

Seasonal variation of heavy metals in coastal water of the Coromandel coast, Bay of Bengal, India

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Received 5 January 1998, revised 21 June 1999

This report presents the dissolved heavy metals and associated hydrographic and nutrients data. Concentrations of heavy metals such as Cu, Zn, Ni, Co, Cd and Hg were showed a rather homogeneous distribution (except Hg) within the coastal region, with high values of Cu ($63.20 \mu\text{g l}^{-1}$) and Cd ($66.80 \mu\text{g l}^{-1}$) at Mahabalipuram and Zn ($130.20 \mu\text{g l}^{-1}$), Ni ($14.60 \mu\text{g l}^{-1}$), Co ($9.60 \mu\text{g l}^{-1}$) and Hg ($0.12 \mu\text{g l}^{-1}$) at Pondicherry during the premonsoon and monsoon seasons respectively. High concentrations of these metals in water may be due to the discharge of monsoonal rains carrying discharge of industrial and agricultural wastes and sewage directly into the coast. This is substantiated by a highly significant positive correlation between concentrations of heavy metals in seawater and nutrients. The metal concentrations in seawater were in order of $\text{Zn} > \text{Cu} > \text{Cd} > \text{Ni} > \text{Co} > \text{Hg}$ at Mahabalipuram and $\text{Zn} > \text{Cd} > \text{Cu} > \text{Co} > \text{Ni} > \text{Hg}$ at Pondicherry. Enrichment of heavy metals contaminations were more in the Coromandel coast, when compared to other marine environs of the Indian coast and also compared to natural seawater level.

A study on distribution of heavy metals in seawater is very important to understand their role in various biogeochemical processes of the sea. Significant contributions have been made with reference to oceanic and coastal distribution of various heavy metals¹. However, information on the distribution of heavy metals in the coastal waters of India is limited. In the coastal waters, the different processes controlling metal distribution tend to be superimposed. Inputs can be from rivers, sediments, atmospheric and degradation of material formed *in situ*; removal can be by biological uptake, sorption in or on to the sedimentary particles both organic or inorganic and by flushing with ocean and coastal waters². Further, a knowledge of the distribution and concentrations of heavy metals in coastal water helps to detect the sources of pollution in the aquatic systems³ and for this reason, water should be included as one of the environmental parameters monitored, in major marine pollution programmes. Present study has been undertaken to understand the seasonal distribution pattern of heavy metals (Cu, Zn, Ni, Co, Cd and Hg) and the provenance of Coromandel coastal seawater, Bay of Bengal.

Materials and Methods

The study areas selected for the present study viz. Mahabalipuram (lat. $12^{\circ} 37' \text{ N}$; long. $80^{\circ} 12' \text{ E}$) lo-

cated 58 km south of Madras, covers an area of 8 km^2 (Fig. 1). The tide is semi diurnal type, influenced by the northeast monsoon cycles. In regards to pollution sources anthropogenic inputs due to tourism are present in this area. The river input around this area is only through the river Palar which opens into the sea near Kalpakkam (6 km south of Mahabalipuram). This river generally transports pesticides and fungicides containing heavy metals originating from agricultural fields. Pondicherry (lat. $11^{\circ} 53' \text{ N}$; long.

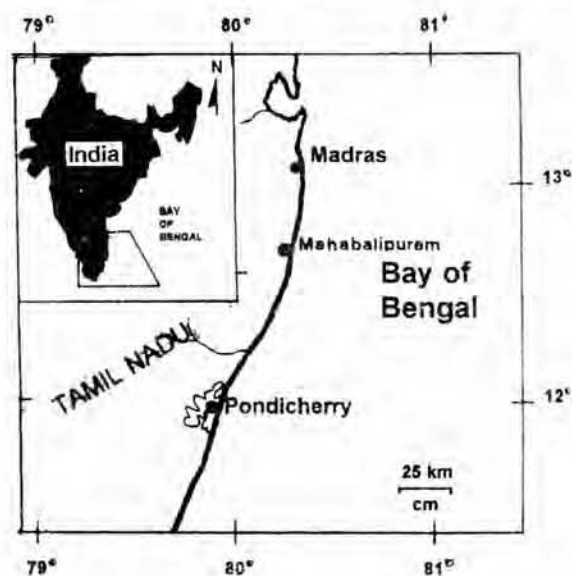


Fig. 1—Map showing the study area.

79° 49' E) is located at a distance of about 100 km south of Mahabalipuram (Fig. 1). Here the littoral region is sandy in nature. Pondicherry coastal area is polluted by the discharge of bulk quantities of industrial, domestic and agricultural wastes directly into the sea. Some major and some small industries such as Anglo French textiles, Chemfab alkalins, Pondicherry paper mills, SICA breweries (nearly 16) and Ponds and Soap division, Golden paper boards, Shasum durgs etc. are situated in this area. All the industrial and domestic wastes are discharged into the sea through four major drains viz. Vaithikuppam drains, Kurachikuppam drain, Grand canal drain and Uppar canal drain. Anthropogenic inputs including faecal contamination are also very high in this area as it is frequented by a large number of tourists.

Nearshore surface (one metre depth) seawater samples were collected from intertidal region at monthly intervals using a wooden dug-out canoe for a total period of two years (April 1989 to March 1991) from both the stations. For the analysis of dissolved nutrients, water samples collected in one liter clean polythene containers and immediately kept in an ice box and transported to the laboratory to avoid contamination. The water samples were then filtered through a millipore filtering unit using HA membrane millipore filter paper (mesh 0.45 μm). The filtered samples were deep frozen and the nutrients were analyzed the next day. Analyses of $\text{PO}_4\text{-P}$, $\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{SiO}_3\text{-S}$ were carried out according to the standard methods⁴.

For the analysis of dissolved heavy metals, surface seawater samples were collected in one liter clean polypropylene bottles of a liter capacity and immediately kept in an ice box and transported to the laboratory to avoid contamination. The water samples were then filtered through a millipore filtering unit using millipore filter paper (mesh 0.45 μm). The filtered samples were pre-concentrated immediately with APDC-MIBK⁵ extraction procedure.

Filtered seawater (1 liter) was divided into 500 ml aliquot and the pH was adjusted to 4 ± 0.1 by addition of 5% HNO_3 . Immediately the heavy metals were pre-concentrated including Hg and separated from the bulk matrix by complexation with APDC and extraction into MIBK. The organic layer containing the metal chelate was collected and back extracted with 50% HNO_3 and diluted with metal free double distilled water. The resulting solution was then stored in acid washed borosil glass vials for Hg and polypro-

pylene containers for other metals. This solution was aspirated into a flame atomic absorption spectrophotometer (Perkin-Elmer model 373) for the determination of Cu, Zn, Ni, Co and Cd and a standard mercury analyzer (ECIL) was used for Hg estimation by Cold vapor atomic absorption spectrophotometry. Re-extraction of each sample with the addition of APDC and MIBK to each aliquot was treated as the blank⁵.

A series of standard metal solutions (Cu, Zn, Ni, Co, Cd and Hg) were prepared in the optimum concentration range with metal free double distilled water. Calibration curves were prepared by plotting the absorption against concentration of the working solution for each element. Metal concentrations in the samples were calculated with the help of these calibration curves and expressed as $\mu\text{g l}^{-1}$. No detectable amounts of these metals were found in the reagent blank. The accuracy of the method was verified using biological tissue reference material (NIES No. 6) of the Sargasso sample obtained from the National Institute of Environmental Studies, Japan shown in Table 1.

For the sake of convenience and interpretation, a calendar year was divided into four seasons based on the northeast monsoon which alone brings bulk rainfall to the southeast coast of India where the present study area is situated. The seasons are: monsoon (October-December), postmonsoon (January-March), summer (April-June) and premonsoon (July-September).

Results and Discussion

Heavy metals such as copper, zinc, nickel, cobalt, cadmium and mercury occur in the seawater in different forms at different concentrations. Concentrations of Cu, Zn, Ni, Co, Cd and Hg measured in the coastal waters of Mahabalipuram and Pondicherry were within the ranges reported for other areas of the world oceans^{3, 6-11}.

Annual mean concentrations of heavy metals in seawater varied spatially as Cu, Ni, and Cd concentrations were high at Mahabalipuram and of Zn and Co were high at Pondicherry. Hg concentration was more or less equal at both the stations. Seasonal variation in the mean concentrations of metals (Table 2) revealed the fact that Zn and Co ($100.30 \mu\text{g l}^{-1}$ and $5.80 \mu\text{g l}^{-1}$) and ($98.30 \mu\text{g l}^{-1}$ and $6.20 \mu\text{g l}^{-1}$) at Mahabalipuram and Pondicherry respectively and concentrations were high during the premonsoon at both the stations. Hg concentrations were high ($0.09 \mu\text{g l}^{-1}$)

during the postmonsoon and monsoon seasons at Mahabalipuram and Pondicherry. But Cu ($40.00 \mu\text{g l}^{-1}$) and Ni ($9.20 \mu\text{g l}^{-1}$) showed high concentration during the premonsoon (Mahabalipuram) and postmonsoon (Pondicherry) seasons. Cd concentrations of $44.30 \mu\text{g l}^{-1}$ and $51.10 \mu\text{g l}^{-1}$ were high during the postmonsoon season at both the stations (Table 1). In general, the order of abundance of these metals was as follows;

Mahabalipuram - Zn > Cu > Cd > Ni > Co > Hg
Pondicherry - Zn > Cd > Cu > Co > Ni > Hg

At both the stations, concentrations of metals in water were high during the premonsoon and postmonsoon seasons with the peak at the latter. Cu concentration was high during the premonsoon season in November 1989 ($63.20 \mu\text{g l}^{-1}$) and December 1990 ($31.50 \mu\text{g l}^{-1}$) at Mahabalipuram and Pondicherry re-

Table 1—Certified values and concentrations found values and recovery trial (%) of the present study sample for the accuracy and precisions of the data

Sample ($\mu\text{g g}^{-1}$)	Cu	Zn	Ni	Co	Cd	Hg
NIES No. 6 Certified values	5.04±0.17	108±20	2.50±0.05	—	0.80±0.03	0.06±0.001
Concentration found	4.90±0.20	106±0.25	2.00±0.09	—	0.68±0.07	0.04±ND
Recovery Trial %	95%	98%	96%	—	95%	95%

Table 2—Seasonal, annual and total mean concentrations of heavy metals in water ($\mu\text{g l}^{-1}$) at Mahabalipuram and Pondicherry from April 1989 to March 1991.

Metal	Year	Summer	Pre monsoon	Monsoon	Post monsoon	Annual mean	Total mean
Mahabalipuram							
Cu	1989-1990	5.00	2.20	29.20	6.80	10.80	14.10
	1990-1991	9.50	40.00	18.00	2.10	17.40	
Zn	1989-1990	20.00	45.30	33.20	36.10	33.70	45.80
	1990-1991	26.00	100.30	68.90	36.00	57.80	
Ni	1989-1990	2.10	1.80	5.20	6.10	3.80	4.60
	1990-1991	3.90	7.50	4.20	6.20	5.40	
Co	1989-1990	0.00	0.03	3.50	0.10	1.00	1.90
	1990-1991	0.20	5.80	4.50	0.50	2.70	
Cd	1989-1990	26.00	9.30	7.20	2.60	11.30	25.60
	1990-1991	39.90	15.30	36.10	44.30	33.90	
Hg	1989-1990	0.05	0.07	0.05	0.04	0.05	0.06
	1990-1991	0.02	0.08	0.06	0.09	0.06	
Pondicherry							
Cu	1989-1990	1.40	2.60	7.50	3.10	3.70	7.70
	1990-1991	1.70	4.90	18.70	21.40	11.70	
Zn	1989-1990	47.30	36.00	61.00	37.00	45.30	61.90
	1990-1991	68.50	98.30	86.10	60.40	78.30	
Ni	1989-1990	0.30	0.70	1.30	1.00	0.80	3.10
	1990-1991	0.70	2.40	9.20	9.10	5.40	
Co	1989-1990	0.10	6.20	5.20	0.30	3.00	2.90
	1990-1991	0.40	2.70	3.70	4.40	2.80	
Cd	1989-1990	5.00	7.60	26.10	10.50	12.30	20.70
	1990-1991	20.20	10.40	34.40	51.10	29.00	
Hg	1989-1990	0.04	0.04	0.05	0.06	0.05	0.06
	1990-1991	0.03	0.04	0.09	0.07	0.06	

spectively and low during the summer season in June ($0.80 \mu\text{g l}^{-1}$) at Mahabalipuram and in April ($0.30 \mu\text{g l}^{-1}$) 1989 at Pondicherry (Fig. 2). Such a seasonal variation of Cu in water was perhaps due to the presence of major sources of metal pollution, intensive human activity, discharge of domestic wastes and land run-off reaching the coastal area at Mahabalipuram and also discharge of industrial effluents, sewage outlets and municipal wastes at Pondicherry. Phytoplankton activity¹² might have also facilitated the seasonal variation in Cu as this metal is an essential one for phytoplankton. Further, higher concentrations of Cu, nitrate and phosphate were recorded during October-December, perhaps due to the monsoonal discharges, from land run-off in the washing of polluted coast.

Further the statistical analysis revealed a significant negative correlation between Cu and salinity ($r = -0.898$; $p < 0.001$) and a significant positive correlation between Cu and silicate ($r = 0.855$; $p < 0.001$) at Mahabalipuram. Such a relationship between Cu concentration with salinity and nutrient was also observed^{8, 13}. At Pondicherry, positive correlation of Cu with phosphate ($r = 0.699$; $p < 0.01$) and nitrite ($r = 0.852$; $p < 0.001$) was also significant.

Zn concentration was high during the premonsoon season ($115.00 \mu\text{g l}^{-1}$ and $135.50 \mu\text{g l}^{-1}$ in August, 1990) at Mahabalipuram and Pondicherry respectively. High Zn concentration in water could have resulted due to the release of this metal from the sediment and abundant organic matter¹⁴ derived from the seaweeds at Mahabalipuram and freshwater inputs along with various drainage at Pondicherry. Further, during the premonsoon season when Zn concentration was high, phosphate and nitrate ($3.90 \mu\text{g -at. l}^{-1}$ at Mahabalipuram; $4.60 \mu\text{g -at. l}^{-1}$ at Pondicherry and $12.00 \mu\text{g -at. l}^{-1}$ at Mahabalipuram; $4.50 \mu\text{g -at. l}^{-1}$ at Pondicherry) concentrations in water were also high (Fig. 3). This is evidenced by the statistical analysis which revealed a positive significant relationship between Zn and phosphate ($r = 0.670$; $p < 0.01$) and nitrite ($r = 0.622$; $p < 0.01$).

Zn concentration was low during the summer season at both the stations. This would have resulted due to the utilization and uptake of zinc along with other nutrients by the biota including phytoplankton. Evidently, the phytoplankton population density was high ($77,250 \text{ cells l}^{-1}$) during the summer season at Mahabalipuram (Fig. 3). Zn could get strongly de-

pleted from the surface waters as it has a nutrient type of distribution in seawater¹⁵.

Concentrations of Ni, Co and Hg in the coastal waters at Mahabalipuram and Pondicherry were also low during the summer season due to the removal of a substantial portion of these metals from water by phytoplankton¹⁶ and binding to other suspended matter. At Mahabalipuram, high concentration of Ni ($12.50 \mu\text{g l}^{-1}$) and Co ($6.50 \mu\text{g l}^{-1}$) were recorded during the premonsoon season while at Pondicherry, Ni ($9.60 \mu\text{g l}^{-1}$) and Co ($14.60 \mu\text{g l}^{-1}$) were recorded during the premonsoon and postmonsoon seasons respectively. This differential seasonal distribution of heavy metals could be attributed to variations in different environmental parameters such as salinity, sediment load, nutrient chemistry, discharge of domestic and industrial effluents (station 1) and land run-off, tourism (station 2) reaching the coastal area.

Metals are best correlated with a combination of nutrients^{9, 10}. This is evident by the statistical analysis which revealed a significant relationship between some heavy metals (Ni and Co) and nutrients (phosphate, nitrate, nitrite and silicate).

Mahabalipuram

Ni: $r = 0.866$ (PO_4) and $r = 0.813$ (NO_3) Both at $p < 0.001$ level.

Co: $r = 0.736$ (PO_4); $r = 0.817$ (NO_3); $r = 0.716$ (SiO_2); all at $p < 0.001$ level; $r = 0.670$ (NO_2); $p < 0.01$ level.

Pondicherry

Ni: $r = 0.886$ (PO_4) and $r = 0.795$ (NO_3) Both at $p < 0.001$ level.

Co: $r = 0.706$ (PO_4); $r = 0.687$ (NO_3); Both at $p < 0.001$ level; $r = 0.816$ (SiO_2); $p < 0.001$ and $r = 0.498$ (NO_2); $p < 0.01$ level.

The average concentrations of Ni and Co in surface waters showed a strong correlation with the available nutrients and a combination of phosphate, nitrate, nitrite and silicate⁸.

There was a narrow range of fluctuation in Cd concentration in seawater. Pondicherry recorded more Cd ($61.60 \mu\text{g l}^{-1}$) than Mahabalipuram. Cd concentration was more during the postmonsoon season at both the stations and less during the summer season. Cd is released into the atmosphere by fossil fuel and by the burning of agricultural and municipal wastes, including dried sewage sludge¹⁷. These activities are relatively more at Pondicherry, facilitating atmospheric

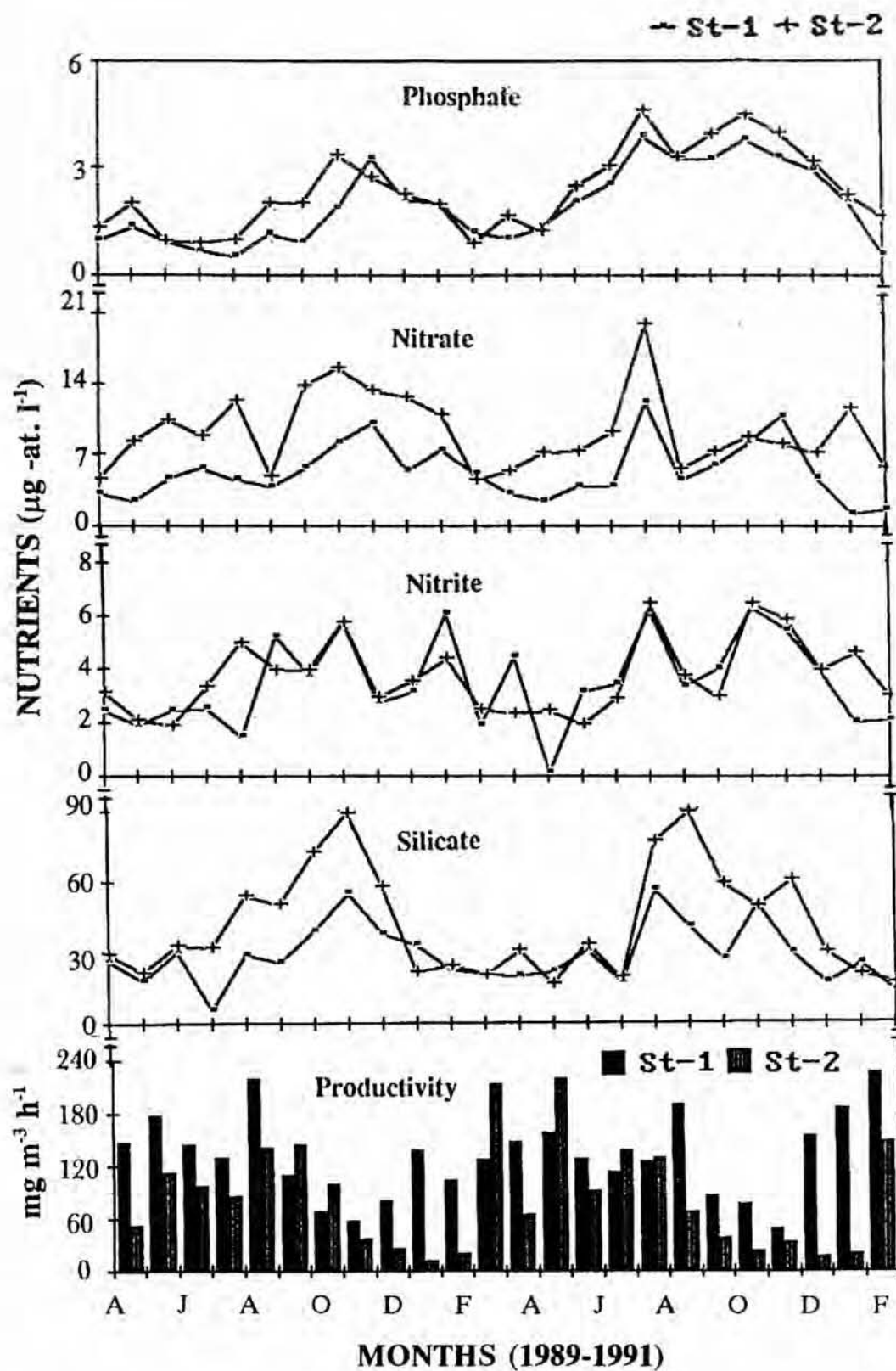


Fig. 2—Monthly variations of phosphate, nitrate, nitrite, silicate and primary production in water were recorded at Mahabalipuram and Pondicherry from April 1989 to March 1991.

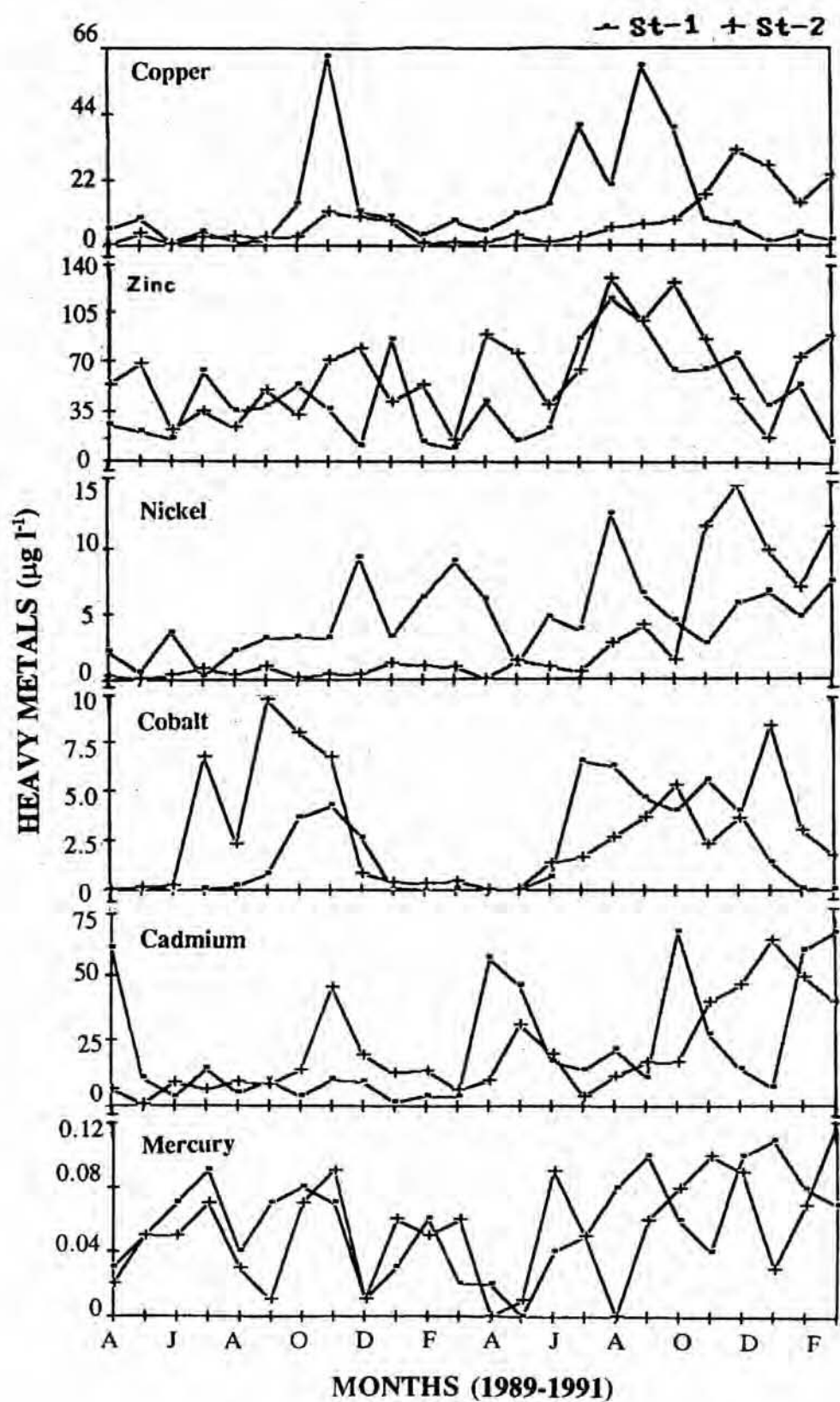


Fig. 3—Monthly variations of copper, zinc, nickel, cobalt, cadmium and mercury concentration in water recorded at Mahabalipuram and Pondicherry from April 1989 to March 1991.

Table 3—Concentration of heavy metals ($\mu\text{g l}^{-1}$) in water reported from various marine environs of the India.

Location	Cu	Zn	Ni	Co	Cd	Hg	Reference
Coromandel coast, India	0.31-50.70	9.00-130.60	ND-14.60	ND-9.60	0.30-66.80	ND-0.12	Present study
Bay of Bengal	4.90	8.00	4.80	3.60	-	-	19
Bay of Bengal (Coastal water)	5.40	25.40	-	1.10	-	-	12
Bay of Bengal	1.20-17.50	1.90-174.00	0.80-30.30	-	0.30-2.90	0.05-0.30	20
Bombay Harbour	16.00	27.00	0.50	0.50	0.10	0.23	21
Madras Coast	6.00-170.00	15.00-290.00	5.00-17.00	-	1.00-4.00	1.00-1.20	22
Pondicherry Coast	0.70-61.50	16.70-135.70	ND-14.80	ND-9.50	3.20-69.00	ND-0.15	3

ND-Not detectable

input of Cd into the coastal waters, in addition to the direct discharge of agricultural, municipal and industrial wastes. In general, higher values of metal concentrations were associated with large amount of land and river drainage during the monsoon (October-December) season at both the stations. When the concentrations of heavy metals (Cu, Zn, Ni, Co, Cd and Hg) in seawater observed in the present study are compared with the levels reported from the other regions of the Indian coast (Table 3), most of the regions showed lower concentrations than the Coromandel coast indicating the increased load of heavy metals pollution along this coast due to various factors such as river run-off, discharge of industrial wastes and municipal sewage, anthropogenic inputs and harbor activities.

Enrichment ratios, used as the tool of quantification of contamination, were compared for water samples with respect of natural and local (Indian coast) background concentration values separately. It was observed that for water the contamination was more when compared with natural and local values (Tables 3, 4). Moreover, concentrations of the heavy metals are increasing from year to year. So it is concluded from the present study that the Coromandel coast of India is rapidly getting polluted with these metals, thus substantiating the view of Govindasamy³, who reported that the coastal waters of the Tamil Nadu state are definitely polluted with heavy metals. So these results clearly indicate that local hydrography,

Table 4—Metal levels in natural seawater and coastal water of Mahabalipuram and Pondicherry of the present study

Metals	Natural seawater * ($\mu\text{g l}^{-1}$)	Present study ($\mu\text{g l}^{-1}$)	
		Mahabalipuram	Pondicherry
Cu	0.092-0.240	0.80-059.70	0.30-031.50
Zn	0.007-0.640	9.00-115.00	15.00-130.60
Ni	0.228-0.693	0.50-012.50	ND-014.60
Co	-	ND-006.50	ND-009.60
Cd	0.015-0.118	0.80-006.50	0.30-063.30
Hg	0.011-0.033	ND-000.11	ND-000.12

Source: * 23

seasonal variability and physico-chemical state are factors which cannot be neglected in studies of the occurrence of dissolved trace metals in coastal waters. Thus Pondicherry is relatively more polluted than Mahabalipuram. Therefore, strict enforcement of laws to prevent pollution in these coastal areas should be made. Attention should be paid immediately to Pondicherry coastal region failing which there will be concomitant loss of valuable marine resources. In Mahabalipuram, which is comparatively less polluted at present, permission for commencing the works in the new industries should be granted only when the industries set up efficient waste water treatment plants. Further, human activities in the form of tourism etc. should be streamlined in order to minimise pollution.

Acknowledgement

The first author (CG) thanks the University of Madras for facilities and also thank the Council of Scientific and Industrial Research, Government of India, for the financial support.

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