.* (1990) suggested that a significant fraction of the carbon in slope and rise sediments is



**Fig. 1.1:** Comparative nutrient cycling in coastal and open ocean.

derived from primary production on the continental shelf. Jorgensen (1983) reported that coastal and continental margin sediments receive about 80% of the freshly produced organic matter that reaches the sediment in the world's oceans; this amounts to 10-50% of the annual primary production in the overlying waters. Thus, continental margin sediments have been considered to be important sites of organic carbon oxidation and also depocentres for organic carbon burial (Walsh *et al.*, 1985; Walsh, 1991). Organic rich debris derived from pelagic primary production is deposited in sediments in a relatively labile state (Rittenberg *et al.*, 1955; Borodovskiy, 1965; Sholkovitz, 1973; Suess, 1976). Microbially mediated benthic mineralization of this material is a major recycling pathway of nutrients, supplying a significant fraction of the nutrients required by primary producers in the overlying water column (Nixon *et al.*, 1976; Rowe, *et al.*, 1977; Billen, 1978).

Klump and Martens (1983) observed that benthic regeneration can meet as much as 50%

or more of the algal nutrient demand. Blackburn and Henriksen (1983) found that the release of inorganic nitrogen from sediments supplied from 30 to 100% of the N required to support primary production in the Danish coastal areas. Numerous other studies have also confirmed that estuarine and shelf sediments supply a substantial fraction of nitrogen required for phytoplankton production in the overlying water (Rowe *et al.*, 1975, 1983; Nixon *et al.*, 1980; Hopkinson & Wetzel, 1982; Florek & Rowe, 1983).

Benthic nitrogen cycling is especially critical in coastal systems due to denitrification (Seitzinger & Giblin, 1996) since it is the largest sink (*i.e.* > 50%) of N in continental shelf sediments (Codispoti, 1989). In coastal systems experiencing large anthropogenic N inputs, benthic denitrification can control the extent of eutrophication. As primary production in many coastal systems is generally N limited (Ryther & Dunstan, 1971), the loss of N<sub>2</sub> via benthic denitrification can regulate productivity and hence withdrawal of CO<sub>2</sub> from the atmosphere. Thus, although benthic nutrient regeneration may support ecosystem productivity, sediment may also limit overall productivity by acting as a sink for combined nitrogen.

Apart from nitrogen, phosphate also plays a major role in controlling algal production in lakes, lagoons, estuarine and coastal bodies. It has been a major limiting nutrient in ocean on the geological time scale (Van Cappellen & Ingall, 1994 & 1996). Many freshwater systems have been reported to be P-limited and a number of estuaries and bays have been found to be also seasonally P-limited (Hecky & Kilham, 1988). While unlike nitrogen, phosphorus is not lost from the system through the formation of any gaseous product, its adsorption and chemical precipitation with ferric oxides and its release or desorption from above minerals under anoxic condition (Krom & Berner, 1981), control its bioavailability in estuarine and coastal environments. With increasing anthropogenic inputs many estuarine and coastal systems may tend towards seasonal P limitation, which are otherwise considered to be N limited (Mortimer *et al.*, 1999). However, Boynton *et al.* (1980) observed that benthic phosphate flux satisfied 52-330% of daily algal P demand. This shows that benthic P cycling in shallow systems is controlled by several factors which need a thorough understanding.

The rate of benthic remineralization and the quantum of nutrient exchanges between the sediment and overlying water are controlled by several factors such as biogeochemical

zonations, especially the redox status, organic matter content, temperature, porosity, bioturbation and episodic resuspension of surficial sediment. Therefore, a quantitative understanding of coupling between benthic regeneration and fluxes with pelagic nutrient cycles and primary productivity is necessary for a complete understanding of biogeochemical cycles and quantification of budgets of key biogenic elements.

### **1.2 Significance of benthic exchange study in the coastal Arabian Sea**

Although the Arabian Sea is a small ocean basin, it hosts several diverse biogeochemical provinces such as eutrophic, oligotrophic and oxygen-deficient areas (Banse, 1994). This region is strongly influenced by the phenomenon of monsoons – the biannual reversal of winds and surface currents. The two monsoons – the summer or the south-west monsoon (June to September) and the winter or the north-east monsoon (December to February) – are associated with large-scale fertilization of surface waters with nutrients derived from depth through upwelling and vertical mixing (Naqvi *et al.*, 2003). It is estimated that the annually-averaged primary production (PP) in the Arabian Sea may be as high as the PP in the North Atlantic Ocean during the spring blooms (Barber *et al.*, 2001). The high PP leads to a high oxygen demand at depth, and this in conjunction with limited oxygen supply due to land-locked nature of the Arabian Sea results in the formation of the thickest and most intense oxygen minimum zone (OMZ;  $O_2 < 0.1$  ml/l or  $\sim 4 \mu\text{M}$ ) (Naqvi & Norohna, 1987, Codispoti *et al.*, 1989, Morrison, 1999) found anywhere in the world. This OMZ impinges upon a large area of the seafloor. It is estimated that about two-thirds of the global continental margin area in contact with the severely oxygen depleted waters ( $O_2 < 0.1$  ml/l or  $\sim 4 \mu\text{M}$ ) occurs in the North Indian Ocean, most of it in the Arabian Sea. This implies that benthic processes over the continental margin in the Arabian Sea should be different from those in most other parts of the ocean.

Moderate upwelling occurs along the west coast of India during June-November (Banse, 1959; 1968). However, one unique aspect of the hydrography of this region is that the upwelled water is capped by 5-10 m thick low-salinity lens formed as a result of very high rainfall in the coastal zone (Naqvi *et al.*, 2000). This sustains extremely strong thermohaline stratification very close to the surface. The upwelled water, which is not much oxygenated to begin with, is thus prevented from exchanging oxygen with the atmosphere while whatever little dissolved oxygen it carries is quickly and fully

consumed for the oxidation of organic matter. As a result, by mid-southwest monsoon (in August) reducing conditions develop over the inner shelf that gradually extend to the mid-shelf north of at least Lat. 12°N. The system is initially buffered by high nitrate concentrations and it takes approximately one month before nitrate is fully denitrified and the system becomes truly anoxic (*i.e.* sulfate reducing). During the transition from the oxic to anoxic conditions nitrous oxide (N<sub>2</sub>O, a potent greenhouse gas) has been found to accumulate in the water column in very high concentrations (~ 0.8 μM) (Naqvi *et al.*, 2000). The western continental shelf is perhaps the only region where all three types of redox environments – oxic, suboxic and anoxic – occur over the same segment of the shelf with such regularity (Naqvi *et al.*, 2006). However, it is believed that SO<sub>4</sub><sup>2-</sup> reduction in the water column is a recent phenomenon caused by an intensification of oxygen deficiency due to anthropogenic fertilizer runoff from land (Naik, 2003; Naqvi *et al.*, 2006).

The prevalence of reducing conditions in the water column is seasonal, as during the winter season when the coastal currents are not conducive for upwelling, the water column is well oxygenated. The sediments over the continental shelf therefore experience a wide range of physico-chemical conditions (temperature, oxygen concentration, nutrient loading) and receive varying quantities of organic matter from the surface. The quality and quantity of benthic respiration (supported by various electron acceptors viz. O<sub>2</sub>, NO<sub>3</sub><sup>-</sup>, MnO<sub>2</sub>, Fe-oxides and SO<sub>4</sub><sup>2-</sup>) are thus expected to undergo large seasonal changes not observed in other areas. There is not much information available on this aspect; the present study was conceived to address this lacuna.

### **1.3 Previous work**

The prevalence of reducing conditions exerts an enormous impact on N cycling in both the water column and sediments. However, most of the work carried out so far has been focused on the water column (Naqvi *et al.*, 2000, Naik, 2003, Naqvi *et al.*, 2006) although an attempt has been made to investigate benthic N cycling, especially for quantifying the rate of sedimentary denitrification along the central west coast of India (Naik, 2003). The effect of benthic exchange on biogeochemistry (e.g., nutrient cycling and primary production) has not been studied at all. In other coastal areas, the coupling of sediment-water exchange process with pelagic algal productivity has been investigated

and found to be very significant, often the key term of the nutrient cycles, as pointed out earlier.

Limited pore water analyses were previously carried out in the Mandovi Estuary by Naik (2003) to provide supporting data for sedimentary denitrification measurements. The frequent occurrence of higher concentration of  $N_2O$  (21-466 nM) in the surficial sediments of the estuary than in the overlying bottom water implied that the sediments serve as an important source of  $N_2O$  to the overlying water. This was supported by the results of *in-situ* benthic flux chamber experiments that yielded an estimated  $N_2O$  flux of  $1.43 \mu\text{mol m}^{-2} \text{d}^{-1}$  to the overlying water column. An average DIN flux of  $26 \text{mmol m}^{-2} \text{d}^{-1}$  to the overlying water was observed which indicated that estuarine sediment could be an important contributor to the pelagic nutrient inventory of the estuary. Also significant accumulation of  $p\text{CO}_2$  was observed during the chamber incubations which agreed well with the previously observed increase of  $p\text{CO}_2$  in the estuarine water by Sarma *et al.* (2001).

#### **1.4 Objectives of the study**

The above-mentioned work involving benthic flux measurements was very preliminary and it was not followed-up in detail. It was confined only to the exchange of nitrogen species ( $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$  and  $\text{N}_2\text{O}$ ) and other nutrients ( $\text{PO}_4^{3-}$  and  $\text{SiO}_4^{4-}$ ) were not measured, and their role in supporting PP was not investigated. Moreover, no attempt was made to compare estuarine and near shore environments. Although it is a well established fact that the eastern Arabian Sea is highly productive due to upwelling during the SW monsoon season, the contribution from benthic flux to the nutrient inventories of the overlying water column has been overlooked. Therefore, the overarching goal of the present study was to understand benthic biogeochemistry of nutrients and assess its potential in fertilizing the overlying water column to fuel PP. The specific objectives are:

- To quantify fluxes of various nutrients across sediment-water interface, and their impact on pelagic nutrient cycles.
- To understand physico-chemical and biological factors, and processes controlling the rate of benthic exchange of biogenic elements, especially phosphorus.
- To assess the degree of coupling between benthic fluxes and pelagic primary productivity and its implications in the estuarine and near shore waters of the west

coast of India.

In order to fulfill these objectives extensive measurements were carried out and the results are presented here. The organization of the thesis is as follows.

**Chapter 2** describes the attributes of the study area. This includes the geographical setting, and various physical, chemical and biological processes that have become known as a result of previous research. Seasonal variations in meteorological factors, coastal currents, riverine runoff, nutrient cycling and primary productivity are discussed in detail.

**Chapter 3** provides comprehensive description of materials and methods followed in sampling, collection and analyses of water and sediment samples.

**Chapter 4** contains the methodology followed for *benthic flux* measurements and describes in detail the results pertaining to factors causing the seasonal variability of flux, benthic turnover time, contribution of benthic nutrient fluxes to pelagic productivity and comparison of flux results between the estuarine and the shelf environments.

**Chapter 5** focuses on benthic P cycling. This aspect was investigated in order to understand the effect of extreme changes in the physical environment (periodic switchover from almost fully riverine to almost fully marine conditions in the estuary) on P exchange between sediments and the overlying water column. Following description of the experimental designs, results on benthic fluxes of  $\text{PO}_4^{3-}$ , its inventory, bioavailability, its variations with salinity and adsorption on sediments are presented and discussed. Factors controlling the sorption dynamics, buffering of estuarine sediments, mobilization of  $\text{PO}_4^{3-}$  in relation to changing salinity and oxygen levels of the overlying water are discussed in detail.

**Chapter 6** presents results of nutrient-enrichment experiments carried out at two sites, one each located in the estuarine and open coastal zones. Results of these experiments, carried out for the first time in Indian coastal waters, provide an insight into nutrients uptake by phytoplankton.

**Chapter 7** contains an integrated discussion of results presented in chapters 4, 5 and 6. It summarizes the major findings and identifies the limitations of the existing data sets and makes recommendations for further studies. ■