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Benthic mineralization and nutrient exchange

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Benthic mineralization and nutrient exchange over the inner continental shelf of western India

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Abstract

The western Indian continental shelf is one of most productive coastal systems of the world ocean. This system undergoes extreme change in oxygen regime being normoxic from November to May and suboxic/anoxic from June to October owing to the biogeochemical response to cyclical monsoonal influence. In order to understand its impact on benthic mineralization, nutrient exchange and in turn on the shelf ecosystem, we carried out first ever intact core incubation experiments by covering two contrasting seasons i.e. Spring intermonsoon and fall intermonsoon (late southwest monsoon). The results show that the shelf sediments act as a perennial net source of DIN, PO_4^{3-} and SiO_4^{4-} to the overlying water column. DIN efflux increased from 1.4 to 3.21 $\text{mmol m}^{-2} \text{d}^{-1}$ from April to October of which NH_4^+ comprises 59–100%. During oxic regime about 75% of diffusing NH_4^+ appears to be nitrified ($2.55 \text{ mmol m}^{-2} \text{d}^{-1}$) of which about 77% remains coupled to benthic denitrification. Consequently 58% of NH_4^+ flux gets lost in active coupled nitrification-denitrification process causing substantial N loss ($1.98 \text{ mmol m}^{-2} \text{d}^{-1}$) in the sediment. The continental shelf sediment switches over from being a NO_3^- source during oxic regime to a NO_3^- sink during low oxygen regime. During suboxia benthic denitrification being fed by NO_3^- from overlying water causes N loss at a rate of $1.04 \text{ mmol m}^{-2} \text{d}^{-1}$. N loss continues even in sulfidic condition during October possibly through chemolithoautotrophic denitrification at a potential rate of $3.21 \text{ mmol m}^{-2} \text{d}^{-1}$. PO_4^{3-} flux increased more than 4 fold during October as compared to April due to reductive dissolution of Fe and Mn oxides. The SiO_4^{4-} flux increases during anoxia due to higher availability of siliceous ooze as a result of diatom blooms during the monsoon season.

Porewater was found to be enriched with NH_4^+ , PO_4^{3-} and SiO_4^{4-} while depleted in NO_3^- and NO_2^- in these organic rich sediments. Sedimentary oxygen consumption decreased by $\sim 28\%$ under anoxia presumably due to the decrease of temperature as well as lower abundance of benthic fauna. Anoxia also appears to re-

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duce benthic mineralization by 25% as C_{org} mineralization rate decreased from 63.83 $mmol\ C\ m^{-2}\ d^{-1}$ in April to 47.83 $mmol\ C\ m^{-2}\ d^{-1}$ in October. This is explained as due to slow oxidation of refractory C_{org} under anoxia apart from effect of lower temperature and lower benthic faunal abundance indicating higher preservation of organic carbon. Benthic nutrient fluxes support about 10%, 16%, 30% and 13%, 40%, 23% of N, P and Si to the pelagic primary productivity during oxic and anoxic period respectively.

1 Introduction

Nutrients form the base of food chain in marine ecosystems as their availability is vital to the primary productivity. The balance between uptake and regeneration is necessary for the maintenance of the pelagic nutrient stock and in turn functioning of the marine ecosystem. In tropical and subtropical open oceans, most of the photosynthetically produced organic matter is lost to deeper depths and the entrainment of remineralized nutrients is largely prevented by thermocline during most part of the year although sporadic mixing events reintroduce these nutrients (e.g. new N) to the euphotic zone (Kumar et al., 2004; Pennington et al., 2006). In contrast, shallowness of continental shelves (< 200 m) results in higher (> 80%) downward export of plankton derived POC (Jørgensen, 1983). The consequent organic matter enrichment of underlying sediment, triggers intense geochemical, microbial and benthic faunal activities which control organic carbon oxidation and accumulation and regeneration of biogenic elements. The ensuing microbially mediated benthic remineralization occurring through sequential use of oxidants i.e. $O_2 > MnO_2 = NO_3^- > Fe_2O_3 > SO_4^{2-} > CO_2$ (Kristensen, 2000), nitrifies the sedimentary porewater and the nutrients are released to the overlying water column mainly via molecular diffusion (Devol and Christensen, 1993; Meile and Van Cappellen, 2003), macrobenthic activities (Karlson et al., 2007; Laverock et al.,

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2011), advective transport of porewater (Huettel et al., 2003; Cardenas and Jiang, 2011) and resuspension of surficial sediment (Johnson et al., 1999; Corbett, 2010).

Continental shelves are known to be biogeochemically active regions in the world ocean. Though they occupy just 8.6 % of the global oceanic area (Jørgensen, 1983), > 15 % of the primary productivity of the global ocean occurs here (Naqvi and Unnikrishnan, 2009) which accounts for ~ 90 % of fisheries resource (Pauley et al., 2002) thereby sustaining livelihood of millions of people worldwide. Of the world Ocean 80 % of the organic carbon burial (Naqvi and Unnikrishnan, 2009) and 83 % of sedimentary remineralization (Jørgensen, 1983) take place in the shelf sediments. Conspicuously pelagic-benthic coupling assumes importance in the biogeochemical cycling of biogenic elements (e.g. C, O, N, P and Si etc) in shelf environments. Benthic regeneration of essential macro and micronutrients and their fluxes to overlying pelagic realm, play key role in the sustenance and functioning of coastal ecosystems (Nixon et al., 1981; Devol and Christensen, 1993; Jahnke et al., 2000; Ferrón et al., 2009a). As benthic supply can control pelagic primary productivity, it has implications for CO₂ fixation, carbon burial and ultimately gives feedback to global climate.

Seasonal anoxia is a unique biogeochemical feature of western shelf of India (Naqvi et al., 2000), which has inspired numerous physical, geochemical and biological investigations (Naik and Naqvi, 2002; Agnihotri et al., 2008; Krishnan et al., 2008; Kurian et al., 2009; Ingole et al., 2010; Roy et al., 2011; Maya et al., 2011; Shenoy et al., 2012) over the last decade and is considered as a biogeochemical hotspot in the world ocean due to the recent intensification of oxygen deficiency and its possible implications on nitrogen cycling and feedback to the global climate change. (Naik and Naqvi, 2006; Naqvi et al., 2009). Western Indian shelf is one of the most productive regions of the Arabian Sea owing to nutrient enrichment through monsoonal upwelling (Sheyte et al., 1990) and land/river run-off during southwest monsoon season (June–September) (Naqvi et al., 2000, 2006), nitrogen fixation during spring intermonsoon (February–April) (Roy et al., 2011; Parab et al., 2012) and atmospheric DIN deposition (Naqvi et al., 2009). The system undergoes extreme change in oxygen regime in a year as the shelf water

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column remains oxygenated from November to May and suboxic/anoxic from July to October. Hypoxia starts in June followed by suboxia during July–August and anoxia during September–October (Naqvi et al., 2006). Longitudinal coexistence of hypoxia, suboxia and anoxia over the shelf in the late monsoon season (Naqvi et al., 2006) makes it a unique biogeochemically active region in the world Ocean. Though western Indian shelf occupies only ~ 8 % of the area of the Arabian Sea, it accounts for 11 % of total pelagic denitrification (Naik and Naqvi, 2002) and 59 % of total N_2O emission from the Arabian Sea (Naqvi et al., 2000). However benthic metabolism, sedimentary nutrient cycling and pelagic-benthic coupling have not been assessed so far which could exert profound influence on the shelf ecosystem. Naqvi et al. (2006) have hypothesized that anoxia during late southwest monsoon would result in dissolution of sedimentary ferric oxyhydroxide minerals and lead to release of Fe-bound phosphate to the overlying water and the mobilized PO_4^{3-} along with other inorganic nutrients (e.g. NH_4^+) is extensively taken up by successive phytoplankton community during post monsoon and later by N_2 fixers e.g. cyanobacteria during spring intermonsoon (February–March). This indicates the potential of benthic supply in meeting nutrient demand of phytoplankton community and thus benthic-pelagic coupling needs to be evaluated in this region. The sediments over the continental shelf experience a wide range of physico-chemical conditions (temperature, oxygen concentration, nutrient loading) and receive varying quantities of organic matter from the surface over a year. The quality and quantity of benthic respiration (supported by various electron acceptors i.e. O_2 , NO_3^- , MnO_2 , Fe-oxides and SO_4^{2-}) and nutrient exchanges are thus expected to undergo large seasonal changes not observed in other areas in the global ocean.

The aim of this study is to quantify the rates of benthic respiration and nutrient fluxes in two contrasting oxygen regimes during premonsoon and late monsoon, assess the impact of anoxia on benthic exchange and to evaluate the role of benthic nutrient supply in sustaining the primary productivity over the continental shelf. Benthic flux rates measured by intact core incubation methods have been found to be comparable to that by in-situ lander methods for shelf/margin sediments (Miller-Way et al., 1994; Hammond

et al., 2004; Woulds et al., 2009). We carried out a series of laboratory based intact core incubation experiments (Rysgaard et al., 1998; Hopkinson et al., 2001; Jahnke et al., 2005) to quantify the benthic exchange rates of dissolved oxygen and nutrients and assess their significance in this unique shelf system. Though benthic nutrient flux studies have previously been done in the eastern Arabian Sea (Pakistan margin) by Woulds et al. (2009) and Schwartz et al. (2009), to our knowledge this is the first ever study on benthic respiration and nutrient exchange on the western shelf of India and we hypothesize that benthic input plays a very significant role in maintaining the productivity of this ecosystem especially during nitrogen poor non-upwelling period (October–May).

1.1 Study site

Our study site (G5) is located at 15°31' N and 73°39' E about ~ 10 km off Candolim, Goa, central west coast of India (Fig. 1) and has an average depth 28 m. It lies on our regularly studied shelf transect since 1997 under ongoing *Candolim Time Series* (CaTS) program. Physical, chemical and biological parameters e.g. temperature, salinity, oxygen, nitrous oxide, nutrients, hydrogen sulphide, chlorophyll, primary productivity and phytoplankton biomass, are being monitored monthly or fortnightly on this transect.

This region is strongly influenced by the monsoons i.e. the biannual reversal of winds and surface currents. Moderate upwelling occurs along the west coast of India during June–November (Naqvi et al., 2006). Due to unique hydrographical and biogeochemical changes induced by southwest monsoon, reducing condition develops over the inner shelf that gradually extends to the mid-shelf north of 12° N. Dissolved oxygen progressively decreases to < 4 μM in July/August in subsurface and bottom waters. The system is initially buffered by high nitrate concentrations (~ 20 μM) and it takes approximately one month before nitrate is fully denitrified and the system becomes truly anoxic (i.e. sulphate reducing). During peak suboxia NO_2^- accumulates up to 6 μM coinciding with high N_2O (180 nM). During the transition from the suboxic to anoxic conditions (late August/early September) N_2O has been found to accumulate in the water

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column in record high concentration ($\sim 0.8 \mu\text{M}$) (Naqvi et al., 2000). As anoxia intensifies during late September–October, O_2 falls below detection limit, the subsurface and bottom water turns sulfidic ($7 \mu\text{M H}_2\text{S}$) and the water column especially bottom water remains depleted in NO_3^- and NO_2^- but enriched in NH_4^+ ($8 \mu\text{M}$), and PO_4^{3-} ($2.17 \mu\text{M}$) (Naqvi et al., 2006). The western continental shelf is perhaps the only region where all three types of redox environments i.e. oxic, suboxic and anoxic co-occur over the same segment of the shelf with such regularity. However sulfidic condition which develops in late monsoon is a recent phenomenon and presumably caused by an intensification of oxygen deficiency due to anthropogenic fertilizer run off from land (Naqvi et al., 2006). During northeast monsoon (November–February) the prevailing west India coastal current causes downwelling which reoxygenates the water column over the shelf and the oxic regime continues till May. Further details of seasonal variation in physical and biogeochemical features of this region have been provided in earlier publications (Naqvi et al., 2006 and 2009).

Surficial sediments in the northern part (north to 13°N) of western Indian shelf is composed of 61 % silt, 21 % clay and 18 % sand and particularly the transect at 15°N (close to CATS transect) is dominated by fine grained particles ($\sim 72\%$ silt and $\sim 27\%$ clay) (Jacob et al., 2009) and has been found to be organic rich (5.8 % TOM) with $\sim 22\%$ labile organic matter (Carbohydrates and proteins) (Jacob et al., 2008). Sedimentation rate over the shelf has been found to be 1.5 mm yr^{-1} (Kurian et al., 2009). Inner shelf sediments along western India are mainly silty clayey and contain 1–4 % organic carbon (Rao and Wagle, 1997). The C/N ratios and $\delta^{13}\text{C}$ value suggests that these are of marine origin (Agnihotri et al., 2008). The shelf sediment is inhabited by 81 species of macrofauna such as polychaetes, crustaceans, bivalves, arachnides and oligochaetes of which polychaetes (85–95 %) remains the dominant group (Jayaraj et al., 2007; Ingole et al., 2010).

2 Materials and methods

2.1 Sample collection

The sampling was carried out at G5 during October 2005 when the bottom water was anoxic and then in April 2006 when the water column was oxic. Water samples were collected at different depths for dissolved oxygen, H₂S, nitrous oxide, nutrients using a 5 L Niskin sampler. Temperature and salinity were recorded by a Seabird CTD profiler. The vertical profiles of above parameters at this site have been presented and described earlier by Naqvi et al. (2009). For the core incubation 10 L of bottom water was also collected in a plastic carboy and was kept in dark at 4 °C.

For the incubation experiment, sediment core was collected in indigenously designed core liners (as described in Sect. 2.2) by divers with minimal disturbance. Three additional sediment cores i.e. each one for porosity, organic carbon and porewater nutrients, were collected in 6.4 cm ID, 30 cm long acrylic core liners by gravity corer. The core for porewater was immediately covered by aluminium foil and kept at 4 °C until pore water extraction.

2.2 Experimental set up

Indigenously fabricated acrylic core liners (ID 10.1 cm, length 48 cm, thickness 0.5 cm) were used for the experiment (Fig. 2). The core liners are fitted with nylon caps at both the ends. The top nylon cap is attached to two 1.5 mm ID Teflon tubings through the holes, which is further attached to 3-way leur locks. The caps have nylon O-rings to make the liners completely air-tight. Two more Teflon tubings are attached through the holes roughly at the centre of the liners. One was used to pass air in case of aerobic incubation and the other one was used for drawing water sample through a syringe. Two 60 mL syringes are fixed to the upper portion of the liner so as to contain the overlying water and replace the withdrawn water sample. The syringes were made impermeable to O₂ by wrapping with multiple layers of adhesive tapes and insulation

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tapes. The syringes were tested for O₂ permeability before they were cut and fitted into the core liner. They were wrapped with tapes, filled with low oxygen water and kept in dark for 5 days. O₂ was checked 24 hourly. No increase in O₂ was observed in the syringes rather O₂ decreased confirming the impermeability of the syringes to O₂. The average length of sediment column was 22 cm and was overlain by a water column of ~ 1.9 L. A Teflon coated magnetic stirrer was positioned at ~ 10 cm above the sediment surface and rotated at 60 rpm ensuring effective mixing of the overlying water without causing resuspension of surficial sediments. The stirrer was remotely coupled with a bar magnet positioned outside the core liner and rotated by a motor.

2.3 Intact core incubations

After retrieval, the core was immediately covered with aluminum foil or black cloth and kept in a container filled with bottom water. Later the core was transferred to a temperature controlled room. After 1–2 h when the suspended particles were settled, the overlying water was carefully siphoned out without disturbing the surficial sediment. Fresh bottom water was slowly introduced over the sediment with minimal resuspension and the core was pre-incubated in dark at temperature close ($\pm 0.5^\circ\text{C}$) to in-situ temperature for 12 h for acclimatization to the laboratory condition. During October, the pre-incubation was done anaerobically as the in-situ bottom water was anoxic, but during April, it was done aerobically since the bottom water remains oxic at G5. Three incubations in October and three in April were carried out in total which are listed in Table 1.

(i) Anaerobic incubations in October

After pre-incubation, the overlying water was siphoned out and fresh bottom water (thawed to laboratory temperature) was put over the sediment and the incubation was started. Since the bottom water at G5 was anoxic at this time, all incubations were done anaerobically. In *Experiment 1*, the core was kept airtight and the overlying water

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was purged with N_2 for 30 min to remove oxygen before the start of incubation in order to mimic the existing natural condition during anoxia and incubation was done for 48 h. In *Experiment-2*, the overlying water was not N_2 purged but the core was kept airtight and incubated for 56 h. *Experiment-3* was done in a similar way as *Experiment 2* but with NO_3^- spiked fresh bottom water as overlying water and incubated for 48 h.

(ii) Aerobic and anaerobic incubations in April

Since the bottom water during April was well oxygenated at the site, the core was incubated both aerobically and anaerobically successively. In *Experiment 4*, the overlying water was aerated continuously by bubbling air through the tubing fixed at the centre of the core. Since the air bubbles were introduced at ~ 10 cm above the sediment-water interface, the air flow did not disturb the surficial sediment. One of valves at the top cap was kept open to release the over pressure created in the headspace due to air influx and the core was incubated for 48 h. In *Experiment 5*, the core was incubated aerobically for first 24 h similarly to Exp. 4 and then kept airtight and incubated anaerobically for another 60 h to observe the effect of progressive shift from oxic to suboxic condition on benthic exchange. *Experiment 6* was done anaerobically from time zero for 48 h but with NO_3^- enriched fresh bottom water.

2.4 Sampling and analysis

The overlying water was sampled at every 4–6 h through one of the tubing attached to the middle portion of the core liner using 5 mL glass or plastic syringe. As the sample was drawn, the plunger of the fixed syringe (on the upper part of the liner) was slowly pushed inward simultaneously in order to replace the withdrawn sample. Oxygen samples were collected in a He flushed 5 mL Hamilton gastight syringe and the sample was fixed by adding 100 μ L of each of Winkler's solutions and then after 30 min the oxyhydroxide precipitate was dissolved by adding 200 μ L of 50 % H_2SO_4 (Grasshoff et al.,

1983). The absorbance of the color was immediately measured at 456 nm (Pai et al., 1993) by a Shimadzu UV-visible spectrophotometer with a precision of $\pm 0.03 \mu\text{M}$.

H_2S sample was collected in a He flushed 5 mL Hamilton gastight glass syringe and was fixed by addition of 100 μL each of dimethyl-*p*-phenylene diamine and FeCl_3 . The absorbance was spectrophotometrically measured at 670 nm (Grasshoff et al., 1983) with precision of $\pm 0.05 \mu\text{M}$.

Nutrient samples were collected in 5 mL BD plastic syringes and kept at -20°C until analysis. Later they were thawed, mixed well and analyzed for NO_3^- , NO_2^- , NH_4^+ , PO_4^{3-} and SiO_4^{4-} by a SKALAR segmented flow autoanalyzer within 48 h following colorimetric method (Grasshoff et al., 1983) with precisions ± 0.06 , ± 0.006 , ± 0.01 , ± 0.003 , $\pm 0.06 \mu\text{M}$ respectively.

5 mL of N_2O samples were taken in case of NO_3^- amendment experiments in a He flushed 10 mL Hamilton gastight syringe and immediately poisoned by addition of 100 μL saturated HgCl_2 solution. N_2O was analyzed by a Hewlett–Packard gas chromatograph equipped with electron capture detector following multiphase analysis method (McAuliff, 1971) with precision of 4 %.

2.5 Processing of additional sediment cores

For porosity the core was sectioned at 1 cm interval and the slices were immediately weighed. After drying at 110°C , the dry weight was taken to determine the pore water content. Volume of the sediment was determined and porosity was expressed as the ratio of pore water volume to the total volume of sediment (sediment + pore water).

For sedimentary organic carbon (C_{org}), the core was sectioned at 1–2 cm and the subsamples were freeze dried and homogenized followed by decalcification using 1N HCl. C_{org} were measured using an IR-MS (Delta V plus; [®] Thermo) coupled with an Elemental Analyzer (EA) in a continuous flow mode. Calibrations were carried out using a laboratory standard (n-Caprioic acid, $\text{C}_6\text{H}_{15}\text{NO}_2$; ACA) following Higginson and

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Altabet (2004) and references therein. Analytical precision of the analysis was found to be $\leq 2\%$. The details of the analytical procedure is given in Agnihotri et al. (2008).

For porewater extraction, the core was sectioned at 1 cm interval and collected in 50 mL centrifuge tubes inside a N_2 flushed glove box. These were centrifuged at 4000 rpm for 20 min at 4°C (Sundby et al., 1992; Schulz, 2006). The extracted pore water was filtered, transferred to plastic vials inside the glove box (Schulz, 2006) and kept at -20°C until nutrient analysis and later analyzed within 48 h as described in the Sect. 2.4.

2.6 Flux calculation

In case of intact core incubations, the appreciable change in volume of overlying water might introduce non-linearity in the change in concentration with time and can lead to overestimation of flux rates. Thus the ratio of time/water column height for each sampling interval was calculated and the concentration of overlying water was plotted against the sum of elapsed time/height for all preceding intervals (Hammond et al., 2004).

$$F = \partial C / \partial T_h$$

where F is the flux in $\text{mmol m}^{-2} \text{d}^{-1}$ and $\partial C / \partial T_h$ is the slope of the plot between concentration and sum of time/height. In case of nutrients, very good linear correlation was observed between concentration and day m^{-1} ($r^2 > 0.9$) and thus the slope of linear regression fit was directly taken as flux rate but in case of oxygen, the slope of the polynomial fit at time zero ($\partial C / \partial T_h t = 0$) was considered (Hammond et al., 2004) since curvature appeared usually after a concentration of $\sim 100 \mu\text{M}$. Positive flux (efflux) values denote flux into overlying water from sediment and negative flux (influx) values stand for fluxes into sediment from overlying water.

Concentration gradient existing between sediment pore water and bottom water results in molecular diffusion of nutrients across sediment-water interface. Diffusive flux

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can form a significant part of the total measured flux and was calculated following modified Fick's first law of diffusion appropriate for sediment (Berner, 1980).

$$F = -\phi \cdot D_s \cdot (\partial C / \partial z)_{z=0}$$

Where F = diffusive flux in $\text{mmol m}^{-2} \text{d}^{-1}$, ϕ = porosity of the surficial sediment, $(\partial C / \partial z)_{z=0}$ is the concentration gradient across sediment-water interface ($\text{mmol m}^{-3} \text{m}^{-1}$) and D_s is the whole sediment diffusion coefficient ($\text{m}^2 \text{d}^{-1}$) after correction for temperature and tortuosity (Krom and Berner, 1980).

$D_s = D_0 / \theta^2$ where D_0 is the molecular diffusion coefficient in seawater (Boudreau, 1997) at a particular temperature and θ is the tortuosity of the sediment and is expressed as

$$\theta^2 = 1 - \ln \phi^2 \quad (\text{Boudreau, 1996})$$

All the flux values are presented in Table 2.

3 Results

3.1 Oxygen consumption rates

Exp. 1 started with $23 \mu\text{M O}_2$ at 0 h but rapidly went below detection limit within 6 h and was not detectable till the end of the experiment (Fig. 3a). However since the preserved bottom water was used, overlying water in Exp. 2 and 3 was oxic at time zero. In Exp. 2 the oxygen decreased from $186 \mu\text{M}$ to $< 8 \mu\text{M}$ after 40 h (Fig. 3a). However overlying water in Exp. 3 turned to be anoxic after 24 h as O_2 was below detection at 36 h and afterwards (Fig. 3a). Possibly it became anoxic even before that i.e. around 30 h, but we did not sample at that time. In these incubations O_2 decreased below $8 \mu\text{M}$ or became undetectable after 24–30 h. No significant variation ($p = 0.5$) was observed between oxygen decrease pattern between Exp. 2 and 3 and very consistent DO flux

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was observed in Exp. 2 ($-48.07 \text{ mmol m}^{-2} \text{ d}^{-1}$) and Exp. 3 ($-47.57 \text{ mmol m}^{-2} \text{ d}^{-1}$) (Table 2).

During April the overlying water remained oxic ($\text{O}_2 > 183 \mu\text{M}$) in Exp. 4 (Fig. 4a), which is well above the hypoxic threshold ($62.5 \mu\text{M}$). Thus the thin upper oxic layer of the sediment column is expected to remain intact which in turn would not have affected the nutrient exchange. This condition was close to the naturally existing condition during pre-monsoon when the bottom water remains oxygenated ($\text{O}_2 > 82 \mu\text{M}$). In Exp. 5 dissolved oxygen remained almost same till 24 h, but after that, it decreased substantially to $36 \mu\text{M}$ at 48 h and remained almost same till the end of the experiment (Fig. 4a). It exhibited a slow transition from oxic to nearly suboxic condition.

In Exp. 6 O_2 decreased non-linearly from $193 \mu\text{M}$ at 0 h to $29 \mu\text{M}$ within 24 h and then remained almost same till 48 h (Fig. 4a). Similar non-linear decrease in O_2 was also noticed in Exp. 2, 3 and 5 as also observed by Sundby et al. (1986), Anderson et al. (1986), Malecki et al. (2004) and Skoog and Arias-Esquivel (2009) elsewhere which occurs due to (i) decrease in concentration gradient across the benthic boundary layer and (ii) decrease in thickness of surficial oxic layer and in turn decrease in number of oxygen respiring microorganisms (Sundby et al., 1986). Oxygen decrease pattern in Exp. 6 did not vary significantly ($p = 0.9$) from that of Exp. 5 and O_2 flux observed in Exp. 5 ($-64.70 \text{ mmol m}^{-2} \text{ d}^{-1}$) Exp. 6 ($-68.21 \text{ mmol m}^{-2} \text{ d}^{-1}$) are consistent (Table 2). The noticeable fact in these three experiments is that, unlike in October incubations, O_2 was not completely consumed and $20\text{--}23 \mu\text{M}$ was still present till the end of incubation.

3.2 Sulfide fluxes

Sulfide accumulated in all the incubations during October. In Exp. 1 sulfide was detectable just after O_2 became zero at 6 h and increased at a rate of $4.299 \text{ mmol m}^{-2} \text{ d}^{-1}$ after 12 h (Fig. 3b). In Exp. 2 S^{2-} was undetectable till 28 h, but it increased linearly at a rate of $1.956 \text{ mmol m}^{-2} \text{ d}^{-1}$ till 48 h and then exponentially to $19.67 \mu\text{M}$ (Fig. 3b). Similar flux pattern and rate ($2.241 \text{ mmol m}^{-2} \text{ d}^{-1}$) were also observed in Exp. 3 after

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O_2 level decreased substantially (Fig. 3b) and the variation in flux pattern between these 3 experiments were statistically insignificant ($p = 0.5$) and the average benthic S^{2-} flux was $2.832 \text{ mmol m}^{-2} \text{ d}^{-1}$ (Table 2). No sulfide was detected in overlying water in Exp. 4, 5 and 6 (not presented in figures) as it is evident that at least $20 \mu\text{M}$ DO was still present at the end. Absence of benthic sulfide flux during normoxia and higher sulfide release during anoxia were also reported earlier by Hansen and Blackburn (1991), McCarthy et al. (2008), Bartoli et al. (2009) and Faganeli and Ogrinc (2009) in other coastal systems.

3.3 Nutrient fluxes

During October NO_3^- and NO_2^- were rapidly consumed between 16–36 h in Exp. 1 and 2 and no NO_2^- build up was observed (Fig. 3c). In Exp. 3, $\text{NO}_3^- + \text{NO}_2^-$ decreased linearly to $0.22 \mu\text{M}$ at the end (Fig. 3c) and NO_2^- increased and peaked ($1.8 \mu\text{M}$) at 24 h coinciding with a prominent N_2O peak (36 nM) and then decreased (Fig. 3d). No significant variation was observed between NO_3^- and NO_2^- consumption patterns between Exp. 1 and 2 ($p = 0.7$). Highest $\text{NO}_3^- + \text{NO}_2^-$ flux ($-3.216 \text{ mmol m}^{-2} \text{ d}^{-1}$) was observed in the NO_3^- amended experiment (Exp. 3) (Table 2). No significant variation was observed NH_4^+ , PO_4^{3-} and SiO_4^{4-} release pattern between Exp. 1, 2 and 3 ($p > 0.05$) and the fluxes were found to be consistent between these three incubations.

During April, N species exhibited different exchange behaviors in aerobic and anaerobic incubation. In Exp. 4, NO_3^- increased from 6.5 to $11.24 \mu\text{M}$. NO_2^- initially decreased till 18 h and then increased to $0.42 \mu\text{M}$ at the end (Fig. 4b). Similarly NH_4^+ decreased initially till 24 h and then showed increasing trend (Fig. 4d). Both PO_4^{3-} (Fig. 4e) and SiO_4^{4-} (Fig. 4f) increased linearly. In Exp. 5, NO_3^- increased till 36 h and then decreased (Fig. 4b). Similarly NO_2^- initially increased to $0.34 \mu\text{M}$ at 60 h and then decreased steeply (Fig. 4c). NH_4^+ showed two increase patterns i.e. a steady increase till 36 h and sharp increase afterwards (Fig. 4d). In first half of the experi-

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ment, lower NH_4^+ efflux and simultaneous increase in NO_2^- and NO_3^- influx was observed. However as oxygen decreased further, NH_4^+ flux increased and downward fluxes of NO_3^- and NO_2^- were observed. NH_4^+ flux was $0.919 \text{ mmol m}^{-2} \text{ d}^{-1}$ till 36 h and increased to $3.221 \text{ mmol m}^{-2} \text{ d}^{-1}$ afterwards. $\text{NO}_3^- + \text{NO}_2^-$ initially increased at a rate of $0.579 \text{ mmol m}^{-2} \text{ d}^{-1}$ and then decreased with flux rate of $-0.583 \text{ mmol m}^{-2} \text{ d}^{-1}$ after 36 h. The initial (0–36 h) $\text{NO}_3^- + \text{NO}_2^-$ efflux rate in Exp. 5 are consistent with the rates observed in Exp. 4. In Exp. 6, NO_3^- showed negative flux and decreased linearly from $11.68 \mu\text{M}$ to $0.33 \mu\text{M}$ (Fig. 4b). NO_2^- remained almost same till 36 h and then steeply peaked ($4.96 \mu\text{M}$) at 36 h and then decreased. A prominent N_2O peak coincided with NO_2^- peak (Fig. 4c). Higher and faster NO_2^- build up was observed in Exp. 6 compared to Exp. 3 but rapid decrease was noticed in both cases. Similar pattern of NO_3^- decrease and accumulation of NO_2^- and N_2O has also been observed by Naqvi et al. (2000) which clearly indicates denitrification. The highest $\text{NO}_3^- + \text{NO}_2^-$ influx ($-1.047 \text{ mmol m}^{-2} \text{ d}^{-1}$) was observed in the NO_3^- amendment experiment (Exp. 6). NH_4^+ initially steadily increased till 30 h followed by steep increase afterwards till end (Fig. 4d). Pattern of NH_4^+ release did not vary significantly between Exp. 5 and 6 ($p = 0.8$) but both varied significantly ($p < 0.05$) from NH_4^+ increase pattern in Exp. 4. PO_4^{3-} and SiO_4^{4-} showed positive fluxes in all above experiments (Fig. 4e and f) without any significant variation ($p > 0.05$) in the flux pattern between 3 experiments during April. Significant variation ($p < 0.001$) in NH_4^+ flux was found between aerobic incubations in April and anaerobic incubations in October. PO_4^{3-} ($p < 0.001$) and SiO_4^{4-} ($p < 0.05$) flux patterns in October significantly varied from those in April.

3.4 N_2O production

Transient build up of nitrous oxide coinciding with NO_2^- peak was observed during both the seasons (Figs. 3d and 4c) in NO_3^- amendment experiments (Exp. 3 and 6) which indicates active benthic denitrification. N_2O accumulation in October was slower rela-

tive to that in April but the decrease was rapidly after peaking up at 36 h which happens due to its further reduction to N_2 . No significant variation was observed between N_2O accumulation pattern between October and April ($p > 0.05$) and N_2O fluxes between October ($8.85 \mu\text{mol m}^{-2} \text{d}^{-1}$) and April ($10.45 \mu\text{mol m}^{-2} \text{d}^{-1}$) were also comparable (Table 2). This shows that only a minor percent of NO_3^- influx (0.2 % in October and 0.9 % in April) resulted in N_2O .

4 Discussion

4.1 Sedimentary oxygen consumption (SOC) and sulfide oxidation

The anaerobic incubations conducted during April resulted consistent O_2 influx rate which gives an average SOC of $66.46 \text{ mmol m}^{-2} \text{d}^{-1}$ (Table 2). However in none of these experiments in April, O_2 was completely consumed as $20\text{--}23 \mu\text{M } O_2$ was still present at the end. Thus the conditions were not strictly anoxic rather close to suboxic as sulfide was not detected at any time point. During first 36 h, Exp. 5 was an aerobic experiment showing similar nutrient exchange patterns and flux rates as observed in the aerobic experiment (Exp. 4) (discussed in next section). Though this experiment was continued for 3.5 days, sulfide was never detected at any time point which implies that upward diffusing S^{2-} was retained within sediment being directly or indirectly oxidized by oxygen from overlying water.

In contrast complete oxygen consumption was observed in October incubations followed by sulfide release. Oxygen uptake occurred at an average rate of $47.826 \text{ mmol m}^{-2} \text{d}^{-1}$ during this time (Table 2). Similar seasonal change in SOC has also been observed in Corpus Christi Bay (McCarthy et al., 2008), Orbetello lagoon Bartoli et al. (2009) and Gulf of Trieste (Faganeli and Ogrinc, 2009). SOC has been observed to be enhanced by macrofaunal activity (Kristensen, 2000; Nizzoli et al., 2007; Braeckman et al., 2010) and higher temperature (Hargrave, 1969; Thamdrup et al., 1998; Rowe et al., 2002; Forja et al., 2004). Average bottom water temperature at this

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site varies from 28 °C during April to 22 °C during October (Naqvi et al., 2006). Thus the observed 28 % decrease in SOC during October could be due to prevalence of low temperature and absence of benthic fauna (Naqvi et al., 2006; Ingole et al., 2010) during anoxia. Neubacher et al. (2011) observed 50 % decrease in SOC during hypoxia in North Sea and Rowe et al. (2002) reported 5 fold low SOC under anaerobic condition compared to that in aerobic condition in the Gulf of Mexico.

Since the bottom water remains oxygenated in April (Naqvi et al., 2006), the surface sediment remains oxic although oxygen penetration could be up to few mm deep (Revsbech, 1989). In such condition, most of the upward diffusing sulfide gets oxidized by Fe and Mn oxides in the top oxic layer of surficial sediment which are in turn produced by oxidation of Fe^{2+} and Mn^{2+} by downward diffusing oxygen from overlying water (Kristensen, 2000). Thus Fe and Mn rich sediments can be effective traps for sulfide in the coastal sediments (Kristiansen et al., 2002). The shelf sediment at G5 contains high percentage of Fe (7.7 %) and Mn (0.09 %) (Siby Kurian, unpublished data) which indicates that sulfide could be retained in the oxic sediment layer during April resulting in no benthic S^{2-} flux. However as the anoxia sets in during late September, oxic-anoxic interface moves upwards to water column. Sulfide is no longer oxidized as Fe and Mn are reduced and flux to overlying water (Kristiansen et al., 2002) though a smaller portion remains trapped in pyrite (FeS_2). In Corpus Christi Bay, McCarthy et al. (2008) located O_2 - H_2S interface below 30 mm during normoxia, but it moved up to just below the sediment surface (0–7 mm) during hypoxia. As Exp. 1 was preceded by anaerobic pre-incubation and N_2 purging prior to time zero, the surface sediment layer must have been anoxic. Thus the sulfide could not be trapped and escaped to the overlying water soon after O_2 fell below detection limit at 6 h resulting in the highest flux. However, since the overlying water was oxic initially in Exp. 2 and 3, a substantial part of upward diffusing sulfide was apparently oxidized by O_2 and Fe and Mn oxides to SO_4^{2-} in the top oxic sediment layer. Immediate sulfide release after 6 h in Exp. 1 and release at 18–28 h after significant drop in oxygen level in Exp. 2 and 3 implies that S^{2-} underwent substantial oxidation by available oxygen in the overlying water but released

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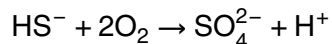
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to the overlying water at an average rate of $2.098 \text{ mmol m}^{-2} \text{ d}^{-1}$. Exp. 2 and 3 nearly represents the condition during late August–early September where S^{2-} is released but was oxidized at a rate of $2.201 \text{ mmol m}^{-2} \text{ d}^{-1}$. Exp. 1 is similar to the in-situ anoxic condition observed during late September–October (Fig. 5c) where S^{2-} is released at a higher rate of $4.299 \text{ mmol m}^{-2} \text{ d}^{-1}$ without being oxidized.

Most of the oxygen is not consumed in decomposition of organic matter in marine sediments but rather in reoxidation of reduced inorganic metabolites e.g. Mn^{2+} , Fe^{2+} , S^{2-} , NH_4^+ and CH_4 close to oxic-anoxic interface chemically or being microbially mediated (Kristensen, 2000). However reoxidation of sulfide has quantitative significance especially during anoxia when pools of Mn-oxides and Fe-oxides are depleted. Up to 85 % of S^{2-} produced by SO_4^{2-} reduction in anoxic zone of sediment is reoxidised in the oxic surface sediment (Thamdrup et al., 1994) and > 50 % of SOC occurs by oxidation of sulfide directly or indirectly (Jørgensen, 1989).



In Exp. 3 sulfide oxidation could also be fuelled by NO_3^- addition in a process known as chemolithoautotrophic denitrification (Lavik et al., 2009) which will be discussed more in the next section. Exp. 1 nearly represents the anoxic condition prevails during October and Exp. 3 represents biogeochemical condition during late August–early September when the transition from suboxia to anoxia occurs. Sulfide accumulates up to $13 \mu\text{M}$ in the subsurface and bottom water in the shelf water off Goa during September–October (Naqvi et al., 2006) and disappears by mid-November owing to its oxidation at oxic-anoxic interface by downwelled oxygenated water during November.

4.2 Nitrification, denitrification and net DIN flux

During April considerably lower NH_4^+ flux in the aerobic incubation (Exp. 4) compared to anaerobic incubations (Exp. 5 and 6) is mainly due to nitrification occurred in the top oxic sediment layer (Fig. 5a). This is further evidenced by positive flux in NO_2^- and

NO_3^- and positive correlation between NH_4^+ and NO_2^- ($r = 0.9, p < 0.001$) and NO_2^- and NO_3^- ($r = 0.96, p < 0.001$). Similar lower NH_4^+ flux under oxic condition has also been reported by Malecki et al. (2004), McCarthy et al. (2008) and Faganeli and Ogrinc (2009) elsewhere.

Exp. 5 represented a slow transition from oxic (0–36 h) to suboxic condition (36–84 h) which is well reflected in nutrient flux pattern. Thus benthic nitrification was active till 36 h resulting in lower NH_4^+ flux, positive NO_3^- and NO_2^- fluxes. As also observed in Exp. 4, nitrification was evidenced by positive correlation between NH_4^+ and NO_2^- ($r = 0.92, p < 0.01$) and NO_2^- and NO_3^- ($r = 0.97, p < 0.001$). This is further substantiated by the fact that the NH_4^+ and $\text{NO}_3^- + \text{NO}_2^-$ fluxes between 0–36 h were consistent with those values from Exp. 4 (aerobic) (Table 2). As the oxygen decreased substantially after 36 h, inhibition of nitrification led to 3.5 fold increase in NH_4^+ flux, which coincided with negative fluxes of NO_3^- and NO_2^- due to benthic denitrification. This resulted in N loss at a rate of $0.583 \text{ mmol m}^{-2} \text{ d}^{-1}$ and NH_4^+ fluxed out at a rate of $3.221 \text{ mmol m}^{-2} \text{ d}^{-1}$ without being nitrified.

In Exp. 6, initial low NH_4^+ flux ($0.76 \text{ mmol m}^{-2} \text{ d}^{-1}$) could be due to partial loss of NH_4^+ through benthic nitrification between 0–30 h. Higher anaerobic NH_4^+ flux in Exp. 6 ($3.552 \text{ mmol m}^{-2} \text{ d}^{-1}$) after 30 h and in Exp. 5 ($3.22 \text{ mmol m}^{-2} \text{ d}^{-1}$) after 40 h was apparently due to suppressed benthic nitrification owing to prevailing low oxygen condition as also observed by Hansen and Balckburn (1991) and Faganeli and Ogrinc (2009) in other regions. $\text{NO}_3^- + \text{NO}_2^-$ showed higher influx compared to that observed in Exp-5 after 30 h as NO_3^- addition in exp-6, enhanced benthic denitrification to a rate of $1.047 \text{ mmol m}^{-2} \text{ d}^{-1}$.

During April NH_4^+ fluxes in aerobic incubation and initial NH_4^+ fluxes in anaerobic incubations are consistent which gives an average aerobic NH_4^+ flux as $0.835 \text{ mmol m}^{-2} \text{ d}^{-1}$ (Table 2). Similarly considering Exp. 4 and Exp. 5, average $\text{NO}_3^- + \text{NO}_2^-$ efflux rate is $0.571 \text{ mmol m}^{-2} \text{ d}^{-1}$ and Exp. 5 and Exp. 6 result $3.386 \text{ mmol m}^{-2} \text{ d}^{-1}$ as average anaerobic NH_4^+ flux. It is conspicuous that in suboxic condition resulted

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in higher NH_4^+ flux ($3.386 \text{ mmol m}^{-2} \text{ d}^{-1}$), but it reduced to $0.835 \text{ mmol m}^{-2} \text{ d}^{-1}$ in aerobic incubation owing to a 75.3% NH_4^+ loss in benthic nitrification at a rate of $2.551 \text{ mmol m}^{-2} \text{ d}^{-1}$. However the lost NH_4^+ did not appear as NO_2^- and NO_3^- at the same rate but rather at a lower rate i.e. $0.571 \text{ mmol m}^{-2} \text{ d}^{-1}$ in the aerobic incubation. This implies that 58.4% of upward diffusing NH_4^+ was apparently lost in coupled nitrification-denitrification process occurring at the oxic-anoxic interface in the surficial sediment (Jenkins and Kemp, 1984; Risgaard-Petersen, 2003; Granger et al., 2011) and 16.8% was released to the overlying water being nitrified to NO_2^- and NO_3^- . Consequently only 24.6% N is released to the overlying water as NH_4^+ . This shows that benthic denitrification coupled with nitrification causes N loss at a rate of $1.98 \text{ mmol m}^{-2} \text{ d}^{-1}$ at sedimentary oxic-anoxic transition zone irrespective of NO_3^- content of the overlying oxic bottom water and 77.6% of benthic nitrification was coupled with denitrification resulting considerable N loss.

Since Exp. 4 represents the prevailing aerobic condition (Fig. 5a) during April, the net benthic DIN release to the overlying water is $1.406 \text{ mmol m}^{-2} \text{ d}^{-1}$ of which NH_4^+ flux comprises 59.3%. Exp. 6 represents the biogeochemical condition of the site during June–July (Fig. 5b) when the bottom water becomes suboxic and NO_3^- rich ($\sim 12 \mu\text{M}$). Two anaerobic incubations results in a benthic denitrification rate of $0.583\text{--}1.047 \text{ mmol m}^{-2} \text{ d}^{-1}$. Considering methodological uncertainties, our results are consistent with Naik and Naqvi (2002) and Naqvi et al. (2006) who reported a sedimentary denitrification rate of $0.233\text{--}1.253 \text{ mmol m}^{-2} \text{ d}^{-1}$ in this region during peak suboxia. Based on NO_3^- consumption, Schwartz et al. (2009) reported benthic denitrification rate $0.51\text{--}1.45 \text{ mmol N m}^{-2} \text{ d}^{-1}$ over Pakistan margin during April–May which is also agreeable with our rates. Sokoll et al. (2012) also observed a benthic denitrification rate of $0.55 \text{ mmol N m}^{-2} \text{ d}^{-1}$ by intact core incubation on slope sediments off Pakistan. However NH_4^+ would be released at an average rate of $3.38 \text{ mmol m}^{-2} \text{ d}^{-1}$ in the following months e.g. June and July but the net DIN release to the overlying water would be at a rate $2.339 \text{ mmol m}^{-2} \text{ d}^{-1}$ as benthic denitrification would cause NO_3^- loss at

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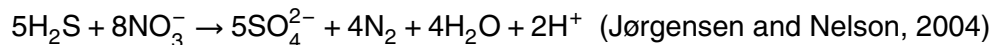
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a rate of $1.047 \text{ mmol m}^{-2} \text{ d}^{-1}$ (Fig. 5b). O_2 concentration largely determined the NO_3^- source for benthic denitrification. Our observation is similar to that reported by Rysgaard et al. (1994) who noticed that in aerobic condition, NO_3^- generated through nitrification within sediment, fed denitrification and during anaerobic condition NO_3^- diffused from the overlying water was found to be the main source for denitrification. Dominance of denitrifiers and low anammox activity in the suboxic water column and sediments has been observed by Jayakumar et al. (2009) and Sokoll et al. (2012) within OMZ of the eastern Arabian Sea margin environments.

During October downward fluxes of NO_3^- and NO_2^- were observed in all experiments and NH_4^+ efflux rates were consistent in all incubations. Though the overlying water was oxic initially, nitrification apparently did not take place due to inhibition by upward diffusing free sulfide (Joye and Hollibaugh, 1995). Moreover during October *nitrifiers* have not been detected in the shelf bottom water while these are found in large numbers during April (Krishnan et al., 2008). Since heterotrophic denitrification and anammox are also inhibited by sulfide (Jensen et al., 2008; Aelion and Warttinger, 2010), the observed loss of $\text{NO}_3^- + \text{NO}_2^-$ seems to be caused by other processes such as DNRA and autotrophic denitrification. DNRA seems unlikely as NH_4^+ flux did not increase significantly in Exp. 3. Moreover very low DNRA activity and interestingly significant autotrophic denitrification in the presence of sulfide, has been observed recently in the bottom water along this transect during late September (S.W.A. Naqvi, unpublished data). NO_3^- is reduced to N_2 by sulfide oxidation mediated by chemolithoautotrophic bacteria such as *Thiobacillus denitrificans*, *Thiomicrospira*, *Thioploca*, *Magnetospirillum* and filamentous *Beggiatoa* with transient build up of intermediates NO_2^- , NO and N_2O (Cordoso et al., 2006; Robertson and Kuenen, 2006). Autotrophic denitrification has been found in several coastal environments (Brettar and Rheinheimer, 1991; Brüchert et al., 2003; Dong et al., 2011 and Shao et al., 2011). These chemolithoautotrophic bacteria are often found in sulfidic surficial sediments (Lam and Kuypers, 2011) and are responsible for massive N loss in anoxic (sulfidic) shelf systems (Lavik

et al., 2009).



In fact Krishnan et al. (2008) have reported the presence of large number of *Thiobacillus denitrificans* in the bottom waters of shelf off Goa during both April and October. Moreover concomitant build up of NO_2^- and N_2O in Exp. 6 substantiates the fact that N loss pathway in October was autotrophic denitrification in contrast to heterotrophic denitrification which caused N-loss in non-sulphidic bottom water and surface sediments during suboxia. NO_3^- addition in Exp-3, stimulated autotrophic denitrification to a rate of $3.216 \text{ mmol m}^{-2} \text{ d}^{-1}$. Similar enhancement in N loss due to autotrophic denitrification has also been reported by Zhang et al. (2009), Shao et al. (2011) and Dong et al. (2011) in sulfidic estuarine and coastal sediments in south east Asia. As *Thioploca* (a known chemolithotrophic S^{2-} oxidizer) mats have been sighted on Pakistan margin sediments (Schmaljohann et al., 2001), Chemoautotrophy plays significant role in benthic biogeochemical processes over there (Cowie, 2005) and also perhaps in other parts of eastern Arabian Sea. As Exp-1 and Exp-2 represent in-situ NO_3^- condition during October, the average autotrophic denitrification rate would be $0.527 \text{ mmol N m}^{-2} \text{ d}^{-1}$ (Table 2). However Exp. 3 nearly represents the biogeochemical condition sometime during late August to September (Fig. 5c) when transition from suboxia to anoxia takes place. Bottom water remains close to anoxic with modest NO_3^- concentration ($8\text{--}10 \mu\text{M}$). Though sulfide has not been detected during this time, it is highly possible that the released sulfide is quickly oxidized by NO_3^- and NO_2^- creating an impression of non-sulphidic condition (Lavik et al., 2009; Canfield et al., 2010). Naqvi et al. (2000) have reported the highest N_2O build up (765 nM) during this transition time. Exp. 3 resulted in an N_2O accumulation of 63 nM compared to 36 nM during April (Exp. 6). Our results show that autotrophic denitrification can potentially cause N loss at a rate of $3.216 \text{ mmol N m}^{-2} \text{ d}^{-1}$ during this time (Table 2). As the bottom water remains NO_3^- depleted during October, NH_4^+ was the only available form of DIN being released at an average rate of

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3.745 mmol m⁻² d⁻¹ (Table 2). The noticeable seasonal change was that the sediment switches from being NO₃⁻ source in oxic period to NO₃⁻ sink in anoxic period.

4.3 Benthic PO₄³⁻ and SiO₄⁴⁻ release

Benthic PO₄³⁻ flux is mainly controlled by interplay of processes such as (1) remineralization from sedimentary organic matter (2) adsorption to Fe-oxides also co-precipitation with ferric minerals (Krom and Berner, 1981) and (3) the formation of authigenic carbonate fluorapatite (Ruttenberg and Berner, 1993) in the top oxic zone of sediment. Positive fluxes of PO₄³⁻ in all experiments during April and October shows that the benthic PO₄³⁻ regeneration rate always exceeds the rate of its adsorption and precipitation in the upper oxic layer. During April PO₄³⁻ flux did not vary significantly between the aerobic and anaerobic incubations. It is evident that O₂ in the anaerobic incubation (Exp. 6) did not decrease to a level to cause anoxia in the upper sediment layer. As ~20 μM O₂ was present at the end of Exp. 6, the upper benthic layer was not truly anoxic which could not cause reductive dissolution of Fe-oxides and in turn release of Fe bound PO₄³⁻. Ferric minerals such as FeOOH and Fe₂O₃ are known to adsorb and bind PO₄³⁻ chemically in the oxic sediment layer (Krom and Berner, 1981). PO₄³⁻ was released to overlying water at an average rate of 0.143 mmol m⁻² d⁻¹ during April (Table 2). Similarly SiO₄⁴⁻ fluxes were always directed to water column at consistent rates in aerobic and anaerobic incubations with an average rate of 3.839 m⁻² d⁻¹.

PO₄³⁻ flux rates increased significantly during October as the condition became anoxic in all three incubations. Anoxia induced reductive dissolution of FeOOH apparently released PO₄³⁻ (Ingall and Jahnke, 1994; Gunnar and Blomqvist, 1997; Slomp et al., 1998) from Fe-minerals in the upper layer which added up to pore water PO₄³⁻ pool and ultimately resulted in higher PO₄³⁻ fluxes. Higher benthic PO₄³⁻ release has also been observed by Rozan et al. (2002), Bartoli et al. (2009) and Skoog and Arias-Esquivel (2009) during anoxia in other coastal systems. Average PO₄³⁻ flux during Oc-

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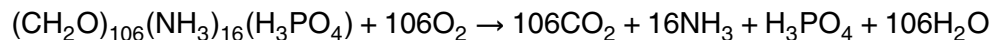
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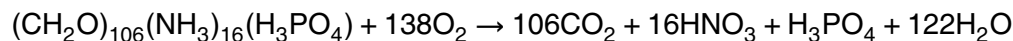
tober was $0.594 \text{ mmol m}^{-2} \text{ d}^{-1}$ which was more than 4 fold higher than PO_4^{3-} flux rates observed during April (Table 2). Faganeli and Ogrinc (2009) observed 3–10 fold higher PO_4^{3-} flux under anoxic condition compared to oxic condition in the Gulf of Trieste. Skoog and Arias-Esquivel (2009) also reported 26 times higher benthic PO_4^{3-} release under anoxic condition than under oxic condition in Long Island Sound. 36–50 % increase in benthic PO_4^{3-} efflux was noticed by Bartoli et al. (2009) during anoxia in Orbetello lagoon, Italy. Average SiO_4^{4-} flux of $5.093 \text{ mmol m}^{-2} \text{ d}^{-1}$ during this period, is ~ 1.3 times higher than that observed during April (Table 2). Diatom remain the dominant phytoplankton in the shelf water off Goa during southwest monsoon (Parab et al., 2006; Roy et al., 2006) due to higher NO_3^- availability through coastal upwelling. In contrast N_2 fixing *Trichodesmium* dominate the phytoplankton community with frequent patchy blooms across the shelf during February–March (Parab et al., 2006; Roy et al., 2011). Higher diatom growth during south west monsoon could result in higher downward flux of siliceous frustules to the underlying sediments during late monsoon. Dissolution of diatom frustules could enrich pore water with SiO_4^{4-} and ultimately lead to higher fluxes in October. Similar enhancement in SiO_4^{4-} flux has also been reported by Grenz et al. (2000) in San Francisco Bay.

4.4 Stoichiometry of fluxes

The aerobic mineralization of planktonic organic matter can be expressed in the following equations.



and with ultimate oxidation of NH_4^+ to NO_3^- the equation becomes as



The flux of biogenic elements are expected to occur in the Redfield ratio but interplay of several processes such as nitrification, denitrification, adsorption, desorption,

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and macrobenthic activities may cause deviation from the expected ratio (Koop et al., 1990; Cowan and Boynton, 1996; Giblin et al., 1997; Ferguson et al., 2004; Faganeli and Ogrinc, 2009). $O : NH_4^+$ flux varied from 38.4–40.4 during April to 23.7–28.6 during October. Such departure from the expected Redfieldian $O : NH_4^+$ ratio (13.25) indicates that a part of NH_4^+ pool is lost or retained through nitrification and/or adsorption. $NH_4^+ : PO_4^{3-}$ flux ratio varied from 16.4 to 40.8 in anaerobic incubations in April. Lowest $NH_4^+ : PO_4^{3-}$ (5.5) in the aerobic incubation is due to substantial loss of NH_4^+ in nitrification and subsequent denitrification (Jenkins and Kemp, 1984) and NH_4^+ adsorption on to clay minerals (Rosenfeld, 1979; Mackin and Aller, 1984) also accounts for the departure from the expected value (16). Decrease in $NH_4^+ : PO_4^{3-}$ flux ratio (5.2–7.3) during October is due to anoxia induced higher PO_4^{3-} release. Closeness of $NH_4^+ : SiO_4^{4-}$ flux ratio (0.8–1.02) to Redfield–Brzezinski value (1.06) during April suggests that stoichiometry of DIN and SiO_4^{4-} release would favor diatom growth in the water column in coming months. However lower $NH_4^+ : SiO_4^{4-}$ flux ratio during October (0.55–0.78) apparently would favor the growth of non-siliceous phytoplankton during late monsoon. This is substantiated by the fact that diatom remains the dominant community during April–May but dinoflagellates become the major phytoplankton during September–October (Parab et al., 2006; Naqvi et al., 2009).

4.5 Organic matter mineralization

Sedimentary oxygen consumption is usually considered as one of the principal determinants of oxidation rate of total organic carbon in marine sediments (Canfield et al., 1993; Glud, 2008). DIC (Tco_2) flux has been observed to be fairly linear with benthic oxygen uptake (Giblin et al., 1997; Hopkinson et al., 2001; Ferrón et al., 2009b) which indicates that oxygen is directly or indirectly responsible for benthic respiration. Oxygen directly oxidizes organic carbon in aerobic mineralization but reoxidizes only the reduced inorganic products of anaerobic mineralization e.g. Fe^{2+} , Mn^{2+} and H_2S fluxing into the top oxic zone (Canfield et al., 1993). However since reduction of Mn oxides,

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Fe oxides and SO_4^{2-} and subsequent reoxidation of Fe^{2+} , Mn^{2+} and H_2S by oxygen have the same net stoichiometry as aerobic carbon oxidation by oxygen (Jørgensen, 1977; Canfield et al., 1993), SOC can be used to calculate organic carbon oxidation rate. Total organic carbon oxidation rate is quantified by taking oxygen consumption in aerobic nitrification and carbon oxidation through denitrification into consideration (Canfield et al., 1993) as follows.

$$\text{TC}_{\text{oxid}} = \text{O}_2 \text{ flux} - \text{O}_{2\text{NH}_4\text{-oxid}} + \text{C}_{\text{denit}}$$

where TC_{oxid} is the depth integrated rate of total organic carbon oxidation, $\text{O}_{2\text{NH}_4\text{-oxid}}$ is the oxygen consumed in NH_4^+ oxidation to NO_3^- and C_{denit} is the organic carbon oxidized through denitrification. In aerobic mineralization C : O_2 is 1, O_2 : NH_4^+ ratio is 2 in complete nitrification process and C : N in heterotrophic denitrification is 1.25 (Canfield et al., 1993).

During April considering nitrification rate $2.551 \text{ mmol m}^{-2} \text{ d}^{-1}$, the O_2 consumption for NH_4^+ oxidation will be $5.102 \text{ mmol m}^{-2} \text{ d}^{-1}$ and benthic denitrification (coupled to nitrification) of $1.98 \text{ mmol N m}^{-2} \text{ d}^{-1}$ would oxidize 2.475 mmole of C_{org} per m^2 per day in oxygenated condition. Thus the net organic carbon oxidation rate during this time is $63.83 \text{ mmol C m}^{-2} \text{ d}^{-1}$. However as suboxia develops, nitrification would cease and benthic denitrification would be represented solely by NO_3^- influx rate i.e. $0.513 \text{ mmol m}^{-2} \text{ d}^{-1}$ initially and followed by $1.047 \text{ mmol m}^{-2} \text{ d}^{-1}$. Thus the net carbon oxidation rate would apparently increase further to $68.21 \text{ mmol C m}^{-2} \text{ d}^{-1}$ presumably between June and July.

However as both NH_4^+ oxidation and heterotrophic denitrification are inhibited by sulfide during October, O_2 flux can directly be considered as C_{org} oxidation rate (Canfield et al., 1993). Considering Exp. 2 and 3 the average C_{org} oxidation rate will be $47.826 \text{ mmol C m}^{-2} \text{ d}^{-1}$ during this sulfidic event. C_{org} mineralization has been found to be faster under aerobic condition than anaerobic condition (Benner et al., 1984; Henrichs and Reeburgh, 1987; Lee, 1992; Dauwe et al., 2001) especially where sediment

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has more refractory organic matter, although aerobic degradation rate could be comparable to the anaerobic one in some cases (Kristensen et al., 1995; Hulthe et al., 1998). Thus during oxic regime 63.83 mmole of organic carbon is mineralized aerobically per m^2 in a day which is equivalent to 70.6% of the pelagic primary productivity ($90.3 \text{ mmol C m}^{-2} \text{ d}^{-1}$; Ram et al., 2003). Similarly an equivalent of 30.9% of PP (154.7 $\text{mmol C m}^{-2} \text{ d}^{-1}$; Ram et al., 2003) is anaerobically mineralized during October. Since the percent of labile C_{org} does not change considerably between two oxic and anoxic regimes (Jacob et al., 2009) it appears that the 25% decrease in C_{org} mineralization rate from oxic to anoxic regime arises due to slower oxidation of refractory C_{org} under anoxic condition (Kristensen et al., 1995; Hulthe et al., 1998; Holmer, 1999). Neubacher et al. (2011) observed 46% decrease in N remineralization in North Sea under hypoxic condition. Similarly Dauwe et al. (2001) reported anoxic C_{org} mineralization 50% less than the oxic one in North Sea. Wouldts et al. (2007) reported 40% decrease in organic matter mineralization by benthic macrofauna on Pakistan margin when condition changed from oxic in April to suboxic in October as oxygen threshold for macrofauna is observed to be $0.1\text{--}0.2 \text{ mL L}^{-1}$ (Levin et al., 2009). Moreover prevailing low temperature (22°C ; Naqvi et al., 2006) and absence of benthic macrofaunal activity (Naqvi et al., 2006; Ingole et al., 2010) during anoxia would slow down carbon mineralization as higher temperature (Kristensen et al., 1992; Middelburg, 1996; Sanz-Lázaro et al., 2011) and benthic faunal activity (Rysgaard et al., 2000; Heilskov and Holmer, 2001; Nascimento et al., 2012) are known to stimulate remineralization of organic matter in marine sediments.

4.6 Porewater nutrients and diffusive fluxes

Porewater at the study site was enriched with NH_4^+ , PO_4^{3-} and SiO_4^{4-} during both the seasons (Fig. 6 d–f). Vertical distribution of pore water NH_4^+ and SiO_4^{4-} did not vary significantly ($p > 0.05$) between April and October. However, in April PO_4^{3-} varied significantly ($p = 0.01$) from October which could happen because of immobilization by

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Fe and Mn oxide minerals owing to bioirrigation. But macro benthic activity stops due to anoxia and sulfidic condition (Rowe et al., 2002) during October which apparently caused reductive dissolution of Fe and Mn oxides and release of PO_4^{3-} to pore water. Similar seasonal variation in porewater PO_4^{3-} profile has also been observed by Woulds et al. (2009) in the sediments Pakistan margin. Low NO_3^- and NO_2^- was observed in the porewater which usually occurs because of N loss through benthic denitrification as O_2 penetration is limited to upper few mm of the sediment. Bioirrigation is conspicuous in NO_3^- and NO_2^- profile in April (Fig. 6c) which apparently caused penetration of oxic bottom water to the deeper anoxic layers thereby nitrifying a part of pore water NH_4^+ to NO_2^- and NO_3^- . In contrast, low porewater NO_3^- and NO_2^- was observed in October due to anoxia related inhibition of macrobenthic activity and also because of enhanced benthic denitrification. Vertical distribution of sedimentary organic carbon (C_{org}) did not vary significantly ($p = 0.6$) between oxic and anoxic regime (Fig. 3b). However, the differences in C_{org} and porewater nutrients were observed in upper ~ 2 cm between April and October. Higher C_{org} in October (Fig. 6b) is possibly due to relatively higher sedimentation of phytoplankton detritus during preceding productive months (June–September) and slower oxidation of refractory organic mater. Upward shift of oxic-anoxic interface and remineralization of labile planktonic organic matter possibly increased pore water NH_4^+ , PO_4^{3-} and SiO_4^{4-} concentration in the surface layer during October. Lower NH_4^+ , PO_4^{3-} in the surficial layer during April, could be due to presence of oxidized surface layer resulting in nitrification of NH_4^+ and PO_4^{3-} adsorption to Fe and Mn oxides. Higher oxidation rate of refractory C_{org} in oxic condition can be a reason for relatively lower C_{org} in the surficial sediment during April. Lower SiO_4^{4-} in April occurred due to frequent dominance of non-siliceous phytoplankton e.g. *Trichodesmium* bloom over diatom population in the preceding months (February–March).

Porosity of surficial sediment did not vary significantly ($p = 0.2$) between April and October (Fig. 6a) but concentration gradient varied between two seasons owing to changing biogeochemical condition in bottom water and sediment. Thus higher diffu-

sive fluxes observed during October was induced by higher concentration gradients across sediment-water interface compared to that during April (Table 2). Higher bioturbation during April could also cause relatively lower diffusive flux compared to that in October when benthic activity practically ceases. Diffusive NH_4^+ flux was especially high comprising 73–92% of total benthic NH_4^+ flux because of higher concentration gradient across sediment-water interface and higher diffusivity of NH_4^+ . Diffusion coefficient (D_s) of NH_4^+ is 3.4 and 1.9 times higher than that of PO_4^{3-} and SiO_4^{4-} respectively (Schulz, 2006). Flux enhancement factor (ratio of measured flux to calculated flux) during oxic period are 14.7, 1.3, 4.7 and 6.6 and during anoxic period are 11.6, 1.03, 9.2 and 8.2 for $\text{NO}_3^- + \text{NO}_2^-$, NH_4^+ , PO_4^{3-} and SiO_4^{4-} respectively. It implies that macrobenthic activity, advective pore water transport and resuspension of sediments greatly enhance the benthic nutrient exchange rate. However the latter two factors apparently play greater role in the anoxic regime.

4.7 Benthic turnover time

Days required to replenish the pelagic nutrient inventory of a system by benthic nutrient supply under steady state is referred as benthic turnover time and it is calculated by dividing depth integrated pelagic nutrient stock by benthic nutrient efflux rate for a particular nutrient (Warnken et al., 2000). Considering Exp. 4 and aerobic part of Exp. 5, the turnover time of NH_4^+ is 16 days (Table 3) during April. However taking nitrification into consideration the turnover time of DIN is longer (~ 67 days) during this period. Considering Exp. 6, the turnover time of DIN (40 days) decreases due to inhibition of nitrification at low oxygen. As Exp. 6 nearly represents the biogeochemical condition of the system during July–August, it is evident that prevailing suboxic condition during July and August will cause quicker replenishment of pelagic DIN stock by benthic flux. Apparently, turnover time of PO_4^{3-} (165 days) and SiO_4^{4-} (29 days) will not change significantly between April and July–August as the fluxes did not vary significantly between aerobic and anaerobic incubations.

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Increased NH_4^+ flux during October led to shorter turnover time of NH_4^+ (20 days) and DIN (24 days) compared to that in April. Similar decrease in PO_4^{3-} turnover time (91 days) was also observed in October as PO_4^{3-} flux increased 4 fold than April. However a longer turnover time for SiO_4^{4-} (136 days) was noticed during this time compared to that in April (29 days) despite higher SiO_4^{4-} flux which is due to higher pelagic Si inventory in October.

4.8 Benthic-Pelagic coupling

Primary productivity in the shelf waters of western India undergoes substantial variation from premonsoon to post monsoon period. Owing to choppy sea during April–May, the occurrence of cyanobacterial bloom ceases (Parab et al., 2006, 2012) and water column remains nutrient poor which leads to low primary productivity i.e. $90.3 \text{ mmol C m}^{-2} \text{ d}^{-1}$ (Ram et al., 2003). Upwelling induced nutrient enrichment stimulates PP to $107.5 \text{ mmol C m}^{-2} \text{ d}^{-1}$ in July and it peaks to $282.5 \text{ mmol C m}^{-2} \text{ d}^{-1}$ in August (Naqvi et al., 2006). Modest PP ($154.7 \text{ mmol C m}^{-2} \text{ d}^{-1}$) is observed during post monsoon i.e. late September–October (Ram et al., 2003). Using Redfield ratio the calculated nutrient demand and percent contribution of benthic supply is presented in Table 3. Lowest nutrient demand is observed during April and benthic nutrient fluxes supplies 10.3% of N, 16.8% of P and 30% of Si required for primary production. During July nutrient demand increases owing to higher productivity and the released NH_4^+ , PO_4^{3-} and SiO_4^{4-} to the overlying suboxic water can potentially meet 14.4% of N demand of algal community with similar P and Si contribution from sediments. With progressive intensification of low oxygen condition, the release of Fe bound P would increase and peak in sulfidic condition during October. Nutrient demand remains moderate during this time and benthic supply would meet 13.7%, 40.7% and 23.2% of N, P and Si requirement of primary producers respectively (Table 3). NH_4^+ and PO_4^{3-} flux during this period play crucial role in maintaining the pelagic nutrient stock which is efficiently used by non-diatom species dominating this period. Anoxia related enhanced

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PO_4^{3-} flux primes the system with much needed P which along with Fe subsequently triggers N_2 fixing cyanobacterial bloom during late October–early November and February–March (Roy et al., 2011; Parab et al., 2012). N_2 fixation in turn brings new N to this seasonally low NO_3^- shelf waters. Apparently anoxia plays indirect role in maintaining pelagic P inventory. Thus benthic nutrient cycling seems well coupled to the pelagic system in this shelf environment.

4.9 Ecological impact and implications of benthic exchange

Coastal upwelling seems to be the major factor in controlling primary productivity in the shelf waters. The study site not much influenced by river discharge as it far from Mandovi–Zuari river mouth. But the exhaustion of upwelled NO_3^- by denitrification (Naqvi et al., 2000) and algal uptake leads to NO_3^- limiting condition during late monsoon. However, significant benthic fluxes of NH_4^+ and PO_4^{3-} during this anoxic period sustain primary production in the overlying water column. Benthic released NH_4^+ escapes nitrification and accumulates in the anoxic bottom water which apparently causes a shift in phytoplankton composition during October. Though SiO_4^{4-} flux remains significant, this NO_3^- depleting and NH_4^+ rich subsurface water favors preferential proliferation of non-diatom species such as dinoflagellates during late monsoon (Naqvi et al., 2006). Benthic release of NH_4^+ , PO_4^{3-} and SiO_4^{4-} remains most important during non-upwelling oxic regime (November–May) as it enriches the pelagic nutrient inventory especially N stock during N limiting period. Though benthic DIN flux supports 10–13% of pelagic primary production, anoxia induced high PO_4^{3-} flux certainly plays significant role in influencing annual productivity in this seasonally N limited system. As hypothesized by Naqvi et al. (2006) and observed in this study, anoxia related reductive dissolution of Fe-P minerals replete the water column with bioavailable Fe and PO_4^{3-} which is essential for N_2 fixing bacterioplankton. *Trichodesmium* bloom has been frequently observed during fall intermonsoon (Naqvi et al., 2009; Roy et al., 2010) presumably stimulated by the availability of these nutrients. With the onset of northeast monsoon,

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the regenerated NH_4^+ gets nitrified to NO_3^- which along with benthic released SiO_4^{4-} favors repopulation of diatoms. By February, NO_3^- gets used up by algal uptake but the system still remains PO_4^{3-} replete owing to prior non-Redfieldian release of NH_4^+ and PO_4^{3-} during anoxia leading to secondary bloom of *Trichodesmium* during spring intermonsoon. Slower benthic mineralization during anoxia indicates higher preservation of organic carbon (Henrichs and Reeburgh, 1988; Hartnett et al., 1998) and burial in the sediments thereby giving a negative feedback to oceanic CO_2 emission.

H_2S released during anoxia creates unfavorable condition for benthic fauna, demersal fishes and other larger organisms living in the bottom waters. However it leads to proliferation of sulfur bacteria e.g. *Thiobacillus denitrificans* (Krishnan et al., 2008) which mediates sulfide oxidation by NO_3^- at the sediment-water interface during late August–early September thereby negating the toxic effect of H_2S atleast for a month before the observed sulfidic event and aggravating NO_3^- loss. It is possible that NH_4^+ generated in the anoxic subsurface water and sediments diffuses upward, undergoes nitrification at the oxic-anoxic interface and subsequent denitrification driven by sulfide. Higher denitrification rate due to the coupled nitrification-denitrification process has been substantiated experimentally by Krishnan et al. (2008).

Continental shelf of western India exhibits spatial heterogeneity on the context of sediment texture (Rao and Wagle, 1997). Soft (silty clayey) sediments dominate the inner shelf where as coarse, permeable (sandy) sediments mainly comprise the outer shelf (Jacob et al., 2009). Benthic respiration and nutrient flux rates in the sandy sediments could be inconsistent with the values from the silty clayey sediments (Janssen et al., 2005; Rao et al., 2007) in this region and that remains a subject of future research. Thus considering the spatial heterogeneity of benthic realm, the present study does not tend to represent the entire western Indian shelf, but nevertheless it depicts a decent picture of benthic exchange of biogenic elements and pelagic-benthic coupling in response to changing oxygen regime in the organic rich nearshore environment of eastern Arabian Sea.

5 Conclusions

Seasonally developing contrasting oxygen regime exerts profound effect on the benthic exchange of essential nutrients and benthic respiration. During oxic condition 58 % of upward diffusing NH_4^+ gets lost in coupled nitrification-denitrification in the sediments, 16 % fluxes out as NO_2^- and NO_3^- and 24 % is released as NH_4^+ . Benthic nitrification occurs at a rate of $2.55 \text{ mmol m}^{-2} \text{ d}^{-1}$ of which 77 % remains coupled to denitrification. Sediment remains a net perennial source of DIN with release rate of $1.6 \text{ mmol m}^{-2} \text{ d}^{-1}$ during oxic condition which progressively increases to $3.21 \text{ mmol m}^{-2} \text{ d}^{-1}$ during October and NH_4^+ comprises 59–100 % of released DIN. Benthic denitrification causes benthic NO_3^- loss at a rate of $1.04 \text{ mmol m}^{-2} \text{ d}^{-1}$ during suboxia. Released sulfide presumably gets oxidized by NO_3^- and NO_2^- at the sediment-water interface by chemolithoautotrophs such as *Thiobacillus denitrificans* and causes NO_3^- loss to N_2 with intermediates mainly N_2O . This sulfide driven denitrification can potentially cause N loss at a rate of $3.21 \text{ mmol m}^{-2} \text{ d}^{-1}$ during anoxia. Shelf sediments behave as NO_3^- source during April but turns into a NO_3^- sink during June–October. PO_4^{3-} flux increases by > 4 fold during anoxia owing to possible reductive dissolution of FeOOH-P minerals in sediments. Organic carbon is mineralized at a rate of $63.83 \text{ mmol C m}^{-2} \text{ d}^{-1}$ during premonsoon, but reduces by 25 % during October apparently due to lower temperature, absence of benthic fauna and slower oxidation of refractory organic matter under anoxia, lower temperature and absence of benthic activity. C_{org} equivalent of 70 % of PP is remineralized in shelf sediments during oxic period but it reduces to 30 % during anoxia. Benthic fluxes of DIN, PO_4^{3-} and SiO_4^{4-} potentially contributes to 10 %, 16 % and 30 % of N, P and Si respectively needed for primary production during premonsoon period and 13 % of N, 40 % of P and 23 % of Si during late monsoon period. Thus at least 10–13 % of phytoplankton production is sustained by benthic nutrient supply on annual scale.

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Table 1. Details of the sediment-water flux incubations done in Oct 2005 and Apr 2006.

Experiment no.	Month	Mode of Incubation	Description	Duration (hour)
1	Oct	Anaerobic	N ₂ purged overlying water + sediment	48
2	Oct	Anaerobic	Overlying water + sediment	56
3	Oct	Anaerobic	NO ₃ ⁻ enriched overlying water + sediment	48
4	Apr	Aerobic	Aerated overlying water + sediment	48
5	Apr	Aerobic/ Anaerobic	Aerated overlying water + sediment for first 24 h and then Anaerobic overlying water + sediment	84
6	Apr	Anaerobic	NO ₃ ⁻ enriched overlying water + sediment	48

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Table 2. Sediment-water flux values at G5, off Goa during Apr and Oct. All values are in $\text{mmol m}^{-2} \text{d}^{-1}$.

Parameter	Incubation	Apr		Oct	
		Measured flux	Diffusive flux	Measured flux	Diffusive flux
O ₂ NO ₃ +NO ₂	Anaerobic	66.46 ± 2.49	– *	47.826 ± 0.36	– *
	Aerobic	0.571 ± 0.01			
	Anaerobic	–0.583, –1.047	–0.071	–0.527 ± 0.05, –3.216	0.277
NH ₄	Aerobic	0.835 ± 0.08			
	Anaerobic	3.387 ± 0.23	2.474	3.745 ± 0.36	3.477
PO ₄	Aerobic/Anaerobic	0.143 ± 0.05	0.03		0.046
	Anaerobic			0.594 ± 0.06	
SiO ₄	Aerobic/Anaerobic	3.839 ± 0.39	0.577		
	Anaerobic			5.093 ± 1.0	0.625
H ₂ S	Anaerobic	0.00	– *	2.832 ± 1.28	– *
N ₂ O	Anaerobic	0.01045	– *	0.00885	– *

* Pore water profile could not be obtained.

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Table 3. Seasonal variation in benthic turnover time, nutrient demand and percent contribution of benthic nutrient flux to primary production (PP) at G5.

Month	Intgrated PP (mmolCm ⁻² d ⁻¹) ^a	Benthic turn over time (day)			Nutrient demand (mmolm ⁻² d ⁻¹)			Contribution of flux to PP (%)		
		DIN	PO4	SiO4	DIN	PO4	SiO4	DIN	PO4	SiO4
Apr	90.3	66.9	165.2	29.7	13.63	0.85	12.77	10.32	16.82	30.06
Oct	154.7	24.1	91.6	136.1	23.35	1.459	21.89	13.78	40.71	23.27

^a data taken from Ram et al. (2003).

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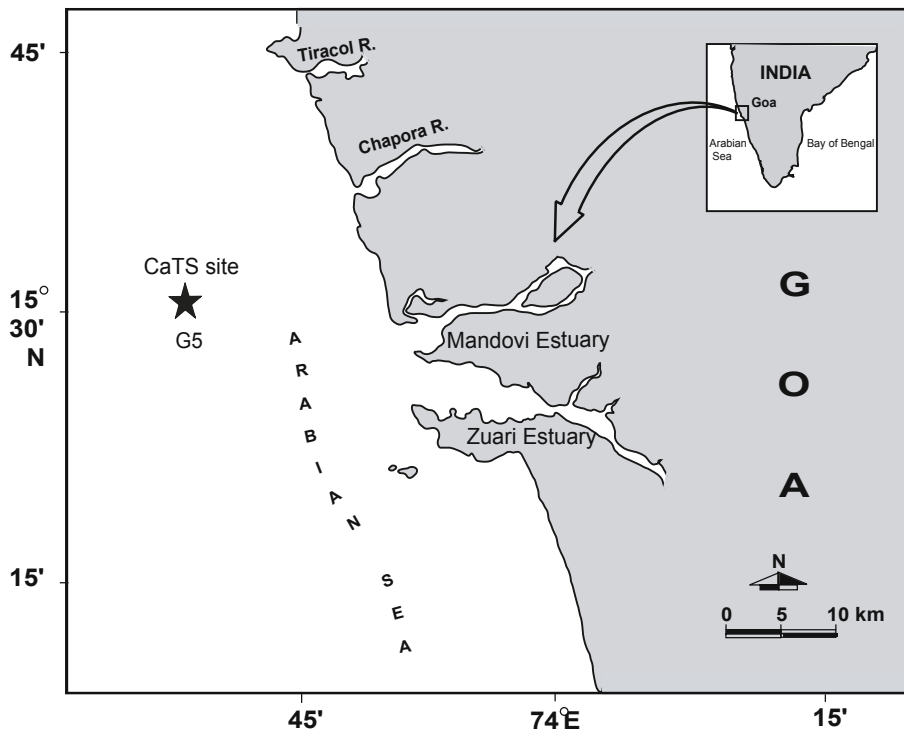


Fig. 1. Location of the study area along west coast of India.

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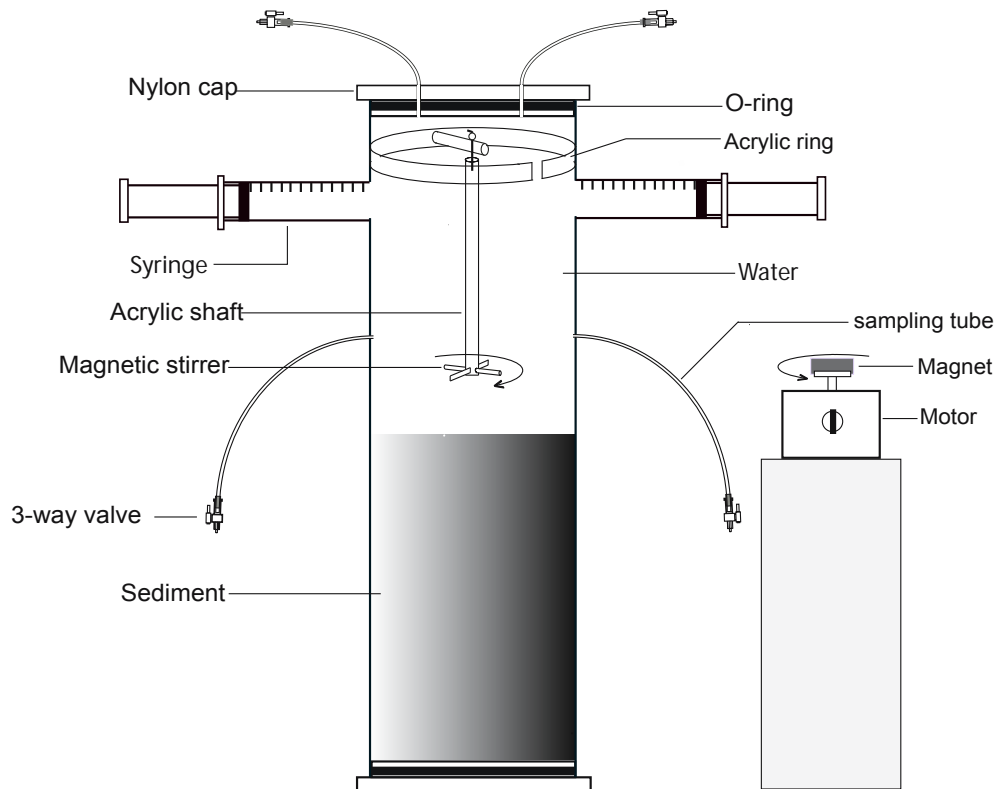


Fig. 2. Experimental design for the intact core incubation.

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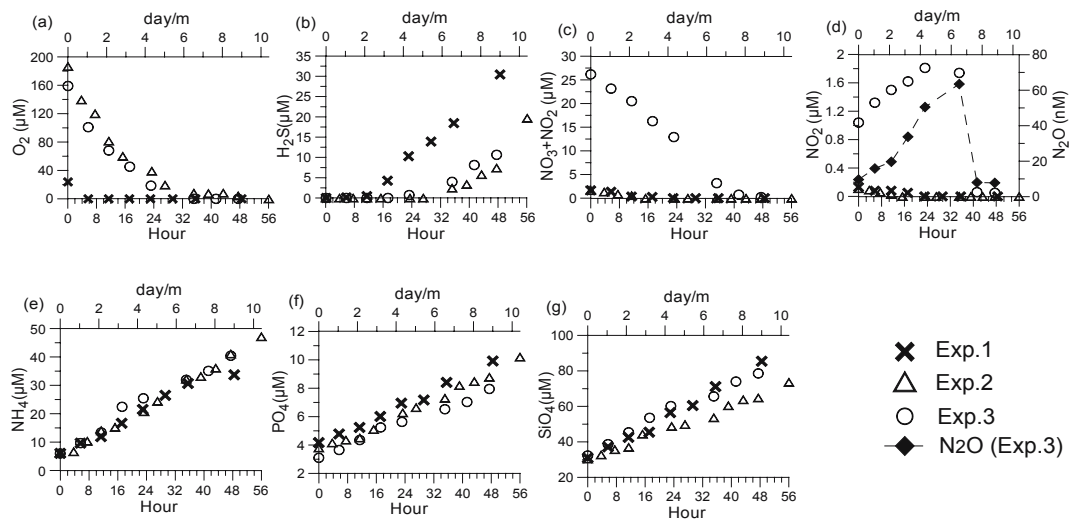


Fig. 3. Variation of parameters with time in the incubation during October.

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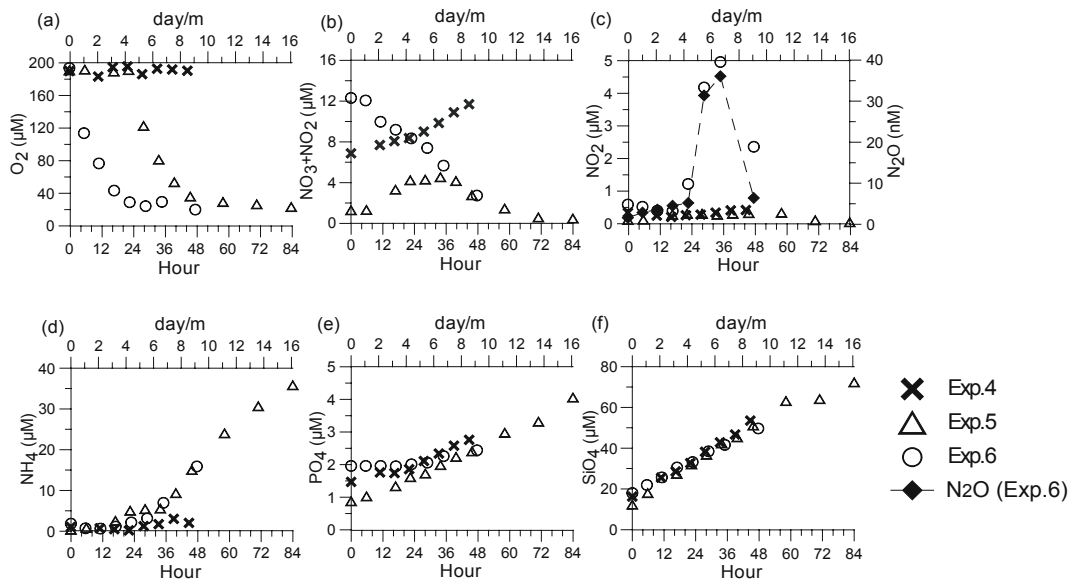


Fig. 4. Variation of parameters with time in the incubation during April.

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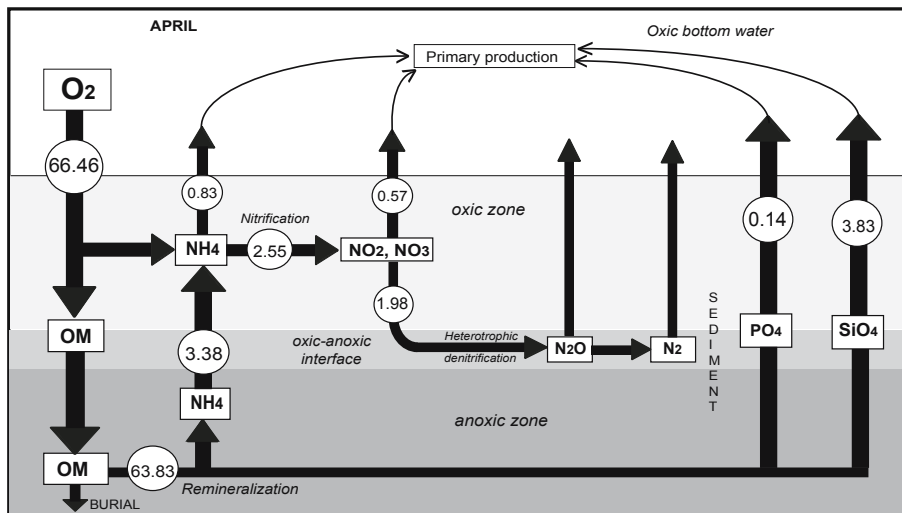


Fig. 5a. Sedimentary oxygen consumption and nutrient exchange during oxic regime. All the flux values are in $\text{mmol m}^{-2} \text{d}^{-1}$.

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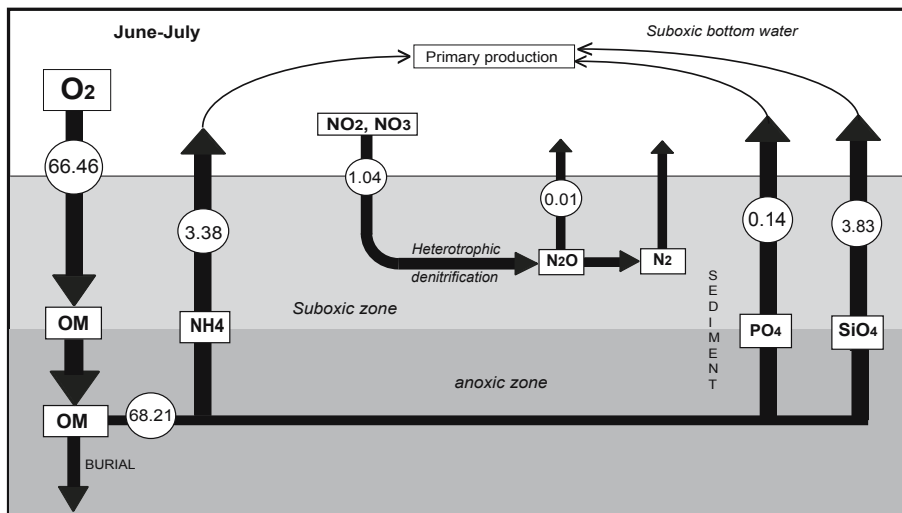


Fig. 5b. Sedimentary oxygen consumption and nutrient exchange during suboxic period. All the flux values are in $\text{mmol m}^{-2} \text{d}^{-1}$.

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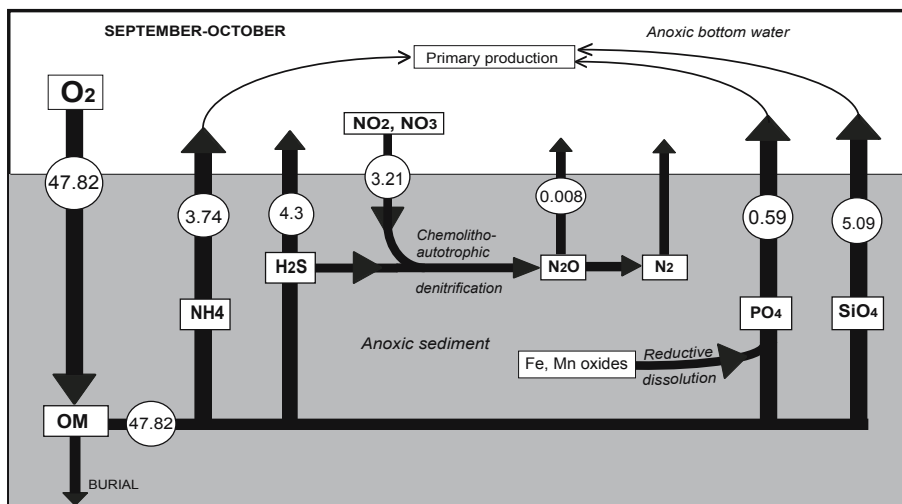


Fig. 5c. Benthic oxygen consumption and nutrient exchange during anoxic regime. All the flux values are in $\text{mmol m}^{-2} \text{d}^{-1}$.

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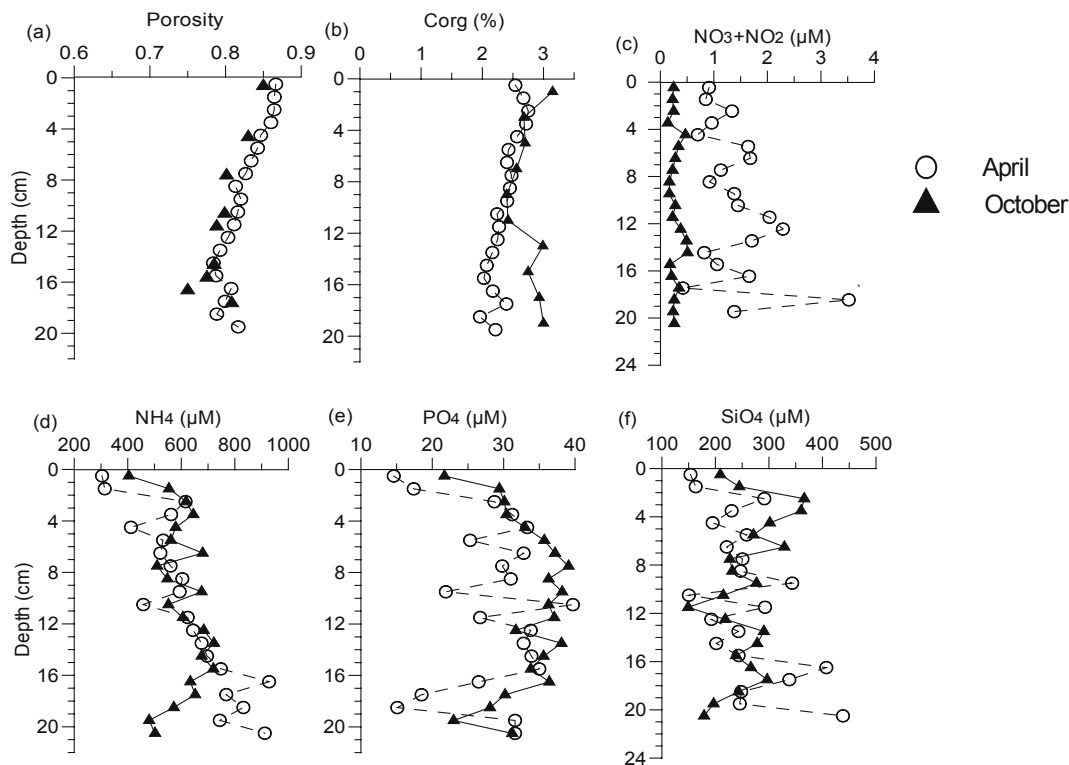


Fig. 6. Seasonal variability in profiles of porosity, sedimentary C_{org} and pore water nutrients at G5, off Goa.

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