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# Trace metal contamination of the marine environment in Palk Bay and Gulf of Mannar

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**Abstract**

The effect of anthropogenic activities has been studied in two stations, each in Palk Bay and Gulf of Mannar, and compared with an offshore site in the former bay for one year on a monthly basis. The mean level of trace metals (Cd, Cu, Pb and Zn) in sediment from polluted areas was 1.23 ppm, 5.42 ppm, 15.52 ppm and 7 ppm respectively. The maximum Cd, Cu, Pb and Zn level in seawater from polluted areas were 1.11 ppb, 26.78 ppb, 21.35 ppb and 247.12 ppb respectively. The mean level of these metals in zooplankton and clam from polluted areas were 1.12 ppm, 14.47 ppm, 24.03 ppm and 267.2 ppm respectively. Analysis of variance (ANOVA) showed no significant difference in the trace metal levels in water, tissue and sediment between polluted and reference station. The paper draws attention to the concentrations of trace metals in the marine environment and biota of Palk Bay and Gulf of Mannar along with other hydrological parameters.

**Keywords**: Trace metals, marine environment, hydrobiology, Palk Bay, Gulf of Mannar

## Introduction

The coastline of Palk Bay and Gulf of Mannar comprises of estuaries, river outlets, tank outlets, lagoons, saltpans and creeks. The former is more or less an enclosed bay while the latter is wide open at the southern end and subjected to incursions of water masses from Indian Ocean and the Arabian Sea (Prasad, 1954). Water exchange in bays is often limited and shipping activities introduce contaminants, which include oil, trace metals, nutrients and organochlorine compounds (UNEP, 1990). There are fish processing, salt, textile and petrochemical industries situated near the coastline of Palk Bay and Gulf of Mannar. Major and minor ports are also present, in addition to the famous pilgrim centre at Rameswaram. The quality of water and sediment affects all the living organisms in this diverse and complex region. The contaminants such as trace metals, phosphorous, pesticides, PCBs and polycyclic aromatic hydrocarbons, get accumulated in the sediments and suspended matter in aquatic systems (Jenne, 1977; Forstner and Wittmann, 1981). Trace metal uptake by sediments and suspended matter occurs by three main mechanisms such as physico-chemical adsorption from water column, biological uptake and physical accumulation of metal enriched particulate matter (Barry, 1982). The present study is an attempt to assess the influence of anthropogenic activities in these two areas with specific reference to the concentrations of trace metals. Three- tier detection mechanism of trace metal Cd, Cu, Pb and Zn from water, sediment and tissue (Kaladaran, *et al.* 2005) has been followed. The trends in hydrobiological parameters for the stations monitored were also compared.

## Materials and methods

In Palk Bay, off Coast Guard Jetty - PB (Lat. 9º 17' 05.8"N, Long. 79º 9' 29.8" E) and Gulf of Mannar, off INP Jetty - GM (Lat. 9º 16' 39.1" N, Long.79º 9' 22.3" E), stations adjacent to fish processing unit effluent disposal sites were selected (Fig.1). In Gulf of mannar, near Sethukarai Estuary - SK (Lat.9º 15' 13.1" N, Long. 78º 50' 17" E), station adjacent to the effluent disposal sites from aquaculture farm was monitored. At Rameswaram - RM (Lat. 9º 17' 20.3" N, Long. 79º 19' 15" E) station adjacent to disposal site of sewage near Bathing Ghat area was selected. Station near a relatively clean area in Palk Bay was taken as reference site-R (Lat.9º 18' 26.9" N, Long.79º 10' 41.9" E).

The latitude and longitude of sampling stations were marked using portable Global Positioning System (Garmin GPS, Model etrex). Water, sediment and zooplankton/ clam samples were collected from each of the above-mentioned stations after following standard sampling procedure (APHA, 1995). *In situ* observations of atmospheric and surface water temperature were taken. The *p*H, dissolved oxygen, gross primary productivity, net primary productivity and total suspended solids were estimated on a monthly basis from April 2003- March 2004.

The *p*H of water samples was measured using ELICO *p*H meter. The dissolved oxygen was determined by Wrinkler's method. The gross and net primary productivity was determined after keeping the light and dark bottles in lab condition for 3 hrs and then the dissolved oxygen values were estimated by Wrinkler's method. The same was converted for carbon equivalent using a PQ of 1.25 for obtaining gross production. The total suspended solids were estimated gravimetrically by weighing the residue retained on glass fibre filters after filtration through Millipore filtration unit and drying in an oven.

Trace metal analysis of seawater samples was carried out using voltameteric analyzer (757 computrace , metrolm, Switzerland ) following the method outlined by (Anoop *et al*., 2007). The sediment samples were taken by Van-Veen grab, the surface layer was sampled, and metals extracted using acid digestion procedure (Dalziel and Baker, 1984). Zooplankton or clam sample tissues were collected from the stations and 1g was digested with 10ml mixture of $HNO_3$ and $H_2O_2$ (1:1 ratio) following standard procedure (Robisch and Clark, 1993). The trace metals in the digested samples were detected on a Perkin Elmer AAnalyst -700 in air-acetylene flame (Geetha *et al.*, 2006).

**Results**

***Variation in hydrobiological parameters***

A maximum atmospheric temperature of 35.2ºC and a minimum of 26ºC were observed for the period, while surface water temperature varied between 26ºC and 32.8ºC. The mean *p*H of water samples for polluted stations combined was 8.3. Maximum dissolved oxygen of 5 ml/l was observed for the reference station. The mean gross and net primary productivity for polluted stations combined were 4.461mgC/l/day and 3.569 mgC/l/day respectively. The maximum total suspended solid of 144 mg/l was observed in RM (Figs. 2 to 8).

***Trace metal level in seawater, tissue and sediment***

***Cadmium***: Mean Cd level in seawater of polluted stations was 0.259 ppm. Mean level in tissue of clam was observed to be highest in PB (Fig. 13). The mean level in tissue from polluted area was 1.12 ppm (Fig.9). The mean cadmium level in sediment was highest in RM (Fig.17; Tables 1, 2).

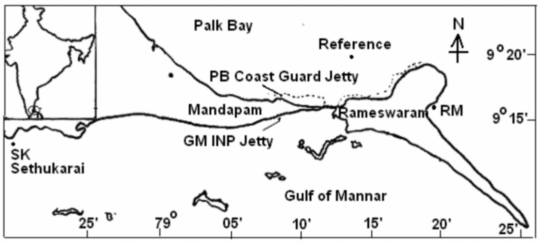


Fig. 1. Location of study area

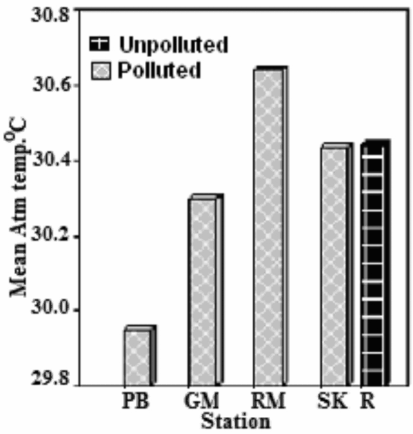


Fig. 2. Mean atmospheric temperature

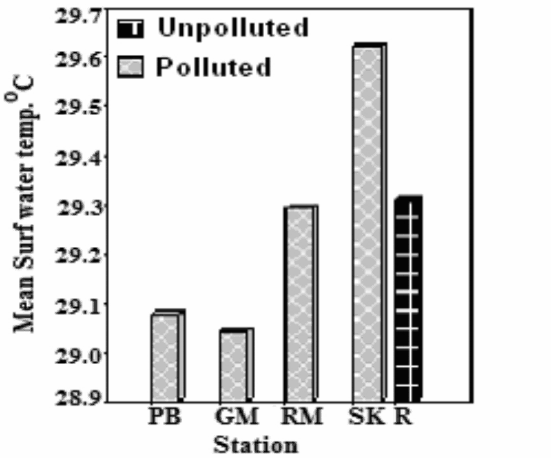


Fig.3. Mean sea surface temperature

***Copper:*** Mean copper level was highest in seawater of SK, while in sediment and tissue it was in Palk Bay reference station (Figs.10, 14 and 18). The mean level in sea water of polluted areas was 6.78 ppb while in sediment and tissue the maximum was 25.41 ppm and 18.96 ppm respectively.

Table 1. *Heavy metal level in tissue for different stations*

| Station | | Cd | Cu | Pb | Zn |
|---|---|---|---|---|---|
| P B | S | 4.10 | 17.50 | 47.89 | 1464.98 |
| | Min. | 0.00 | 0.00 | 0.00 | 0.00 |
| | Max. | 10.56 | 52.19 | 151.09 | 4975.00 |
| G M | S | 0.09 | 25.56 | 34.56 | 121.86 |
| | Min. | 0.00 | 0.00 | 0.00 | 0.00 |
| | Max. | 0.23 | 75.40 | 102.32 | 395.61 |
| RM | S | 2.09 | 14.54 | 150.87 | 64.16 |
| | Min. | 0.00 | 0.00 | 0.00 | 0.00 |
| | Max. | 5.49 | 34.54 | 426.73 | 187.09 |
| SK | S | 1.15 | 9.68 | 18.42 | 122.00 |
| | Min. | 0.00 | 0.00 | 0.00 | 0.00 |
| | Max. | 2.73 | 24.80 | 53.80 | 304.40 |
| Ref. | S | 1.78 | 27.20 | 32.64 | 655.55 |
| | Min. | 0.00 | 0.00 | 0.00 | 0.00 |
| | Max. | 6.00 | 99.99 | 112.44 | 2416.66 |

S = Std. deviation, Ref = Reference, Min.= Minimum, Max.= Maximum

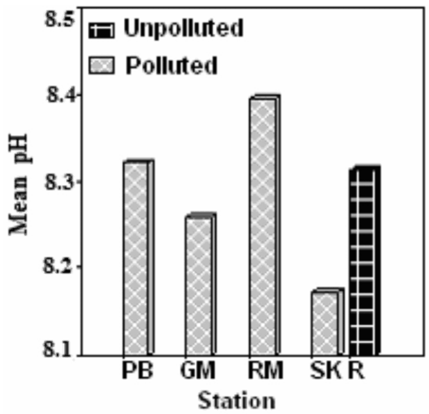


Fig. 4. Average *pH of seawater*

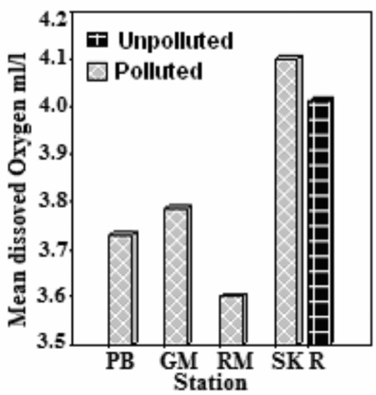


Fig.5 Dissolved oxygen in seawater

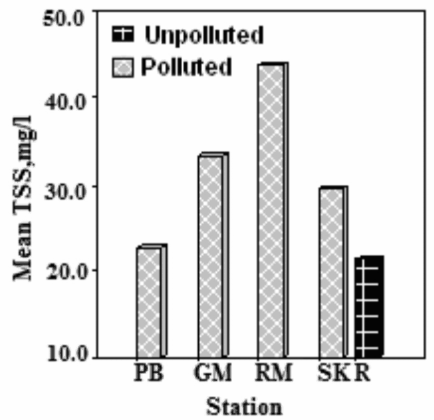


Fig. 6. Total suspended solids in seawater

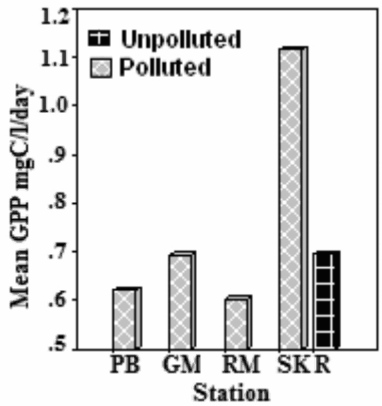


Fig. 7.Gross primary productivity

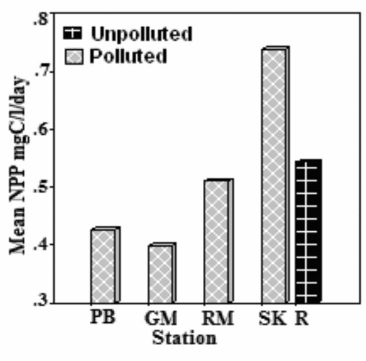


Fig. 8. Net primary productivity

***Lead***: The maximum lead level of 21.4 ppb was observed in seawater of SK (Fig. 11). In tissue and sediment, mean lead was highest in RM and GM respec-

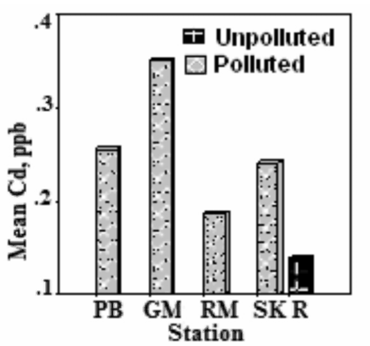


Fig. 9.Cadmium level in sea water

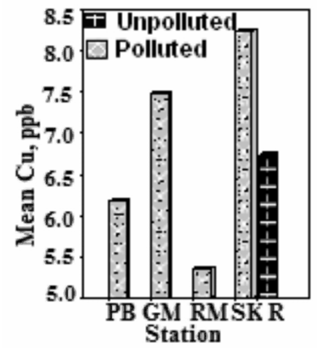


Fig. 10. Copper level in seawater

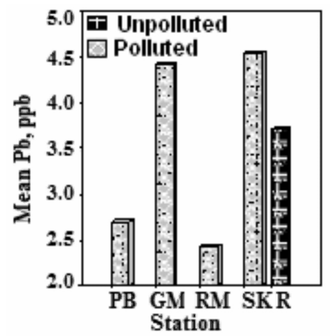


Fig.11. Lead level in seawater

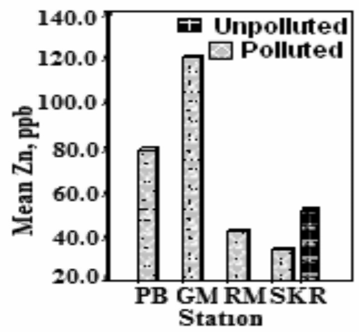


Fig. 12. Zinc level in seawater

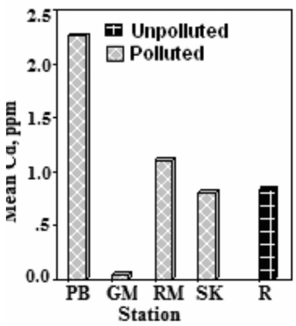


Fig.13. Mean cadmium level in tissue

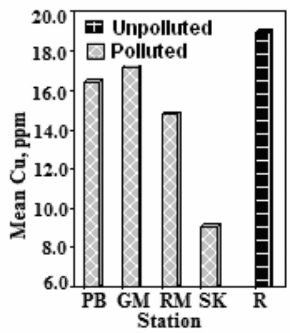


Fig. 14. Mean copper level in tissue

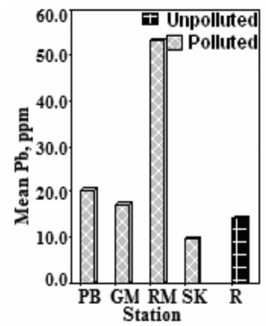


Fig. 15. Mean lead level in tissue

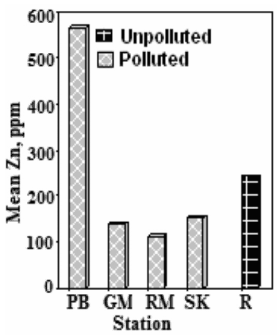


Fig.16. Mean zinc level in tissue

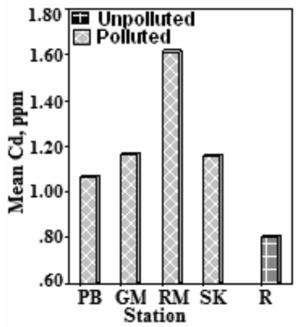


Fig. 17. Mean cadmium level in sediment

tively (Figs.15, 19). There was no significant difference between the polluted stations combined and reference station for heavy metal level in tissue based on ANOVA (Table 3). Maximum lead level in sediment and tissue of zooplankton from RM was 55.5 ppm and 426.73 ppm .

***Zinc***: In seawater, the mean Zn level was highest in GM near INP jetty site 119.8 ppb (Fig. 12). In tissue and sediment the mean level was highest in PB and GM (Figs.16, 20). Maximum Zn level in sediment and tissue for polluted station was 21.1 ppm and 4975 ppm respectively.

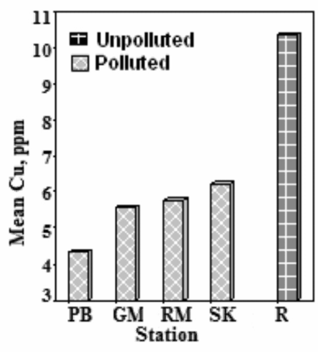


Fig. 18. Mean copper level in sediment

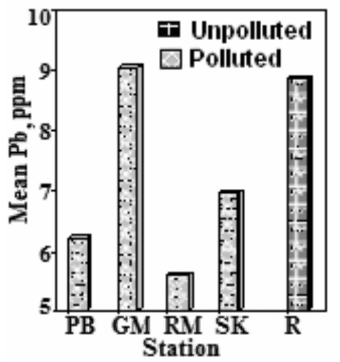


Fig. 19. Mean lead level in sediment

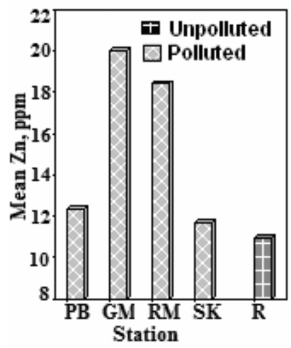


Fig. 20. Mean zinc level in sediment

Fig. 21. Untreated sewage let into Palk Bay near Rameswaram Jetty

Table 2. *Heavy metal level in sediments for different stations*

| Station | | Cd | Pb | Cu | Zn |
|---|---|---|---|---|---|
| PB | S | 1.64 | 15.22 | 4.04 | 5.88 |
| | Min. | 0.00 | 0.00 | 0.00 | 0.00 |
| | Max. | 4.40 | 44.10 | 10.60 | 17.70 |
| GM | S. | 1.66 | 18.52 | 6.02 | 8.66 |
| | Min | 0.00 | 0.00 | 0.00 | 0.00 |
| | Max. | 4.40 | 55.50 | 21.00 | 21.10 |
| RM | S | 1.60 | 15.56 | 3.61 | 2.82 |
| | Min. | 0.00 | 0.00 | 0.00 | 0.00 |
| | Max. | 5.00 | 36.60 | 12.60 | 8.75 |
| SK | S | 1.59 | 10.59 | 7.43 | 5.44 |
| | Min. | 0.00 | 0.00 | 0.00 | 0.00 |
| | Max. | 4.40 | 24.80 | 25.41 | 16.70 |
| Ref. | S | 1.25 | 15.46 | 15.47 | 9.16 |
| | Min. | 0.00 | 0.00 | 0.00 | 0.00 |
| | Max. | 4.00 | 45.70 | 53.50 | 29.40 |

S = Std. deviation, Ref = Reference,
Min.= Minimum, Max.= Maximum

Table 3. *ANOVA table for tissue heavy metal between polluted stations combined and reference station*

| | | | Sum of Squares | df | Mean Square | F | Sig. |
|---|---|---|---|---|---|---|---|
| Cd * Type | Between groups | Com. | 0.770 | 1 | 0.77 | 0.14 | 0.71 |
| | Within groups | | 272.6 | 48 | 5.68 | | |
| | Total | | 273.4 | 49 | | | |
| Cu * Type | Between groups | Com. | 194.7 | 1 | 194.69 | 0.47 | 0.50 |
| | Within groups | | 19772.6 | 48 | 411.93 | | |
| | Total | | 19967.2 | | 49 | | |
| Pb * Type | Between groups | Com. | 943.3 | 1 | 943.34 | 0.21 | 0.65 |
| | Within groups | | 216679.0 | 48 | 4514.15 | | |
| | Total | | 217622.3 | 49 | | | |
| Zn* Type | Between groups | Com. | 5561.3 | 1 | 5561.32 | 0.01 | 0.92 |
| | Within groups | | 28294312.8 | 47 | 602006.66 | | |
| | Total | | 28299874.2 | 48 | | | |

Com. = Combined

## Discussion

The atmospheric and seawater temperature range observed in Palk Bay and Gulf of Mannar were similar to those observed earlier by Subramanian and Kannan (1988). The mean *p*H and dissolved oxygen values were within the range of 6-8.5 and 3ml/l respectively, specified by WHO for coastal waters. The surface association of metal ions with oxide surfaces normally occurs over a very narrow *p*H range of 1to 2 Units (Benjamin and Leckie, 1980). Easterson and Mahadevan (1980) have reported that the dissolved oxygen (DO) of the surface water at Mandapam varied between 2.96 to 5.59 ml/l. The mean DO for polluted waters combined was 3.79ml/l while it was higher in Gulf of Mannar pollution site than in Palk Bay. Organic materials which are similar to those naturally found in the sea, such as domestic sewage and food processing wastes are decomposed more rapidly. However, the release of elements essential for plant nutrition and productivity from these materials leads to eutrophication (Qasim and Sankaranarayanan, 1972). The gross primary productivity in the present study was 0.16-4.461mgC/l/day for the polluted stations combined and in the reference station it varied between 0.16-1.956mgC/l/day. ANOVA did not show any significant difference between the mean total suspended solids from polluted water and reference station. Nevertheless, the discharge of untreated sewage on a long term basis (Fig. 21) can damage adjacent sensitive seagrass and coral reef ecosystem. ANOVA for atmospheric and surface water temperature, *p*H, dissolved oxygen, NPP and GPP did not show significant difference for polluted and non-polluted stations.

The Cd level in seawater has not exceeded the permissible level of 2.5 ppb specified by European Economic Committee in any of these stations. In tissue and sediment it has not exceeded 9 ppm, the permissible limit in seafood specified by WHO (1987) and 4.2 ppm indicated by Long *et al*. (1995) respectively. The Cu level in seawater was greater than 5 ppb level specified by EEC (Fig. 10), but was within the safe limit of 25 ppb specified by Boyd (1990). Copper has entered the aquatic environment by leaching from paints on the hulls of ships (Lloyd, 1992). In addition, copper is used as fungicides and algicides. In tissue and sediment, copper level has not exceeded the permissible limit of 130 ppm and 108 ppm respectively. Mean Pb level in seawater has not exceeded the safe limit of 15ppb (Fig.11). Kumaresan *et al.* (1988) studied the distribution of Zn in sediments of coral and seagrass beds of Manali and Hare islands in Gulf of Mannar and it was 20.08 and 21.75 ppm respectively. In the present study a maximum Zn level of 29.4 ppm was observed in Palk Bay sediment. The mean Pb and Zn level in sediment have not exceeded the permissible limit of 112 ppm and 271ppm respectively. In sea water, the Zn level is greater than the permissible limit of 40 ppb specified by EEC.

In comparison with water and sediment in all the stations observed, the level of heavy metals Pb and Zn in tissue were higher. These trace metals can be removed from the water column only by accumulation in the biota or by sedimentation. Major sources of Pb to aquatic systems include atmospheric deposition of exhaust from vehicles, disposal of batteries, sewage discharge, agricultural runoff from fields fertilized with sewage sludge (Ronald *et al*.,1999). It is seen that high Pb level was observed in tissue samples collected from pollution sources in PB, GM and RM station. Statistically there was no significant difference in the presence of heavy metal in tissue, between samples of polluted and non-polluted stations. The presence of higher heavy metal Pb and Zn in tissue indicates that the movement of metals is not localized but spread out and depends on various other factors like embayed condition, wind velocity and current pattern of the region.

The reversal of winds associated with northeast and southwest monsoons entirely changes oceanographic phenomena in the area as well as the current pattern in the Palk Bay. More long-term studies with specific reference to sensitive ecosystems in the region are necessary to ascertain the anthropogenic impact and remedial measures to be adopted.

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