

RESEARCH ARTICLE

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Key Points:

- First time series N_2O coupled upwelling study on the hypoxic-anoxic western Indian shelf system
- Initial O_2 levels of upwelling waters play crucial role in defining the shelf nitrogen biogeochemistry
- Four-times lower revised N_2O fluxes than previous estimate may compensate to some extent its increase due to ongoing intensification of seasonal anoxia

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Upwelling intensity modulates N_2O concentrations over the western Indian shelf

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Abstract Repeat measurements of dissolved nitrous oxide (N_2O) along two transects of the western continental shelf of India in 2012 revealed high concentrations of 45 ± 32 nM (off Kochi) and 73 ± 63 nM (off Mangalore) during the summer monsoon (SM). N_2O concentrations increased nonlinearly during the peak of the SM upwelling, when low O_2 ($<25 \mu M$) conditions prevailed in the water column. Off Kochi, N_2O levels fell gradually from the fall intermonsoon (20 ± 8 nM) to the winter monsoon (8.8 ± 2 nM) and remained low (9.2 ± 5.2 nM) through the spring intermonsoon season. The N_2O supersaturation off Kochi ($574 \pm 720\%$) was presumably due to its high yield during sediment denitrification, whereas the higher N_2O supersaturation observed off Mangalore ($1046 \pm 885\%$) was due to its production during denitrification in both the anoxic water column and the underlying sediments. Such distinctive biogeochemical behavior between these two shelf segments is at first augmented by the natural origin of intense upwelling at Mangalore relative to Kochi wherein suboxic to anoxic oxygen minimum zone waters spread from offshore to the shelf of Mangalore, over which the runoff and terrestrial nutrients supply acts in unison. Following new zonal extrapolation approach, our revised estimate of N_2O effluxes from the southwestern Indian shelf ($7\text{--}14^\circ N$) was four times lower ($0.019\text{--}0.039 \text{ Tg y}^{-1}$) than previous estimate. Nevertheless, further studies are needed to refine the N_2O effluxes from the entire western Indian shelf to monitor its modification due to expansion/intensification of the coastal low- O_2 zones and also to ascertain its actual N_2O contribution to the world oceans.

1. Introduction

Nitrous oxide (N_2O) is a biogenic trace gas that contributes to ozone depletion in the stratosphere [Crutzen, 1970]. Moreover, it is the third most abundant greenhouse gas after carbon dioxide (CO_2) and methane (CH_4) with a global warming potential of ~ 300 times that of CO_2 [International Panel on Climate Change (IPCC), 2013]. Since the industrial revolution, anthropogenic activities have led to an increase in global N_2O emissions by 40–50% [Hirsch et al., 2006] and the globally averaged atmospheric dry mole fraction of N_2O for 2012 (325 ppb) was 1.2 times the preindustrial value (270 ppb) [World Meteorological Organization, 2013; IPCC, 2013]. The oceans are estimated to account for one-third of all natural emissions of N_2O to the atmosphere [IPCC, 2013]. Coastal areas including estuaries contribute up to 35–60% to the total marine N_2O emissions [Bange et al., 1996; Seitzinger et al., 2000]. N_2O is mainly produced as an intermediate during denitrification and as a by-product during nitrification, and accumulates under oxygen-deficient conditions [Codispoti et al., 2005]. While production under well-oxygenated conditions is reported to be dominant [Freitag et al., 2012], the highest N_2O concentrations have been recorded in the oxygen minimum zones (OMZ), especially in coastal areas experiencing upwelling [Naqvi et al., 2000; Arévalo-Martínez et al., 2015]. Oxygen deficiency over the continental shelves is regulated by factors such as regional circulation, shelf width, O_2 content of the upwelled waters, eutrophication, and primary production.

Globally, major mesopelagic OMZs are found in the eastern tropical Pacific Ocean and the northern Indian Ocean. In the Pacific Ocean, the intense OMZs are associated with the productive eastern boundary upwelling systems [Capone and Hutchins, 2013] whereas in the Indian Ocean, midwater oxygen deficiency is maximal in the northern and central Arabian Sea [Naqvi, 1991; Banse et al., 2014]. The restricted renewal of intermediate waters that also experience elevated O_2 demand for the oxidation of organic matter sinking

from the productive surface layer facilitates the development of the world's thickest (between ~ 100 and 1200 m) OMZ in the central Arabian Sea [Naqvi, 1987; Warren, 1994; Codispoti *et al.*, 2001; Banse *et al.*, 2014]. Moreover, due to its semienclosed nature, the northern Indian Ocean contains about two-third of the global continental-margin area affected by natural O_2 deficiency (<0.2 mL L^{-1} or 9 μM) [Helly and Levin, 2004]. During the summer monsoon (SM), advection of low O_2 water through upwelling leads to seasonal prevalence of hypoxic/anoxic conditions along the west coast of India. This shallow low- O_2 system is two orders of magnitude smaller in volume than the perennial open ocean OMZ, but it experiences more severe conditions [Naqvi *et al.*, 2000, 2006a]. The low- O_2 zone of the western Indian shelf, the largest of its kind in the world (area $\sim 200,000$ km²), is primarily of natural origin, but it appears to have intensified in recent years due to enhanced nutrient loading from land that might have enhanced N_2O production [Naqvi *et al.*, 2006b, 2010]. The coastal upwelling systems in the north-western Indian Ocean (Arabian Sea) and southeastern Pacific Ocean (off central Chile and Peru) have been identified as "hot spots" of N_2O production with N_2O saturations up to 8250% and 2426–12,244%, respectively [Naqvi *et al.*, 2005; Cornejo *et al.*, 2007; Arévalo-Martínez *et al.*, 2015].

The N_2O flux per unit area to the atmosphere is three times higher than from the Arabian Sea as compared to the Bay of Bengal [Naqvi and Noronha, 1991; Naqvi *et al.*, 1994]. Of the estimated global oceanic N_2O emission of ~ 9 Tg y^{-1} [Ciais, 2013], the contribution from the Arabian Sea (0.4 – 1.1 Tg y^{-1}) is 5–13%. The emission from the western Indian continental shelf (0.06 – 0.39 Tg of N_2O y^{-1}), which accounts for only 4% of the area of the Arabian Sea, alone has been reported to be 15–35% of total emission from the Arabian Sea [Naqvi *et al.*, 2000], making it a globally important site of N_2O production [Naqvi *et al.*, 2000, 2006b]. However, previous studies mainly focussed on the open ocean and the shelf regions of central eastern Arabian Sea (CEAS) with very few observations in the south eastern Arabian Sea (SEAS). The aim of the present study is to fill this gap through a comparative study involving time series observations off Kochi (KoTS—Kochi Time Series) in the SEAS and seasonal sampling off Mangalore in the CEAS. This is the first time series study of N_2O from the shelf waters off Kochi ($\sim 10^\circ N$) and the only one other than that carried out off Goa (the Candolim Time Series, CATS, $\sim 15.5^\circ N$). The study also intends to find the role of upwelling intensity and O_2 concentration in its source water in ascertaining shelf biogeochemical response. The new data are used to revise estimate of annual flux of N_2O from the southwestern Indian shelf.

2. Study Area

The dynamics of upwelling from its evolution to decay and the associated nutrient biogeochemistry and net ecosystem metabolism from the KoTS have been recently documented in detail by Gupta *et al.* [2016]. The SEAS (Figure 1) is a biologically productive region [Prakash and Ramesh, 2007] due to upwelling [Gupta *et al.*, 2016]. The biogeochemistry of the SEAS is closely linked to the seasonally reversing coastal currents viz. northward and southward flowing West India Coastal Current during winter monsoon (WM) and SM, respectively. The spring intermonsoon (SIM) and fall intermonsoon (FIM) periods experience transitional conditions between the two monsoons. The northerly current during WM carries low salinity water originating in the Bay of Bengal which enhances stratification in the upper water column of the SEAS. During SM, the upwelling-induced nutrient enrichment leads to high biological production over the western continental shelf of India. An important feature of the SEAS is the seasonal hypoxia/anoxia arising principally from the low O_2 content of the upwelling water that is further depleted as a result of high O_2 demand for mineralization of locally produced organic matter. It is this feature that makes the western continental shelf of India a "hot spot" for N_2O production. In addition to upwelling, the western shelf also receives substantial amounts of nutrients through terrestrial input which influence the biogeochemistry and ecology of the region. Many small and medium rivers like Mandovi and Zuari in Goa, the Kalinadi in North Kanara, and the Netravati in South Kanara flow across the coastal plain into the central Arabian Sea. Cochin (Kochi) estuary (CE) and the Ashtamudi Lake are the two major estuaries debouching freshwater into the Arabian Sea in the south. The study site is located off CE, one of the largest estuarine systems along the southwest coast of India. The CE receives 104×10^3 m³ of industrial and 260 m³ of domestic wastes daily, most of which are untreated [Balachandran *et al.*, 2002; Martin *et al.*, 2008]. The export of significant fraction of these anthropogenic wastes to the adjacent coastal sea [Thottathil *et al.*, 2008; Gupta *et al.*, 2009] has been shown to exert considerable influence on local biogeochemistry [Gupta *et al.*, 2016].

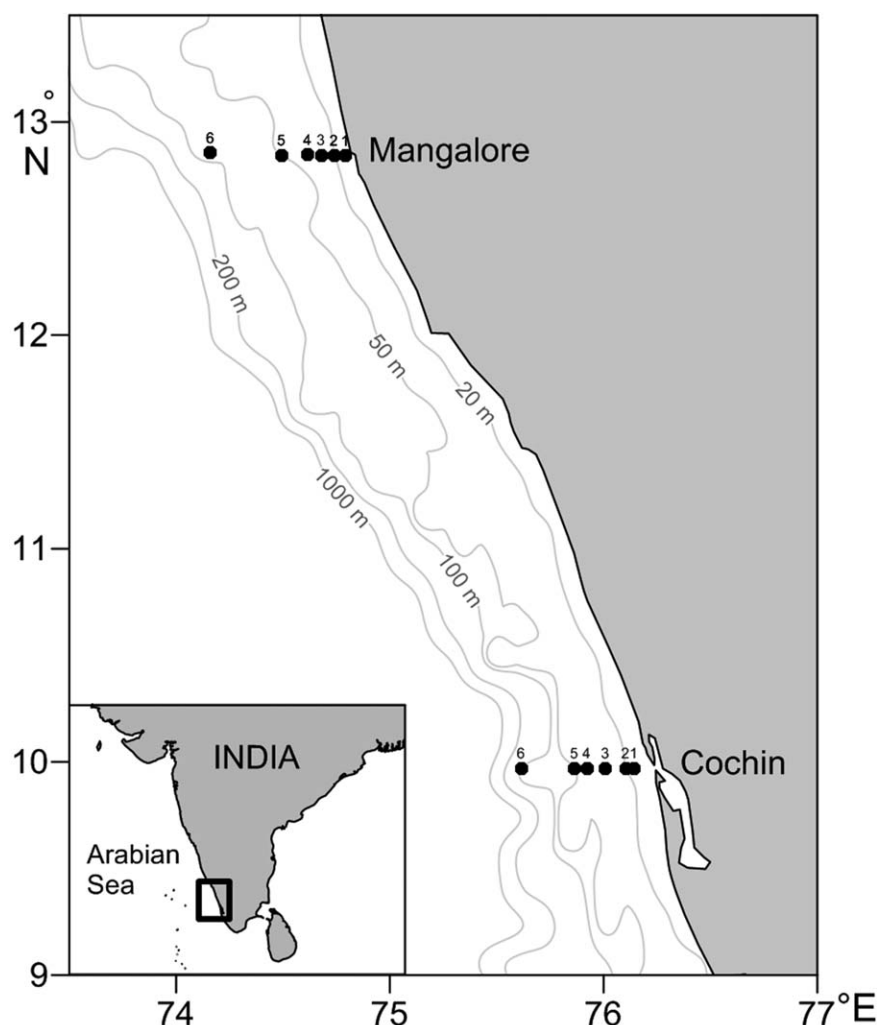


Figure 1. Stations location map.

3. Materials and Methods

As a part of the Kochi Time Series (KoTS) study during January to December 2012, sampling for N_2O was carried out along a transect off Kochi seven times between April and December 2012. Observations were also made along another transect off Mangalore three times—in April, September, and December 2012. Along both transects (KoTS and Mangalore), six stations were occupied at water depths of 13, 20, 30, 40, 50, and 100 m (Figure 1). The sampling periods are classified into four seasons viz., spring intermonsoon (SIM: April), summer monsoon (SM: June to September), fall intermonsoon (FIM: October), and winter monsoon (WM: November to December). For the convenience of discussion, each transect is segmented as follows: station 1—nearshore; stations 2 and 3—inner shelf; stations 4 and 5—midshelf; and station 6—outer shelf (shelf entrance).

Temperature and salinity profiles at each station were obtained using a Sea-Bird CTD (model 911 plus). Water samples were collected using Niskin samplers mounted on the CTD rosette. Subsamples for dissolved oxygen (O_2) were taken in 60 ml glass bottles. The O_2 was fixed by adding 0.5 ml each of Winkler reagents, and titrated against 0.001N Hypo (Dosimat 655, Metrohm, Switzerland) using visual end point detection [Grasshoff *et al.*, 1999]. Subsample size for titration varied based on color intensity of precipitate following the addition of Winkler reagents: 10–25 ml when the color is substantial and whole volume of reagent bottle for samples with pale yellow to white. The small amount of O_2 carried by the reagents was not subtracted and sodium azide was not used to prevent interference by nitrite. The detection limit of the method

is approximately 2 μM . Apparent Oxygen Utilization (AOU) was estimated as a difference between the theoretical O_2 solubility, calculated according to *Garcia and Gordon* [1992], and the measured concentration. Samples for nutrients (nitrate, nitrite, and ammonium) were analyzed spectrophotometrically (Thermo Evolution 201) onboard within few hours of collection following standard procedures [*Grasshoff et al.*, 1999]. The analytical precision, expressed as standard deviation based on replicate analyses, was ± 0.05 , ± 0.01 , and ± 0.07 μM for NO_3^- , NO_2^- , and NH_4^+ , respectively. Samples (2 L) for chlorophyll (Chl *a*) estimation were filtered onboard through Whatman 47 mm GF/F filter (0.7 μm) under gentle vacuum (< 50 mm Hg) and kept at -20°C until analysis. Chl *a* was extracted from the filters with 90% acetone at 4°C in the dark for 12 h and measured fluorometrically [*Joint Global Ocean Flux Study*, 1994]. Phaeopigments were also measured by adding 1 N HCl to the chlorophyll extract immediately after the Chl *a* measurement. Wind speed was measured continuously during the cruise using automated weather station (AWS) installed onboard ~ 10 m above from the sea surface.

Water samples for N_2O were collected in 60 ml glass bottles immediately after the sampling for O_2 . Samples were poisoned using saturated mercuric chloride (0.3 ml/60 ml) to arrest microbial activity. The tightly stoppered bottles were kept in dark until analysis. Dissolved N_2O concentration was determined following the multiple phase equilibration technique [*McAuliffe*, 1971]. Briefly, 25 ml of sample was equilibrated successively with an equal volume of ultrapure helium in a gas tight syringe by vigorously shaking the syringe at room temperature for 5 min using a wrist action shaker. After equilibrium, the gas mixture from the headspace was injected through a 5 ml sampling loop into a gas chromatograph (Shimadzu) and separated over a Chromosorb column (80/100 mesh) at 40°C . N_2O was detected with a ^{63}Ni Electron Capture Detector (ECD). Precision of the analysis was $\sim 4\%$. Calibration was achieved using a gas mixture of N_2O in nitrogen (Alltech Associated Inc., IL, USA).

The percentage saturation of N_2O was calculated as

$$\text{N}_2\text{O saturation} = (C_w/C_a) \times 100$$

where C_w is the measured concentration of dissolved N_2O and C_a is the equilibrium concentration in seawater. C_a was calculated using

$$C_a = \beta (T, S) x' P$$

where x' is the atmospheric dry mole fraction of N_2O , P is the atmospheric pressure, and β is the Bunsen solubility, as a function of in situ temperature and salinity [*Weiss and Price*, 1980]. The surface saturation of N_2O was calculated relative to an average atmospheric concentration of 323 ppb as reported recently by *Rao et al.* [2013] for the east coast of India. $\Delta\text{N}_2\text{O}$ is derived as the difference between C_w and C_a .

The sea-air exchange flux density was computed from

$$F = k_w(u) (C_w - C_a)$$

where k_w is the gas transfer velocity which depends on factors such as wind speed, temperature, turbulence in both the atmosphere and the water [*Liss and Merlivat*, 1986; *Upstill-Goddard*, 2006]. In this study, we used three different parameterizations [*Liss and Merlivat*, 1986 (LM86); *Wanninkhof*, 1992 (W92), *Nightingale et al.*, 2000 (N00)] to calculate k_w . k_w was adjusted by multiplying with $(Sc/600)^{-n}$ ($n = 2/3$ for wind speeds < 3.6 m s^{-1} and $n = 1/2$ for wind speeds > 3.6 m s^{-1}) for LM86, $(Sc/660)^{-0.5}$ for W92, and $(Sc/600)^{-0.5}$ for N00, where Sc is the Schmidt number for N_2O . Sc was calculated using empirical equations for the kinematic viscosity of seawater [*Siedler and Peters*, 1986] and the diffusion coefficient (in $\text{m}^2 \text{s}^{-1}$) of N_2O in water [*Rhee*, 2000]. Hourly measured wind speed was averaged to obtain daily mean and was used for transfer velocity calculations.

4. Results

4.1. Variation in Shelf Hydrography

Sea surface temperatures (SST) off Kochi were high ($> 28^\circ\text{C}$) during both the SIM and WM with an intermittent cool phase ($< 28^\circ\text{C}$) during the SM season. The water column temperature and salinity remained almost uniform at least up to the inner shelf during nonupwelling periods, but the water column was highly stratified with very shallow mixed layer when upwelling occurred (Figure 2). Coastal waters off Mangalore also

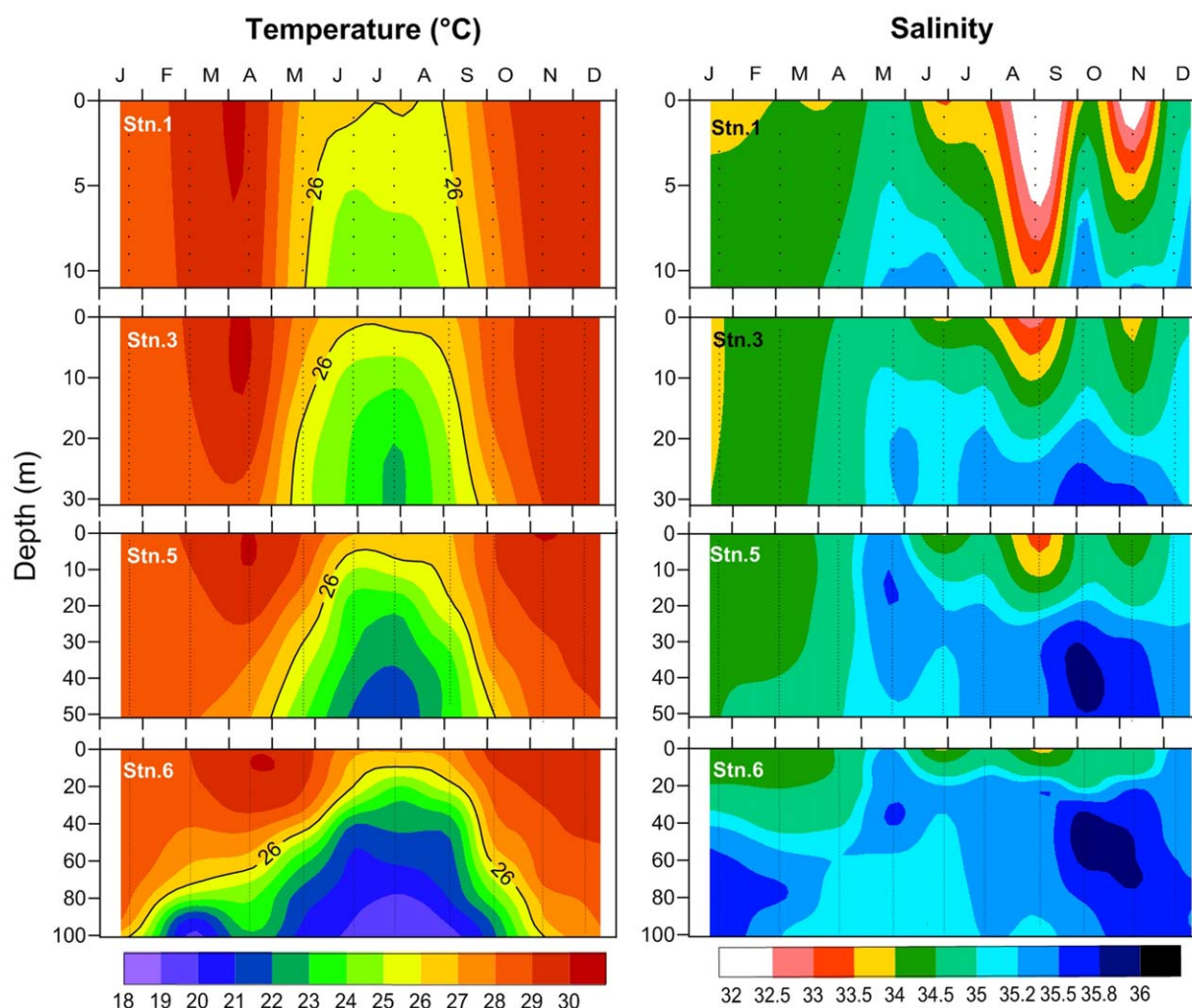


Figure 2. Time-series distribution of temperature and salinity at nearshore (stn.1), inner (stn.3), mid (stn.5) and outer shelf (stn.6) stations of Kochi during 2012.

exhibited similar seasonal variations; however, the nearshore and inner shelf water column temperatures during the SIM were higher and upper column salinity during the SM was lower than off Kochi (Figure 3). The temperature distribution during 2012 showed that upwelling signatures began to appear at the shelf break during January to March, covered the entire shelf at its most active phase during June to September, and collapsed abruptly and ended completely by the end of October [Gupta *et al.*, 2016]. The winds during January to March are predominantly from northwest which are not favorable for upwelling. However, the coastal circulation (West India Coastal Current, WICC) along the eastern Arabian Sea is seasonally reversed with poleward surface and equatorward under currents during northeast monsoon (December to February) and opposite during southwest monsoon (May to September) [Shankar and Shetye, 1997]. These seasonally reversing currents carry different watermasses from the Bay of Bengal and the northern Arabian Sea, respectively. It has been shown that poleward flowing WICC favors formation of anticyclonic gyre resulting in Lakshadweep high [Shankar and Shetye, 1997] which can influence in initiating the advection of offshore waters toward coast as upwelling along the bottom [Gupta *et al.*, 2016]. The reverse phase of WICC favor in intensifying the upwelling to spread entire shelf.

The relatively low surface salinity during the SIM, especially off Kochi, was due to the advection of fresher waters originating in the Bay of Bengal, which were later displaced away from the shelf by the upwelled Arabian Sea High Salinity Watermass (ASHSW) [Gupta *et al.*, 2016]. Surface salinity was highly variable during the SM months: low during June and September with an intermittent increase during July which is

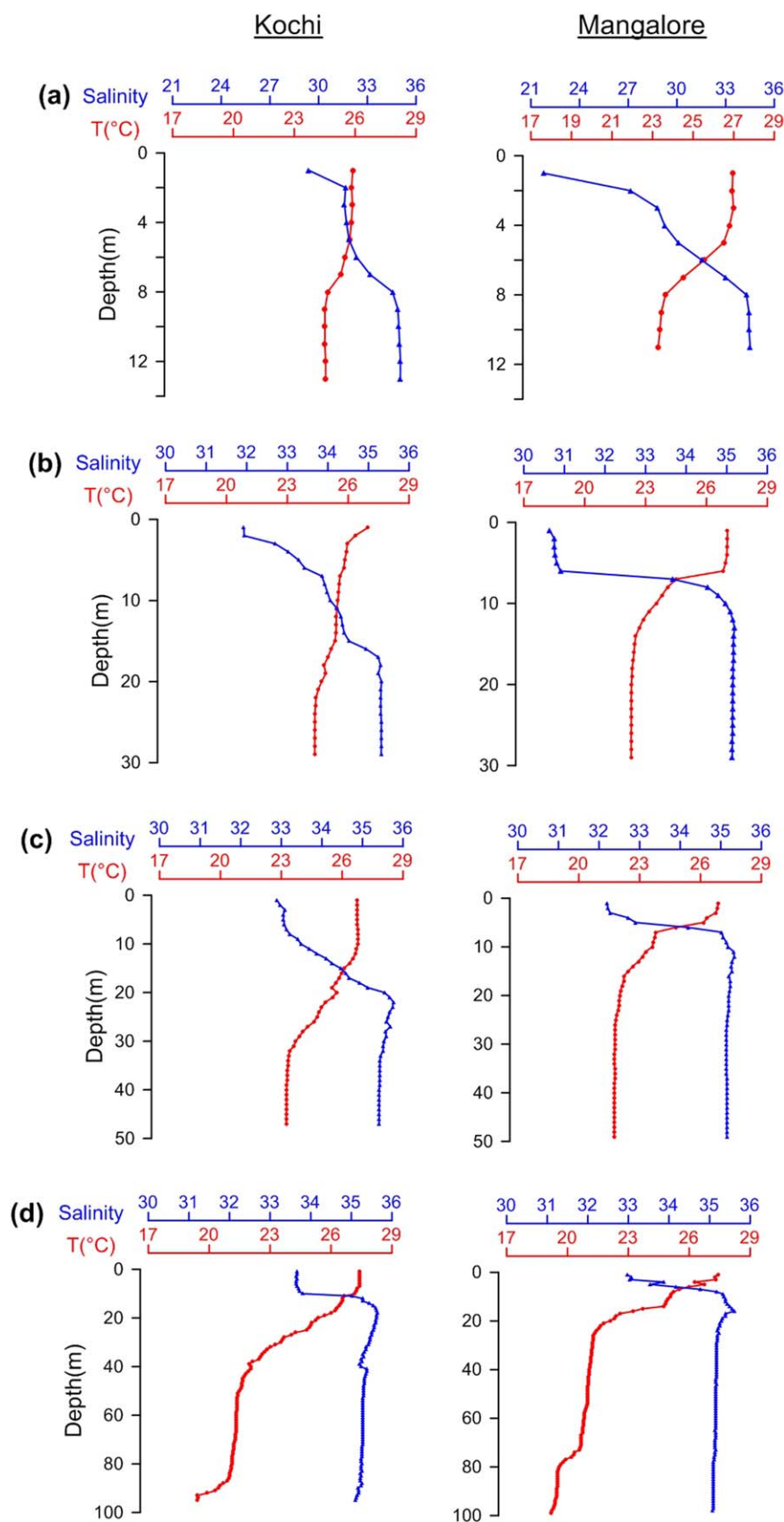


Figure 3. Comparison of vertical profiles for temperature and salinity between Kochi and Mangalore for (a) nearshore, (b) inner shelf, (c) midshelf, and (d) outer shelf during September 2012.

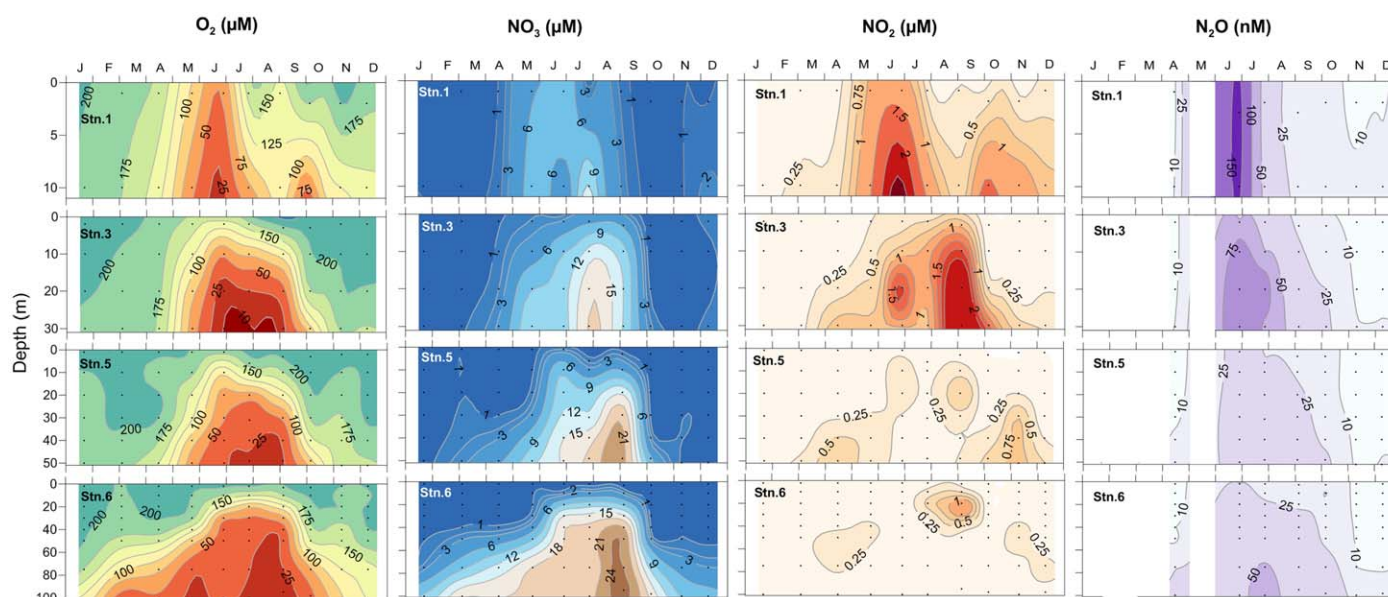


Figure 4. Time series distribution of O_2 , NO_3^- , NO_2^- , and N_2O at nearshore (stn.1), inner (stn.3), mid (stn.5), and outer shelf (stn.6) stations of Kochi during 2012.

consistent with the corresponding precipitation pattern following the oscillations of Indian Ocean Dipole (IOD) effect during 2012. The IOD index was near neutral during June to July that resulted in deficit rainfall but it became positive thereafter and the rainfall was normal to above normal [India Meteorological Department, 2013]. Because of this, lowest salinity was recorded in September. Together with the peak cold water intrusion through upwelling, the drop in surface salinity due to SM rains and runoff led to very strong stratification associated with a shallower MLD off Mangalore (Figure 3) than off Kochi.

4.2. Dissolved O_2 , Nutrients, and N_2O

The time series distribution of O_2 , NO_3^- , NO_2^- , and N_2O off Kochi (Figure 4) shows significant variability with the progression of upwelling (April to September). In April, the upper 50 m of the water column was well oxygenated before the advection of upwelled waters. The already low O_2 content of the upwelled water gets further diminished as it ascends toward the coast [Gupta et al., 2016]. O_2 depletion in nearshore surface waters was observed in May when the upwelled waters spread over the entire shelf. The O_2 saturations varied from 23% to 116% (avg. $88 \pm 23\%$), 3.7% to 138% ($37 \pm 37\%$), 4% to 112% ($80 \pm 33\%$), and 61 to 116% ($96 \pm 17\%$), respectively, during SIM, SM, FIM, and WM. Nutrient depleted (NO_3^- : $0.49 \pm 0.54 \mu M$; NO_2^- : $0.13 \pm 0.19 \mu M$; PO_4^- : $0.24 \pm 0.15 \mu M$) conditions prevailed during January to April. Upwelling intensified between May and June as a result of which the water column below 30 m turned hypoxic ($<50 \mu M$) and the euphotic zone got enriched with nutrients (NO_3^- : $\sim 8 \pm 7 \mu M$; NO_2^- : $0.7 \pm 0.9 \mu M$; PO_4^- : $0.7 \pm 0.4 \mu M$). The O_2 concentrations reached a minimum of $7 \mu M$ and nitrite attained a maximum of $3.2 \mu M$ in June. Following the sharp recession of upwelling, the shelf waters again became oxic and oligotrophic during FIM and WM.

The O_2 and nutrients distributions off Mangalore during April and December remained almost similar and comparable to that off Kochi. However, the bottom waters in September displayed significant difference (Figure 5) with anoxic off Mangalore and hypoxic off Kochi. The anoxia off Mangalore (despite our O_2 minimum detection limit of $2 \mu M$) is in accordance to its well established seasonal recurrence over the CEAS shelf [Naqvi et al., 2000, 2009]. The strongly reducing environment resulted in accumulation of NO_2^- (up to $6.2 \mu M$) and decrease in NO_3^- concentrations up to the midshelf off Mangalore. Even at the outer shelf off Mangalore, measured O_2 was $<5 \mu M$ below 30 m depth (not detectable at 100 m) while off Kochi it was $<60 \mu M$ ($14.3 \mu M$ at 100 m). These data clearly indicate that upwelling waters are associated with different O_2 concentrations, i.e., anoxic and hypoxic, respectively, in these shelf regions. The monthly observed N_2O concentrations are listed in Table 1. The data off Kochi show a well defined seasonal pattern with an increase in N_2O concentration from 9.2 ± 5.2 nM during SIM to 45 ± 32 nM during SM, followed by a progressive decrease to 20 ± 8 nM during FIM and 8.8 ± 2 nM during WM. Maximum N_2O concentrations (61 ± 47 nM) were recorded in June. High N_2O concentrations during the SM were clearly associated with hypoxic

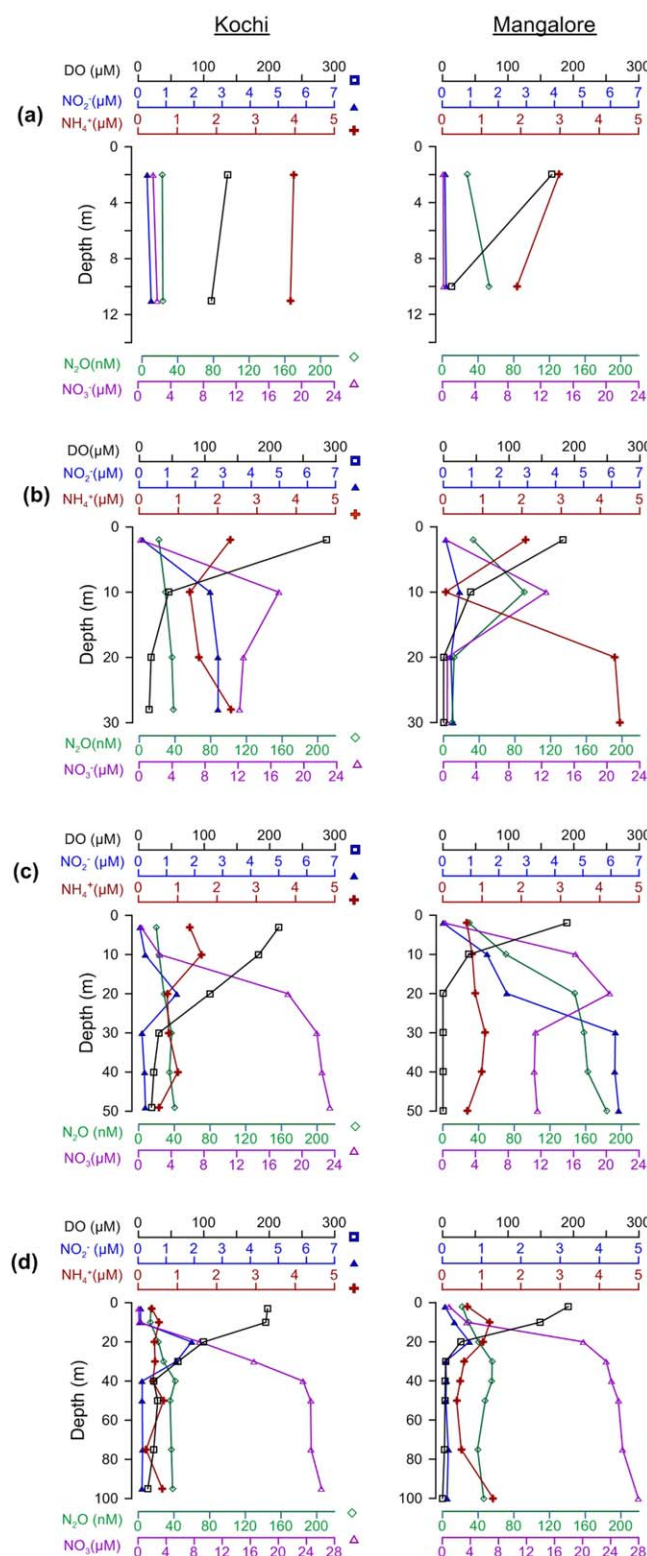


Figure 5. Comparison of vertical profiles for O_2 , nutrients, and N_2O between Kochi and Mangalore for (a) nearshore, (b) inner shelf, (c) midshelf, and (d) outer shelf during September 2012.

conditions arising from upwelling. The ranges (means $\pm$ SD) of N_2O concentrations off Mangalore were 4.2–29 nM (7.6 ± 5.7 nM), 9.5–202 nM (73 ± 63 nM), and 6.6–13 nM (8.5 ± 1.5 nM) in April, September, and December, respectively. The observed concentrations in September were significantly higher than those recorded off Kochi (31 ± 9.6 nM) and were apparently related to lower O_2 concentrations (Figure 5). However, the measured N_2O concentrations off Mangalore are lower than those reported earlier [Naqvi *et al.*, 2009]. The highest values were mostly associated with elevated nitrite in O_2 depleted waters, consistent with earlier observations [Naqvi *et al.*, 2000].

5. Discussion

5.1. Factors Controlling N_2O Production

During the WM and SIM seasons, the water column in the entire study region remained well oxygenated with low N_2O concentrations (<10 nM) in the mixed layer, as observed earlier [Naqvi *et al.*, 2010]. Nitrification has been considered to be the major process responsible for N_2O production in well oxygenated waters, as evident from the significant linear correlations ($p < 0.001$) between N_2O and ($NO_3^- + NO_2^-$), and between ΔN_2O and AOU in both the regions (Figure 6). By contrast, under O_2 depleted conditions, such as that prevailing in our study area during the SM, N_2O production via denitrification becomes significant. Bange and Andreae [1999] estimated that about 35% of the oceanic N_2O is produced through denitrification while the rest is produced through nitrification. According to Freing *et al.* [2012], however, contribution by denitrification is smaller ($\sim 7\%$), except in the OMZs of Arabian Sea [Law and Owens, 1990; Naqvi and Noronha, 1991] and eastern tropical Pacific Ocean [Kock *et al.*, 2016] where $\sim 90\%$ of N_2O production occurred via denitrification. The nonlinear increase in N_2O concentration at $O_2 < 25 \mu M$

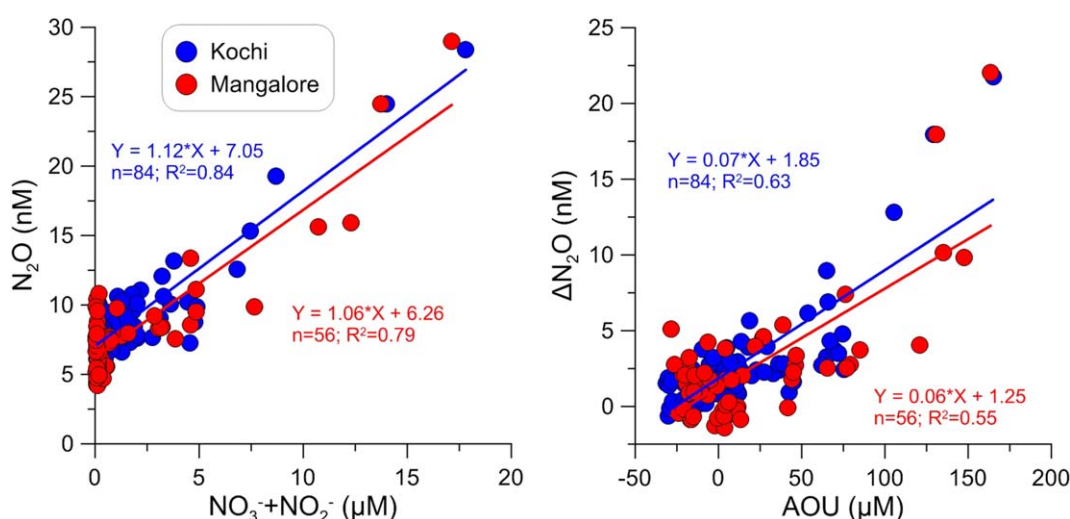
Table 1. Monthly Variation in Concentration and Air-Sea Fluxes of N₂O in the Study Region

Month	Surface Conc. (nM)	Maximum Subsurface (depth) Conc.(nM)	Surface Saturation (%)	Sea to Air Fluxes ($\mu\text{mol m}^{-2} \text{d}^{-1}$)		
				LM86	W92	N00
Kochi						
April	5.6–7.6	28(100 m)	100–135	0.15–5.9	0.29–11	0.2–7.6
June	25–164	164(10–20 m)	418–2652	28–216	58–467	40–329
July	17–35	107(20 m)	272–566	20–54	39–108	27–74
September	14–30	54(40 m)	231–474	8–18	20–50	14–36
October	10–22	41(100 m)	174–380	2.4–91	8.4–31	6.3–23
November	7.1–8.9	19(100 m)	126–155	1.0–2.1	3.1–6.7	2.5–4.9
December	6.5–9	15(100 m)	115–160	0.1–1.4	0.6–6.2	0.5–4.6
Mangalore						
April	4.4–7.6	29(100 m)	82–137	–0.18–0.1	–1.3–2.7	–1.1–2.1
September	22.1–40.1	54(40 m)	361–648	19–40	51–92	37–66
December	6.6–11.1	15 (100 m)	116–194	0.06–0.5	0.22–2.02	0.2–2.03

observed in the present study (Figure 7) is in part due to production through denitrification. This critical O₂ concentration is well in agreement with the earlier reported value of 22 μM toward enhanced yield of N₂O [Goreau *et al.*, 1980; Codispoti *et al.*, 2005].

5.2. N₂O Dynamics Off Kochi

The results clearly show greater accumulation of N₂O in the water column over the inner shelf as compared to midshelf and outer shelf. The mean N₂O concentration over the inner shelf was low during April (8.0 ± 1.2 nM), but increased by an order of magnitude in June (119 ± 50 nM). The seasonal N₂O concentration in the inner shelf varied from 6.6 to 10.2 nM (average: 8 ± 1.2 nM) during the SIM, from 22 to 164 nM (68 ± 49 nM) during the SM, from 10 to 27 nM (15.7 ± 6.4 nM) during the FIM, and from 7.6 to 13.2 nM (9.2 ± 1.5 nM) during the WM. Biogeochemical cycling over the inner shelves is to a large extent influenced by anthropogenic discharges from adjacent estuaries, the waters of which are expected to be highly supersaturated with N₂O [Barnes and Owens, 1999; Bange, 2006; Barnes and Upstill-Goddard, 2011]. However, the Indian estuaries show low N₂O concentrations due to their capacity for rapid assimilation of nitrogen [Rao and Sarma, 2013]. The Kochi estuary is no exception to this and due to its very fast turnover times for anthropogenic nitrogen [Bhavya *et al.*, 2016] its N₂O concentrations are very low during both the dry (12 ± 5.6 nM) and wet (28 ± 15 nM) seasons (unpublished data), which is in agreement with earlier studies [Rao and Sarma, 2013]. Moreover, most of our nearshore observations were made during the flood tide (see Table 1 of Gupta *et al.* [2016]) when the influence of estuarine inputs to the shelf is expected to be negligible. So, the prevailing well-oxygenated conditions over the entire shelf would have favored nitrification as the dominant source of N₂O during dry periods (Figure 6). By contrast, during the SM elevated N₂O concentrations


Figure 6. Relationship of N₂O versus NO₃⁻ + NO₂⁻, and ΔN₂O versus AOU in the study area during dry (nonupwelling) periods.

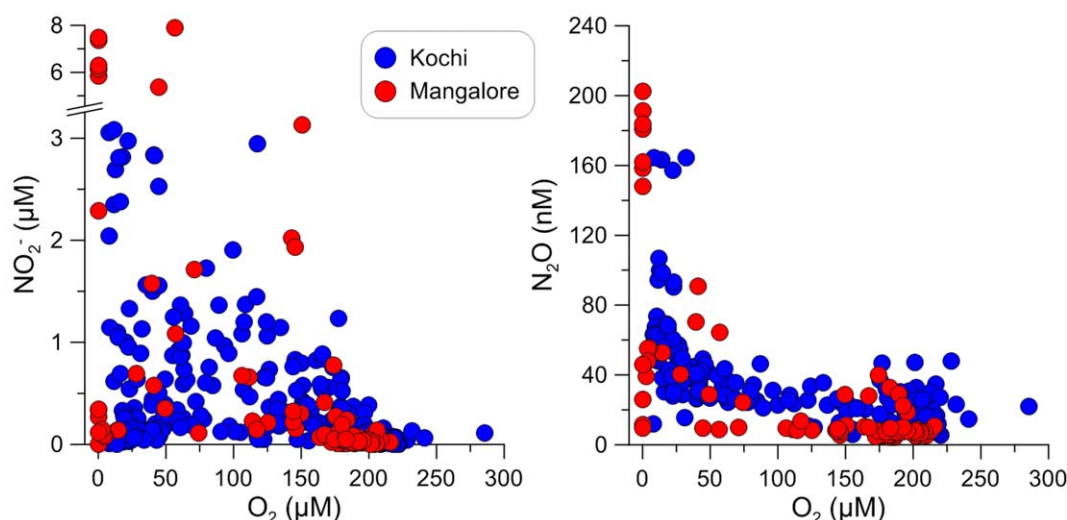


Figure 7. Relationship between O_2 , nitrite, and N_2O in the study area during 2012.

in subsurface were associated with hypoxic/suboxic waters indicating its possible production through denitrification. However, it should be noted that denitrification is triggered only when Winkler O_2 values fall well below our detection limit ($\sim 2 \mu M$); the actual threshold values are much lower ($< 0.09 \mu M$) [Dalsgaard *et al.*, 2012; Banse *et al.*, 2014]. This condition was never achieved off Kochi even during the peak upwelling in June when the minimum measured O_2 concentration being only $8.4 \mu M$. It is possible, though, that occurrence of denitrifying events were missed due to inadequate temporal resolution. The observed O_2 concentrations were often $< 20 \mu M$ and elevated NO_2^- ($\sim 3 \mu M$, Figure 4) levels up to the inner shelf ($> 10 m$), pointing to occasional, transient events of denitrification in the water column or close to sediment-water interface. But more so it is likely that the observed NO_2^- and N_2O are predominantly mixed upward from denitrification in the underlying anoxic sediments. The stratification over the Kochi shelf is relatively weak during the SM (Figure 2), which enables vertical mixing of nutrient-rich upwelled waters thereby enhancing primary production [Gupta *et al.*, 2016]. The subsequent organic sinking flux is expected to result in high O_2 demand in bottom waters, but the surplus ventilated upwelling waters together with weaker stratification seems to ensure enough oxygen supply to keep the subpycnocline waters just short of being denitrifying. Nitrification or/and assimilatory reduction of NO_3^- by phytoplankton [Vaccaro and Ryther, 1960] can also be possible mechanisms in such conditions, but they cannot elevate NO_2^- and N_2O to the observed levels under hypoxic conditions. Therefore, denitrification in the underlying anoxic sediments appears to be quite significant, over weak nitrification and short-lived denitrification in the water column, which builds-up 18-fold high N_2O concentrations ($119 \pm 43 nM$) over its saturated value ($6.5 \pm 0.2 nM$) close to the coast (up to station 2) in June (Figure 4).

The N_2O concentrations in the outer and midshelf regions were much lower, ranging from 5.6 to $28 nM$ (average: $9.8 \pm 6.2 nM$) during the SIM, 14 to $58 nM$ ($34 \pm 10 nM$) during the SM, 13 to $41 nM$ ($22 \pm 8 nM$) during the FIM, and 6.5 to $19 nM$ ($8.7 \pm 2.3 nM$) during the WM. These regions are not much affected by anthropogenic activities evidenced by no marked change in O_2 concentrations when compared to five decades ago [Gupta *et al.*, 2016]. Therefore, the conditions encountered here, including relatively modest N_2O buildup under hypoxic/suboxic conditions (Figure 4), are mostly of natural origin (upwelling source water) with the variability associated with seasonal hydrographic changes.

5.3. Differences in Biogeochemical Responses of Kochi and Mangalore Shelves to Upwelling

It has been reported that the hypoxic zone in the western Indian shelf has intensified in recent decades as a result of elevated nutrient loading through atmospheric deposition and runoff [Naqvi *et al.*, 2000, 2006a, 2009]. In contrast, results of the present study show that during September, propagation of anoxic upwelled waters over Mangalore shelf exerts a huge impact on the biogeochemical processes relative to off Kochi. This is evident from the much higher concentrations of N_2O off Mangalore in September (maximum

202 nM; average 73 ± 63 nM) than off Kochi (maximum 55 nM; average 23 ± 9). The results of the present study are consistent with earlier observations indicating that waters off Kochi do not lose oxygen completely [Banse, 1959, 1968; Gupta *et al.*, 2016] while those off Mangalore shelf recurrently turn anoxic during SM [Naqvi *et al.*, 2009]. The extent of O_2 depletion over the shelf depends on several factors: (i) initial O_2 concentration in the upwelling water, (ii) upwelling intensity associated with horizontal circulation, (iii) stratification resulting from a combination of upwelling of cold saline water and runoff of warm freshwater plus local precipitation, which restricts aeration of subsurface waters, and (iv) subpycnocline O_2 demand that in turn depends on organic matter supply from the surface layer following fertilization by upwelling as well as anthropogenic supply.

The 21°C isotherm observed at shallow depths (~ 50 m) at the Mangalore shelf entrance was found to be much deeper (~ 80 m) off Kochi (Figure 3). This shows that upwelling waters at Mangalore are cooler by $\sim 1^\circ\text{C}$ than at Kochi. Accordingly, at 100 m depth while the O_2 concentration was $\sim 14 \mu\text{M}$ off Kochi, it was below detection limit off Mangalore (Figure 5). The permanent OMZ exists in the Arabian Sea has a southern boundary to the south of Mangalore up to $\sim 12^\circ\text{N}$ [Naqvi, 1991]. The upwelling waters at Mangalore are therefore sourced from the core of OMZ which are already denitrified. It is also likely that the upwelling off CEAS (Mangalore) is stronger, i.e., upwelling waters are originated from the deeper depths in the open ocean than in the SEAS (Kochi) [our unpublished data]. This is consistent with the reported highly O_2 depleted to anoxic bottom waters at the shelf entrance of Mangalore all through SM months ($0 < 10 \mu\text{M}$) [Naqvi *et al.*, 2009] relative to those observed in the present study at Kochi ($14\text{--}33 \mu\text{M}$). Thus the difference in upwelling source water characteristics viz. relatively cooler and suboxic/anoxic waters advection at Mangalore compared to Kochi is highly important leading to contrasting biogeochemical status of these shelves. The discernible very poor NO_3^- and NO_2^- concentrations at surface followed by steep rise at 10 m at least in the inner shelf clearly shows that nutrients input into upper stratified column from runoff, especially during September being late summer monsoon, is negligible compared to that supplied through upwelling (Figures 3b and 5b). This is supported by recent findings that monsoonal estuaries of India including those on its western shelf assimilate anthropogenic nutrients as high as $\sim 91\%$ thereby their discharge to coastal seas are very less [Bhavya *et al.*, 2016; Krishna *et al.*, 2016]. Thus nutrients derived from relatively strong upwelling might have largely enhanced the biological production as evidenced by higher Chl *a* off Mangalore ($9.7 \pm 11 \text{ mg m}^{-3}$) than off Kochi ($4.4 \pm 3.8 \text{ mg m}^{-3}$). Consequently, a higher O_2 demand for sinking dead plankton flux at Mangalore (Phaeophytin: $3.2 \pm 3.5 \text{ mg m}^{-3}$) relative to Kochi ($1.4 \pm 1.3 \text{ mg m}^{-3}$) in the already anoxic subpycnocline waters intensifies denitrification in the former region. The strong near-surface stratification off Mangalore act in unison to ensure a complete removal of O_2 beneath the thermocline not only over the inner shelf but also over the mid and outer shelf as well (Figure 5). This restriction in O_2 supply further adds stress on benthic mineralization to intensify the sedimentary anoxia leading to denitrification especially up to the midshelf. Complete deficiency of O_2 results in N loss mainly through denitrification [Naik, 2003; Naqvi *et al.*, 2009], and when nitrate is fully exhausted sulfate reduction takes place in the sediments over the inner shelf of CEAS [Naqvi *et al.*, 2009].

High NH_4^+ ($\sim 5 \mu\text{M}$) associated with highly depleted NO_3^- ($< 0.5 \mu\text{M}$) concentrations in the anoxic subpycnocline waters of Mangalore (Figure 5) indicate the anaerobic oxidation of sinking surface production while such signals are weak in the suboxic waters of Kochi. CEAS region has been found to exhibit high benthic denitrification rate of $0.58\text{--}1.04 \text{ mmol N m}^{-2} \text{ d}^{-1}$ [Pratihary *et al.*, 2014] which are consistent with those of $0.23\text{--}1.25 \text{ mmol m}^{-2} \text{ d}^{-1}$ reported earlier in this region [Naik and Naqvi, 2002; Naqvi *et al.*, 2006a]. The N_2O concentrations in the subpycnocline waters of Mangalore during September are distinctly low in the inner shelf ($9.5\text{--}11.7$ nM) than at midshelf ($65\text{--}202$ nM) despite NO_3^- is highly depleted ($< 0.5 \mu\text{M}$) under anoxic conditions in the former region (Figures 5b and 5c). H_2S smell was noticed from the bottom waters and surface sediments up to inner shelf during this period, but its concentration was not measured. It is likely that chemolithoautotrophic bacteria often present in such sulfidic sediments [Lam and Kuypers, 2011] would have reduced NO_3^- to N_2 through sulfide oxidation [Jørgensen and Nelson, 2004]. The near absence of intermittent reduced forms like NO_2^- and N_2O (Figures 5a and 5b) up to inner shelf explains almost complete loss of N to molecular N_2 . Such autotrophic denitrification has been found earlier in the sulfidic bottom waters off Goa also during late September (S. W. A. Naqvi *et al.*, National Institute of Oceanography, unpublished data) and benthic experiments estimated its potential rate as high as $3.21 \text{ mmol N m}^{-2} \text{ d}^{-1}$ [Pratihary *et al.*, 2014]. However, the suboxic to anoxic (nonsulfidic) sediments of midshelf with moderate

subpycnocline NO_3^- concentrations ($\sim 12 \mu\text{M}$) follows usual heterotrophic denitrification wherein the organic matter is oxidized by NO_3^- or NO_2^- resulting in N_2O production. It has been shown that nonsulfidic sediments overlaid by suboxic waters of CEAS with moderate NO_3^- concentrations could cause significant N loss through heterotrophic denitrification during July to August which switched to autotrophic denitrification by late September to October when sediments turned to sulfidic [Pratihary *et al.*, 2014]. It is pertinent to note that these periods coincided with a salient drop in O_2 content of the upwelling waters at the shelf entrance of Mangalore from being suboxic during July to August to anoxic by September [Naqvi *et al.*, 2009], as was the case in our September observation also. This perhaps is a vital first-step (apart from primary productivity) in controlling the observed shift in sediment nature from nonsulfidic to sulfidic. This transition period was found to have highest buildup of N_2O (765 nM) in the CEAS [Naqvi *et al.*, 2000] and, in particular, at Mangalore (554 nM) [Naqvi *et al.*, 2009]. Though no such studies were ever made for the SEAS, the nonsulfidic suboxic conditions prevailed over Kochi shelf all through SM upwelling would induce heterotrophic benthic denitrification and the N_2O thus produced is diffused into the water column above. The availability of moderate NO_3^- concentrations in the suboxic bottom waters of Kochi inner shelf ($\sim 12 \mu\text{M}$) when compared to its near absence from the similar region of Mangalore ($< 0.5 \mu\text{M}$) indicate the highest degree of denitrification in the anoxic later region (Figure 5b). Overall, the shelf off Mangalore exhibited a clear gradient with sulfate reducing nearshore, autotrophic denitrifying inner shelf, strong heterotrophic denitrifying midshelf and mildly denitrifying outer-shelf, whereas the inner shelf of Kochi appears to have been influenced predominantly by heterotrophic sediment denitrification due to hypoxic/suboxic water column. These differences in biogeochemical responses over the western shelf of India are therefore predominantly governed by the varying upwelling intensities and associated O_2 concentrations.

5.4. Revised Estimate of N_2O Emission From the Southwestern Indian Shelf

The N_2O saturation levels off Kochi ranged from 101% to 2652% (Table 1) with high values occurring during the SM ($574 \pm 720\%$) followed by the FIM ($246 \pm 76\%$), the WM ($140 \pm 12\%$), and the SIM ($123 \pm 12\%$). Overall, oceanic surface waters are supersaturated with respect to atmospheric N_2O ($\sim 3.5\%$) [Nevison *et al.*, 1995]. However, higher saturation levels are commonly seen in coastal upwelling zones [Bange *et al.*, 1996, 2001a]. N_2O saturations observed in the surface waters of the western Arabian Sea (300%) [Bange *et al.*, 1996; de Wilde and Helder, 1997] and the north/central Arabian Sea (400%) [Jayakumar, 1999] appear modest when compared to those recorded over the shelf off Goa and Mangalore in the CEAS (up to 8250%) [Naqvi *et al.*, 2006b, 2009] and off Kochi in the SEAS (2652%, present study). The coastal waters of Peru, experiencing similar upwelling conditions, accumulate even higher quantity of N_2O (up to 12,244%) [Arévalo-Martínez *et al.*, 2015]. The N_2O emissions estimated following Wanninkhof [1992] ranged from 0.29 to $467 \mu\text{mol m}^{-2} \text{d}^{-1}$ off Kochi, and from -1.3 to $92 \mu\text{mol m}^{-2} \text{d}^{-1}$ off Mangalore (Table 1). High efflux off Kochi in June and July is mainly due to relatively stronger winds; data are not available off Mangalore for this period. In September, when the SM winds are weak, nearly 2-fold higher effluxes are recorded off Mangalore than off Kochi. Both regions served as sources of N_2O to the atmosphere with one exception: off Mangalore (up to midshelf) weak N_2O flux was directed from the atmosphere to the sea in April. The sea-to-air fluxes obtained in the present study are significantly higher when compared to most other naturally occurring hypoxic systems (Table 2).

Naqvi *et al.* [2000] quantified the N_2O emission from the entire western continental shelf of India as 0.06 – 0.39 Tg y^{-1} by extrapolating the sea-to air fluxes (derived by multiplying average N_2O concentration with LM86 and W92-based transfer velocities assuming wind speeds of 5 – 10 m s^{-1}) linearly to the entire western shelf area for a period of 6 months. This is significant when compared to the N_2O emission of 0.33 – $0.70 \text{ Tg N}_2\text{O y}^{-1}$ from the open Arabian Sea [Bange *et al.*, 2001b] considering that the western Indian shelf accounts for only 4% of the total area of the Arabian Sea. It must be noted that the high N_2O concentrations are confined mainly to the central shelf (11 – 17°N including Mangalore-Goa regions) as this region is only recurrently witnessing seasonal anoxia while the northern and southern shelves have always been reported with hypoxia and low N_2O concentrations, as was the case in the present study also. Thus linear extrapolation to entire western shelf without considering its significant O_2 and N_2O gradients would have resulted in overestimation of N_2O effluxes. We therefore attempt here to refine this estimate from the southwestern Indian shelf using present data and following a zonal and gridded extrapolation concept. For this, we divided the western shelf into three zones viz. 7 – 11°N , 11 – 14°N , and 14 – 21°N . The total N_2O emission estimated by Naqvi *et al.* [2000] was proportioned into these three zones as per the area of each zone (Table 3). N_2O

Table 2. Comparison of N₂O Concentrations and Fluxes From Major Naturally Hypoxic Shelf Systems Around the World

Region	Surface/Mixed Layer Concentration (nM)	Max. Subsurface (depth) Concentration (nM)	Sea to Air Fluxes ($\mu\text{mol m}^{-2} \text{d}^{-1}$)	Reference
Off Peru. (ETSP)	7.6–986		27–1825	Arévalo-Martínez <i>et al.</i> [2015]
Off central Chile (ETSP)	6.7–59	245 (30 m)	–9.8–195	Cornejo <i>et al.</i> [2007]
	5.1–30.1	206 (40 m)	–7.7–42.9	Farias <i>et al.</i> [2009]
Oman shelf	9.7–24.7	48.8 (50 m)	N.G.	Naqvi <i>et al.</i> [2010]
Eastern Indian shelf	4.9–12.0	42.0 (120 m)	–0.1–10.7	Naqvi <i>et al.</i> [1994]
	4.8–8.1	60 (80 m)	–54.8–45	Rao <i>et al.</i> [2013]
Western Indian shelf	5.3–436	765 (19 m)	–1.2–3243	Naqvi <i>et al.</i> [2006b]
	4.4–165	202 (30 m)	–1.1–467	Present study

fluxes from the zone 7°N to 11°N (SEAS) were estimated based on the year-long data off Kochi (~10°N) generated in the present study. The annual emission for the zone 11–14°N was computed by combining present seasonal data (in April, September, and December) off Mangalore (12.8°N) with earlier data for peak upwelling months (June to August which also include high buildup signals during transition period as explained above) from Naqvi *et al.* [2009]. The Kochi and Mangalore segments of the shelf were subdivided into six grid boxes according to the water depth (viz. 0–15, 15–25, 25–35, 35–45, 45–75, 75–200 m) and the fluxes were computed for each grid box by multiplying the surface area of each grid box with the corresponding N₂O flux density. An extrapolation of these grid box fluxes to the 7–11°N area of the SEAS yielded a total N₂O flux of 0.007, 0.016, and 0.010 Tg y^{–1}, based on LM86, W92 and N00 transfer velocity parameterizations, respectively. Similarly, the N₂O emission from the zone 11 to 14°N was estimated at 0.012, 0.023, and 0.016 Tg y^{–1}, respectively, based on the above parameterizations. Combining these estimates, the revised estimate of N₂O efflux from the southwestern Indian shelf (7–14°N) comes to 0.019–0.039 Tg y^{–1} which is almost one-fourth of the earlier estimate (Table 3). It is likely that the emission from the northern zone (14–21°N) may also be lower than that reported previously, and so application of similar revised approach in conjunction with higher resolution sampling in space and time is needed for further refining the estimate of N₂O emission from the entire western Indian shelf. This is important in view of intensification of seasonal anoxia in recent times owing to the expansion of OMZ which may yield an upward-rise of N₂O concentrations. In such case, the elevated N₂O concentrations to some extent may compensate the lower effluxes due to revised approach.

6. Conclusion

The SEAS has been identified as a significant source of N₂O to the atmosphere, especially during the summer monsoon. The coastal upwelling results in seasonal buildup of N₂O in oxygen-depleted (<25 μM of O₂) waters. N₂O accumulation is much higher off Mangalore than off Kochi. This difference is mainly attributed to the stronger upwelling and associated anoxic conditions coupled with higher productivity and stronger near-surface thermohaline stratification off Mangalore relative to Kochi. This leads to the development of intensely reducing conditions in bottom waters and underlying sediments off Mangalore that support enhanced production of N₂O. Off Kochi, by contrast, bottom waters remain just short of turning anoxic, thereby the modest buildup of N₂O may be largely limited to its production through sediment denitrification. Utilizing the high-resolution data of the present study, our revised estimate of N₂O emission from the southwestern Indian shelf (south of 14°N) was only one-fourth (0.019–0.039 Tg y^{–1}) of the earlier estimate which is attributed to our new approach adopted in computing the annual fluxes. In view of the growing

Table 3. Revised N₂O Budget (Tg y^{–1}) Along the Southwestern Indian Shelf Based on Different Parameterizations for Gas Transfer Velocity

Zone (°N)	Surface Area (km ²)	Earlier Budget [Naqvi <i>et al.</i> , 2000]	Revised Budget (Present Study)			
			LM86	W92	N00	Updated Range
7–11	30,871	0.010–0.067	0.007	0.016	0.011	0.007–0.016
11–14	39,368	0.013–0.085	0.012	0.023	0.016	0.012–0.023
14–21	109,761	0.036–0.241				
Total	180,000	0.060–0.390				

concerns about expanding OMZ and its influence on global climate change (via emissions of climate-relevant trace gases such as N_2O), further studies are essential to refine the sea to air fluxes of greenhouse gases including N_2O and also to predict the responses of the biogeochemical processes over the entire shelf off west India to the ongoing regional (developmental activities) to global (e.g., warming) environmental changes.

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