Chemical Oceanography of the Arabian Sea: Part IV—Laccadive Sea

R SEN GUPTA, CAROLINE MORAES, T W KUREISHY, V N SANKARANARAYANAN, T K JANA,
S W A NAQVI & M D RAJAGOPAL

National Institute of Oceanography, Dona Paula, Goa 403 004

Data collected during the 10th (October 1976) and 31st (March-April 1978) cruises of *RV Gaveshani* suggest that water movements, considered typical of island-arc regions, are responsible for high levels of productivity observed in the Laccadive Sea. Patterns of distribution of nutrients and nutrients-oxygen relationships are similar to those observed in other parts of the Arabian Sea. High magnesium and low fluoride concentrations in the water indicate probable loss of the latter as insoluble ion-pairs and as apatites.

Detailed oceanographic studies of the Laccadive Sea have not been made, although isolated studies have been made on hydrography, chemistry and biology of the waters[1-7]. In the present paper, data on the chemical characteristics of the waters are given, which facilitate comparison with other parts of the Arabian Sea, with special reference to factors influencing marine productivity. Data collected during the 10th (October 1976) and 31st (March-April 1978) cruises of *RV Gaveshani* are presented here.

Materials and Methods

Water samples were collected from standard hydrographic casts using transparent TPN samplers (Hydro Bios, Kiel, FRG) and metallic Nansen bottles up to a depth of 2000 m from stations shown in Fig. 1.

Temperature, salinity, dissolved oxygen, PO_4^{3-}-P, NO_3^--N, NO_2^--N, NH_4^+-N, SiO_3-Si and F^- were measured. Temperature was read off reversing thermometers, oxygen and nutrients were measured using standard analytical methods[8]. Fluoride was analysed by the lanthanum alizarine complexone method[9].

Results and Discussion

Hydrographical characteristics around Laccadive islands—Inter-atoll variations in the depths of the isopycnal layers between (i) Kavaratti and Androth (Fig. 2A), (ii) Androth and Kalpeni (Fig. 2B), and (iii) Kalpeni and Suheli Par (Fig. 2C) were studied. Similar variations along a north-south transect between 13°45′ and 8°30′N (Fig. 2D) were also investigated.

In Fig. 2A, σ_t values from 22.5 to 23.5 show westward upsloping. At $\sigma_t > 24$, there is downsloping. The values from 26.5 to 27.1 increase with depth from east to west. In Fig. 2B, except σ_t 22, all the other isopycnals slope

towards the north. In Fig. 2C, σ_t values from 22 to 23.5 show westward upsloping. Below these, up to σ_t 26.5 the upsloping is eastward. The values between 27 and
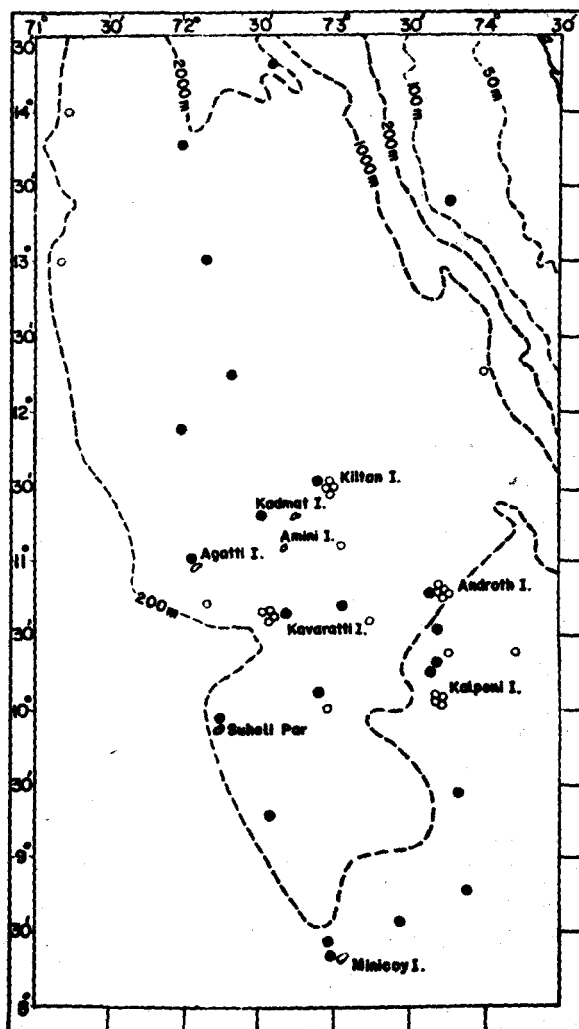

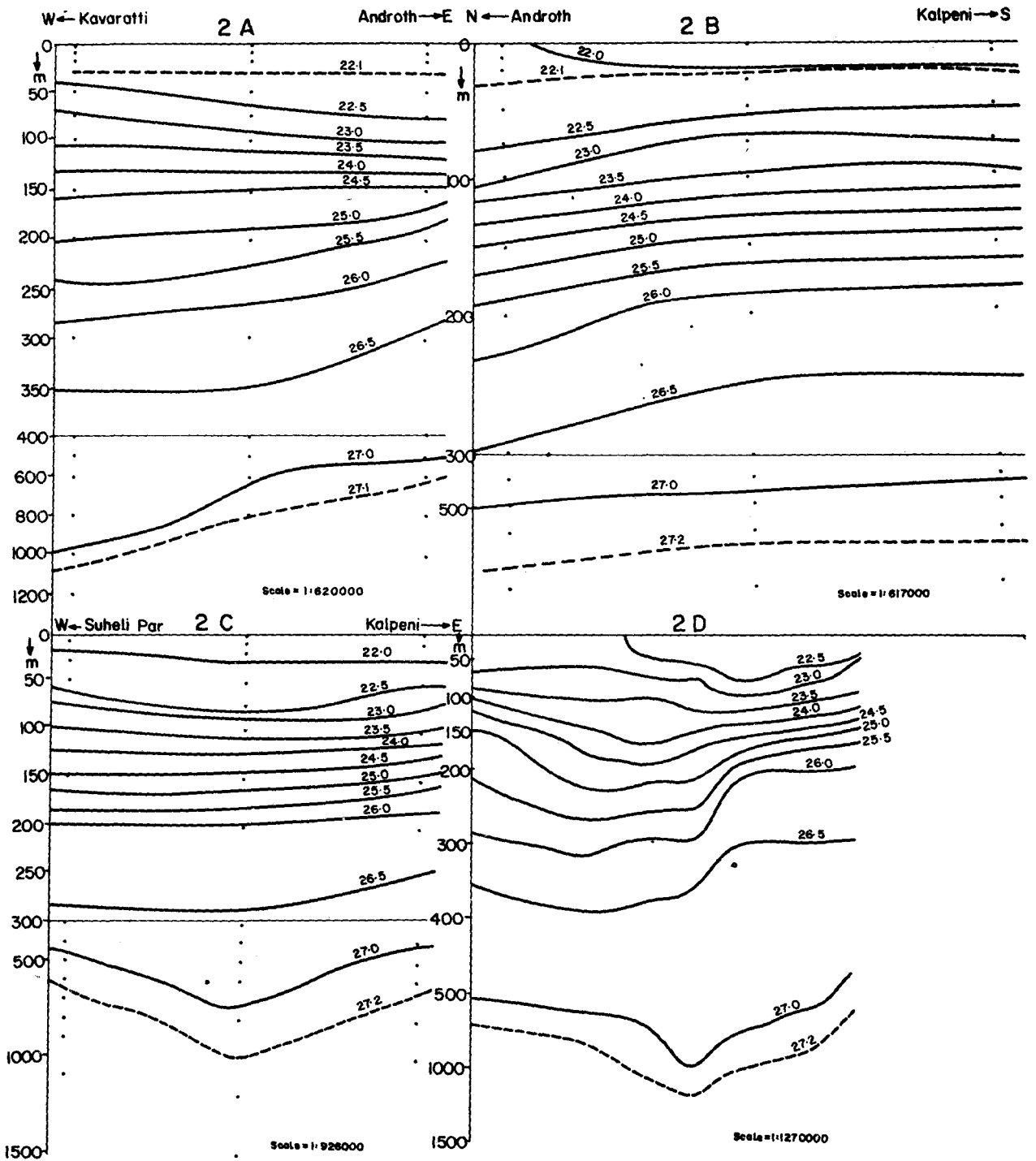Fig. 1—Observation stations (O, 10th cruise and ●, 31st cruise)

Fig. 2—Isopycnals along a transect between (A) Androth and Kavaratti. (B) Androth and Kalpeni, (C) Kalpeni and Suheli Par islands and (D) along a north-south transect between 13°45' and 8°30'N

27.2, maintain almost the same depth both towards east and west, but deepen at the centre of the figure. The σ_t values from 22.5 to 26.5 in Fig. 2D are almost similar to those in Fig. 2B. They slope down northwards.

There is a general upsloping (upwelling) of the water mass towards the west between Kavaratti and Androth and between Androth and Suheli Par islands (Fig. 2A and C). Wind directions at these stations are N to

NNW. Displacement of water as a result of such winds will be in the direction WNW to NW. The upsloping of the isopycnals is, therefore, the effect of the prevailing wind system. The downward slopes of the isopycnals indicate a compensatory sinking of the water mass below the vertical displacement. A similar upsloping of the isopycnals at depths above 100 m on the left slope of Bermuda island, looking downstream, has been

observed; the explanation given from model studies is that it is due to vertical turbulent mixing which results from the labile nature of the water mass[10].

At or near the island arcs the water moves clockwise around the land mass resulting in a general upward transfer of the deeper water[11]. As has been verified experimentally, such a closed circulation around the islands is due to tangential wind stress and Coriolis force[12].

Rao and Jayaraman[13] observed an upsloping of isopycnals which was limited to the upper 150 m near a station south of Minicoy island along an eastwest transect. This depth agrees well with the present observations. However, similar features could not be observed at a station NE of Minicoy, worked during the 31st cruise, presumably due to seasonal variations in wind-induced upwelling.

It has been shown earlier that because of a stable eddy system present downstream close to Barbados island, the littoral animals with long pelagic larval stages become more abundant than in the exposed areas[14]. Similar eddies seem to be present downstream near the Laccadive islands. The abundance of decapod larvae, including the red prawns, observed in this area in plankton hauls during both the cruises is probably a result of such eddies. Existence of anticyclonic eddies around the islands of Laccadives in the upper 100 m, probably supporting a high productivity in these waters, is also suggested by Jayaraman *et al.*[2].

The northsouth sloping of the isopycnals agrees with the general idea of transport of water masses in the Arabian Sea. The waters coming out from the Persian Gulf (Arabian Gulf) and the Red Sea seek their own density levels as they move towards the equator. Between 13°45' and 8°30'N, σ_t values of 26.5 and 27.2 slope up by about 100 m (Fig. 2D).

The water masses can also be characterised by the silicate-density relationship such as has been found for waters of the Arabian Sea[15]. The water mass from 0 to 200 m has σ_t values ranging between 22 and 26 and the silicate concentration ranges from 0 to about 35 μg-at/litre (Fig. 3). In the earlier study[15], the range of silicate is from 0 to about 25 μg-at/litre. Higher values, in this study, may be the effect of the upsloping of the isopycnals. The water mass from 201 to 500 m depth has σ_t ranging between 26 and 27 and silicate concentration ranges from 25 to 55 μg-at/litre. The cluster of points at lower silicate values indicates that this water mass is probably from the Arabian Gulf. Similarly, the water between 501 and 1000 m depth with σ_t from 27 to 27.3 and silicate concentration from 45 to 75 μg-at/litre is from the Red Sea. Overlapping of values and points in the figure indicates mixing of different water masses.

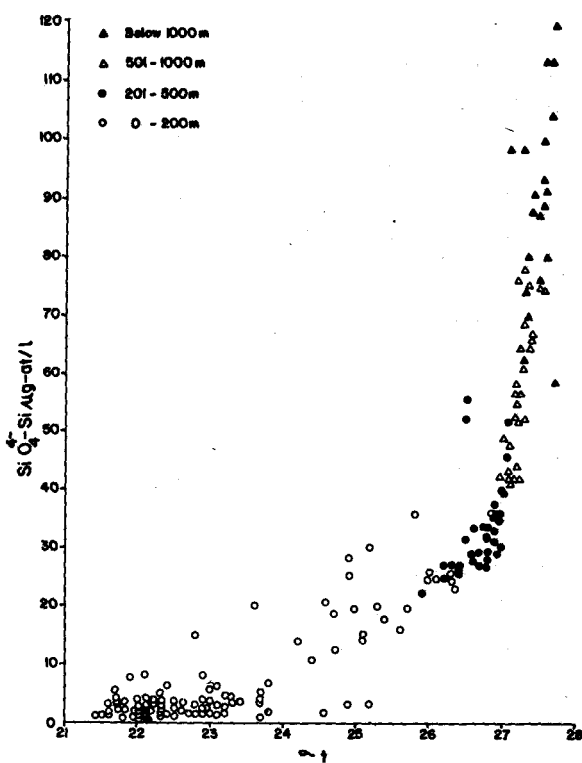*Nutrients-oxygen relationships*—Two oxygen mi-

Fig. 3—Silicate—σ_t relationships for different water masses in the Laccadive Sea

nima in the water column have been noted at 150 and 800 m depths in the northern and northeastern basins of the Arabian Sea[16]. These basins occur north of lat. 18°N. Vertical distribution of oxygen in the Laccadive Sea has been studied at 3 selected stations (Fig. 4). It is clear from the Figure that 2 oxygen minima start appearing in this area close to lat. 11°N. Curve A in Fig. 4 shows that the upper oxygen minimum layer starts at about 200 m. This is associated with a sharp increase in PO_4^{3-}-P, NO_3^--N and SiO_3-Si and a decrease in pH. Maximum value of oxygen is observed at 500 m which is associated with a decrease in silicate and nitrate and an increase in pH. This is the effect of mixing of Arabian Gulf and Red Sea waters (Fig. 2D) both of which have low nutrient concentrations, compared to the corresponding depths of the Arabian Sea[17]. The second oxygen minimum appears around 800 m and is the result of denitrification[16]. Although NO_3^--N continues to increase with depth, it is far less than the theoretical amount, determined later in this paper.

Similar features have been observed at the station at 9°15.5'N (Fig. 4C). Here, the oxygen maxima at 500 m are lacking. This indicates the completion of mixing of water masses resulting in homogeneity. At all the stations, nitrite is present in a very thin layer close to the first oxygen minimum layer. Its concentration ranges from 0.16 to 0.20 μg-at/litre.
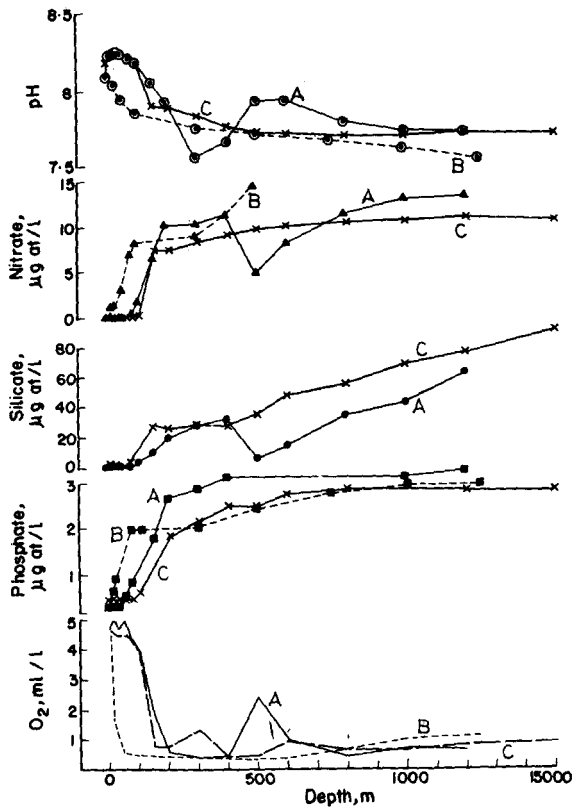
Fig. 4—Depth profiles of chemical components at 3 stations (A) 10°36′N; 72°43′E, (B) 14°00′N; 71°12′E, and (C) 09°15.5′N; 72°35′E

These processes are either absent or not pronounced at the station north of lat. 11°N. This can be seen from curve B (Fig. 4). At this station there is a thick oxygen minimum layer extending from about 100 to about 500 m.

Oxygen, productivity and nutrients—During the 10th cruise, the saturation of water with oxygen between 0 and 50 m ranged from − 6 to + 10%, while during the 31st cruise the range of oxygen saturation at that depth range was + 4 to + 12%. During the 10th cruise in October the surface water was fairly warm and undersaturated with respect to oxygen. In the 31st cruise during March-April, which is the transition period from colder to warmer months, the water in 0-50 m zone was normally super-saturated with oxygen.

Photosynthetic productivity ranged from 0.02 to 0.35 gC/m²/day during the 10th cruise[18]. The values during the 31st cruise ranged from 0.08 to 0.83 gC/m²/day[19]. Differences in the productivity values between the cruises are, presumably, due to seasonal variations in the wind-induced upwelling.

Average values for NO_3^--N and PO_4^{3-}-P in the uppermost 100 m depth were 4.21 and 0.97 µg-at/litre respectively during the 10th cruise. In the 31st cruise NO_3^--N decreased to 0.29 µg-at/litre and PO_4^{3-}-P to 0.46 µg-at/litre. During the 31st cruise at almost all the stations NO_3^--N was absent from surface to about 50-

75 m depth. Dense patches of the blooms of blue-green alga *Trichodesmium*[20] were associated with NH_4^+-N ranging from 0.5 to 5.5 µg-at/litre at the surface.

Thus, it can be concluded that the constant upward movement of water around the islands becomes an important source for the supply of nutrients in the upper layers of the Laccadive Sea.

The ratios of the change in the concentration of nutrients and dissolved oxygen in water were then calculated as described earlier[15,16]. For this purpose, the values between 150 m and depths of maximum apparent oxygen utilization (AOU) at all stations were used during both the cruises. Oxidative ratios from the depth of the appearance of positive value of AOU up to the depth where it was maximum were determined for all stations. Results obtained are as below:

Ratio	AOU positive to AOU_{max}	150 m to AOU_{max}
$\Delta AOU:\Delta P$	263:1	249:1
$\Delta AOU:\Delta N$	15:1	19:1
$\Delta N:\Delta P$	17:1	13:1

The intercept on the phosphate axis, for the depth range, AOU positive to AOU_{max}, is 1.3 µg-at/litre. This phosphate concentration includes both oxidative and reserved fractions, used in the same sense as used by Sen Gupta et al.[16], and indicate that some phosphate is left in the water when nitrate concentration approaches zero. The intercept on the phosphate axis, during the calculation of phosphate-oxygen utilization relationship at 0.66 µg-at/litre indicates only the reserved fraction of phosphate as it is at zero AOU. The balance 0.64 µg-at/litre of phosphate is left at the surface when nitrate concentration approaches zero. This would mean that nitrate would act as a limiting factor for the production of phytoplankton. This accords well with the recent laboratory experiments indicating that below the optimal cell N:P of 30 algal growth is determined solely by nitrogen limitation and above 30 by phosphorus limitation[21].

The amount of phosphate left in the water at zero nitrate value shows a seasonal variation. Calculations from data of 10th cruise in October 1976, give a value of 0.17 µg-at/litre; while the value for the 31st cruise (March-April 1978) is 0.48 µg-at/litre. Similar calculations from the data of *INS Darshak* cruises, in January-May 1974, give 0.1 µg-at/litre[16]; while the values from ISMEX, in monsoon 1973, give 0.29 µg-at/litre[15].

Silicate and oxygen utilization—From silicate concentrations of 0-150 µg-at/litre and AOU values of 25 to 550 µg-at/litre, the following relationship between these 2 variables is deduced[15].

$$AOU = 32 + Si^2/(0.12065 + 0.01025 Si + 0.00197 Si^2)$$

$$... \quad (1)$$

To test the present values, silicate concentrations are pooled into each 5 μg-at/litre intervals up to a concentration of 10 μg-at/litre and then into each 10 μg-at/litre intervals after calculating the averages for the corresponding AOU values. The values when fitted to eq. 1 the results as shown in Table 1 are obtained.

No zero values of silicate are observed at the surface. Such values are, however, observed during ISMEX 1973 and have been used as $(AOU)_0$ to deduce eq. 1. It appears that silicate values in the surface layers of the Arabian Sea reach about zero only during monsoon. The differences between $(AOU)_{calc}$ and $(AOU)_{obs}$ in silicate concentrations up to 10 μg-at/litre is due to this factor.

The difference in the other ranges lies within the analytical and computational errors. The differences at higher concentrations of silicate agree well with the earlier observations[15]. These are from the samples collected at depths greater than maximum values of AOU. Below this depth oxygen increases steadily resulting in positive deviations (Table 1). It can be concluded that the relation between silicate and oxygen utilization in eq. 1 agrees well with the data obtained from the Laccadive Sea.

Silicate-phosphate relationship—Normally these 2 parameters do not show a linear relation in the ocean. However, in some areas a linear relationship between these 2 has been approximated at selected depth intervals[22,23]. The slope of the regression line between 150 m and AOU maxima for silicate-phosphate relationship, for the present values, gives a ratio of 36:1 by atoms.

Consolidated ratios: Using all the positive values of AQU up to the depths where it is found to be maximum the following atomic ratios are obtained:

$$\Delta AOU : \Delta N : \Delta P = 263 : 17 : 1 \qquad \cdots (2)$$

Table 1—Observed and Calculated Values of AOU at Different Silicate Concentrations

[Values are expressed in μg-at/litre]

Si		AOU		$AOU_{calc} - AOU_{obs}$
Range	Average	Observed	Calculated	
0-5	2.73	104	78	−26
5-10	6.84	91	197	+106
10-20	15	338	345	+7
20-30	25.5	445	423	−22
30-40	34.32	478	454	−24
40-50	43.6	512	473	−39
50-60	54.73	516	487	−29
60-70	65.96	512	496	−16
70-80	75.07	516	502	−14
80-90	84.05	490	506	+16
90-100	95.05	506	510	+4
100-110	104	450	513	+63
110-120	115.23	456	515	+59

Atomic ratios for the same parameters from 150 m to AOU maxima become

$$\Delta AOU : \Delta N : \Delta P = 249 : 13 : 1 \qquad \cdots (3)$$

The ratio between silicate and phosphorus is calculated as

$$\Delta Si : \Delta P = 36 : 1 \qquad \cdots (4)$$

Biochemical relationships—Oxidative ratios have been used to deduce composition of plankton in the Arabian Sea[15]. A similar attempt in respect of Laccadive Sea plankton is described here. Assuming what has been suggested by Richards[24] and by applying the relation given in eq. 2, phytoplankton organisms will have the composition $(CH_2)_n(NH_3)_{17}H_3PO_4$.

The overall reaction for oxidation would be

$$(CH_2)_n(NH_3)_{17}H_3PO_4 + (n+34)O_2 =$$
$$nCO_2 + 17NH_3 + H_3PO_4 + (n+17)H_2O \qquad \cdots (5)$$
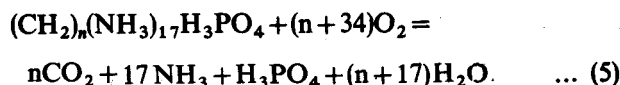
Since $\Delta AOU : \Delta P$ ratio is 263:1 by atoms, it would give

$$(n+34)O_2 = 263O = 131.5O_2 \text{ or } n \approx 98 \text{ atoms} \qquad \cdots (6)$$

The relation in eq. 3 when treated similarly would result in

$$n = 99 \text{ atoms} \qquad \cdots (7)$$

Thus, for all positive values of AOU from the depth of its appearnace to the depth of its maximum

$$C : N : P = 98 : 17 : 1 \qquad \cdots (8)$$

Similarly, between 150 m depth and the depth of AOU maximum

$$C : N : P = 99 : 13 : 1 \qquad \cdots (9)$$

In the eq. 8, the relation $\Delta AOU : \Delta P = 262:1$ will give

$$\Delta AOU : \Delta C = 263 : 98 \text{ or } 2.7 \qquad \cdots (10)$$

In the eq. 9, $\Delta AOU : \Delta P = 249:1$ will give

$$\Delta AOU : \Delta C = 249 : 99 \text{ or } 2.5 \qquad \cdots (11)$$

Earlier, Sen Gupta *et al.*[15] obtained

$$\Delta AOU : \Delta C : \Delta N : \Delta P = 280 : 108 : 16 : 1 \text{ or}$$
$$\Delta AOU : \Delta C = 2.6 \qquad \cdots (12)$$

The theoretical relation[25] between oxygen consumption and carbon production is 2.6.

The ratio $\Delta Si : \Delta P = 36.1$ by atoms obtained for the Laccadive Sea is not significantly different from 40:1 deduced earlier[15] for the Arabian Sea. Thus, we get

$$\Delta AOU : \Delta C : \Delta Si : \Delta N : \Delta P = 263 : 98 : 36 : 17 : 1 \text{ by atoms}$$

$$\cdots (13)$$

It can, therefore, be concluded that the atomic relation

$$\Delta AOU : \Delta C : \Delta Si : \Delta N : \Delta P = 280 : 108 : 40 : 16 : 1 \quad \ldots (14)$$

deduced from the ISMEX and *Meteor* data will be valid for the Laccadive Sea also.

Denitrification—The Arabian Sea and the Bay of Bengal have been observed to be areas where the process of denitrification takes place at an intermediate depth[15,16,26]. The process has been identified to be at the stage of ammonia, without reaching its completion, in the Arabian Sea.

Assuming that the ratio $\Delta NO_3 : \Delta PO_4 = 94.5$ occurs during denitrification[24] and that a maximum of 14 μg-at/litre of nitrate can be reduced during the process[27], it can be calculated that 14.2 μg-at/litre of nitrate-ion is lost in the waters of the Laccadive Sea. This amount of nitrate would have gone in the accumulation of 2.6 μg-at/litre of ammonia[27]. The average concentration of ammonia between 150 m and AOU maximum in this area has been 1.8 μg-at/litre (ranging 1.4 and 2.4 μg-at/litre). The average concentration of nitrate between 150 m and AOU maximum layer is 17.6 μg-at/litre. This would mean that about 45% of the available nitrate is lost due to denitrification. The data from ISMEX and *Meteor* cruises show a rate of denitrification of 41% for the entire Arabian Sea.

Calcium, magnesium and fluoride—These are generally considered to be major ions in the oceans. Taking into consideration their conservative and semi-conservative properties in seawater, it is thought that their concentrations or their relations with chlorinity may be useful in delineating the characteristics of different water masses.

Measurements of these 3 constituents in the Indian Ocean are few and far between. Calcium and fluoride from the Arabian Sea have been measured earlier[17]. A preliminary analysis of the fluoride values has been presented[28]. Study on these 3 ions at a few stations in the Bay of Bengal and southeastern Arabian Sea has been reported[29]. During the 31st cruise of *RV Gaveshani* 178 samples were analysed on board for fluoride. Sixty samples, collected and preserved on board in sealed polythene bottles, were examined in the shore laboratory for their calcium and magnesium concentrations applying the procedures of Culkin and Cox[30]. In this communication only the general features of these constituents in the waters of the Laccadive Sea are highlighted.

Calcium: Although the average of values in the lagoons (416 ± 0.5 mg/litre for Kavaratti and Minicoy atolls[31]) are somewhat lower than those from the open ocean (425 ± 1 mg/litre), the difference is not very significant being only of the order of ± 2% in standard errors.

Measurements made earlier[29] have given an average value of 428 mg/litre for the Gulf of Mannar and SE Arabian Sea and 431 mg/litre for the entire Arabian Sea. The closeness of these values with those from the Laccadive Sea indicates similarities in the chemical nature of calcium all over the Arabian Sea.

Magnesium: The average concentration in the Laccadive Sea is 1339 ± 6 mg/litre while in the lagoons it is 1335 mg/litre[31]. The difference is not significant. Its concentration in the Gulf of Mannar and SE Arabian Sea is 1280 ± 10 mg/litre[29]. The difference may be due to either geographic variation of magnesium in the oceans or spatial changes in its chemical complex formations.

Fluoride: Its concentration in sea water lies more or less well defined at about 1.4 mg/litre at $35°/_{oo}$ salinity.

Fluoride concentration of 1.36 ± 0.01 mg/litre has been observed in the SE Arabian Sea[29]. *Meteor* cruise[17] has indicated an average concentration of 1.19 mg/litre. For Laccadive Sea the average concentration is 1.17 ± 0.01 mg/litre. This appears to be low compared to the SE Arabian Sea and the global mean value. However, it is almost similar to *Meteor* observations. Abnormalities in fluoride values have been reported from time to time. Their causes have been attributed to mainly the localized volcanic activities at the ocean bottom. Fluoride can be removed from the seawater as the sparingly soluble ion-pairs CaF^+ and MgF^+. The formation constants of these ion-pairs decrease with increasing chlorinity[32]. Fluoride can also be removed from seawater as apatite at low pH at or near the bottom[33]. It appears that these factors, either individually or collectively, are responsible for these variations of fluoride and magnesium in the Laccadive Sea waters.

Acknowledgement

References

1 Qasim S Z, Bhattathiri P M A & Reddy C V G, *Int Rev ges Hydrobiol*, **57** (1972) 207.
2 Jayaraman R, Ramamritham C P, Sundararaman K V & Nair C P A, *J mar biol Ass India*, **2** (1960) 24.
3 Darbyshire M, *Deep-Sea Res*, **14** (1967) 295.
4 Tranter D J & George G, *J mar biol Ass India*, **21** (1969) 16.
5 Qasim S Z, *Deep-Sea Res*, **17** (1970) 655.
6 Qasim S Z & Sankaranarayanan V N, *Limnol Oceanogr*, **15** (1970) 574.
7 Sankaranarayanan V N, *Indian J mar Sci*, **2** (1973) 23.

8 Grasshoff K, *Methods of seawater analysis* (Verlag Chemie, Weinheim) 1976, 317pp.

9 Greenhalgh R & Riley J P, *Anal Chim Acta*, **25** (1961) 179.

10 Hogg N G, *Geophys fluid dynam*, **4** (1972) 55.

11 Defant A, *Physical oceanography*, Vol. 1 (Pergamon Press, New York) 1961, 729pp.

12 Zyryanov V N & Felzenbaum A T, *Okeanologia*, **16** (1976) 766 (In Russian-English abstract).

13 Rao L V G & Jayaraman R, *Curr Sci*, **35** (1966) 378.

14 Emery A B, *Carib J Sci*, **12** (1972) 121.

15 Sen Gupta R, Rajagopal M D & Qasim S Z, *Indian J mar Sci*, **5** (1976) 201.

16 Sen Gupta R, Sankaranarayanan V N, De Sousa S N & Fondekar S P, *Indian J mar Sci*, **5** (1976) 58.

17 Dietrich G, Düing W, Grasshoff K & Koske P H, *Meteor Forschungergebnisse, Reihe*, A2, 1967.

18 Bhargava R M S, Bhattathiri P M A, Devassy V P & Radhakrishna K, *Indian J mar Sci*, **7** (1978) 267.

19 Bhattathiri P M A & Devassy V P, *Indian J mar Sci*, **8** (1979) 222.

20 Devassy V P, Bhattathiri P M A & Qasim S Z, *Indian J mar Sci*, **7** (1978) 168.

21 Rhee G Y, *Limnol Oceanogr*, **23** (1978) 10.

22 Richards F A, *J mar Res*, **17** (1958) 449.

23 Stefansson U, *Deep-Sea Res*, **15** (1968) 541.

24 Richards F A, in *Chemical oceanography*, Vol. 1, edited by J.P. Riley and G. Skirrow (Academic Press, London) 1965, 611.

25 Redfield A C, Ketchum B H & Richards F A, in *The sea*, Vol. 2, edited by M.N. Hill (Interscience, New York) 1963, 26.

26 Sen Gupta R, De Sousa S N & Joseph T, *Indian J mar Sci*, **6** (1977) 102.

27 Cline J D & Richards F A, *Limnol Oceanogr*, **17** (1972) 885.

28 Grasshoff K, *Kieler Meeresforsch*, **22** (1966) 42.

29 Sen Gupta R, Naik S & Singbal S Y S, *Mar Chem*, **6** (1978) 125.

30 Culkin F & Cox R A, *Deep-Sea Res*, **13** (1966) 789.

31 Naqvi S W A & Reddy C V G, *Mar Chem*, **8** (1979) 1.

32 Elgquist B, *J inorg nucl Chem*, **32** (1970) 937.

33 Arrhenius G, in *The sea*, Vol. 3, edited by M.N. Hill (Interscience, New York) 1963, 655.