Seasonal variations in mercury concentrations in the coastal waters of Kalpakkam, southeast coast of India

K. K. Satpathy^{1,*}, Usha Natesan², S. Sarguru², A. K. Mohanty², M. V. R. Prasad¹ and S. K. Sarkar³

¹Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India ²Centre for Environmental Studies, Anna University, Chennai 600 025, India

³Department of Marine Science, University of Calcutta, Kolkata 700 019, India

Studies were carried out in the coastal waters of Kalpakkam to monitor the seasonal variation in mercury (Hg) concentration. The Hg level (dissolved + acid leachable) ranged from 3 to 50 ppb for surface and 1.5 to 47.9 ppb for bottom-water samples, yielding an annual average concentration of 20.42 ± 11.44 and $23.11 \pm$ 13.06 ppb for surface and bottom waters respectively. Strong positive correlation of Hg with salinity and its relatively low concentrations during monsoon and post-monsoon showed that concentration of Hg in this coastal water was mainly of marine origin, indicating absence of any other external source of input. Relatively high Hg concentrations were encountered in bottom samples compared to the surface. Madras Atomic Power Station (MAPS) outfall discharge water did not show elevated Hg level compared to ambient surroundings. The present observed values are significantly lower (30 times) than the earlier reported values from this coast.

Keywords: Coastal waters, mercury concentration, seasonal variations, surface and bottom water.

URBAN and industrial activities in and around coastal areas introduce significant amounts of pollutants into the marine environment. In many cases these started more than two decades ago and are still continuing, causing significant and permanent disturbances in marine systems and. consequently, environmental and ecological degradation. Among other pollutants, heavy-metal contamination of sea water due to industrial effluent discharge and dumping of land-based solid waste is of great concern today. Although mercury (Hg) occurs as one of the rare elements of the crust, its wide range of industrial applications in the past 50 years has led to the contamination of coastal water, among others. Though the anthropogenic sources of Hg in the marine environment are numerous, until recently, effluents from chloro-alkali plants contributed significantly to its load in many coastal and inshore areas. Hg is considered to be a particle-reactive element in the aquatic environment. It is easily associated with the sus-

pended particulate matter (SPM)¹⁻³ and transferred to the bed material on settling. Moreover, although the change in the electrolytic process has largely eliminated the use of Hg in chloro-alkali plants, the past emissions deposited in the aquatic environment and those emanating from other sources continue to exhibit its distinct signature in water, sediment and biota of regions influenced by its fluxes. In India, awareness about Hg pollution came into limelight when the possible adverse implications of Hg loss from 38 chloro-alkali plants to the tune of 180 t yr⁻¹ was reported by Choudhury⁴. Further, observations of elevated levels of Hg in water, sediment and biota from the coastal waters around India⁵⁻¹⁴ strongly supported Choudhury's contentions.

Selvaraj *et al.*¹⁵ had implicated the condenser cooling water discharge from the Madras Atomic Power Station (MAPS) into the coastal waters as the sole cause for the elevated levels of Cu and Hg in the Kalpakkam coastal waters. A detailed scientific refutal on the role of MAPS on dissolved copper concentration of Kalpakkam coastal waters was published¹⁶. However, Hg concentration could not be estimated at that time due to operational difficulties. In this communication, the seasonal variation of dissolved Hg in the coastal waters of Kalpakkam is shown and a comparison is made with the earlier reported values¹⁵. Hydrographical parameters such as pH, salinity, turbidity and dissolved oxygen (DO) were also measured to correlate them with Hg concentration.

Kalpakkam is situated at 12°34'N lat. and 80°11'E long. on the east coast of India. MAPS, consisting of two pressurized heavy water reactors (PHWRs), each of 235 MW(e) capacity, is located on this coast. Unit-1 reactor went operational on 23 July 1983, whereas Unit-2 went operational on 18 September 1985. Sea water at a rate of about 35 m^3 /s is used for cooling the condenser and for process (pump, biological shield, etc.) sea water cooling, when both the units are operational. Sea water is drawn through a submarine tunnel of 468 m length, built 53 m below the seabed. The tunnel is connected at the landward end to the pump house through a vertical shaft called forebay. After extracting heat, sea water is discharged on-shore to the north of the reactor. MAPS uses aluminium brass (an alloy of Cu and Zn) tube as condenser as well as process water heat exchanger material. The submarine tunnel in particular and the sea-water cooling system in general, are prone to biofouling causing nuisance value to the power-plant operation. In order to overcome this unavoidable problem, liquefied chlorine gas is being injected (for the last 20 years) continuously at the entry of the sea-water tunnel and the residual maintained at the outfall discharge point is $\sim 0.5 \text{ mg l}^{-1}$. The tunnel is inaccessible and thus no other antifouling techniques such as antifouling coatings can be used inside the system. Chlorine is ineffective at the entry of the tunnel (where different meshsize screens are located to prevent entry of relatively large-sized organisms) due to free flow and unidirectional

^{*}For correspondence. (e-mail: satpathy@igcar.gov.in)

flow condition. The screens made up of mild steel, which act as a first line of defence, are periodically removed, cleaned and then coated with coal tar epoxy paint, essentially to prevent corrosion. Besides this, no other coating is used for any other purposes. Two backwaters, namely the Edaiyur and the Sadras backwater systems are important features of this coast. During the period of the NE monsoon and seldom during the SW monsoon, these two backwaters get opened to the coast, discharging considerable amount of freshwater to the coastal milieu for a period of 2-3 months. This part (Tamil Nadu) of peninsular India receives the bulk of its rainfall (~70%) from the NE monsoon. The average rainfall at Kalpakkam is about 1000 mm. After the monsoon, a sand bar is formed between the backwaters and the sea, due to littoral drift, which is a prominent phenomenon in the east coast of India. The Sadras backwater receives discharge from the Kalpakkam Township, whereas anthropogenic influences in the Edaiyur backwater is negligible. During the present study, the Sadras backwater remained disconnected from the sea from the later part of March 2006 and reopened during December 2006–January 2007, whereas the mouth of the Edaiyur backwater remained open throughout the study period. Five sampling stations were chosen along the coast stretching over a length of about 8 km and about 600 m into the sea, where the water column depth varied from 7 to 9 m. These stations are located in the same area from where Selvaraj et al.¹⁵ had also collected their samples. The stations were chosen such that the first and fifth are situated opposite to the opening of the Sadras and Edaiyur backwaters respectively. The third station is near the intake point while the fourth station is situated close to the mixing zone of the heated condenser cooling water discharge representing the outfall discharge water sample.

Surface (1 m below the sea surface) and bottom (1 m above the bottom) water samples were collected from the five stations (Figure 1), fortnightly, using Transparent Plastic Nansen (TPN) water sampler of 1.51 capacity during February 2006–January 2007. Samples from the TPN sampler were transferred to acid-cleaned Pyrex glass bottles. Winkler's titrimetric method¹⁷ was followed for the estimation of DO. Salinity measurements were carried out using Knudsen's method¹⁷. pH and turbidity measurements were carried out using CyberScan pH (PCD 5500) and turbidity meter (IR TB 100) respectively. During the collection of samples for Hg analysis, precautions were taken to avoid contamination, following the procedure of Schmidt¹⁸. Samples were acidified using 2 ml of HNO₃ per litre of sample to prevent deterioration and were deep-frozen until analyses. Thus the Hg content represents both the soluble (dissolved) and acid-leachable fractions. Samples were filtered within 3-4 h, after reaching the laboratory. Mercury was extracted based on the liquidliquid extraction procedure of Mentasti et al.¹⁹, in which the filtered water sample was placed in an acid-cleaned separating funnel and pH was adjusted to 2.70 with conc. HNO₃. After the addition of 2 ml of ammonium pyrrolidine dithiocarbamate (APDC), the chelates were extracted into 10 ml of iso-butyl methyl ketone (IBMK), $100.16 \text{ g mol}^{-1}$ concentration, under agitation. The aqueous phase was removed and the mercury present in IBMK was brought to aqueous phase with conc. HNO₃ and HCl. The final sample volume was kept at 10 ml to achieve a high concentration factor (100). Mercury Analyser, ECIL India, Model MA 5840 was used for estimation. Relative standard solutions were run with the samples concurrently to check the precision of the instrument. Quantitative recovery of standards used during analysis was 95%. The calibration curve prepared with standard solution was found to be linear up to 200 ppb. The detection limit of the method is 0.1 ppb. Accuracy and precision of the data were found to be ± 5 ppb. The presence of Cu, Pb and Cd in the sample has been reported to enhance the recovery of each of them in the presence of one another. The present sample contains about 42.5 ppb of Cu¹⁶, 60 ppb of Pb and 12 ppb of Cd (unpublished data). Thus their presence could have enhanced the efficacy of this method. All samples were analysed in triplicate and the average value is reported.



Figure 1. Study area showing sampling locations.

Hydrographical parameters such as pH, salinity, turbidity and DO were measured to know their role on the seasonal variation of Hg in coastal waters. Data generated were pooled into monthly average values and station-wise average values.

pH values varied from 7.7 to 8.4 in surface waters and 7.7 to 8.3 in bottom waters during the present study. The highest and lowest monthly average values for both surface and bottom waters were observed during February and June respectively (Figure 2 *a*). There was no conspicuous variation in the station-wise (Figure 2 *b*) average values of pH. However, a marginal variation between months was observed; particularly the values were relatively low during the monsoon period. The pH change in a coastal milieu is governed by freshwater influx, phytoplankton production and respiration, and the extensive buffering capacity of the sea water that causes a change in pH within a very narrow limit²⁰.

The observed surface and bottom salinity values ranged from 23.38 to 35.97 and 25.41 to 35.97 psu respectively. The lowest and highest salinity values were observed in November and May respectively. As expected, during the present study salinity increased from January to May (Figure 2c), which can be attributed to the dilution of coastal water by the addition of freshwater from the two backwaters in January and during monsoon period in November-December. However, this dilution decreased in the subsequent months (January-August), resulting in an increase in salinity. It remained almost constant during summer and till the arrival of the SW monsoon. Salinity started decreasing from August, reaching a minimum in November, coinciding with the peak monsoon period. Marginally high bottom-water salinity was observed at all the locations, as evident from the station-wise average values (Figure 2d). Freshwater discharge from the rivers causes a decline in the salinity of the surface water²¹ during the monsoon. In the subsequent months, restoration occurs as salinity continuously increases up to May/June, as recorded in the present investigation. In addition, a typical marine and isohaline condition was observed at this location even beyond June up to August, as relatively less precipitation is received at this locality from the SW monsoon. Similar behaviour of salinity in the coastal waters has also been reported earlier^{22,23}.

The DO content varied from 3.3 to 6.6 mg l⁻¹ and 4.4 to 5.9 mg l⁻¹ for surface and bottom samples respectively. As expected, the surface values were marginally higher than the bottom values throughout the study period. The monthly average value showed a decrease in DO concentration from February to May, after which it increased gradually up to January (Figure 2 *e*). No clear trend in DO content was observed with respect to the stations (Figure 2*f*). The noticeable increase in DO observed from October to January could be attributed to the input of freshwater rich in DO during the NE monsoon period. The range of DO observed during different months and at

different stations showed that the coastal water is not well saturated. In aquatic systems, oxygenation is the result of an imbalance between the process of photosynthesis, degradation of organic matter, reaeration²⁴ and physico-chemical properties of water²⁵. Due to involvement of such multiple factors, which determines the DO level in coastal waters, no typical trend was observed. However, salinity was found to be the most important factor that controlled the level of DO in coastal waters during the present study, as evident from its strong negative correlation ($P \ge 0.001$) with DO, both in station-wise and month-wise average values (Figure 3 *a* and *b*).

The turbidity values ranged from 1.69 to 17.76 NTU for surface water and 1.85 to 92.77 NTU for bottom water during the present study. Monthly values showed relatively high water turbidity during summer and values were almost similar during the rest of the period (Figure 2 g). It has been reported that wave action increases during summer due to the northerly wind and the northward current prior to the onset of the SW monsoon²⁶⁻²⁸, resulting in turbulent condition in the coastal waters favouring resuspension of the bottom sediment due to stirring action that causes low water transparency^{29,30}. This perhaps could be the plausible reason for bottom water showing higher turbidity than the surface, as otherwise expected between the surface and bottom in deeper waters. Moreover, the role of phytoplankters for the increased turbidity values³¹ in April and May cannot be overlooked, as phytoplankton production in the Bay of Bengal during summer is generally high compared to the remaining periods of the year. The fourth and fifth locations showed marginally higher turbidity compared to the other three locations. These two locations are close to MAPS outfall discharge and Edaiyur backwater opening respectively. Thus they have relatively high turbulence, leading to relatively high turbidity at these locations. A distinct variation in turbidity values of surface and bottom waters was noticed at all the locations (Figure 2h). However, at the fifth location the difference between the surface and bottom values was the least, which could be attributed to the debouchments from the Edaiyur backwater throughout the study period.

Since water samples were treated with conc. HNO_3 immediately after their collection, the Hg content represents both soluble and acid-leachable fractions. Hg concentration during this study ranged from 1.50 to 50.00 ppb, with both highest and lowest values encountered during December. Undetectable values were never encountered during this study. Monthly average values showed that surface-water Hg concentration gradually increased from February to May, after which it marginally decreased till October. Then the rate of decrease accelerated up to January (Figure 4 *a*). Except February and December, the bottom values were higher than the surface values for the rest of the period. During February, the surface and bottom values were almost equal, whereas during December



Figure 2. Monthly variation in physical parameters.



Figure 3. Maps showing the correlation between different parameters in monthly average values (a) and station-wise average values (b). (The directions of lines in squares from left to right show positive correlation and those from right to left show negative correlation between the parameters. The gap between the lines in a square is directly proportional to the strength of the correlation, i.e. more the gap, stronger the correlation.)

the surface value was higher compared to the bottom value. The station-wise values showed that, the second and fifth locations were marginally lower in Hg content than the other three locations (Figure 4 *b*). Except in the second location, Hg values remained relatively high in the bottom samples compared to the surface. Surface Hg concentration was highest at the first location and was almost equal at the third and fourth locations; the lowest value was observed at the fifth location. The highest bottom-water Hg concentration was observed at the fifth location. The highest bottom-water Hg concentration of mercury for surface and bottom waters during this study was found to be 20.42 ± 11.44 and 23.11 ± 13.06 ppb respectively.

Distribution of Hg in coastal waters is governed by several factors such as adsorption onto suspended particulate matter (SPM), chemical precipitation and coagulations, biological uptake, etc. However, adsorption of Hg into SPM has been considered as the dominating mechanism leading to effective sink of Hg to the bottom. Moreover, elemental mercury has been evidenced to volatilize from the natural waters to the atmosphere. This escape has important biological connotations because it not only decreases the half life of mercury in the water, but also its wider geographical dispersion to other environments. The processes suggested to be responsible for volatilization are many: demethylation, bacterial reduction from water or sediments, reduction of Hg (I) and (II) to Hg (0) by humic and fluvic acids, physiological reduction by phytoplankton as a means of detoxification and photochemical reduction of Hg (II) to Hg (0). In the present study Hg showed a strong positive correlation with salinity and strong negative correlation with DO (Figure 3 a) in monthly

average values. According to Frenet-Robin and Ottmann³², release of Hg into the water column back from the sediments is favoured by increase in salinity, which describes the above correlation between salinity and Hg. It has been proposed that the exchange mechanism of Hg between water and sediments is based on resuspension of the bed sediment, which results in an increase in Hg concentration in water³³. Both contention of salinity and Hg correlation, and exchange mechanisms between sediment and water appear to be true for Kalpakkam coastal waters owing to the tangible fact that relatively high Hg concentrations were encountered during the period of comparatively high salinity and bottom samples registered higher Hg content than the surface. This shows that Hg concentration in this coastal waters is mainly of marine origin and absence of any other external source of input supports the above observation. Moreover, relatively low concentrations observed during the monsoon and post-monsoon periods further strengthen the earlier conclusion that the allochthonous origin of Hg in the coastal waters is negligible. Though marginally higher concentrations of Hg in the surface water during peak monsoon period was observed, which could have been due to the surface run-off leading to enhanced levels, it did not exceed the magnitude found during summer. Hg also showed a weak positive correlation $(P \ge 0.01)$ with turbidity, which could be due to the release of Hg into the water from SPM. According to Campbell et al.³⁴, removal of Hg from SPM is greatly favoured at salinities ~25 psu and above. The highest Hg concentration for surface water at the first location compared to the others could be due to its input from the Sadras backwater, which receives drainage from the Kalpakkam Township. During the present study, the Sadras backwater remained open to the sea for a period of



Figure 4. Seasonal variation in Hg concentration in coastal waters of Kalpakkam. (a) Monthly variations and (b) Station-wise variations.

four months. Higher surface-water concentration compared to the bottom-water concentration at the second location could be due to the fact that the coast at this location is comparatively thickly populated with the fishermen community, which uses a large number of mechanized fibre boats, and thus could be a source for the observed elevated Hg levels. Lowest concentrations of Hg, both in the surface and bottom samples at the fifth location showed that this sampling point is relatively clean, as there is no anthropogenic input at this location.

A comparison between the Hg levels reported earlier from different coastal waters other than that by Selvaraj et al.15 and the values observed during this study showed that the present concentration at Kalpakkam coast sur-passes all the others^{5,10,35–37}. The highest value reported earlier (20 years ago) was 1.2 ppb in the Madras coastal waters³⁶. The most reasonable explanation for the relatively high Hg values encountered in this study is that, the present values include both dissolved and acidleachable fractions of Hg. However, all reported values referred to the dissolved fractions only. Moreover, to our knowledge the latest literature available in this regard from the east coast of India from the Gulf of Mannar and Palk Bay³⁸ is about seven years old, wherein the Hg value was reported to be 2.05 ppb. Thus, it is difficult and inappropriate to compare the present values with those of relatively old data, as rapid industrialization and general increase in pollution level have been taking place in the recent past. No recent data even from the west coast as well as from northern part of the east coast of India are available to compare with the present observed values. Surprisingly, values reported from the Pakistan coast, northern Arabian Sea³⁹ ranged from 61 to 450 ppb, which is significantly higher than the present observed values, without pointing at point source. To substantiate and strengthen the marginally elevated Hg levels observed in the present study, role of the tsunami as one of the factors cannot be ruled out. It devastated this coast during December 2004, as a result of which inner-shelf bottom

CURRENT SCIENCE, VOL. 95, NO. 3, 10 AUGUST 2008

sediment had mixed with the shallow coastal waters. Also the frequency of roughness of the sea has increased since then. A perusal of turbidity values between pre- and posttsunami revealed increased turbidity during the posttsunami period⁴⁰. Therefore, increased suspended matter content aftermath of the tsunami possibly contributed to the leachable fraction of Hg, thereby marginally pushing the level up.

To get a clear picture of the behaviour of Hg distribution at different locations (surface and bottom), similarity and dissimilarity cluster analyses were carried out. The similarity cluster showed that all the surface samples formed one cluster, whereas the other cluster was formed by all the bottom samples (Figure 5a). In the present study the surface concentration of Hg was found to be lower compared to the bottom concentration in almost all the observations, and thus only two clusters were formed. The dissimilarity cluster also developed two classes. Surface and bottom observations of stations 1 and 3 formed one cluster, and the other cluster was formed by the stations 2, 4 and 5 (Figure 5 b). This showed that the behaviour and concentration of Hg at the first and third locations was similar, as concentration of Hg was marginally higher at these locations compared to the other three locations. Similarly, the variation in Hg concentrations at the second, fourth and fifth locations was minimal and is reflected by the fact that they formed one cluster.

Although Hg values observed during the present study are marginally higher than those reported^{5,10,35–37}, the values reported by Selvaraj *et al.*¹⁵ were found to be significantly higher than ours (>30 times). The values reported by Selvaraj *et al.*¹⁵ ranged from 64 to 1374 ppb in the surface and 0 to 1664 ppb in bottom-water samples during the pre-monsoon period, and 0 to 526 ppb in the surface and 0 to 321 ppb in the bottom-water samples during the post-monsoon period. Values in the present study ranged from 3 to 50 ppb for surface and 1.5 to 47.9 ppb for bottomwater samples. This showed that the highest value observed during the present study is about 30 times less



Figure 5. Dendrograms showing similarity (a) and dissimilarity (b) clusters between surface and bottom samples of various locations.

than the earlier reported values. It is difficult to understand how the Hg concentration as reported by Selvaraj et al.¹⁵ was so high. The only simple and possibly convincing reason for such high values could be due to analytical error either during extraction or during instrumental analysis or long duration between acidification and filtration leading to significant contribution of the leachable fraction. Selvaraj et al.¹⁵ had attributed the higher concentration of Hg to anthropogenic input from the coastal industries. But interestingly, there is no coastal industry located at the Kalpakkam coast, except MAPS, which does not use Hg for any purpose. Moreover, such a conclusion has been drawn without knowing the content of the discharge. The above conclusion could have been dialectical had the MAPS outfall water been analysed for Hg. During the present study, the fourth location represented the outfall discharge from MAPS, and Hg values at this station throughout the year were comparable with the remaining stations. In fact, most of the values from this location were relatively low compared to the other stations. Thus the discharge outfall from MAPS is no way different from the coastal water with respect to Hg content, as evident from the present study. Selvaraj *et al.*¹⁵ have reported that to control biofouling and bio-corrosion in the cooling water system of MAPS, chlorine has been used intermittently - a distorted fact as only low-dose continuous chlorination⁴¹ has been in vogue at MAPS since 1988. Similarly, the source of chlorine used by MAPS, as mentioned by Selvaraj et al.¹⁵, was through the electrolytic chlorination process, which they had attributed as the cause of elevated levels of Hg observed at Kalpakkam coast. On the contrary, at MAPS, chlorination is done by injection of liquefied chlorine gas in sea water⁴². Selvaraj et al.¹⁵ have assumed MAPS as a pollution source. The results of the present study clearly show that the discharge from MAPS condenser does not contain elevated levels of Hg. It not only gives credence to the comment made by Kureishy⁴³, but also parleys with him.

The present results form a baseline data for future impact studies considering the fact that a few major projects are expected to be commissioned at this location in the near future. A general increase in the pollution level in the last decade coupled with tsunami impact has pushed the Hg level marginally up in the Kalpakkam coastal waters. The present observed Hg values are found to be far less than (30 times) the values reported by Selvaraj *et al.*¹⁵.

- Shaw, B. P., Sahu, A. and Panigrahi, A. K., Comparative toxicity of an effluent from a chlor-alkali industry and HgCl. *Bull. Environ. Contam. Toxicol.*, 1990, 45, 280–287.
- Matty, J. M. and Long, D. T., Early diagenesis of mercury in the Laurentian Great Lakes. J. Great Lake Res., 1995, 21, 574–586.
- Mason, R. P., Lawson, N. M., Lawrence, A. L., Leaner, J. J., Lee J. G. and Sheu, G. R., Mercury in Chesapeake Bay. *Mar. Chem.*, 1999, 65, 77–96.
- Choudhury, N., Increasing danger of mercury pollution. *Indian* Express, 1980, 48, p. 9.
- Singbal, S. Y. S., Sanzigiri, S. and Sen Gupta, R., Total mercury concentration in the Arabian Sea waters. *Indian J. Mar. Sci.*, 1978, 7, 124–126.
- Sanzigiri, S., Sen Gupta, R. and Singbal, S. Y. S., Total mercury concentration of the Laccadive Sea. *Indian J. Mar. Sci.*, 1979, 8, 252–253.
- Zingde, M. A. and Desai, B. N., Mercury in Thane creek, Bombay harbour. Mar. Pollut. Bull., 1981, 12, 237–241.
- Kureishy, W., Sanzigiri, S., Gorge, N. D. and Brayanca, A., Mercury, cadmium and lead in different tissues of fishes and in zooplankton from the Andaman sea. *Indian J. Mar. Sci.*, 1983, 12, 60–63.
- Sasmal, S. K., Sahu, B. K. and Panigrahy, R. C., Mercury in the estuarine and nearshore sediments of the western Bay of Bengal. *Mar. Pollut. Bull.*, 1987, 18, 135–137.

CURRENT SCIENCE, VOL. 95, NO. 3, 10 AUGUST 2008

- Qasim, S. Z., Sen Gupta, R. and Kureyshi, T. W., Pollution of seas around India. Proc. Indian Acad. Sci., 1988, B97, 117–131.
- Shaw, B. P., Sahu, A. and Panigrahy, A. K., Mercury in Rushikulya river estuary. *Mar. Pollut. Bull.*, 1988, 19, 233–234.
- Patel, B. and Chandy, J. P., Mercury in biotic and abiotic matrices along Bombay coast. *Indian J. Mar. Sci.*, 1988, 17, 55–58.
- Daniel, A., Mercury concentration in water, sediment and biological samples of Madras coast. In *Marine Pollution and Toxicology* (eds Venugopalan, V. K. and Balasubramanian, T.), Annamalai University, 1990, pp. 229–239.
- Krishnakumar, P. K. and Pillai, V. K., Mercury near a caustic soda plant at Karwar, India. *Mar. Pollut. Bull.*, 1990, 21, 304–307.
- Selvaraj, K., Total dissolvable copper and mercury concentrations in inner shelf waters off Kalpakkam, Bay of Bengal. *Curr. Sci.*, 1999, 77, 494–497.
- Satpathy, K. K., Natesan, U., Kalaivani, S., Mohanty, A. K., Rajan, M. and Baldev Raj, Total dissolved copper concentrations in coastal waters of Kalpakkam. *Curr. Sci.*, 2006, **91**, 1008–1010.
- Grasshoff, K., Ehrhardt, M. and Kremling, K., Methods of Sea Water Analysis, Wiley-VCH, New York, 1983.
- Schmidt, D., Sampling and analysis for the monitoring of trace heavy metals in sea water: Achievements in analytical quality assurance. In *Advances in Environmental Science* (ed. Iyer, C. S. P.), Educational Book Publisher and Distributors, New Delhi, 1997, pp. 7–29.
- Mentasti, F., Nicolotti, A., Porta, V. and Sarzanini, C., Comparison of different pre-concentration methods for the determination of trace levels of arsenic, cadmium, copper, mercury, lead and selenium. *Analyst*, 1989, **114**, 1113–1117.
- Riley, J. P. and Chester, R., An Introduction to Marine Chemistry, Academic Press, London, 1971.
- La Fond, E. C., On upwelling and sinking off the east coast of India. Andhra Univ. Mem. Oceanogr., 1954, 1, 117–121.
- Varma, P. U. and Reddy, C. V. G., Seasonal variation of the hydrological conditions of the Madras coastal waters. *Indian J. Fish.*, 1959, 6, 298–305.
- Subramanyan, R. and Sen Gupta, R., Studies on the plankton of east coast of India. *Proc. Indian Acad. Sci.*, 1965, **B56**, 125–131.
- Granier, J., Billen, G. and Palfner, L., Understanding the oxygen budget and related ecological processes in the river Mosel: The RIVERSTRAHLER approach. *Hydrobiology*, 2000, **410**, 151– 166.
- Aston, S. R., Nutrients dissolved gasses and general biochemistry in estuaries. In *Chemistry and Biogeochemistry of Estuaries* (eds Olausson, E. and Cato, I.), John Wiley, New York, 1980, pp. 233– 262.
- Varkey, M. J., Murty, V. S. N. and Suryanaryan, A., Physical oceanography of the Bay of Bengal and Andaman Sea. In *Oceanography and Marine Biology* (eds Ansell, A. D., Gibson, R. N. and Barnes, M.), UCL Press, 1996, vol. 34, pp. 1–70.
- McCreary, J. P., Han, W., Shankar, D. and Shetye, S. R., Dynamics of the East India coastal current. 2. Numerical solutions. J. Geophys. Res., 1996, 101, 13993–14010.
- Haugen, V. E., Vinayachandran, P. N. and Yamagata, T., Comment on 'Indian Ocean: Validation of the Miami Isopycnic Coordinate Ocean Model and ENSO events during 1958–1998'. J. Geophys. Res., 2003, 108, 3179.
- Qasim, S. Z., Bhattathiri, P. M. A. and Abidi, S. A. H., Solar radiation and its penetration in a tropical estuary. *J. Exp. Mar. Biol. Ecol.*, 1968, 2, 87–103.
- Nixon, S. W., Physical energy inputs and the comparative ecology of lake and marine ecosystems. *Limnol. Oceanogr.*, 1988, 33, 1005–1025.
- Kalimurthy, M., Observations on the transparency of the waters of the Pulicat Lake with particular reference to plankton production. *Hydrobiology*, 1973, 41, 3–11.

- Frenet-Robin, M. and Ottamann, F., Comparative study of the fixation of inorganic mercury on the principal clay minerals and the sediment of the Loire estuary. *Estuarine Coastal Mar. Sci.*, 1978, 7, 425–436.
- Linderberg, S. E., Andren, A. W. and Harris, R. C., Geochemistry of mercury in estuarine environment. In *Estuarine Research* (ed. Cronin, L. E.), Academic Press, London, 1975, pp. 64–108.
- Campbell, J. A., Chan, E. Y. L., Riley, J. P., Head, P. C. and Jones, P. D., The distribution of mercury in the Mersey estuary. *Mar. Pollut. Bull.*, 1986, 17, 36–40.
- Qasim, S. Z. and Sengupta, R., Marine pollution studies in India. In *Water Pollution and Management Review* (ed. Varshney, E. D.), South Asian Publisher Pvt Ltd, New Delhi, 1983, pp. 139–159.
- Somasundaram, M. V., Ravichandran, G. and Ramasamy, A., Pollution in Coovum estuary and adjoining wells. In Proceedings of the National Seminar on Estuarine Management, Government of Kerala, 1987.
- 37. Daniel, A., The effect of pollution on some organisms in the zooplankton, benthos and nekton, contributing to the food chain in the marine environment. In Completed projects under environmental research programme: Objectives and salient findings, ENVIS, Government of India, Project 36/ERC, 1984, pp. 58–59.
- Palanichamy, S. and Rajendran, A., Heavy metal concentration in sea water and sediment of Gulf of Mannar and Palk Bay, southeast coast of India. *Indian J. Mar. Sci.*, 2000, 29, 116–119.
- Tariq, J., Jaffar, M., Ashraf, M. and Moazzam, M., Distribution of trace metals in sediments and sea water from the continental shelf of Pakistan. *Indian J. Mar. Sci.*, 1994, 23, 147–151.
- Satpathy, K. K., Mohanty, A. K., Prasad, M. V. R., Natesan, U. and Sarkar, S. K., Post-tsunami changes in water quality of Kalpakkam coastal waters, east coast of India with special references to nutrients. *Asian J. Water Environ. Pollut.*, 2008 (in press).
- 41. Satpathy, K. K., Saravanane, N., Nair, K. V. K. and Durairaj, G., Studies on the recovery of potential of phytoplankton after entrainment in the cooling system of a nuclear power plant. In *Emerging Trends in Environmental Science* (ed. Iyer, C. S. P.), Asiatech Publishers Inc, New Delhi, 2001, pp. 111–120.
- 42. Satpathy, K. K., Nair, K. V. K. and Mathur, P. K., Chlorine demand and chemical control of biofouling in power plant cooling systems. In Proceedings of the Indo-US Meeting on Recent Developments in Biofouling Control (ed. Thompson, M. F.), Oxford and IBH Publishing Co Pvt Ltd, New Delhi, 1994, pp. 397–407.
- Kureishy, T. W., Measurement of mercury and copper. *Curr. Sci.*, 1999, **77**, 1387–1388.

ACKNOWLEDGEMENT. We are grateful to the Director, Indira Gandhi Centre for Atomic Research, Kalpakkam for encouragement, support and valuable suggestions during the study.

Received 5 December 2007; revised accepted 2 July 2008