DECADAL VARIATIONS IN OCEANIC PROPERTIES OF THE ARABIAN SEA WATER COLUMN SINCE GEOSECS

Ravi Bhushan^{1,2} • Koushik Dutta^{1,3} • Rajesh Agnihotri^{1,4} • R Rengarajan¹ • Satinder Pal Singh¹

ABSTRACT. This article reports temporal changes in the measured oceanic geochemical properties of the Arabian Sea and the equatorial Indian Ocean by reoccupying six stations investigated during the GEOSECS expedition in 1977 and 1978. Observed differences are interpreted in terms of plausible changes in the environment and climate that have occurred in response to natural or anthropogenic processes. The depth profiles of major parameters such as dissolved oxygen, ΣCO_2 , major nutrients (silicates, nitrates, and phosphates), and radiocarbon in dissolved inorganic carbon were measured during the cruises between 1994 and 1998 along with temperature and salinity. Most stations in the Arabian Sea show an increase in salinity by ~0.2 to 0.3 salinity units in the top 400 m, whereas one station in the equatorial Indian Ocean showed a decrease in salinity by ~0.1 units, indicating a likely change in the evaporation-precipitation (E-P) balance. The ΣCO_2 increased by an average of 8 μ M within the top 1200 m of the Arabian Sea. The depth profiles of nitrates and dissolved oxygen for the central Arabian Sea stations show significant variations, while only marginal changes are seen for silicates and phosphates relative to the GEOSECS data. The decrease in Δ^{14} C of surface waters is due to the steady decrease in atmospheric ¹⁴C concentration since GEOSECS, and the Δ^{14} C increase in subsurface waters is attributed to the downward vertical diffusion of bomb ¹⁴C interpreted in terms of atmosphere to ocean transfer and lateral advection of water masses.

INTRODUCTION

The northern Indian Ocean comprises two major oceanic regions, the Arabian Sea and the Bay of Bengal. The oceanography of the northern Indian Ocean region is significantly influenced by seasonal changes in the atmospheric and oceanic circulations induced by the seasonal monsoon winds. This is a classic example of coupled ocean-atmosphere interaction, which leads to significant changes in sea surface temperature, salinity, and biogeochemistry of the northern Indian Ocean. The seasonal monsoon winds lead to coastal upwelling along the western margins of the Arabian Sea and the Bay of Bengal (Currie et al. 1973; Shankar et al. 2002). The intense upwelling in the Arabian Sea feeds nutrients to its surface waters, making it one of the most productive oceanic regions (Prasanna Kumar et al. 2002; Naqvi et al. 2006 and references therein). The deep waters of the Arabian Sea are composed of waters from south of the Equator and marginal seas like the Red Sea and the Persian Gulf (Shetye et al. 1994). Bower et al. (2000) investigated the initial transformation, dynamics, and spreading pathways of Red Sea and Persian Gulf outflow waters into the Arabian Sea on the basis of historical hydrographic data and a numerical plume model. Depending on the temperature-salinity characteristics of the outflow sources and the product water masses, Bower et al. (2000) concluded that the Red Sea and the Persian Gulf outflows are diluted by factors of ~ 2.5 and ~ 4 , respectively. It is concluded that the product water from both the outflows are advected away from the sill region in narrow boundary currents during some part of the year, whereas during other times the same occurs in isolated patches.

The Redfield ratio of carbon, nitrogen, and phosphorous (C:N:P) of sinking particle flux to the deep ocean is one of the crucial factors in the marine biogeochemical cycle, which for many years was assumed to be constant (106:16:1) in the modern ocean. However, there is evidence of a temporal shift in the ratio in deep waters of the Northern Hemisphere (Pahlow and Riebesell 2000). Pahlow and Riebesell (2000) observed a rise in N:P in the North Atlantic Ocean and C:N and C:P in the North Pacific Ocean. They suggested that the rise in N:P ratio in the North Atlantic Ocean might be due to an enhanced invasion of atmospheric nitrous oxide derived from an-thropogenic sources. The increased C:N and C:P ratios accompanied by increased remineralization

^{1.} Geosciences Division, Physical Research Laboratory, Ahmedabad 38009, India.

^{2.} Corresponding author. Email: bhushan@prl.res.in.

^{3.} Department of Earth and Planetary Sciences, Northwestern University, Evanston, Illinois 60208, USA.

^{4.} Radio and Atmospheric Science Division, National Physical Laboratory, New Delhi 110012, India.

rates suggest an enhanced export of carbon in this region perhaps due to the enhanced bioavailability of eolian iron. Hupe and Karstensen (2000) suggested that $\Delta C_{org}/\Delta N/\Delta P/\Delta O_2$ remineralization ratios in the Arabian Sea are not constant but depth dependent throughout the water column. Activities like N fixation at the surface and denitrification within the OMZ of the Arabian Sea are expected to have their imprints on organic matter remineralization within upper and intermediate waters. However, the remineralization ratios in the deeper waters should be invariant. The first measurements of radiocarbon in the water column of the Arabian Sea and the Bay of Bengal were done during 1977 and 1978 as a part of the international GEOSECS program (Stuiver and Östlund 1983). Based on reoccupation of three Arabian Sea GEOSECS stations, Somayajulu et al. (1999) and Bhushan et al. (2000) described temporal changes in ¹⁴C distribution about 2 decades after GEOSECS.

Arabian Sea waters have been undergoing significant changes both at the surface (in terms of biological productivity, sea surface temperature [SST], E-P balance) and subsurface waters (denitrification or consumption of nitrates) in response to anthropogenic global climate change. For instance, SSTs of the Arabian Sea have been reported to be increasing with a rate of 0.4° C/100 yr since the beginning of the 20th century (Mitra et al. 2002). In addition, Stramma et al. (2010) reported that large areas of the subsurface tropical oceans are undergoing decreasing oxygen levels during the past few decades. Following the same ramp, evidence from recent sedimentary records reveals enhancement of surface biological productivity on both the western and eastern sides of the Arabian Sea (Anderson et al. 2002; Agnihotri et al. 2008). A plausible enhancement of denitrification and consequent increased production of N₂O has been projected in an anthropogenic climate change scenario by Naqvi et al. (2000). Although much of the activity is anticipated to take place on the western and eastern side productive zones, decadal-scale changes in open-ocean intermediate and deeper waters of the Arabian Sea provide an opportunity to investigate the overall impacts of the aforesaid processes.

This study has determined the water column distributions of dissolved oxygen, ΣCO_2 , nutrients, and dissolved inorganic ¹⁴C in the Arabian Sea and examined their decadal variations as deduced by comparison with the GEOSECS data (Stuiver and Östlund 1983). This study attempts to understand the varying dissolved oxygen (though statistically insignificant for intermediate and deeper waters at times) and nitrate levels (statistically significant) for the north-central and central part of the Arabian Sea, known as the core of the perennial denitrification zone of the Arabian Sea. Being an oligotrophic and low surface biological productivity zone, the observed changes plausibly indicate overall enhanced rates of subsurface denitrification in response to enhanced surface biological productivity and E-P changes.

METHODS

The GEOSECS stations 413, 416, 417, 418, 419, and 448 (occupied in the Arabian Sea and the equatorial Indian Ocean between December 1977 and March 1978) were reoccupied during three different phases in this study between 1994 and 1998. The locations of the GEOSECS and the corresponding reoccupation stations are shown in Figure 1 and listed in Table 1. The first reoccupation was undertaken during the cruise SS-118 of *FORV Sagar Sampada* in March 1994, wherein GE-OSECS station 416 was reoccupied (SS-118/H12). During the cruise SS-132 to the Arabian Sea in March 1995, GEOSECS stations 417 (SS-132/3271), 418 (SS-132/3274), and 419 (SS-132/3273) were reoccupied. During cruise SS-152 in 1997, GEOSECS station 448 (SS-152/3846) and other stations in the Bay of Bengal were reoccupied (Dutta and Bhushan 2012). During the third Arabian Sea cruise SS-164 in 1998, GEOSECS stations 413 (SS-164/4018), 416 (SS-164/4016), 417 (SS-164/4021), 418 (SS-164/4020), and 419 (SS-164/4019) were reoccupied.

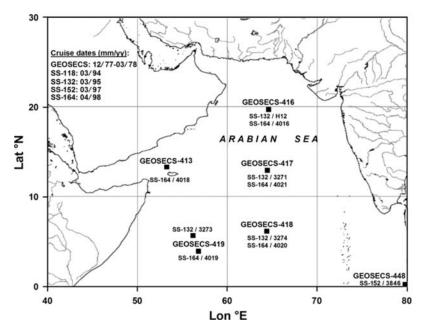


Figure 1 Sampling stations in the Arabian Sea occupied during GEOSECS and this study

While all GEOSECS stations were occupied during winter (December 1977 to January 1978), the reoccupation cruise of SS-164 was during late spring (April 1998). Among the geochemical parameters, only ΣCO_2 and ¹⁴C were measured during the SS-118 and SS-132 cruises. Measurements of dissolved oxygen, ΣCO_2 , and nutrients (silicates, nitrates, and phosphates) were carried out during SS-152 and SS-164.

Collection of Seawater and Measurements of Temperature and Salinity

Seawater samples were collected using eight 30-L PVC Go-Flo bottles (General Oceanics, Miami, Florida, USA) attached with a 12-position rosette. Continuous profiles of temperature, salinity, dissolved oxygen, and beam attenuation (particles) were obtained using a Sea-Bird CTD instrument. The temperature sensor of the CTD was calibrated before each cruise. The software package SEASOFT (v 4.232; http://www.seabird.com/software/SeasoftDosRev. htm) was used for processing the raw CTD data and deriving potential temperature (θ) and potential density (σ_{θ}). The CTD temperature and salinity values are expressed following the conventions of ITS-90 (°C) and PSS-78 units, respectively. Salinity of the seawater samples

| Table 1 | Sampling | locations d | uring | GEOSECS | and the | ir reoccupations. |
|---------|----------|-------------|-------|---------|---------|-------------------|
|---------|----------|-------------|-------|---------|---------|-------------------|

| Station | Location (Lat°N; Long°E) | Sampling date | Reoccupa- tion for other parameters | Sampling date | Reoccupation for ¹⁴ C | Sampling date |
|-------------|--------------------------------|---------------|---|---------------|----------------------------------|---------------|
| GEOSECS 413 | 13.35; 53.27 | 12/1977 | SS-164/4018 | 04/1998 | SS-164/4018 | 04/1998 |
| GEOSECS 416 | 19.75; 64.62 | 12/1977 | SS-164/4016 | 04/1998 | SS-118/H12 | 03/1994 |
| GEOSECS 417 | 12.97; 64.47 | 01/1978 | SS-164/4021 | 04/1998 | SS-132/3271 | 04/1995 |
| GEOSECS 418 | 6.18; 64.42 | 01/1978 | SS-164/4020 | 04/1998 | SS-132/3274 | 05/1995 |
| GEOSECS 419 | 3.95; 56.80 | 01/1978 | SS-164/4019 | 04/1998 | SS-132/3273 | 05/1995 |
| GEOSECS 448 | 0.00; 80.10 | 03/1978 | SS-152/3846 | 02/1997 | SS-152/3846 | 03/1997 |

was determined using an AutoSal 8400A salinometer (Guildline Instruments Ltd., Smiths Falls, Ontario, Canada). The salinometer was calibrated using IAPSO standard seawater. The precision of salinity measurements by Autosal was typically ± 0.0005 units, based on repeat measurements of seawater samples. CTD salinity values were calibrated using the salinometer-based values.

Measurements of Dissolved Oxygen

Dissolved oxygen (DO) was measured by a modified Winkler titration method (Carpenter 1965). A Metrohm 655 Dosimat autotitrator (Metrohm USA Inc., Riverview, Florida, USA) was used for the titration. The end point of titration was detected using starch solution as a visual indicator. Based on repeat analyses, the average precision of dissolved oxygen measurements by the Winkler titration method was $\pm 2 \mu M (1\sigma)$.

Measurements of Dissolved Inorganic Carbon (ΣCO₂)

The dissolved inorganic carbon (ΣCO_2) in the seawater samples was measured by the coulometric method following the procedures outlined by Johnson et al. (1985) and Dickson and Goyet (1994). Aliquots of seawater samples were collected in 60-mL borosilicate glass bottles. Immediately after collection, the samples were poisoned with 25 µL of saturated (5%) HgCl₂ solution to inhibit biological production. The bottles were sealed with greased ground glass stoppers and kept refrigerated at ~2°C until their analysis. ΣCO_2 was measured using a UIC model 5012 CO_2 coulometer (UIC Inc., Joliet, Illinois, USA). Typical precision of ΣCO_2 measurements was better than ±3 µM (1 σ) based on repeat analyses of seawater samples. The accuracy of ΣCO_2 measurements was checked from analyses of certified reference seawater (Batch#42, December 1997), supplied by Prof Andrew G Dickson, Scripps Institute of Oceanography, USA. The mean ΣCO_2 measured for this standard seawater was 1983.2 ± 2.3 µM (1 σ , *n* = 20), in good agreement with its certified value of 1985.1 ± 0.8 µM.

Measurements of Nutrients

About 500 mL of seawater samples were collected for the analysis of nutrients. The samples were kept refrigerated until analysis. Silicates and nitrates were measured onboard using a Technicon Auto-Analyzer (Technicon Instruments Corp., New York, New York, USA). Phosphates were measured by spectrophotometry using a Beckman model 26 spectrophotometer (Beckman Instruments, Palo Alto, California, USA) using the procedure of Strickland and Parsons (1972). Based on repeat measurements of seawater samples, the precisions (1σ) of silicates, total nitrates and phosphates measurements were $\pm 1.3\%$, $\pm 1.4\%$ and $\pm 1.6\%$, respectively, of the measured values. Accuracies of silicate and nitrate measurements were within $\pm 5\%$ of the measured values as checked by analyzing CSK standard solutions (Wako Pure Chemical Industries Ltd., Osaka, Japan).

Radiocarbon Measurements

Details of the analytical methods for DIC ¹⁴C analysis have been described earlier (Bhushan et al. 1994, 1997, 2000; Dutta et al. 2006). About 100 L of seawater was collected using 30-L PVC Go-Flo bottles and CO₂ was extracted from the seawater by addition of concentrated H₂SO₄ within a continuous closed circulation system using a peristaltic pump. The liberated CO₂ was trapped in 2N NaOH solution, which was brought back to the laboratory for ¹⁴C assay. The trapped CO₂ was liberated in the laboratory and converted to benzene. ¹⁴C was measured by liquid scintillation counting (LSC) of benzene prepared from the seawater samples (Bhushan et al. 1994). All ¹⁴C results are expressed as Δ^{14} C following Stuiver and Polach (1977). The internal precision of Δ^{14} C was ±5‰ (1 σ) based on repeat measurements of 3-mL modern benzene samples.

Comparison with GEOSECS Data

Oceanographic data of the GEOSECS Indian Ocean expedition (Stuiver and Östlund 1983) were obtained from the digital archive of IRI/LDEO Climate Data Library (http://iridl.ldeo.columbia. edu/SOURCES/.GEOSECS). Comparisons of dissolved oxygen, ΣCO_2 , and the nutrients were done only for the Arabian Sea data collected during the SS-164 cruise. The vertical sampling resolution of both GEOSECS and SS-164 cruises were similar, between 14 and 20 samples per station. To determine the temporal changes, the GEOSECS data were first interpolated and differences were obtained for the depths sampled during the SS-164 cruise.

RESULTS AND DISCUSSION

Changes in Salinity

Profiles of potential temperature versus salinity (θ -S) for the Arabian Sea and equatorial Indian Ocean stations are shown in Figures 2a-f. The Arabian Sea is characterized by four distinct water masses in the top 1000 m of the water column, namely the Arabian Sea High Salinity Water (ASW), the Persian Gulf Water (PGW), Indian Central Water (ICW), and Red Sea Water (RSW). These water masses can be located at approximate depths of 20–100, 200–300, 300–400, and 500–800 m, respectively (Figure 2b). The ASW and RSW can be traced at most of the stations, whereas PGW can be traced in just a few northern Arabian Sea stations. It is evident from the θ -S plots that the salinity has increased at all stations in the Arabian Sea by ~0.2 to 0.3 salinity units for waters up to 400 m (Figures 2a–e). θ -S plot at the equatorial Indian Ocean (GEOSECS 448) reoccupied in 1997 (SS-152/3846) shows a slight decrease in salinity by ~0.1 units (Figure 2f). The increase in salinity suggests a net increase in evaporation over precipitation in the Arabian Sea over 2 decades. This observation is consistent with the observed pattern of global salinity changes as a result of intensification of the global water cycle, which shows increased salinity in the Arabian Sea and reduced salinity in the equatorial Indian Ocean and the Bay of Bengal (Durack et al. 2012). Average changes in salinity for the deep waters (>2000 m) observed at the stations SS-164/4016, SS-164/4021, SS-164/4020, and SS-164/4019 (GEOSECS 416, 417, 418), were 0.00, 0.07, and 0.03, respectively (uncertainty ± 0.02 units). Using the salinity data from SS-118 and SS-132 cruises, Somayajulu et al. (1999) reported deep-water salinity changes of 0.07, 0.11, and 0.00 units, for the corresponding stations SS-118/H12, SS-132/3271, and SS-132/3274.

Changes in Dissolved Oxygen

The depth profiles of dissolved oxygen (DO), ΣCO_2 , and nutrients for the Arabian Sea stations are shown in Figures 3a-e. DO concentrations in the upper 1000 m of the seawater column are governed by both overhead column productivity as well as ventilation of subsurface waters through circulation of the water masses. Since the Arabian Sea is a highly productive region associated with seasonally reversing monsoonal winds, any change in the overhead productivity would be strongly reflected in the upper 1000-m water column, where most of the organic matter remineralization occurs. A decreasing trend in DO concentration within 200-1000 m is mainly indicative of increasing productivity and strengthening of the oxygen minimum zone. The northernmost station (GEOSECS 416 and SS-164/4016; Figure 3b) happens to be within the core of the perennial denitrification zone of the Arabian Sea (Nagvi 1994; Nagvi et al. 2000). However, as seen in the profiles in Figures 3a-e, the DO concentrations do not show any significant deviations since the GEOSECS measurements except in the western Arabian Sea, specifically (i) near the Red Sea mouth (GEOSECS-413; Figure 3a) where DO appears to have decreased by $\sim 12 \ \mu M$ below 1000 m and (ii) $\sim 10-20 \ \mu M$ in the southwestern Arabian Sea (GEOSECS-419; Figure 3e), where the upper water column shows a decrease in DO. The central and northeastern Arabian Sea is known to be an intense perennial denitrification zone. The overhead productivity of these regions is quite low and regions of high

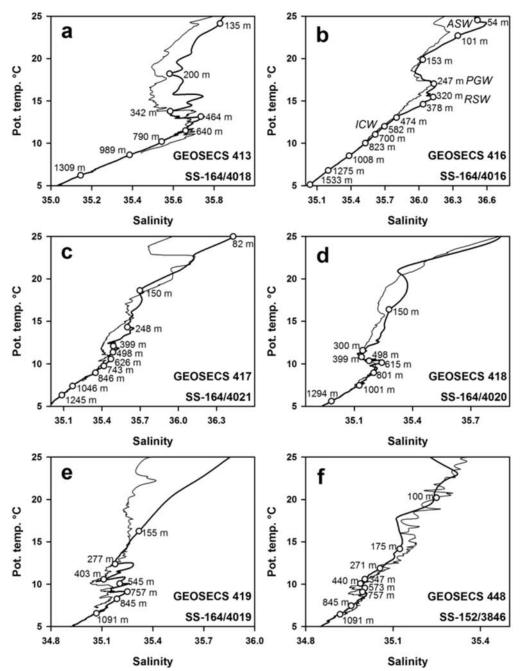


Figure 2 θ -S profiles of the GEOSECS sampling stations during 1977–1978 (thin lines) and the reoccupied stations (thick lines) during 1997 and 1998 for the top 1200 m of the water column. Main water masses of the Arabian Sea (ASW, PGW, RSW, and ICW) are shown in (b). All stations in the Arabian Sea have recorded an increase in salinity in the 2 decades since GEOSECS.

productivity are located far from this region. One of the plausible reasons for this phenomenon is increased mineralization of the sinking particles due to the supply of denitrifying bacteria from the western continental margin of India or the seasonal suboxic zone of the eastern Arabian Sea (Naqvi

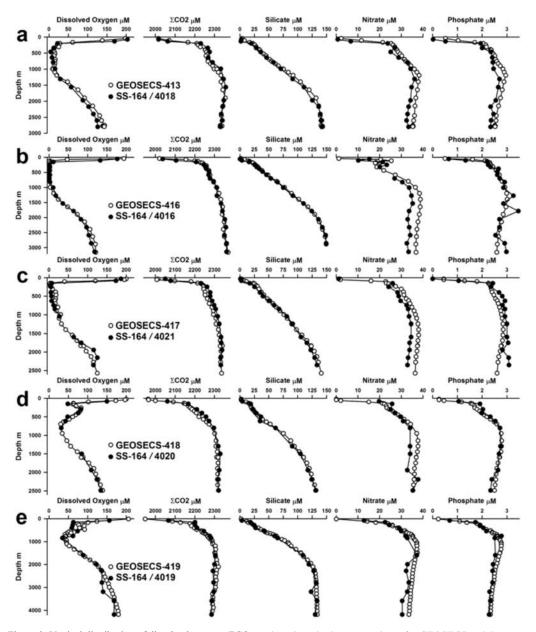


Figure 3 Vertical distribution of dissolved oxygen, ΣCO_2 , and nutrients in the water column for GEOSECS and the reoccupied stations in the Arabian Sea.

et al. 2000, 2006). While there is an expected enhanced denitrification in the seasonal suboxic zone off the coast of India and Pakistan (Naqvi et al. 2000), no significant changes are noted since GEO-SECS in deep-water DO below 1000 m in the central Arabian Sea (GEOSECS-416, 417, and 418; Figures 3b, 3c, and 3d). This indicates that the influence of enhanced productivity has not caused significant change in subsurface DO in the last 2 decades or the threshold of lower limits of subsurface DO concentration had already been crossed (due to enhanced surface biological productivity) during GEOSECS times. It is also important to mention here that subtle changes in deep-water DO

concentration related to productivity variations are difficult to detect considering the relatively high uncertainty ($\pm 2 \mu M$) of the Winkler titration method. Therefore, it is important to examine the nutrient profiles in tandem with other species, especially nitrates, as it is the next exploitable species (after DO) that heterotrophic bacteria consume for carrying out organic matter remineralization.

Changes in Dissolved Inorganic Carbon (ΣCO₂)

The ΣCO_2 content in the whole water column of the Arabian Sea shows an increasing trend from south to north. This is apparent in view of the increasing northward trend of productivity in the Arabian Sea. The northern Arabian Sea station (SS-164/4016) shows ΣCO_2 decreased by ~15 µM in top the 1000 m with respect to GEOSECS (Figure 3b), possibly due to enhanced productivity leading to the consumption of ΣCO_2 supported by subsurface DO. The southernmost region shows enhanced ΣCO_2 (~30 to 40 µM) with respect to GEOSECS (Figures 3c, 3d, and 3e), which could either be attributed to decreased productivity or anthropogenic increase of CO_2 . Figure 4 shows the net changes in ΣCO_2 for all stations in the Arabian Sea. The ΣCO_2 within the top 1200-m water column of the Arabian Sea increased by an average of 8 µM over 2 decades since 1978. This compares with the anthropogenic CO₂ invasion of ~10 to 20 µM in the Arabian Sea reported by Sabine et al. (1999).

Changes in Nutrients (Nitrates, Phosphates, and Silicates)

Some of the studied chemical parameters such as silicates have remained invariant since the GE-OSECS measurements. However, some apparent differences in nitrate depth profiles mainly in the northern-central and central Arabian Sea are noteworthy, e.g. in the stations GEOSECS-416 (SS-164/4016, Figure 3b) and GEOSECS-417 (SS-164/4021, Figure 3c). Silicate and phosphate contents remain invariable since GEOSECS at almost all the stations, indicating diatom (siliceous productivity) dissolution rates and organic matter remineralization rates in general have not varied significantly over a period of 2 decades. In the northern-central (GEOSECS-416) and central part (GEOSECS-417) of the Arabian Sea, nitrate values of the intermediate and deeper waters measured during SS-164 in 1998 show a marginal ($2 \pm 3 \mu$ M) decrease with respect to those measured by GEOSECS at the corresponding depths (Figures 3b and 3c). The southernmost central Arabian Sea station (GEOSECS-418 and SS-164/4020; Figure 3d) shows higher values of nitrates in the upper water column, which remain similar or slightly lower than corresponding GEOSECS measurements. Figures 5a–d show relative changes in the nutrients along with Σ CO₂ and DO for the GEOSECS

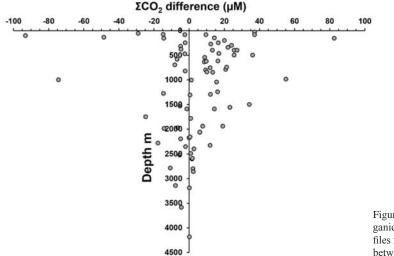


Figure 4 Changes in dissolved inorganic carbon (ΣCO_2) in vertical profiles for all stations in the Arabian Sea between 1977–1978 and 1998.

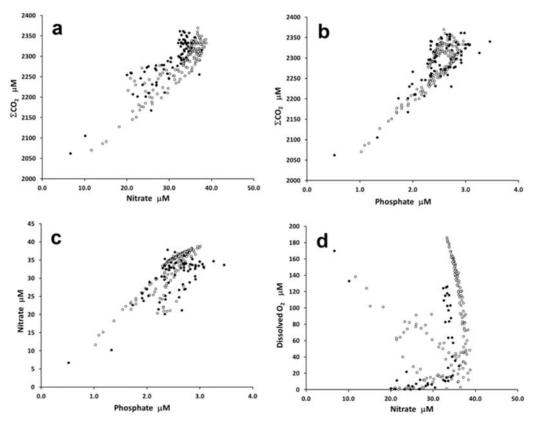


Figure 5 Relative changes in 2 decades for ΣCO_2 , nutrients (nitrate and phosphate) and dissolved oxygen for GEOSECS (open circles) and SS-164 cruise (filled circles). (a) ΣCO_2 versus nitrate showing reduction of nitrate mainly in deeper water; (b) ΣCO_2 versus phosphate showing no discernible shift; (c) nitrate versus phosphate; and (d) dissolved oxygen versus nitrate showing distinct reduction in deep water nitrate.

stations and the reoccupied stations. The scatter plots in Figures 5a, 5c, and 5d show a reduction in nitrates from ~37 to ~32 μ M for the waters with nitrates >30 μ M (~1000 m or deeper). The relative change in phosphates with respect to ΣCO_2 , is negligible (Figure 5b). Reduction in deeper water nitrates in the north-central and central parts of the Arabian Sea indicates enhanced denitrification (consumption of nitrates by heterotrophic bacteria) over a period of 2 decades. A corresponding decrease in DO concentrations in the northern central Arabian Sea may not be that apparent, but in the central part of Arabian Sea (GEOSECS-417 and SS-164/4021; Figure 3c) can be seen at upper depths. As stated previously, if subsurface waters had already crossed the lower threshold limits of DO significant changes are not expected in DO profiles. Even if some subtle changes would have occurred in the last 2 decades, they are difficult to record due to the uncertainty of the Winkler titration method. It is important to note the distinct decline of nitrates in the central Arabian Sea, which is within core of the perennial denitrification zone, indicative of enhanced utilization of nitrates due to intensification of denitrification. The nutrient and DO depth profiles of the central Arabian Sea are known to be governed by the availability of nutrients from subsurface waters of adjacent productive zones of the eastern and western Arabian Sea, even though the open-ocean and coastal suboxic zones are not contiguous (Naqvi et al. 2006). Hence, enhanced productivity, and thereby intensification of denitrification, in adjacent productive zones can be expected to leave their imprint in intermediate to deeper water nitrate contents of the central Arabian Sea as well. Thus, decreased values of nitrates

in the north-central and central Arabian Sea (Figures 3b and 3c) are probably indicative of enhanced denitrification due to increased surface biological productivity in the last 2 decades. This observation is consistent with observations made in the high-productivity zone of the Arabian Sea, mainly situated at the western and eastern coast lines, which indicates enhanced surface biological productivity in response to both direct (via enhanced nutrient supply from coastal rivers and eolian pathways; Naqvi 2000; Duce et al. 2008) and indirect (enhanced upwelling caused by increased land-ocean thermal contrast in a global warming scenario; Goes et al. 2005) influences of anthropogenic forcing in recent decades. If it is so, the central Arabian Sea could possibly be acting as a locale for nitrate loss and sink for anthropogenically added nitrates in the adjacent coastal areas. Plausible changes in the nitrate:phosphate ratios induced by such a scenario may not still be significant on decadal timescales; the deficiency of nitrates with respect to phosphates is still possibly able to stimulate nitrogen fixation in the central oligotrophic regions of the Arabian Sea (Hupe and Karstensen 2000).

These observations have to been seen in the realm of similar observations made in the North Pacific, where Keller et al. (2002) reported nitrate concentrations and apparent oxygen utilization (AOU) appear to have decreased in intermediate waters (at depths ~1000 m), whereas in shallow waters both have increased (though not statistically significant) when comparing GEOSECS (1970s) and WOCE (1990s) data.

Decadal Changes in Radiocarbon

The surface DIC Δ^{14} C of the reoccupation stations show values that were lower by 17 to 58‰ (mean 32‰) as compared to GEOSECS (Figure 6). This is due to the steady decrease in atmospheric 14 C concentration since GEOSECS as the Δ^{14} C of the atmosphere was much higher during GEOSECS than during this study. The average Δ^{14} C of atmospheric CO₂ in the maritime air over the Arabian Sea was 120% in 1993 and 99% in 1998 (Bhushan et al. 1997; Dutta et al. 2006), compared to 313‰ in 1977 (during GEOSECS) as recorded in tree rings from peninsular India (Chakraborty et al. 2008). However, the subsurface Δ^{14} C values at most of the stations in the upper 1000 m were higher than the GEOSECS values due to increased penetration of bomb ¹⁴C in the water column of the Arabian Sea mainly by downward transfer through mixing with deeper waters. The deep waters below 1000 m at most of the stations do not show any significant change in Δ^{14} C values except at station SS-164/4018 (reoccupation of GEOSECS 413; Figure 6). The increase in Δ^{14} C values at this station since GEOSECS at depths between 1200–2200 m is most likely due to gradual sinking of more saline and dense Red Sea surface water (Bhushan et al. 2003; Dutta and Bhushan 2012). A similar increase is also noted in the DO concentration at the same depths in this station, hinting at increased penetration of oxygen-rich surface waters from the Red Sea since GEOSECS. The bomb ¹⁴C penetration and its inventory in the equatorial Indian Ocean is significantly higher than that in the Arabian Sea stations. This has been attributed to advection of low-salinity waters enriched in ¹⁴C from the Indonesian Throughflow from the Pacific along the Equator to the 10° latitudinal belt (Bard et al. 1988, 1989). This can be noticed with enhanced Δ^{14} C values at depths of 100–500 m depth at stations 4018, 419, and 3846. The small changes in the bomb ¹⁴C inventories, significant increase in the mean penetration depths, and lowering of the surface Δ^{14} C values in the Arabian Sea indicate that the temporal variation of bomb ¹⁴C in 2 decades is mainly by downward transfer through mixing with deeper waters.

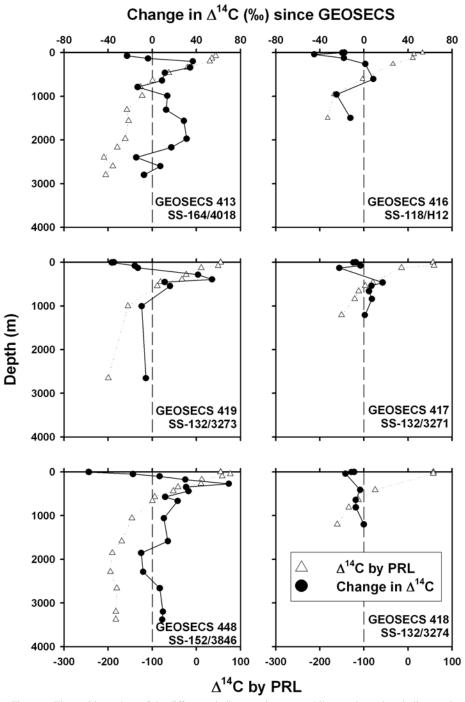


Figure 6 The positive values of the difference indicate an increase, while negative values indicate a decrease in ¹⁴C since GEOSECS. The vertical dashed lines signify zero changes in ¹⁴C.

CONCLUSIONS

Changes in various oceanographic parameters such as salinity, dissolved oxygen, ΣCO_2 , and nutrients are studied from measurements at five stations in the Arabian Sea reoccupied 2 decades following the GEOSECS expedition. A distinct increase in salinity can be seen in most stations in the Arabian Sea, indicating enhanced evaporation over precipitation. Differences in the nutrients since GEOSECS indicate an increase in productivity in the Arabian Sea since 1977. The observed differences in the concentration of nutrients, DIC, and oxygen could be affected by water mass mixing and remineralization processes taking into account denitrification and anthropogenic CO_2 . Denitrification appears to dominate the effect of nitrogen fixation, thereby making this region a potential sink for fixed nitrogen. This study indicates a net increase in the biological pump of the Arabian Sea, possibly due to changes in the nutrient inventory and their basin-wide recycling via circulation. Increased inventory of ¹⁴C in the top 1000 m is due to the penetration of bomb ¹⁴C since the 1950s.

ACKNOWLEDGMENTS

We are highly indebted to Prof B L K Somayajulu for his inspiration in initiation of this program. We are thankful to the captain and crew of the *FORV Sagar Sampada* for providing onboard logistics support. We are grateful to the Ministry of Earth Sciences (previously Dept. of Ocean Development), Govt. of India, for providing ship time. We thank the Director and staff of the Centre of Marine Living Resources in Cochin for the management of various cruises, and the technical staff of NORINCO for operation and maintenance of the shipboard instruments. We are highly grateful to Dr S W A Naqvi (from National Institute of Oceanography, Goa) for his help in setting up the Auto-Analyzer onboard. The onboard help and laboratory sample processing of ¹⁴C samples provided by Mr J P Bhavsar is sincerely acknowledged. We thank the two anonymous reviewers for comments that helped in improving this manuscript.

REFERENCES

- Agnihotri R, Kurian S, Fernandes M, Reshma K, D'Souza W, Naqvi SWA. 2008. Variability of subsurface denitrification and surface productivity in the coastal eastern Arabian Sea over the past seven centuries. *The Holocene* 18(5):755–64.
- Anderson DM, Overpeck JT, Gupta AK. 2002. Increase in the Asian Southwest Monsoon during the past four centuries. *Science* 297(5581):596–9.
- Bard E, Arnold M, Ostlund GH, Maurice P, Monfray P, Duplessy JC. 1988. Penetration of bomb radiocarbon in the tropical Indian ocean measured by means of accelerator mass spectrometry. *Earth and Planetary Science Letters* 87(4):379–89.
- Bard E, Arnold M, Toggweiler JR, Maurice P, Duplessy J-C. 1989. Bomb ¹⁴C in the Indian ocean measured by accelerator mass spectrometry: oceanographic implications. *Radiocarbon* 31(3):510–22.
- Bhushan R, Chakraborty S, Krishnaswami S. 1994. Physical Research Laboratory (Chemistry) radiocarbon date list I. *Radiocarbon* 36(2):251–6.
- Bhushan R, Krishnaswami S, Somayajulu BLK. 1997. ¹⁴C in air over the Arabian Sea. *Current Science* 73(3):273–6.
- Bhushan R, Somayajulu BLK, Chakraborty S, Krishnaswami S. 2000. Radiocarbon in the Arabian Sea water column: temporal variations in bomb ¹⁴C inventory since the GEOSECS and the CO, air-sea

exchange studies. *Journal of Geophysical Research* 105(C6):14,273–82.

- Bhushan R, Dutta K, Mulsow S, Povinec PP, Somayajulu BLK. 2003. Distribution of natural and man-made radionuclides during the reoccupation of GEOSECS stations 413 and 416 in the Arabian Sea: temporal changes. *Deep Sea Research II* 50(17–21):2777–84.
- Bower AS, Hunt HD, Price JF. 2000. Character and dynamics of the Red Sea and Persian Gulf outflows. *Journal of Geophysical Research* 105(C3):6387– 414.
- Carpenter JH. 1965. The Chesapeake Bay Institute technique for the Winkler dissolved oxygen method. *Limnology and Oceanography* 10(1):141–3.
- Chakraborty S, Dutta K, Bhattacharyya A, Nigam M, Schuur EAG, Shah SK. 2008. Atmospheric ¹⁴C variability recorded in tree rings from peninsular India: implications for fossil fuel CO₂ emission and atmospheric transport. *Radiocarbon* 50(3):321–30.
- Currie RI, Fisher AE, Hargreaves PM. 1973. Arabian Sea upwelling. In: Zeitzschel B, Gerlach SA, editors. *The Biology of the Indian Ocean, Volume* 3. New York: Springer. p 37–52.
- Dickson AG, Goyet C, editors. 1994. Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Seawater, Version 2. CDIAC-74, Oak Ridge National Laboratory, Oak

Ridge, Tennessee, USA.

- Duce RA, LaRoche J, Altieri K, Arrigo KR, Baker AR, Capone DG, Cornell S, Dentener F, Galloway J, Ganeshram RS, Geider RJ, Jickells T, Kuypers MM, Langlois R, Liss PS, Liu SM, Middelburg JJ, Moore CM, Nickovic S, Oschlies A, Pedersen T, Prospero J, Schlitzer R, Seitzinger S, Sorensen LL, Uematsu M, Ulloa O, Voss M, Ward B, Zamora L. 2008. Impacts of atmospheric anthropogenic nitrogen on the open ocean. *Science* 320(5878):893–7.
- Durack PJ, Wijffels SE, Matear RJ. 2012. Ocean salinities reveal strong global water cycle intensification during 1950 to 2000. *Science* 336(6080):455–8.
- Dutta K, Bhushan R. 2012. Radiocarbon in the Northern Indian Ocean two decades after GEOSECS. *Global Biogeochemical Cycles* 26: GB2018, doi:10.1029/2010GB004027.
- Dutta K, Bhushan R, Somayajulu BLK, Rastogi N. 2006. Inter-annual variation in atmospheric Δ^{14} C over the Northern Indian Ocean. *Atmospheric Environment* 40(24):4501–12.
- Goes JI, Thoppil PG, Gomes H do R, Fasullo JT. 2005. Warming of the Eurasian landmass is making the Arabian Sea more productive. *Science* 308(5721):545–7.
- Hupe A, Karstensen J. 2000. Redfield stoichiometry in Arabian Sea subsurface waters. *Global Biogeochemical Cycles* 14(1):357–72.
- Johnson KM, King AE, Seiburth JM. 1985. Coulometric TCO₂ analyses for marine studies; an introduction. *Marine Chemistry* 16(1):61–82.
- Keller K, Slater RD, Bender M, Key RM. 2002. Possible biological or physical explanations for decadal scale trends in North Pacific nutrient concentrations and oxygen utilization. *Deep-Sea Research II* 49(1– 3):345–62.
- Mitra AP, Dileep Kumar M, Kumar KR, Abrol YP, Kalra N, Velayutham, M, Naqvi SWA. 2002. Global change and biogeochemical cycles: the south Asia region. In: Tyson P, Fuchs R, Fu C, Lebel L, Mitra AP, Odada E, Perry J, Steffen W, Virji H, editors. *Global-Regional Linkages in the Earth System*. Berlin: Springer. p 75–107.
- Naqvi SWA. 1994. Denitrification processes in the Arabian Sea. Proceedings of the Indian Academy of

Sciences 103(2):279-300.

- Naqvi SWA, Jayakumar DA, Narvekar PV, Naik H, Sarma VVSS, D'Souza W, Joseph S, George MD. 2000. Increased marine production of N₂O due to intensifying anoxia on the Indian continental shelf. *Nature* 408(6810):346–9.
- Naqvi SWA, Naik H, Pratihary A, D'Souza W, Narvekar PV, Jayakumar DA, Devol AH, Yoshinari T, Saino T. 2006. Coastal versus open-ocean denitrification in the Arabian Sea. *Biogeosciences* 3:621–33.
- Pahlow M, Riebesell U. 2000. Temporal trends in deep ocean Redfield ratios. *Science* 287(5454):831–3.
- Prasanna Kumar S, Muraleedharan PM, Prasad TG, Gauns M, Ramaiah N, de Souza SN, Sardesai S, Madhupratap M. 2002. Why is the Bay of Bengal less productive during summer monsoon compared to the Arabian Sea? *Geophysical Research Letters* 29:2235, doi:10.1029/2002GL016013.
- Sabine CL, Key RM, Johnson KM, Millero FJ, Poisson A, Sarmiento JL, Wallace DWR, Winn CD. 1999. Anthropogenic CO₂ in the Indian Ocean. *Global Biogeochemical Cycles* 13(1):179–98.
- Shankar D, Vinayachandran PN, Unnikrishnan AS. 2002. The monsoon currents in the north Indian Ocean. Progress in Oceanography 52(1):63–120.
- Shetye SR, Gouveia AD, Shenoi SSC. 1994. Circulation of the water masses of the Arabian Sea. *Proceedings* of the Indian Academy of Sciences 103(2):107–23.
- Somayajulu BLK, Bhushan R, Narvekar PV. 1999. Δ^{14} C, Σ CO₂ and salinity of the western Indian Ocean deep waters: spatial and temporal variations. *Geophysical Research Letters* 26(18):2869–72.
- Stramma L, Schmidtko S, Levin LA, Johnson GC. 2010. Ocean oxygen minima expansions and their biological impacts. *Deep-Sea Research I* 57(4):587–95.
- Strickland JDH, Parsons TR. 1972. A Practical Handbook of Sea-water Analysis. Ottawa: Fisheries Research Board of Canada.
- Stuiver M, Östlund HG. 1983. GEOSECS Indian Ocean and Mediterranean radiocarbon. *Radiocarbon* 25(1):1–29.
- Stuiver M, Polach HA. 1977. Discussion: reporting of ¹⁴C data. *Radiocarbon* 19(3):355–63.