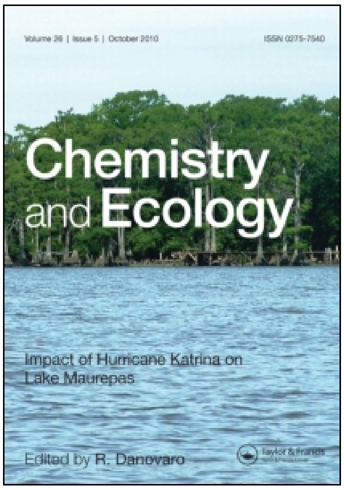

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Variability of dissolved reactive phosphate and apparent oxygen utilization along the west coast of India

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Variability of dissolved reactive phosphate and apparent oxygen utilization along the west coast of India

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This work focuses on the spatial variability of dissolved reactive phosphate along the west coast of India. In this study, samples of surface and bottom water was collected from each of the 27 sites during a single pre-monsoon transect along the west coast of India to study the variation of dissolved reactive phosphate. Phosphate showed an enrichment pattern with increase in depth of the water column. In addition to this, an offshore increase in phosphate concentrations was noticed for both surface and bottom stations. Almost all the surface stations of this study area were found to be characterized by negative apparent oxygen utilization (AOU) values, and bottom stations of the deeper offshore zone (200 m depth) displayed large positive AOU values. The bottom stations of shallow near coastal waters and the deeper offshore zone are characterized by an inverse relationship between phosphate and dissolved oxygen, whereas at these depths, a direct relation was observed between phosphate and AOU. AOU is calculated as the difference between oxygen saturation value at the in situ temperature and salinity and the actual measured concentration. This oxidative re-mineralization mechanism decreases the observed dissolved oxygen well below the expected theoretical values, which is concordant with the higher concentration of phosphate and high positive AOU values.

Keywords: Reactive phosphate; Apparent oxygen utilization; Dissolved oxygen; Re-mineralization; Shallow near coastal waters

1. Introduction

Besides the conservative major elements and the trace metals, there are several components of sea water that are of fundamental importance to the growth of phytoplankton, the base of the food chain in the marine environment. These components include soluble inorganic phosphate, nitrite, nitrate, and ammonium and hydrated silicate ions. These marine fertilizers are consumed in the upper layer of the water body where light conditions permit photosynthesis and are often limiting to growth. Nitrogen and phosphorus are the two major nutrients taken up by phytoplanktons for their healthy growth. Recent ecosystem level nutrient limitation studies support the evidence that phosphorus is the primary limiting nutrient in fresh waters, and N is the limiting nutrient in marine systems [1].

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Phosphorus occurs in both the reactive (inorganic) and unreactive (organic) forms and is an important biogenic element connected with the economy and productivity of the water column. An understanding of the phosphorus cycle in different water masses—focusing on the utilization and regeneration of phosphorus—helps to predict productive and non-productive areas in the oceanic systems. In the marine environment, phosphorus exists in different forms: (1) associated with biological matter, (2) present as dissolved P (which passes through a 0.45 μm filter), (3) present as particulate P, bound onto suspended inorganic and organic particulate matter (which is retained on a 0.45 μm filter), or (4) associated with bottom sediments [2]. The present work focuses on the distributional characteristics of dissolved inorganic phosphate in the surface and bottom water samples of 27 stations off the west coast of India between Cape Comorin and Mumbai. The phosphate distribution pattern off the west coast of India has been influenced by the increasing water discharges from major industrial establishments and from sewage through a network of large and small canals. Geographically, the region of study plays an important role either directly or indirectly in the livelihood and recreational activity of a large number of inhabitants of the coast.

2. Materials and methods

2.1 *Study area*

Water samples were collected during Cruise No. 162 of FORV SAGAR SAMPADA in the pre-monsoon period (18–28 February 1998). Both surface and bottom water samples were collected from 27 stations, off the west coast of India lying between latitudes 8° 3.96′ and 20° 34.05′ N and longitudes 77° 21.96′ and 70° 44.69′ E. The samples collected were categorized as shallow near coastal water samples (collected from a depth of 30 m), deeper offshore zone samples (collected from a depth of 200 m) and samples of Mumbai region (eight stations were sampled in Mumbai region). Figure 1 shows the location map of stations sampled.

2.2 *Sampling and storage of water samples*

Samples were collected using a Niskin sampler (Model 1010) with a capacity of 1.7 l, connected to a conductivity, temperature, depth probe. Immediately after the collection, samples were filtered through Whatman GF/C and were kept frozen in acid-washed plastic containers until analysis. All the apparatus used was cleaned thoroughly with HCl, washed in deionized water, and finally washed with MilliQ water. All the reagents and standards used were of Merck/Suprapur BDH grade.

2.3 *Analytical techniques*

The measurement of hydrographical parameters such as salinity and temperature was done using a conductivity, temperature, depth probe. The estimation of dissolved oxygen (DO) was done chemically onboard using Winkler's method [3]. Estimation of phosphorus was done colorimetrically (using a Hitachi UV-visible spectrophotometer) in which a known volume of sample was allowed to react with a composite reagent containing molybdic acid, ascorbic acid, and trivalent antimony. The resulting complex, heteropoly acid, was reduced in situ to give a blue solution, the extinction of which was measured at 885 nm [3] using the Hitachi UV-visible spectrophotometer. Blank corrections were applied to all sets of readings. The precision of the analysis was checked by performing the standard spiking technique with triplicates.

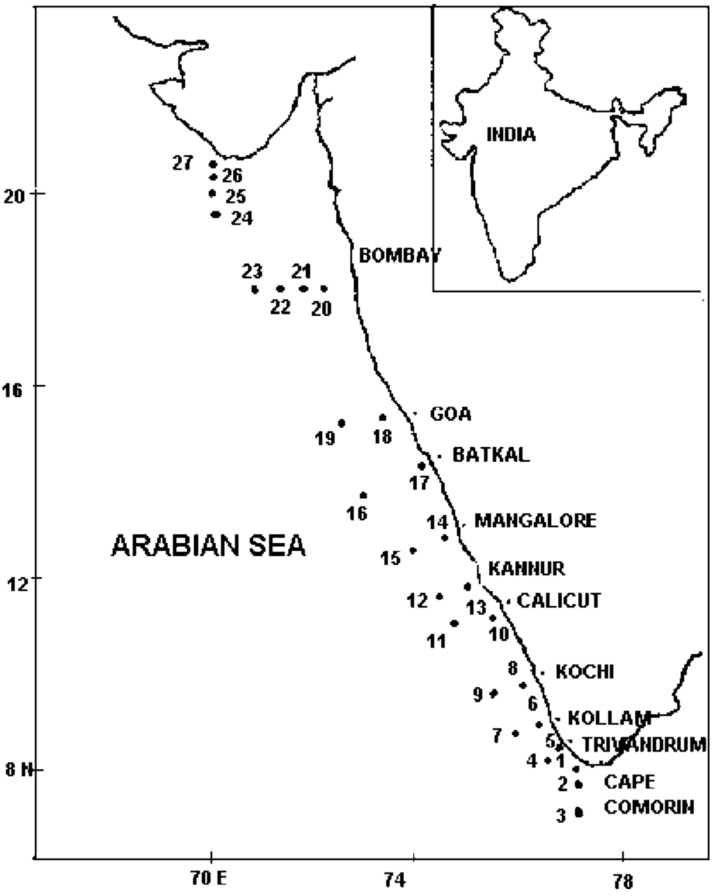

Figure 1. Map of the sampling stations.

3. Results and discusssions

3.1 *Hydrographical parameters*

The spatial variability of general hydrographical parameters like temperature, pH, and salinity is given in table 1.

The temperature-distribution pattern was found to be almost uniform in the surface stations. The surface water temperature of both coastal and offshore stations varied between 27.67 and 29.68 °C. However, the bottom temperature distribution was not in a uniform manner, which showed a variation of 12.90–29.40 °C. For Mumbai region, the surface temperature variation observed was 23.41–27.12 °C, whereas for bottom samples it was 23.39–26.49 °C. Bottom water samples of offshore stations were also unique in their behaviour because the temperature distribution of these samples was in the range 12.9–14.3 °C, and they are also characterized by low values of DO (0.3–0.6 ml l^{-1}). The temperature-distribution pattern of offshore stations showed a decreasing trend with depth of the water column. In the surface waters, the temperature showed a slightly decreasing trend towards the north (from the Mumbai region). The relatively high temperature within the surface layer associated with moderate thermal gradients in the southern part shows a seasonal heating effect. The thermocline gradually spreads towards north with its thickness varying from <100 m in the south to >200 m in

Table 1. List of stations and the general hydrographical features.

Station no. (km)	Locality	Depth (m)	Shore distance (km)	Hydrographical parameters: Temperature (°C) S	Temperature (°C) B	pH S	pH B	Salinity (‰) S	Salinity (‰) B
1	Cape Comorin	30	4	28.87	28.32	8.76	8.77	33.76	33.69
2	Cape Comorin	50	12	29.26	28.06			33.94	33.74
3	Cape Comorin	208	55	29.36	13.91			33.95	35.06
4	Trivandrum	124	21	29.32	17.30			34.06	35.04
5	Trivandrum	28	1.5	29.61	29.40	8.21	8.32	34.63	34.19
6	Kollam	29	6.5	29.49	29.38	8.44	8.41	34.00	34.01
7	Kollam	238	33	29.40	13.55	8.41	7.86	34.03	35.13
8	Kochi	30	13	29.39	29.28	8.33	8.32	34.07	34.07
9	Kochi	202	38	29.68	14.44	8.29	8.12	33.91	35.12
10	Kozhikkode	30	9	29.24	29.24	8.15	8.22	34.59	34.60
11	Kozhikkode	200	50	29.19	12.90	8.37	8.28	34.29	35.21
12	Kannur	203	50	29.08	14.30	8.56	8.32	34.27	35.22
13	Kannur	31	6	29.05	29.07	8.40	8.39	34.69	34.69
14	Mangalore	30	6	29.60	29.13	8.41	8.40	35.04	35.02
15	Mangalore	205	41.5	29.08	13.73	8.51	8.23	34.63	35.27
16	Baikal	204	66	28.96	13.78	8.58	8.12	35.36	35.31
17	Baikal	31	9	28.26	28.16	8.52	8.45	34.78	35.07
18	Goa	32	9	27.67	27.50	8.49	8.43	35.38	35.36
19	Goa	204	54	28.41	14.35			35.59	35.42
20	Mumbai	33	14	25.76	25.76	7.52	7.38	35.55	35.55
21	Mumbai	51	46	26.53	26.49	7.53	7.36	35.73	35.74
22	Mumbai	96	69	27.12	26.26	7.57	7.43	35.86	35.96
23	Mumbai	90	104	26.74	25.81	7.50	7.46	35.91	36.06
24	Mumbai	86	40	25.73	24.99	7.56	7.46	35.96	35.84
25	Mumbai	80	42	25.52	25.39	7.56	7.48	35.96	35.95
26	Mumbai	51	17	23.52	23.68	7.51	7.46	35.46	35.47
27	Mumbai	32	9	23.41	23.39	7.53	7.49	35.41	35.40

Note: S: surface; B: bottom.

the northern part with a corresponding decrease in its thermal gradient [4]. The bottom water samples collected from the offshore stations are found to be having the characteristics (salinity 35.04–35.42‰ and temperature 12.9–14.4 °C) of Indian Ocean Equatorial water according to the classification of Darbyshire [5]. According to his classification based on the salinity and temperature distribution pattern of different water masses, the Indian Ocean equatorial water is characterized by a temperature below 17 °C and a minimum salinity of 34.9‰.

pH is an important hydrochemical feature indicating the level of dissolved carbon dioxide in the water which may in turn reflect the activity of phytoplankton and the level of DO in the sea [6]. The pH values were found to be almost uniform along the surface and bottom up to the Mumbai region. The surface values ranged from 8.15 to 8.58, whereas for the bottom stations it was 8.12–8.77. In the Mumbai region (stations 20–27), the surface pH showed a variation of 7.51–7.56, and for bottom stations the range was 7.36–7.49. The slightly lower pH recorded in the Mumbai region may be due to the biochemical decomposition of organic matter brought to these shallow near coastal waters by land runoff, which may increase the carbon dioxide content and a subsequent lowering of pH.

Salinity or salt concentration plays an important role in sustaining aquatic life. Discussing the salinity variations of the coastal stations, the surface and the bottom stations recorded negligible variations in their salinity. Here, surface and bottom stations showed a range of

33.7–35.4‰. The surface stations sampled at 200 m depths exhibited a narrow range of salinity content (33.9–35.6‰). Here, the bottom salinities were slightly higher than that of surface values (35.1–35.4‰). In Mumbai region also, a narrow range of salinity variation characterized the surface and bottom stations. Salinity showed a slightly increasing trend on moving from Cape Comorin to Mumbai region. The increasing trend of salinity from south to north suggests a gradient towards the south. The southward decrease in salinity towards south may be attributed to a slow spreading of high saline water towards south, which loses the high saline characteristics [7–8]. During winter, the low saline Bay of Bengal water joins the northward flowing Equatorial Indian Ocean water and flows as a northward current along the west coast of India. This in turn causes a considerable reduction in surface salinity along the southwest coast of India, which can extend up to 17° N in February–March [9]. The salinity showed a slightly increasing trend towards offshore for both surface and bottom water samples (for stations sampled at 200 m depth). The low-saline waters (<34.5‰) in the shelf region of the southwest coast of India are the result of lateral advection from the south during the northeast monsoon season [4]. The general high values of salinity in the study region showed that evaporation is high in this region compared with precipitation increasing the salinity, whereas in the east coast of India, a lower salinity was observed due to the high rate of river runoff. Stations off Cochin are characterized by a low salinity, $<$ 34‰, that can be the effect of land runoff through the large backwater system opening into the sea near Cochin due to moderate rainfall.

In this study, DO values showed considerable variations (figure 2). The Indian Ocean, especially the Arabian Sea is unique with respect to the amount of DO. Tracing the distributional pattern of DO at various stations, at 30 m depth, the surface stations recorded a variation of 4.5–5.0 ml l^{-1}, whereas for bottom stations, the range was 3.8–4.6 ml l^{-1}. A characteristic observation made in this study is the wide fluctuation in the DO content of surface and bottom samples collected from 200 m depth. An average concentration of around 4 ml l^{-1} was obtained in the surface waters, whereas <1 ml l^{-1} is obtained in the bottom layer waters in the euphotic zone. These low values were may be due to the utilization of oxygen for the biological degradation of organic matter. DO maximum in the surface layer especially during the premonsoon period season (February–May) was reported earlier [10–11]. The intensity of incident solar radiation is very high during this period, which causes the maximum primary productivity to occur a few metres below the sea surface together with the high vertical stability, may result in the observed oxygen maximum. For Mumbai region, with the exception

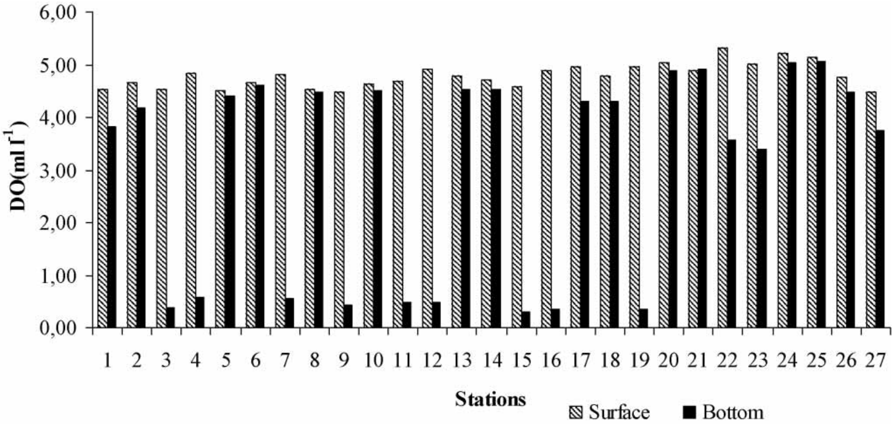

Figure 2. Distribution of dissolve oxygen (ml l^{-1}) along the west coast of India in the Arabian Sea.

of stations 26 and 27, all stations (stations 20–25) displayed a higher DO content than other stations sampled at 30 and 200 m depths (for both surface and bottom stations). Because of the high temperature in the surface layers and low oxygen content in the intermediate waters of the equatorial Indian Ocean, the oxygen concentrations are comparatively lower in the Arabian Sea [10]. Compared with other oceanic regions, photosynthetic activity is much higher in the Arabian Sea waters [10, 12]. High photosynthetic activity leads to a high concentration of organic matter in the surface waters, which accumulates in the deeper layers, thereby reducing the oxygen concentration due to decay and degradation.

3.2 *Spatial variability of dissolved reactive phosphate*

On tracing the distributional characteristics of dissolved reactive phosphate (figure 3) in the coastal stations (30 m depth stations), most of the bottom water samples displayed higher phosphate concentrations than that of surface. The offshore stations (200 m depth stations) were also typical in their behaviour in the sense that bottom concentrations of dissolved reactive phosphate exceeded the surface, except at station 3. Water samples of Mumbai region were also characterized by a similar pattern of distribution. The concentrations of dissolved phosphate reported in this study more or less coincide with those of the earlier studies conducted by several workers [11, 13–14] in the nearby regions of the Arabian sea.

One of the salient features observed was that the bottom concentrations of dissolved reactive phosphorus were higher than the surface values at most of the stations. Particularly in the offshore stations, wide variations in surface and bottom phosphate contents were noticed, except at station 3, i.e. Cape Comerin. The upper 200 m water column includes both the euphotic zone and the thermocline, and so any change in nutrient concentration within this depth has to be correlated with productivity and regenerative processes. Such a type of distribution pattern can also be correlated with changes in the hydrographical rhythm of the water column. In the present work, the highest surface and bottom values of phosphate (0.34 μmol l^{-1} for surface and 0.99 μmol l^{-1} for bottom samples) were observed at station 19. At the higher water column depth, comparatively higher values were observed in the central region of the west coast (stations 12, 16, and 19). In this region, an offshore increase in phosphate concentration was observed for both surface and bottom stations. The productivity in a water column will be highest within the upper strata where light penetration is maximum. As a result, the concentration of nutrients will be low, and DO will be high in the surface compared with bottom layers. The bottom stations of the deeper offshore zone (i.e. stations 3, 7, and 11 in the southern region and 12, 15, 16, and 19 in the central region) characterized by comparatively higher phosphate concentrations were also highlighted by low values of DO (0.398–0.557 ml l^{-1}) as well as temperature (12.9–14.4 °C). Nutrients are taken up in the euphotic zone and released back into the sea water following remineralization of sinking detritus, and the concentrations that build up in deeper water from which they can be brought to the surface again via physical processes, such as upwelling and seasonal increases in depth of the wind-mixed upper layer (stratification), i.e. the ‘biological pump’. The effect of these processes is to generate vertical nutrient distributions that exhibit a characteristic ‘surface water depletion, deep-water enrichment’ profile [2]. It should also be taken into account that hypoxic conditions may also give rise to P release from sediments [15–16].

Changes in concentrations of reactive phosphorus at various depths can also be correlated with changes in DO (table 2). In the surface waters of the coastal stations, phosphate was positively correlated with DO ($r = 0.872$, $p < 0.001$), and so also at surface stations of 200 m depth ($r = +0.675$, $p < 0.02$) (table 3). The surface phosphate concentration of Mumbai region displayed an inverse relationship with DO ($r = -0.622$, $p < 0.05$). A similar feature

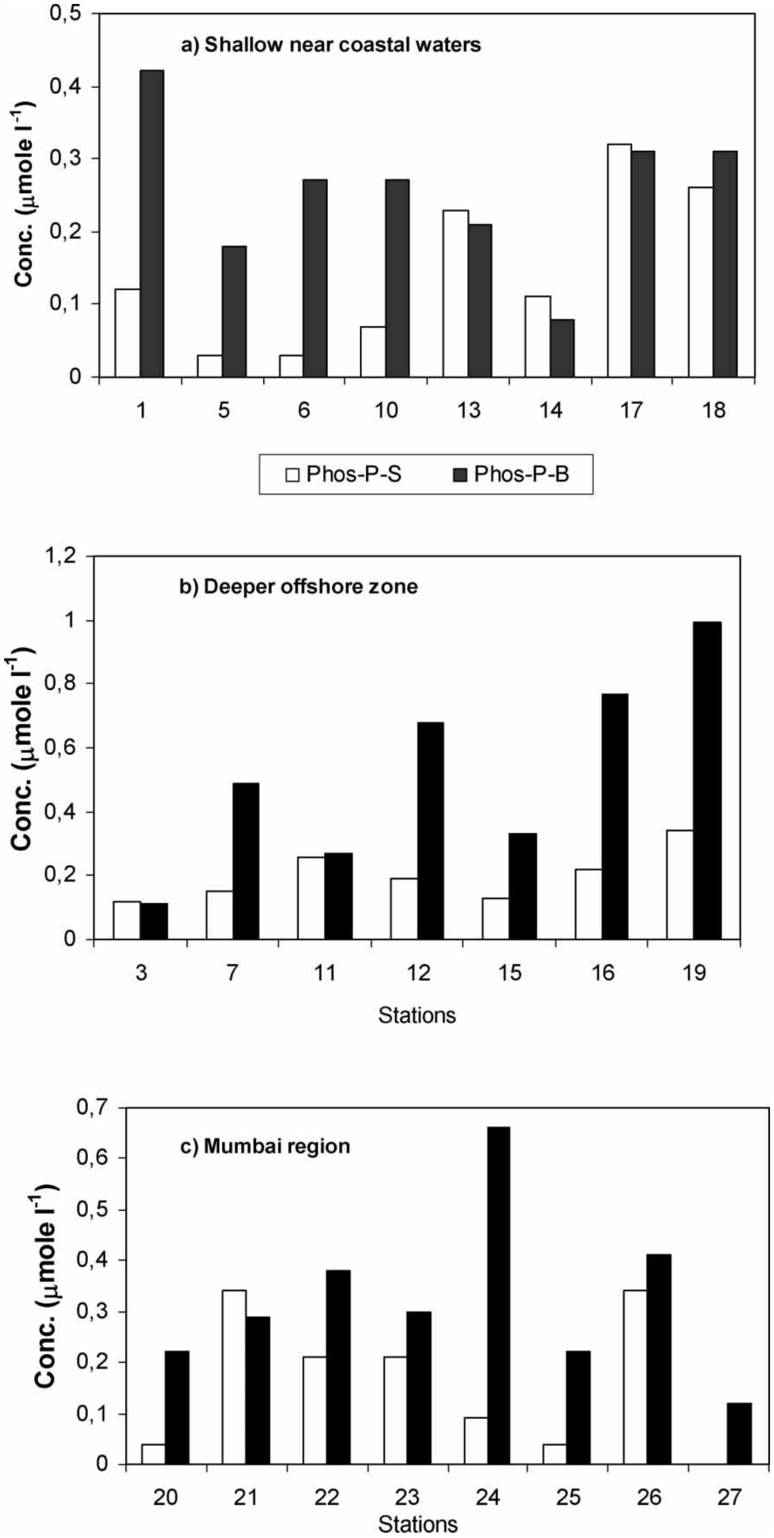

Figure 3. Distribution of dissolved reactive phosphates along the west coast of India in the Arabian Sea.

Table 2. Correlation between dissolved phosphates and DO.

Collection area	Pearson's correlation coefficient and level of significance
30 m depth	
Surface	$r = 0.872$, $p < 0.001$; 99.9%
Bottom	$r = -0.734$, $p < 0.01$; 99%
200 m depth	
Surface	$r = 0.675$, $p < 0.02$; 98%
Bottom	Not significant
Mumbai region	
Surface	$r = -0.622$, $p < 0.05$; 95%
Bottom	Not significant

was noticed in the bottom water samples collected from coastal stations, where phosphorus was negatively correlated with DO ($r = -0.734$; $p < 0.01$). The bottom waters of the coastal zone (i.e. stations 3, 7, and 11 in the southern region and 12, 15, 16, and 19 in the central region) were also characterized by higher values of reactive phosphorus and low values of DO (0.398–0.557 $\mathrm{ml\,l^{-1}}$). This can be explained on the basis of the productivity potential and regenerative mechanism taking place at this depth. At a higher water column depth, the regenerative process is active because of the decay of dead organisms and other organic matter. The oxidative process removes oxygen from these waters, and the end-products of decomposition accumulate at these depths. This process of decomposition depletes the oxygen

Table 3. Spatial variability of AOU along the study area.

Region and station no.	AOU ($\mu\mathrm{mol\,l^{-1}}$)	
	Surface	Bottom
30 m depth region		
1	−18.7	31.7
5	−6.3	1.5
6	−12.6	−8.3
10	−8.7	−2.9
13	−16	−4.6
14	−12.3	−4.6
17	−19.4	6.6
18	−11.4	6.6
200 m depth region		
3	−18.2	79.3
7	−20.2	232.2
11	−11.4	241.5
12	−20.8	235.7
15	−6.5	243.2
16	−19.7	241.4
19	−22.9	241.3
Mumbai region		
20	−19.5	−12.7
21	−15.3	−16.2
22	−34.5	47.1
23	−24.2	54.1
24	−27	−14.8
25	−23.9	−15.9
26	0.9	13.1
27	13.5	49.5

content of these layers, thereby leading to an inverse relation between phosphate and DO. A similar work pointed out a negative correlation between nitrate concentration (bottom stations) and DO with a coefficient of correlation $r = 0.921$, at a depth of 200 m [17].

Shirodkar and Jayakumar [11] also noticed that the relationship between DO and nutrients in the upper 1000 m in the equatorial western Indian Ocean shows a good negative correlation $r = -0.86$. A similar feature was noticed between DO and nutrients in the Lakshadweep waters, Arabian Sea [18]. The inverse relationship between phosphate and DO in these deeper layers indicates that the DO content of these bottom layers is utilized for the breakdown of organic matter and regeneration of nutrients.

3.3 *Correlation with apparent oxygen utilization*

Apparent oxygen utilization (AOU) indicates biologically induced changes in oxygen concentrations that have taken place after water has ceased to be in direct exchange with the atmosphere. It is calculated as the difference between the oxygen saturation value at the in situ temperature and salinity, and the actual measured concentration i.e. $O_2' - O_2$, where O_2' is the theoretical value, and O_2 is the observed value [19]. Characterizing the distribution pattern of AOU in the surface waters of 27 stations (table 3), it was found that with the exception of stations 26 and 27 (Mumbai High region), all stations are characterized by negative AOU values. In the bottom waters, some of the coastal stations, i.e. 6, 8, 10, 13, and 14 (and thus also some of the stations of the Mumbai High region: 20, 21, 24, and 25) displayed negative AOU values. In the offshore stations, bottom water samples are characterized by very high positive AOU values (216.1–243.2 $\mu\text{mol}\,\text{l}^{-1}$). The negative AOU values of surface stations indicate that productivity-related changes in oxygen concentration are more pronounced in these surface layers, which makes the measured oxygen higher than that of theoretical values. Increased photosynthetic activity due to maximum light availability of surface layers leads to a low concentration of nutrients and high DO content compared with that of bottom layers. In addition to this, surface layers have a chance of direct deoxygenation from the atmosphere, thereby leading to negative AOU values. Bottom water samples collected from 30 m depths are also characterized by negative AOU values. One of the reasons for this observation may be the shallowness of the water column. The competing processes of photosynthesis and respiration are responsible for changes in oxygen concentration of sea water. At a lower water column depth, photosynthesis overwhelms respiration or decomposition of organic matter, which makes the oxygen content slightly higher than the theoretical values. At stations 26 and 27 (Mumbai High region), both surface and bottom water samples are characterized by positive AOU values. These two stations are inshore stations (distance from the shore being 17 and 9 km, respectively). Therefore, terrestrial input of organic matter and other decomposable materials accumulating may be oxidized here, tending to decrease observed DO values well below the theoretical values. The surface stations at depths of 30 m as well as 200 m are characterized by an inverse relationship between dissolved phosphate and AOU ($r = -0.623$ ($p < 0.05$) and -0.351 ($p < 0.1$), respectively, for 30 (coastal) and 200 m (offshore) depths) (figure 4). At a shallow water column depth, oxygenation from the atmosphere increases the oxygen content of the surface layers, so changes related to regeneration are insignificant at this depth. In bottom stations at these depths, phosphate was positively correlated with AOU ($r = 0.738$ ($p < 0.01$) and 0.581 ($p < 0.1$), respectively, at 30 and 200 m depths). A depth of 200 m is below the compensation point where net production is taken to be zero. Stations at 200 m depth are characterized by high positive AOU values and low DO values concordant with slightly higher phosphate concentrations. Oxidative decomposition of organic matter and other dead organisms takes place as they fall from the surface, and the end-products of this

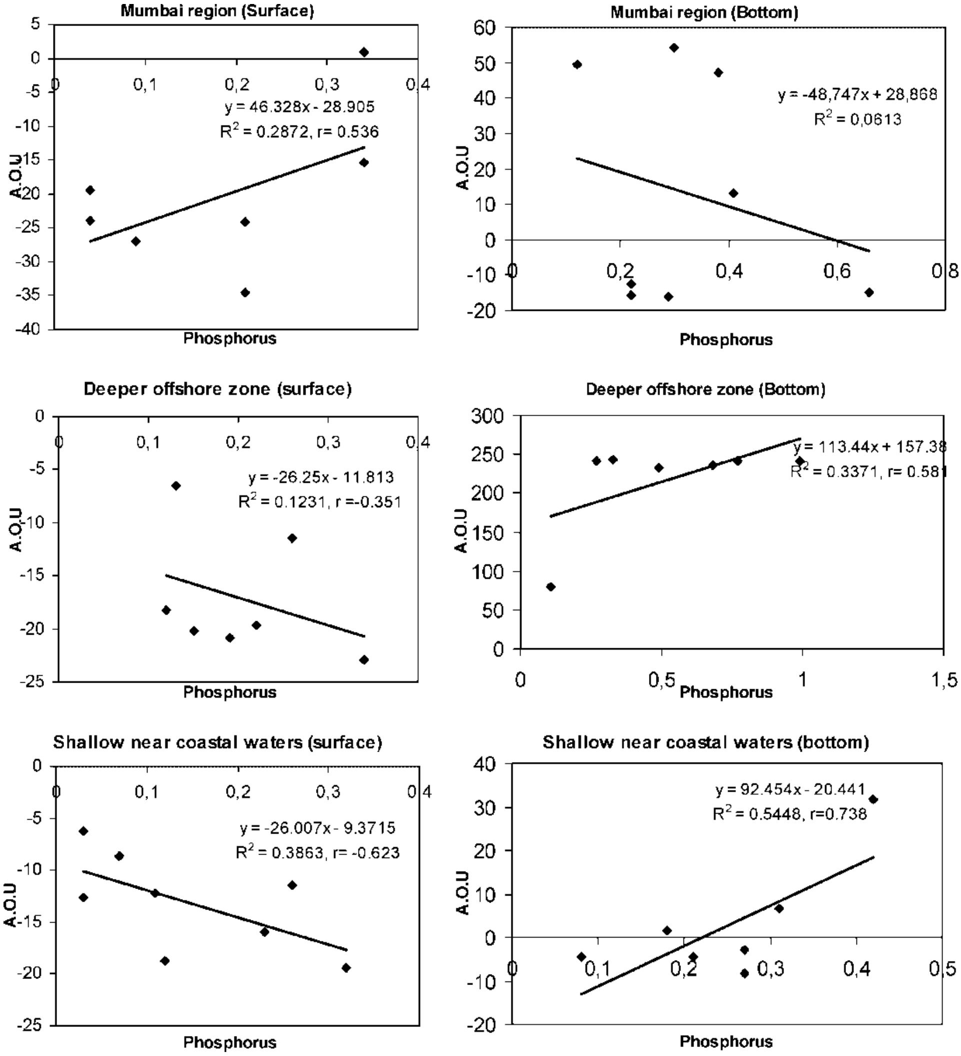

Figure 4. Spatial variability of dissolved phosphates (μmol l^{-1}) and AOU.

regeneration, mainly nutrients, accumulate in the deeper layers, thereby reducing the oxygen concentration below the true values leading to high positive AOU values. A similar pattern of positive correlation was reflected in the comparison between the AOU values of the bottom water samples (200 m depth) and the respective nitrate concentrations ($r = 0.50$, $p > 0.01$) and also with the respective nitrite concentrations ($r = 0.38$, $p > 0.05$) along the west coast of India [17]. Any anomaly between theoretical and measured oxygen concentration is ascribed to photosynthesis or to the biological oxidation of organic matter, and AOU should be related to nutrient changes, which accompany these processes [17, 20].

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