

## CHAPTER - VII

## OVERALL DISCUSSION, SUMMARY &amp; RECOMMENDATIONS

**7.1. Ecological implications of benthic fluxes**

In the Mandovi estuary benthic fluxes of dissolved oxygen and nutrients appear to be controlled mainly by temperature, river runoff and activities of benthic organisms. Large variations in these parameters/processes on the annual scale introduce large seasonality in the fluxes, with the largest difference occurring between the premonsoon and monsoon seasons. The fluxes attained maxima in April and became negligible when peak monsoon conditions prevailed in the estuary. Shifts in salinity arising from the variable freshwater influx exert a significant control on benthic nutrient exchanges both directly and indirectly. Fluxes of ammonium and phosphate under varying salinity conditions are mainly controlled by their adsorption (desorption) on to (from) the sediments, whereas nitrate and silicate fluxes are largely affected by their concentrations in the water column (or concentration gradients across sediment-water interface). Ammonium fluxes were found to be high when highly saline conditions prevailed in the estuary (*i.e.* in February, March and April) and low when the estuary was freshwater dominated (*i.e.* in August). Significant increase in the ammonium flux with salinity was also observed experimentally. This indicates that apart from other factors such as temperature and availability of labile sedimentary organic matter, geochemical processes associated with salinity variations are important modulators of benthic ammonium release.

The benthic  $\text{NH}_4^+$  release was the highest ( $4 \text{ mmol m}^{-2} \text{ d}^{-1}$ ), but the sedimentary  $\text{NO}_3^-$  uptake from the overlying water was low ( $0.1 \text{ mmol m}^{-2} \text{ d}^{-1}$ ) because of the low  $\text{NO}_3^-$  concentration ( $0.3 \text{ }\mu\text{M}$ ) in the water column during the premonsoon season. With the onset of the southwest monsoon,  $\text{NH}_4^+$  flux decreased considerably (to  $0.8 \text{ mmol m}^{-2} \text{ d}^{-1}$ ) in response to the lowered salinity ( $\sim 4$ ), whereas the sedimentary  $\text{NO}_3^-$  uptake increased by an order of magnitude (to  $1.23 \text{ mmol m}^{-2} \text{ d}^{-1}$ ) due to the greatly elevated  $\text{NO}_3^-$  concentration in the water column ( $7.1 \text{ }\mu\text{M}$ ). The net release of DIN during the monsoon was, therefore, due to a higher  $\text{NH}_4^+$  efflux and a lower  $\text{NO}_3^-$  uptake; conversely, the net

uptake of DIN during the premonsoon period can be explained by a lower  $\text{NH}_4^+$  efflux and a higher  $\text{NO}_3^-$  uptake. However, since the environmental conditions changed from the premonsoon to the monsoon period (salinity decreased and water column  $\text{NO}_3^-$  increased), the behavior of the estuarine sediment in regard to DIN exchange could not be unequivocally established from fluxes measured *in-situ* with the benthic chamber. In the core incubation experiments, though, where salinity was high ( $\sim 33$ ) and  $\text{NO}_3^-$  was also quite high (26  $\mu\text{M}$ ),  $\text{NH}_4^+$  efflux ( $4.1 \text{ mmol m}^{-2} \text{ d}^{-1}$ ) still surpassed benthic  $\text{NO}_3^-$  uptake ( $1.5 \text{ mmol m}^{-2} \text{ d}^{-1}$ ). Thus, it seems reasonable to conclude that under the higher salinity regime, which prevails in most of the estuaries along the Indian west coast for larger part (2/3) of the year, the sediments should serve as a net source of DIN for the overlying water column, irrespective of the water-column  $\text{NO}_3^-$  concentration.

The rate of  $\text{NO}_3^-$  uptake by the sediments during the monsoon, derived from the benthic chamber deployment, and that during the premonsoon, measured through core incubation in the lab, under comparatively high overlying-water  $\text{NO}_3^-$  concentrations are of similar magnitude, implying that the estuarine sediments serve as a significant sink of  $\text{NO}_3^-$  (especially when the overlying water is  $\text{NO}_3^-$ -rich). Thus, these sediments hold the potential to get rid, at least partially, of the extra load of  $\text{NO}_3^-$  entering the estuary from anthropogenic sources, river discharge or land run off.

The high rate of benthic  $\text{NO}_3^-$  uptake ( $1.5 \text{ mmol m}^{-2} \text{ d}^{-1}$ ) observed in the estuary was associated with low water-column build up of  $\text{N}_2\text{O}$  indicating net  $\text{N}_2\text{O}$  consumption via sedimentary denitrification. However, in the laboratory incubation of cores, substantial accumulation of  $\text{N}_2\text{O}$  was noticed in the overlying water as well as in the headspace.  $\text{N}_2\text{O}$  fluxes from sediment to the overlying water and, from the water to the overlying air were calculated as 391 and 182  $\text{nmole m}^{-2} \text{ d}^{-1}$ , respectively. These apparently contradicting observations imply that the estuarine sediments can act as both a net source and a net sink of  $\text{N}_2\text{O}$ , which is not unexpected for a (N) species having an intermediate oxidation state in an environment where near surface redox gradients are sharp and highly variable both in space and with time.

Rapid uptake of nutrients observed in the nutrient enrichment experiments and high benthic fluxes measured during the premonsoon period, when nutrient concentrations in the water column were rather low, suggest that nutrients released by the sediments are quickly utilized by the phytoplankton. Although for the estuarine phytoplankton,  $\text{NO}_3^-$  was experimentally observed to be the preferred N species over  $\text{NH}_4^+$ , under low- $\text{NO}_3^-$  conditions that seem to be characteristic of most of non-monsoon periods,  $\text{NH}_4^+$  diffusing out of the sediments should be a more important source for phytoplankton N uptake. Given that the Mandovi estuary remains highly productive during these periods in spite of low  $\text{NO}_3^-$  concentrations, and is less productive (presumably due to light limitation) during the monsoon season when the water column  $\text{NO}_3^-$  is high, it would appear that overall PP in the Mandovi estuary is supported largely by  $\text{NH}_4^+$  rather than  $\text{NO}_3^-$ .

The estuarine sediments were experimentally found to have a high  $\text{PO}_4^{3-}$  adsorbing capacity and a high  $\text{PO}_4^{3-}$  buffering capacity which tends to maintain  $\text{PO}_4^{3-}$  concentration of the estuarine water around 0.7-0.9  $\mu\text{M}$ . This indicates that the estuarine sediments have the potential to remove excess  $\text{PO}_4^{3-}$ , which may be added to the system from various natural and anthropogenic sources, as well as to release  $\text{PO}_4^{3-}$  to the water column when the uptake by organisms lowers its concentration thereby preventing P-limitation of PP during any season.

Unlike the Mandovi estuary, benthic fluxes over the inner shelf off Goa appear to be influenced mainly by bottom water temperature, the amplitude of seasonal oscillations of which exceeds  $5^\circ\text{C}$ . Since the estuary is very shallow and remains well mixed in premonsoon, nutrients coming out of the seafloor are readily available to primary producers. In the shelf region, on the other hand, even though benthic fluxes are higher than in the estuary, deeper water column, longer turnover time and seasonal vertical stratification together make the regenerated nutrients relatively less readily available for photosynthesis. Also, unlike the Mandovi estuary, the coastal region experiences suboxia ( $\text{O}_2 < 4 \mu\text{M}$ ) during the monsoon season followed by anoxia ( $\text{O}_2 \sim 0 \mu\text{M}$ ) during the early post monsoon period. Persistence of anoxic conditions almost for one month results in the release of oxidized-Fe-bound  $\text{PO}_4^{3-}$  to the overlying water, enhancing bottom water  $\text{PO}_4^{3-}$

concentrations to 4  $\mu\text{M}$  or more during October. Thus, the contribution of benthic fluxes to pelagic productivity could still be very high in the shelf region.

Going on the results of lab incubations, the flux of  $\text{NO}_3^-$  across the sediment-water interface seems to be directed out of the sediment over the shelf, in contrast with what happens in the estuarine region, whereas the flux of  $\text{NH}_4^+$  from sediments to the oxic overlying water is higher in the estuary. It is possible, however, that the lower  $\text{NH}_4^+$  and higher  $\text{NO}_3^-$  fluxes out of the sediment over the shelf owe to, at least in part, higher nitrification activity. The shallower estuarine site is expected to be more illuminated than the deeper shelf site, except during the monsoon months when the estuarine water is highly turbid. Thus, nitrification rates in the benthic boundary layer are expected to be lower in the estuary.

## 7.2. Summary

The Arabian Sea is a unique natural environment since it hosts several distinct biogeochemical provinces. Features such as semiannual reversal of winds and currents, large scale upwelling and perennial existence of a thick and intense OMZ make it a unique natural laboratory for biogeochemical investigations. International research initiatives undertaken over the past few decades, especially the JGOFS (Joint Global Ocean Flux Study), have led to a tremendous improvement of our understanding of open ocean biogeochemical processes, but ironically the areas closest to the land (*i.e.* the inshore and coastal waters) still continue to be relatively ignored.

The Mandovi estuary of Goa has been subjected to numerous investigations because of its proximity to the NIO, India's premier research institution for marine sciences. As a result, there exists a fairly good understanding of general physico-chemical and hydrographical processes operating in the estuary (Qasim & Sen Gupta, 1981; Shetye *et al.*, 1995). One of the most striking features of this estuary, and in fact of all estuaries along the Indian west coast, is the strong seasonality. That is, during the dry period (October-May) the river flow is almost non-existent, and the tidal domination makes the estuary an inseparable part of the coastal sea. During the wet season (June-September), on the other hand, the estuary becomes almost like a freshwater body, and the heavy riverine discharge brings in large amounts of nutrients not only to the estuary but also to the coastal sea. Thus, the estuarine system remains well coupled with the adjacent coastal

systems throughout the year and these seasonally contrasting features exert a large impact on the estuarine and coastal biogeochemistry. As a result, nutrient inventory, primary productivity and benthic faunal activity are known to undergo dramatic variations with season. And yet, some very basic processes such as the sedimentary nutrient cycling and its role in supporting the pelagic primary production have remained uninvestigated or, at best, poorly known.

The biogeochemical cycling in the coastal environment off Goa also exhibits strong seasonality but due to different forcing processes. On the annual scale it is predominantly affected by the monsoon-induced upwelling which is the principal mechanism of nutrient-enrichment of the water column, because of which productivity is quite high within the coastal zone during the monsoon season. However, moderately high production persists even in March-April because of episodic blooms of diazotrophs, while it is much higher in September-October due to continuation of upwelling, coupled with high insolation. In contrast to the estuary, persistence of subsurface oxygen deficiency between August and October is the most remarkable feature of the coastal region. Quite opposite to the summer-early autumn upwelling regime, downwelling caused by the northward moving WICC ensures a well oxygenated water column between November and February. This period is therefore relatively less productive.

The present study is the first of its kind that addresses the important question of benthic-pelagic coupling in the Indian estuarine and coastal waters. It was conceived and designed for quantifying benthic exchange of essential nutrients and to assess their contribution to pelagic productivity in the Mandovi estuary and over the inner shelf off Goa. Major results of the investigation are summarized below:

### **7.2.1. Salient Findings**

- Benthic respiration rate and fluxes of nutrients across sediment-water interface in the Mandovi estuary are found to exhibit strong seasonality with large differences between the premonsoon and monsoon seasons owing to variations in temperature, salinity, macrobenthic activities, etc. Fluxes of oxygen and nutrients attain peak values during premonsoon and reach minima in the monsoon season. Ammonium is the dominant species of benthic regenerated N in premonsoon comprising 70-100% of the benthic DIN flux. However, owing to the effect of

reduced salinity during the monsoon, benthic  $\text{NH}_4^+$  flux decreases to 1/5th of the premonsoon value.

- The estuarine sediments of Mandovi serve as net source of DIN during the premonsoon period mainly in the form of  $\text{NH}_4^+$ , but act as a net sink of DIN in the monsoon season owing to suppressed flux of  $\text{NH}_4^+$  and enhanced benthic denitrification. The net loss of DIN to the sediment is found to be  $229 \mu\text{mol m}^{-2} \text{d}^{-1}$  during the monsoon season. The estuarine sediment is an active site for benthic denitrification as it removes  $1065 \mu\text{mol}$  of  $\text{NO}_3^- + \text{NO}_2^-$  per square meter in a day during the monsoon season, and also has a potential to remove  $\text{NO}_3^-$  added to the estuary due to natural or anthropogenic processes during other seasons as well. The estuarine sediment may also act as a source of  $\text{N}_2\text{O}$  to the water column with an estimated flux of  $391 \text{ nmol m}^{-2} \text{d}^{-1}$  and, in turn, to the atmosphere at a rate i.e.  $182 \text{ nmol m}^{-2} \text{d}^{-1}$ .
- The estuarine sediments exhibit high adsorbing capacity for  $\text{PO}_4^{3-}$  due to the presence of high amount of ferric oxyhydroxides. The sediments also possess a high  $\text{PO}_4^{3-}$  buffering capacity which tends to maintain the  $\text{PO}_4^{3-}$  concentration in estuarine water around  $0.7\text{-}0.9 \mu\text{M}$ . The maximum buffering capacity seems to correspond to a concentration of  $0.75 \mu\text{M}$ . Benthic  $\text{PO}_4^{3-}$  flux is controlled by  $\text{PO}_4^{3-}$  concentration and salinity of the overlying water,  $\text{PO}_4^{3-}$  production rate in sediment and buffering capacity of the sediment.
- In simulated enrichment experiments, the added nutrients were consumed rapidly after a lag phase of  $\sim 24$  hours and their concentrations were reduced to negligible levels within the next 24 hours by the estuarine phytoplankton. Contrary to common belief,  $\text{NO}_3^-$  was the preferred form of nitrogenous nutrient over  $\text{NH}_4^+$  for estuarine phytoplankton, and the pennate form of diatoms comprised a larger fraction of all diatoms that were the dominant algal group in the estuary. Nutrient uptake by estuarine phytoplankton appears to be tightly coupled to benthic supply of nutrients, ensuring complete utilization of benthic regenerated nutrients during non-monsoon periods. Benthic fluxes were found to contribute 49%, 25% and 55% of algal N, P and Si demands, respectively, during the premonsoon period.

- In the shelf region, benthic respiration rate, especially denitrification, and nutrient fluxes are higher than those in the estuary due to higher sediment porosity and possibly also due to higher labile organic matter content in the sediment during premonsoon.  $\text{NH}_4^+$  comprised 51-100 % of the DIN released from the sediment. Results of incubation experiments revealed that shelf sediments are a perennial source of DIN to the water column. However, though sediments can supply  $\text{NO}_3^-$  at a rate of  $179 \mu\text{mol m}^{-2}\text{d}^{-1}$  during the premonsoon and northeast monsoon seasons, they act as an effective sink of  $\text{NO}_3^-$  during the monsoon and post monsoon seasons by removing it at a rate of  $1047 \mu\text{mol m}^{-2}\text{d}^{-1}$  from the water column through benthic denitrification.
- Nutrient enrichment experiment in the coastal region revealed rapid uptake but after a longer time lag as compared to the estuary. The longer response time (~ 48 hours), of the coastal phytoplankton community to sudden, pulsed nutrient availability could be because of their slower physiological adaptation. As in case of the estuary,  $\text{NO}_3^-$  was taken up preferentially over  $\text{NH}_4^+$  also in the coastal waters. Although a higher benthic regeneration rate and comparatively lower gross primary production in the shelf region suggest a greater potential of benthic fluxes for satisfying the algal nutrient demands, deeper water column and thermal stratification may lead to a less tight coupling between benthic fluxes and algal uptake. Still, benthic fluxes can potentially meet 16, 10 and 25 % of the algal N, P and Si demands, respectively, in the shelf region. Effective vertical transport of benthic regenerated nutrients during periods of enhanced vertical mixing may contribute more substantially to the pelagic primary production.

### 7.3 Recommendations for future research

- Although the present study provide the first ever quantitative estimates of benthic fluxes, these pertain to only the premonsoon and monsoon periods as *in-situ* measurements could not be carried out in post-monsoon period when the estuary reverts back to the high saline regime. The immediate effect of this increase in salinity on benthic exchange processes needs further study.
- This study focused only on a fixed intertidal site. Spatial flux measurements along the salinity gradient in different seasons will give a better insight into

- geochemical controls on benthic nutrient exchanges in the estuary.
- The Mandovi estuary is richly endowed with extensive mangrove growth. Since the mangrove swamp sediments probably play an important role in the estuarine nutrient budgets, future research should also include this biogeochemically important ecosystem.
  - Although several important aspects of phosphorus dynamics has been covered in the present study, quantification of different sedimentary P pools by sequential extraction could not be carried out. Future research should remedy this shortcoming.
  - Direct flux measurement by using benthic chambers could not be carried out in the shelf area because of technical reasons, such that the seasonality of benthic-pelagic coupling in the open coastal region remains to be evaluated.
  - Sediments of shallow systems are often inhabited by benthic primary producers. The role of benthic primary production on sediment-water exchange of nutrients was outside the scope of the present study but this aspect should be addressed by future studies.
  - Simultaneous direct measurement of nutrient fluxes, nutrient uptake and primary production through *in-situ* incubation of sediment-water system in a mesocosm will certainly be a holistic approach to be followed in future.
  - A series of benthic flux measurements across the western Indian shelf at different latitudes will provide the much needed information on benthic cycling of biogenic elements and their exchanges with overlying waters at various depths and locations in this biogeochemically unique area.
  - Sedimentary cycles of N, P, S and Fe are closely coupled with each other especially in shallow marine environments. A more integrated approach than attempted here, especially addressing key processes such as sulphate and Fe reduction, would have put the bar too high to be achievable. However, considering that the data generated in the study are the first of their kind not only for the Mandovi estuary but for any estuary in India, future researchers will hopefully build on these results and aim towards a more comprehensive



understanding of the benthic biogeochemistry and ecology and their interactions in the coastal environments. ■

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