Seasonal variations in inorganic carbon components in the central and eastern Arabian Sea

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Extensive observations have been made on the carbon dioxide system in the Arabian Sea during three different seasons as part of the Indian Joint Global Ocean Flux Study (JGOFS) Programme. Concentrations of total carbon dioxide and partial pressure of carbon dioxide exhibited seasonal variability, with pronounced north–south gradients in surface layers. Total carbon dioxide in surface waters was higher by ~100 μM during winter compared to the intermonsoon period due to winter cooling and convective mixing. The partial pressure of carbon dioxide (pCO_2) in surface layers was generally in excess over the atmospheric value, suggesting that the central and eastern Arabian Sea is a perennial source to atmospheric carbon dioxide. The flux of carbon dioxide to atmosphere reached a maximum of ~40 mmole $m^{-2}d^{-1}$ around 16° N in the central Arabian Sea during monsoon season. The carbon dioxide regenerated from soft tissue was higher during winter and is the least in monsoon. The aragonite saturation horizon occurred around 500 m.

THE northwestern Indian Ocean (Arabian Sea) is a region of negative water balance where evaporation far exceeds precipitation and run-off. Consequently, the upper layers in the region are more saline and weakly stratified[1]. This region, strongly affected by seasonal changes associated with monsoon, is one of the most productive areas of the world oceans[2]. The northwestern Arabian Sea is more affected by these changes since intense upwelling occurs in this region during the southwest monsoon season. The northeastern Arabian Sea, on the other hand, experiences winter cooling and convective mixing resulting in the upward transport of nutrients[3]. These processes make the Arabian Sea important with respect to air–sea exchange of biogenic gases. Carbon dioxide is estimated to be released to the atmosphere at a rate of 74–79 Tg C yr^{-1} from this region[4–6]. Intense oxygen-deficient conditions develop within intermediate layers in the north because of oxidation of large amounts of organic matter that leads to nitrate consumption through denitrification[7,8]. This results in reducing conditions in the Arabian Sea that could influence the carbonate equilibria and raise the partial pressure of carbon dioxide (pCO_2) in water. Here, we present results of extensive measurements on carbon dioxide components made as a part of JGOFS (India) programme, in the central and eastern Arabian Sea and discuss their seasonal and spatial variability.

The measurements were made during intermonsoon (SK 91; April to May), winter (SK 99; February to March) and southwest monsoon (SK 104; July to August) seasons on board ORV *Sagar Kanya*. A Seabird CTD rosette system fitted with 1.8/12/30 litre Niskin bottles was used to collect water samples. Sub-samples were drawn into 125 ml stoppered glass bottles taking due care to avoid trapping of air bubbles. All analyses were completed within 24 hours of the collection. Oxygen analyses were done by Winkler's titration during SK 91 while it was done by spectrophotometry on SK 99 and SK 104. Total carbon dioxide (TCO_2) was measured using a Coulometer (Model 5011 of UIC Inc., USA) following the procedure detailed elsewhere[6] but with a semi-automated sample drawing system. The pH was measured by multiwavelength spectrophotometry at 25°C using Cresol red indicator[9]. The measured pH, on free ion scale, was converted to pH on total scale as described in George *et al.*[6]. Ionization constants of carbonic acid were computed using the relations of Goyet and Poisson[10]. Analytical precisions for TCO_2 and pH are ±2.0 μM and ±0.002, respectively, while those for the calculated parameters, pCO_2 and CO_3^{2-}, are ±4.0 μatm and ±1.7 μM, respectively. The accuracy of TCO_2 measurements was checked using the Certified Reference Materials supplied by Dr A. G. Dickson of Scripps Institution of Oceanography, USA, and was found to be 0.2–0.3%. The carbon dioxide fluxes were computed according to Wanninkhof[11] using the measured wind speeds.

The surface TCO_2 concentrations were the highest in winter and are comparable in monsoon and intermonsoon (Figure 1). The north–south gradient is clearly seen in the intermonsoon and winter seasons where sampling could be done from 11° to 22°N. The presence/absence of such a trend during monsoon could not be ascertained as sampling was restricted to 11°–18°N. However, during monsoon there was a patch of low TCO_2 in surface waters around 16°N (Figure 1) which may be related to upwelling driven by the Findlater Jet[12] or to a gyral circulation[13]. In intermediate layers the TCO_2 levels were higher at all depths in the north than

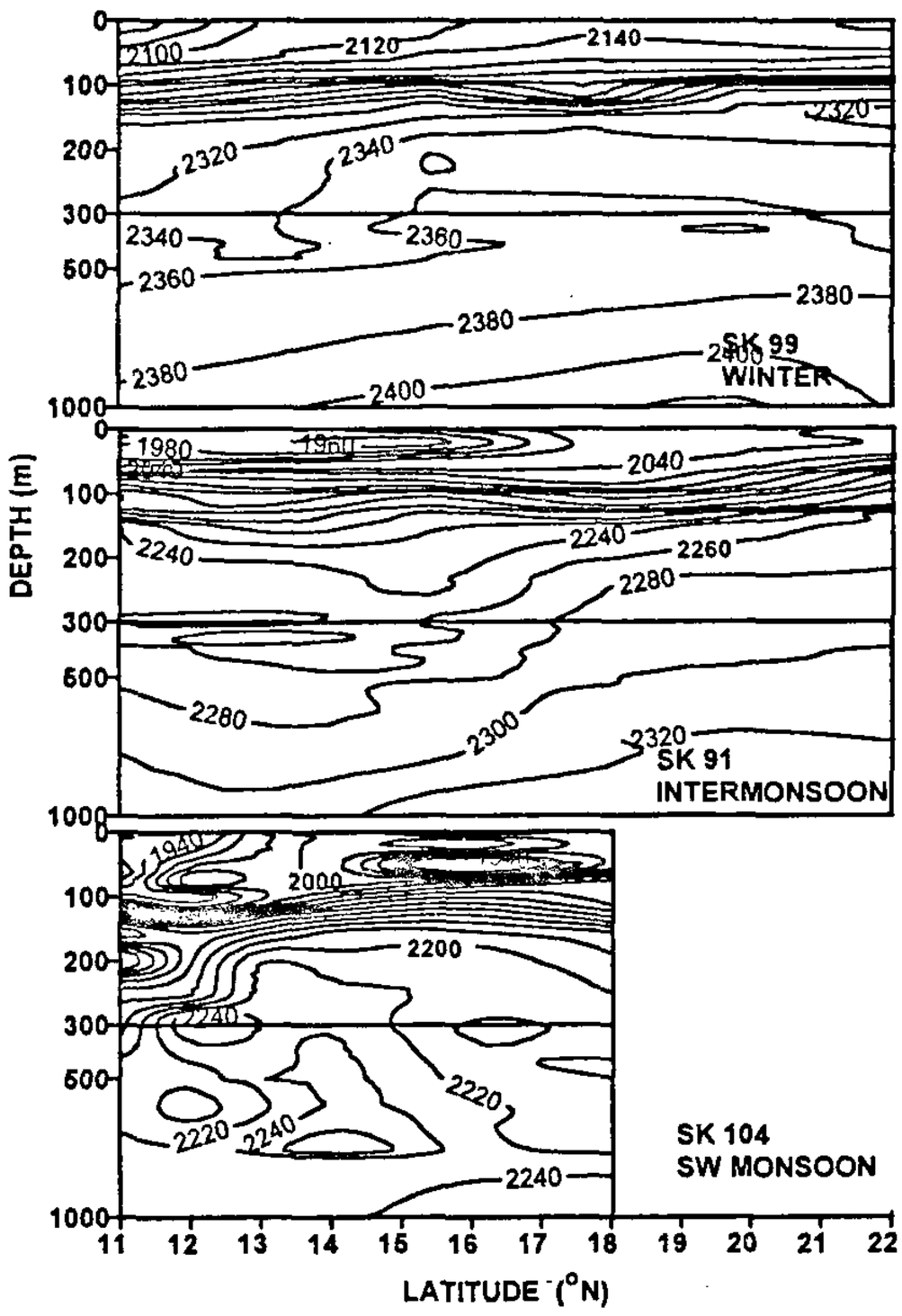

Figure 1. Distribution of TCO_2 (μM) along 64° E during three different seasons winter, intermonsoon and southwest monsoon in the Arabian Sea.

those in the southern Arabian Sea during winter and intermonsoon seasons. This results from a combination of higher biological production, and the consequent regeneration processes and aging of subsurface waters towards the north. The seasonal trends in deep TCO_2 concentrations are consistent with those observed in surface layers. This is because of the fact that the increased surface TCO_2 shall be associated with the supply of nutrients from thermocline region that could enhance production in the upper layers. The subsequent sinking and regeneration of this material in the subsurface layers would lead to proportional increase in TCO_2. The differences in TCO_2 have, however, decreased from ~100 μM in the upper layers to ~80 μM around 1000 m between winter and intermonsoon. The seasonal gradients in TCO_2 agreed well with the nitrate distribution shown by de Sousa *et al.*[14]. The nitrate concentrations were less than expected from the general trends and consequently nitrate deficit was significant in winter than that in intermonsoon. This larger nitrate deficit is caused by enhanced decomposition of sinking organic material, following higher surface production[15] in winter. The salinity distribution in intermediate layers (Figure 2) indicated increased influence of Persian Gulf Water (PGW), farther south, in southwest monsoon compared to other seasons. This could be due to seasonal variations in the distribution of outflowed PGW in the Arabian Sea. For instance, the wind fields suggest that the PGW outflow might be carried along the western Arabian Sea in winter but along the eastern part in monsoon (Dr S. Prasanna Kumar, pers. comm.). The PGW is relatively depleted in TCO_2 with ~2150 μM (ref. 16) compared to that in intermediate waters of even the south Arabian Sea. Hence, comparatively low TCO_2 was observed in monsoon in intermediate layers of the Arabian Sea due to dilution by PGW. This is augmented by Figure 3, where PGW (rich in oxygen with ~190 μM) leads to relatively higher oxygen concentrations (~50 μM) in monsoon compared to those in winter in subsurface waters of the Arabian Sea.

The higher average TCO_2 (>2120 μM) levels in surface waters north of 16°N, during winter, can be attributed to winter cooling and convective overturning[3]. On the other hand, relatively higher TCO_2 at shallower depths also occurred in waters off the southwest Indian coast during monsoon. This is due to upwelling induced by the prevailing winds[12,17] that results in the shoaling of 27°C isotherm from 100 m at 64° E to about 10 m at

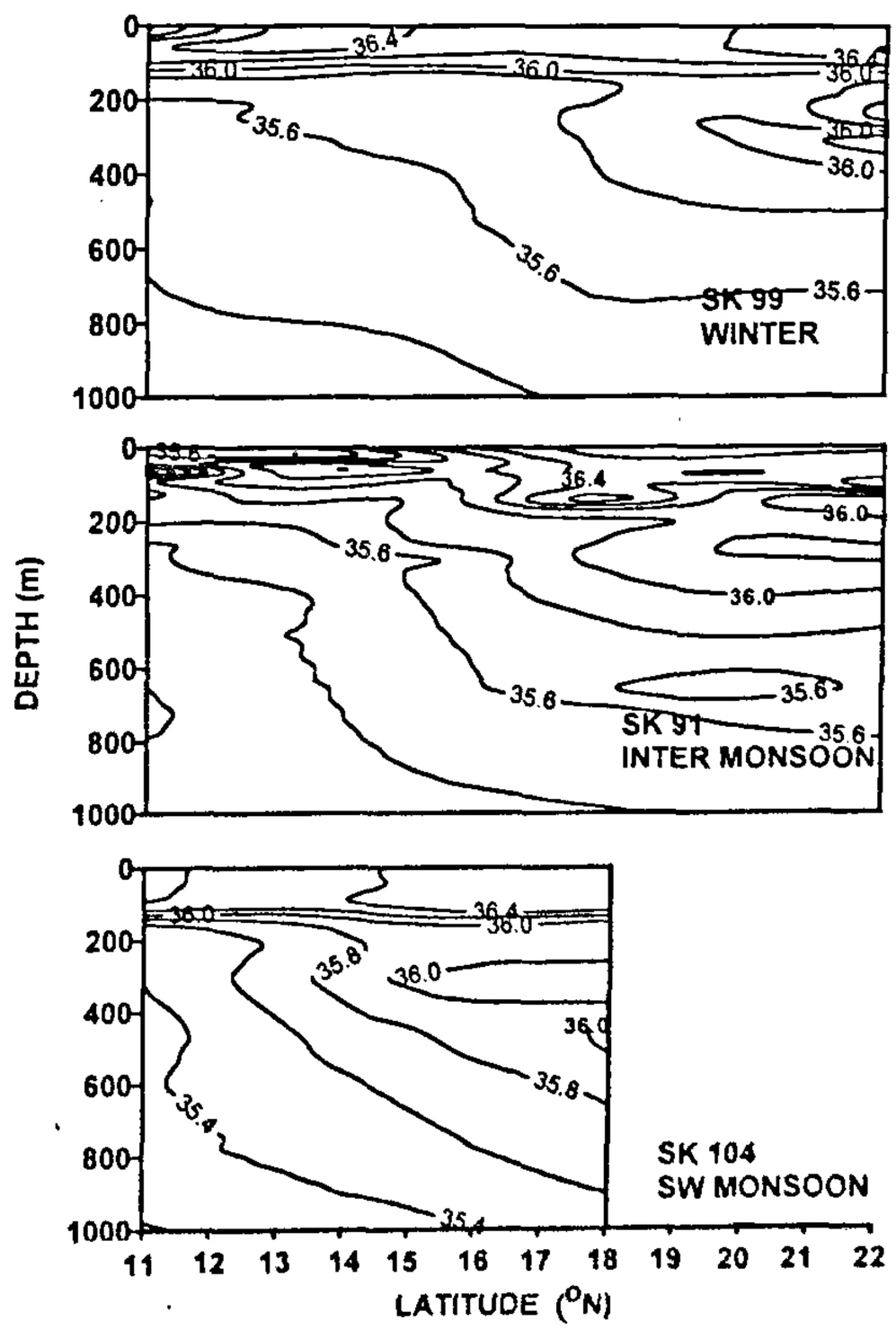

Figure 2. Distribution of salinity (psu) along 64° E during three different seasons winter, intermonsoon and southwest monsoon in the Arabian Sea.

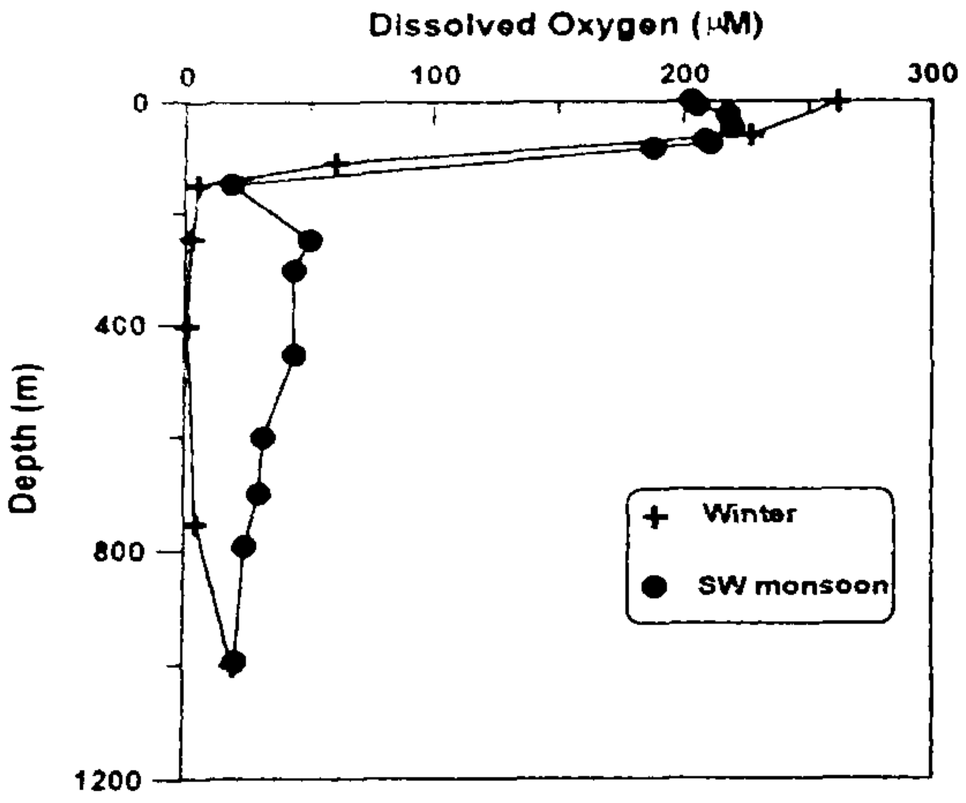

Figure 3. Variation in oxygen between winter (SK 99) and monsoon (SK 104) at 16° N.

76° E (Figure 4). Similarly, isolines of pH (8.00) and TCO_2 (2000 μM) became progressively shallow towards the east which also is the case with pCO_2 (Figure 4). However, there was a large variation in surface TCO_2 along this section that parallels the eastward decrease in salinity, due to the influx of fresh water with lower TCO_2 from land.

Relatively low pH values are observed in the northern Arabian Sea than elsewhere in the North Indian Ocean due to prevailing reducing conditions in the former region[6]. The depth distribution of pCO_2 (calculated from the measured TCO_2 and pH) is shown in Figure 5 that essentially conform with pH trends. The pCO_2 values in surface waters were generally higher than that in the atmosphere; they mostly centered around ~420 μatm in winter, but with a range of 360–420 μatm during the other two sampling periods. This is again a result of high surface production in winter that subsequently leads to higher pCO_2 levels in subsurface layers. The relatively higher subsurface pCO_2 seems to have been transported into the surface effectively by winter convection. The pCO_2 increased to 1100±100 μatm in intermediate waters (200–1000 m) with discernible seasonal variations (Figure 5). In general pCO_2 in the intermediate waters was higher during winter compared to other two seasons. A patch of high pCO_2 surface water was observed during the monsoon at ~16°N. This results from the offshore upwelling and also from the build up of carbon dioxide partial pressure in intermediate layers in the north. This differential gradient of pCO_2 between subsurface and surface layers drives relatively more carbon dioxide into the surface layers in the north in general. The calculated average carbon dioxide fluxes from sea to air around 21°N and 11°N were about 13 and 0.21 mmol $m^{-2} d^{-1}$ in intermonsoon and 1.2 and 0.3 mmol $m^{-2} d^{-1}$ during winter, respectively. In monsoon, the flux was about 40 mmol $m^{-2} d^{-1}$ around 16°N in the Arabian Sea, where a gyral upwelling was noticed, while it was ~8 mmol $m^{-2} d^{-1}$ in the south. Although the fluxes during intermonsoon were as expected from the north–south gradient in regeneration intensities those in win-

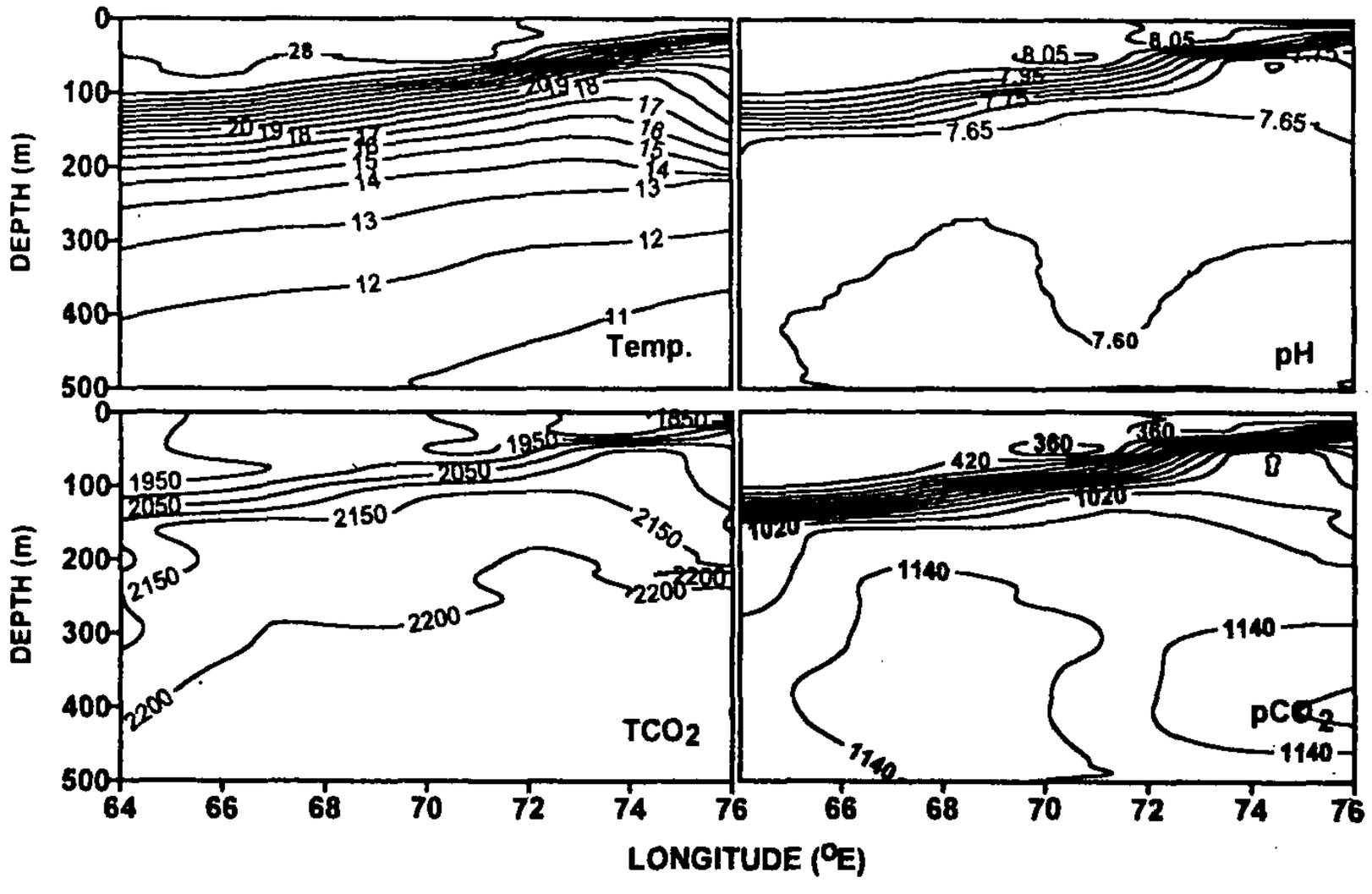

Figure 4. Distribution of temperature (°C), pH, TCO_2 (μM) and pCO_2 (μatm) along an east-west section around 10–11° N.

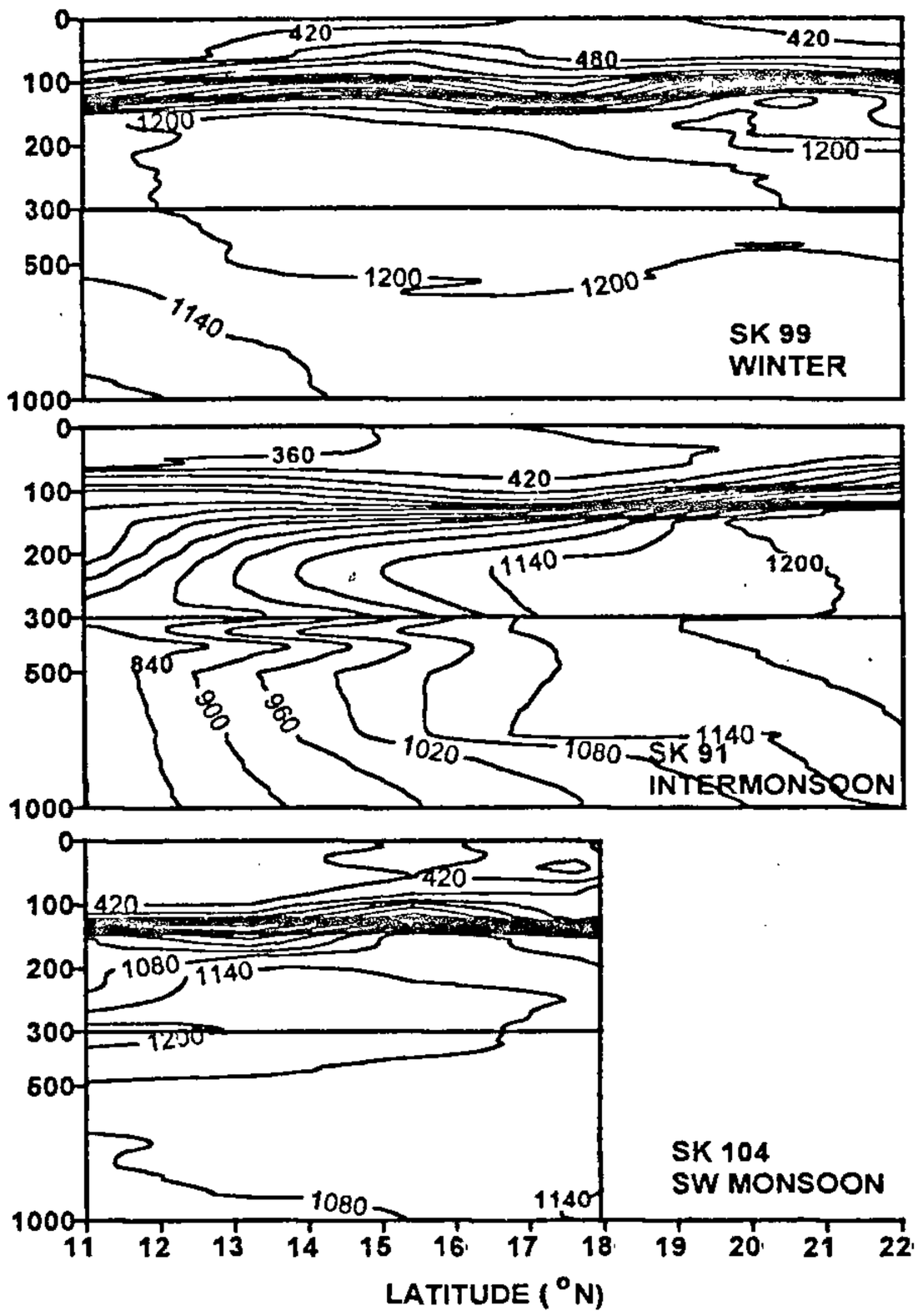

Figure 5. Distribution of pCO_2 (μatm) along 64° E during three different seasons winter, intermonsoon and southwest monsoon in the Arabian Sea.

ter were not proportional since the evaluated fluxes depend on prevailing wind speeds as well. We observed higher north–south gradients in wind speeds in intermonsoon than in winter. Our results thus reveal that the central and eastern Arabian Sea serves as a perennial source of CO_2 to the atmosphere.

Regenerated carbon (Figure 6) was also found to behave similar to that of TCO_2 (Figure 1). During winter it is higher by 70–80 μM than in intermonsoon and by more than 100 μM compared to that in monsoon. The regenerated carbon dioxide was evaluated, following the generalizations made for global oceans[18], from

$$TCO_2\,(n) = (TCO_2 * 35.000)/S$$

$$TCO_2\,(pre)(n) = 2233 - 10.36*\theta$$

$$TCO_2\,(reg) = TCO_2\,(n) - TCO_2\,(pre)(n),$$

where suffixes 'n', 'pre' and 'reg' indicate normalized, predicted and regenerated components, respectively. θ is the potential temperature. The regeneration amounted to a CO_2 release of 140 mM at 200–300 m in intermonsoon whereas it was about 80 μM and 230 μM, respectively, during monsoon and winter seasons (Figure 6).

The regional variability in calcium carbonate saturation was studied with respect to calcite and aragonite. Saturation carbonate ion concentrations were estimated following the equations of Mucci[19] for the effects of temperature and salinity and of Millero[20] for the influence of pressure on the solubility products of aragonite and calcite. Surface waters of the northern Indian Ocean have been found to be supersaturated with respect to both calcite and aragonite[5,6,21,22]. The present computations suggest that a change-over from supersaturation to undersaturation of aragonite occurs around 500 m while it is ~2000 m for calcite in the northern Arabian Sea. But the southern Arabian Sea (~11°N) is supersaturated even at 3000 m with respect to calcite. The present observations support the view that the deep northern Arabian Sea is relatively more corrosive to carbonate skeletal materials than the southern part[5,6].

This study thus establishes a strong seasonal variability in CO_2 components in the Arabian Sea. The TCO_2 and pCO_2 are higher in winter and are driven by cooling

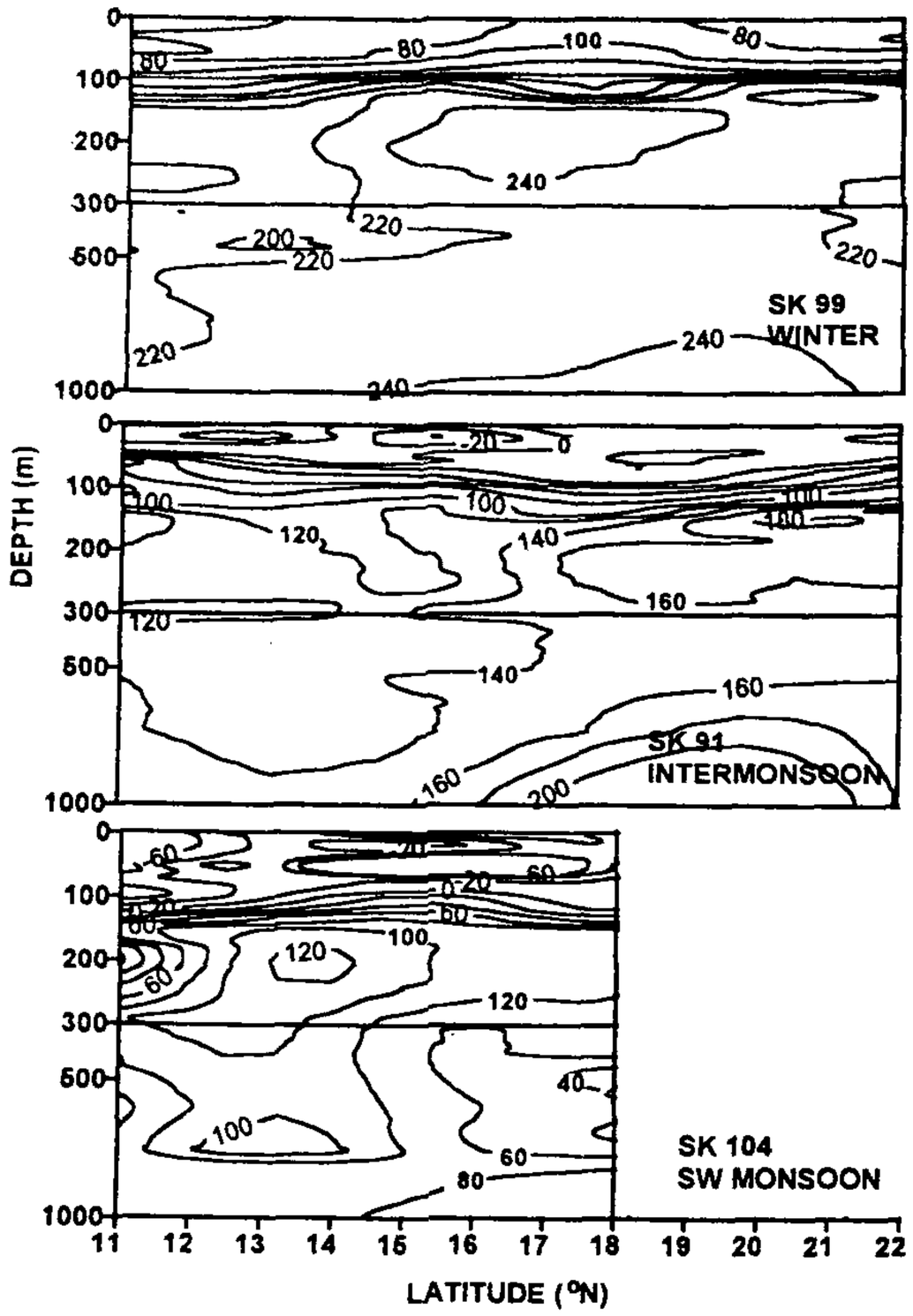

Figure 6. Distribution of regenerated CO_2 (μM) along 64° E during three different seasons winter, intermonsoon and southwest monsoon in the Arabian Sea.

and convective mixing. Intense winds cause larger sea-to-air exchange of CO_2 to atmosphere. The CO_2 regeneration is also intense in winter.

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