

## Concentrations of Particulate Iron in Estuarine & Coastal Waters of Goa

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**Particulate iron concentrations in the waters in and around Goa showed very high values (0.65 to 180 mg/litre). The high values were attributed to the influence of river runoff flowing through a terrain rich in iron ore. Concentration of iron was maximum during south-west monsoon when the runoff is at its peak. Increase in the concentrations was observed from the river mouth towards offshore due to flocculation and settling. Particulate iron present in the environment was of mineral origin. Chlorinity/particulate iron relationship showed that about 11% of the iron was precipitated within the chlorinity range 15-20‰ as was about 21% in the chlorinity range 15-20‰.**

IRON is one of the biogeochemically important trace elements in the marine environment. Harvey<sup>1</sup> and Goldberg<sup>2</sup> have shown that algae utilize particulate iron for their growth. There is very little information available on the distribution of iron in the Indian waters. Subrahmanyam and Sen Gupta<sup>3</sup> have studied the total iron concentration in the waters off Madras and Jagatheesan and Venugopalan<sup>4</sup> have reported trace metal concentrations in the particulate matter of Porto Novo waters. A study on the distribution of iron in the waters in and around Goa is important because of the mining of iron ore in this region and its probable influence on the estuarine and marine environment. In the present paper seasonal variations of particulate iron in the Mandovi and Zuari estuaries and its distribution in the coastal waters of Goa are reported.

### Materials and Methods

Samples for the measurement of particulate iron were collected at monthly intervals for 1 yr (1972-73) from 3 stations each in Mandovi (stations 1-3) and Zuari (stations 15-17). Details of station positions and the collection of surface and subsurface samples from upper reaches of rivers as well as from coastal waters are same as given earlier<sup>5</sup>. For the estimation of particulate iron 200 ml of samples were filtered on a membrane filter pad of 0.45  $\mu$ m pore size. Iron present in water, filtered through the membrane filter, was estimated as soluble iron ( $Fe_{sol}$ ). For the estimation of  $Fe_{part}$  and  $Fe_{sol}$  the methods described by Lewis and Goldberg<sup>6</sup> were applied.  $Fe_{part}$  was also determined by treating the filters with dilute HCl for a few minutes as described by Strickland and Parsons<sup>7</sup>, who have termed the iron measured by this method as biologically active, and this includes the iron liberated in ferric form which is likely to be utilized by the marine algae. Hereafter, the particulate iron estimated by this method will be referred to as biologically active iron ( $Fe_{b}$ ).

### Results and Discussion

Annual variation in the concentration of  $Fe_{part}$  in both Mandovi and Zuari estuaries was abnormally high during the whole year (Fig.1). The values were low during November to April, when there was very little runoff. During June to October, when the monsoon was active,  $Fe_{part}$  values showed a sharp increase at the surface as well as at the bottom. Variation in the concentration of  $Fe_{part}$  at stations 1-3 in the Mandovi estuary was in the range of 4-105 mg/litre, and the variation in Zuari estuary at stations 15-17 was between 5 and 180 mg/litre. The data clearly show that in both the estuaries concentrations of  $Fe_{part}$  were maximum during the monsoon months (June to October). Concentrations of  $Fe_{part}$  estimated at different stations from the upper reaches of both the rivers are given in Table 1. Concentration levels in the Mandovi varied between 5 and 44 mg/litre whereas in the Zuari the values ranged between 21 and 63 mg/litre. As both these rivers flow through iron ore-bearing terrain, the high values of  $Fe_{part}$  observed in both the rivers are possibly due to the influence of these deposits. Concentrations of  $Fe_{part}$  measured at different stations (18-29) in the nearshore waters are given in Table 2. There was a significant lowering in the concentrations of iron relative to estuarine values. Concentrations varied between 0.65 and 12.7 mg/litre. There was a general lowering in the levels of  $Fe_{part}$  concentration towards the offshore waters.  $Fe_{part}$  concentrations in Goa waters showed abnormally high values. Such high concentrations have been reported from rivers and nearshore waters where terrigenous influences are significant<sup>8-11</sup>. Ryther *et al.*<sup>10</sup> reported high values of iron observed at the Amazon river mouth which decreased by almost a thousandfold offshore. The authors attributed this to sedimentation of particulate matter. Concentrations of  $Fe_{part}$  and  $Fe_{biol}$  observed during different seasons are given in Table 3. Biologically

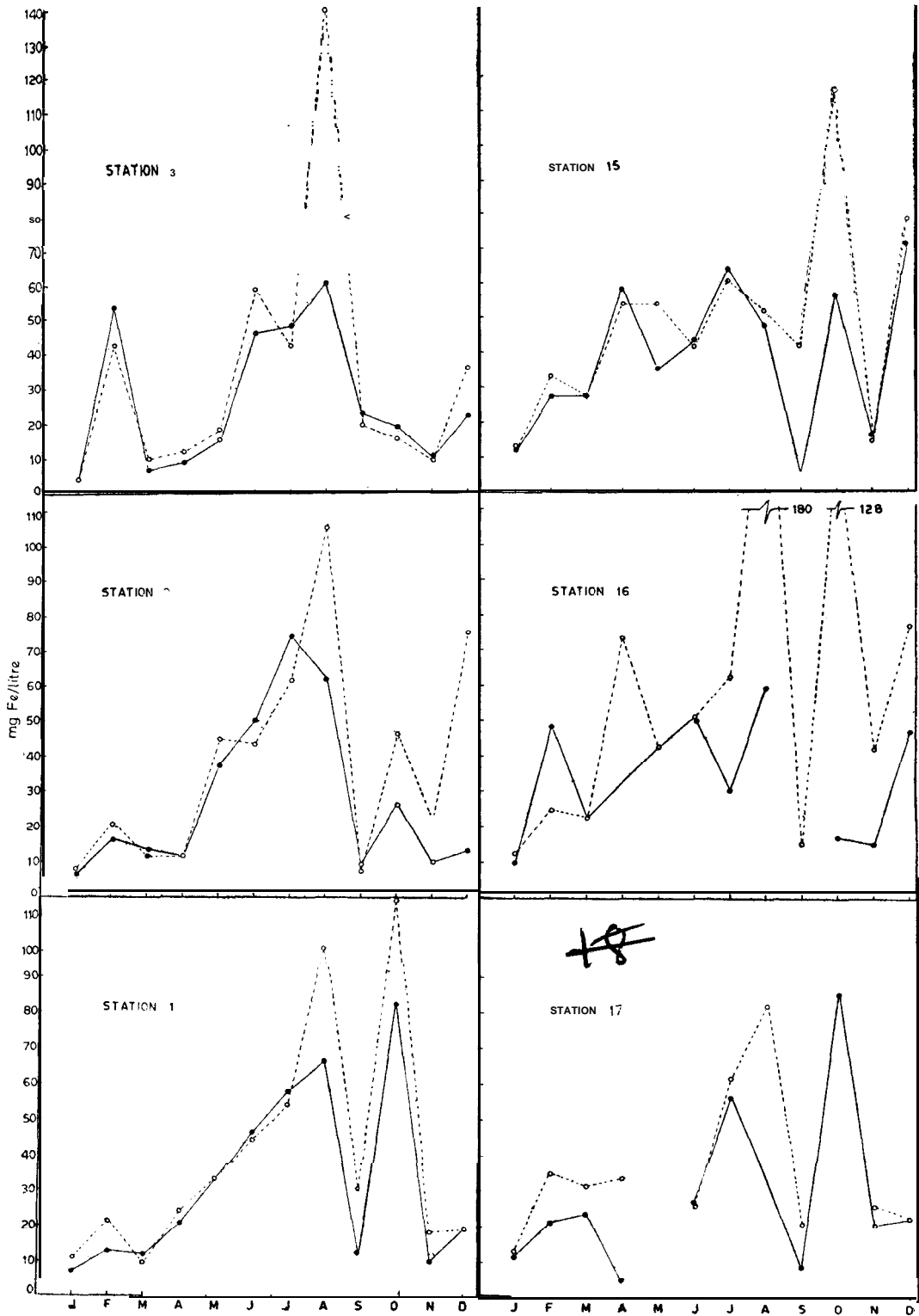


Fig. 1 Monthly variation in particulate iron concentrations at stations in Mandovi (stations 1-3) and Zuari (stations 15-17) estuaries [Solid lines indicate surface values and broken lines bottom values]

active fraction of iron is an insignificant part of the total Fe<sub>part</sub> present in the environment. Concentrations of Fe<sub>part</sub> and Fe<sub>biol</sub> (Table 4) varied from 0.6 to 7 mg/litre and 0.04 to 0.22 mg/litre respectively. There was a significant reduction in the concentrations of particulate Fe<sub>part</sub> and Fe<sub>biol</sub> in the coastal waters. It appears from the data that a considerable portion of the Fe<sub>part</sub> which is of

mineral origin may be subjected to flocculation and sedimentation when the river water comes in contact with sea water. Aston and Chester<sup>12</sup> found that some of the inorganic factors responsible for controlling the precipitation of iron in the estuarine waters are suspended particles and chlorinity.

TABLE 1 — MEAN CONCENTRATIONS OF PARTICULATE IRON (MG/LITRE) IN THE UPPER REACHES OF MANDOVI AND ZUARI RIVERS

Station No.	Mandovi river		Station NO.	Zuari river	
	Surface	Bottom		Surface	Bottom
1			9	20.6	44.4
2	34.2	38.5	10	31.3	29.2
4	24.8	40.3	11	50.9	36.6
5	15.5	17.2	12	62.7	49.1
			13	43.0	53.2
6	5.9	6.6	14	47.5	55.1
7	—	4.9	17	32.5	50.6

TABLE 4 — PARTICULATE AND BIOLOGICALLY ACTIVE IRON CONCENTRATIONS IN NEARSHORE WATERS

(Values expressed in mg/litre are mean values)

Station NO.	Depth m	Fe <sub>part</sub>	Fe <sub>biol</sub>
18	Surface	5.7	0.06
	11	6.6	0.22
19	Surface	2.5	0.09
	15	0.6	0.04
20	Surface	7.1	0.05
	14	3.6	0.10
22	Surface	7.0	0.08
	2.0	2.7	0.08
23	Surface	2.7	0.07
	20	1.2	0.05

TABLE 2 — PARTICULATE IRON CONCENTRATIONS (MG/LITRE) IN THE INSHORE WATERS OF GOA

Station No.	Off Vengurla		Station No.	Off Aguada		Station No.	Off Cape Ramas		Station No.	Off Karwar	
	Depth (m)	Fe <sub>part</sub>		Depth (m)	Fe <sub>part</sub>		Depth (m)	Fe <sub>part</sub>		Depth (m)	Fe <sub>part</sub>
18	0	5.5	21	0	6.3	24	0	4.6	27	0	7.8
	10	4.9		10	6.2		10	1.3			
	15	4.0			20		3.0				
	2.0	5.3									
19	0	3.1	22	0	2.4	25	0	2.7	28	0	2.2
	10	1.0		15	1.2		25	1.2			
	25	6.7		2.0	1.3		30	1.3			
20	0	1.8	23	0	0.6	26	0	1.8	29	0	2.4
	10	0.9		10	0.5		10	0.6			
	20	0.9			30		1.2	20		0.9	
	35	0.9		40	1.3		30	1.1			

TABLE 3 — CONCENTRATIONS OF PARTICULATE AND BIOLOGICALLY ACTIVE IRON (MG/LITRE) IN MANDOVI AND ZUARI ESTUARIES

	Station No.	Mandovi estuary		Station No.	Zuari estuary	
		Fe <sub>part</sub>	Fe <sub>biol</sub>		Fe <sub>part</sub>	Fe <sub>biol</sub>
28-8-72	1	66.5	0.48	15		
	2			16	47.3	—
	3	60.1	0.21	17	30.4	0.19
18-9-72	1	12.8	0.04	15		
	2			16	4.8	0.05
	3	22.4	0.04	17	9.1	0.06
12-10-72	1			15	56.3	0.34
	2	82.6	0.22	16	16.7	0.12
	3	18.7	0.10	17	85.6	0.14
21-12-72	1			15		
	2	19.8	0.44	16	70.7	1.50
	3	13.7	0.82	17	46.9	0.34
21-2-73	1	21.9	0.48	17	22.8	0.53
	2			15	27.4	0.29
	3	53.6	0.10	16		
				17	48.8	0.23

In the two Goa rivers, the total suspended load and the large variations in chlorinity values, especially during the monsoon months, may be aiding in flocculation and sedimentation of iron in large quantities. Williams and Chan<sup>11</sup> reported that  $Fe_{sol}$  transported by the rivers undergoes precipitation and flocculation in contact with saline water present in estuaries and is probably the result of an increase in the ionic strength and pH. Data on particulate and biologically active iron clearly show that the major part of the  $Fe_{part}$  is of mineral origin which may be 'biologically inactive' for healthy plant cells. Concentrations of  $Fe_{sol}$  for different seasons in both estuaries (Mandovi and Zuari) are given in Table 5. Values in both the estuaries varied between 0.12 and 0.86 mg/litre and 0.10 and 0.59 mg/litre respectively. Maximum values were observed during the postmonsoon season at all stations. Increase in  $Fe_{sol}$  during postmonsoon months could be explained as due to the release of soluble iron during the decay of organisms following blooms.

**Chlorinity-particulate iron relationship** — Decrease in iron concentrations from the estuarine region towards offshore was very marked and therefore the chlorinity  $Fe_{part}$  relationship and the approximate loss of  $Fe_{part}$  by flocculation and sedimentation were also studied. For this purpose, the range from zero chlorinity to 20‰, has been chosen because the system is fresh water dominated during monsoon months and becomes an extension of the sea during the pre- and postmonsoon periods. To reduce the number of values, average chlorinities at every 5‰ interval and corresponding  $Fe_{part}$  concentrations have been calculated and presented in Fig. 2. The curve is extrapolated from the lowest chlorinity value to the iron axis to obtain iron values at zero chlorinity, and the value thus obtained is used as  $Fe_0$ . It is clear from the figure that there is no linear relationship between the iron content and chlorinity. The curve is concave at low chlorinity ranges but it is asymptotic at higher chlorinities. As a consequence of removal of iron the curve representing the iron concentration as a function of chlorinity is concave along the direction of iron axis. Simplest relationship corresponding to this has been provided by Sen Gupta<sup>13</sup>.

$$Fe = Fe_0 + \frac{Cl^2}{a + a_1Cl + a_2Cl^2} \quad ..(1)$$

substituting  $Fe_0 = 83$  mg/litre and using the observations at salinities below 20‰ we find the best fit

to be

$$Fe = 83 - \frac{Cl^2}{0.0187 + 0.0379 Cl + 0.0204 Cl^2} \quad ..(a)$$

Starting with low chlorinities, chlorinity 0-5‰ range will give an iron concentration of 54.63 mg/litre which implies that 5.79 mg/litre or 11 % of the iron has been removed from the water. But at the chlorinity range 15-20 ‰, the loss was 8 mg/litre or 21% of the iron. The possible explanation is that iron is removed with particles in suspension from the river water as it joins the saline water. Kullenberg and Sen Gupta<sup>14</sup>, while studying the fluoride concentration in sea water, have observed that 17% of the fluoride was removed from the water by settling with particles at the confluence of river water with saline water. Present observations indicate that iron is removed from the water in a similar manner.

Any universal applicability of Eq. (2) is not claimed since the iron carried by rivers does vary considerably from place to place. Therefore, we restrict its validity according to treatment of data noted above.

We shall now try to compute the amount of iron in particulate form which may be expected to settle down at the confluence of river with sea water off Goa. The runoff from both the rivers (Mandovi

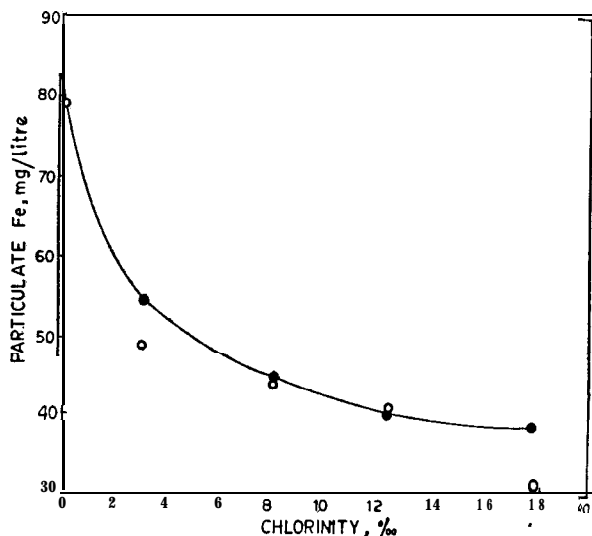


Fig. 2 — Particulate iron-chlorinity relationship [●, calculated values; and ○, observed values]

TABLE 5 — MEAN CONCENTRATIONS OF SOLUBLE IRON (MG/LITRE) IN MANDOVI AND ZUARI ESTUARIES (1972-73)

Station No.:	Mandovi						Zuari					
	1		2		3		15		16		17	
	S	B	S	B	S	B	S	B	S	B	S	B
Premonsoon (March)	0.17	0.29	0.17	0.16	0.37	0.44	0.14	0.21	0.38	0.14	0.37	0.34
Monsoon (July)	0.50	0.25	0.19	0.18	0.15	0.12	—	—	—	—	—	—
Postmonsoon (Dec.)	—	0.75	0.86	0.32	0.59	0.33	0.59	0.21	0.28	0.10	0.28	0.22

S=surface, and B= bottom

and Zuari) is mainly regulated by monsoon precipitation. Runoff during pre- and postmonsoon periods is mainly dominated by tidal variations. It is assumed that the freshwater discharge outside the monsoon period is either insignificant or negligible.

The average rate of runoff from the Zuari, calculated from the discharge values from June to October in 1963, 1964 and 1966, was  $9 \text{ km}^3$  (ref. 15). With some reservations this may be accepted as the annual runoff from the river Zuari. From Fig. 3, concentration of  $\text{Fe}_{\text{part}}$  at zero chlorinity is  $83 \text{ mg/litre}$ , which would mean that approximately  $700 \times 10^3$  tonnes of  $\text{Fe}_{\text{part}}$  is carried annually by the river Zuari into the sea. From chlorinity  $\text{Fe}_{\text{part}}$  relation it is found that about 10% of this settles in estuarine region and 20% in nearshore area. That is of the iron, carried annually by the river Zuari in particulate form, about 70000 tonnes is deposited in the estuary and about 140000 tonnes in nearshore regions. Assuming that the runoff from the Mandovi is of the same order as the river Zuari, a similar amount can be expected to be added annually to this area as well. The sediments in the nearshore up to 15 m depth contain 7-9% of iron (dry weight).

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