

## **POLLUTION INDUCED TIDAL VARIABILITY IN WATER QUALITY OF MAHIM ESTUARY**

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Variability of water quality due to release of wastewater in Mahim estuary and associated nearshore waters is discussed. The mixing of low salinity contaminated estuary water with high salinity bay water was considerably hindered inducing lateral as well as intermittent vertical stratification which severely polluted the northern bay as compared to the southern region. The high wastewater fraction varying between 0.3 (spring) and 0.98 (neap) of estuarine volume in absence of river runoff, resulted in severe deterioration in water quality due to weak tidal flushing. The overall character of the particulate suspended matter changed considerably with increase of inorganic component from 50 per cent in the estuary to 65 and 80 per cent in the bay and in the offshore respectively. The low estuarine pH increased with increase in salinity and attained seawater values in the coastal water. The stress of anthropogenic organic load though marginal outside the bay, the dissolved oxygen (DO) replenished with the incursion of high tide was quickly consumed leaving very low to undetectable levels in the northern bay unlike in the southern bay. Low to undetectable concentrations of  $\text{NO}_3^-$ -N and  $\text{NO}_2^-$ -N and occurrence of  $\text{S}^2$  along with high concentration of  $\text{NH}_4^+$ -N during low tide indicated active denitrification and limited sulphate reduction in the bay. The estuary was often devoid of DO,  $\text{NO}_3^-$ -N and  $\text{NO}_2^-$ -N during dry season except for brief periods of tidal floods and  $\text{S}^2$  concentration frequently exceeded  $75 \mu\text{M}$ . On the contrary the estuary sustained high concentrations of  $\text{NO}_3^-$ -N and  $\text{NO}_2^-$ -N particularly during flood tides in monsoon due to aerobic oxidation of organic matter by additional DO associated with the monsoonal runoff. In such situations a good correlation between  $\text{NO}_3^-$ -N and  $\text{NO}_2^-$ -N was evident. However, this additional DO was

soon consumed inducing nitrate diagenesis. The high flux of  $\text{NH}_4^+$ -N through the estuary was only partially oxidised in the bay and hence influenced the levels beyond the bay mouth. The concentrations of  $\text{PO}_4^{3-}$ -P were very high in the estuary and the bay and often decreased with increase in salinity.

## INTRODUCTION

Mahim estuary and the adjoining Mahim Bay are under extreme environmental stress due to the release of domestic and industrial wastewaters draining a variety of pollutants into the receiving water. Abnormal concentrations of phosphate, nitrate, nitrite and ammonia have been reported in the estuary (Zingde and Desai, 1980). Dissolved oxygen (DO) which varied considerably with the tidal stage was often below  $1 \text{ mg l}^{-1}$  in the estuary and high levels of biochemical oxygen demand (BOD) were frequently encountered (Zingde and Desai, 1980). Although the semidiurnal tides sweeping the bay induced considerable flushing, the tidal influence reduced markedly in the estuary due to an abrupt bed elevation and sudden narrowing of the channel cross-section at the head of the bay. It has been estimated that the estuary retained  $9.3 \times 10^4 \text{ m}^3$  of wastewater which was over 15 per cent of the spring high tide and 40 per cent of the low tide volumes of the estuary (Sabnis and Zingde, 1989). The bay which was an important centre for clams and rock oysters (Subrahmaniam *et al.*, 1949) in the past has at present no commercial fishery. A decrease in diversity of chaetognaths, copepods and planktonic fish eggs and larvae off Mahim has been attributed to the prevailing pollution stresses (Nair *et al.*, 1981; Gajbhiye *et al.*, 1981, 1982). A distinct deterioration of marine life along the northern part of the bay as compared to the southern region has been considered to be due to greater impact of pollutants on the northern shores (Govindan and Desai, 1980-81).

Spatial and temporal variabilities of some physico-chemical parameters are discussed in this paper.

## MATERIALS AND METHODS

Sampling in Mahim estuary, the adjacent bay and the nearshore water was undertaken during 1979-81 at 8 stations marked in Fig. 1. Stations

1 to 3 were sampled during high and low tides every month from Nov 79 to Dec 80 except during the monsoon months of June to August. Stations 4,5 and 6 were synergically monitored over a tidal cycle on 4 Jan 1980 (spring), 18 Sept 1980 (neap) and 25 Sept 1980 (spring). Station 5 was also monitored over a tidal cycle on 29 Aug 1980 and station 3 on 19 Feb 1981. Stations 7 and 8 were sampled during high and low tides during April 1980.

A clean polyethylene bucket was used for sampling at the surface while a Niskin sampler was employed to obtain subsurface samples when the depth of water column exceeded 3 m. The samples were analysed for salinity, (sal); pH; total suspended solids, (SS); DO;  $PO_4^{3-}$ -P (P),  $NO_3^-$ -N, (NA);  $NO_2^-$ -N, (NI); and  $NH_4^+$ -N, (A) by using standard procedures (Grasshoff, 1976). Selected samples were also analysed for BOD and sulphide (Grasshoff, 1976).

## RESULTS AND DISCUSSION

### Study area

The shallow semi-enclosed Mahim bay which provides shelter to several fishing crafts is open to the Arabian Sea on the west and is connected to the Mahim estuary on the north-east. The bay is formed by differential weathering aided by sea erosion, of the interlayered soft tuffs and hard basaltic flows of Deccan Volcanics. The subtropical climate with torrential rainfall, the easily alterable mineral assemblages, such as olivine, pyroxenes and labradorite of the basalt, provide the bay with rich lithogenic flux, characterised by predominance of the sorptive smectite group of minerals and several hydrolyzates. The northern shores of the bay are predominantly rocky with mud patches in-between while the southern shores are mainly sandy with scattered rock crops. The estuary harbours extensive growth of mangroves which form a prominent green belt separating south and north Bombay. The narrow meandering Mahim River which passes through industrial areas terminates at the base of the Vihar and Powai lakes.

The river experiences pronounced cycle of freshwater discharge mainly through the overflow from the lakes during July-August which leads to yearly flushing of the river and the estuary. The average freshwater flow

**Table 1:** Physico-chemical characteristics (mean) at stations 1, 2, and 3 during different months.

Month	Station	Sal $\times 10^{-3}$	pH	SS $\text{mg l}^{-1}$	DO $\text{mg l}^{-1}$	$\text{PO}_4^{3-}\text{-P}$ $\mu\text{M}$	$\text{NO}_3\text{-N}$ $\mu\text{M}$	$\text{NO}_2\text{-N}$ $\mu\text{M}$	$\text{NH}_4\text{-N}$ $\mu\text{M}$	TN/P ratio
Nov.	1	35.4	8.1	90	5.7	2.9	1.7	0.2	-	0.6
	2	35.0	8.1	92	5.9	3.4	4.2	2.0	1.5	2.3
	3	35.0	7.9	99	4.6	4.3	6.5	2.6	5.4	3.4
Dec.	1	35.5	8.1	52	6.2	0.9	1.5	0.9	-	2.7
	2	35.2	7.9	70	5.4	1.9	5.4	2.1	7.9	7.6
	3	35.3	7.8	97	4.5	2.4	5.7	2.4	10.7	7.8
Jan.	1	36.0	8.2	50	6.7	0.4	2.0	0.7	0.5	8.0
	2	35.4	8.0	44	5.7	1.7	10.9	2.1	4.4	10.2
	3	35.6	7.9	42	5.1	3.1	9.8	3.2	6.9	6.4
Feb.	1	35.6	8.2	60	6.6	0.4	0.8	0.1	0.3	3.0
	2	35.3	8.3	62	6.7	0.6	1.6	0.8	0.8	5.3
	3	35.3	8.2	66	5.9	1.6	3.4	4.0	3.5	6.8
Mar.	1	35.3	8.1	86	5.4	0.5	1.1	0.5	0.4	4.0
	2	35.4	8.1	85	5.5	0.9	3.0	1.5	0.9	6.0
	3	35.0	7.9	79	4.5	2.2	4.4	7.2	10.1	9.9
Apr.	1	36.0	8.2	76	6.7	0.3	2.6	0.6	0.4	12.0
	2	35.8	7.9	72	6.6	0.6	4.3	2.5	0.4	12.0
	3	35.6	7.8	73	4.8	1.4	6.1	2.6	2.0	7.6
May.	1	35.8	8.1	67	6.3	0.4	1.7	0.1	0.8	6.5
	2	35.8	8.1	46	6.4	1.1	3.4	0.4	1.4	4.7
	3	35.4	7.8	68	5.3	1.3	7.3	0.5	2.9	8.2
Sep.	1	28.8	8.2	-	6.8	0.4	5.2	1.1	2.8	22.7
	2	27.8	8.2	-	6.2	0.4	5.5	1.0	0.6	17.8
	3	30.4	8.0	-	5.7	0.4	6.0	0.9	0.6	18.7
Oct.	1	35.2	7.9	59	5.0	1.2	1.7	0.6	0.5	2.3
	2	35.1	7.9	65	4.9	1.3	1.1	0.7	0.7	1.9
	3	35.1	7.9	71	5.2	1.6	2.2	0.9	1.0	2.5
Nov.	1	35.7	7.9	87	4.7	1.7	1.1	1.6	0.5	1.9
	2	35.4	7.8	100	4.4	1.8	1.5	1.6	1.1	2.3
	3	35.5	7.8	112	3.2	2.0	1.9	2.0	2.3	3.1
Dec.	1	35.6	8.0	43	7.5	2.0	7.9	1.1	2.3	5.6
	2	35.4	7.8	58	5.9	2.9	10.6	7.8	5.1	8.1
	3	35.2	7.6	47	5.6	2.9	10.5	5.8	8.4	8.5

of around  $85 \text{ m}^3 \text{ sec}^{-1}$  during August decrease considerably after the withdrawal of monsoon and stagnant conditions exist in the river and the estuary after September.

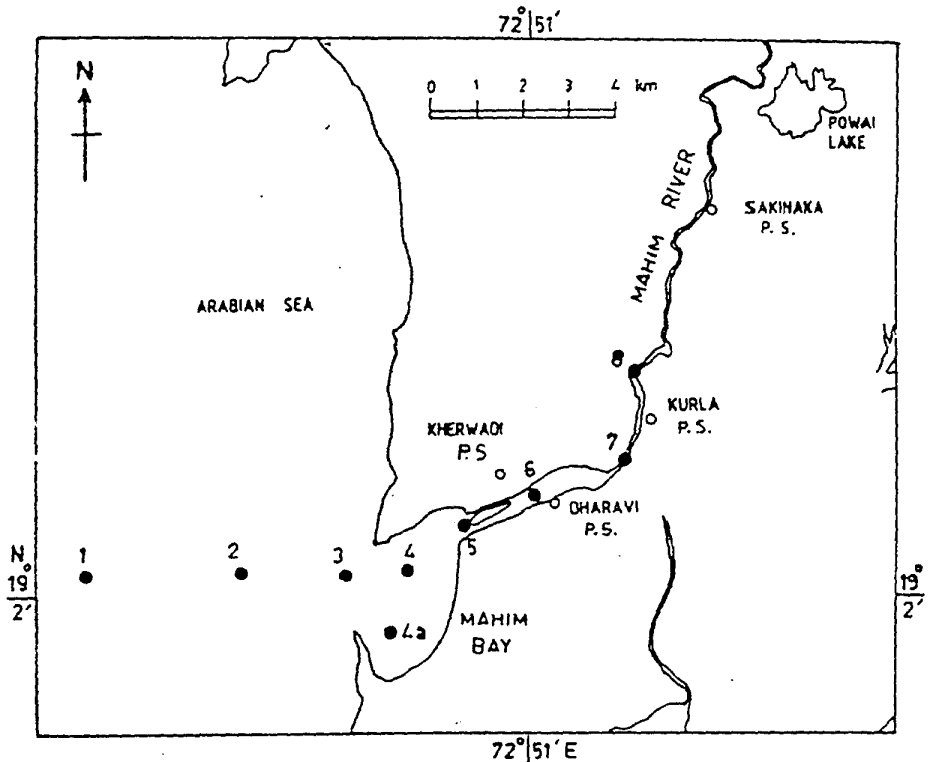


Fig.1: Locations of sampling and major sewage pumping stations (PS)

The Bay experiences considerable tidal influence with the spring of about 3 m at the head. An abrupt bed elevation around station 5 and considerable narrowing of the channel upstream markedly reduces the tidal ingress into the estuary. Thus, as against 3 m spring rise in the bay, the rise in the estuary is under 1 m decreasing to 0.1 m during neap tide. The tidal influence which is upto 10 km in the estuary during spring decreases to 5 km during neap tide. Flushing time of the estuary of 19 tidal cycles has been estimated by applying the modified tidal prism method for spring tidal conditions (Sabnis and Zingde, 1989).

### Fluxes of pollutants

Total domestic wastewater flow of  $1.6 \times 10^5 \text{ m}^3 \text{ day}^{-1}$  added 43 t

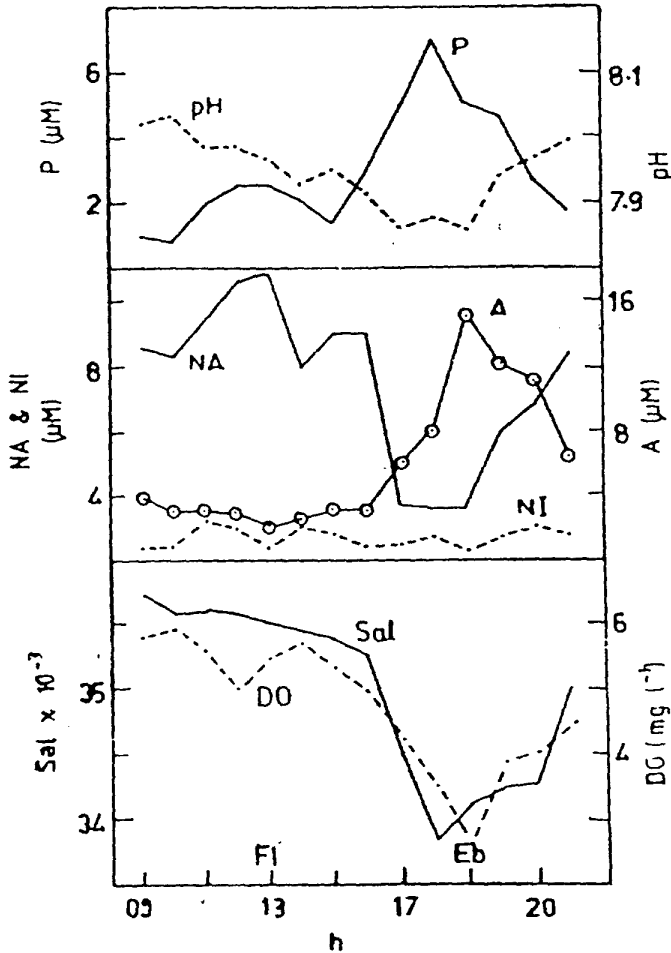


Fig. 2: Hourly variation of surface water quality at station 3 on 19 Feb 1981. NA =  $\text{NO}_3^-$ -N; NI =  $\text{NO}_2^-$ -N; A =  $\text{NH}_4^+$ -N; P =  $\text{PO}_4^{3-}$ -P; Fl = flood tide; Eb = ebb tide

of suspended solids, 45 t of BOD, 13 t of sulphate, 6 t of nitrogen and 1 t of phosphorus in the estuary (Sabnis, 1984). In addition, the estuary and the river received a variety of wastes through point discharges from the industries located along the banks. These industries have been estimated to add 0.7 t of suspended solid and 0.7 t of BOD in the receiving water (Sabnis, 1984). The wastewater load retained in the estuary was

**Table 2:** Physico-chemical characteristics at station 4 a.

Parameter	May 80			Jan 81		
	Max	Min	Mean	Max	Min	Mean
Sal x 10 <sup>-3</sup>	35.6	34.9	35.2	35.5	34.1	34.9
pH	8.1	7.7	7.9	8.2	7.7	7.8
SS (mg l <sup>-1</sup> )	105	38	73	82	30	68
DO (mg l <sup>-1</sup> )	5.0	2.2	3.5	5.3	3.8	4.1
BOD (mg l <sup>-1</sup> )	12.1	2.6	4.9	10.3	3.1	5.2
PO <sub>4</sub> <sup>3-</sup> -N (µM)	7.6	2.8	5.2	6.7	2.6	4.8
NO <sub>3</sub> <sup>-</sup> -N (µM)	32.9	6.3	14.2	28.3	5.3	15.2
NH <sub>4</sub> <sup>+</sup> -N (µM)	13.8	4.2	9.1	12.6	2.7	10.9

estimated at  $9.3 \times 10^4 \text{ m}^3$  which formed 16 per cent of the spring tide and 40 per cent of the low tide volume of the estuary (Sabnis and Zingde, 1989). The bay also received wastewater - largely sewage, through several point discharges. Of these, the major discharge was through a pipeline terminating above the low water mark in the southern bay.

### Salinity

High premonsoon nearshore surface salinity ( $35.5 \times 10^{-3}$  -  $36.5 \times 10^{-3}$ ) off Bombay decreased considerably ( $25 \times 10^{-3}$  -  $27 \times 10^{-3}$ ) accompanied with the development of lateral salinity gradient across the shoreline into the creek under the influence of monsoonal runoff during July-August followed by a steep increase to the premonsoon levels with the withdrawal of monsoon after September (Zingde and Desai, 1980). The salinities recorded during the present investigation at stations 1 to 3 agreed well (Table 1) with those reported earlier. Although the bay receiving low saline waste, drained water of lower salinity into the sea during ebb, its influence was not evident beyond station 3. This can be explained on the basis of the circulation pattern in the area. During flood, the seawater ingress in the bay is preferentially from the north-east while the water largely ebbs along south-east (NIO, 1978). Hence, the water leaving the bay during ebb would tend to move in the south-east direction and not directly across the coast to influence the salinities at stations 1 and 2. However, as the coastal circulation is elliptical (Major and minor axes of the ellipse varying from 5 to 6 km and

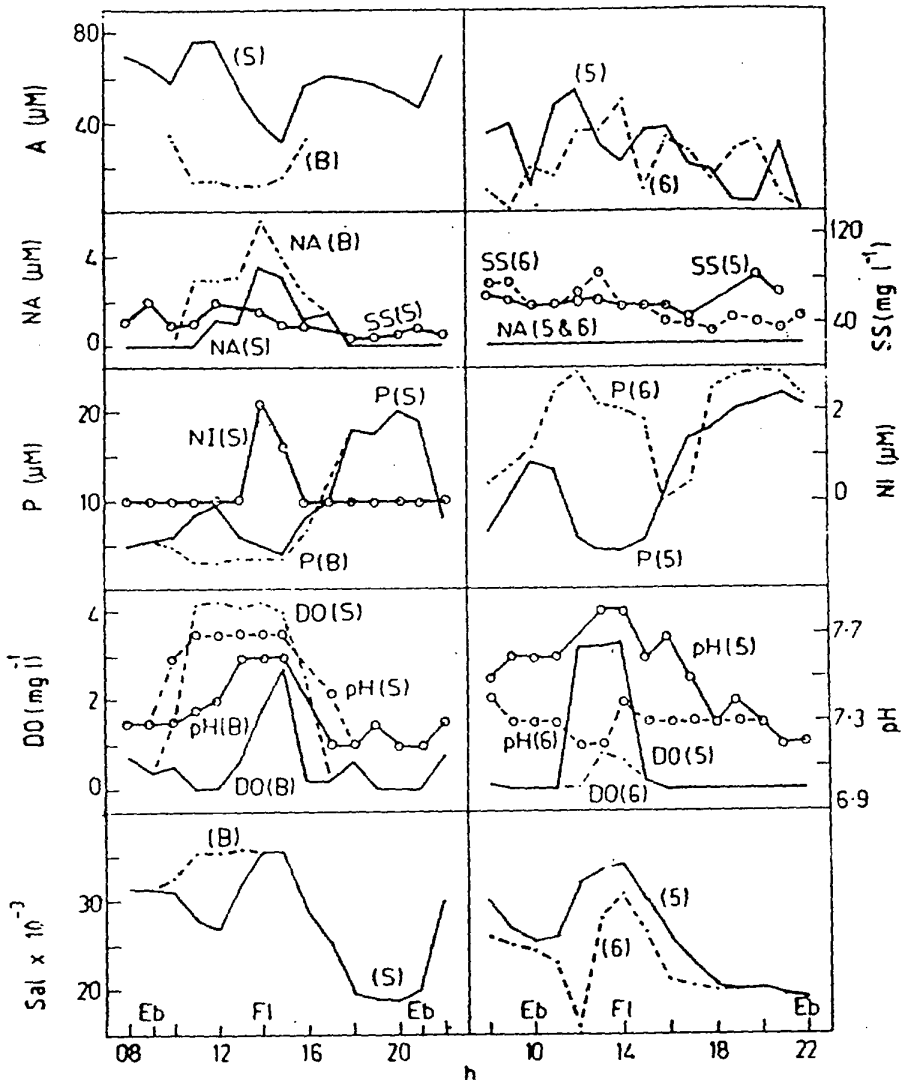


Fig. 3: Hourly variation of water quality at stations 4, 5 and 6 on 4 Jan 1980 (near spring). Only surface values are represented for stations 5 and 6. NA =  $\text{NO}_3^-$ -N; NI =  $\text{NO}_2^-$ -N; P =  $\text{PO}_4^{3-}$ -P; SS = suspended solids; S = surface; B = bottom.

0.5 to 2 km respectively), a contaminant leaving the bay can influence the water quality at coastal stations though the impact would be considerably



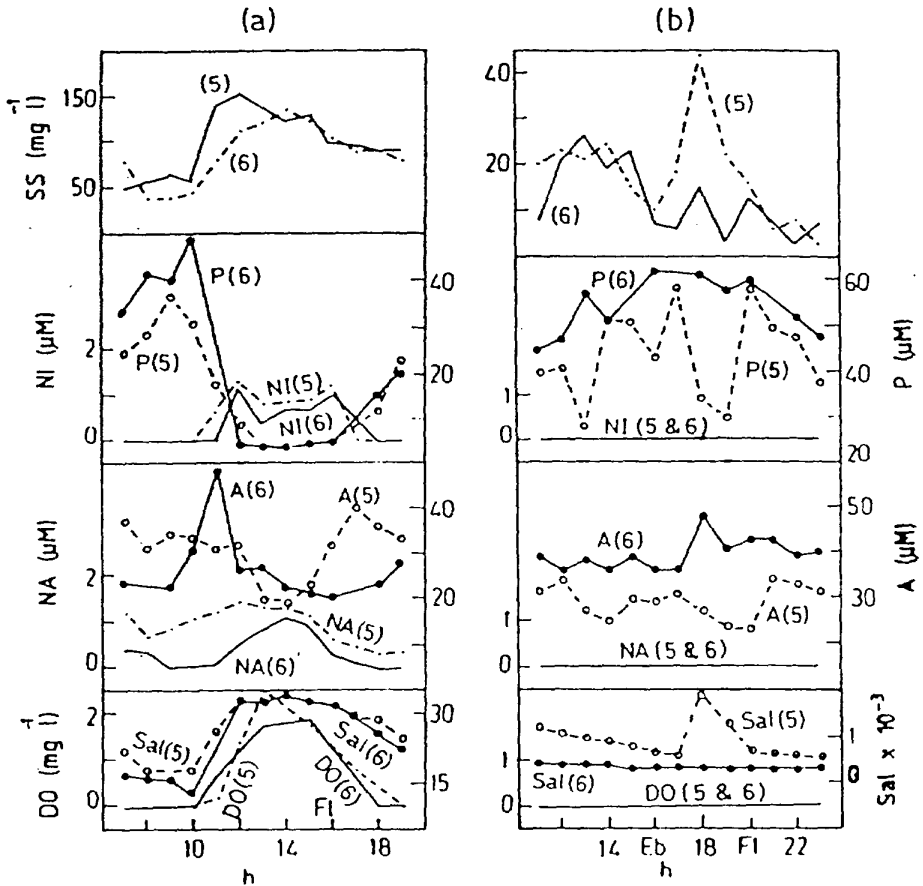


Fig. 4: Hourly variation of water quality at stations 5 and 6 on (a) 25 Sep 1980 (spring) and (b) 18 Sep 1980 (neap); NA =  $\text{NO}_3^-$ -N; NI =  $\text{NO}_2^-$ -N; A =  $\text{NH}_4^+$ -N; P =  $\text{PO}_4^{3-}$ -P.

reduced because of dilution. Station 3 being at the mouth of the bay however showed fluctuating salinities. Thus for instance, on 19th Feb 1981, the high tide salinity of  $35.5 \times 10^{-3}$  decreased to  $33.6 \times 10^{-3}$  around the low tide (Fig. 2) although vertical gradient was negligible throughout the tide cycle.

The volume of spring tidal prism upstream of station 5 was estimated at  $6.89 \times 10^5 \text{ m}^3$ . Hence,  $6.89 \times 10^5 \text{ m}^3$  of contaminated seawater with an average salinity of  $31.6 \times 10^{-3}$  drained into the bay during ebb (Sabnis

and Zingde, 1989). Using the bathymetry reported by Sabnis (1984) the spring low and high tide volumes of the bay were estimated at  $7.7 \times 10^6$   $m^3$  and  $60.2 \times 10^6$   $m^3$ , respectively. If complete mixing was achieved in the bay, the salinity would be around  $35.3 \times 10^{-3}$ , marginally lower than the salinity of seawater ( $35.5 \times 10^{-3}$ ) ingressing into the bay during flood tide. Wide temporal variations in salinity at station 4 from  $36 \times 10^{-3}$  at high tide to  $19 \times 10^{-3}$  during low tide (Fig. 3) however indicated that the mixing was considerably hindered. The incomplete mixing of high saline bay water and low saline estuary water favoured intermittent stratification during certain part of the tidal cycle. It could therefore be presumed that the contaminated low saline estuary water retained its signature in the bay prior to its removal to the sea. Significant temporal variation in salinity also occurred at stations 5 and 6 with markedly lower salinities at station 6 (Fig. 3) as expected because of its proximity to the wastewater release location. With more or less constant wastewater flow during the dry season, salinities within the estuary were dependent on the quantum of seawater ingressing during flood tide. Hence, as evident from Fig. 4 though salinities of  $15 \times 10^{-3}$  -  $31 \times 10^{-3}$  prevailed during spring tide, during neap tide the salinities seldom exceeded  $1 \times 10^{-3}$ . Hence, with the lack of riverine freshwater flow during dry season, the wastewater fraction in the estuary could be estimated from the relation

$$f = \frac{S_o - S}{S_o}$$

where  $f$  = fraction of wastewater

$S_o$  = salinity of seawater entering the estuary

and  $S$  = salinity of water in the estuary.

The wastewater fraction calculated with average salinities of  $24.6 \times 10^{-3}$  and  $0.4 \times 10^{-3}$  during spring and neap tides respectively (Fig. 4), increased from 0.3 during spring to 0.98 during neap tide. Hence, severe pollution conditions were expected in the estuary as the neap approached. Even during monsoon when the riverine flow was  $85 \text{ m}^3 \text{ sec}^{-1}$  (Sabnis, 1984), the salinities within the estuary were largely dependent on the tidal phase, though maximum salinity during spring tide was below  $20 \times 10^{-3}$  (Fig. 5). Considerable seawater influence in the estuary was also evident during August (Fig. 6).

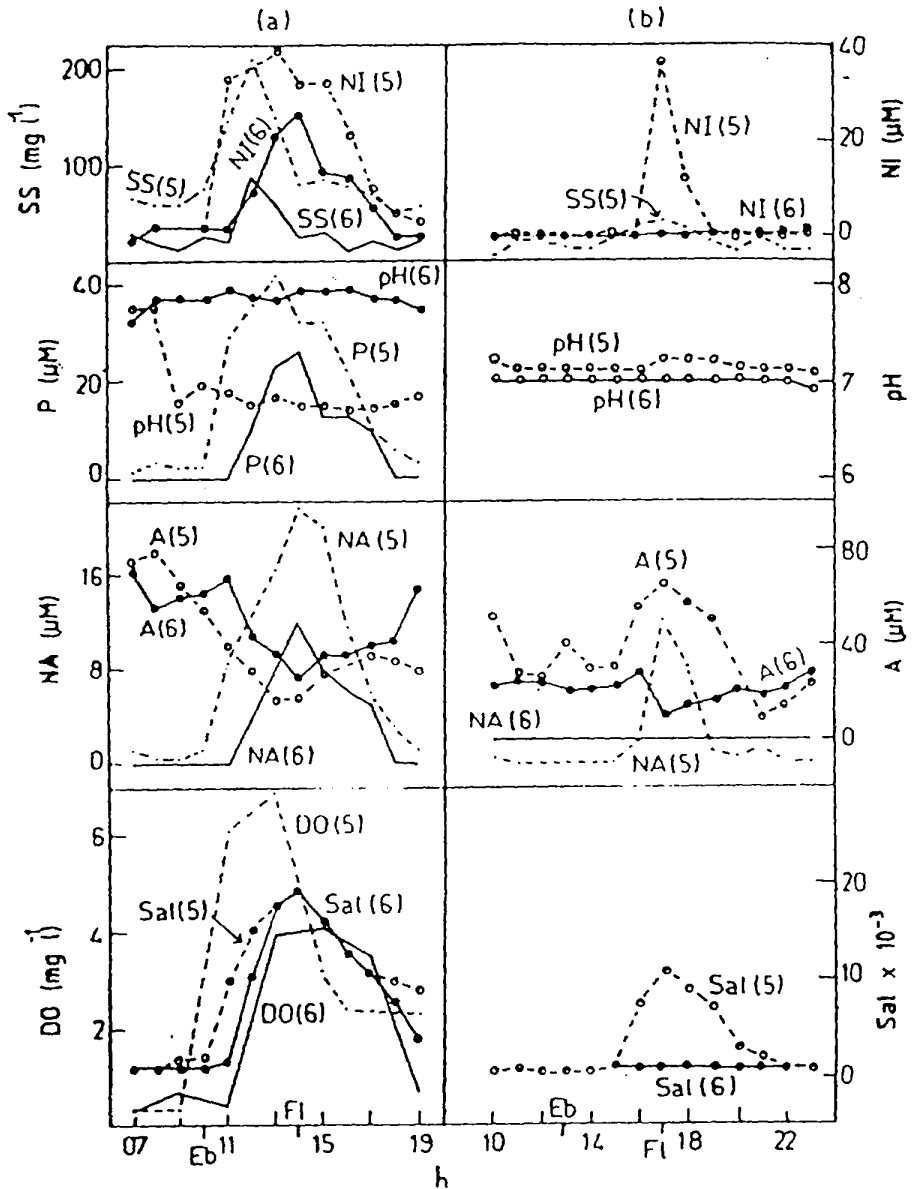


Fig. 5: Hourly variation of water quality at stations 5 and 6 on (a) 29 July 1980 (spring) and (b) 21 July 1980. NA = NO<sub>3</sub><sup>-</sup>-N; NI = NO<sub>2</sub><sup>-</sup>-N; A = NH<sub>4</sub><sup>+</sup>-N; P = PO<sub>4</sub><sup>3-</sup>-P; SS = suspended solids. DO was below detection at both stations on 21 July 1980.

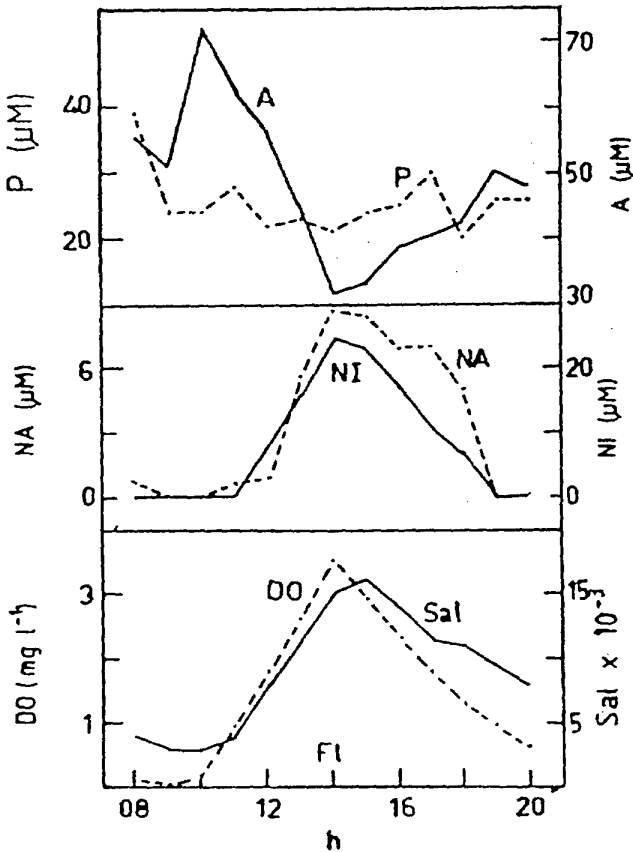


Fig. 6: Hourly variation of water quality at station 5 on 29 Aug 1980. NA= $\text{NO}_3^-$ -N; NI =  $\text{NO}_2^-$ -N; A =  $\text{NH}_4^+$ -N; P =  $\text{PO}_4^{3-}$ -P;

### Suspended solids

The SS varied randomly in a relatively narrow range of 42 to 112  $\text{mg l}^{-1}$  (Table 1) in the coastal water and was largely derived from the tidal dispersion of fine grained bed material in the water column. The concentrations in the bay were also of the same order (Fig. 7). Almost 43 t of SS entered the estuary every day from the domestic waste alone. A substantial portion of this load was deposited within the estuary (Zingde and Desai, 1980). As a result of sedimentation and inputs of materials largely

organic, the overall character of the SS changed along the length of the estuary and the bay. Within the estuary, the SS contained on average 50 per cent inorganic material defined as the fraction which was non-volatile at 600°C. In the bay this fraction increased to around 65 per cent while outside the bay, the inorganic component increased to over 80 per cent.

Tidal variations though not large, a definite tendency of increase during flood tide was evident in the estuary (Figs. 4 and 5).

### pH

The pH of the coastal water varied in 7.6-8.3 range (Table 1) with lower values often at station 3. Temporal variations revealed that the pH at station 3 decreased from 8.0 at high tide to 7.8 at low tide (Fig. 2). This decrease was also accompanied with decrease in salinity as well as DO due to considerable influence of bay water at this location. The tidal dependance of pH was also evident in the bay as well as in the estuary (Fig. 3) though on some occasions the pH remained more or less constant in the estuary particularly during neap tide (Fig. 5). In the absence of riverine flow marked decrease in pH from station 1 to station 8 (Fig. 7) was associated with the influence of wastewater.

The nature of the pH-salinity relationships encountered in the estuary and the bay are illustrated by profiles drawn in Fig. 8. Nearing the seaward boundary of the bay, the pH approached values in the range 7.9-8.2. Low salinity pH values were normally smaller and there was generally a pattern of increasing pH with increasing salinity, although not always in a regular manner.

### Dissolved oxygen

Distribution of DO in the coastal water of Bombay has been investigated in fair details (Zingde *et al.*, 1979). The dissolved oxygen profiles were characterised by maxima in July-August and January-February. The former was associated with the monsoonal influence and the later was due to lower temperature and increase in photosynthetic activity. From Table 1 it is evident that the DO levels off the bay do not conform to above observations which can be due to the variable anthropogenic load of organic

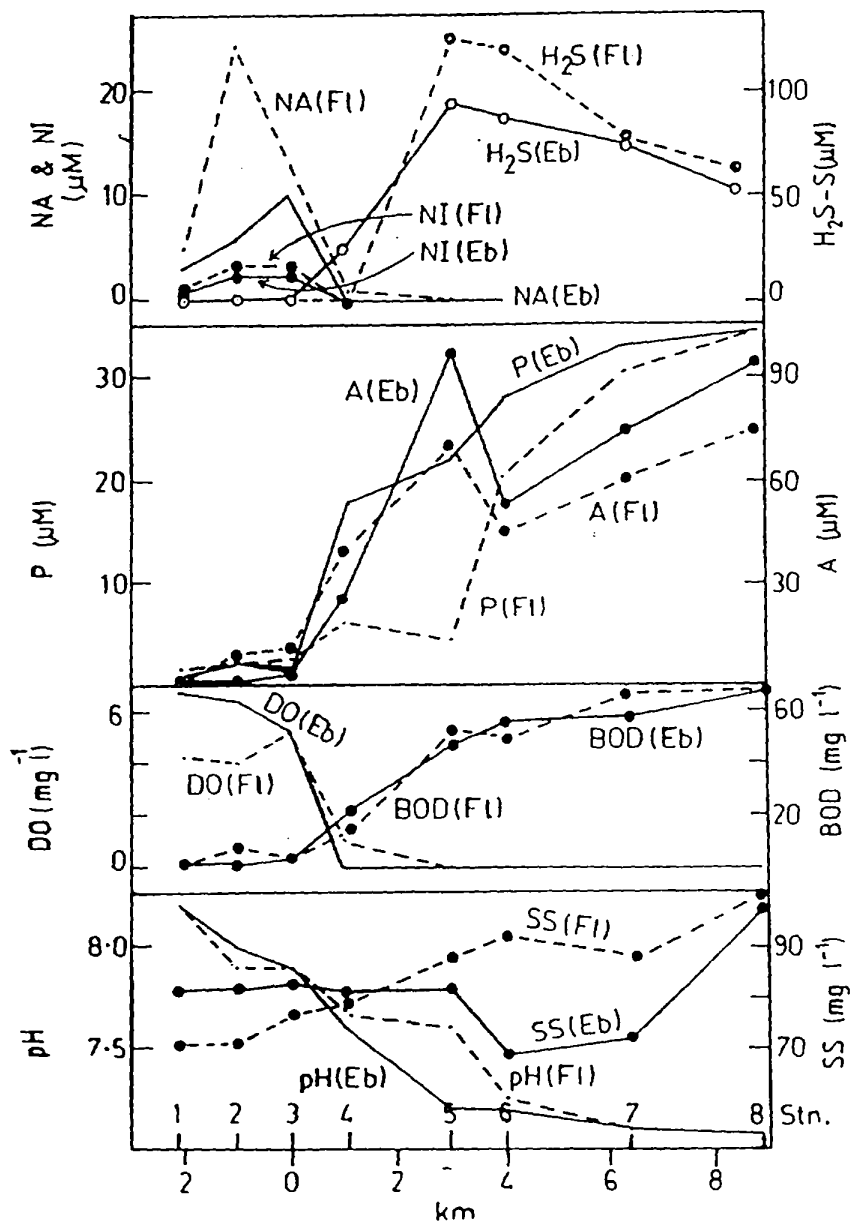


Fig. 7: Variation of water quality with distance during April 1981. NA= $\text{Na}_3\text{-N}$ ; NI =  $\text{NO}_2\text{-N}$ ; A =  $\text{NH}_4\text{-N}$ ; P =  $\text{PO}_4\text{-P}$ ; SS = suspended solids; FI = flood tide; Eb = ebb tide.

matter transported to the coastal water. Under the influence of organic load the average BOD though low ( $2.5 \text{ mg l}^{-1}$ ), varied widely ( $1.5 - 8.5 \text{ mg l}^{-1}$ ) in the coastal water with higher values often confined to station 3 thus affecting DO which was tide dependent decreasing considerably during low tide (Fig. 2). No doubt, the relatively high photosynthetic activity (Varshney, 1982) favoured by high concentrations of nutrients arrested the decrease to critical levels but the DO was generally undersaturated sometimes upto 60 per cent.

The tide dependent fraction of organic-rich wastewater controlled DO in the norther bay which decreased close to the detection limit ( $0.1 \text{ mg l}^{-1}$ ) on several occasions during a tide cycle, at the surface (Fig. 3). With the ingress of coastal water during flood tide, the DO steadily increased attaining maximum around the high tide followed by sudden and steep decrease within an hour of commencement of the ebb tide (Fig. 3). Thus the DO transported into the northern bay was quickly utilized largely for the breakdown of organic matter and partly for the oxidation of ammonia and sulphide. The DO levels were however relatively higher in the southern bay (Table 2) perhaps because of better flushing of this portion of the bay.

High salinity and hence high density coastal water entered the bay preferentially along the bottom as a salt wedge resulting in vertical stratification. Due to the density inhibited mixing, the less saline, low DO and high  $\text{NH}_4^+\text{-N}$  containing bay water formed the surface layer while the high saline, high DO and low  $\text{NH}_4^+\text{-N}$  containing coastal water predominantly remained at the bottom during flood tide (Fig. 3).

Although the bay water entering the estuary during spring flood tide across station 5 had DO of  $2\text{-}3 \text{ mg l}^{-1}$ , considerable reduction in incursion of coastal water in the bay during neap flood resulted in severe depletion of DO in the water entering the estuary (Figs. 3 and 4). The incursion of seawater was upto the station 8 but the DO was consumed within the lower estuary even during spring tide and the segment upstream of station 6 was devoid of DO throughout the dry season revealing the severity of estuary pollution. Evidently, the BOD was variable and abnormally high ( $30\text{-}90 \text{ mg l}^{-1}$ ) in the estuary and decreased considerably in the bay ( $4\text{-}20 \text{ mg l}^{-1}$ ) due to better tidal flushing and relative high rate of aerobic oxidation of organic matter.

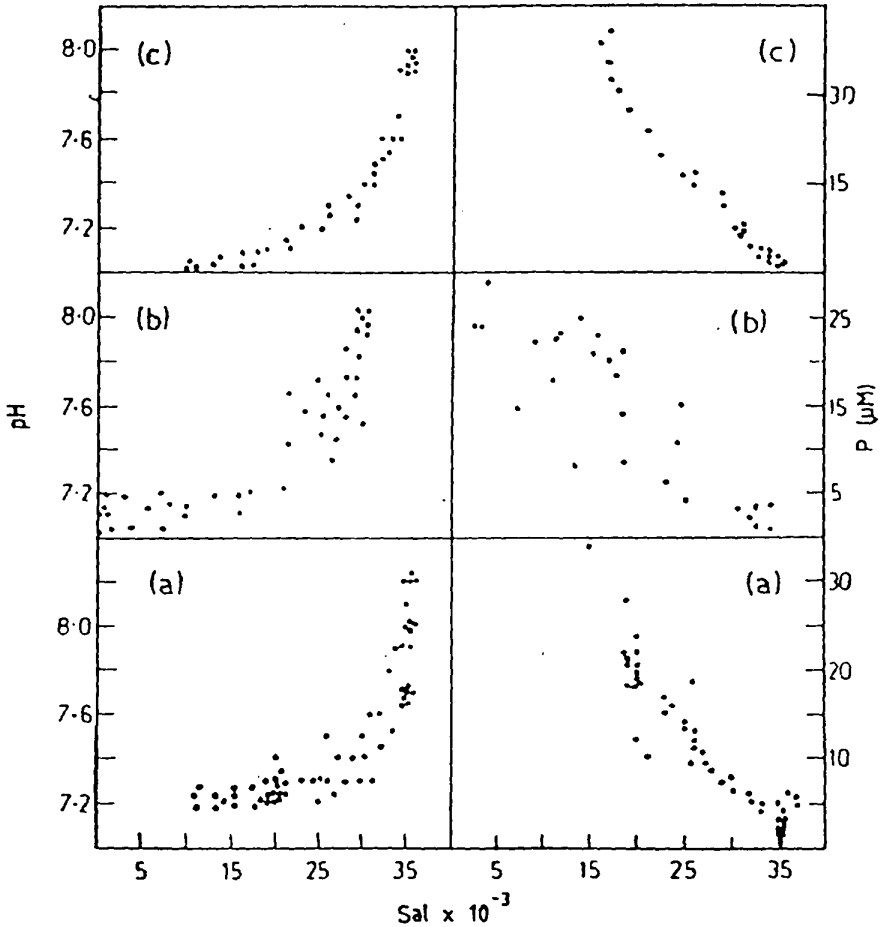


Fig. 8: Variation of pH and  $\text{PO}_4^{3-}\text{-P}$  (Represented as P) with salinity on (a) 4 Jan 1980, (b) 29 July 1980 and (c) 25 Sep 1980.

During monsoon (July-August) when the DO rich runoff drained into the estuary, the DO levels though improved during spring tide (Figs. 5 and 6) the situation was no better during neap tide and the estuary was devoid of DO (Fig. 5). It was therefore apparent that the DO associated with the runoff was quickly consumed and the major source of DO to the estuary was through the ingress of tidal water.



### Nitrate, nitrite and ammonium

Nitrogen occurs in aquatic systems in the oxidation states from -III to +IV. The most important chemical forms are  $\text{NH}_4^+$ , dissolved and particulate organic nitrogen,  $\text{N}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}_2^-$  and  $\text{NO}_3^-$ . Of these only  $\text{NH}_4^+$ ,  $\text{N}_2$  and  $\text{NO}_3^-$  are thermodynamically stable under the pE-pH conditions found in natural waters.

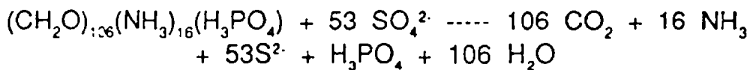
The levels of  $\text{NH}_4^+$ -N,  $\text{NO}_3^-$ -N and  $\text{NO}_2^-$ -N in the coastal water varied considerably (Table 1) though the general trend of increasing concentrations from station 1 to station 3 was maintained. The relative concentrations of  $\text{NH}_4^+$ -N were high particularly at station 3 and were tide variable (Fig. 2) indicating that  $\text{NH}_4^+$ -N was not fully oxidised in the bay but was partly transported to the coastal water.

Within the bay as well as in the estuary, the concentrations of  $\text{NH}_4^+$ -N were abnormally high (20-80  $\mu\text{M}$ ) with a general tendency to decrease during high tide (Figs 3, 4 and 6). The  $\text{NO}_3^-$ -N and  $\text{NO}_2^-$ -N concentrations were on the contrary very low and often decreased to zero specially during neap tide. This behaviour of  $\text{NH}_4^+$ -N,  $\text{NO}_3^-$ -N and  $\text{NO}_2^-$ -N could be explained on the basis of general mechanism of decomposition of organic matter. The simplest plausible model of organic diagenesis is one in which marine organic matter having the Redfield composition  $[(\text{CH}_2\text{O})_{106} (\text{NH}_3)_{16} (\text{H}_3\text{PO}_4)]$  is oxidised by the oxidant yielding greatest free energy change per mole of organic carbon oxidised. When this oxidant is depleted, oxidation proceeds utilizing the next most efficient oxidant and so on until either all oxidants are consumed or oxidizable organic matter is depleted. The electron acceptors responsible for oxidation of organic matter in the marine environment are  $\text{O}_2$ ,  $\text{NO}_3^-$ ,  $\text{MnO}_2$ ,  $\text{Fe}^{3+}$ ,  $\text{SO}_4^{2-}$  and  $\text{CO}_2$  in the decreasing order of their preference. The domestic waste released in the estuary was rich in dissolved organic matter (DOM) as well as particulate organic matter (POM). Although DOM would be mostly oxidised in the water column, POM would primarily settle on the bed and broken down in sediments. Due to the anoxic conditions prevailing in the estuary, a considerable fraction of the organic matter would be transported to the bay. From the bathymetry and the current speeds reported by Sabnis (1984) the water entering the bay during neap flood tide was roughly estimated at  $37 \times 10^6 \text{ m}^3$ . This water with an average DO content of  $5 \text{ mg l}^{-1}$  during April (Table 1) would transport  $1.49 \times 10^6$

kg of DO into the bay during flood tide which if efficient mixing had occurred would be sufficient to assimilate 22.5 t of BOD released in the estuary per tide cycle. However due to density inhibited mixing, the contaminated creek water tended to retain its identity because of which the northern portion of the bay had distinct deterioration of water quality as compared to the southern part of the bay. As the estuary opened at the northern bay, the water contained in the bay during low tide was pushed into the estuary during flooding. As the DO transported into the northern bay was quickly consumed the redox potential would be driven low enough to favour the next most efficient oxidant, i.e. nitrate which was also completely consumed at station 4. At station 4a in the southern bay on the contrary the oxidation of organic matter was largely by DO which was relatively high (Table 2) accompanied with high concentration of  $\text{NO}_3^-$ -N.

The aerobic oxidation of organic matter in the estuary during spring tide in monsoon (Figs 5 and 6) resulted in high concentrations of  $\text{NO}_3^-$ -N and  $\text{NO}_2^-$ -N in the estuary with  $\text{NO}_2^-$ -N often exceeding  $\text{NO}_3^-$ -N. It was possible that the conditions in the estuary were conducive for the growth of *Nitrosomonas* sp. which oxidise ammonia to nitrite. Preferential growth of *Nitrosomonas* sp under certain circumstances leading to the accumulation of nitrite has been reported in several instances (Richards, 1971). The correlation between  $\text{NO}_3^-$ -N and  $\text{NO}_2^-$ -N was fairly good as evident from Fig. 9. The Figs. 5 and 6 also revealed considerable denitrification occurring in the estuary particularly during neap tide even during monsoon.

In the absence of DO, nitrate and nitrite, the oxidation of organic matter in the estuary would primarily proceed through the utilization of sulphate which is abundantly available in seawater, via reaction of the type.



which results in the liberation of sulphide and ammonia in the stoichiometric ratio of 3.31. The sulphide in the estuary varied in 50-125  $\mu\text{M}$  range with a mean of 84  $\mu\text{M}$ . The corresponding range for  $\text{NH}_4^+$ -N was 44-101  $\mu\text{M}$  with a mean of 80  $\mu\text{M}$  (Fig. 7). The molar ratio  $\text{S}^{2-}$  to  $\text{NH}_3$  varied widely from 0.6 to 2 with a mean of 1. Wide variation in the ratio could result from the arial oxidation of  $\text{S}^{2-}$  to elemental sulphur or from its loss to the atmosphere.

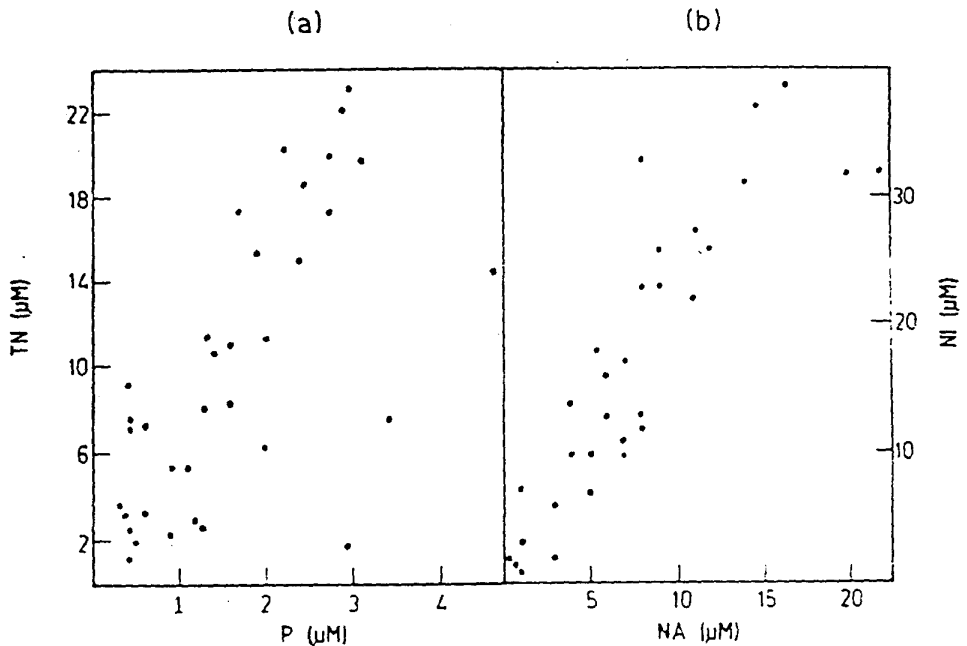


Fig. 9: Variation of (a)  $\text{PO}_4^{3-}\text{-P}$  (Represented as P) with TN ( $\text{NO}_3^- \text{-N} + \text{NO}_2^- \text{-N} + \text{NH}_4^+ \text{-N}$ ) in the coastal water and (b)  $\text{NO}_3^- \text{-N}$  with  $\text{NO}_2^- \text{-N}$  (Represented as NA and NI respectively) in the Mahim estuary during July-Aug 1980.

The loss of ammonia to the atmosphere was unlikely at the prevailing low pH of the estuary, the conditions under which ammonia would exist in ionised form as  $\text{NH}_4^+$ . Presuming that  $\text{S}^{2-}$  and  $\text{NH}_3$  were produced in the stoichiometric ratio of 3.31 via above type of reaction the  $\text{S}^{2-}$  deficit was estimated at 5.2 t at mean  $\text{NH}_4^+$  concentration of  $80\mu\text{M}$  in the estuary.

The sulphide transported into the bay was quickly oxidised by DO during flood tide. Evidently,  $\text{S}^{2-}$  was not detected in the bay water, though lower concentrations ( $25\mu\text{M}$ ) were measured during low tide when DO and nitrate were completely consumed (Fig. 7).

During spring flood tide,  $6.89 \times 10^5 \text{ m}^3$  of bay water with an average DO content of  $1.5 \text{ mg l}^{-1}$  transported about 1 t of DO into the estuary which would at the most oxidise 0.8 t of organic matter. Actual organic matter oxidised could be considerably less since the DO would be quickly

consumed for the oxidation of  $S^{2-}$ . Likewise the organic matter oxidised through the utilization of nitrate and nitrite would be negligible in view of the low nitrate and nitrite contents of water.

### Phosphate

Concentration of  $PO_4^{3-}$ -P in the coastal water varied considerably though general decrease from station 3 to station 1 was maintained. The temporal changes in the concentration at station 3 ranged from as low as  $1 \mu M$  to as high as  $7 \mu M$  around the low tide under the influence of the polluted bay water (Fig. 2). The N:P ratio calculated adding the concentrations of  $NO_3^-$ -N,  $NO_2^-$ -N and  $NH_4^+$ -N (Represented as TN in Table 1) varied considerably and was generally lower than the Redfield value (1:16) except during September (Table 1). Although the concentrations of  $NO_3^-$ -N,  $NO_2^-$ -N and  $NH_4^+$ -N were of the same order as observed during previous months, the concentration of  $PO_4^{3-}$ -P decreased leading to enhanced N:P ratios. Combined concentrations of  $NO_3^-$ -N,  $NO_2^-$ -N and  $NH_4^+$ -N are plotted as a function of the concentration of soluble  $PO_4^{3-}$ -P in Fig. 9. The relation was fair with a correlation coefficient of 0.75. The low N:P ratio did not appear to be due to the influence of wastewater as the waters of the central west coast of India generally exhibit lower N:P ratios.

The  $1.6 \times 10^5 m^3 day^{-1}$  of domestic wastewater entering the estuary, was a major source of  $PO_4^{3-}$ -P in the receiving water. The concentrations of  $PO_4^{3-}$ -P were abnormally high often attaining maxima during low tides similar to the levels of  $NH_4^+$ -N. The N:P ratios however were markedly low and varied widely. Thus for instance for the data in Fig. 3, the ratio varied from 0.1 to 14.2 with a general tendency of decrease from station 4 to station 6. The total N and total P content of sewage entering the estuary was 35 and 6  $mg l^{-1}$  respectively with N:P molar ratio of 13.1 (Sabnis, 1984). The possible reason for low ratio could be that the phosphorus in sewage is mineralised to inorganic phosphate quicker than nitrogen and hence not measured fully as ammonia. Part of the nitrogen would also be lost to the atmosphere during nitrate diagenesis.

As the domestic wastewater was a major source of  $PO_4^{3-}$ -P to the estuary, mixing of low saline, high phosphate estuary water and high saline,

low phosphate seawater resulted in intermediate concentrations with often linear relationships between  $\text{PO}_4^{3-}\text{-P}$  and salinity (Fig. 8).

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