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**Intensified oxygen minimum zone on the western shelf of Bay of Bengal during summer monsoon:
Influence of river discharge**

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Abstract

A study on biogeochemical cycling in the west coastal Bay of Bengal was undertaken during peak discharge period to understand the influence of enhanced stratification and primary production on possible intensification of oxygen minimum zone (OMZ). Our study reveals that oxygen concentrations were below the detection limits in the northwestern (NW) coastal Bay of Bengal between 100 and 500 m associated with strong stratification and high phytoplankton biomass. Such low oxygen concentrations have never reported so far from the coastal Bay of Bengal. Despite existence of conducive environment for occurrence of denitrification in the coastal Bay of Bengal, accumulation of neither secondary nitrite nor nitrous oxide (N₂O) was observed. Absence of denitrification was reported to be caused by faster scavenging of organic matter and low bacterial respiration rates, in contrast, our results suggest that neither of them were potential reason for absence of denitrification in the coastal Bay of Bengal than hitherto attributed.

Keywords: suboxic zone, continental shelf, denitrification, nutrients, river discharge, Bay of Bengal

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1. Introduction

The Bay of Bengal (northeastern Indian Ocean) receives immense fresh water runoff from major rivers, such as the Ganges, Brahmaputra, Godavari, Mahanadi, Cauvery, Irrawady, and Krishna ($1.6 \times 10^{12} \text{ m}^3 \text{ a}^{-1}$; UNESCO 1979). Both river runoff and precipitation are more intense during the summer (southwest monsoon; June to September; Unger et al. 2003). As a result, salinity of the surface waters is 3 to 7 units lower in the Bay of Bengal throughout the year than in the adjacent basin, the Arabian Sea (LaViolette 1967; Varkey et al. 1996), which leads to strong stratification (Shetye et al. 1991, Shetye 1993). The river system also delivers major parts of its annual average sediment load (1.1×10^9 tonnes) during the summer (Milliman and Meade 1983; Milliman and Syvitski 1992). The fluvial inputs are major sources of nutrients to the Bay of Bengal. The annual supply of nutrients (dissolve silicate) by the Ganges and Brahmaputra rivers to the Bay of Bengal is $133 \times 10^9 \text{ mol a}^{-1}$, which is $\sim 2\%$ of the riverine input to the world ocean (Sarin et al. 1989).

Occurrence of oxygen minimum zone (OMZ) ($<5 \mu\text{mol kg}^{-1}$ of dissolved oxygen) in the Bay of Bengal is well debated in the literature. Wyrski (1971) reported an intense depletion of dissolved oxygen (DO) at intermediate depths of Bay of Bengal. Based on the data collected during International Indian Ocean Expedition (IIOE), Deuser (1975) reported that OMZ exists in the northeastern Bay and stressed on the possible occurrence of reducing conditions. Sen Gupta et al. (1977) and Naqvi et al. (1978) noticed nitrate deficiencies in the Bay, suggesting that sizable denitrification might be occurring in this area. Hattori (1983) and later Rao et al. (1994) did detailed study on the possibility of denitrification in the Bay of Bengal during spring (pre-southwest; March-April 1991) and winter (northeast monsoon; December 1991) and observed pockets of low oxygen waters ($4\text{-}10 \mu\text{mol kg}^{-1}$) in the western Bay, but they did not notice secondary nitrite maxima associated with low oxygen layer. Such low oxygen water pockets were attributed to advection of water from close to sediment where intense decomposition of organic matter or diffusion of oxygen into the pore waters led to decrease in oxygen levels. Madhu et al. (2006) observed that $<20 \mu\text{mol kg}^{-1}$ of DO was found between 100 and 150 m during summer. Sardesai et al. (2007) also observed concentration close to $\sim 10 \mu\text{mol kg}^{-1}$ between 100 and 150 m in the near shore waters during summer. No reports have been made so far from the coastal Bay of Bengal on existence of intense OMZ. No secondary nitrite maximum was observed associated with decrease in

high nitrous oxide (N₂O) concentrations (Rao et al. 1994; Sardesai et al. 2007). The absence of denitrification in the Bay was attributed to lower bacterial respiration rates and rapid sinking of organic matter (Ittekkot et al. 1991; Rao et al. 1994). In all these studies, measurements were made only in the upper 100-150 m during summer and no measurement were made close to the coast where maximum impact of river discharge can be noticed as the entire coastal region is topped with low saline water and strongly stratified (Shetye et al. 1991). Gomes et al. (2000) observed that primary productivity increases during summer (0.1 to 0.2 gC m⁻² d⁻¹) due to enhancement of nutrients by river discharge. Here we report first ever observations on influence of river discharges on intensification of OMZ, with reference to thickness and concentrations, in the coastal Bay of Bengal during summer and impact of water column biogeochemical processes.

2. Material and methods

Samples were collected on board ORV Sagar Nidhi (#SN 42) during 23rd July to 10th August 2010, representing peak river discharge period, along the east coast of India covering major rivers such as Krishna, Godavari and Mahanadi and minor rivers - Vamsadara and Hyadri. Seventy three stations were occupied in 9 transects (8 stations in each transect except off Godavari river where 9 stations) covering both south and north of riverine mouths. Transect V (off Visakhapatnam city) was chosen to represent no discharge location. In each transect, water samples were collected at standard depths from a water column depth of 25 to 1000 m (**Fig. 1**).

Water sampling was carried out at standard depths using a Seabird Conductivity-Temperature-Depth (CTD)-rosette system fitted with 10 L Niskin bottles. Analysis for nutrients (nitrate, nitrite, phosphate and silicate) and oxygen were completed shortly after collection of the samples. Dissolved oxygen (DO) was estimated following Winkler titration using automated end point potentiometric detection (Carritt and Carpenter 1966) by Tritrinado 835 Metrohm autotitrator. Nutrients were analyzed following standard colorimetric procedures (Grashoff et al. 1983). In addition to this, dissolved oxygen was also measured continuously at every one meter depth using DO sensor (JFE ALEC Co Ltd, Japan). In order to ensure consistency between calibrations, we used the same nutrient standards during entire cruise. These standards were prepared in bulk and stored in sealed sterilized ampoules. The analytical precision,

expressed as standard deviation, was $\pm 0.07\%$ RSD for DO whereas for nitrate+nitrite, ammonium, phosphate and silicate were ± 0.02 , 0.02 , 0.01 and $0.02 \mu\text{mol l}^{-1}$ respectively. The DO measured using Winkler method and sensor agreed within $0.2 \mu\text{M kg}^{-1}$ in the sub-oxic region. A 2 to 5 L of water sample was filtered through GF/F filter (Whatman) and phytoplankton biomass retained on that was extracted with N, N dimethyl formamide for Chl-a at 4°C in dark for 12 h, and then analyzed spectrofluorometrically (Varian Eclipse Fluorescence spectrophotometer, USA) following Suzuki and Ishimaru (1990). The analytical precision for Chl-a analysis was $\pm 4\%$. The dissolved carbohydrates were measured using spectrophotometric method following Dubois et al. (1956) and Gerchako and Hatcher (1972) using Shimadzu UV-1800 spectrophotometer. The analytical precision was $\pm 0.02 \mu\text{M}$ of glucose equivalent with analytical precision of $\pm 3\%$. Total organic carbon (TOC) was measured using high temperature catalytic oxidation (HTCO) method (TOC CPH, Shimadzu, Japan). The suspended particulate matter (SPM) was measured based on weight difference of the matter retained on $0.22 \mu\text{m}$ pore size polycarbonate filters (Millipore). Dissolved nitrous oxide (N_2O) was determined by a multiphase head space equilibration technique (McAullife 1971) coupled with Gas Chromatographic (GC) analysis. Predetermined volume (25 ml) was equilibrated with equal volume of helium in a gas tight syringe. Equilibration was achieved by vigorously shaking the syringe at room temperature for 5 minutes. This method has been used before by several authors (e.g. Jayakumar et al. 2001). After equilibrium, the head space was dried over drierite and then injected through a 5-ml sampling loop into a gas chromatograph (Agilent- 6820). The configuration of the instrument was similar to the one described by Weiss (1981). Chromosorb 102 (80/100 mesh) column, and a ^{63}Ni Electron Capture Detector (ECD) was used for N_2O detection. The detectors were calibrated using dilutions made from the standard gas mixtures which were made and certified by Spectra gases, USA. The concentrations of the gases in the water samples were calculated from the concentrations measured in the head space, using the functions for the Bunsen solubility given by Weiss and Price (1980) for N_2O . Also atmospheric concentrations in the study region were measured by collecting the air samples in previously evacuated gas sampling bulbs, and injecting known amount of sample (5 ml) into GC with gas tight syringes through the same injection module used for the headspace analysis of water samples. The analytical uncertainty (1σ) for N_2O measurements at any depth was less than $\pm 2\%$, which is estimated from the analysis of duplicate water samples stored for different periods of time in a refrigerator. The precision of N_2O measurement was always better than 1% (at 1σ level).

Particulate organic carbon (POC) and their isotopic values were measured by filtering about 2-5 litres of water sample through pre-combusted GF/F filter, at 300° C for 6 h, at low vacuum and dried at 60° C for at least 24 h. Filters were acid (hydrochloric acid) fumigated for 12 h in the desiccators to remove inorganic carbon. The content and isotopic ratios of organic carbon in the particulate matter was measured on elemental analyser coupled with Isotope Ratio Mass Spectrometer (EA-IRMS-Delta V, Finnigan, Germany) and results are expressed relative to conventional standards i.e., PDB limestone for carbon (Coplen 1996) as δ values. Standard deviation on twenty aliquots of the same samples was lower than 0.2‰ for $\delta^{13}\text{C}$.

3. Results and Discussion

Salinity varied between ~22 and 34 psu in the study region along the west coastal Bay of Bengal in the upper 20 to 50 m and relatively lower salinities were observed in the northwestern (NW) (transects VD, HD, MS, MN) compared to southwestern (SW) coast (KS, KN, GS, GN) (**Fig. 2**). The East India Coastal Current (EICC) flow poleward during the study period from southern tip of India to nearly transect VD and southward from NW region and both merges at ~18° N and moves offshore (Shetye et al. 1991; Varkey et al. 1996). As a result equatorward movement of Ganges river outflow decreases salinity in the NW region. The salinity gradient between surface and subsurface (50 m) was low (<1 psu), where less river outflow influence was observed (KN, GS and V transects), in contrast, ~3 psu difference was noticed off Krishna (KS) and Godavari (GN) river mouths and increased sharply to ~13 psu in the north off Mahanadi river (MN) (**Fig. 3a**). Heavy discharge from the Ganges river to the NW region led to intense stratification.

The SPM was brought to the coastal Bay through freshwater discharge. The SPM ranged between 9.1 and 33.7 mg l⁻¹ and displayed significant spatial distribution pattern (**Fig. 3b**). Though discharge influence was high in the NW region, as evidenced from salinity, high SPM was observed in the SW region. The contribution of SPM from Ganges river to the peninsular region was small as the westward major SPM flow towards east was evidenced from the distribution of clay mineralogy (Rao et al. 1988). Similarly, nitrate concentrations decreased from SW (5.5±3 $\mu\text{mol kg}^{-1}$) to NW region (0.6±0.3 $\mu\text{mol kg}^{-1}$) whereas phosphate did not show significant difference (0.3±0.2 $\mu\text{mol kg}^{-1}$) except at GN transect. (**Fig. 3c, d**). Though higher nitrate concentrations were found in the SW region, Chl-a concentrations

increased towards NW (3.6 to 5.3 mg m⁻³) compared to SW region (0.8 to 1.2 mg m⁻³) (**Fig. 3e**). The contrasting distribution of nutrients and Chl-a was mainly caused by low SPM in the NW (9.2 to 12.4 mg l⁻¹) than SW (30-34 mg l⁻¹) region that led to increase in light availability for phytoplankton to grow. Madhuratap et al. (2003) also suggested light availability controls the phytoplankton growth in the Bay of Bengal during summer (June to September). The decrease in nutrient levels in the NW region was probably due to high biological consumption as evidenced from high Chl-a (**Fig. 3e**).

The DO concentrations in the surface water ranged between 155 and 215 $\mu\text{mol kg}^{-1}$ (**Fig. 4**) and increased towards NW and it was consistent with the Chl-a distribution (**Fig. 3e**). The sharp decrease in DO concentrations were observed below halocline (~30-50 m) and were close to detection limits at depth below 100 to 150 m in the entire study region. Based on the high depth resolution DO data collected using DO sensor, the variations in boundary and thickness of the OMZ was estimated. The upper boundary of the OMZ ($<5 \mu\text{mol kg}^{-1}$) was varied between ~70 and 115 m in the study region and gradual deepening was noticed from SW (81 m) to NW region (94 m) (**Fig. 5a**). On the other hand, the lower boundary of the OMZ varied between ~260 to 550 m and again gradual deepening was noticed towards NW (**Fig. 5b**). Hence, the thickness of the OMZ increased from ~200 m in the SW to 460 m in the NW region (**Fig. 5c**). It was observed that OMZ occurs close to the coast in the NW region (3.5 km from the coast) than in the SW region (7.5 km; **Figure 5d**). The OMZ was found to be away from the coast ($\sim 7.5 \pm 1$ kms) in the SW region and was sharply moved towards coast ($\sim 3.5 \pm 1$ kms) in the NW region. This pattern is again consistent with the Chl-a distribution pattern. In addition to this, the DO levels in the OMZ were also decreased towards NW region as they were $\sim 5 \mu\text{mol kg}^{-1}$ in the SW and were sharply decreased and were under detection limits in the NW region. This study suggests that OMZ was intensified towards NW with reference to both thickness and DO levels. Such intensification was associated with increase in vertical stratification (**Fig. 3a**) and biological production (**Fig. 3e**) suggesting that enhanced sinking flux of fresh organic carbon supported by river-derived nutrients led to formation of intense OMZ in the intermediate depths. Madhu et al. (2006) observed that DO concentration was $<20 \mu\text{mol kg}^{-1}$ between 100 and 150 m during summer; however, they did not sample at the core of the OMZ. Sardesai et al. (2007) also observed concentration close to $\sim 10 \mu\text{mol kg}^{-1}$ during summer in near shore waters between 100-150 m. They suggested that water column nutrients and oxygen concentrations in the Bay of Bengal were mainly driven by physical process alone through advection of

water masses and faster scavenging of organic matter via mineral particles. All these studies noticed DO concentrations relatively higher than the levels found in this study during summer. The potential reason could be under sampling in the core OMZ in other studies (Madhu et al. 2006 and Sardessai et al. 2007) as they sampled mostly upper 100 m of water column, hence they missed the low DO concentrations in the core of OMZ region. In addition to summer, Rao et al. (1994) noticed pockets of water with DO levels close to $4 \mu\text{mol kg}^{-1}$ during winter and spring seasons suggesting that perennial existence of OMZ in the coastal Bay of Bengal but it was intensified during summer due to strong vertical stratification due to high river discharge associated with enhanced biological production.

Such low oxygen concentrations are conducive for occurrence of denitrification. Naqvi et al. (2000) observed occurrence of seasonal suboxic conditions along the west coast of India accompanied with denitrification in the water column and the associated enhancement of secondary nitrite and production of N_2O . In this study, although similar DO levels were found, like in the west coast of India, significant accumulation of neither nitrite nor N_2O was observed in the suboxic zone. The nitrite ranged only between 0.1 and $2 \mu\text{mol kg}^{-1}$ in the entire study area and mostly found above 50 m, which was caused by excretory products of zooplankton or oxidation of ammonium (**Fig. 6a**), and no secondary nitrite was found in the water column associated with low oxygen. Though no secondary nitrite was observed, low nitrate concentrations were noticed close to the shelf, and such pockets were observed mainly along KS, KN and GS transects suggesting that possible denitrification in the shelf waters close to sediments (**Fig. 7**). Rao et al. (1994) also observed pockets of low nitrate concentrations in the offshore region during December 1991 and attributed to advection of denitrified water from the marginal sediments to the water column. The N_2O distribution suggests that it ranged between 1 to $\sim 90 \text{ nmol kg}^{-1}$ and higher concentrations were noticed between 100 to 250 m depth (**Fig. 6b**). Increase in N_2O in the subsurface waters was noticed from SW to NW region. Despite relatively low oxygen concentrations during summer compared to spring and winter periods (Naqvi et al. 1994), the distribution pattern of N_2O during summer is almost similar that of other seasons.

In order to confirm possible occurrence of denitrification in the OMZ, samples from the 250 m on transect V was collected in 40 glass bottles and were crimped. These bottles were kept in the incubator at the water temperature and inert gas (argon) was passed through the incubator for possible

contamination of atmospheric oxygen. The incubation was conducted for 10 days and on each day four bottles removed from the incubator and measured for dissolved oxygen, nutrients (nitrate and nitrite) and N₂O (**Fig. 8**). During the incubation the dissolved oxygen was decreased from ~8.1 to 2.8 μM whereas nitrate was increased from 25 to 38 μM albeit with some variations. Increase in nitrite from undetection limits to 8.7 μM was noticed whereas N₂O decreased ~10 to 2 nM during experiment period. We noticed some problem with the stoichiometry balance between oxygen consumption and nitrate release during nitrification in our experiment. In case of nitrification, for every moles of ammonium oxidised, two moles of oxygen is consumed whereas in our experiment ~8 μM of dissolved oxygen was consumed for ~13 μM of nitrate released. This could possibly due to leak of some oxygen from the atmosphere during incubation experiment. Nevertheless our data suggest that denitrification did not trigger despite oxygen levels decreased to low levels (~2 μM). The decrease in oxygen, N₂O and increase in nitrate and nitrite strongly suggests that organic matter decomposition and nitrification process are active and oxidation of N₂O to nitrate occurs. This experiment further suggests that denitrification do not occur in the OMZ of coastal Bay of Bengal.

The almost equal intense OMZ and absence of denitrification in the Bay of Bengal compared to Arabian Sea was attributed to low bacterial respiration and faster sinking of organic matter (Rao et al. 1994) in the former region. Naqvi et al. (1996) noticed that bacterial respiration rates in the central Bay of Bengal were 2.4 times less than in the central Arabian Sea during winter. Neither spatial nor temporal variability in bacterial respiration rates were known and no such measurements were carried out especially in the shelf regions. Therefore attributing absence of denitrification to low bacterial respiration in the central Bay of Bengal compared to Arabian Sea based on central Bay of Bengal data collected during winter may not be appropriate. In order to examine bacterial consumption of organic matter in the subsurface waters in the coastal Bay of Bengal, dissolved carbohydrate distribution was studied at selected stations in the NW and SW coastal Bay of Bengal (**Fig. 9**). Interestingly, the mean dissolved carbohydrate concentration in the depth range between 150 and 750 m in the SW (KS and GS) was 6.3±0.6 μmol glucose equivalents kg⁻¹ whereas it decreased to 4.2±0.7 μmol glucose equivalents kg⁻¹ in the NW (MN and MS) region. Similarly total organic carbon was also decreased from SW (123.5±5 μmol kg⁻¹) to 108.3±4 μmol kg⁻¹ in the NW region (**Fig. 9**). This, taken together with apparent oxygen utilization (AOU) values for the two regions (264±4 μmol kg⁻¹ for the former and 282±3 μmol kg⁻¹ for the latter

transects) strongly suggests that organic carbon and carbohydrate, the latter is the labile fraction of dissolved organic matter, was efficiently utilized in the NW region. Therefore, low bacterial respiration rates may not be a possible reason for the absence of denitrification in the coastal Bay of Bengal. Recently, Fernandes et al. (2009) observed relatively low C/N, POC/Chl-a and POC/DOC ratios and high Chl-a in the coastal Bay of Bengal during SW monsoon indicating the POM was relatively fresh. The isotopic ratios of particulate organic carbon (POC) was heavier ($\delta^{13}\text{C}_{\text{POC}} = -22.8 \pm 1.0\%$) in the NW, which is close to marine plankton signal of -23.2% (Thornton and McManus 1994), than in the SW region ($\delta^{13}\text{C}_{\text{POC}} = -25.4 \pm 2.1\%$) suggesting POC in the former region was mainly contributed through *in situ* primary production. Despite high water column POC in the NW, the sediment organic carbon in the NW region was lower ($0.73 \pm 0.11\%$) than that of in the SW region ($1.09 \pm 0.19\%$) suggesting that efficient bacterial degradation of organic matter in the water column of the former region. The mean SPM in the NW region was also relatively low ($\sim 10 \pm 3 \text{ mg l}^{-1}$) and hence may be less efficient scavenging of organic matter to the sediments compared to that of SW region facilitating organic matter to decompose in the water column through increasing particle residence time in the water column. It is therefore suggested that neither low bacterial respiration rates nor faster scavenging of organic matter can be potential reasons for the absence of denitrification in the coastal Bay of Bengal during summer. Nevertheless, it is difficult to derive possible reasons on absence of denitrification in the coastal Bay of Bengal with the present data and more work is needed to undertake to address this issue in future.

4. Summary and conclusions

The present study on biogeochemical cycling along the west coast of Bay of Bengal during peak discharge period (summer) suggests that river discharge has significant impact on stratification and primary production that led to the intensification of OMZ in the western coastal Bay of Bengal than other seasons. The thickness of OMZ layer increased towards NW region and was consistent with enhanced stratification and biological production due to heavy river discharge. Though conducive conditions for occurrence of denitrification were encountered, however, the accumulation of neither secondary nitrite nor of N_2O was observed. Unlike it was attributed before, neither low bacterial respiration rates nor faster sinking organic matter was responsible for absence of denitrification.

Therefore, more work is needed to understand potential reasons for the absence of denitrification in the Bay of Bengal through high resolution time-series observations.

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Legends to Figures:

Figure 1: Sampling locations in the western coastal Bay of Bengal. The flow of Ganges discharge was shown with arrows.

Figure 2: Distribution of salinity along different transects in the western coastal Bay of Bengal.

Figure 3: Variations in a) salinity in the surface (closed circle) and 50 m (open circle), b) SPM, c) nitrate, d) phosphate, and e) Chl-a in the surface.

Figure 4: Distribution of dissolved oxygen ($\mu\text{M kg}^{-1}$) along the different transects in the east coast of Bay of Bengal. The 5 μM dissolved oxygen contour shown in thick line.

Figure 5. Spatial variations in a) upper boundary, b) lower boundary, c) thickness and d) distance between western boundary of OMZ and coast along the west coast of Bay of Bengal.

Figure 6. Vertical distribution of a) nitrite and b) nitrous oxide (N_2O) in the western Bay of Bengal. Nitrite at all stations was plotted whereas N_2O showed at selected stations (KN-closed diamond, GN open diamond, MS-open circle and MN-closed circle).

Figure 7: Distribution of nitrate ($\mu\text{M kg}^{-1}$) along different transects in the west coast of Bay of Bengal

Figure 8: Time-series variations in a) DO (μM), b) dissolved nitrate (μM), c) nitrite (μM) and d) N_2O (nM) during laboratory experiment.

Figure 9: Vertical distribution of dissolved oxygen (closed circles), total organic carbon (open circles) and dissolved carbohydrates (plus) in the deep station of a) KS, b) GS, c) MS and d) MN.

Figure 1:

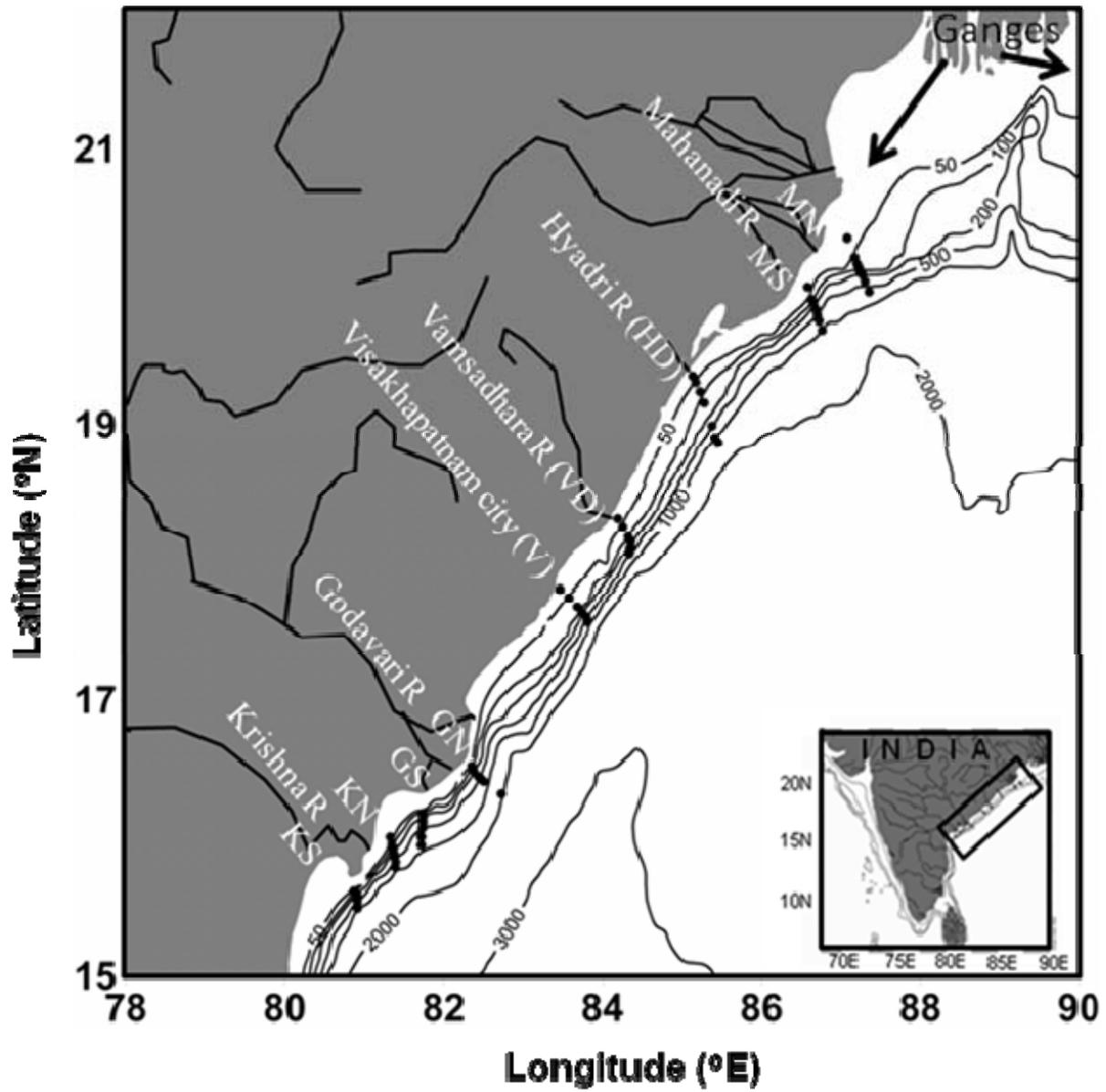


Figure 2:

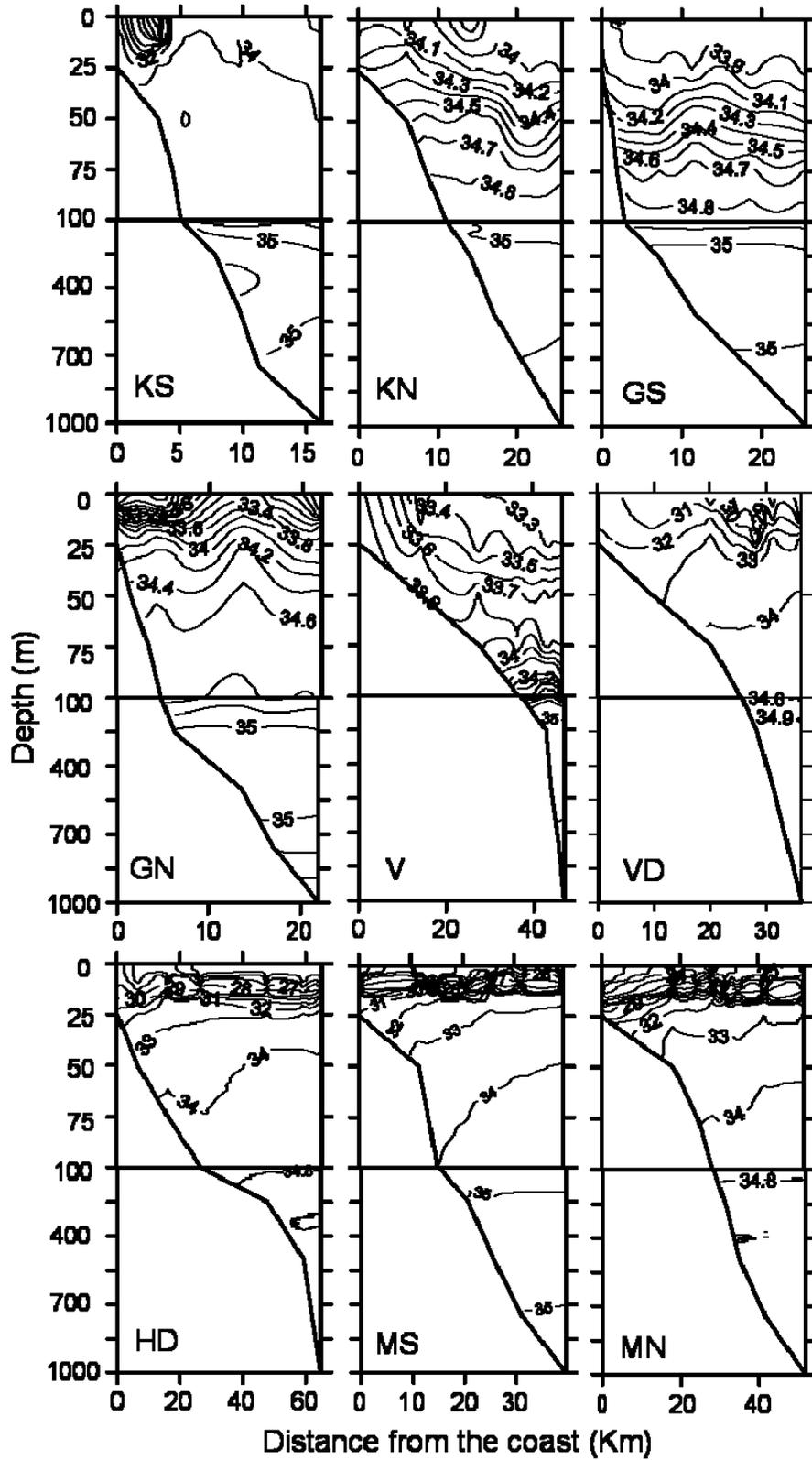


Figure 3:

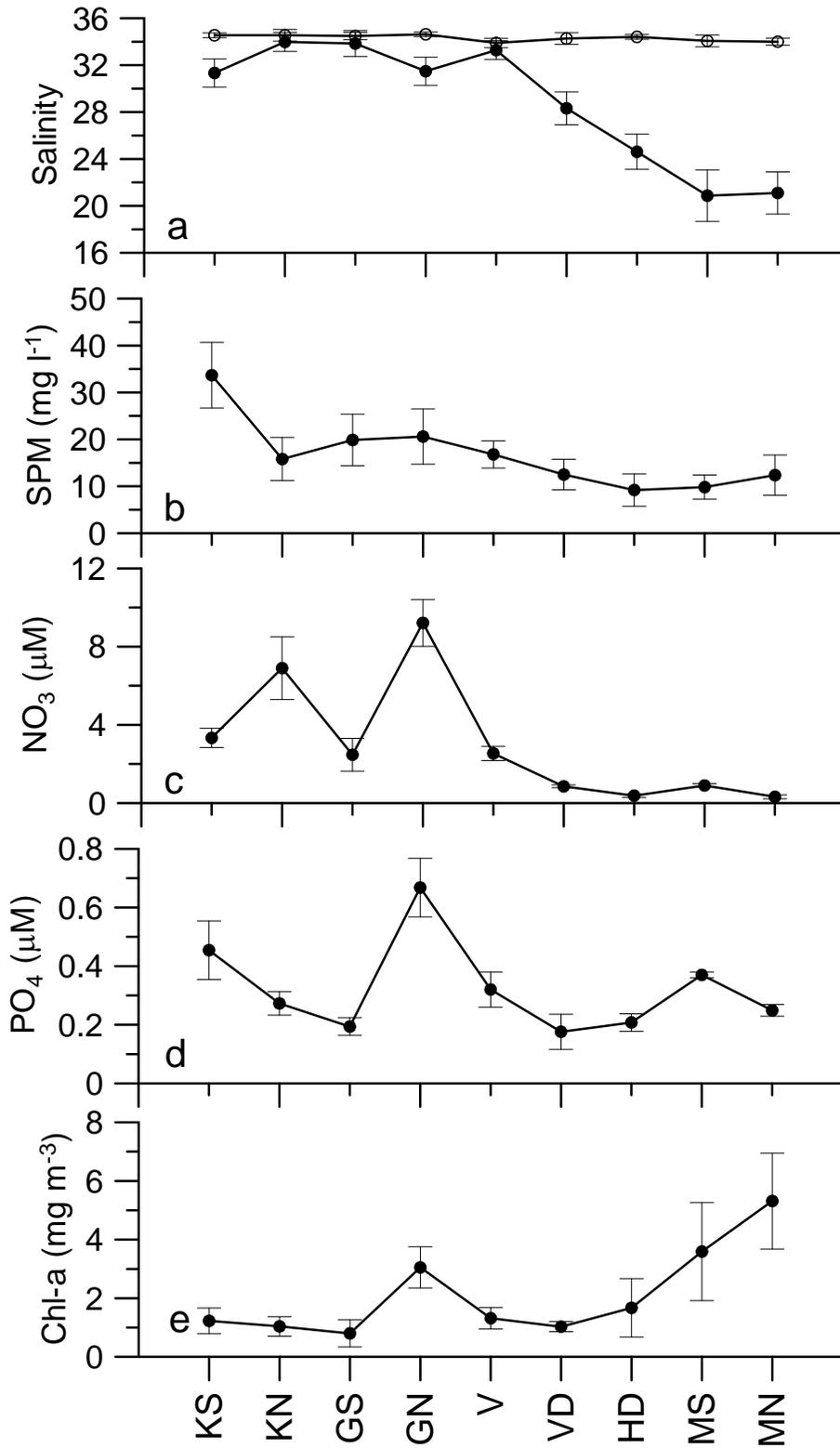


Figure 4:

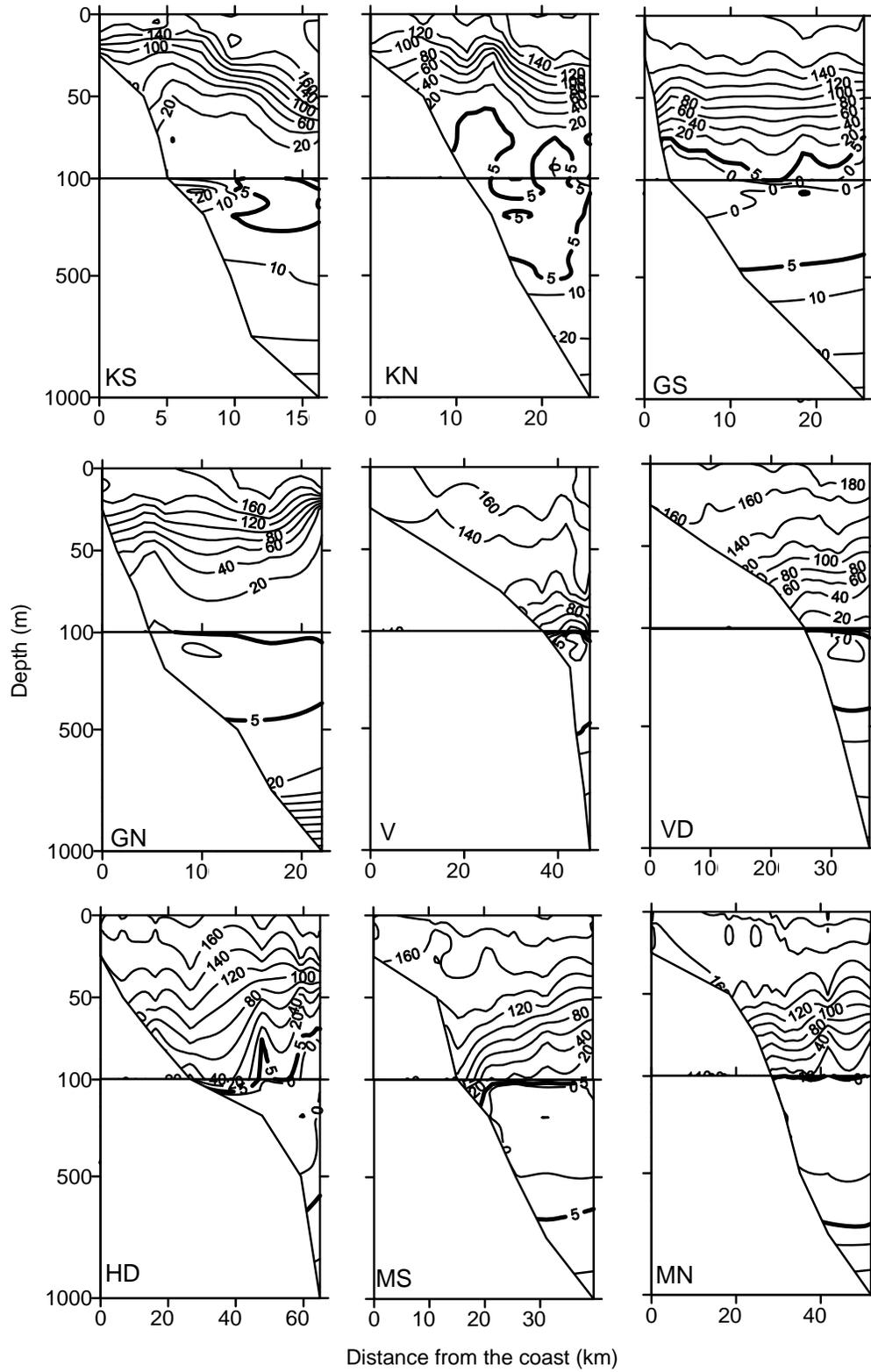


Figure 5:

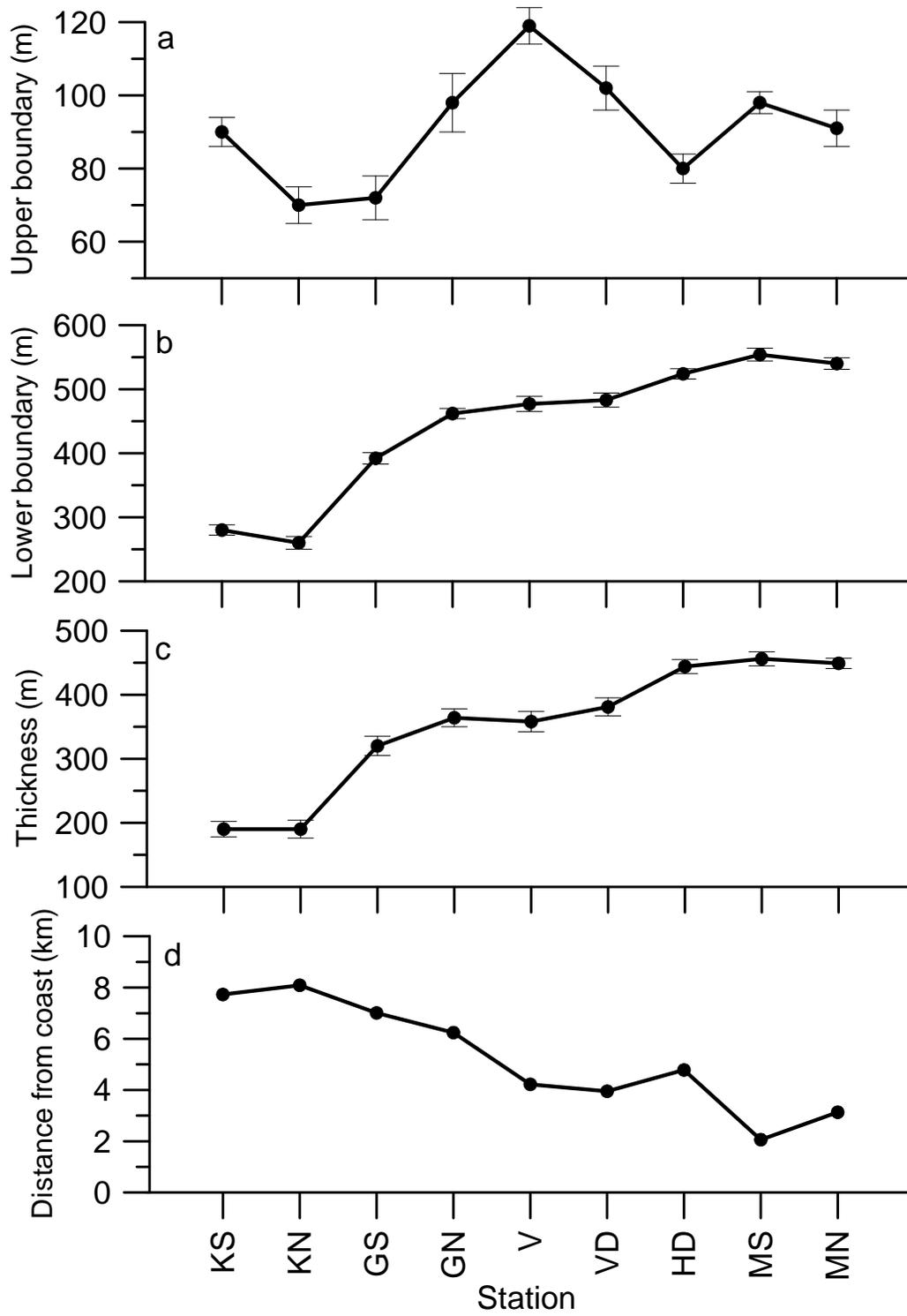


Figure 6:

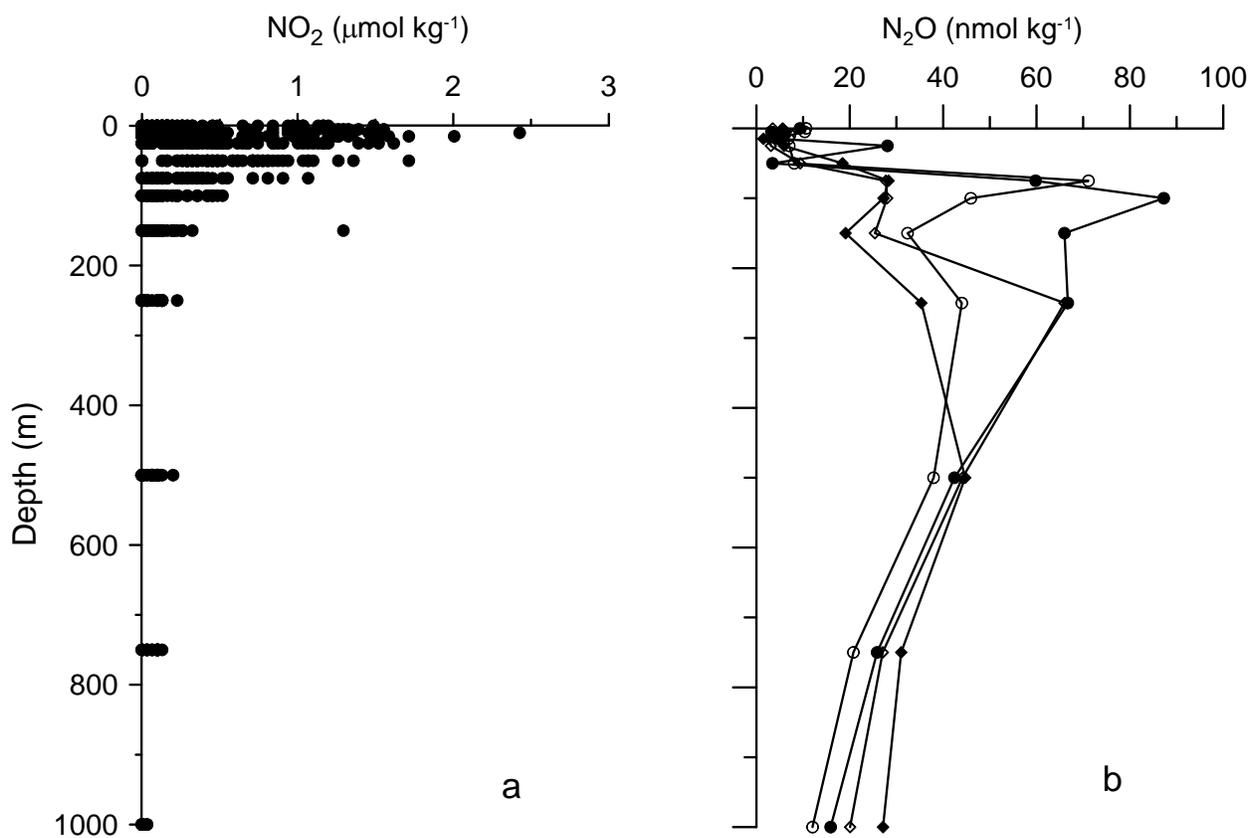


Figure 7:

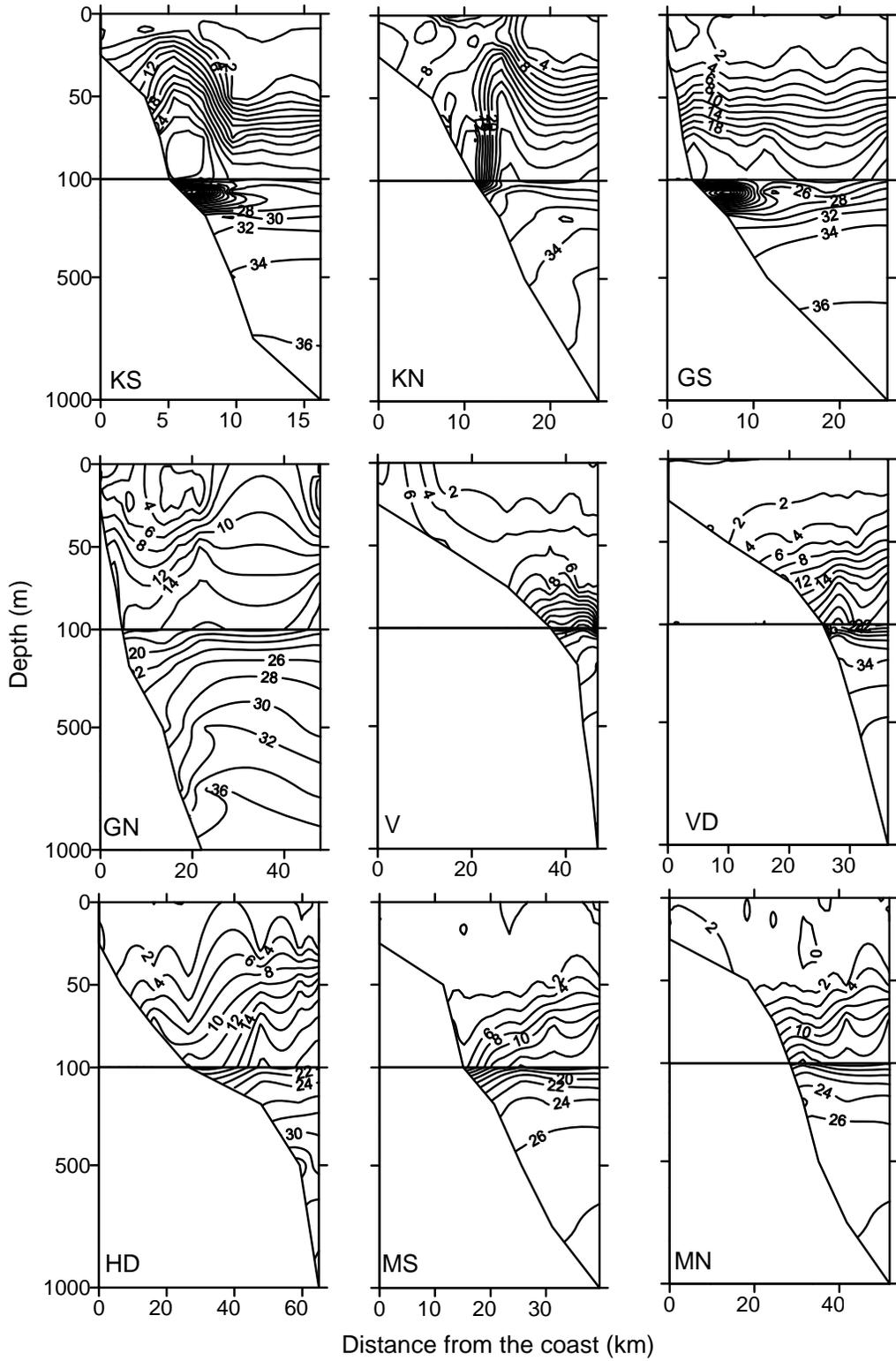


Figure 8:

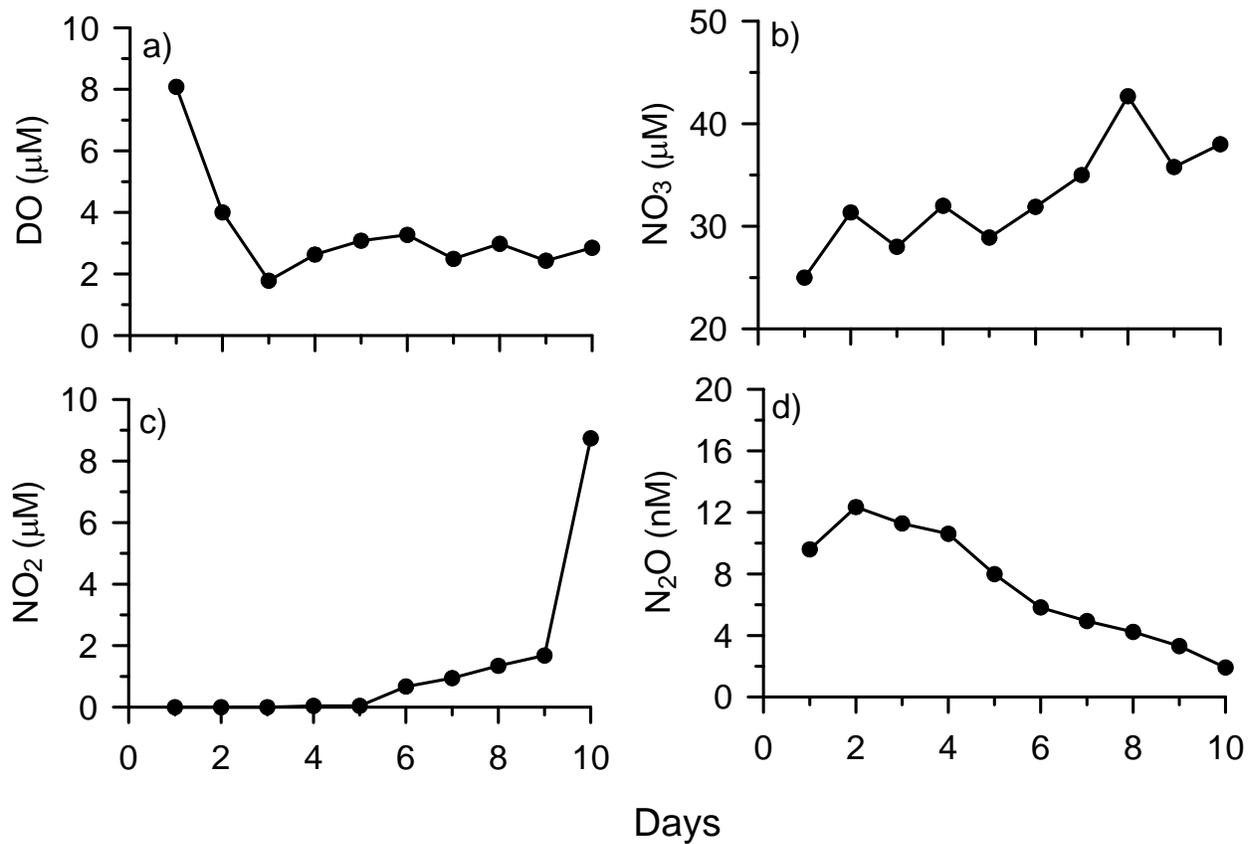


Figure 9:

