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N. Jayaraju<sup>a</sup>, B. C. Sundara Raja Reddy<sup>b</sup> & K. R. Reddy<sup>b</sup> <sup>a</sup> Department of Geology & Geoinformatics, Yogi Vemana University, Kadapa, India

<sup>b</sup> Department of Geology, S.V. University, Tirupati, India

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# Anthropogenic metal pollution in surface sediments of the Tambaraparni River Estuary

N. Jayaraju<sup>a</sup>\*, B.C. Sundara Raja Reddy<sup>b</sup> and K.R. Reddy<sup>b</sup>

<sup>a</sup>Department of Geology & Geoinformatics, Yogi Vemana University, Kadapa, India; <sup>b</sup>Department of Geology, S.V. University, Tirupati, India

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Estuarine sediments in the <63  $\mu$ m size fraction were collected from 15 stations within the Tambaraparni River Estuary, located on the east coast of India. The distribution of the heavy metals Cd, Co, Cr, Cu, Ni, Pb and Zn was recorded. Our analysis distinguished two groups of elements. First, Cd, Pb and Zn, which occurred in higher than expected concentrations indicative of pollution, and second, Co, Cr, Cu and Ni, which occurred at background levels. The highest metal concentration found in the study area was for Zn (1200  $\mu$  g  $\cdot$  g<sup>-1</sup>), and the lowest was for Cd (0.42  $\mu$ g  $\cdot$  g<sup>-1</sup>). It is presumed that river run-off, industrial waters and untreated domestic waters are major contributors to heavy metal pollution in the Tambaraparni River Estuary. The concentrations of heavy metal species in surface sediments (<2 m water depth) of the Tambaraparni Estuary were studied to determine the extent of anthropogenic inputs from catchment areas and to understand anthropogenic effects on geochemical process in this tropical estuarine system.

Keywords: sediments; heavy metal pollution; river; estuary; elemental concentrations

## 1. Introduction

Estuarine sediments can be a sensitive indicator of both spatial and temporal trends when monitoring contaminants in estuarine environments [1–4]. Estuaries around the world receive a large amount of waste from the catchments that surround them and have become repositories for heavy metals, hydrocarbons and pesticides. In small quantities, metals such as Fe, Cu, Co and Zn are essential for the healthy growth of marine organisms. However, these same metals are toxic if present in excess. By contrast, metals such as Hg, Pb and Cd are said to have little or no biological role [5]. Sediment contamination poses one of the worst environmental problems for marine ecosystems. Sediments may act as sinks and also as sources of contaminants in aquatic systems [6,7]. Heavy metals are defined as metals having densities  $>5 \text{ g} \cdot \text{cm}^{-3}$  [8]. In aquatic ecosystems, heavy metals are in dynamic equilibrium with pore water and the overlying water column, and have pathways that are primarily associated with sediment substrates [9,10]. Aquatic sediments constitute the most important sink of heavy metals and other pollutants [11,12] in

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<sup>\*</sup>Corresponding author. Email: nadimikeri.jayaraju@gmail.com

aquatic ecosystems. Determining sediment quality is therefore essential in assessing the pollution status of any aquatic ecosystem.

In concentrated amounts, heavy metals are lethal to organisms including humans. Accumulation of Pb and Cd in the body may result in brain and kidney damage [8]. Lead contamination may also lead to metabolic interference and central nervous system toxicity, while Cd causes skeletal illness, high blood pressure and sterility among males [13]. Other heavy metals are also known to have deleterious effects when introduced into the environment in undesirable amounts. Grain size plays a significant role in determining elemental concentrations in sediments [14–18]. Salomons and Forstner [19] recommended that the sediment particle size fraction  $<63 \,\mu$ m be analysed for heavy metals as this fraction is the most likely to be carried in suspension, the most important system for transport of sediments.

Recently, reports have stated that water quality in many estuaries is deteriorating day by day due to different human activities [15,16]. However, few studies have been conducted in the estuarine waters of south India with reference to heavy metal contaminants. This study is intended to provide data regarding the levels of heavy metals in one of the major estuarine systems of the region. The aim of the study is to generate a database on heavy metal concentrations at selected stations within the Tambaraparni Estuary and to compare metal levels here with those in different estuarine sediments from both the east and west coasts of the Indian subcontinent. Assessment of heavy metal pollution in marine sediments requires knowledge of preanthropogenic metal concentrations were not available assessment of metal pollution in marine sediments is not possible [20].

# 2. Materials and methods

#### 2.1. Study area

The Tambaraparni River rises in the Western Ghats and flows eastwards for  $\sim 120 \text{ km}$  before debouching into the Gulf of Mannar, through three small distributaries, near Punnaikayal, 20 km south of Tuticorin, Tamil Nadu (Figure 1). The hydrological and lithological details of the rivers draining both Indian coasts (east and west) are given in Table 1.

The Tambaraparni is one of the key rivers of south India that discharges into the Bay of Bengal. The river has a very wide mouth and its estuary extends  $\sim 20$  km in to the Bay of Bengal because of considerable freshwater influx (Table 1). The coast in the immediate vicinity of the estuary is characterised by the occurrence of a large number of small sand bars. The Tambaraparni River Estuary lies at 78°4′E and 8°40′ which forms part of topographic sheet No. 58 L/2, Survey of India. The river drains predominantly agricultural land, industrial zones (comprising haulage, construction and dredging activities), and residential and commercial areas. The Tambaraparni River is known to be highly contaminated by wastes derived from industrial sources, sewage and agricultural activities, which accounts for 76% of the total pollutants in India. The data obtained by this study have been found to be particularly useful for a variety of purposes because of the relatively high concentration of heavy metals and significant changes in the ambient physico-chemical conditions of the estuarine ecosystem. Unfortunately, the discharge of industrial and household waste into water resources (both direct discharge and indirect discharge through leakages in the sewage system) causes excessive contamination of surface and subsurface water. Consequently, water quality and irrigation value are lost. Therefore, it is imperative to know the mechanism by which heavy metals and their complexes are transported into rivers in order to understand their cycle in nature [21]. River hydrodynamics have been significantly altered in the last decades as a result of the construction of roads and industry. Two zones with contrasting hydrological

and environmental features can be distinguished in the study area: (1) a tidal zone, comprising broad salt marshes crossed by a meandering tidal channel; and (2) a lacustrine zone, consisting of streams of dendritic network.

#### 2.2. Experimental

In total, 15 sediment samples were retrieved using a manually operated dredge from fixed sampling stations across the upper, middle and lower regions of the estuary covering a distance of  $\sim$ 60 km (Figure 1). Each sample consisted of  $\sim$ 300 g of surface layer sediment (0–2 cm). Polyethylene scoops and cans were used exclusively for sampling and storage [21]. Samples were transferred to polyethylene bags, sealed, refrigerated and sent to the laboratory on the same day. In the laboratory, the sediment samples were left to settle, the supernatant water was removed and the sediment was spread out on a polyethylene tray and left to dry at room temperature. Dried sediments were sieved mechanically and the fraction of grain size <63  $\mu$ m was collected for the subsequent studies. A total of 1 g of wet sediment was digested with nitric acid and hydrogen peroxide on



Figure 1. Tambaraparni River Estuary showing sampling stations.

Table 1. Lithological and hydrological details of rivers.

River	Lithology	Area $(10^{6}  \text{km}^{2})$	Discharge (km <sup>3</sup> yr <sup>-1</sup> )	Run-off
Narmada <sup>a</sup>	Basalts, Alluvium	0.099	47	418
Tapi <sup>a</sup>	Basalts, Alluvium	0.065	19	282
Mahi <sup>a</sup>	Shale, Gneisses	0.035	12	339
Sabarmati <sup>a</sup>	Shale, Gneisses	0.022	4	189
Vishwamitra <sup>a</sup>	Trappean, Alluvium	0.003	1	250
Mandovi <sup>a</sup>	Basalts, Laterites, Alluvium	0.011	61	600
Hoogly <sup>a</sup>	Granites, Alluvium	0.750	52	657
Mahanadi <sup>b</sup>	Gneisses, Alluvium	0.150	25	420
Godavari <sup>b</sup>	Gneisses, Alluvium	0.145	22	500
Krishna <sup>b</sup>	Gneisses, Alluvium	0.110	21	335
Cauvery <sup>b</sup>	Gneisses, Alluvium	0.095	18	320
Tambaraparni <sup>c</sup>	Gneisses, Alluvium	0.065	16	270

Notes: aRahaman and Singh [43]; bAshraf et al. [5]; CThis study.

a hot plate at 100°C inside a fume hood until white fumes evolved. The resulting digest was cooled, filtered with Whatman filter paper and made up to the mark in a 25 cm<sup>3</sup> standard flask with deionised water [22]. The very fine particles in the supernatant were removed although they belong to the <63  $\mu$ m fraction. Data were analysed statistically with Pearson's correlation matrix and factor loadings using XL STAT 2010 [23] (Table 2).

## 2.3. Preparation of standards

Instrumental calibration was carried out prior to metal determination using standard solutions of metal ions prepared from their salts. Commercial analytical grade 1000 ppm stock solutions of  $Cd^{2+}$ ,  $Co^{2+}$ ,  $Cr^{2+}$ ,  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Pb^{2+}$  and  $Zn^{2+}$  were diluted in 25 cm<sup>3</sup> standard flasks and made up to the mark with deionised water to obtain working standard solution of 2.0, 3.0 and 4.0 ppm of each metal ion. Heavy metals (Cd, Co, Cr, Cu, Ni, Pb and Zn) were analysed using an atomic absorption spectrophotometer [19]. The detection limits of the technique are optimised to 0.01 ppb for all the analysed heavy metals, but they were also calculated statistically for each element, obtaining values <2 ppb in all cases [24].

#### 3. Results and discussion

Sampled sediments were usually <2 mm which includes sand, silt and clay. Concentration ranges in the <63  $\mu$ m sediments were: Cd 0.42–0.92  $\mu$ g · g<sup>-1</sup>; Co 14.3–21.3  $\mu$ g · g<sup>-1</sup>; Cr 64.5–110  $\mu$ g · g<sup>-1</sup>; Cu 62.8–115  $\mu$ g · g<sup>-1</sup>; Ni 36.4–76.0  $\mu$ g · g<sup>-1</sup>; Pb 50–170.0  $\mu$ g · g<sup>-1</sup> and Zn 473–1200 (Table 2). Sediments contaminated with Cd, Cu and Zn (Figure 2) are considered to be polluted and sediments contaminated with Cr, Pb and Ni are considered to be moderately polluted [25]. Validation of methodology is achieved by analytical performance characteristics using statistical control. The accuracy and confidence of the results were assumed by using certified reference materials and control samples [21].

# 3.1. Cd

The range of sedimentary Cd values  $(0.42-0.92 \,\mu g \cdot g^{-1})$  is somewhat lower than reported from other estuaries (Table 3). Cadmium (Cd) levels reported from Izmit, Turkey  $(3.3-8.9 \,\mu g \cdot g^{-1})$  [3] are higher than in other studies including this one. Therefore, the Tambaraparni Estuary can be considered to be moderately polluted with respect to Cd. The recorded values are higher than the 0.01–0.09 and 0.04 ppm found for sedimentary rocks [26] and this relative higher content is most likely contained in the biogenon's carbonates [27].

# 3.2. Co

Cobalt values ranged from 14.3 to  $21.3 \mu g \cdot g^{-1}$ . No comparison was made with other estuaries because Co had not been determined previously. In general, Co concentrations were low in the study area. No strongly elevated Co levels were observed, although Co is apparently enriched above normal values. The most significant positive relations were detected with Ni (0.628), Cr (0.564) and Cu (0.544). The most pronounced negative relation was Pb (-0.512) and Zn (-0.173) (Table 4). Cobalt is an active element in biological systems. The negative correlation between Co and Pb and Zn (Table 4) excludes an organic origin for cobalt. Similar results are also noticed in Mabahiss Bary, North Hurghada, Red Sea, Egypt [28] and Buyak Menderes and Gediz rivers, Turkey [21]. The Co pollution originates from industrial wastes and may increase if action is not taken.

									Sa	ampling	stations							
Element	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	Mean	Median	Variance
Cd	0.42	0.58	0.46	0.57	0.59	0.79	0.84	0.69	0.76	0.43	0.56	0.64	0.73	0.92	0.65	0.642	0.69	0.022
Co	19.1	15.6	14.3	15.7	19.5	20.3	18.6	19.5	21.3	16.5	18.4	17.6	18.9	20.2	16.9	18.16	19.5	4.003
Cr	75.4	70.5	58.9	64.5	75.3	90.5	110.3	110.1	96.5	87.6	96.4	98.5	79.9	86.4	90.3	86.07	110.1	234.81
Cu	86.2	74.6	62.8	77.2	78.4	75.3	90.8	115.3	110.4	96.9	89.5	96.5	95.4	89.5	91.2	88.66	115.3	189.71
Ni	36.4	37.8	44.5	46.9	55.8	58.6	72.6	64.5	76.0	58.5	68.5	49.5	72.3	68.4	53.9	57.61	64.51	62.21
Pb	156	130	146	170	110	78.4	68.4	65.3	68	75.2	70.2	69	65.3	57.6	50.3	91.98	65.31	5191.11
Zn	530	989	790	650	560	520	1200	850	810	745	685	598	610	590	473	706.68	50	38738

Table 2. Heavy metal concentrations in the sediments of the study area ( $\mu g \cdot g^{-1}).$ 

SD 0.148 2.001 5.326 3.777 2.736 23.25 196.82



Figure 2. Location of different rivers on the east and west coasts of India. The rectangle indicates the study area.

Table 3. Comparative evaluation of heavy metal concentrations  $(\mu g \cdot g^{-1})$  reported in the Indian estuaries.

Location	Cd	Cr	Cu	Pb	Zn
This study	0.42-0.49	58.9-110.3	62.8–115.35	0.3–170	473-1200
Mumbai Coast <sup>a</sup>	2-24	0-30	_	_	0-46
Mandovi (Goa) <sup>b</sup>	_	_	11.5-77.5	4.5-46.5	19.9-83.5
Cochin Coast <sup>c</sup>	8.14	_	17.14	5.94	318
Astamudi (Kerala Coast) <sup>d</sup>	0–9	0-35	0-60.3	0-19.7	0-88
Godavari <sup>e</sup>	15	25	59	110	132
Krishna <sup>e</sup>	_	45	129	80	105
Kaveri <sup>e</sup>	0.28	36	38	40	83

Notes: <sup>a</sup>Dhage et al. [41]; <sup>b</sup>Alagarsamy [31]; <sup>c</sup>Krishankumar et al. [42]; <sup>d</sup>Ashraf et al. [5]; <sup>e</sup>Paropkari et al. [39].

#### 3.3. Cr

High  $(110 \,\mu g \cdot g^{-1})$  and low  $(58.9 \,\mu g \cdot g^{-1})$  Cr levels were found at stations 7 and 3, respectively (Table 2). The high level  $(76 \,\mu g \cdot g^{-1})$  at station 9 and low level  $(36 \,\mu g \cdot g^{-1})$  at station 1 for Cr followed the same trend as for other heavy metals. The higher values at stations 7 and 8 may be

Variables	Cd	Co	Cr	Cu	Ni	Pb	Zn
Cd	1						
Co	-0.186	1					
Cr	-0.197	0.564	1				
Cu	-0.354	0.544	0.762	1			
Ni	0.109	0.628	0.650	0.596	1		
Pb	0.025	-0.512	-0.791	-0.646	-0.760	1	
Zn	0.205	-0.173	0.277	0.110	0.196	0.001	1

Table 4. Correlation matrix [Pearson (n)] for heavy metal concentrations.

attributed to the unbranching river course because the sediment tends to absorb the heavy metals. The river estuary is contaminated by agricultural, food processing, industrial and urban waste from various sources located along its course. Moreover, this area is comparatively shallow, and no high wave depositions regularly contaminate the upstream region. The low values at stations 12–15 may be due to the branching of river course, which ultimately disperses the heavy metal concentrations non-uniformly throughout the estuarine sediment. A similar trend has also been noticed in the Ojo and Ojora River Lagos, Nigeria Buyak Menderes and Gediz rivers, Turkey [21,22,29]. The levels of Cr and Ni were indicative of sites that were moderately to heavily polluted, whereas levels of Pb in sediments showed great spatial variation. The results show that Cr, which has high toxicity, is present in considerable levels. This is because of waste water discharge from industries located along the river banks.

## 3.4. Cu

Copper contamination in the estuarine system mainly comes from agricultural inputs such as Cu-containing pesticides, fungicides, and antifouling paints from tourist/recreational and fishing craft. It is also considered that long-term manure application can be responsible for the elevated Cu content in surface soils [30]. It should be mentioned here that there is no significant relation between salinity and the Cu concentration for inshore and estuarine waters along the Indian coasts [31]. The levels of Cu in the sediments in the present study varied from 64.5 to  $110 \,\mu g \cdot g^{-1}$  and are higher than those reported from various other estuarine sediments (Table 3). These values are not far from the average copper content (85 ppm) of limestones and agree with the average copper content of the marine sediments of north Red Sea wadies [27].

# 3.5. Pb

In this study, Pb concentrations varied from 50 to  $170 \,\mu g \cdot g^{-1}$ . The primary sources of Pb are manufacturing processes, atmospheric deposition and domestic waste. Sediments are the primary sinks for Pb in aquatic environments. For deep-sea sediments, the average background value is  $\sim 47 \,\mu g \cdot g^{-1}$ , although this fluctuates widely [32]. Lead levels in bay, estuarine and other coastal sediments have been much altered by anthropogenic activities. The average Pb level in Indian river sediment is  $\sim 14 \,\mu g \cdot g^{-1}$  [33], which is lower than the world average. The average Pb level in Indian river particulates is  $\sim 51 \,\mu g \cdot g^{-1}$  [25], which is also lower than the world average of  $150 \,\mu g \cdot g^{-1}$  [34]. This study showed that the variation in Pb levels in the region is high (50.3–170  $\,\mu g \cdot g^{-1}$ ). The high and fluctuating concentrations indicate the importance of anthropogenic input. In the Lapeter Sea, anthropogenic inputs are considered to be the major source of elevated Pb concentrations in marine sediments [35]. The Pb content of Gediz River Turkey (105–140 ppm), indicates that the river has a Pb pollution risk [21].

## 3.6. Zn

Zinc values ranged from 47 to  $120 \,\mu\text{g} \cdot \text{g}^{-1}$ . The relatively high levels of Zn were indicative of sites that were moderately to heavily polluted. Zinc was found at high levels at most stations. Anaerobic conditions lead to the formation of ZnS regardless of pH (within the range 1–14) [5]. Zn concentrations in the Tambaraparni estuarine sediments were generally higher than other metal species. Zinc can enter the aquatic environment from a number of sources including industrial discharge, sewage effluent and run-off [36]. Input of organic wastes from municipal sewage into the estuary likely contribute to increases in the Zn levels in sediments. The relations between zinc and other parameters are shown in a correlation matrix (Table 4). The most significant positive relation is that with Cr (0.277) and Cd (0.205). A negative relationship is found with Co (-0.173). Zinc is an essential element, therefore its uptake by marine biota may be increased at high temperatures. This may explain the decreased Zn concentration in sediment from the study area which is characterised by high temperatures, especially in summer, when the samples were collected. The most important cause of Zn pollution is industrial waste [21].

# 3.7. Ni

In this study, Ni values ranged from 36.4 to  $76.0 \,\mu\text{g} \cdot \text{g}^{-1}$ . Ni concentrations were elevated in all sediment samples. Historically, the focus of concern about this metal was in terms of occupational safety, but researchers are now paying more attention to its role in the health of estuarine ecosystems [5]. Environmental contamination by Ni occurs both naturally and anthropogenically. Natural enrichment includes chemical and physical weathering of igneous and metamorphic rocks and soils, which leads to the release of heavy metals into the sediments. Other contributions include the decomposition of plant and animal detritus, the precipitation of air-borne particles from volcanic activity, wind erosion, plant exudates and oceanic spray [37]. Some of the heavy metals in feed additives, such as Zn, Cu and Ni, end up in animal waste and be are concentrated in the catchment area of the Tambaraparni River. Nickel sulfate is released during the burning of fossil fuels and in waste incineration. The fractionation pattern of Ni for Buyak Menderes and Gediz rivers surface sediments of Turkey, indicates that Ni binds to organic and sulfide compounds in the strong acid-soluble fraction. It is normal to find Ni in the silicate phase when its compounds properties are considered [21]. The elevated Ni concentrations in this study may be primarily anthropogenic.

#### 3.8. Factor analysis

The available data (Table 2) were subjected to factor analysis which explained  $\sim$ 65.57% of the variance (Table 5, Figures 3 and 4). Factor 1 accounted for 48.88% of the variance with Pb, Cr, Ni, Cu and Co the dominant heavy metal species. Factor 2, comprising Zn, accounts for 17.08% of the variance. Factor 3, comprising Cd, accounts for 9.61% of the variance (Figures 3 and 4). The first factor corresponds to the change from the river mouth to the inner part of the study area and the second factor corresponds to the change from areas under the direct influence of seawater towards the central part of the study area. Thus, the main factor deferring the distribution of heavy metal concentrations is related to the geographical position of the sample, which may be strongly influenced by pollution from anthropogenic activities [38].

The distribution figures (Figures 3 and 4) show that heavy metals have a strong affinity with estuarine sediment samples. The majority of heavy metals are diverted on the positive values of axes 1 and 2. With the exception of Zn and Pb, all heavy metals are negatively correlated with factors 1, 11 and 111 [23]. Thus sediments are most affected by pollution in the central part of

Elements	F1	F2	F3
Cd	0.152	0.261	-0.605
Co	-0.615	-0.120	0.152
Cr	-0.863	0.211	0.200
Cu	-0.814	0.028	0.355
Ni	-0.822	0.156	-0.224
Pb	0.938	0.056	0.253
Zn	-0.049	0.997	0.053

Table 5. Factor loading for metal concentrations.



Figure 3. Factor loadings with heavy metal concentrations (Factor 1 and Factor 2).

the study area. It is important to note that different estuarine wetlands are subjected to various impact factors. A combination of these factors under specific conditions ultimately defines the sediment condition for a given area. In particular, this study stresses the alarming features of the sediement conditions in many Indian estuaries. As this study indicates, although estuaries and coastal zones make up 10% of the world's ocean surface and <3% of its volume, the main pressures of anthropogenic impact are concentrated here [37].

#### **3.9.** Comparison of data with other estuarine systems

There are significant differences in the concentrations of heavy metals between the east and west coasts of India (Table 3), indicating potential differences in their incorporation into sediments ( $<63 \,\mu$ m fraction). The sedimentation processes operating along the east and west coasts are significantly different. This is mainly because large sedimentary loads are discharged by the peninsular rivers along the east coast, while relatively low sediment fluxes are supported along the west coast. This may be responsible for the observed differences in elemental concentrations [40]. Annually, Indian rivers add  $\sim 1600$  million tones of sediments to the surrounding seas, a major





Figure 4. Factor loadings with heavy metal concentrations (Factor 1 and Factor 3).

Table 6. Population-related data and some estimates of pollutants entering the sea around India (as of 2004).

Population ( $\times 10^6$ )	
Total	1020
Coastal (20% of total population)	250
Area ( $\times 10^6$ km <sup>2</sup> )	
Country	3.276
Agricultural land	1.95
Exclusive economic zone	2.015
Annual mean river run-off (km <sup>3</sup> )	1645
Rainfall per year ( $\times 10^9 \text{ m}^3$ )	
On land	3500
Bay of Bengal	6500
Arabian Sea	6100
Domestic sewage added to the sea	
by coastal population per year	
(at 60 per head per day) ( $\times 10^{6} \text{ m}^{3}$ )	3900
Industrial effluents added to the	
sea by coastal industries per year ( $\times 10^6 \text{ m}^3$ )	390
Sewage and effluents added by the	
rivers to the sea per year ( $\times 10^6 \text{ m}^3$ )	45
Solid waste and garbage generated by	
coastal population per year	
(at 0.8 kg per head per day) ( $\times 10^6$ m <sup>3</sup> )	50
Fertilizer used per year (at $30.5 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ )	$5 \times 10^6$ tonnes
Pesticides used per year (at $336 \text{ g} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ )	55000 tonnes <sup>a</sup>
Synthetic detergents used per year	125000 tonnes <sup>a</sup>
Tar deposition on beaches along the	
coasts of India per year	1500-2000 tonnes

Note: <sup>a</sup>Approximately 20% of this is expected to end up in the sea.

River	Sediment load ( $\times 10^9$ kg)
Brahmaputra	597.000
Indus	450.000
Ganga	329.000
Narmada	44.358
Godavari	38.839
Brahmani	13.277
Mahanadi	13.204
Tapti	10.522
Baitarni	0.954
Subarnarekha	5.911
Mahi	5.879
Vamsadhara	1.836
Netravathy	1.223
Chellar	0.613
Cauvery	0.471
Bharatpuzha	0.444
Bhadar	0.354
Banas	0.322
Krishna	0.320
Pennar	0.257
Purna	0.238
Periyar	0.199
Muvattupuzha	0.157
Gundlakamma	0.064
Kallada	0.058
Vamanapuram	0.053
Shatrunji	0.041
Achenkovil	0.036
Sabarmati	0.018
Tambaraparni	0.011

Table 7. Annual sediment load by Indian rivers at terminal points in 1984.

portion of which may settle in the near shore regions. Most of the heavy metals are transported into the sea this way (Table 1).

#### 3.9.1. West coast

The average concentrations of heavy metals along west coast were found to be: Cu (103.5  $\mu$ g · g<sup>-1</sup>); Ni (65.9  $\mu$ g · g<sup>-1</sup>) and Zn (54.7  $\mu$ g · g<sup>-1</sup>) [40]. The distribution of bulk concentrations of elements along the west coast shows that Ni concentrations decrease, whereas Cu and Zn increase towards the south (Tables 6 and 7). The higher Cu content in the southern region reflects a significant contribution from coastal rocks [39].

#### 3.9.2. East coast

The average bulk concentrations of metals along the east coast are Cu  $(59.6 \,\mu g \cdot g^{-1})$ ; Ni  $(115.5 \,\mu g \cdot g^{-1})$  and Zn  $(103.45 \,\mu g \cdot g^{-1})$  [39,40]. These data are for the central part of the eastern coast, particularly off the major peninsular rivers such as Godavari, Krishna and Tambaraparni, rather than the northern regions (Tables 6 and 7). Observations may be explained in terms of the geology of the drainage basins (Table 1). This study revealed a significantly higher level of Zn and Cu and their presence was maximal in the Tambaraparni Estuary, indicating a highly polluted

estuarine ecosystem. Concentrations of Cd, Pb and Zn were comparable with levels reported to occur in polluted areas.

#### 4. Conclusions

Spatial variations in metal concentrations in our study area might be a result of the cosmopolitan nature of environment. The highest metal concentration observed  $(1200 \,\mu\text{g} \cdot \text{g}^{-1})$  was for Zn, whereas Cd levels tended to be lowest  $(0.42 \,\mu\text{g} \cdot \text{g}^{-1})$ . It is presumed that road traffic, run-off, industrial waters, untreated domestic waters and other anthropogenic sources are major contributors of heavy metals in the Tambaraparni Estuary. The metal concentration data indicate that the surface sediments are moderately to strongly contaminated, probably as a result of anthropogenic activities, and provide a useful means of distinguishing between natural and anthropogenic sources of metals entering the coastal zone through river inputs. Comparison of the metal levels from the estuary indicated that there is a detectable anthropogenic input into the Tambaraparni Estuary. It is proposed that continuous monitoring and further studies in the area should be carried out in the near future to ascertain the long-term effects of anthropogenic impacts and to assess the effectiveness of minimising human activity to upgrade the marine environment in the estuary.

To prevent severe heavy metal contamination of the estuary, especially at and in the vicinity of communities exposed to agricultural and industrial metal loadings, it is imperative to implement timely monitoring and remediation strategies to alleviate the loadings and cumulative concentrations of heavy metals in near-shore sediments. It is emphasised that industrial plants in and around the river must develop suitable treatment systems to reduce the loadings of toxic heavy metals. Furthermore, international regulations and standards designed to protect the environment must be adopted by all companies and countries that are currently polluting the estuarine environment beyond international guidelines.

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#### References

- M. Ergin, C. Saydam, O. Bastwrk, E. Erden, and R.Yoruk, *Heavy metal concentration in surface sediments from* the two coastal inlets (Golden Horn Estuary and Izmit Bay) of the North eastern sea of Marmara, Chem. Geol. 91 (1991), pp. 269–285.
- [2] P.W. Balls, S. Hall, B.S. Miller, J.M. Pirie, and W. Proctor, *Trace metals in Scottish estuarine and coastal sediments*, Mar. Pollut. Bull. 34 (1997), pp. 2–50.
- [3] H. Pekey, Heavy metal pollution assessment in sediments of Izmit Bay, Turkey, Environ. Monit. Assess. 123 (2006), pp. 219–231.
- [4] J.R. Fianko, S. Osae, D. Adomako, D.K. Adotey, and Y. Serfor-Armah, Assessment of heavy metal pollution of the Iture Estuary in the central region of Ghana, Environ. Monit. Assess. 131 (2007), pp. 467–473.
- [5] P.M. Ashraf, L. Edwin, and B. Mennakumari, *Trace metal pollution in estuaries of south India*, Asian J. Water Environ. Pollut. 5 (2008), pp. 63–69.
- [6] A.P. Mucha, M.S.T.D. Vasconcelos, and A.A. Borodalo, Macro benthic community in the Dauro estuary: relation with trace metals and natural sediment characteristics, Environ. Pollut. 121 (2003), pp. 169–180.
- [7] P.S. Ajay, C.S. Prakash, and S. Prashant, Relationship of heavy metals in natural lake waters with physico-chemical characteristics of waters and different chemical fractions of metals in sediments, Water Air Soil Pollut. 188 (2008), pp. 181–193.
- [8] C.M. Ademoriti, Environmental Chemistry and Toxicology, Folundex Press, Ibadan, 1996, pp. 171–204.

- [9] P.M. Chapman, G.P. Rooberg, and G.A. Vigers, *Design of monitoring studies of priority pollutants*, J. Water Pollut. Cont. Fed. 54 (1982), pp. 277–292.
- [10] R.W. Joline and I.B. Leah Young, *Heavy metal levels in suspended sediments*, Crassostrea gigas, and the risk to humans, Arch. Environ. Contam. Toxicol. 55 (2008), pp. 442–450.
- [11] W.J. Adams, R.A. Kimerle, and J.W. Barnett, Sediment quality and aquatic life assessment, Environ. Sci. Technol. 26 (1992), pp. 1865–1875.
- [12] N. Jayaraju, B.C. Sundara Raja Reddy, and K.R. Reddy, The response of benthic foraminifera to various pollution sources: a study from Nellore coast, east coast of India, Environ. Monit. Assess. 142 (2008), pp. 319–323.
- [13] E. Suren, S. Yilmaz, M. Turkoglu, and S. Kaya, Concentration of cadmium and lead heavy metals in Dardanelles seawater, Environ. Monit. Assess. 125 (2007), pp. 91–98.
- [14] P. Szefer, K. Szefer, G.P. Glasby, J. Pempkowiak, and R. Kaliszan, *Heavy metal pollution in surficial sediments from the southern Baltic Sea of Poland*, J. Environ. Sci. Health 31(10) (1996), pp. 2723–2754.
- [15] J. Ridgway and G. Shimmield, Estuaries as repositories of historical contamination and their impact on shelf seas, Estuar. Coast. Shelf Sci. 55 (2002), pp. 903–928.
- [16] R. Wolfgang, L. Maria, D. San, M. Glone, and S.J. Gil, Organic pollution and its impact on the microbiology of coastal marine environments: a Philippine perspective, Asian J. Water Environ. Pollut. 4 (2006), pp. 1–9.
- [17] M. Ponti, C. Casselli, and M. Abbiati, Anthropogenic disturbance and spatial heterogeneity of macrobenthic invertebrate assemblages in coastal lagoons: the study case of Pialassa Baiona (northern Adriatic Sea), Helgol. Mar. Res. 65 (2011), pp. 25–42.
- [18] S. Khedhiri, K. Semhi, and J. Duplay Fadila Darragi, Comparison of sequential extraction and principal component analysis for determination of heavy metal partitioning in sediments: the case of protected Lagoon El Kelbia (Tunisia), Environ. Earth Sci. 62 (2011), pp. 1013–1025.
- [19] W. Salomons and V. Forstner, Metals in the Hydrocycle, Springer, Berlin, 1984.
- [20] G.M.S. Abrahim and R.J. Parker, Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamki estuary, Auckland, New Zealand, Environ. Monit. Assess. 136 (2010), pp. 227–238.
- [21] H. Akcay, A. Oguz, and C. Karapire, Study of heavy metal pollution and speciation in Buyak Menderes and Gediz river sediments, Water Res. 37 (2003), pp. 813–822.
- [22] J.A. Adekoya, A.B. Williams, and O.O. Ayejao, Distribution of heavy metals in sediment of Igbede, Ojo- and Ojoja rivers of Lagos, Nigeria, Environmentalist 26 (2006), pp. 277–280.
- [23] N. Jayaraju, B.C. Sundara Raja Reddy, and K.R. Reddy, Anthropogenic impact on Andaman Coast monitoring with benthic foraminifera, Andaman Sea, India, Environ. Earth Sci. 62 (2011), pp. 821–829.
- [24] C. Barba Briso, J.C. Fernandez Caliani, A. Miras, J. Cornejo, and E. Galan, *Multi-source water pollution in a highly anthropized wetland system associated with the estuary of Huelva (SW Spain)*, Mar. Pollut. Bull. 60 (2010), pp. 1259–1269.
- [25] L. Rosales-Hoz, A. Carranza-Edwards, and O. Celis-Hernandez, Environmental implications of heavy metals in surface sediments near isla de Sacrificios, Mexico, Bull. Environ. Contam. Toxicol. 78 (2007), pp. 353–357.
- [26] A.A. Beus and C.V. Grigorian, Geochemical Methods of Prospecting for Ore Deposits (in Russian). Nedra, Moscow, 1975.
- [27] M.H. El-Mamony, Elevation of terrestrial contribution to the Red Sea sediments, Egypt, PhD thesis, Alexandria University, 1995.
- [28] O.E.A. Attia, A.M.A. Kahadra, A.H. Nawwar, and G.E. Radwan, *Impacts of human activities on the sedimentological and geochemical characteristics of Mabahiss Bay, North Hurghada, Red Sea, Egypt*, Arab J. Geosci. (2010), doi 10.1007/s12517-010-0193-3 (available online).
- [29] M.L.M. Tackx, N. De Pauw, R. Van Miegham, F. Azemar, A. Hannouti, S. Van Damme, F. Fiers, N. Daro, and P. Meire, Zooplankton in the schelde estuary Belgium and The Netherlands. Spatial and temporal patterns, J. Plankton Res. 26 (2004), pp. 133–141.
- [30] P.L. Monbet, Dissolved and particulate flexes of copper through the Morlaix river estuary (Brittany, France): mass balance in a small estuary with strong agricultural catchment, Mar. Pollut. Bull. 48 (2004), pp. 78.
- [31] R. Alagarsamy, Distribution and seasonal variation of trace metals in surface sediments of Mandovi estuary, West coast of India, Estuar. Coast. Shelf Sci. 67 (2006), pp. 333–339.
- [32] P.J. Craig, Metal cycles and biological methylation, in Handbook of Environmental Chemistry, 1(A), The Natural Environment and the Biological Cycles, O. Hutzinger, ed., Springer-Verlag, Berlin, 1980, pp. 169–227.
- [33] V.M. Dekov, V. Subramanian, and R. Van Grieken, Chemical compotation of reverine suspended maters and sediments from the Indian subcontinent, in Biochemistry of Rivers in Tropical South and South East Asia, V. Ittekkot, V. Subramanian, S. Anandavani, eds., Heft 82, Scope sonderband, Mitteilugenans dern Geologisch-Palaontalogischem-Instituteder Universital, Hamburg, 1999, pp. 99–109.
- [34] J.M. Martin and M. Meybeck, Elemental mass balance of material carried by world major rivers, Mar. Chem. 7 (1979), pp. 173–206.
- [35] R.F. Notling, A. Ramkema, and J.M. Everaats, The geochemistry of Cu, Cd, Zn, Ni and Pb in sediments cores from the continental slope of the Banc d'Arquin (Mauritani), Cont. Shelf Res. 19 (1999), pp. 665–691.
- [36] A.B.A. Boxall, S.D. Comber, A.U. Conrad, J. Howcroft, and N. Zamer, *Inputs monitoring and fate modeling of antifouling biocides in UK estuaries*, Mar. Pollut. Bull. 40 (2000), pp. 898–905.
- [37] M.J. Kennish, Ecology of Estuaries: Anthropogenic Effects, CRC Press, Boca Raton, CA, 1992, pp. 1–494.
- [38] J.P. Debenay, E. Tsakiridis, R. Soulardc, and H. Grossel, Factors determining the distribution of foraminiferal assemblages in Port Joinville Harbor (Ile d'Yeu, France): the influence of pollution, Mar. Micropaleontol. 43(1–2) (2001), pp. 75–118.

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- [39] A.L. Paropkari, P.V. Shirodkar, R. Algarsamy, S. Kaisary, and A. Mesquita, *Trace elements in near shore sediments along the east and east coasts of India*, Proceedings of an International Workshop, Japan, 1999, pp. 300–305. Available at http://drs.nio.org/drs/handle/2264/1755.
- [40] R.B. Clark, Marine Pollutants, 3rd edn, Van Nostrand Reinhold, New York, 1986, pp. 110–121.
- [41] S.S. Dhage, A.A. Chandorka, R. Kumar, A. Srivastava, and I. Gupta, *Marine water quality assessment at Mumbai West Coast*, Environ. Int. 32 (2005), pp. 149–158.
- [42] P.K. Krishankumar, G.S. Bhat, and M. Ragagopala, Monitoring the concentration of cadmium, lead, copper and zinc from the coastal waters of India using voltammetric technique, Presented in International Workshop on Marine Pollution and Ecotoxicology, 25–26 February, 2004 at NIO, Goa, India.
- [43] W. Rahaman and S.K. Singh, *Rhenium in rivers and estuaries of India: sources, transport and behavior*, Mar. Chem. 118 (2010), pp. 1–10.