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Environment degradation by chemical effluents along the Kayalpatinam coast of Gulf of Mannar with special reference to mercury

*P. S. Asha, M. Selvaraj and K. Diwakar

*Tuticorin Research Centre of CMFRI, South Beach Road, Karapad, Tuticorin – 628 001, Tamil Nadu, India. *E-mail: ashasanil@gmail.com*

Abstract

Studies were carried out on the level of mercury and other water quality parameters in the effluent lagoon of Dharangadhara Chemical Works, Tuticorin and the adjacent open sea over a period of three years and the impact of effluent discharge in bulk quantity into the coastal marine environment, over a distance of 18 km. The present study indicated that the presence of mercury, acidity and low oxygen concentration are the major impacts of effluent discharge. The mean concentration of mercury in the open sea during 1999 – 2002, was 4.7 µg. l^{-1} which got reduced to 1.68 µg. l^{-1} after five years, indicating the improvement of effluent treatment measures. However the mercury levels are still higher compared to those reported elsewhere. Except for salinity and pH, no statistically significant difference was observed in the variation of other parameters between stations during 1999-2002, but highly significant differences were observed in the variation of dissolved oxygen, chlorophyll, pH and salinity between stations during 2007-2008.

Keywords: Mercury, effluent discharge, acidity

Introduction

Mercury is a potential toxin even at extremely low levels in aquatic environment. Thermal power plants, steel industries and cement plants are the major sources of mercury pollution in India (Lenk *et al.*, 1992). Investigations have been carried out on mercury pollution in the Indian waters (Patel and Chandy, 1988; Sivadasan and Nambisan, 1988; Krishnakumar *et al.*, 1990; Marichamy *et al.*, 1995; Kaladharan *et al.*, 1999).

In Kayalpatinam, Tuticorin the Dharangadhara Chemical Works Ltd. (DCW) is a major industrial complex which produces a variety of chemicals such as caustic soda, liquid chlorine, HCl, trichloroethylene, polychloroethylene, beneficiated elmenite and vinyl chloride monomer (Easterson, 1996). The effluent discharge from this plant is yellowish-brown in colour, which flows towards the southern side due to prevailing current when the industry lets out the lagooned effluent into the sea. Discoloration of coastal waters in this area could be noticed due to the discharge during the peak of northeast monsoon. Pollution and related fish mortality have been reported during this industrial discharge in and around Kayalpatinam coast in 1982, 1983, 1986, 1987 and 1989 (Kasim *et al.*,1991).

Acidity and high concentration of mercury have been detected in the effluents of DCW (Kasim *et al.*, 1991; Marichamy *et al.*, 1995). However recent data are not available on the current level of mercury contamination in this area. This paper summarizes the data on hydrological parameters and concentration of mercury in the effluent lagoon and the adjacent open sea during the period 1999 - 2002 and compares with the impact of effluent discharge, associated with monsoon over a distance of 18 km in the coastal waters for one year during December 2007 – December 2008.

Material and Methods

Water samples were collected once in a month for analyzing parameters like temperature, pH, dissolved oxygen and mercury from three stations during the years 1999 - 2002. Station 1 (8^{0} 35′654″

Fig. 1. Open sea area where the effluent from DCW joins the sea (station 1)

N lat.; 78^0 08′201″ E long.) is open sea area where the effluent water joins the sea (Fig.1). Station 2 (8^0 35′638″ N lat.; 78^0 08′165″ E long.) is the lagoon of DCW, which is about 3 km long and 1 km wide, protected by a bund nearer to the open sea. To study the impact of effluent discharge in bulk, for the period from December 2007 to December 2008, monthly water sampling and analysis of parameters like temperature, pH, dissolved oxygen, mercury, carbon dioxide, chlorophyll and total suspended solids were carried out from six stations *i.e.*, the first two stations 1 and 2 were covered during 1999-2002; station 3 (8^0 34′984″ N lat.; 78^0 06′121″ E long.) is a part of the lagoon on the opposite side of station 2, where pumping of saline water from the backwaters was continued for reducing the effect of pollution; station 4 (8^0 34′838″ N lat.; 78^0 08′244″ E long.) was one km away from station 2; station 5 (8^0 30′958″ N lat.; 78^0 07′370″ E long.) was eight km away from station 4; station 6 (8^0 29′668″ N lat.; 78^0 07′730″ E long.) was three km away from station 5, where the pilgrims visit the Thiruchendoor temple to take sea bath; and station 7 (8^0 27′917″ N lat.; 78^0 06′078″ E long.) was 6 km away from station 6. The station locations are shown in Fig. 2.

In situ measurements of air and water temperatures were made using a high precision thermometer. The water quality parameters namely salinity, dissolved oxygen, pH, productivity, total suspended solid concentration (TSS) and chlorophyll were determined following the standard procedures

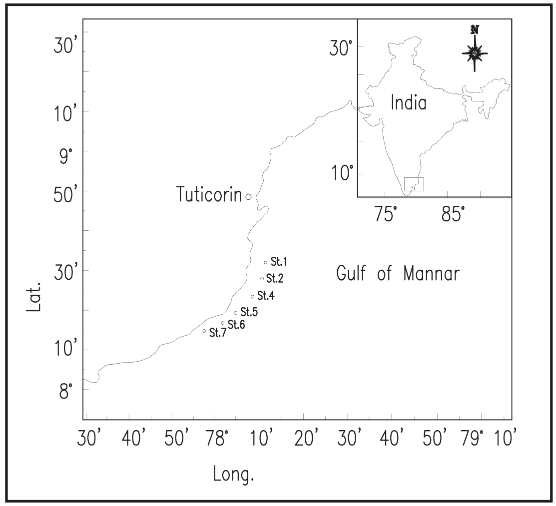

Fig. 2. Map showing location of sampling stations in the year 2007-08 (Station 3 is not part of the coastal area)

(Strickland and Parson, 1968). Carbon dioxide concentration was estimated by acid - base titrimetry method (Dickson, 1998), mercury by ECIL mercury analyser (model Ma 5800 E) after a pre-concentration step for seawater by cold vapour method with sensitivity at one nanogram level. The accuracy of estimation was tested with standard techniques using known value of mercury. The mean values of all parameters were used for statistical analysis to test one way analysis of variance (ANOVA) using SPSS 7.5 statistical package.

Results and Discussion

Mean values of mercury concentration and hydrological parameters obtained during 1999-2002 are given in Table 1 and the mean values of water quality parameters including mercury concentration along the coastal areas during December 2007-2008 are given in Table 2.

No variations in the air and water temperatures of three stations were noticed during the period 1999-2002 and among the six stations during 2007-2008, which confirm the absence of thermal pollution caused by the effluent discharge. Wide fluctuation was noticed in the dissolved oxygen concentration in three stations and the DO was comparatively low in the lagoon water. The impact of effluent discharge

Table 1. Mercury concentration and hydrological parameters (mean ± S.E., n = 216) at three stations during 1999 - 2002

Year	Station	Hg (μg. l^{-1})	Air temp (ºC)	SST (ºC)	Salinity (ppt)	pH	D.O (ml. l^{-1})
1999	1	4.63 ± 2.50	30.3 ± 0.99	27.8 ± 0.60	34.2 ± 1.61	8.26 ± 0.07	3.16 ± 0.36
"	2	20.5 ± 7.31	30.6 ± 0.94	28.7 ± 0.25	50.9 ± 11.1	6.60 ± 0.62	2.75 ± 0.35
"	3	16.9 ± 5.75	30.9 ± 0.84	29.7 ± 0.63	45.5 ± 5.13	7.02 ± 0.49	2.78 ± 0.52
2000	1	3.46 ± 0.77	28.9 ± 0.95	27.9 ± 0.60	34.8 ± 1.47	8.31 ± 0.08	4.12 ± 0.45
"	2	3.28 ± 0.41	29.1 ± 0.94	27.0 ± 0.53	43.9 ± 3.65	6.45 ± 0.30	3.40 ± 0.39
"	3	4.49 ± 1.35	28.9 ± 0.77	27.0 ± 0.56	36.6 ± 3.64	6.34 ± 0.28	3.62 ± 0.54
2001	1	5.33 ± 1.96	28.0 ± 0.88	27.0 ± 0.74	29.5 ± 1.56	7.71 ± 0.13	3.01 ± 0.42
"	2	8.51 ± 3.37	27.5 ± 0.86	26.4 ± 0.85	41.1 ± 7.01	6.17 ± 0.50	2.74 ± 0.51
"	3	5.35 ± 2.07	27.6 ± 0.79	26.6 ± 0.63	36.4 ± 5.63	7.49 ± 0.11	2.30 ± 0.52
2002	1	5.48 ± 1.84	28.8 ± 1.09	29.5 ± 0.84	30.9 ± 0.70	7.78 ± 0.09	2.12 ± 0.20
"	2	9.03 ± 2.46	27.7 ± 0.95	27.9 ± 0.70	60.5 ± 7.29	3.38 ± 0.72	1.01 ± 0.42
"	3	6.21 ± 1.83	28.4 ± 1.14	28.3 ± 0.87	41.5 ± 5.70	3.25 ± 0.57	0.79 ± 0.18

Table 2. Mercury concentration and hydrological parameters (mean ± S.E., n = 72) at six stations during 2007 - 2008

	hydrological parameters								
Station	Hg (μg. l^{-1})	Air temp (ºC)	SST (ºC)	Salinity (ppt)	pH	D.O (ml. l^{-1})	Chlorophyll (μg. l^{-1})	TSS (g. l^{-1})	CO_2 (mg. l^{-1})
1	8.27 ± 6.28	29.6 ± 0.64	29.3 ± 0.52	10.6 ± 2.91	2.44 ± 0.22	0.55 ± 0.19	1.55 ± 0.38	0.19 ± 0.03	9.54 ± 5.53
2	1.69 ± 0.14	29.8 ± 0.68	30.0 ± 0.51	26.1 ± 2.27	4.98 ± 0.27	1.80 ± 0.24	2.20 ± 0.74	0.26 ± 0.04	13.2 ± 6.75
*									
4	1.97 ± 0.25	30.7 ± 0.84	30.3 ± 0.58	29.5 ± 1.11	6.07 ± 0.15	2.19 ± 0.17	2.98 ± 0.88	0.24 ± 0.03	3.46 ± 3.46
5	1.97 ± 0.32	31.2 ± 0.69	30.7 ± 0.36	30.4 ± 0.75	6.89 ± 0.14	2.12 ± 0.10	6.44 ± 1.41	0.22 ± 0.03	0
6	3.10 ± 0.89	31.1 ± 0.59	30.3 ± 0.37	30.8 ± 0.75	7.56 ± 0.11	2.25 ± 0.09	2.66 ± 0.68	0.23 ± 0.03	0
7	1.97 ± 0.48	32.0 ± 0.66	31.3 ± 0.40	30.3 ± 1.10	7.86 ± 0.07	2.29 ± 0.12	5.15 ± 0.98	0.27 ± 0.03	0

* Station 3 is outside the coastal area, it is part of the lagoon and hence not shown here

was severe, evidenced by the anoxic conditions, observed for most of the period in the lagoon water and open sea (stations 1 and 2) during 2007-2008. Statistically very high significant difference was observed in the variation among stations (p< 0.01) (Tables 3 and 4). The pH was acidic in the lagoon water and not much variation was observed in the pH of open sea. During 2007-2008, the pH was lower in the first two stations and it increased from station 4 to 6. Marichamy *et al.* (1988) and Kasim *et al*. (1991) showed that acidity is one of the major concerns caused by the discharge of DCW.

Extreme monthly variations in salinity were observed in the lagoon water during 1999-2002. However, such extreme variations were not observed in the lagoon water during 2007 – 2008. Salinity was comparatively low at all the stations, indicating the impact of discharge. Statistically very high significant difference was noticed in the variation among stations during 2007-2008 (p< 0.01) (Table 4). The presence of carbon dioxide could be detected in the first three stations and the highest 13.2 mg.ml^{-1} was observed in station 2, showing the impact of effluent discharge on dissolved carbon dioxide content and it was found to be zero at stations 5, 6 and 7. The chlorophyll concentration was the lowest (1.55 μg.ml^{-1}) in the lagoon water and highest (6.44 μg.ml^{-1}) at station 5. Significant difference was also observed in the variation of chlorophyll concentrations among stations (p< 0.01). The total suspended solid concentration (TSS) was the lowest (0.19 g.l^{-1}) at station 1 and the highest (0.27 g.l^{-1}) at station 7. Low variation in the TSS among stations indicated less influence of effluents. Mercury

Table 3. ANOVA on the annual variation in hydrological parameters between stations during 1999 – 2002

Parameters	Treatment	Sum of Squares	df	Mean Square	F	Sig.
	Between stations	104.609	3	34.87	4.662	0.004*
Air Temp	Within station	777.914	104	7.48		
	Total	882.523	107			
	Between stations	52.763	3	17.588	8.565	0.000*
D.O.	Within station	199.179	97	2.053		
	Total	251.942	100			
	Between stations	1189.28	3	396.427	5.472	0.002*
Mercury	Within station	6882.583	95	72.448		
	Total	8071.863	98			
	Between stations	81.208	3	27.069	11.781	0.000*
pH	Within station	238.964	104	2.298		
	Total	320.172	107			
	Between stations	1222.787	3	407.596	1.635	0.186
Salinity	Within station	25184.017	101	249.347		
	Total	26406.805	104			
	Between stations	73.31	3	24.437	5.544	0.001*
SST	Within station	458.381	104	4.408		
	Total	531.692	107			

* $p < 0.001$

concentrations during 1999-2002 was 4.72 µg. l^{-1} , 9.36 µg. l^{-1} and 7.38 µg. l^{-1} in stations 1, 2 and 3 respectively. These values are higher when compared to those reported elsewhere (Krishnakumar *et al*., 1990; Krishnakumar and Bhat, 1998; Kaladharan *et al.,* 1999). Statistically significant difference was observed between stations in the variations ($p < 0.01$) (Table 3). Chester *et al*. (1973) reported mercury concentration at the surface waters of Indian Ocean to range from 0.005 to 0.127 µg. l^{-1}. Singbal *et al.* (1978) noted an average of 0.013 to 0.187 µg. l^{-1} in the coastal waters of the Arabian Sea. The present study revealed that the concentration of mercury in the open sea adjacent to the effluent lagoon was several times higher than the normal range of values reported. The Ministry of Environment and Forestry has stipulated an upper limit of 10 µg. l^{-1} of mercury for the effluent discharge into the coastal waters. The mercury in the effluent of the lagoon exceeded the permissible limit on several occasions and the mean value (9.36 µg. l^{-1}) was close to the limit. Marichamy *et al.* (1988) also estimated higher values of mercury concentration in the effluent of the lagoon of DCW in the year 1987.

In 2007-2008, the mercury concentration was found to have decreased to a mean of 2.136 µg. l^{-1} at the lagoon exit point and 1.68 µg. l^{-1} at the open sea due to conversion of old Mercury Cell Process to an environmentally cleaner Membrane Cell Process for the manufacture of caustic soda, by the DCW, which totally eliminate the usage of mercury from the processing system (Murali, 2007). The biological effects of mercury are strongly dependent on its concentration, chemical form, organisms and the resident time. Goldberg and Arrhenius (1958) estimated the residence time of mercury in the sea as 4.2 x 10^4 years. The present study indicates that the presence of mercury, acidity and low oxygen concentration was the major threat in the effluent discharge from the chemical plant. The low pH and salinity would improve the bioaccumulation rate, which may facilitate the dissolution of metals as indicated by Das *et al*. (2001).

In Tuticorin waters, Marichamy *et al*. (1988, 1995) estimated the median lethal concentration (LC 50) of mercury as 5.1 ng. ml^{-1} for the bivalve *Crassostrea madrasensis* and 2.8 ng. ml^{-1} for

Table 4. *ANOVA on the annual variation in hydrological parameters between stations during 2007 – 2008*

Parameters	Treatment	Sum of Squares	df	Mean Square	F	Sig.
	Between stations	43.420	5	8.684	1.311	0.270
Air Temp	Within station	437.279	66	6.625		
	Total	480.699	71			
	Between stations	1064.578	5	212.916	1.351	0.254
CO_2	Within station	10398.647	66	157.555		
	Total	11463.224	71			
	Between stations	229.692	5	45.938	4.556	0.001*
Chlorophyll	Within station	665.536	66	10.084		
	Total	895.227	71			
	Between stations	27.395	5	5.479	15.159	0.000*
D.O	Within station	23.855	66	0.361		
	Total	51.249	71			
	Between stations	14.197	5	2.839	0.915	0.477
Mercury	Within station	204.728	66	3.102		
	Total	218.926	71			
	Between stations	245.866	5	49.173	119.785	0.000*
pH	Within station	27.094	66	0.411		
	Total	272.960	71			
	Between stations	3915.675	5	783.135	23.175	0.000*
Salinity	Within station	2230.251	66	33.792		
	Total	6145.927	71			
	Between stations	27.049	5	5.410	1.928	0.101
SST	Within station	185.150	66	2.805		
	Total	212.199	71			
	Between stations	0.060	5	0.012	1.387	0.241
TSS	Within station	0.573	66	0.009		
	Total	0.633	71			

* $p < 0.001$

Mesodesma glabratum; 0.26 ng. ml^{-1} for the prawn *Penaeus indicus* and 0.22 ng. ml^{-1} for the teleost *Liza macrolepis*. Asha (unpublished) estimated high concentration of mercury beyond the WHO permissible limit of 2.2 µg. g^{-1} in the tissue samples of the fish *Sphyraena obtusata* and *Euthynnus affinis*, the crab *Portunus pelagicus*, cephalopod *Sepia remani* and clam *Donax* sp. caught off Tuticorin during 2008-2009. The level of acidic toxicity has not been reported in any of the fauna off Tuticorin. The present study suggests the need for the assessment on the tolerance limits of acidity and mercury for major organisms in Tuticorin waters.

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