Indian Journal of Marine Sciences
Vol. 15, June 1986, pp. 67-71

Variations of Dissolved Oxygen in Mandovi & Zuari Estuaries

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Received 24 April 1985; revised received 12 December 1985

During non-monsoon months the estuaries were well mixed showing uniform oxygen concentrations from surface to bottom. However, during monsoon months both the estuaries showed stratified conditions with surface water showing high oxygen concentration and bottom water very low concentration. The stations at the freshwater-end showed relatively higher oxygen concentration than the stations at the sea-end. Plots of oxygen against salinity showed peaks at the extreme ends (freshwater and seawater). Another peak at intermediate salinity 18 to 24×10^{-3} was also observed. The upper reaches of Mandovi showed supersaturation with respect to dissolved oxygen while the lower reaches showed undersaturation. The Zuari showed under-saturation through the entire length.

Studies on dissolved gases help understanding physical, chemical and biological processes taking place in natural waters. Accurate data on solubility of gases in natural waters are of special importance because any departure of these from equilibrium with the atmospheric gases provide information on many types of processes. For example, supersaturation by non-reactive gases such as nitrogen or argon may be related to the role which entrapped air bubbles play in gas exchange[1]. Whereas supersaturation by oxygen in waters which are equilibrated with respect to non-reactive gases may suggest photosynthetic production of oxygen[1], and undersaturation by oxygen may reflect its biological and chemical utilization for respiratory and oxidation processes[2]. Solubility data for nitrogen, oxygen and argon are summarized by Weiss[3] who has developed an expression representing dependance of solubilities of these gases in seawater on temperature and salinity. Using Weiss relationship it is possible to compute solubilities of the above gases in estuarine waters of varying salinities and temperatures. In the present paper, salinity dependance of oxygen solubility in estuarine waters of Mandovi and Zuari is reported.

Materials and Methods

Stations in Mandovi and Zuari estuaries were chosen to represent marine, estuarine and freshwater zones (Fig. 1). In Mandovi, water samples were collected monthly (Feb. 1980 to March 1981) from surface and bottom at sts. M_1 to M_4. In Zuari however, observations were made at sts. Z_1 to Z_4 for a few months representing premonsoon (Feb., March, May) monsoon (Aug., Sept.) and postmonsoon (Oct., Dec.). In addition a series of surface water samples covering the salinity range 0 to 35×10^{-3} were collected from both the estuaries during postmonsoon (19 Oct. and 19 Nov. 1982) at low tide starting from the freshwater-end of the estuaries in order to study the effect of change in salinity on dissolved oxygen concentration. Surface samples were collected using a clean plastic bucket while bottom samples were collected using a Niskin sampler. Temperature was measured immediately after collection using a thermometer while chlorinity was measured by Mohr-Knudsen titration technique[4]. Salinity was computed from chlorinity using Knudsen Hydrographic Tables. Dissolved oxygen was determined by the modified Winkler method[5].

Results and Discussion

Salinity and dissolved oxygen—At all stations salinity was highest during premonsoon; but it decreased during monsoon and increased again during

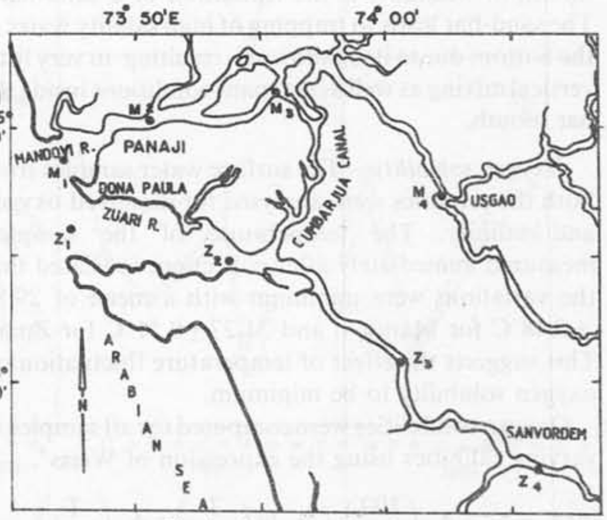

Fig. 1—Location of stations

postmonsoon (Fig. 2). During premonsoon the change in salinity was not significant from surface to bottom with the bottom water showing slightly higher values. However, during monsoon, stations at the sea-end (sts. M_1, M_2, Z_1 and Z_2) showed vertical stratification with the bottom water having high salinity while the surface water showed almost freshwater condition. Stations at the freshwater-end (sts. M_3, M_4, Z_3 and Z_4) showed complete freshwater condition from surface to bottom during monsoon. During postmonsoon salinity at the sea-end stations increased rapidly while the stations at the freshwater-end showed gradual increase in salinity with sts. M_4 and Z_4 still showing very low salinity.

At any time, the highest oxygen concentration was observed at the freshwater sts. M_3 and M_4 in Mandovi and Z_3 and Z_4 in Zuari (Fig. 2). The surface and bottom water showed almost the same trend of variation in concentration with little difference from surface to bottom, indicating that these estuaries were always well mixed from surface to bottom, except for the brief period of monsoon season when the stations at the sea-end showed vertical stratification with surface water having higher concentration than the bottom water. This feature was more pronounced in Mandovi than in Zuari.

Since the solubility of oxygen in sea water is inversely related to salinity[6], it can be one of the reasons for the low oxygen concentration of the bottom water during monsoon at the mouth of the estuaries. Another factor may be that during monsoon the subsurface seawater enters the estuaries at the bottom while freshwater flows out into the sea at the surface leading to the formation of salt-wedge[7]. The subsurface seawater will have lower oxygen concentration than the surface seawater and freshwater from river. The third important factor that might have caused lower oxygen concentration at the mouth of Mandovi is the formation of a sand-bar[7]. The sand-bar leads to trapping of high salinity water at the bottom due to its shallow sill, resulting in very little vertical mixing as well as stagnant conditions inside the bar mouth.

Oxygen solubility—The surface water samples from both the estuaries were analysed for dissolved oxygen and salinity. The temperature of the samples, measured immediately after collection, indicated that the variations were minimum with a mean of $29.82 \pm 0.48°C$ for Mandovi and $31.27 \pm 0.51°C$ for Zuari. This suggests the effect of temperature fluctuation on oxygen solubility to be minimum.

Oxygen solubilities were computed for all samples at varying salinities using the expression of Weiss[3].

$$\ln C'' = A_1 + A_2\left(\frac{100}{T}\right) + A_3 \ln\left(\frac{T}{100}\right) + A_4\left(\frac{T}{100}\right) + S\left[B_1 + B_2\left(\frac{T}{100}\right) + B_3\left(\frac{T}{100}\right)^2\right] \quad \ldots (1)$$

where C″ is the solubility of gas in seawater in units same as the units used for the constants $A_1, A_2, A_3, A_4, B_1, B_2$, and B_3; S is the salinity of the seawater sample and T is its absolute temperature. For the solubility of oxygen in seawater relative to air at 760 mmHg total pressure and at 100% relative humidity, the values for constants A_1 to A_4 and B_1 to B_3 (in $cm^3.l^{-1}$) are given by Kester[1] as follows:

$A_1 = -173.4292$; $A_2 = +249.6339$;
$A_3 = +143.3483$;
$A_4 = -21.8492$; $B_1 = 0.033096$; $B_2 = +0.014259$;
$B_3 = -0.0017$

Table 1 gives observed oxygen concentrations (C) at increasing salinities in Mandovi and Zuari and also oxygen solubility (C″) values calculated using Weiss expression (1) and the oxygen saturation anomaly Δ_G given by

$$\Delta_G = \frac{C - C''}{C''} \times 100 \quad \ldots (2)$$

Fig. 3 shows the observed oxygen concentrations at increasing salinities in Mandovi and Zuari. Dissolved oxygen concentration was highest in the freshwater zone of both the estuaries and it decreased with increasing salinity. A secondary peak was observed at salinity between 20.8 and 22.1×10^{-3} in Mandovi and between 17.8 and 20.5×10^{-3} in Zuari. A further increase was observed at the mouth in both the estuaries. The observed oxygen concentrations (C) in Mandovi (Table 1) were close to the saturation values C″. Except in few cases, the water was supersaturated with dissolved oxygen between salinity 0 and 4.25×10^{-3} while between salinities 11.53 and 31.67×10^{-3}, the water was undersaturated. However, at the mouth of the estuary oxygen supersaturation was noticed again. In Zuari the oxygen concentration showed undersaturation throughout the estuary (Table 1), the maximum oxygen saturation anomaly ranged from -13.1 to -25.2 in the salinity range 2.05 to 32.7×10^{-3}. Of the 2 estuaries Zuari showed higher saturation anomaly values than Mandovi (Table 1).

Relatively higher oxygen values observed during the monsoon season might be due to higher solubility of this gas because of low salinities, while the lower oxygen values during the premonsoon were due to its lower solubility as the salinity increased rapidly in this season. During the non-monsoon months the estuaries were well mixed showing almost the same oxygen concentration at surface and bottom. However, with the onset of the monsoon and increase in the freshwater outflow, estuaries became stratified

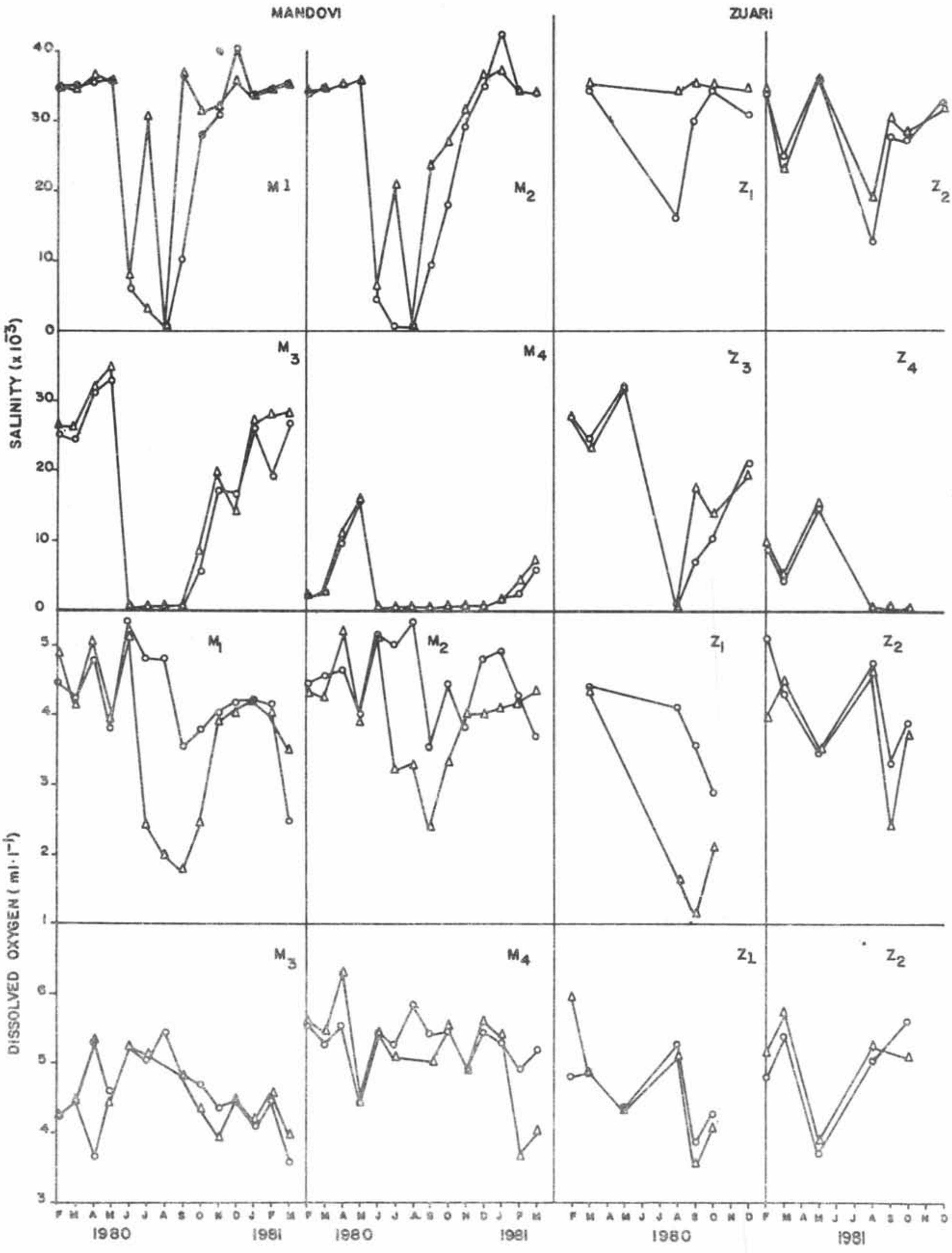

Fig. 2—Variation of salinity and dissolved oxygen in Mandovi and Zuari estuaries (○——○ surface; Δ——Δ bottom)

Table 1—Variations of Temperature, Dissolved Oxygen and the Oxygen Saturation Anomaly at Varying Salinities in Mandovi and Zuari Estuaries

Mandovi estuary					Zuari estuary				
Temp. (°C)	S($\times 10^{-3}$)	Obs. DO (ml.l^{-1}) C	Cal. DO (ml.l^{-1}) C″	Oxygen Sat. Anomaly Δ_G	Temp. (°C)	S($\times 10^{-3}$)	Obs. DO (ml.l^{-1}) C	Cal. DO (ml.l^{-1}) C″	Oxygen Sat. Anomaly Δ_G
30.5	0.045	5.25	5.24	+0.19	30.5	0.130	4.75	5.24	−9.35
30.0	0.045	5.30	5.29	+0.19	30.7	0.270	4.46	5.22	−14.56
30.2	0.045	5.19	5.25	−1.14	31.0	0.400	4.60	5.19	−11.37
29.5	0.090	5.10	5.33	−4.31	31.0	0.510	4.40	5.18	−15.06
29.5	0.090	5.07	5.33	−4.88	31.2	0.650	4.47	5.16	−13.39
29.5	0.090	5.40	5.33	+1.31	31.5	1.010	4.84	5.12	−5.47
29.5	0.135	5.46	5.23	+4.39	32.0	1.280	4.73	5.04	−6.15
30.0	0.135	5.45	5.28	+3.22	32.0	1.480	4.72	5.07	−6.90
29.5	0.226	5.35	5.33	+0.37	31.5	2.050	4.50	5.18	−13.13
29.5	0.515	5.31	5.33	−0.37	31.2	2.610	4.15	5.24	−20.80
29.5	1.192	5.12	5.30	−3.39	31.5	2.970	3.90	5.23	−25.43
29.5	2.500	5.11	5.26	−2.85	31.5	4.250	3.88	5.03	−22.86
29.5	3.330	5.30	5.24	+1.14	31.7	5.910	3.85	4.97	−22.53
30.5	4.250	5.25	5.12	+2.54	31.5	8.370	3.68	4.92	−25.20
30.2	11.530	4.43	4.94	−10.32	32.2	11.910	3.89	4.78	−18.61
31.0	13.870	4.62	4.82	−4.15	31.5	17.770	4.19	4.68	−10.47
30.5	17.120	4.35	4.77	−8.80	32.0	20.550	4.32	4.57	−5.47
30.0	23.190	4.00	4.66	−14.16	31.5	23.770	3.98	4.53	−12.14
30.0	20.880	4.62	4.71	−1.91	31.0	27.850	3.82	4.47	−14.54
29.8	22.120	4.54	4.70	−3.40	31.0	28.910	3.90	4.44	−12.16
30.0	25.140	4.36	4.61	−5.42	31.0	31.110	3.78	4.39	−13.89
29.5	28.860	3.78	5.02	−24.70	30.5	32.700	3.70	4.38	−15.52
29.2	31.670	3.86	4.50	−14.22	30.5	33.150	4.28	4.37	−2.06
29.0	34.470	4.90	4.45	+10.11	30.5	33.310	4.29	4.37	−1.83
29.5	34.130	4.81	4.42	+8.82					

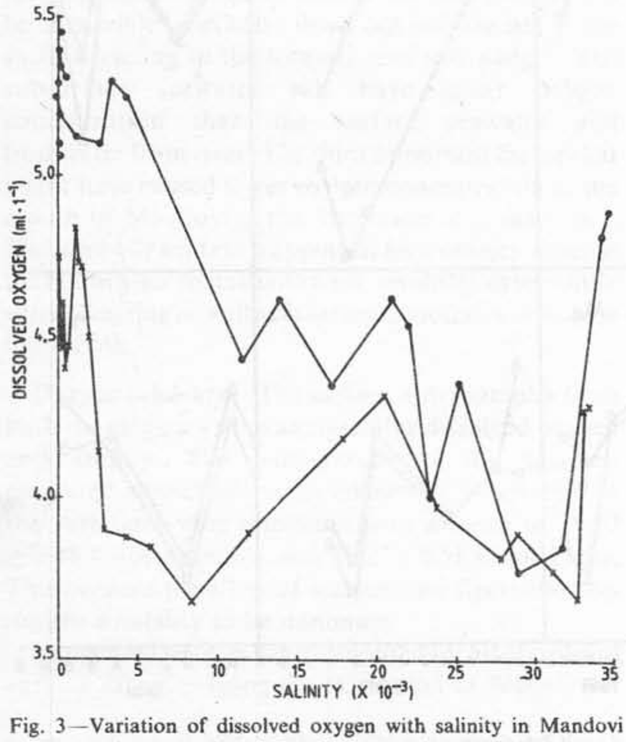

Fig. 3—Variation of dissolved oxygen with salinity in Mandovi (●——●) and Zuari (×——×) estuaries

showing wide differences in dissolved oxygen between surface and bottom. An interesting feature observed (Fig. 2) was the very low (1.78 ml.l^{-1}) oxygen concentration in the bottom water at st. M_1 and to some extent at st. M_2 in Mandovi in Sept. This water also showed an unusually high salinity (Fig. 2) and may be representing high salinity, oxygen deficient water which might have been trapped at the bottom due to the shallow sill formed by the sand-bar at the mouth. This water also showed[8] high concentration of major ions Ca^{2+}, Mg^{2+}, F^-. However, the dissolved oxygen content of this bottom water, showed recovery during the postmonsoon season when the salt-wedge subsided and the sand-bar got disturbed.

According to expression (1), the solubility of oxygen in seawater depends on the temperature and the salinity of the water. If the temperature is constant (as was almost the case in the present study, Table 1), the oxygen solubility should then depend on the salinity, with the highest solubility being at the lowest salinity (freshwater-end) and the same decreasing towards higher salinity regimes.

The high concentration of oxygen observed at the freshwater-end (Fig. 3 and Table 1) was due to the high solubility of this gas in the less saline waters. Another factor which might be responsible for this was the high photosynthetic activity in these clear waters. The nutrient concentration at the mouth of these 2 estuaries was reported[9] to be showing 2 peaks one during monsoon season and the other during postmonsoon season. Bhattathiri *et al.*[10] reported increasing trend in the primary production and chlorophyl *a* in these waters from July to September. According to some reports[11,12] at low salinity the oxygen concentration decreased due to respiratory activity of organism while at higher salinity the oxygen concentration decreased as a result of its reduced solubility; the result being maximum oxygen concentration at mid-salinity (10×10^{-3}). The same factors might have been responsible for the high oxygen concentration at salinities around 22×10^{-3} in both Mandovi and Zuari estuaries.

The upper reaches of Mandovi showed supersaturation with respect to dissolved oxygen probably due to higher photosynthetic activity as the water in this region was very clear. Another factor which might have been responsible for this was the supply of oxygen by freshwater from numerous streams discharging into this estuary, while the undersaturation in the lower reaches might have been caused by the reduced photosynthetic activity due to high turbidity of the water caused by the discharge of mine wastes from iron ore processing plants. It might have also been caused by high chemical and biological oxidation[2]. In the case of Zuari, the entire estuary was undersaturated with respect to dissolved oxygen.

The organic matter floating in the estuaries consisted principally of leaves and small stems mainly from thick growths of grass along the banks in the upper reaches of the streams and also from the mangroves fringing the lower reaches. A substantial portion of this together with the organic matter from the catchment area deposited in the bottom sediment would have been responsible for the benthic oxygen demand.

Acknowledgement

The authors are grateful to Dr V V R Varadachari, former Director, for facilities.

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