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Petroleum hydrocarbons and trace metals in Visakhapatnam harbour and Kakinada Bay, east coast of India

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High concentrations of PHC were observed in the inner channels (viz., South lighter canal, Northern arm, North western arm and Western arm) of Visakhapatnam harbour. The estimation of trace metals (Cu, Zn, Pb, Cd, Co, Ni and Cr) in surficial sediments indicated higher contamination in Visakhapatnam harbour than in Kakinada Bay. Positive correlations between Cu, Zn, Pb and Cd suggests common sources of these metals. Lack of correlation between Co, Ni with the other metals indicates point sources. High concentrations of chromium reflects intense discharges due to electroplating and battery operations.

Several reports are available on hydrography[1] and various aspects of pollution[2-7] in the Visakhapatnam harbour and coastal waters. However, no such reports have been made in Kakinada Bay. The present study consists the status of pollution through studies on petroleum hydrocarbons and trace metals in Visakhapatnam harbour and Kakinada Bay waters.

Surface waters and surficial sediments were collected thrice viz., in March '93, in October '93 and in March '94 from seven stations in Visakhapatnam harbour and five stations in Kakinada Bay (Fig. 1). Petroleum hydrocarbons (PHC) were determined UV Spectrophotometrically[8] after extracting an aliquot (1 l) of water sample with *n*-hexane. Trace metals were estimated after digesting the sediment samples with a mixture of hydrofluoric acid and aqua regia and using atomic absorption spectrophotometric method[9]. The coefficient of variation for Pb, Cd, Zn, Cu, Co, Ni and Cr were 2.0, 0.7, 0.6, 0.77, 0.67, 0.53 and 1.2 respectively.

Petroleum hydrocarbons in surface waters—Petroleum hydrocarbon (PHC) concentrations in different channels of Visakhapatnam harbour and Kakinada Bay are presented in Table 1. Average PHC concentrations varied between 11.5 and 123.8 $\mu g.l^{-1}$ in different channels of Visakhapatnam harbour and between 1.6 and 14.8 $\mu g.l^{-1}$ in different stations of Kakinada Bay. Low concentrations of PHC observed in the entrance channel (12.9 $\mu g.l^{-1}$); fishing harbour (11.5 $\mu g.l^{-1}$) of Visakhapatnam harbour and Kakinada

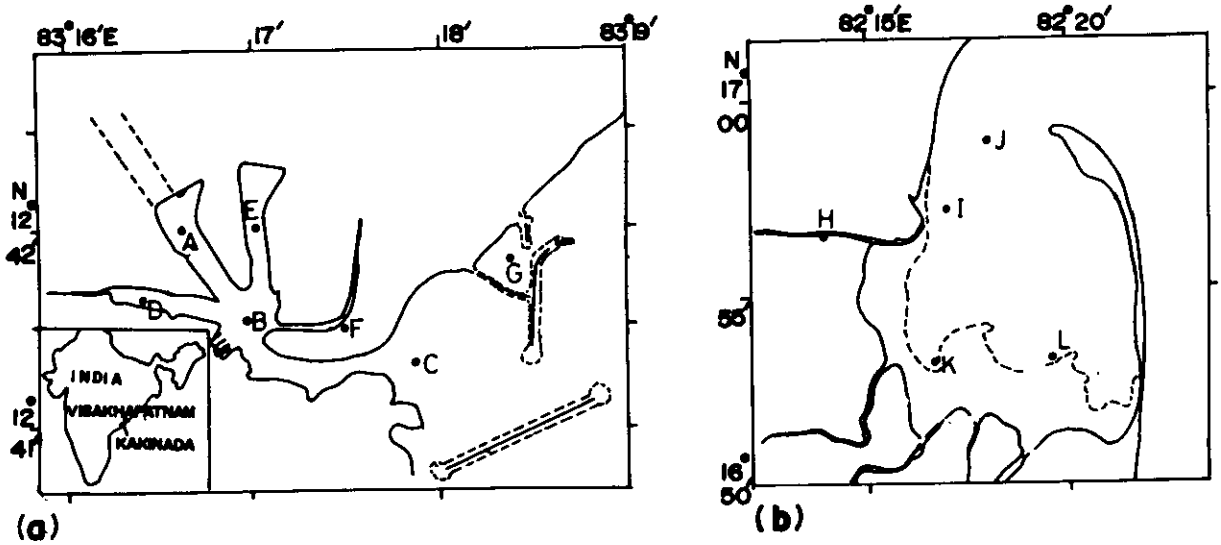

Fig. 1—Station location map (a) Visakhapatnam harbour | (b) Kakinada Bay

Bay (1.6-14.8 $\mu g.l^{-1}$) in all the stations revealed no oil pollution in these regimes. Concentrations of PHC were high along western arm (128 $\mu g.l^{-1}$); south lighter canal (48.1 $\mu g.l^{-1}$); north western arm (33.6 $\mu g.l^{-1}$) and northern arm (38.9 $\mu g.l^{-1}$) of Visakhapatnam harbour. Urban run off enriched with heavy oils such as lubricating oils and polycyclic hydrocarbons might be responsible for this hydrocarbon pollution[10,11]. The range of PHC during October, 1993 in the inner channels (2.0-28.9 $\mu g.l^{-1}$) of Visakhapatnam harbour indicated the dilution effect because of monsoonal run off from Meghadrigadda into these harbour waters. High concentrations of PHC during March, 1993 and March, 1994 (premonsoon season) revealed stagnant conditions as reported by Sarma *et al.*[2].

Trace metals in surficial sediments—The average concentrations of trace metals (Pb, Zn, Co, Cu, Ni, Cd and Cr) in surficial sediments of Visakhapatnam harbour and Kakinada Bay are given in Table 2. Increased levels of metals (Pb, Zn, Cr and Cd) in the inner channels (sts A, D and F) of Visakhapatnam habour indicate the influence of industrial discharges, shipping activities and sewage respectively. Lu & Chen[12] have shown that Cd, Cu, Ni, Pb and Zn became relatively static under reducing conditions because of increased organic load and hence accumulated in the sediment. Thus the industrial complex consisting of fertiliser, refinery, smelters, etc., discharging their effluents through monsoon run off via Meghadrigadda to this harbour channels might be responsible for the accumulation of heavy metals in sediments. Further, the reduced flushing in Visakhapatnam harbour[2] may increase the organic load, leading to settlement of particles in the bottom. High concentrations of zinc in the harbour channels (231-328 $\mu g.gm^{-1}$) may be due to increased harbour and port activities and also due to adsorption onto ferromanganese oxides precipitated in sediment. Further, organic matter in anoxic sediments in the presence of sulphide ions is a concentrated source of heavy metals (Zn, Cd, Pb and Cu)[13]. Cr showed high concentrations in the entire study region (67-245 $\mu g.gm^{-1}$). It may be due to the electropolating work and battery operations through Visakhapatnam harbour and Kakinada port activities.

Correlation matrix Correlation matrix for all trace metals calculated with the data (N = 36) of three collections are given in Table 3. The positive significant correlations between Pb, Cu, Zn and Cd indicated the enrichment of these metals and adsorption onto ferromanganese oxides precipitated in the sediment. However, Co and Ni do not correlate with any other metal indicating discrete sources. Positive correlations between Cr and Co, Ni and Cu show that these metals are discharged from common source probably through electroplating and port operations. The hydroxides and hydroxy complexes of Cr in seawater formed as filaments on shelly materials[14] and this negatively charged chromium hydroxides act as cation adsorbers[15]. Thus high correlation between Cr and Co, Ni may also be due to the adsorption capacity of chromium hydroxide for Co and Ni.

Pollution indices Pollution Load Index (PLI) as proposed by Tomlinson[16] was evaluated and presented in Table 2. South lighter canal, western arm and

Table 1—Petroleum hydrocarbon concentrations ($\mu g.l^{-1}$) in surface waters

Station	March '93	October '93	March '94	Mean	SD
Visakhapatnam harbour					
North western arm (A)	38.6	14.2	48.0	33.6	17.4
Turning basin (B)	13.0	28.9	22.4	21.4	8.0
Entrance channel (C)	10.8	10.9	17.0	12.9	3.5
Western arm (D)	123.2	24.3	224.0	123.8	99.8
Northern arm (E)	64.1	10.3	27.3	33.9	27.5
South lighter canal (F)	100.2	22.0	22.0	48.1	45.1
Fishing harbour (G)	15.0	2.0	17.6	11.5	8.4
Kakinada Bay					
Kakinada canal (H)	24.3	9.6	10.5	14.8	8.2
Opp. Nagarjuna Fertiliser Park (I)	2.3	1.0	2.0	1.8	0.7
Fishing harbour (J)	3.0	1.0	1.2	1.7	1.1
Coringa (K)	2.3	1.0	1.5	1.6	0.7
Gaderu (L)	5.0	1.0	2.0	2.7	2.1

SD—Standard deviation.

Table 2—Average metal concentrations ($\mu g.gm^{-1}$) in surficial sediments

Station	Cd	Pb	Zn	Co	Cu	Ni	Cr	PLI*
Visakhapatnam harbour								
North western arm (A)	36	199	270	40	72	60	122	4.64
Turning basin (B)	28	180	231	37	76	60	109	4.25
Entrance channel (C)	13	86	172	31	30	33	81	2.37
Western arm (D)	42	288	321	38	89	53	103	5.25
Northern arm (E)	6	119	323	30	71	44	106	2.95
South lighter canal (F)	38	236	328	30	79	63	245	4.87
Fishing harbour (G)	7	104	160	40	51	56	111	2.71
Kakinada Bay								
Kakinada canal (H)	14	113	82	41	73	63	67	3.01
Opp. Nagarjuna Fertilizers Park (I)	7	86	65	51	73	65	124	2.56
Fishing harbour (J)	5	61	67	48	71	66	117	2.27
Coringa (K)	5	58	64	52	80	65	121	2.31
Gaderu (L)	5	66	70	55	68	58	136	2.31

*PLI values excluding Cr.

Table 3—Correlation matrix among trace metals (N = 36)

	Pb	Zn	Co	Cu	Ni	Cr	Cd
Pb	1.00	0.64	−0.41	0.64	−0.10	−0.08	0.78
Zn	—	1.00	−0.61	0.52	−0.24	0.01	0.36
Co	—	—	1.00	−0.10	0.70	0.41	0.58
Cu	—	—	—	1.00	0.26	0.32	0.25
Ni	—	—	—	—	1.00	0.58	0.24
Cr	—	—	—	—	—	1.00	−0.21
Cd	—	—	—	—	—	—	1.00

north western arm to be heavily polluted (PLI values >4.5). Because of stagnation of the harbour waters and combined effects of discharges, turning basin (Stn. B) is also considered to be polluted zone (PLI = 4.25). Northern arm, entrance channel and fishing harbour of Visakhapatnam harbour and Kakinada Bay (PLI ranged between 2.0 and 3.0) are moderately polluted zones.

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