



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 the most productive coastal systems of the world ocean. This system experiences extreme changes in its oxygen regime, being normoxic from November to May and suboxic (denitrifying)/anoxic from June to October, owing to the biogeochemical response to cyclical monsoonal influence. In order to understand the impact of the seasonally varying oxygen regime on benthic mineralization, nutrient exchange and, in turn, on the shelf ecosystem, we carried out the first ever intact-core incubations during two contrasting seasons – spring intermonsoon and fall intermonsoon (late southwest monsoon) at a 28 m-deep fixed site on the inner shelf off Goa, dominated by fine-grained cohesive sediments. The results showed that incomplete sediment oxygen consumption (SOC) occurred during April as opposed to the complete SOC and subsequent sulfide flux observed in the fall intermonsoon incubations. The sediments acted as a perennial net source of DIN (dissolved inorganic nitrogen i.e. $\text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+$), PO_4^{3-} and SiO_4^{4-} to the overlying water column. The efflux of DIN increased from 1.4 to 3.74 $\text{mmol m}^{-2} \text{d}^{-1}$ from April to October, of which NH_4^+ flux comprised 59–100%. During the oxic regime, ~75% of diffusing NH_4^+ appeared to be nitrified (2.55 $\text{mmol m}^{-2} \text{d}^{-1}$), of which ~77% remained coupled to benthic denitrification. Consequently, 58% of NH_4^+ flux was lost in active coupled nitrification–denitrification, resulting in substantial N loss (1.98 $\text{mmol m}^{-2} \text{d}^{-1}$) in the sediments. The continental shelf sediments switched over from being a NO_3^- source during the oxic regime to a NO_3^- sink during the anoxic regime. During suboxia, benthic denitrification that is fed by NO_3^- from the overlying water caused N loss at the rate of 1.04 $\text{mmol m}^{-2} \text{d}^{-1}$. Nitrogen

loss continued even under sulfidic conditions during October, possibly through the chemolithoautotrophic denitrification, at a potential rate of 3.21 $\text{mmol m}^{-2} \text{d}^{-1}$. Phosphate 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 increased during October apparently due to the higher availability of siliceous ooze from diatom blooms commonly occurring in the monsoon season.

Slow oxidation of organic carbon (C_{org}) under anoxia, lower temperature and reduced benthic faunal activity appeared to decrease benthic mineralization by 25% as suggested by the drop in the C_{org} oxidation rate from 63.8 $\text{mmol C m}^{-2} \text{d}^{-1}$ in April to 47.8 $\text{mmol C m}^{-2} \text{d}^{-1}$ in October. This indicated a higher preservation of C_{org} during the late southwest monsoon. Sediment porosity, C_{org} content and nutrients did not show significant variations from April to October. Porewaters were found to be enriched with NH_4^+ , PO_4^{3-} and SiO_4^{4-} but depleted in NO_3^- and NO_2^- in these organic-rich sediments. Significant DIN, PO_4^{3-} and SiO_4^{4-} effluxes indicate the potential of benthic input in meeting nutrient demand of the phytoplankton community in this seasonally N-limited shelf system.

1 Introduction

Nutrients form the basis of the marine food chain, as their availability is essential to the primary production. Balance between uptake and regeneration is necessary for the maintenance of the pelagic nutrient stock and, in turn, for the functioning of the marine ecosystem. In tropical and

subtropical open oceans, most of the photosynthetically produced organic matter is lost to greater depths and the entrainment of remineralized nutrients is largely prevented by the thermocline during most parts 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 (Jahnke, 1996) compared to that in open oceans. The consequent organic matter enrichment of underlying sediments triggers intense geochemical, microbial and benthic faunal activities, which control organic carbon oxidation/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), nutrifies the sedimentary pore water, and over time 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., 2011), flow-induced advective pore water transport (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 of 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 fishery resources (Pauley et al., 2002), thereby sustaining the livelihoods of millions of people worldwide. In the world ocean, 80 % of the organic carbon burial (Naqvi and Unnikrishnan, 2009) and 83 % of sedimentary remineralization (Jørgensen, 1983) take place in shelf sediments. Conspicuously, benthic–pelagic coupling is important in the biogeochemical cycling of C, O, N, P and Si in shelf environments. Benthic regeneration of essential macro- and micronutrients, and their fluxes to the overlying pelagic realm, play a 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 CO_2 fixation and carbon burial, and ultimately impacts the global climate.

Seasonal anoxia is a characteristic biogeochemical feature of the 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. It is considered as a biogeochemical hotspot in the world ocean due to the recent intensification of O_2 deficiency and the possible implications thereof for nitrogen cycling and feedback to global climate (Naik and Naqvi, 2006; Naqvi et al., 2009). The western Indian shelf is one of the

most productive regions of the Arabian Sea, owing to nutrient enrichment through monsoonal upwelling (Shetye et al., 1990) and land/river runoff during the southwest monsoon season (June–September) (Naqvi et al., 2000, 2006), nitrogen fixation during the 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 over the course of a year: the shelf water column remains oxygenated from November to May and becomes suboxic/anoxic during July–October. Hypoxia ($O_2 \leq 62.5 \mu M$; Levin et al., 2009) starts in June, followed by suboxia (denitrifying condition, $O_2 \leq 4.46 \mu M$; see Naqvi et al., 2010, and references therein) during July–August and often by anoxia (sulfidic condition; Naqvi et al., 2010, and references therein) during September–October (Naqvi et al., 2006). However, anoxia (sulfidic condition) remains limited only to the nearshore region of the shelf and is not a regular occurrence (e.g., years 1997, 2000, 2003 and 2007). Longitudinal coexistence of hypoxia, suboxia and anoxia¹ over the shelf in the late monsoon season (Naqvi et al., 2006) makes it a unique biogeochemically active region in the world ocean. Though the 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 the total N_2O emission from this basin (Naqvi et al., 2000). However, benthic metabolism, sedimentary nutrient cycling and benthic–pelagic coupling, which could exert a profound influence on the shelf ecosystem, have not been assessed so far. Naqvi et al. (2006) hypothesized that anoxia during the late southwest monsoon would culminate in the dissolution of sedimentary ferric oxyhydroxide minerals and lead to the release of Fe-bound phosphate to the overlying water. The mobilized PO_4^{3-} , along with other inorganic nutrients (e.g., NH_4^+), is extensively taken up by the phytoplankton community (e.g., dinoflagellates) and later by N_2 fixers during the spring intermonsoon (February–March). This indicates the potential of benthic supply to meet the nutrient demands of the phytoplankton community, and thus benthic–pelagic coupling needs to be evaluated. The sediments over the continental shelf experience a wide range of physico-chemical conditions (temperature, dissolved O_2 concentration and nutrient loading) and receive varying quantities of organic matter from the surface over the course of a year. The rate of benthic respiration (supported by various electron acceptors (i.e., O_2 , NO_3^- , MnO_2 , Fe oxides and SO_4^{2-}) and nutrient ex-

¹As per our consideration:

Hypoxic: dissolved $O_2 \leq 62.5 \mu M$ (Levin et al., 2009);

Suboxic: dissolved $O_2 \leq 4.46 \mu M$, NO_3^- , $NO_2^- > 0 \mu M$, $H_2S = 0 \mu M$ (Naqvi et al., 2010);

Anoxic: dissolved $O_2 = 0 \mu M$, NO_3^- , $NO_2^- = 0 \mu M$, $H_2S > 0 \mu M$ (Naqvi et al., 2010).

The term *anaerobic* was used in the text to represent low-oxygen conditions (below hypoxic threshold) in general.

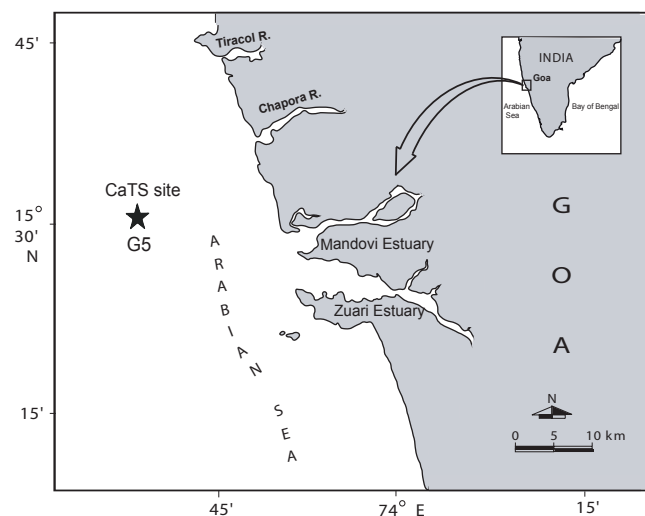


Figure 1. Geographical location of the studied site (G5) over the western continental shelf of India.

changes are thus expected to undergo large seasonal changes, not observed in other areas of the global ocean.

In the present study, we have tried to simulate the natural conditions using ex-situ incubations at a fixed 28 m deep site on the inner shelf during two contrasting seasons. The aim of this study was to assess the impact of varying O_2 regime on benthic respiration, C_{org} mineralization and nutrient fluxes over the inner continental shelf. Although 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 Indian shelf. We hypothesize that the benthic input has the potential to meet the nutrient demand of the phytoplankton community in the shelf ecosystem, especially during the nitrogen-poor, non-upwelling period (October–May).

A large portion (~66%) of the western Indian shelf (i.e., outer shelf) is covered by sandy, C_{org} -poor and reactive permeable sediments, whereas cohesive (silty-clayey) sediments dominate the inner shelf. The benthic respiration, C_{org} mineralization and nutrient fluxes in permeable sediments can be radically different from those observed in cohesive sediments (Janssen et al., 2005; Rao et al., 2007; Cook et al., 2007). Our results are based on the flux measurement at a fixed study site on the inner shelf where the sediments are cohesive in nature. We do not intend to extrapolate our findings to the entire western shelf considering uncertainties associated with substantial spatial heterogeneity in C_{org} and granulometric composition across the shelf; rather, we confine our results and inferences only to the inner shelf environments.

Study site

Our study site (G5) is located at $15^{\circ}31'N$ and $73^{\circ}39'E$, ~10 km off Candolim, Goa, on the central west coast of India (Fig. 1) at a depth of 28 m. It lies on our regularly studied shelf transect that has been studied monthly or fortnightly since 1997 under the ongoing Candolim Time Series (CaTS) program. Physical, chemical and biological parameters (e.g., temperature, salinity, O_2 , H_2S , N_2O , CH_4 , pH, nutrients, chlorophyll, primary productivity, phytoplankton community and bacterial counts) are monitored under this program.

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. Due to the unique hydrographical and biogeochemical changes induced by the southwest monsoon, a reducing condition develops over the inner shelf that gradually extends to the mid-shelf north of $12^{\circ}N$ (Naqvi et al., 2006). Dissolved O_2 progressively decreases to $<4\mu M$ in July/August in subsurface and bottom waters. The system is initially buffered by high nitrate concentrations (~ $20\mu M$) and it requires approximately one month before nitrate is fully denitrified and the system becomes truly anoxic (i.e., sulfate-reducing). During peak suboxia, NO_2^- accumulates up to $6\mu M$, coinciding with high N_2O (180 nM). During the transition from suboxic to anoxic conditions (late August/early September), N_2O has been found to accumulate in the water column in record high concentrations (~ $0.8\mu M$; Naqvi et al., 2000). As anoxia intensifies during late September–October, O_2 falls below the detection limit, the subsurface and bottom waters turn sulfidic ($7\mu M H_2S$) and NO_3^- - and NO_2^- -depleted but enriched in NH_4^+ ($8\mu M$) and PO_4^{3-} ($2.17\mu M$) (Naqvi et al., 2006). However, substantial interannual variability in the duration and intensity of the O_2 deficiency has been observed (Naqvi et al., 2009). The intensity of the O_2 deficiency also varies both longitudinally and latitudinally at a given time. The western continental shelf is perhaps the only region where all three types of redox environments – i.e., normoxia, suboxia and anoxia – co-occur over the same segment of the shelf with such regularity. However, the sulfidic conditions that develop in the late monsoon are a recent phenomenon presumably caused by the recent intensification of O_2 deficiency on account of increased atmospheric DIN deposition and/or anthropogenic fertilizer runoff from land (Naqvi et al., 2006). During the northeast monsoon (November–February), the prevailing West India Coastal Current causes downwelling, which reoxygenates the water column over the shelf, thereby re-establishing the oxic regime that continues until May. Further details of seasonal variation in physical and biogeochemical features of this region have been provided by Naqvi et al. (2006, 2009).

The western Indian shelf covers an area of $310\,000\text{ km}^2$, of which the inner shelf (up to a depth 55–60 m) comprises ~33% (Mallik, 2008). The inner shelf sediments are mainly

fine-grained silty clays that contain, in general, 1–4 % organic carbon (Rao and Wagle, 1997). Sediments in the northern part (north of 13° N) of the inner shelf are composed of 61 % silt, 21 % clay and 18 % sand. The transect at 15° N (close to the CaTS transect) in particular is dominated by fine-grained particles (~72 % silt and ~27 % clay) and has been found to be organic-rich (3.2 % C_{org}), with ~22 % labile organic matter (carbohydrates and proteins) (Jacob et al., 2008). The outer shelf (at depth > 60 m) occupies around two-thirds of the total area (Mallik, 2008). Organic-poor ($C_{\text{org}} < 1\%$), coarse, sandy sediments dominate the outer shelf region (Rao and Wagle, 1997; Jacob et al., 2008). The sedimentation rate over the inner shelf (at 45 m depth, off Goa) has been found to be 1.5 mm yr^{-1} (Kurian et al., 2009). The C:N ratios and $\delta^{13}\text{C}$ values suggest that the organic carbon is of marine origin (Agnihotri et al., 2008). At a 30 m deep location (off Goa) on the inner shelf, Jayaraj et al. (2007) observed benthic fauna such as polychaetes, crustaceans, mollusks and others, of which polychaetes comprised 83 %. At a 43 m deep site (off Bhatkal) on the inner shelf, Ingole et al. (2010) also reported 43 taxa of benthic fauna such as polychaetes, crustaceans, oligochaetes, of which polychaetes comprised 85–95 %. Both these locations were dominated by silty-clayey cohesive sediments.

2 Materials and methods

2.1 Incubation method

Over the last couple of decades, benthic respiration and nutrient fluxes have been measured mainly by benthic chambers/landers (in-situ) or by intact-core incubations (ex-situ) over continental shelf environments. Separating a sediment section from its natural setting may affect benthic faunal activity. The turbulence created within a chamber/lander or incubation core may differ from that found under natural conditions which may in turn change the thickness of the benthic boundary layer and O_2 penetration depth, thereby affecting the flux rates. Though in-situ incubation has been preferred over whole-core incubation in some cases (e.g., Hammond et al., 1985; Devol and Christiansen, 1993; Jahnke et al., 2000; Berelson et al., 2003), reliable flux data have been obtained through the latter method (e.g., Rysgaard et al., 1998; Hopkinson et al., 2001; Jahnke et al., 2005; Faganeli and Ogrinc, 2009; Lehrter et al., 2012) over continental shelves. Comparative studies such as those carried out by Miller-Way et al. (1994), Hammond et al. (2004) and Woulds et al. (2009) show that benthic fluxes measured through the chamber/lander and the intact-core incubation method in shallow marine environments such as continental shelves are similar in magnitude and direction with minimal systematic difference, even under anaerobic conditions, with only few exceptions. Apart from NO_2^- and PO_4^{3-} fluxes, Miller-Way et al. (1994) did not observe significant variability

of nutrient fluxes between the in-situ and ex-situ incubation over the Louisiana shelf. They attributed these differences to the increase in O_2 in the overlying water upon core recovery rather than to the inherent differences in two methodologies. They also argued that the differences in the in-situ and ex-situ methodologies cannot be solely attributed to the removal of sediment cores from sea bottom. Hammond et al. (2004) observed variability of fluxes between two methods over the outer shelf and near-anoxic slope on the California margin. Interestingly, they observed a similar degree of variability of fluxes within the replicate measurements in the case of both in-situ and ex-situ methods. This apparently shows the overriding effect of patchiness in causing the variability of fluxes rather than the methodological difference. Over the slope (nearly anoxic) of the Pakistan margin, Woulds et al. (2009) reported considerable differences in some nutrient fluxes through both the methods that were attributed to O_2 contamination in the whole-core incubations. However, significant differences in fluxes may appear in deeper environments (e.g., continental slope and abyssal plain), due to pressure effects on benthic microbial and faunal community metabolism. Due to logistic limitations, we chose to carry out a series of laboratory-based intact-core incubations as suggested by Hammond et al. (2004) while taking precautions to prevent O_2 contamination.

2.2 Sample collection

The sampling was carried out at station G5 during October 2005, when the bottom water was anoxic, and again in April 2006, when the water column was oxic. Water samples were collected at different depths for dissolved O_2 , H_2S , N_2O and nutrients using a 5 L Niskin sampler. Temperature and salinity were recorded by a Sea-Bird CTD profiler. The vertical profiles of the above parameters at this site are described in Naqvi et al. (2009). Bottom water (10 L) was also collected and kept in the dark at 4 °C, to be used for the core incubations.

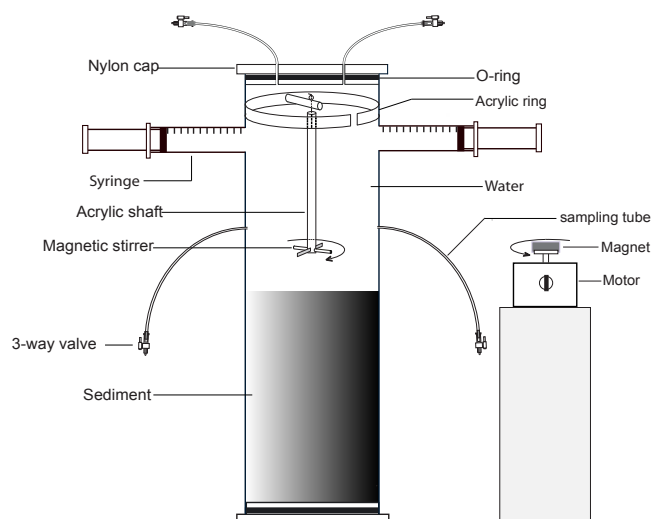
For the incubation experiments, a sediment core was collected with minimal disturbance by divers using specially designed core liners (see Sect. 2.3). Three additional sediment cores, one each for determination of porosity, C_{org} and pore water nutrients, were collected in 6.4 cm inner diameter (ID), 30 cm long acrylic core liners by means of a gravity corer. The core for pore water was covered with aluminum foil within 5–10 min of collection. The headspace was flushed with N_2 for 5 min (only during October), and the core was kept at 4 °C until pore water extraction. Burrows created by benthic fauna were conspicuous on the sediment surface during April, but no burrows were noticed during October.

2.3 Experimental setup

Specially fabricated acrylic core liners (ID 10.1 cm, length 48 cm, thickness 0.5 cm) were used for the experiment

Table 1. Details of the sediment–water flux incubations done in October 2005 and April 2006 at station G5, off Goa.

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

**Figure 2.** Experimental design for the intact-core incubation.

(Fig. 2). The core liners were fitted with nylon caps at both the ends. The top nylon cap was attached to two 1.5 mm ID Teflon tubes through the holes, which was further attached to three-way Leur locks. The caps had nylon O rings to make the liners completely airtight. Two more Teflon tubes were attached through the holes roughly at the center of the liners. One was used to pass air in the case of aerobic incubation and the other one was used for drawing water sample using a syringe. Two 60 mL syringes were 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 insulating tape. The syringes were tested for O₂ permeability before they were cut and fitted into the core liner. They were wrapped with tape, filled with low-oxygen water and kept in the dark for 5 days. Oxygen levels were 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 sedi-

ment 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.

2.4 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. After 2–3 h, the core was transferred to a temperature-controlled room. Later, when the suspended particles had settled (~ 1–2 h), the overlying water was carefully siphoned off without disturbing the surficial sediment. Fresh bottom water was slowly introduced over the sediment with minimal resuspension, and the core was preincubated in the dark at in-situ temperature (± 0.5 °C) for 12 h in order to acclimatize it to the laboratory conditions. During October, the preincubation was done anaerobically as the in-situ bottom water was anoxic; however, during April it was done aerobically to match the prevailing oxic condition of the bottom water at station G5. Three incubations each in October and April were carried out as listed in Table 1.

- (i) *Anoxic incubations in October.* After preincubation of the sediment core, the overlying water was siphoned out and replaced with fresh bottom water (brought to laboratory temperature). The top was covered with the cap, the valves were closed and the incubation was started. As explained earlier, the incubations were done anaerobically. In experiment 1, the core was kept airtight and the overlying water was purged with N₂ for 30 min to remove O₂ before the start of incubation. The incubation was carried out for 48 h. In experiment 2, the overlying water was not N₂ purged but the core was kept airtight and incubated for 56 h. Experiment 3 was done in a way similar to experiment 2 but with NO₃⁻-spiked fresh bottom water as overlying water and incubated for 48 h. Since the bottom water at station G5 remained NO₃⁻-depleted during this time, it was necessary to enrich the overlying water with NO₃⁻ to quantify benthic N loss. To begin with, the overlying water in

experiments 2 and 3 was oxic; however, anoxia developed after 24–36 h with the O₂ concentration decreasing substantially or going below detection, followed by H₂S accumulation. Conditions became similar in experiment 1 (after 6 h), experiment 2 (after 36 h) and experiment 3 (after 24 h), and fully anoxic incubation conditions were thereby replicated within portions of the three experiments.

- (ii) *Aerobic and anaerobic incubations in April.* Since the bottom water during April was well oxygenated at the site, the core was successively incubated both aerobically and anaerobically. In experiment 4, the overlying water was aerated continuously by bubbling air through the tubing fixed at the center 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 the valves on the cap at the top was kept open to release the excess pressure created in the headspace due to the air influx and the core was incubated for 48 h. In experiment 5, the core was incubated aerobically during the initial 24 h, similar to experiment 4, and, later, made airtight and incubated anaerobically for another 60 h in order to study the effect of progressive shift from aerobic to anaerobic conditions on benthic exchange. Experiment 6 was conducted anaerobically up to 48 h but using NO₃⁻-enriched fresh bottom water. Aerobic incubation was replicated by maintaining similar conditions in both experiment 4 and the first 24 h of experiment 5. Similarly, anaerobic incubation was also replicated when conditions became comparable during the last 60 h of experiment 5 and experiment 6. The animal burrows remained intact, and some live benthic fauna were seen throughout the aerobic incubations.

2.5 Sampling and analysis

The overlying water was sampled every 4–6 h with a 5 mL glass or plastic syringe through a tube attached to the middle portion of the core liner. As the sample was drawn, the plunger of the fixed syringe (on the upper part of the liner) was slowly pushed inward simultaneously so as to replace the withdrawn sample. Samples for dissolved O₂ were collected in a He-flushed 5 mL Hamilton gastight syringe, and fixed immediately by adding 100 µL of each of the Winkler's titration reagent solutions. After 30 min, the oxyhydroxide precipitate was dissolved by adding 200 µL of 50 % H₂SO₄ (Grasshoff et al., 1983). The absorbance was immediately measured at 456 nm (Pai et al., 1993) with a Shimadzu UV-visible spectrophotometer with an analytical/method precision of ±0.03 µM.

Sulfide samples were collected in He-flushed 5 mL Hamilton gastight glass syringes and fixed by adding 100 µL each of the dimethyl-*p*-phenylene diamine and FeCl₃. The ab-

sorbance was measured at 670 nm by spectrophotometer (Grasshoff et al., 1983) with a resulting analytical precision of ±0.05 µM.

Nutrient samples were collected in 5 mL BD plastic syringes and kept at -20 °C for analysis within 48 h. Before analyses the samples were thawed, mixed well and evaluated for NO₃⁻, NO₂⁻, NH₄⁺, PO₄³⁻ and SiO₄⁴⁻ using a SKALAR segmented flow autoanalyzer and colorimetry (Grasshoff et al., 1983) with precisions of ±0.06, ±0.006, ±0.01, ±0.003 and ±0.06 µM, respectively. The bottom water collected during October and April was also analyzed for the nutrients using the above method. During October, NO₃⁻+NO₂⁻, NH₄⁺, PO₄³⁻ and SiO₄⁴⁻ concentrations of the bottom water were 0.08, 5.48, 3.52 and 35.18 µM, whereas during April they were 7.06, 1.09, 1.73 and 12.47 µM, respectively.

Five milliliters of sample for N₂O analysis was collected using He-flushed 10 mL Hamilton gastight syringes in NO₃⁻ amendment experiments and immediately poisoned by adding 100 µL of saturated HgCl₂ solution. Nitrous oxide was analyzed with a Hewlett-Packard gas chromatograph equipped with an electron capture detector following the multiphase analysis method (McAuliff, 1971) with a precision of 4 %.

2.6 Processing of additional sediment cores

For porosity determinations, the cores were sectioned at 1 cm intervals and the slices were immediately weighed. After drying at 110 °C, the dry weight was taken in order to determine the pore water content (*w*). Ten grams of dried homogenized sediment was fully soaked with deionized water in a 25 mL calibrated and weighed bottle after removing the entrapped air bubbles. Porosity (*φ*) was expressed as the ratio of pore water volume to the total volume of sediment (sediment + pore water) and was determined as follows:

$$\phi = (Gxw)/[1 + (Gxw)],$$

where *G* (specific gravity) is (W₂-W₁)/[(W₄-W₁)-W₃-W₂], W₁ the weight of the empty bottle, W₂ = the weight of the bottle with dried sediment, W₃ = the weight of the bottle with sediment and water, and W₄ = the weight of the bottle with water.

For sedimentary C_{org}, the core was sectioned at 1–2 cm intervals and the subsamples were freeze-dried, homogenized and subsequently decalcified using 1N HCl. C_{org} was 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, C₆H₁₅NO₂ - ACA) following Higginson and Altabet (2004). Analytical precision of the analysis was found to be ≤ 2 %. The details of the analytical procedure are given in Agnihotri et al. (2008).

For pore water extraction, the core was sectioned at 1 cm intervals and collected in 50 mL centrifuge tubes inside a N₂-flushed glove box. These were centrifuged at 4000 rpm for

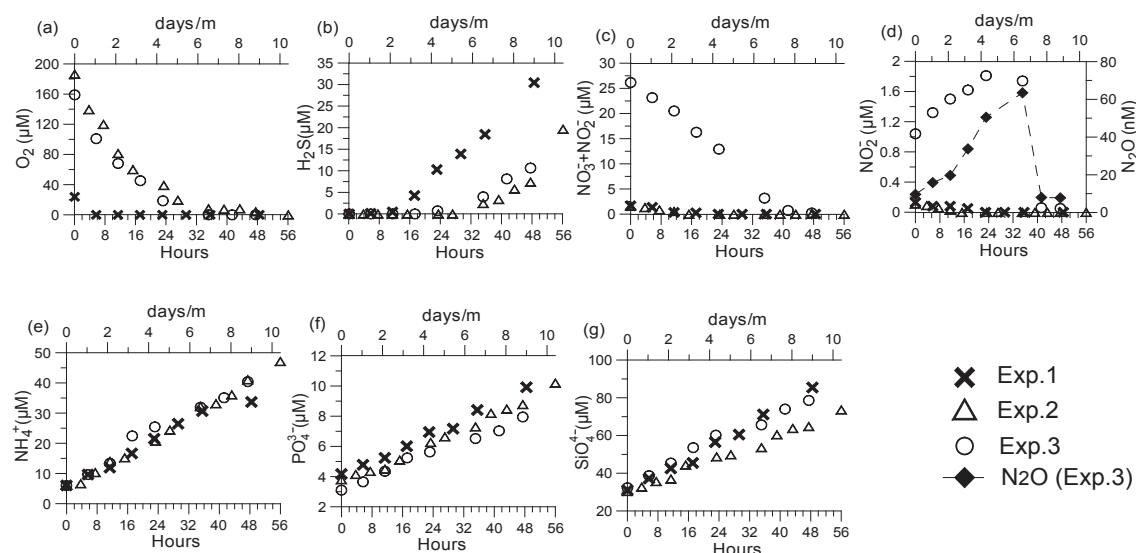


Figure 3. Variation of parameters with the integral of time/water column height (in days/meter) in the incubations during October 2005: (a) dissolved oxygen, (b) H_2S , (c) $\text{NO}_3^- + \text{NO}_2^-$, (d) NO_2^- and N_2O , (e) NH_4^+ , (f) PO_4^{3-} and (g) SiO_4^{4-} .

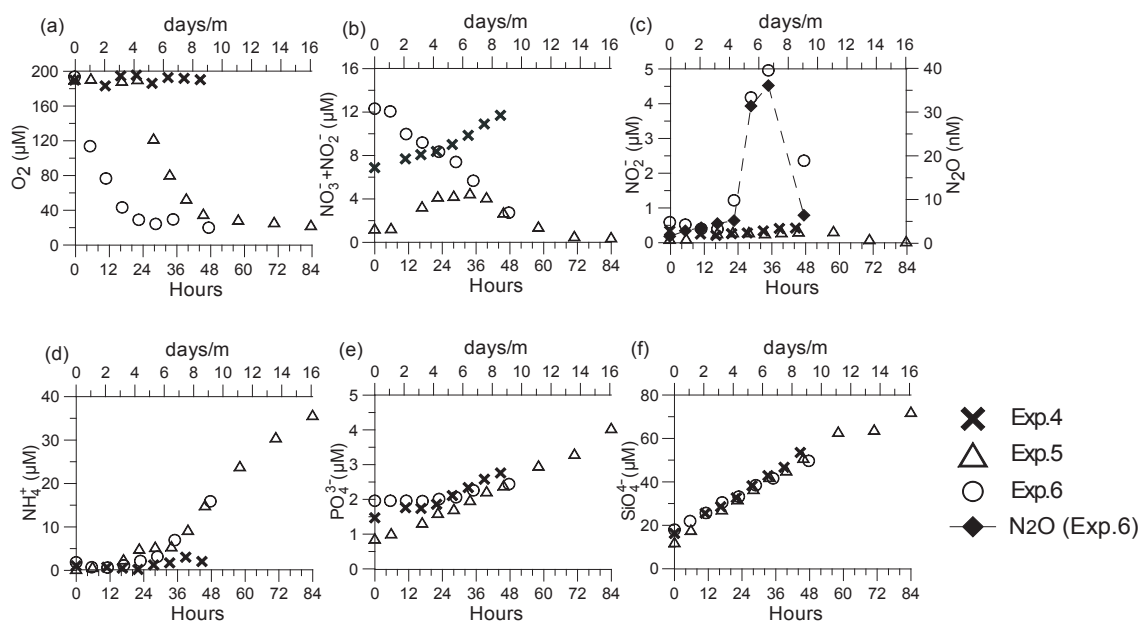


Figure 4. Variation of parameters with the integral of time/water column height (in days/meter) in the incubations during April 2006: (a) dissolved oxygen, (b) $\text{NO}_3^- + \text{NO}_2^-$, (c) NO_2^- and N_2O , (d) NH_4^+ , (e) PO_4^{3-} , and (f) SiO_4^{4-} .

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. The analysis was done within 48 h as described in Sect. 3.4.

2.7 Flux calculation

In the case of intact-core incubations, the appreciable change in volume of overlying water introduces a nonlinearity in concentration change with time that can lead to overestimation of fluxes. Thus, the ratio of time/water column height for each sampling interval was calculated and the concentration in overlying water was plotted against the sum of elapsed time/height for all preceding intervals (Hammond

Table 2. Sediment–water flux rates of dissolved oxygen, nutrients, sulfide and nitrous oxide at station G5, off Goa, during April and October. Mean flux rate was calculated from replicate experiments and the standard deviation is expressed in parentheses. Diffusive fluxes of O₂, H₂S and N₂O are not available as their pore water profiles could not be measured. Positive fluxes denote flux into overlying water from sediment and negative fluxes denote flux into the sediment from overlying water. All values are in mmol m⁻² d⁻¹.

Parameter	Incubation	April		October	
		Measured flux	Diffusive flux	Measured flux	Diffusive flux
O ₂	Anaerobic	-66.46 (±2.49)	-	-47.82 (±0.36)	-
NO ₃ ⁻ + NO ₂ ⁻	Aerobic	0.57 (±0.01)	-0.07		0.27
	Anaerobic	-0.58, -1.04		-0.52 (±0.05), -3.21	
NH ₄ ⁺	Aerobic	0.83 (±0.08)	2.47		3.47
	Anaerobic	3.38 (±0.23)		3.74 (±0.36)	
PO ₄ ³⁻	Aerobic/anaerobic	0.14 (±0.05)	0.03		0.04
	Anaerobic			0.59 (±0.06)	
SiO ₄ ⁴⁻	Aerobic/anaerobic	3.84 (±0.39)	0.57		0.62
	Anaerobic			5.09 (±1.0)	
H ₂ S	Anaerobic	0.00	-	2.83 (±1.28)	-
N ₂ O	Anaerobic	0.01	-	0.008	-

et al., 2004):

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

where F is the flux in mmol m⁻² d⁻¹ and $\partial C / \partial T_h$ is the slope of the plot between concentration and sum of time/height. In the 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 the flux. However, in the case of O₂, 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 the sediment from overlying water. Mean fluxes were calculated from replicate experiments and are presented with standard deviation in Table 2.

A concentration gradient existing between sediment pore water and bottom water results in the molecular diffusion of nutrients across the sediment–water interface. Diffusive flux 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):

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

where F is the diffusive flux in mmol m⁻² d⁻¹, ϕ the porosity of the surficial sediment and $(\partial C / \partial z)_{z=0}$ is the concentration gradient (in mmol m⁻³ m⁻¹) close to sediment–water interface. Depending on the solute profile, $(\partial C / \partial z)_{z=0}$ was calculated differently (Dennis and Grenz, 2003). For NO₃⁻ and NO₂⁻, the concentration difference between bottom water and pore water of the top sediment (0–1 cm) was considered

as the gradient. In the case of NH₄⁺, PO₄³⁻ and SiO₄⁴⁻, the bottom water concentration and pore water concentrations up to 3 cm gave a linear fit ($r^2 > 0.9$) versus depth. Thus, the linear gradient over the upper 3 cm of the sediment was taken as $(\partial C / \partial z)_{z=0}$ for these nutrients.

D_s is the whole sediment diffusion coefficient (m² d⁻¹) after correction for temperature and tortuosity (Krom and Berner, 1980):

$$D_s = D_0 / \theta^2, \quad (1)$$

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 $\theta^2 = 1 - \ln \phi^2$ (Boudreau, 1996). All the flux values are presented in Table 2.

2.8 Statistical analysis

Analysis of variance (i.e., ANOVA) was used to assess the variability of flux patterns between different experiments.

3 Results

3.1 Oxygen consumption rates

Experiment 1 started with 23 μM of O₂ at time zero but rapidly went below the detection limit within 6 h and was not detectable until the end of the experiment (Fig. 3a). However, overlying waters in experiments 2 and 3 were oxic (O₂ > 158 μM) at the beginning but became anoxic after 36 h as O₂ decreased substantially or fell below the detection limit with subsequent sulfide accumulation (Fig. 3a, b). No significant variation ($p = 0.5$) was observed in the O₂ decrease

patterns of experiments 2 and 3, and consistent O_2 flux was observed in experiment 2 ($-48.07 \text{ mmol m}^{-2} \text{ d}^{-1}$) and experiment 3 ($-47.57 \text{ mmol m}^{-2} \text{ d}^{-1}$). Mean fluxes were calculated from replicate experiments and are presented with standard deviation (Table 2).

During April, the overlying water remained oxic ($O_2 > 183 \mu\text{M}$) in experiment 4 (Fig. 4a). Thus, the thin upper oxic layer of the sediment column, as expected, remained intact and did not affect the nutrient exchange. This condition was close to the naturally existing condition during the premonsoon, when the bottom water remains oxygenated ($O_2 > 82 \mu\text{M}$). In experiment 5, O_2 remained almost constant for the first 24 h, decreasing substantially thereafter to $36 \mu\text{M}$ at 48 h and remaining at that level until the end of the experiment (Fig. 4a). In experiment 6, O_2 decreased nonlinearly from 193 to $29 \mu\text{M}$ within 24 h and thereafter remained constant until 48 h (Fig. 4a). A nonlinear decrease in O_2 was also noticed in experiments 2, 3 and 5, similar to observations elsewhere by Sundby et al. (1986), Anderson et al. (1986), Malecki et al. (2004) and Skoog and Arias-Esquivel (2009). These have been attributed to (i) a decrease in the concentration gradient across the benthic boundary layer and (ii) a decrease in the thickness of surficial oxic layer and subsequently a decrease in the number of O_2 -respiring microorganisms (Sundby et al., 1986). The O_2 decrease pattern in experiment 6 did not vary significantly ($p = 0.9$) from that of experiment 5, and the O_2 fluxes observed in experiment 5 ($-64.7 \text{ mmol m}^{-2} \text{ d}^{-1}$) and experiment 6 ($-68.21 \text{ mmol m}^{-2} \text{ d}^{-1}$) were consistent (Table 2). A noticeable feature was that unlike the October incubations, O_2 was not completely consumed and 20–23 μM was still present until the end of incubation.

3.2 Sulfide fluxes

Sulfide accumulated in all the incubations during October. In experiment 1, sulfide was detectable just after O_2 became zero at 6 h and increased at the rate of $4.3 \text{ mmol m}^{-2} \text{ d}^{-1}$ after 12 h (Fig. 3b). In experiment 2, S^{2-} was undetectable until 28 h but increased linearly at the rate of $1.95 \text{ mmol m}^{-2} \text{ d}^{-1}$ up to 48 h and then rose exponentially to $19.67 \mu\text{M}$ (Fig. 3b). Similar flux patterns and rates ($2.24 \text{ mmol m}^{-2} \text{ d}^{-1}$) were also observed in experiment 3 after the O_2 level decreased substantially (Fig. 3b). The variation in S^{2-} flux patterns between these three experiments was statistically insignificant ($p = 0.5$). No sulfide was detected in the overlying water in experiments 4, 5 and 6 (not shown in the figures), which was to be expected, as at least 20 μM of O_2 was still present at the end of the experiment. The absence of benthic sulfide flux during normoxia, as well as sulfide release during anoxia, was also reported 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 and 36 h in experiments 1 and 2, and no NO_2^- buildup was observed (Fig. 3c). In experiment 3, $\text{NO}_3^- + \text{NO}_2^-$ decreased linearly to $0.22 \mu\text{M}$ at the conclusion of the experiment (Fig. 3c), with the NO_2^- peak ($1.8 \mu\text{M}$) coinciding with a prominent N_2O peak (36 nM) at 24 h (Fig. 3d). No significant variation was observed in the NO_3^- and NO_2^- consumption patterns between experiments 1 and 2 ($p = 0.7$). The highest $\text{NO}_3^- + \text{NO}_2^-$ flux ($-3.21 \text{ mmol m}^{-2} \text{ d}^{-1}$) was observed in the NO_3^- -amended experiment (experiment 3, Table 2). No significant variation was observed in the NH_4^+ , PO_4^{3-} and SiO_4^{4-} release pattern between experiments 1, 2 and 3 ($p > 0.05$), and the fluxes were found to be consistent in the three incubations.

During April, N species exhibited different exchange behaviors in aerobic and anaerobic incubations. In experiment 4, NO_3^- increased from 6.5 to $11.24 \mu\text{M}$. Nitrite initially decreased until 18 h and then increased to $0.42 \mu\text{M}$ at the end (Fig. 4b) of the experiment. Similarly, NH_4^+ decreased initially until 24 h and then showed an increasing trend (Fig. 4d). Both PO_4^{3-} and SiO_4^{4-} (Fig. 4e, f) increased linearly. In experiment 5, NO_3^- increased until 36 h and decreased thereafter (Fig. 4b). Nitrite initially increased to $0.34 \mu\text{M}$ at 60 h before registering a steep decrease (Fig. 4c). Ammonium increased in a distinct manner: a steady increase until 36 h followed by a sharp rise (Fig. 4d). In the first half of the experiment, lower NH_4^+ efflux accompanied by simultaneous increases in NO_2^- and NO_3^- influx was observed. However, as O_2 decreased further, NH_4^+ flux increased, while the NO_3^- and NO_2^- fluxed downward. Ammonium flux was $0.92 \text{ mmol m}^{-2} \text{ d}^{-1}$ until 36 h and increased subsequently to $3.22 \text{ mmol m}^{-2} \text{ d}^{-1}$. Nitrate and nitrite flux initially increased at the rate of $0.57 \text{ mmol m}^{-2} \text{ d}^{-1}$ and later decreased at a rate of $-0.58 \text{ mmol m}^{-2} \text{ d}^{-1}$ at 36 h. The initial (0–36 h) $\text{NO}_3^- + \text{NO}_2^-$ efflux rate in experiment 5 was similar to the rates observed in experiment 4. In experiment 6, NO_3^- exhibited a negative flux, decreasing linearly (Fig. 4b). Nitrite remained almost constant until 36 h; thereafter it rose steeply to peak at 36 h and decreased subsequently. A prominent N_2O peak coincided with the NO_2^- peak (Fig. 4c). Higher and faster NO_2^- buildup was observed in experiment 6 as compared to experiment 3, but rapid (subsequent) decreases were observed in both cases. A similar pattern of NO_3^- decrease and accumulation of NO_2^- and N_2O was also reported by Naqvi et al. (2000), indicating denitrification. The highest $\text{NO}_3^- + \text{NO}_2^-$ influx ($-1.04 \text{ mmol m}^{-2} \text{ d}^{-1}$) was observed in the NO_3^- -amendment experiment (experiment 6). Ammonium initially increased steadily until 30 h, followed by a steep increase afterwards, that continued until the end of the experiment (Fig. 4d). During April, the pattern of NH_4^+ release did not vary significantly between experiment 5

(after 36 h) and experiment 6 ($p = 0.8$), but both varied significantly ($p < 0.05$) from that in experiment 4. Phosphate and SiO_4^{4-} showed positive fluxes in all the experiments (Fig. 4e, f), without any significant variation ($p > 0.05$) in the flux pattern between the three experiments. Significant variation ($p < 0.001$) in NH_4^+ flux was found between aerobic incubations in April and anaerobic incubations in October. Phosphate ($p < 0.001$) and SiO_4^{4-} ($p < 0.05$) flux patterns in October significantly varied from those in April.

3.4 N_2O production

Transient buildup of nitrous oxide, coinciding with the peak in NO_2^- , was observed in both the seasons (Figs. 3d and 4c) in the NO_3^- -amended experiments (experiments 3 and 6), which indicated active benthic denitrification. Nitrous oxide accumulation in October was slower relative to that in April, but the decrease was rapid after peaking at 36 h, which results from its further reduction to N_2 . No significant variation ($p > 0.05$) was observed in the N_2O accumulation patterns of October and April incubations. Nitrous oxide 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 percentage of NO_3^- influx (0.2 % in October and 0.9 % in April) had resulted in N_2O .

4 Discussion

In the present study we have simulated the biogeochemical conditions prevailing at station G5 through a series of intact-core incubations. In the course of the experiments, we manipulated O_2 and NO_3^- levels in order to represent the seasonal conditions during oxic and anoxic regimes. We assume that the changes in O_2 and nutrient concentrations over a few days in the experiments would mimic the natural variability occurring over the inner shelf for a longer period. Both aerobic and anaerobic incubations were duplicated during April and October except for the NO_3^- -amendment experiments. Although incubation experiments may not fully represent the natural condition (flow regime and faunal activity), recent studies reveal that ex-situ experiments can be a powerful tool for flux studies in shallow environments. Here we assume that the benthic fluxes determined through the ex-situ method reflect the combined effects of molecular diffusion, faunal activity and advective transport processes.

4.1 Sediment oxygen consumption (SOC) and sulfide oxidation

The anaerobic incubations conducted during April resulted in a consistent O_2 influx rate, giving an average SOC of $66.4 \text{ mmol m}^{-2} \text{d}^{-1}$ (Table 2). However, in none of these experiments was O_2 completely consumed, as 20–23 μM O_2 was still present at the end. Also, the conditions were not anoxic, as sulfide was not detected at any time point. Dur-

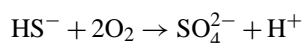
ing the first 36 h, experiment 5 was an aerobic experiment showing similar nutrient exchange patterns and flux rates as observed in experiment 4 (discussed in Sect. 5.2). Although this experiment was continued for 3.5 days, sulfide was never detected at any time, which implied that the upward-diffusing S^{2-} was retained within the sediment, being directly or indirectly oxidized by O_2 from the overlying water.

In contrast, complete O_2 consumption followed by sulfide release was observed in the October incubations. Oxygen uptake occurred at an average rate of $47.8 \text{ mmol m}^{-2} \text{d}^{-1}$ during this time (Table 2). Similar seasonal changes in SOC have also been observed in the Corpus Christi Bay (McCarthy et al., 2008), Orbetello Lagoon (Bartoli et al., 2009) and the 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 the present 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 the prevalence of low temperatures and the absence of benthic fauna (Naqvi et al., 2006; Ingole et al., 2010). Neubacher et al. (2011) observed a 50 % decrease in SOC during hypoxia in the North Sea and Rowe et al. (2002) reported a 5-fold lower SOC under anaerobic conditions compared to aerobic conditions in the Gulf of Mexico.

Since the bottom water remains oxygenated in April (Naqvi et al., 2006), the surface sediment remains oxic (although O_2 penetration may only be to a few millimeters deep in coastal sediments; Revsbech, 1989). In fact, a ~ 0.5 cm thick brown layer (Fe- and Mn-oxide-rich) was conspicuous at the surficial sediment during April but was absent during October. Sediments rich in Fe and Mn can be an effective trap for sulfide in coastal environments (Kristiansen et al., 2002). In such conditions, most of the upward-diffusing sulfide gets oxidized by Fe and Mn oxides in the top oxic layer which are, in turn, produced by oxidation of Fe^{2+} and Mn^{2+} by the downward-diffusing O_2 from the overlying water (Kristensen, 2000). The sediments at station G5 contain a high percentage of Fe (7.7 %) and Mn (0.09 %) (S. Kurian et al., unpublished data), which indicates that sulfide could be retained in the oxic sediment layer during April, culminating in no benthic S^{2-} flux. However, as the anoxia sets in during late September, the oxic–anoxic interface moves upwards to the water column. Consequently, Fe and Mn are reduced and flux to the overlying waters (Kristiansen et al., 2002). Thus, S^{2-} is no longer oxidized by Fe- and Mn oxides, although a smaller portion may be trapped as pyrite (FeS_2). In Corpus Christi Bay, McCarthy et al. (2008) located the 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 experiment 1 was preceded by anaerobic preincubation 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 the detection limit at 6 h, resulting in the highest flux. However, since the overlying water was initially oxalic in experiments 2 and 3, a substantial part of upward-diffusing sulfide was apparently oxidized to SO_4^{2-} by Fe oxides, Mn oxides and O_2 in the top oxalic sediment layer. Following a significant drop in O_2 , there was an immediate sulfide release after 6 h in experiment 1 and after 18–28 h in experiments 2 and 3. This implied that S^{2-} underwent substantial oxidation by available O_2 in the overlying water and was released at a lower rate ($2.09 \text{ mmol m}^{-2} \text{ d}^{-1}$). Experiments 2 and 3 nearly represent the condition during late August–early September, where S^{2-} was released but was oxidized at a rate of $2.2 \text{ mmol m}^{-2} \text{ d}^{-1}$. Experiment 1 is similar to the natural anoxic condition observed during late September–October (Fig. 5b), where S^{2-} was released at a higher rate without being oxidized.

Most of the O_2 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 the oxalic–anoxic interface, being chemically or 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 the anoxic zone of sediment is reoxidized in the oxalic zone of sediments (Thamdrup et al., 1994), and > 50 % of SOC occurs directly or indirectly by oxidation of sulfide (Jørgensen, 1989).



In experiment 3, sulfide oxidation could also be fueled by NO_3^- addition in a process known as chemolithoautotrophic denitrification (Lavik et al., 2009), which will be discussed further in Sect. 5.2. Experiment 1 nearly represents the anoxic conditions prevailing during October and experiment 3 represents the biogeochemical conditions during late August–early September, when the transition from suboxia (denitrifying condition) 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 the oxalic–anoxic interface by downwelled oxalic water during November.

4.2 Nitrification, denitrification and net DIN flux

During April, considerably lower NH_4^+ flux in the aerobic incubation (experiment 4) compared to anaerobic incubations (experiments 5 and 6) is mainly due to nitrification that occurred in the top oxalic sediment layer (Fig. 5a). This is further evidenced by positive fluxes of NO_2^- and NO_3^- and positive correlation between NH_4^+ and NO_2^- ($r = 0.9$, $p < 0.001$) as well as NO_2^- and NO_3^- ($r = 0.96$, $p < 0.001$). Similar lower

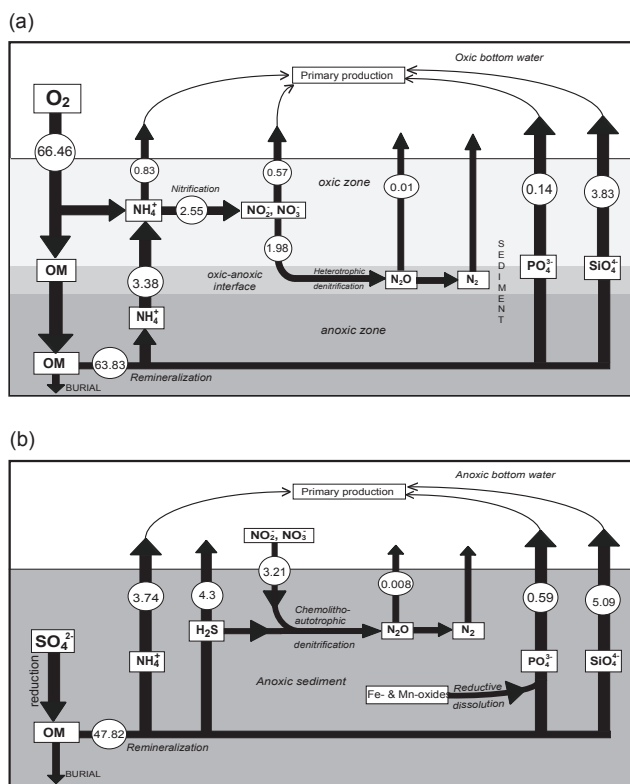


Figure 5. (a) Schematic diagram of sediment oxygen consumption (SOC), organic matter (OM) mineralization and nutrient fluxes during April, based on the results of experiments 4, 5 and 6. (b) Schematic diagram of organic matter (OM) mineralization and nutrient fluxes during October, based on the results of experiments 1, 2 and 3. Numbers inside the circles are flux rates in $\text{mmol m}^{-2} \text{ d}^{-1}$.

NH_4^+ flux under oxalic conditions has also been reported elsewhere by Malecki et al. (2004), McCarthy et al. (2008) and Faganeli and Ogrinc (2009).

Experiment 5 represented a transition from oxalic (0–36 h) to near-suboxalic (denitrifying) conditions (36–84 h), which is well reflected in nutrient flux patterns. Thus, benthic nitrification was active until 36 h, resulting in lower NH_4^+ flux and positive NO_2^- and NO_3^- fluxes. As observed in experiment 4, nitrification was also 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 $NO_3^- + NO_2^-$ fluxes from 0 to 36 h were consistent with those from experiment 4 (Table 2). As the O_2 decreased substantially after 36 h, inhibition of nitrification led to a 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 $0.58 \text{ mmol m}^{-2} \text{ d}^{-1}$ and NH_4^+ fluxed out at a rate of $3.22 \text{ mmol m}^{-2} \text{ d}^{-1}$ without being nitrified.

In experiment 6, initial low NH_4^+ flux ($0.76 \text{ mmol m}^{-2} \text{ d}^{-1}$) could be due to partial loss of

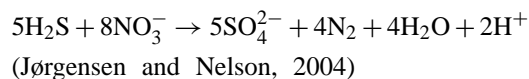
NH_4^+ through benthic nitrification from 0 to 30 h. Higher NH_4^+ anaerobic fluxes in experiment 5 after 40 h ($3.22 \text{ mmol m}^{-2} \text{ d}^{-1}$) and experiment 6 after 30 h ($3.55 \text{ mmol m}^{-2} \text{ d}^{-1}$) were apparently due to suppressed benthic nitrification owing to prevailing low- O_2 conditions as also observed by Hansen and Blackburn (1991) and Faganeli and Ogrinc (2009) in other regions. Nitrate and nitrite showed higher influx compared to that observed in experiment 5 (after 30 h) as NO_3^- addition enhanced benthic denitrification to a rate of $1.04 \text{ mmol m}^{-2} \text{ d}^{-1}$.

During April, NH_4^+ fluxes in experiment 4 and initial NH_4^+ fluxes in experiments 5 and 6 were consistent, with a mean aerobic NH_4^+ flux of $0.83 \text{ mmol m}^{-2} \text{ d}^{-1}$ (Table 2). Similarly, considering experiments 4 and 5 (0–24 h), the average $\text{NO}_3^- + \text{NO}_2^-$ efflux rate is $0.57 \text{ mmol m}^{-2} \text{ d}^{-1}$. Mean anaerobic NH_4^+ flux was $3.38 \text{ mmol m}^{-2} \text{ d}^{-1}$ considering experiments 5 and 6. It is conspicuous that the anaerobic conditions resulted in an NH_4^+ flux of $3.38 \text{ mmol m}^{-2} \text{ d}^{-1}$, but it reduced to $0.83 \text{ mmol m}^{-2} \text{ d}^{-1}$ in the aerobic incubation owing to a 75 % NH_4^+ loss at a rate of $2.55 \text{ mmol m}^{-2} \text{ d}^{-1}$ through benthic nitrification (Fig. 5a). However, the lost NH_4^+ did not appear as NO_2^- and NO_3^- at the same rate but rather at a lower rate ($0.57 \text{ mmol m}^{-2} \text{ d}^{-1}$) in the aerobic incubation. This implies that 58 % of upward-diffusing NH_4^+ was apparently lost in coupled nitrification–denitrification occurring at the oxic–anoxic interface in the surficial sediment (Jenkins and Kemp, 1984; Risgaard-Petersen, 2003; Granger et al., 2011) and 17 % was released to the overlying water being nitrified to NO_2^- and NO_3^- . Consequently, only 25 % 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 the sedimentary oxic–anoxic transition zone (Fig. 5a) irrespective of NO_3^- content of the overlying oxic bottom water, and 78 % of benthic nitrification was coupled with denitrification, resulting in considerable N loss.

Since experiment 4 represents the prevailing aerobic conditions (Fig. 5a) during April, the net benthic DIN release to the overlying water is $1.4 \text{ mmol m}^{-2} \text{ d}^{-1}$, of which NH_4^+ flux comprises 59 %. Experiment 6 represents the biogeochemical condition of the site during June–July, when the bottom water becomes suboxic (denitrifying) and NO_3^- -rich ($\sim 12 \mu\text{M}$). The benthic denitrification rate varied from 0.58 to $1.04 \text{ mmol N m}^{-2} \text{ d}^{-1}$ based on two anaerobic incubations (last 60 h of experiments 5 and 6). Considering methodological uncertainties, our results are consistent with Naik and Naqvi (2002) and Naqvi et al. (2006), who reported a sedimentary denitrification rate of 0.23 – $1.25 \text{ mmol m}^{-2} \text{ d}^{-1}$ in this region during peak suboxia. Based on NO_3^- consumption, Schwartz et al. (2009) reported a benthic denitrification rate 0.51 – $1.45 \text{ mmol N m}^{-2} \text{ d}^{-1}$ on the Pakistan margin during April–May, which is also in agreement 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 incu-

bation on slope sediments off Pakistan. Oxygen 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 under aerobic conditions, NO_3^- generated through nitrification within the sediment fed denitrification, while, under anaerobic conditions, NO_3^- diffused from the overlying water was found to be the main source for denitrification. Dominance of denitrification and low anaerobic ammonium oxidation (anammox) activity in the suboxic (denitrifying) water column and sediments was observed by Jayakumar et al. (2009) and Sokoll et al. (2012) within the oxygen minimum zone (OMZ) of the eastern Arabian Sea margin environments.

During October, influxes of NO_3^- and NO_2^- were observed in all experiments, and NH_4^+ effluxes were consistent in all incubations. Although the overlying water was initially oxic, nitrification apparently did not take place due to the inhibition by upward-diffusing free sulfide (Joye and Hollibaugh, 1995). Moreover, during October, nitrifiers were not detected in the shelf bottom water, whereas these were 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 dissimilatory nitrate reduction to ammonium (DNRA) and autotrophic denitrification. As NH_4^+ flux did not increase significantly in experiment 3, DNRA seems unlikely. In fact, very low DNRA activity (Sarkar et al., unpublished data) and, interestingly, significant autotrophic denitrification (S. W. A. Naqvi et al., unpublished data) have been observed in the sulfidic bottom water along this transect during late September. Nitrate is reduced to N_2 through sulfide oxidation mediated by chemolithoautotrophic bacteria such as *Thiobacillus denitrificans*, *Thiomicrospira*, *Thioploca*, *Magnetospirillum* and filamentous *Beggiatoa*, with transient buildup 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; Shao et al., 2011). Chemolithoautotrophic bacteria are often found in sulfidic surficial sediments (Lam and Kuypers, 2011) and are responsible for extensive N loss in anoxic (sulfidic) shelf systems (Lavik et al., 2009).



In fact, Krishnan et al. (2008) reported the presence of a large number of sulfide-oxidizing denitrifiers (*Thiobacillus denitrificans* like organisms) in the bottom waters of the shelf off Goa during both April and October. Moreover, concomitant buildup of NO_2^- and N_2O in experiment 6 substantiates the fact that the N-loss pathway in October was autotrophic denitrification, in contrast to heterotrophic denitrification, which caused N loss in non-sulfidic bottom water

and surface sediments during July–August. Nitrate addition in experiment 3 stimulated autotrophic denitrification to a rate of $3.21 \text{ mmol m}^{-2} \text{ d}^{-1}$ (Fig. 5b). Similar enhancement in N loss due to autotrophic denitrification was also reported by Zhang et al. (2009), Shao et al. (2011) and Dong et al. (2011) in sulfidic estuarine and coastal sediments in Southeast Asia. As *Thioploca* (a known chemolithotrophic S^{2-} oxidizer) mats have been sighted on Pakistan margin sediments (Schmaljohann et al., 2001), chemoautotrophy apparently plays a significant role in benthic biogeochemical processes there (Cowie, 2005) and also perhaps in other parts of the Arabian Sea. As experiments 1 and 2 represent the nitrate conditions typical of the late monsoon period (October), the average autotrophic denitrification rate would be $0.52 \text{ mmol N m}^{-2} \text{ d}^{-1}$ (Table 2). However, experiment 3 approximately represents the biogeochemical conditions some time during late August to early September (Fig. 5b), when the 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 was not 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-sulfidic conditions (Lavik et al., 2009; Canfield et al., 2010). Naqvi et al. (2000) reported the highest N_2O buildup (765 nM) during this transition time. Nitrous oxide accumulation and subsequent consumption in experiment 3 further indicates denitrification, which occurs under sulfidic conditions. Our results show that autotrophic denitrification can potentially cause N loss at a rate of $3.21 \text{ mmol N m}^{-2} \text{ d}^{-1}$ 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 $3.74 \text{ mmol m}^{-2} \text{ d}^{-1}$ (Fig. 5b). Overall, NH_4^+ comprised 59–100% of the benthic DIN release. The noticeable seasonal change was that the sediment switches from being a NO_3^- source in the oxic period to a NO_3^- sink in the anoxic period. During April, the major N loss was through heterotrophic denitrification, whereas autotrophic denitrification dominated during October.

4.3 Benthic PO_4^{3-} and SiO_4^{4-} release

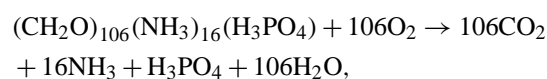
Benthic PO_4^{3-} flux is mainly controlled by the interplay of processes such as remineralization from sedimentary organic matter, adsorption to Fe oxides, co-precipitation with ferric minerals (Krom and Berner, 1981) and the formation of authigenic carbonate fluorapatite (Ruttenberg and Berner, 1993) in marine sediments. Positive fluxes of PO_4^{3-} in all experiments during April and October show that the benthic PO_4^{3-} regeneration rate always exceeds the rate of its adsorption and precipitation in the upper oxic layer. During April, PO_4^{3-} flux did not vary significantly between the aerobic and anaerobic incubations. It is evident that O_2 in the anaerobic incubation (experiment 6) did not decrease to a level that caused anoxia in the upper sediment layer. As $\sim 20 \mu\text{M}$ O_2

was present at the end of experiment 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 PO_4^{3-} . Ferric minerals such as FeOOH and Fe_2O_3 are known to adsorb and bind PO_4^{3-} chemically in the oxic sediment layer (Krom and Berner, 1981). Phosphate was released to overlying water at an average rate of $0.14 \text{ mmol m}^{-2} \text{ d}^{-1}$ during April (Fig. 5a). Similarly, SiO_4^{4-} effluxes were similar under both aerobic and anaerobic incubations, with a mean flux of $3.83 \text{ mmol m}^{-2} \text{ d}^{-1}$ (Fig. 5a).

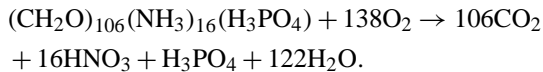
Phosphate fluxes increased significantly in October incubations, as the conditions became anoxic in all three incubations. Anoxia-induced reductive dissolution of FeOOH apparently released PO_4^{3-} (Ingall and Jahnke, 1994; Gunnar and Blomqvist, 1997; Slomp et al., 1998) from Fe minerals and ultimately resulted in higher PO_4^{3-} fluxes. Higher benthic PO_4^{3-} release was also observed by Rozan et al. (2002), Bartoli et al. (2009) and Skoog and Arias-Esquivel (2009) during anoxia in other coastal systems. Average PO_4^{3-} flux in the October incubations was $0.59 \text{ mmol m}^{-2} \text{ d}^{-1}$ (Fig. 5b), which is more than 4-fold higher than that in the April incubations (Fig. 5a). Faganeli and Ogrinc (2009) observed 3–10-fold higher PO_4^{3-} flux under anoxic conditions compared to oxic conditions in the Gulf of Trieste. Skoog and Arias-Esquivel (2009) also reported 26 times higher benthic PO_4^{3-} release under anoxic conditions than under oxic conditions in Long Island Sound. A 36–50% increase in benthic PO_4^{3-} efflux was noticed by Bartoli et al. (2009) during anoxia in Orbetello Lagoon, Italy. The SiO_4^{4-} flux during October is ~ 1.3 times higher than that observed during April (Table 2). Diatoms remain the dominant phytoplankton in the shelf water off Goa during the 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 over the shelf, during February–March (Parab et al., 2006; Roy et al., 2011). Higher diatom growth during the southwest monsoon could result in a higher downward flux of siliceous frustules to the underlying sediments during the late monsoon. Dissolution of diatom frustules could have enriched pore water with SiO_4^{4-} and led to higher fluxes in October incubations (Fig. 5b). 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



The flux of biogenic elements is expected to occur in the Redfield ratio, but interplay of several processes such as nitrification, denitrification, adsorption, desorption, 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). The O : NH_4^+ flux varied from 38.4–40.4 during April to 23.7–28.6 during October. Such a departure from the expected Redfieldian O : NH_4^+ ratio (13.25) indicates that a part of the NH_4^+ pool is lost or retained through nitrification and/or adsorption. The NH_4^+ : PO_4^{3-} flux ratio (16.4–40.8) was higher than the expected value (16) in anaerobic incubations in April. The lowest NH_4^+ : PO_4^{3-} flux ratio (5.5) in the aerobic incubation is due to substantial loss of NH_4^+ in coupled nitrification–denitrification (Jenkins and Kemp, 1984) and NH_4^+ adsorption onto clay minerals (Rosenfeld, 1979; Mackin and Aller, 1984). Decrease in the NH_4^+ : PO_4^{3-} flux ratio (5.2–7.3) during the October incubation is due to anoxia-induced higher PO_4^{3-} release. Closeness of the NH_4^+ : SiO_4^{4-} flux ratio (0.8–1.02) to the Redfield–Brzezinski value (1.06) during the April incubations suggests that it would favor diatom growth in the water column. However, the lower the NH_4^+ : SiO_4^{4-} flux ratio during the October incubations (0.55–0.78) apparently would favor the growth of non-siliceous phytoplankton during the late monsoon. This is substantiated by the fact that diatoms remain the dominant community during April–May, while dinoflagellates become the major phytoplankton during September–October (Parab et al., 2006, Naqvi et al., 2009).

4.5 Organic matter mineralization

Sediment oxygen consumption is usually considered to be one of the principal determinants of the oxidation rate of total C_{org} in marine sediments (Canfield et al., 1993; Glud, 2008). Dissolved inorganic carbon (T_{CO_2}) flux has been observed to be fairly linear with SOC (Giblin et al., 1997; Hopkinson et al., 2001; Ferrón et al., 2009b), which indicates that O_2 is directly or indirectly responsible for benthic respiration. Oxygen directly oxidizes C_{org} 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, Fe oxides and SO_4^{2-} and subsequent reoxidation of Fe^{2+} , Mn^{2+} and H_2S by O_2 have the same net stoichiometry as in C_{org} oxidation by O_2 (Jørgensen, 1977; Canfield et al., 1993), SOC can be used to calculate the C_{org} mineralization rate. The total C_{org} oxidation rate is quantified by taking O_2 consumption in aerobic nitrification and carbon

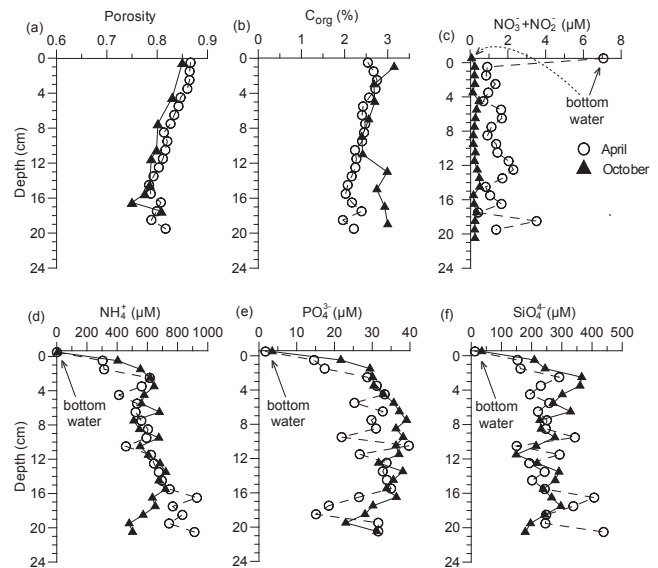


Figure 6. Seasonal variability in vertical profiles of (a) porosity, (b) sedimentary C_{org} , (c) pore water $\text{NO}_3^- + \text{NO}_2^-$, (d) pore water NH_4^+ , (e) pore water PO_4^{3-} and (f) pore water SiO_4^{4-} at station G5, off Goa. The bottom water nutrient concentrations are pointed by arrow marks..

oxidation through denitrification into consideration (Canfield et al., 1993) as follows:

$$T_{\text{C}_{\text{oxid}}} = \text{O}_2\text{flux} - \text{O}_2\text{NH}_4\text{-oxid} + C_{\text{denit}},$$

where $T_{\text{C}_{\text{oxid}}}$ is the depth-integrated rate of total C_{org} oxidation, $\text{O}_2\text{NH}_4\text{-oxid}$ is the O_2 consumed in NH_4^+ oxidation to NO_3^- and C_{denit} is the C_{org} oxidized through denitrification. In aerobic mineralization, C : O_2 is 1, O_2 : NH_4^+ ratio in complete nitrification is 2, and C : N in heterotrophic denitrification is 1.25 (Canfield et al., 1993).

During April, considering the nitrification rate of $2.55 \text{ mmol m}^{-2} \text{ d}^{-1}$, the O_2 consumption for NH_4^+ oxidation will be $5.1 \text{ mmol m}^{-2} \text{ d}^{-1}$, while the benthic denitrification (coupled to nitrification) of $1.98 \text{ mmol N m}^{-2} \text{ d}^{-1}$ would oxidize C_{org} at the rate of $2.47 \text{ mmol m}^{-2} \text{ d}^{-1}$ under the oxic conditions. This leads to a net C_{org} oxidation rate of $63.8 \text{ mmol C m}^{-2} \text{ d}^{-1}$. However, as both nitrification and heterotrophic denitrification are inhibited by sulfide during October, O_2 flux can be directly considered as the C_{org} oxidation rate (Canfield et al., 1993). Considering experiments 1 and 3, the mean C_{org} oxidation rate would be $47.8 \text{ mmol C m}^{-2} \text{ d}^{-1}$ during the sulfidic event. Organic carbon mineralization has been found to be faster under aerobic and compared to anaerobic conditions (Benner et al., 1984; Henrichs and Reeburgh, 1987; Lee, 1992; Dauwe et al., 2001), especially where the sediment has more refractory organic matter, although aerobic and anaerobic degradation rates can be similar in some cases (Kristensen et al., 1995; Hulthe et al., 1998). Thus, during April, 63.8 mmol

of C_{org} were mineralized aerobically square meter in a day, while 47.8 mmol of C_{org} was anaerobically mineralized during October. It appears that the 25 % decrease in the C_{org} mineralization rate from oxic to anoxic regime arises due to a slower oxidation of C_{org} under a stratified water column during October. Neubacher et al. (2011) observed a 46 % decrease in N remineralization in the North Sea under hypoxic conditions. Similarly, Dauwe et al. (2001) reported 50 % less anoxic C_{org} mineralization than oxic mineralization in the North Sea. Higher temperatures (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 C_{org} in marine sediments. As porosity and C_{org} did not change significantly between April and October (see Sect. 4.6 and Fig. 6), the prevailing low temperature (22 °C) and the absence of benthic macrofaunal activity (Naqvi et al., 2006; Ingole et al., 2010) apparently slowed down C_{org} mineralization at the study site during anoxia.

4.6 Porewater nutrients and diffusive fluxes

The porosity of surficial sediment did not vary significantly ($p = 0.2$) between April and October (Fig. 6a). Vertical distribution of C_{org} did not vary significantly ($p = 0.6$) between the oxic and anoxic regimes (Fig. 6b). Porewater at the study site was enriched with NH_4^+ , PO_4^{3-} and SiO_4^{4-} compared to overlying water column during both the seasons (Fig. 6d, e and f). Vertical distribution of pore water NH_4^+ and SiO_4^{4-} did not vary significantly ($p > 0.05$) between April and October. However, $\text{NO}_3^- + \text{NO}_2^-$ and PO_4^{3-} varied significantly ($p < 0.05$) between two seasons. As these profiles were from single core observations, the degree of spatial heterogeneity could not be ascertained. However, the effect of bioirrigation and PO_4^{3-} immobilization/desorption by/from Fe- and Mn-oxide minerals also cannot be ruled out. Macrobenthic activity reduces due to sulfidic conditions (Rowe et al., 2002) during October, and anoxia causes reductive dissolution of Fe- and Mn oxides and release of PO_4^{3-} to pore water. Similar seasonal variation in the pore water PO_4^{3-} profile has been observed by Woulds et al. (2009) in the sediments on the Pakistan margin. Low NO_3^- and NO_2^- were observed in the pore water, which usually occurs because of N loss through benthic denitrification, as O_2 penetration is limited to the upper few millimeters of the sediment. Bioirrigation was conspicuous in the $\text{NO}_3^- + \text{NO}_2^-$ profile in April (Fig. 6c), which apparently caused the penetration of the oxic bottom water to the deeper anoxic layers, thereby nitrifying the pore water NH_4^+ to NO_2^- and NO_3^- . In contrast, low $\text{NO}_3^- + \text{NO}_2^-$ in pore water was observed in October, due to anoxia-related decrease of benthic faunal activity as well as enhanced benthic denitrification.

The calculated diffusive fluxes of nutrients did not vary significantly between April and October except in the case of NO_3^- and NH_4^+ . The diffusive NH_4^+ flux was especially high,

comprising 73–92 % of total benthic NH_4^+ flux, because of a higher concentration gradient across the sediment–water interface and higher diffusivity of NH_4^+ . The 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 factors (the ratio of measured flux to calculated flux) during the oxic period were 14.7, 1.3, 4.7 and 6.6 for $\text{NO}_3^- + \text{NO}_2^-$, NH_4^+ , PO_4^{3-} and SiO_4^{4-} , respectively, and 11.6, 1.03, 9.2 and 8.2, respectively, during the anoxic period. There was clear evidence of benthic faunal activity in the aerobic incubations during April, as some burrows and live benthic organisms were conspicuous throughout the experiments. Interestingly, recent observations (October 2011 and 2012; Badesab et al., unpublished data) showed the presence of live benthic macrofauna (e.g., polychaeta, bivalves and crustaceans) in the G5 sediments during October under sulfidic conditions. These adaptable species survive the anoxia and proliferate afterwards. Polychaetes proliferate even during anoxia. Thus, the benthic faunal activity apparently did not stop during October incubations. Stirred chambers can also cause advective pore water transport (Huettel and Gust, 1992), although its magnitude may differ from that in natural environments. As advective pore water transport depends on the bottom current flow and surface roughness (mounds, ripples etc), it is not necessary that it would occur at the same magnitude during both seasons. Although its role in pore water exchange may be smaller compared to benthic faunal activity (bioirrigation and bioturbation) in cohesive sediments, it may not be negligible. The stirring rate was kept the same during April and October, which possibly created a constant bottom flow. However, surface roughness could have increased during October, thereby increasing the advective transport. Thus, benthic faunal activity and advective pore water transport apparently enhanced the benthic nutrient exchange rate.

4.7 Benthic turnover time

The number of days required to replenish the pelagic nutrient inventory of a system by the benthic nutrient supply under steady state is referred to as the benthic turnover time. It is calculated by dividing the depth-integrated pelagic nutrient stock by the benthic nutrient efflux rate (Warnken et al., 2000). Considering experiment 4 and the aerobic part of experiment 5, the turnover time of NH_4^+ is 16 days (Table 3) during April. However, when nitrification is taken into consideration, the turnover time of DIN is enhanced (~ 67 days) during this period. In experiment 6, the turnover time of DIN (40 days) decreased due to inhibition of nitrification at low O_2 . As experiment 6 nearly represents the biogeochemical condition of the system during July–August, it is evident that prevailing anaerobic conditions during July and August will cause a quicker replenishment of the pelagic DIN stock by the benthic flux. Apparently, the turnover time of PO_4^{3-} (165 days) and SiO_4^{4-} (29 days) did not change significantly be-

Table 3. Benthic turnover time for DIN, PO_4^{3-} and SiO_4^{4-} during April and October at station G5.

Month	Benthic turnover time (days)		
	DIN	PO_4^{3-}	SiO_4^{4-}
Apr	66.9	165.2	29.7
Oct	24.1	91.6	136.1

tween April and July–August, as the fluxes did not vary significantly between aerobic and anaerobic incubations.

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

4.8 Ecological impact and implications of benthic exchange

Coastal upwelling seems to be the major factor in controlling primary productivity (PP) in these shelf waters. The study site is not much influenced by river discharge as it is far from the Mandovi–Zuari river mouth. Exhaustion of upwelled NO_3^- by denitrification (Naqvi et al., 2000) and algal uptake led to NO_3^- -limiting conditions during the late monsoon. However, significant benthic fluxes of NH_4^+ and PO_4^{3-} during this anoxic period may sustain the pelagic PP. Benthic-released NH_4^+ escapes nitrification and accumulates in the anoxic bottom water, which apparently causes a shift in the phytoplankton composition during October. Although the SiO_4^{4-} flux remains significant, the NO_3^- -depleted, NH_4^+ -rich subsurface water favors preferential proliferation of non-diatom species, such as the dinoflagellates, during the late southwest monsoon (Naqvi et al., 2006). The benthic release of NH_4^+ , PO_4^{3-} and SiO_4^{4-} is of great importance during the non-upwelling oxic regime (November–May), as it enriches the pelagic nutrient (especially N) stock during this N-limiting period. Significant DIN flux and the anoxia-induced, high PO_4^{3-} flux possibly can play a 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 supplies the water column with bioavailable Fe and PO_4^{3-} , which are essential for N_2 -fixing bacterioplankton. *Trichodesmium* blooms have been frequently observed during the fall intermonsoon (Naqvi et al., 2009, Roy et al., 2010), presumably stimulated by the availability of these nutrients. With the onset of the northeast monsoon, the regen-

erated NH_4^+ gets nitrified to NO_3^- , which, along with the benthic released SiO_4^{4-} , favors repopulation of the diatoms. By February, NO_3^- gets used up by algal uptake; however the system still remains PO_4^{3-} -replete owing to prior non-Redfieldian release of NH_4^+ and PO_4^{3-} during anoxia that leads to a secondary bloom of *Trichodesmium* during the spring intermonsoon. Slower benthic mineralization during anoxia indicates higher preservation of C_{org} and burial in the sediments, thereby giving a negative feedback to CO_2 emission from the western Indian shelf.

Sulfide released during anoxia creates unfavorable conditions for the benthic fauna, demersal fishes and the other larger organisms living in the bottom waters. However, it leads to the proliferation of the 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 and aggravates NO_3^- loss.

5 Conclusions

Seasonally developing, contrasting oxygen regimes, as simulated by our manipulative ex-situ incubation studies, exerted a profound effect on the benthic exchange of essential nutrients and benthic respiration. During the prevalence of oxic conditions, 58 % of the upward-diffusing NH_4^+ was lost in coupled nitrification–denitrification in the sediments, 17 % was fluxed out as NO_2^- and NO_3^- and 25 % was released as NH_4^+ . Benthic nitrification occurred at the rate of $2.55 \text{ mmol m}^{-2} \text{ d}^{-1}$, of which 77 % remained coupled to denitrification. Sediments remained a net perennial source of DIN, with a flux rate of $1.4 \text{ mmol m}^{-2} \text{ d}^{-1}$ during April, which progressively increased to $3.74 \text{ mmol m}^{-2} \text{ d}^{-1}$ during October, NH_4^+ comprising 59–100 % of the DIN efflux. Benthic denitrification caused NO_3^- loss at the rate of $1.04 \text{ mmol m}^{-2} \text{ d}^{-1}$ during suboxia. Released sulfide was, presumably, oxidized by NO_3^- and NO_2^- at the sediment–water interface by the chemolithoautotrophic sulfide oxidizers such as *Thiobacillus denitrificans* like organisms, resulting in the reduction of NO_3^- to N_2 (plus intermediates, mainly N_2O). This sulfide-driven denitrification can potentially cause N loss at the rate of $3.21 \text{ mmol m}^{-2} \text{ d}^{-1}$ during anoxia. Shelf sediment behaved as a NO_3^- source during April but turned into a NO_3^- sink during October. PO_4^{3-} flux increased > 4-fold during anoxia owing to possible reductive dissolution of FeOOH–P minerals in sediments. Organic carbon was mineralized at the rate of $63.8 \text{ mmol C m}^{-2} \text{ d}^{-1}$ during the premonsoon, which was reduced by 25 % during October, apparently due to lower temperatures, the absence of benthic fauna and a slower oxidation of the organic matter under anoxia.

The continental shelf of western India exhibits spatial heterogeneity in terms of sediment texture and C_{org} . Our results

and inferences based on incubation experiments from the inner shelf may not represent the entire western shelf. Future studies focusing on both the inner and outer shelf might improve the understanding of the benthic mineralization and nutrient fluxes in this region.

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