

Studies on the Behaviour of Nutrients in the Mandovi Estuary During Premonsoon

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Behaviour of silicate, nitrate and phosphate in the Mandovi Estuary was studied during the premonsoon season. The study shows that silicate is removed from the water column while nitrate showed an internal source. This nitrate source has been identified as the wash water from an iron ore screening plant which discharges the muddy waste directly into the river. Applying mixing relations, the distribution of this nitrate both up- and downstream of the outfall has been studied. Phosphate showed very low concentrations in the low salinity region; however, its concentration increased slightly towards the higher salinity region.

Introduction

The behaviour of nutrients during estuarine mixing may vary from one estuary to another, and even within one estuary it may vary seasonally depending upon environmental conditions such as precipitation, change in river flow, biological activity etc. In some estuaries, such as the Clyde Estuary (Mackay & Leatherland, 1976), some nutrients may show conservative behaviour while others may behave non-conservatively. The present study reports the behaviour of silicate, nitrate and phosphate in the Mandovi Estuary during the premonsoon (February–May) season. In this season the estuary is in a stable condition with dry weather and no precipitation. The land drainage being nil, the freshwater in the river is derived entirely from the groundwater. Earlier studies on physical, chemical and biological characteristics of this estuary have been reviewed by Qasim (1979). Recently De Sousa *et al.* (1981) have worked on the nutrients of the Mandovi and Zuari rivers. However, they covered only nine stations in the Mandovi, wide apart from one another especially in the low salinity range. Since many elements undergo major changes in concentration in the low salinity region, it was thought quite possible that these might have been missed in the earlier study. In the present work a series of samples were collected covering the whole salinity range from pure river water to seawater. The sampling was carried out in premonsoon (18 February and 31 March 1981) and monsoon (24 July and 19 August 1981). This paper, however, discusses the behaviour of nutrients in premonsoon only since nothing interesting was observed during monsoon (Table 1) as the entire estuary showed near freshwater conditions at the surface.

Materials and methods

The locations of the sampling stations are indicated in Figure 1. Surface samples were collected from the Institute's motor boat *NIO I* at low tide starting from the freshwater end

TABLE 1. Concentrations of nitrate, phosphate and silicate in the Mandovi during monsoon

Distance from Colem (km)	24 July 1981 ^a				19 August 1981 ^b			
	Cl (‰)	NO ₃ ⁻ -N (μmol l ⁻¹)	PO ₄ ³⁻ -P (μmol l ⁻¹)	SiO ₄ ⁴⁻ -Si (μmol l ⁻¹)	Cl (‰)	NO ₃ ⁻ -N (μmol l ⁻¹)	PO ₄ ³⁻ -P (μmol l ⁻¹)	SiO ₄ ⁴⁻ -Si (μmol l ⁻¹)
31	<0.04	9.8	1.00	136.2	0.02	8.0	0.23	91.9
33	<0.04	6.7	0.06	133.9	0.02	7.8	0.17	87.4
35	<0.04	7.7	ND ^c	127.1	0.02	7.6	0.17	73.7
38	<0.04	8.1	ND	129.4	0.02	7.6	0.13	96.4
41	<0.04	7.7	ND	133.9	0.03	7.6	0.01	105.5
44	<0.04	8.3	ND	131.7	0.03	7.4	0.13	96.4
46	<0.04	8.3	ND	129.4	0.03	7.8	0.06	91.9
48	<0.04	6.9	0.06	120.3	0.03	8.0	0.01	96.4
49	<0.04	7.7	0.13	124.8	0.04	8.2	0.05	112.3
50	<0.04	7.5	0.19	127.1	0.04	8.2	0.17	94.2
52	<0.04	7.5	0.52	115.8	0.04	8.2	ND	98.7
53	<0.04	7.7	0.09	122.6	0.04	7.8	ND	94.2
55	<0.04	7.5	ND	124.8	0.04	8.0	ND	94.2
57	<0.04	6.5	ND	131.7	0.04	9.0	0.01	87.4
59	<0.04	7.7	ND	124.8	0.05	7.8	0.05	90.9
60	<0.04	7.3	ND	127.1	0.05	8.0	0.06	62.4
62	<0.04	8.3	0.02	136.2	0.11	8.0	ND	71.5
63	0.04	8.8	0.02	138.5	0.08	8.0	0.06	73.7
64	0.09	7.5	ND	118.0	0.11	7.3	0.11	91.9

^aIt rained heavily on this day and during the few days preceding it.

^bA bright sunny day which was preceded by 3-4 days of heavy rain.

^cND = not detectable.

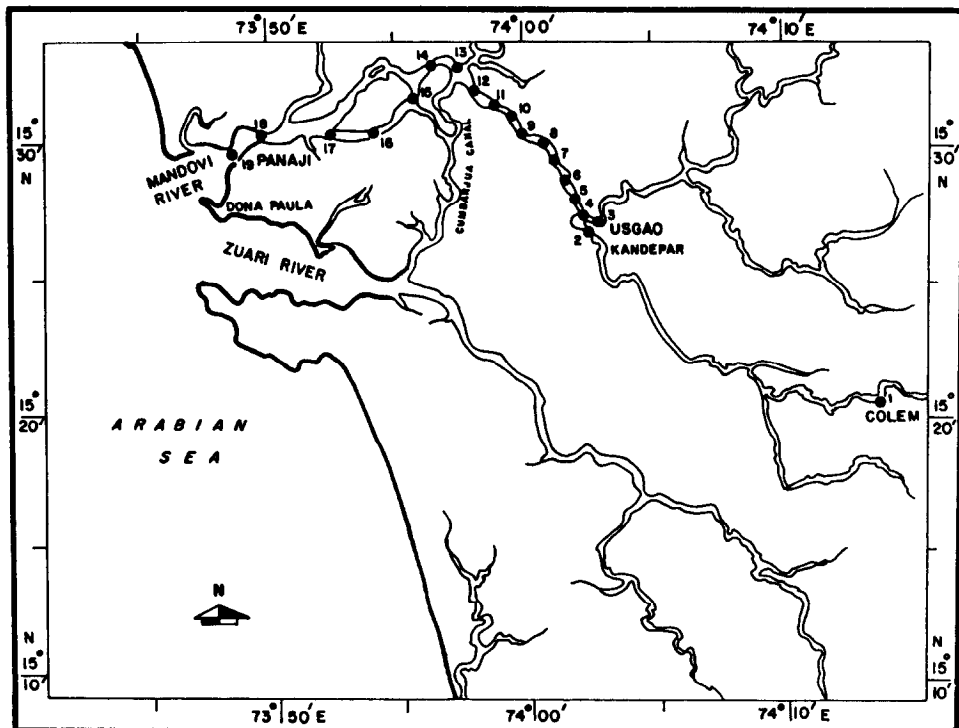


Figure 1. Map showing sampling positions.

of the estuary up to the sea end using a plastic bucket. The sample of river source water was collected by road as the point was not accessible by boat. The samples were filtered immediately after collection and frozen. They were analysed within 24 h of collection. Since the estuary is shallow and remains well mixed in this season (Qasim & Sen Gupta, 1981), it can be expected that the values of surface samples are representative of the entire water column. Reactive silicate was measured according to published methods (FAO, 1965), nitrate was determined by the modified method of Morris and Riley (Grasshoff, 1964), reactive phosphate by the method of Murphy & Riley (1962) and chlorinity was measured by titration with silver nitrate. Salinity values were computed from those for chlorinity.

Results and discussion

The fraction (f) of freshwater at any given location in an estuary is given in terms of salinity (S) at the same location by (Officer, 1976)

$$f = \frac{S_0 - S}{S_0}, \quad (1)$$

where S_0 is the salinity of the coastal water into which the estuary empties. Using equation (1), values for the percentage of freshwater were calculated for all the samples and plotted against distance (Figure 2). De Sousa *et al.* (1981) and Sen Gupta & Naik (1981) reported that the seawater penetration in the Mandovi is maximal in this season (55 km from the mouth). The percentage of freshwater decreases rapidly in the last 30 km towards the mouth (Figure 2).

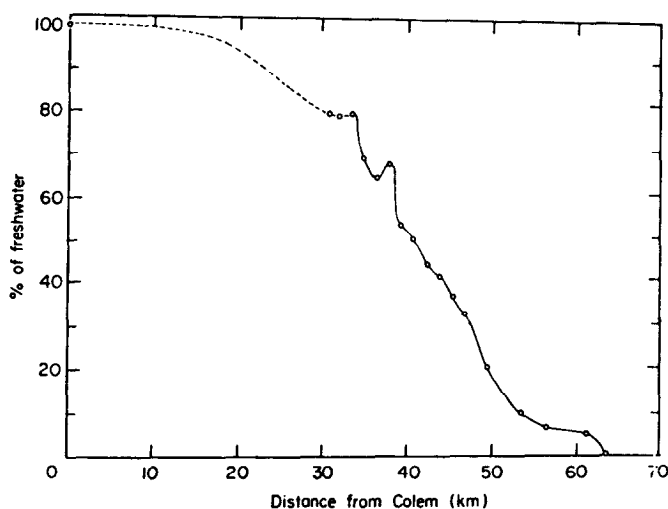


Figure 2. Distribution of freshwater in the Mandovi estuary.

Silicate

The variation of reactive silicate with chlorinity is shown in Figure 3 along with the theoretical dilution line joining the silicate concentration in source river water with that in the coastal seawater where the estuary discharges. From Figure 3 it can be deduced that large amounts of reactive silicate are removed from the water column in the low chlorinity range of 3–13‰. A better picture of silicate removal is obtained from Figure 4 which gives observed silicate distribution with distance. Figure 4 also gives the silicate curve as predicted by simple

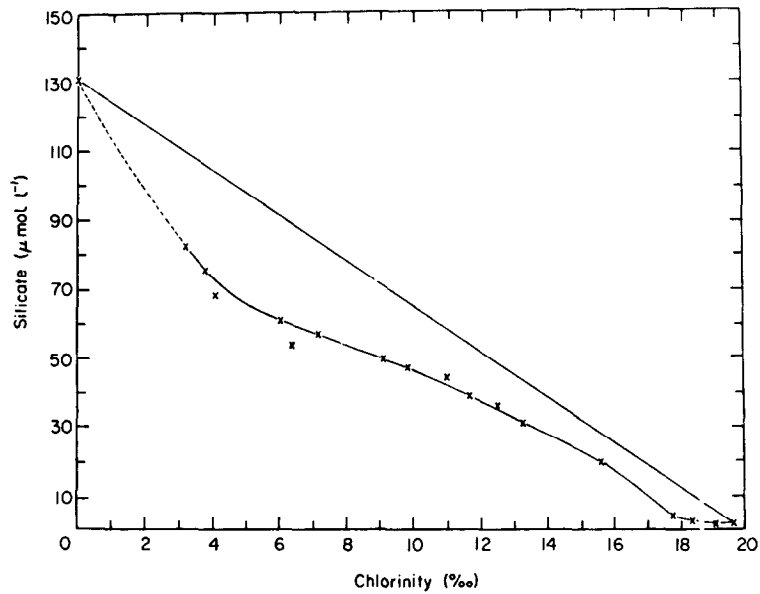


Figure 3. Variation of silicate as a function of chlorinity.

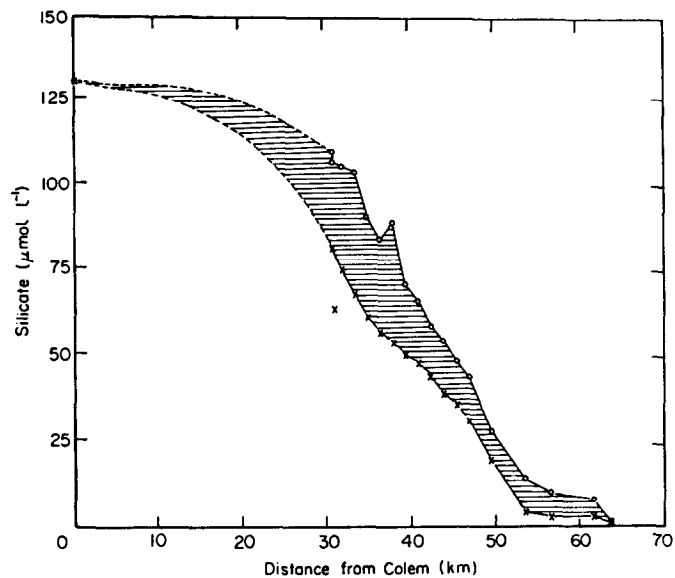


Figure 4. Variation of silicate as a function of distance. \times — \times , observed curve; \circ — \circ , predicted curve; the shaded portion indicates the amount of silicate removed.

mixing of silicate-rich river water with seawater containing low silicate. The predicted values of silicate are obtained using the mixing relation given by Yentsch (1975) as follows.

For any non-conservative property the observed concentration C_f at any point in the estuary having $F\%$ of fresh water is given by

$$C_f = \frac{F\%}{100} (C_{f,r}) - C_u, \quad (2)$$

where $C_{f,r}$ is the concentration of that property in the freshwater source and C_u is the amount removed.

Equation (2) gives the contribution due to the freshwater source, but since estuarine waters consist of a mixture of freshwater and seawater, there will be some contribution though small, from seawater source also, which is given by

$$C_s = \frac{S\%}{100} (C_{s,r}) - C_u, \quad (3)$$

where $C_{s,r}$ is the concentration of the property in the seawater source and $S\%$ is the percentage of seawater in the estuarine sample. The combined effect would be

$$C_x = (C_s + C_f)$$

$$\text{or} \quad C_x = \frac{F\%}{100} (C_{f,r}) + \frac{S\%}{100} (C_{s,r}) - C_u. \quad (4)$$

Equation (4) gives a relation for the observed concentration of any non-conservative property at any location in the estuary in terms of contribution from freshwater and seawater sources and a loss C_u due to some removal mechanism. The sum of first two terms on the right-hand side of (4), i.e.

$$\frac{F\%}{100} (C_{f,r}) + \frac{S\%}{100} (C_{s,r}) = C_p \quad (5)$$

gives the concentration of the property as predicted by simple dilution. Hence (5) was used to calculate the predicted values of silicate, which are plotted in Figure 4 along with the observed values. The difference between the predicted and observed values (shaded portion) gives the amount removed. It is clear from Figure 4 that higher amounts of soluble reactive silicate are removed from the water column between 20 and 45 km from Colem corresponding to the low chlorinity range. Previously, De Sousa *et al.* (1981) reported loss of silicate during this season, and suggested biological utilization and abiological removal by adsorption onto suspended sediments as probable mechanisms of removal.

Nitrate

In this discussion nitrate means sum of nitrate-N and nitrite-N. Variation of nitrate with chlorinity (Figure 5) suggests the presence of an internal source of nitrate in the chlorinity range 3–10‰. To determine the exact position of this possible source the observed nitrate values were plotted against distance (Figure 6). Also shown in Figure 6 is a curve obtained from the predicted values calculated from the mixing of fresh water and seawater. It suggests that there is some mechanism by which nitrate is supplied to the estuary at about 35 km from Colem. There is no industry discharging its effluents in this area nor is there any domestic sewage outfall which could raise the nitrate concentration to such an extent. The only possible source could be the iron ore screening plant situated in this area which uses 1.6×10^5 l day⁻¹ of river water (Anonymous, 1978) to wash the iron ore and discharges the muddy waste directly into the river. Analysis of this waste water showed that it contained 80 $\mu\text{mol NO}_3^- \text{N l}^{-1}$. Hence it can be concluded that it is this nitrate that enriches the estuarine waters. The source of nitrate in iron ore is attributed to the large amount of explosives used in blasting the hard rock. It is reported that this particular mining company uses 10 tonnes month⁻¹ of ammonium nitrate as explosive to blast the rock at their mining site (Anonymous, 1978). Figure 6 shows that the nitrate added is carried both upstream and downstream of the outfall showing nitrate values much higher than the predicted ones.

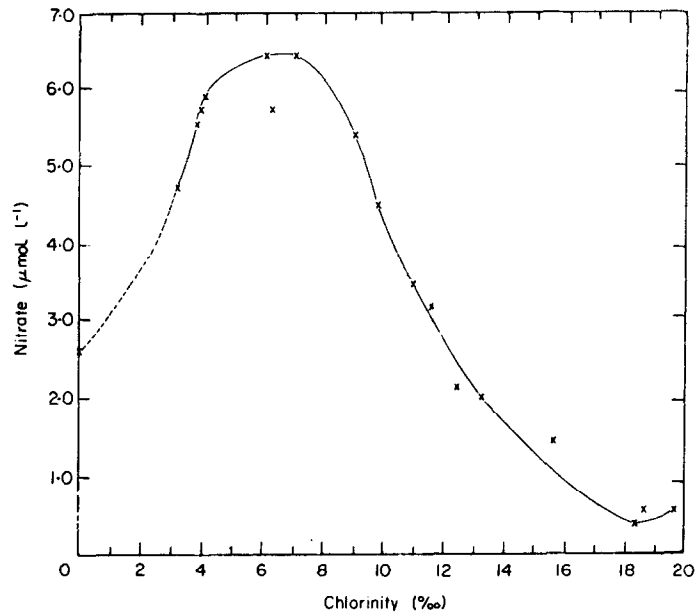


Figure 5. Variation of nitrate as a function of chlorinity.

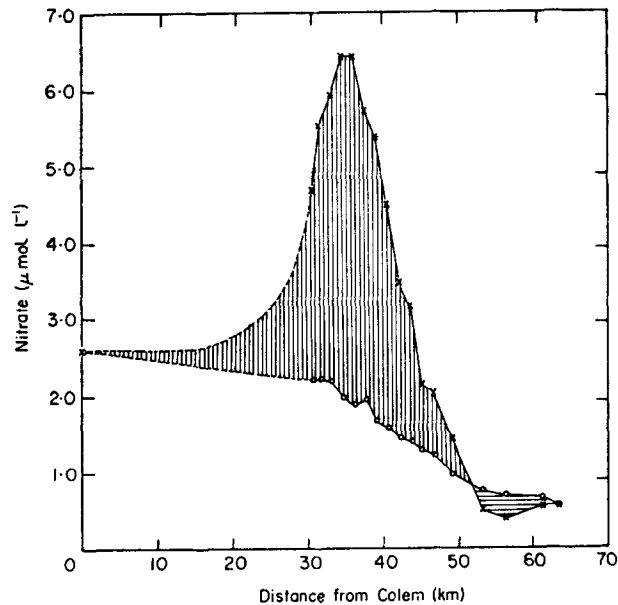


Figure 6. Variation of nitrate as a function of distance. \times — \times , Observed curve; \circ — \circ , predicted curve; ▨, addition of nitrate; ▩, removal of nitrate.

Towards the mouth of the estuary, it shows a net loss of nitrate. However, Figure 6 does not give a clear picture of the processes taking place in the estuary since the high concentrations of nitrate resulting from the outfall mask the effect of any other removal or supply mechanism that might be operating in this area. For this a different approach has been adopted.

According to Officer (1976) the concentration of any conservative pollutant at any point downstream of the outfall is given by

$$C_x = C_o \frac{f_x}{f_o} \quad (6)$$

where C_o is the concentration of the pollutant at the outfall and f_o is the fraction of freshwater at the outfall while f_x is the fraction of freshwater at any point. Similarly the concentration of any conservative pollutant upstream of the outfall is given by

$$C_x = C_o \frac{S_x}{S_o}, \quad (7)$$

where S_o is the salinity at the outfall and S_x is the salinity at any point. In this particular case the estuary can be split into two:

- (i) For any point lying upstream of the outfall, the nitrate concentration will be a result of
 - (a) the contribution from the river water source moving downstream, given by equation (6), where C_o will give the concentration of nitrate in river water source, and $f_o = 1$ is the fraction of freshwater, and
 - (b) the contribution from the outfall moving upstream, given by equation (7).
 - (ii) For any point lying downstream of the outfall, the total nitrate concentration will be a result of
 - (a) the contribution from the outfall moving downstream given by equation (6), and
 - (b) the contribution from the seawater source moving upstream, given by equation (7), where C_o will be the concentration of nitrate in a seawater source having salinity S_o .
- Hence for any point in the estuary the combined effect is given by the expression

$$C_x = C_o' \frac{f_x}{f_o} + C_o'' \frac{S_x}{S_o}. \quad (8)$$

In the present study for any point upstream of the outfall equation (8) becomes

$$C_x = 2.6 \frac{f_x}{1} + 6.44 \frac{S_x}{11.18}, \quad (9)$$

while for any point downstream of the outfall equation (8) can be written as

$$C_x = 6.44 \frac{f_x}{0.67} + 0.57 \frac{S_x}{35.57}, \quad (10)$$

where 2.6, 6.44 and 0.57 are the concentrations of nitrate in $\mu\text{mol l}^{-1}$ in the freshwater source, at the outfall and in seawater source respectively; 1 and 0.67 are the fractions of freshwater in the freshwater source and at the outfall respectively, and 11.18 and 35.57 are the salinities at the outfall and in the seawater source respectively.

Equations (9) and (10) have been used to compute the predicted nitrate values for all the points and plotted against distance (Figure 7). The similarity between this plot and the observed curve is very striking. The difference between the predicted and observed curves (shaded portion) gives the amount of nitrate removed. The possibility of nitrate loss due to denitrification can be ruled out owing to the shallow and well oxygenated nature of the estuary. As biological productivity is maximum in this season (Dehadrai, 1970; Dehadrai & Bhargava, 1972), the nitrate loss can be attributed entirely to the biological utilization.

Unlike silicate, the nitrate removal starts significantly towards the mouth of the estuary (40 km) compared with that in the low salinity region, this is so because, whereas both biological utilization and abiological removal are responsible for silicate loss, only biological utilization is operative in the case of nitrate removal. During the period of observation, it was noticed that the estuarine water from about 45 km upstream was very turbid due to the muddy water from the iron ore processing plant. High turbidity favours higher abiological removal of silicate whereas it hinders the growth of primary producers and in turn the biological removal of nitrate.

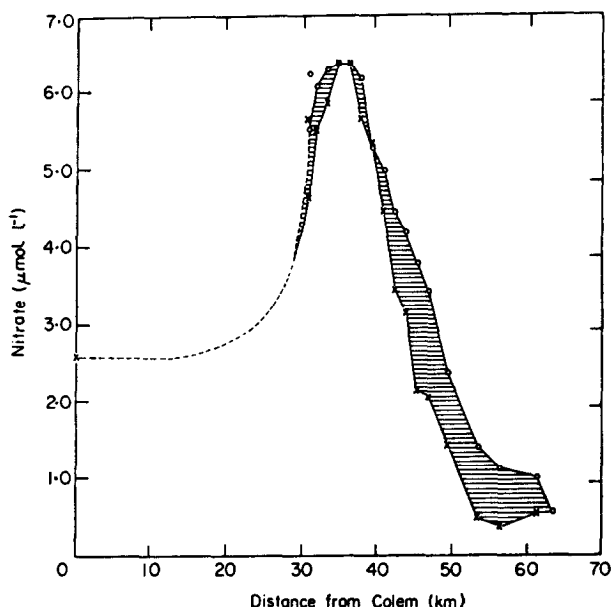


Figure 7. Variation of nitrate as a function of distance considering the nitrate from the outfall from the iron ore screening plant. \times — \times , Observed curve; \circ — \circ predicted curve; Shaded portion indicates amount of nitrate removed.

Phosphate

The variation of soluble reactive phosphate with chlorinity is shown in Figure 8. It can be seen that there is a distinct lack of variation of phosphate in estuarine waters especially of lower salinity. However, towards the higher salinity region there is a slight increase in phosphate. Steffansson & Richards (1963) proposed that the observed lack of variation of dissolved phosphate could be attributed to two main causes:

- (i) the similarity of inorganic phosphate in the river and sea waters which contribute to the estuary;
- (ii) the existence of a buffering mechanism.

Several authors have suggested the presence of some phosphate-buffering mechanism responsible in maintaining low phosphate concentrations in estuaries. From their laboratory experiments, Stirling & Wormald (1977) observed that phosphate is removed from solution by suspended sediments and that the removal is greatly affected by salinity. They observed that up to 99% phosphate adsorption had occurred at a salinity of 2‰ after 48 h of equilibration. They also observed that lowering the pH of the solution enhances the adsorption; this is probably because of the presence of phosphate as H_2PO_4^- at low pH rather than

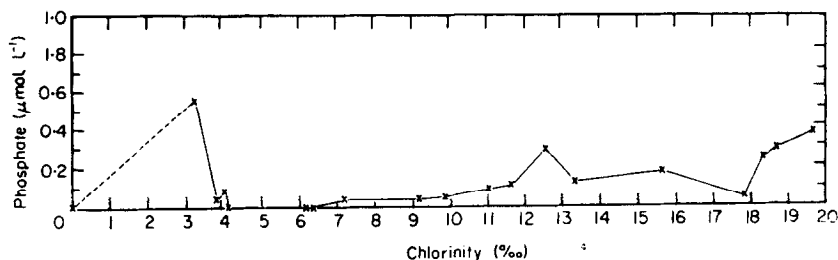


Figure 8. Variation of phosphate as a function of chlorinity.

HPO_4^{2-} ions which dominate the phosphate dissociation systems at higher pH (Kester & Pytkowicz, 1967). This suggests that in estuaries where river water with a low pH mixes with seawater with a pH of about 8, the efficiency of phosphate removal will be greater in the fresh than in the saline part of the estuary. This probably explains the increasing concentration of phosphate towards the mouth of the estuary. A similar feature was observed by Sen Gupta & Naik (1981). Besides adsorption, biological utilization will also play a role in maintaining low phosphate concentrations in the estuary. However, this biological uptake may be small in comparison with the abiological removal. Olsen (1958) has suggested that the biological fixation of phosphate was no more than 5%.

In summary it can be concluded that in the tide-dominated Mandovi Estuary silicate and nitrate behave non-conservatively, since both are removed from solution. Silicate showed a greater loss in the low salinity region, probably due to adsorption on suspended sediments, while higher nitrate loss occurred in the high salinity region because of biological utilization. The source of the nitrate peak observed in the low salinity range is identified as the wash water from an iron ore screening plant. Phosphate showed a distinct lack of variation especially in the low salinity range which is attributed to the phosphate-buffering mechanism of estuarine sediments.

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