

Processes controlling carbon components in the Arabian Sea

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Abstract- Data on carbon dioxide components, collected just before SW monsoon 1986, have been analysed. Total carbon dioxide (TCO₂) and titration alkalinity are higher in the northern and western Arabian Sea compared to those in the southern and eastern regions, while the concentrations are the highest in the northern part. Maximum TCO₂ of about 2650 $\mu\text{mol dm}^{-3}$ was found in near bottom layers at 20°N. Inursion of Red Sea Water around 12°N resulted in the deepening of carbon dioxide isopleths above the levels of 2300 $\mu\text{mol dm}^{-3}$. TCO₂ relations with apparent oxygen utilization and phosphate suggest a northward decrease in carbon dioxide production per unit oxygen consumption. Despite the high biological production in the western Arabian Sea, relatively low CaCO₃ dissolution (~100 mol dm^{-3} near and below 3000m) is attributed to skeletal material incorporation into faecal material and the subsequent faster deposition rates. Arabian Sea water is found to be undersaturated around 200- 400m and 200-600m with respect to aragonite and calcite, respectively. Carbon dioxide added through regeneration processes exceeds 500 $\mu\text{mol dm}^{-3}$ around 20°N, a part of which is transported towards south. Enhanced pCO₂ build up towards north, to maximum of 1000 μatm , results in increased CO₂ transport from sea to air from south to north. Arabian Sea seems to be a CO₂ source for the atmosphere since the fraction of CO₂ in air, calculated based on CO₂ concentration in seawater, is more than 0.5. Although, the Persian Gulf Water and the Red Sea Water influence could be seen from preformed CO₂ levels in the Arabian Sea, the quantum of respective anthropogenic contributions could not be ascertained in view of the large uncertainties involved.

INTRODUCTION

Substantial inputs of anthropogenic greenhouse gases into the atmosphere have been of global concern. The increased carbon dioxide in atmosphere is believed to be countered in part by oceanic uptake and the polar regions are significant in the transportation of atmospheric carbon dioxide to deep oceans. The occurrence of extensive upwelling and the associated high biological productivity in the Arabian Sea (QASIM, 1977) make this region an important area for the air - sea exchange of carbon dioxide. It has been estimated that the Arabian Sea contributes to a carbon flux from the ocean to the atmosphere of 74 Tg y^{-1} (SOMASUNDAR *et al.*, 1990). The Arabian Sea is also found to be a carbon source for the Persian Gulf and the Red Sea bodies and the Arabian Sea in general is negatively balanced by 84 Tg y^{-1} of carbon which might be compensated by northward moving watermasses such as the Antarctic Bottom Water (SOMASUNDAR *et al.*, 1990). Further, due to poor re-oxygenation and high biological production, intermediate layers in the northern Arabian Sea experience intense reducing conditions leading to denitrification (SEN GUPTA *et al.*, 1976). Here, we report on the significance of various processes regulating the carbon dioxide system in this part of the Indian Ocean, with implications on the absorption of anthropogenic carbon dioxide.

MATERIAL AND METHODS

Water samples were collected during cruise 42 of RV SONNE (April-June 1986) in the Arabian sea at 20 stations (Fig.1). A CTD rosette system was used to collect water samples. The analytical methods adopted for various physicochemical parameters,

dissolved organic carbon (DOC) and titration alkalinity (TA) have been described elsewhere (KUMAR *et al.*, 1990). Briefly, DOC was analysed by high temperature catalytic oxidation and TA by the back titration methods. The precisions of these analyses were found to be 2.67% for DOC and 0.2% for TA. pH was measured using NBS buffers to 0.01 units. pH_{NBS} were converted to pH_{sws} (pH on seawater scale) before making further computations, using the relationship given by MILLERO (1979)

$$\text{pH}_{\text{NBS}} - \text{pH}_{\text{sws}} = 0.144$$

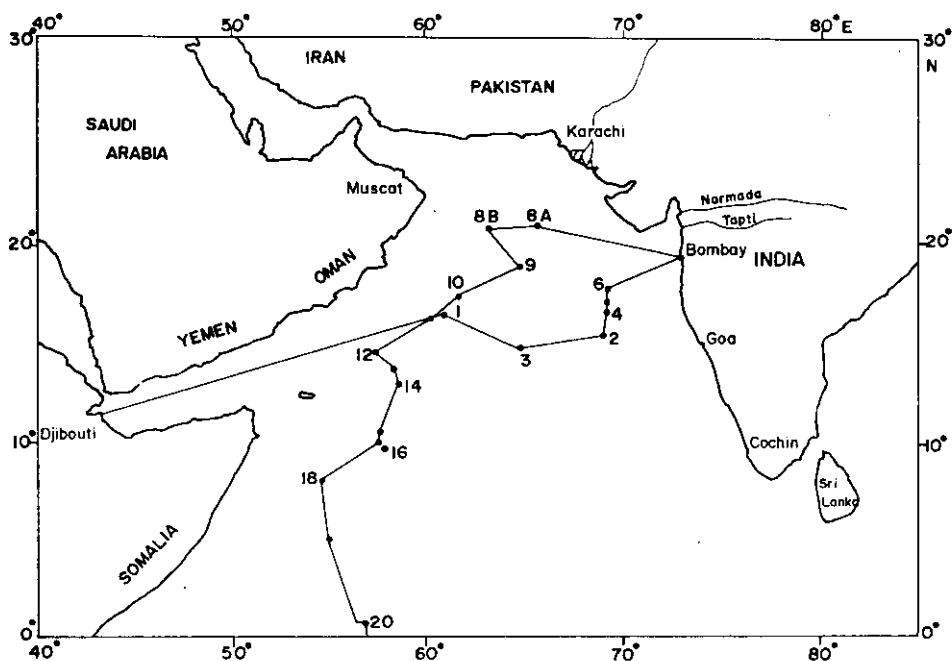


Fig. 1. Station locations in the Arabian Sea.

Various carbon dioxide components such as bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), partial pressure of carbon dioxide (pCO_2) and total carbon dioxide (TCO_2) were estimated using pH_{sws}, TA and Hansson's dissociation constants (HANSSON, 1973) as recommended in UNESCO (1983). Carbon dioxide released due to regeneration processes was estimated using the generalised equations of KROOPNICK (1985) for the world oceans. Apparent oxygen utilization (AOU) was calculated after the oxygen solubilities evaluation from the coefficients of BENSON and KRAUSE (1984).

RESULTS

The distributions of physicochemical parameters during the study period have been described by KUMAR *et al.* (1990). The salient features, relevant to the present topic in brief, are severe depletion of oxygen in the intermediate layers of the northern Arabian Sea (minimum observed is $6 \mu\text{mol dm}^{-3}$) and the consequent occurrence of denitrification (to a maximum of $8 \mu\text{mol dm}^{-3}$). DOC distribution though found to be patchy, in accordance with the productivity pattern, shows a clear increase southward in intermediate and deeper layers. This increase has been found to be due to the

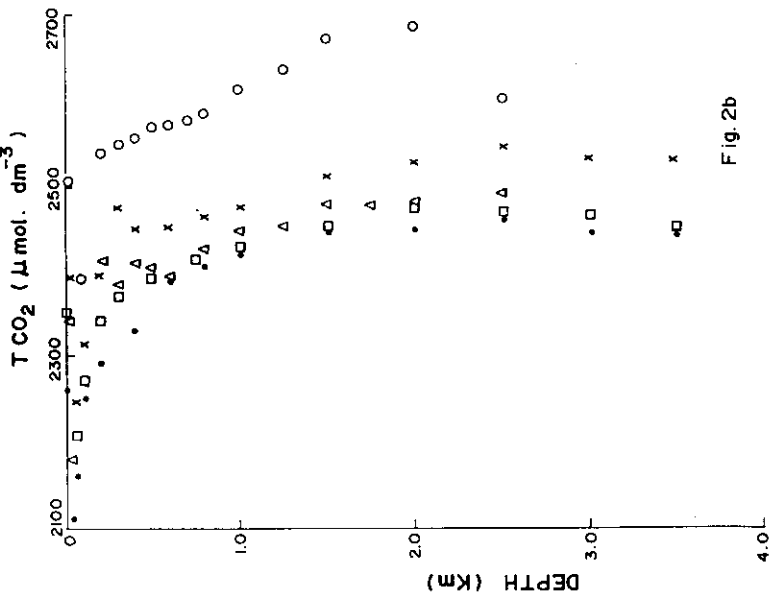


Fig. 2a

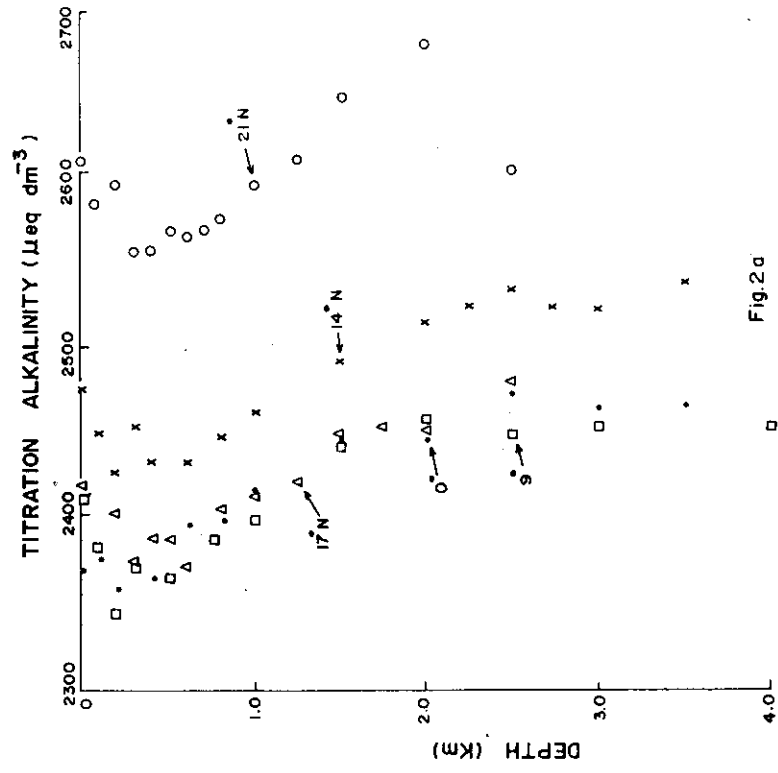


Fig. 2b

Fig. 2. Spatial variations in the vertical profiles of (a) Titration alkalinity ($\mu\text{eq. dm}^{-3}$) and (b) Total carbon dioxide ($\mu\text{mol. dm}^{-3}$) in the Arabian Sea. Symbols indicate: Stn. 8A (o), Stn. 12(x), Stn. 4(Δ), Stn. 16(\square) and Stn. 20(\bullet).

decreased heterotrophic activity southward and/or chemosynthetic production of DOM by nitrifiers (RAJENDRAN *et al.*, submitted).

Fig. 2a shows regional variations in TA. Evidently, TA decreases from north to south and also from west to east. The profiles, in general, depict an initial decrease from surface to 500m before showing an increasing trend as the depth increases. TA values in the north (stn. 8A) are higher than those in the west (stn. 12). TCO₂ also behaved (Fig. 2b) similar to TA but with a very clear decreasing trend southward at all the depth levels. TCO₂ was found to be around 2400 $\mu\text{mol dm}^{-3}$ at equator but in north it was more than 2600 $\mu\text{mol dm}^{-3}$, with a maximum of 2650 $\mu\text{mol dm}^{-3}$ in the deeper layers of Stn. 8A. Salinity normalised TCO₂ (NTCO₂) when plotted against potential temperature (Fig. 3) showed decreasing trend northward. The most significant phenomenon in Fig.3 was the deepening of isopleths ($> 2300 \mu\text{mol. dm}^{-3}$) around 12°N. This could be due to the influx of the Red Sea Water and its influence could be felt even in very deep layers as depicted in Fig.3.

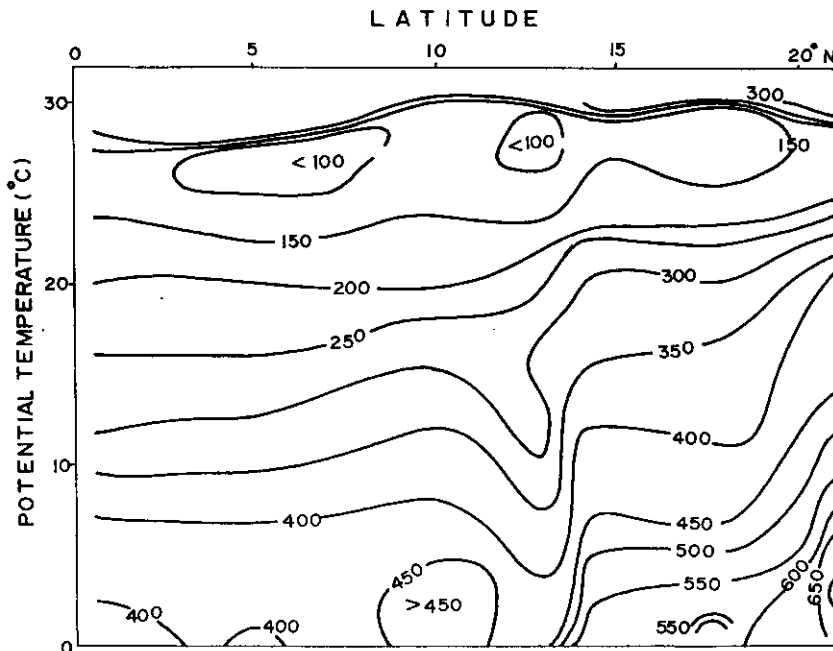


Fig. 3. Latitudinal variation in salinity normalised carbon dioxide ($\mu\text{mol. dm}^{-3}$), expressed as (NTCO₂-2000), against potential temperature.

DISCUSSION

Carbon dioxide inputs to the Arabian Sea could significantly come from the atmosphere as well as the southern Indian ocean, since the river contribution is meagre and adjacent bodies (The Persian Gulf and the Red Sea) are found to receive Carbon from the Arabian Sea (SOMASUNDAR *et al.*, 1990). Carbon, from surface to deep layers of the oceans, will be mainly carried through biogenic debris in addition to CO₂ diffusion downward. TCO₂ showed positive relations with AOU and PO₄ (Fig. 4) indicating the carbon dioxide production during regeneration processes. Further, despite the lower TCO₂ observed at all levels near the equator, compared to those in

the north, the slopes of regression lines of TCO_2 vs AOU and PO_4 are high. For instance, $\Delta\text{TCO}_2/\Delta\text{PO}_4$ ratios at stations 8A, 3 and 20 are 103, 116 and 135, respectively. Obviously, the decrease in TCO_2 towards south is because of the decreased biological production southward and the consequent low oxygen utilization. Further, more CO_2 is added in the north due to CaCO_3 solution which accounts for a low $\Delta\text{CO}_2:\Delta\text{PO}_4$ north ward. DOC oxidation is more effective in the northern Arabian Sea than in the Southern part and also DOC accumulation towards south results in a decrease of TCO_2 almost to a similar magnitude (KUMAR *et al.*, 1990). The northward increase in TCO_2 not only reflects the higher production rate but also higher "ages" of these waters. The carbon dioxide produced due to microbial oxidation of particulate and dissolved organic carbon is higher in the north compared to that in the south because of high biological production in the north. Higher biological production in the north leads to reducing conditions in the intermediate layers thus necessitating denitrification while organic carbon is oxidised to CO_2 (KUMAR *et al.*, 1990). However, biological debris also include skeletal carbonates that dissolve in subsurface layers because of the influence of pressure and temperature. We have attempted to resolve the contribution due to such solution using the equation of KROOPNICK (1985),

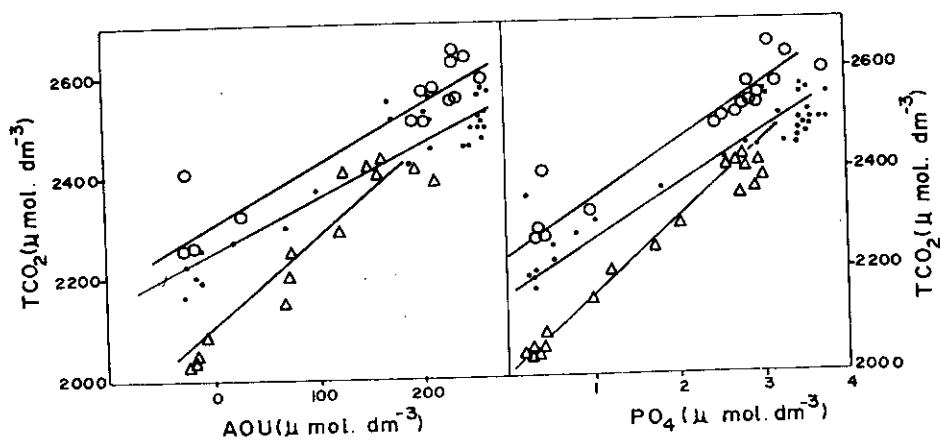


Fig. 4. Variations in TCO_2 relations with AOU and phosphate. Symbols indicate: Stn. 8A(o), Stn. 3 (•) and Stn. 20 (Δ)

Table 1. The geographical variations in the ratios of Org. CO_2 /Inorg. CO_2

Stn.No.	Coordinates	800m	1500m	2500m
8 (North)	21° 00'N 63° 05'E	3.3	2.2	1.8
2 (East)	15° 30'N 68° 45'E	3.9	2.5	1.8
3 (Central)	14° 29'N 64° 44'E	4.0	2.6	2.0
12 (West)	14° 21'N 57° 40'E	7.5	3.4	2.4
20 (South)	00° 38'N 56° 41'E	9.1	6.0	2.7

$$ICO_2 = CO_2 (\text{inorg}) = 1/2 (n \text{ Alk} - n\text{Alk}(z))$$

where

$$n \text{ Alk} = \frac{\text{Alk}_{\text{meas}} \times 35}{\text{Salinity}}$$

and $n \text{ Alk} (z)$ has been estimated from

$$n \text{ Alk} (z) = (2372 - 2.84) \times \theta$$

derived for the upper 100 m of world oceans. $n \text{ Alk}(z)$ is similar to preformed TA and is not to be influenced by variations in temperature and salinity over short time scales (BREWER *et al.*, 1983). The skeletal carbonate dissolved (ICO_2) was found to be a factor of 3 higher in the northern Arabian Sea (stn. 8A) compared to that in the south (Fig. 5) ICO_2 also decreases from east to west in the Arabian Sea. Skeletal carbonate dissolution is in accordance with the productivity pattern which increases northward and also, the waters become progressively more corrosive northward. The contribution of soft tissue decomposition was found to increase from north (65%) to south (74%) to the total carbon dioxide addition at depth (KUMAR *et al.*, 1990). The ratio of carbon dioxide produced by soft tissue decomposition to that of skeletal dissolution was more in south and western regions compared to other regions of the Arabian Sea (Table 1). The ratios were lowest in the north, at all the depth levels examined. This is attributable to the decreased skeletal organism population southward and/or to the increase in the ratio of insoluble skeletal organisms to the soluble ones (KUMAR *et al.*, 1990). As pointed out earlier, the waters in the northern Arabian Sea may be more corrosive than the southern Arabian Sea. The western Arabian Sea experiences pronounced upwelling causing higher productivity, than the eastern part (QASIM, 1977 ; BANSE and

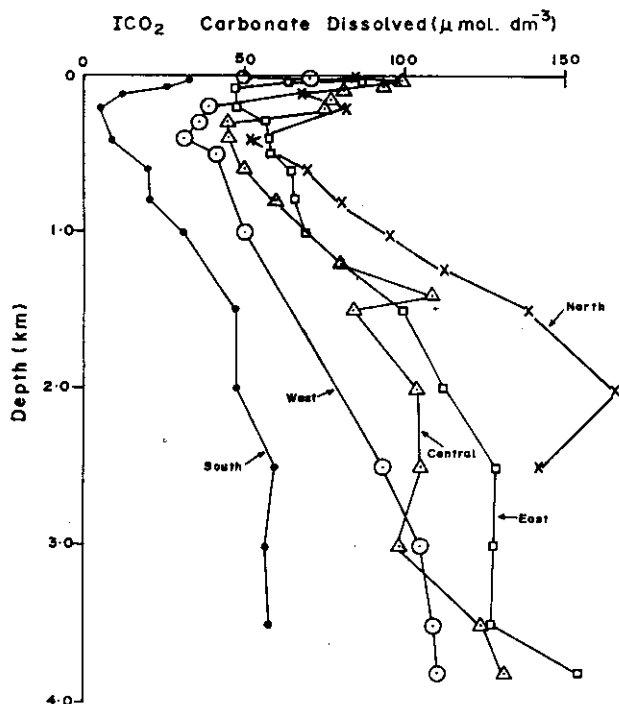


Fig. 5. Regional and depthwise variations in Inorganic carbonate (skeletal) dissolved (ICO_2) in the Arabian Sea. Symbols indicate: Stn. 8A(x), Stn. 2 (□), Stn. 3 (Δ), Stn. 1 (o) and Stn. 20 (•).

McCLAIN, 1986). Hence, higher ICO_2 should have been expected to occur in the west (stn. 1) which is not the case (Fig. 5). Coccoliths and foraminiferal tests have been found to comprise the skeletal material in the sediment traps deployed in the Arabian sea (NAIR *et al.*, 1989). While foraminiferal tests sink rapidly, coccolith skeletal matter remains in the water column for longer times and is more susceptible for dissolution (HONJO, 1977). Due to the higher production rates in the west, the coccoliths might have been preserved because of their incorporation into faecal pellets, as suggested by HONJO (1977). Reduced ICO_2 production (Fig. 5) and the possible coccolith transport alongwith faecal pellets in the western Arabian Sea, thus provide explanation for (i)

Table 2. Inorganic and organic carbon in particle fluxes in the deep Arabian Sea (Data from NAIR *et al.*, 1989)

Area	Carbon components g m^{-2}	March-May	June-Sep	Oct-Nov	Dec-Feb	Total
Western Arabian Sea (3020m)	C Inorg.	0.14	1.45	0.26	0.43	2.28
	C Org.	0.16	1.18	0.14	0.32	1.80
	C Inorg/C org	0.878	1.231	1.826	1.35	1.267
Central Arabian Sea (2900m)	C inorg	0.059	1.117	0.26	0.67	2.11
	C org	0.06	0.74	0.20	0.53	1.53
	C inorg/C org	0.98	1.51	1.29	1.26	1.373
Eastern Arabian Sea (2770m)	C inorg	0.096	0.87	0.41	0.049	1.43
	C org	0.18	1.00	0.33	0.05	1.56
	C inorg/C org	0.533	0.872	1.236	0.984	0.914

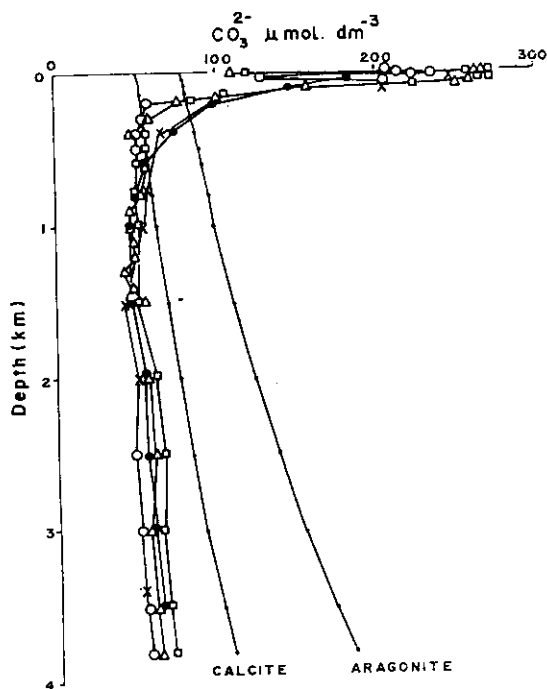


Fig. 6. Vertical profiles of carbonate ion in the Arabian Sea in relation to CaCO_3 saturation levels. Symbols indicate: Stn. 8A(x), Stn. 2 (\square), Stn. 3 (Δ), Stn. 1 (o) and Stn. 20 (\bullet).

eastward decrease in particulate carbonate flux during June-Sept monsoon (Table 2) and (ii) CaCO_3 in sediments (KOLLA *et al.*, 1981). Moreover, as the lower oxygen concentrations occur off the Indian Coast than off Arabia, the waters may be more corrosive for CaCO_3 dissolution in the eastern Arabian sea thus resulting in a reduced particulate carbonate flux. Table 2 suggests extensive seasonal variations in carbonate fluxes. For instance, inorganic carbon flux is low in the central parts as compared to east and western parts of the Arabian Sea during the period between March and May. An reverse trend could be seen during December- February period. Table 2 also reveals seasonality in inorganic carbon to organic carbon flux ratios. During March-Sept, central Arabian Sea experiences relatively larger amounts of C inorg/C org values while the ratio decreases eastward from October to February. Possibly there could be seasonal variations in skeletal carbonate dissolution as well to account for the trends seen in Table 2. During the period of this study, the entire Arabian Sea was found to be undersaturated with respect to skeletal carbonates from 600m downward. Specifically, seawater was undersaturated with respect to aragonite below 200 m whereas it was so with respect to calcite below 600 m (Fig. 6). There was little variation, even regionally, in CO_3^{2-} content with depth below 600m. CO_3^{2-} concentrations were estimated using pH_{sws}, TA, temperature and salinity adopting UNESCO (1983). CO_3^{2-} concentrations for saturation levels at different depths were estimated according to FEELY *et al.* (1988). Ca^{2+} was estimated using Ca^{2+}/Cl ratio of 0.02164 (NAQVI and NAIK, 1983). FEELY *et al.* (1988) found seasonal variations in the depth of occurrence of CaCO_3 saturation levels. Occurrence of similar kind of variations, in the trends of Fig. 6, may perhaps be the reason for seasonal changes of inorganic carbon flux noted in Table 2. Though it was concluded that calcite saturation depth lies between 2500-3000m (NAQVI and NAIK, 1983), the present evaluations clearly depict the occurrence of shallow water CaCO_3 dissolution. In fact, the higher Ca^{2+}/Cl ratios observed by NAQVI and NAIK

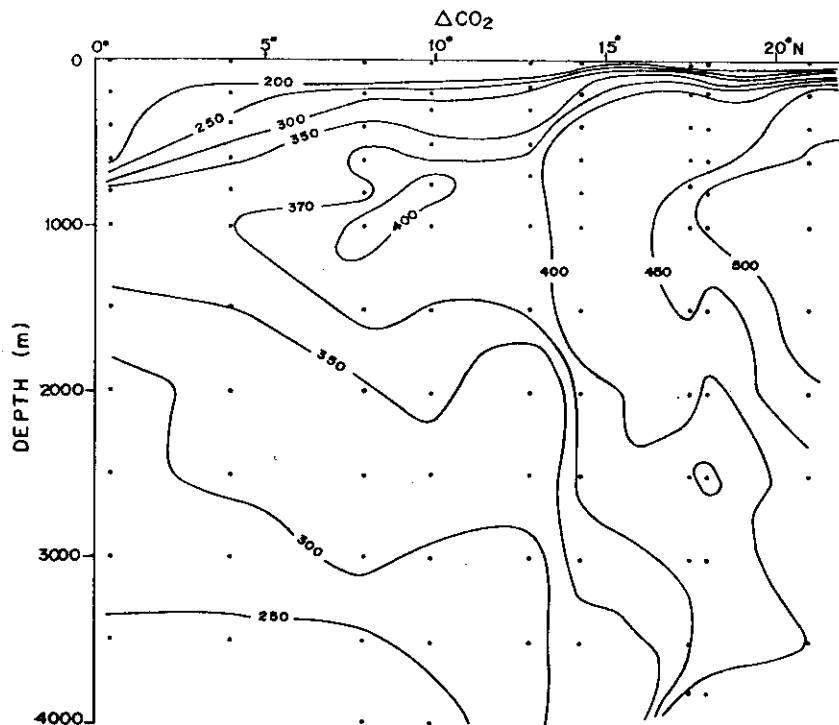


Fig. 7. Latitudinal variations in the regenerated carbon dioxide (ΔCO_2) in the Arabian Sea.

(1983), for the Indian Ocean surface water than the world averages are the result of this shallow water skeletal dissolution but may not be due to river runoff, which is at its minimum during the period of observation. An interesting feature was the higher dissolution of skeletal material in the northern Arabian Sea than in the western part. Both areas are rich in biological production and hence so in the faecal pellet production also. However, the higher bacterial activity northward (KUMAR *et al.*, 1990) has possibly resulted in enhanced decomposition of faecal material at stn. 8A than at stn. 12. Consequently, coccoliths with relatively longer residence times, dissolve more in the north than in the western Arabian Sea (Fig. 5). Further, increased CaCO_3 dissolution in the north is also aided by large CO_2 produced due to soft tissue decomposition. CO_2 released reacts with CaCO_3 to yield bicarbonate ions

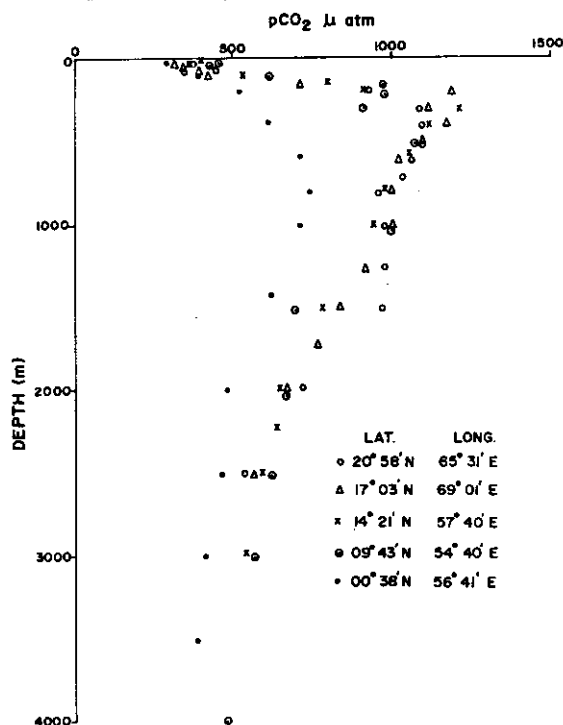
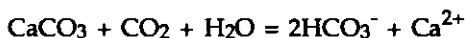


Fig. 8. Regional variations in vertical profiles of pCO_2 in the Arabian Sea.

Carbon dioxide added due to regeneration processes ($\Delta \text{CO}_2 = \text{TCO}_2 - \text{preformed CO}_2$) exceed $500 \mu\text{mol. dm}^{-3}$ in the intermediate layers of the northern Arabian Sea (Fig. 7). Carbon dioxide produced due to these processes at any depth around 21°N is about 1.5 times higher than that produced at the equator. Fig. 7 clearly depicts a southward moving tongue of northern Arabian Sea intermediate water enriched with CO_2 around a depth of 1000m. On an average this layer was evaluated to transport about 3.06 Tg C y^{-1} across the equator to the southern Indian Ocean (SOMASUNDAR *et al.*, 1990).

Because of the enhanced CO_2 regeneration in the intermediate layers of central and northern than in the southern Arabian Sea, partial pressure of CO_2 builds up in the north than near equator (Fig. 8). Significantly, pCO_2 in the oxygen minimum (200-400m) zone of the northern parts is nearly double of that present at the corresponding

depths at the equator. Despite the continuing decrease with depth, $p\text{CO}_2$ does not vary much below 2000m. Increased $p\text{CO}_2$ in surface layers in the north than near equator should result in enhanced carbon dioxide ejection to atmosphere in the former area. In order to evaluate the CO_2 partition pattern between air and surface seawater, an indirect parameter f_{AIR} is used here. f_{AIR} is defined as the ratio of CO_2 in air to

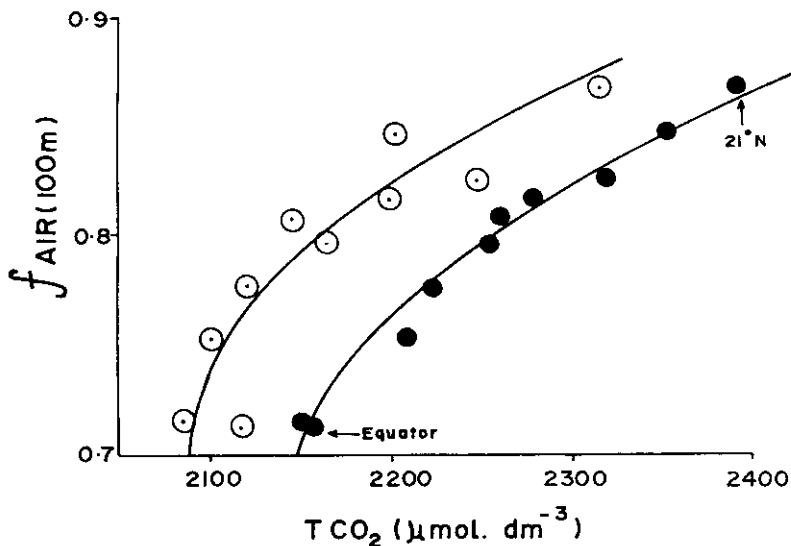


Fig. 9. TCO_2 (•) and salinity normalised TCO_2 (○) relations with the calculated fractions of CO_2 in air (f_{AIR}).

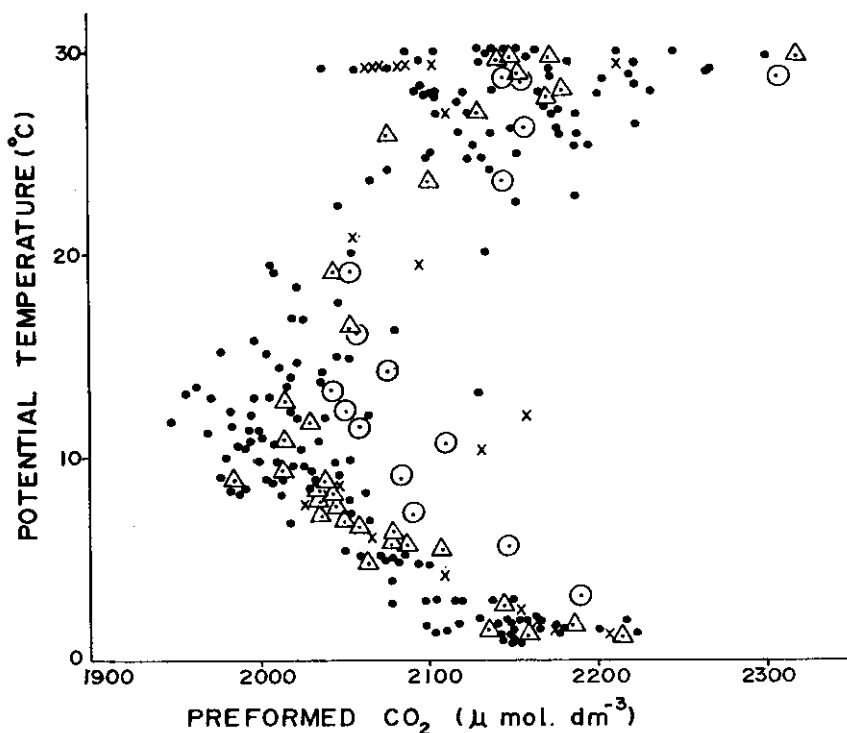


Fig. 10. Relation between potential temperature and preformed CO_2 in the Arabian Sea. Symbols are Stn. 8A (○), Stn. 3 (△), Stn. 20 (X) and others (•).

the total present in air and seawater. f_{AIR} is calculated according to the equation (TAKAHASHI *et al.*, 1980),

$$f_{AIR} = [1 + 29 \times 1.025 \times 10^{-6} \times z(\text{TCO}_2)_0^\gamma \cdot (\text{TCO}_2)^{1-\gamma} / (\text{pCO}_2)_0]^{-1}$$

where 29 is mean molecular weight of dry air (g mole^{-1}), 1.025 is average density of seawater (g cm^{-3}), z is depth of the water column (cm), $(\text{TCO}_2)_0$ and $(\text{pCO}_2)_0$ are total carbon dioxide and its partial pressure at the reference conditions, respectively, and γ is the Revelle factor. In the present computations, a value of 10^4 cm for Z and $(\text{TCO}_2)_0$ and $(\text{pCO}_2)_0$ as averaged TCO_2 and pCO_2 values over the 10^4 m water column were considered. A Revelle factor of 10 was used representing the mean value for surface seawater (TAKAHASHI *et al.*, 1980). As expected, f_{AIR} increases with an increase in TCO_2 implying that CO_2 in the Arabian Sea air should increase northward. For example f_{AIR} at 21°N is 0.86 while it is about 0.72 near the equator (Fig. 9). This indicates the increased inputs from the subsurface layers in north and the resultant northward increase in the input of carbon dioxide from the Arabian Sea to atmosphere in concurrence with the increased remineralization. More significantly, the entire Arabian Sea, including its equatorial region, seems to act as a source for atmospheric carbon dioxide as the minimum f_{AIR} found at stn. 20 is also greater than 0.5. Consequently, the estimated transport of 74 Tg y^{-1} of carbon as CO_2 to atmosphere from the Arabian Sea should be considered as a minimum since SOMASUNDAR *et al.* (1990) computed the flux only for the area between latitudes 10 and 25°N and longitudes 52 and 77°E .

The carbon dioxide observed is the sum of preformed (i.e., CO_2 present when the water parcel was at surface in contact with atmosphere) and regenerated (CO_2 added due to decomposition/dissolution of biogenic debris) fractions. The preformed CO_2 is a conservative parameter and hence a water mass shall retain this quantity of CO_2 even after reaching deep ocean. The preformed CO_2 will, however, consist of natural and anthropogenic components, where the proportions of these depend on location, extent of inputs etc. While preformed quantities are used as conservative watermass tracers (BROECKER *et al.*, 1985), the difference in preformed CO_2 between surface (presently formed water) and deep water (that formed some time ago) may serve to quantify the anthropogenic CO_2 signal in subsurface layers of the oceans (CHEN and MILLERO, 1979). The error in our preformed CO_2 computations is estimated to be about $\pm 35 \mu\text{mol. dm}^{-3}$. Relatively high preformed CO_2 in the northern Arabian Sea, for instance below a potential temperature of 12°C at station 8A, indicates the possible incursion of anthropogenic CO_2 (Fig. 10). The northern Arabian Sea is prone to absorb relatively large amounts of anthropogenic carbon dioxide from all directions, except from south, due to high rates of fossil fuel consumption and deforestation over the years in surrounding landmasses. At the potential temperature of 15°C , characteristic of the Persian Gulf Water, a clear peak for preformed CO_2 could be seen in Fig. 10 at stn. 8A (i.e., northern Arabian Sea). Similarly, high density Red Sea Water intrudes into the Arabian Sea whose signature could be seen at stn. 20 around a θ of 10 - 12°C . Deep water of the northern Red Sea was reported to contain young water and hence significant anthropogenic carbon dioxide (KRUMGALZ *et al.*, 1990). Below a θ of 10°C , preformed CO_2 increases towards the bottom (Fig. 10). A break in the distribution of the preformed CO_2 at a θ of 10°C (Fig. 10) is in accordance with the 9°C discontinuity of SOMASUNDAR *et al.* (1987). Relatively higher preformed carbon dioxide near and below 10°C at stn. 20 (Fig. 10) possibly could have been due to the carbon dioxide component released by oxidants other than oxygen or that could have resulted due to winter overturning mixing processes and the consequent diffusion downward. In the Arabian Sea, deep waters move northward and sizable fractions are derived from Indian Ocean Bottom water and Antarctic Bottom water (WYRTKI, 1971). Antarctic Bottom water has been found to have little anthropogenic CO_2 (POISSON and CHEN, 1987) and

hence can not be expected to result in the higher preformed CO₂ to such an extent as depicted in Fig. 10. The increase in anthropogenic signal with depth in the Red Sea, after a minimum, was attributed to young water sinking from Gulf of Aquaba (KRUMGALZ *et al.*, 1990). Adopting this logic, a water parcel with the least preformed CO₂ may be the oldest water in the region and Fig. 10 depicts this to occur between potential temperatures 14° and 9°C corresponding to an average depth of 750 ± 250 m. From this reasoning the oldest water mass in the Arabian Sea may contain a preformed CO₂ of 2025 µmol. dm⁻³. Also as Fig. 10 suggests, young water may have reached deeper regions of the equator but not those regions of Central (stn. 3) and northern (stn. 8A) parts of the Arabian Sea. However, quantification of anthropogenic CO₂ component in the deep water is rather approximate, since the average difference found for preformed CO₂ between old and present seawater exceeds 100 µmol. dm⁻³ which is unrealistic. SHILLER (1981) has cautioned on neglecting the mixing corrections in evaluation of the preformed CO₂. As SHILLER (1981) doubted CO₂ back calculation for anthropogenic CO₂ component in the Antarctic Intermediate water mass, the present evaluations also might have resulted in higher preformed CO₂ values.

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