Heavy Metal Distribution in the Godavari River Basin

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ABSTRACT / Suspended and bed sediments collected from the entire region of the Godavari River basin were analyzed for Fe, Mn, Cr, Cu, Ni, and Zn. There are pronounced temporal and spatial variations in the heavy metal distributions. The concentrations of heavy metals in the suspended sediments are significantly higher than the bed sediments. Throughout the basin heavy metals are enriched in the finer fractions (<2 μm) of the bed sediments. The average heavy-metal composition of the sediments is higher when compared to the average Indian river sediments. Heavy-metal concentration in the two shallow cores collected shows, to some extent, the influence of urbanization. When compared to the other tropical Indian rivers such as the Krishna, the Godavari appears to be a significant contributor of heavy metals to the Bay of Bengal. Considering the enormous sediment load of the Godavari River—170 million tons/yr, the heavy metal fluxes to the Bay of Bengal is very significant. Except for the Pranhita, other tributaries of the Godavari do not contribute significant loads of heavy metals. All the metals show high correlation among themselves and the correlation is more pronounced in suspended sediments than in the bed sediments. The heavy-metal distribution, fractionation, and its relationship with total suspended sediments and depth in various parts of the basin are discussed in detail.

Introduction

A large part of the anthropogenic discharge of heavy metals into the environment is incorporated in the suspended sediments in rivers, which act as efficient scavengers for these metals (Salomons and Forstner 1984). Therefore, sediments can be an indicator of the extent of pollution in a given area. Suspended sediments in a river contain significantly higher levels of heavy metals than those present in a dissolved form. In order to assess the natural and anthropogenic input, the chemical composition of riverborne sediments needs to be known. So far several attempts have been made to understand the river transport of heavy metals on regional and global scales (Gibbs 1977, Forstner and Wittmann 1981, Subramanian and others 1987, Ramesh and others 1988). Our present knowledge of heavy-metal fluxes on river sediments is based on large rivers with low sediment load. Since more than 70% of the sediment load is transported by Asian rivers (Milliman and Meade 1983), it is essential to understand the behavior of heavy metals in Asian rivers. While some attention has been paid to the Himalayan rivers (Subramanian and others 1987), large rivers in the peninsular region of India (non-Himalayan rivers) have not been studied in detail. With the above facts in view, extensive studies on the heavy metals have been carried out in the core, suspended, bed, and size-fractionated sediments from the Godavari River basin.

Description of the Basin

The Godavari River carries an enormous load (170 million tons/yr; Biksham and Subramanian 1988) and is the largest in peninsular India. The Godavari basin (16°N to 18°N lat. and 73°E to 83.3°E long.) covers an area of 313,147 km^2 in the central and southern part of the Indian subcontinent. The river originates from Nasik in western Ghats and travels 1,465 km before emptying into the Bay of Bengal. The basin area includes major geological formations (Krishnan 1966) such as Tertiary volcanic Deccan Traps (48%), Archaean Granites (39%), pre-Cambrian and Gondwana Sedimentary rocks (11%), and recent Alluvial cover (2%) (Biksham and Subramanian 1988).

The climate in the basin is primarily semiarid (10°C to 45°C) with annual rainfall of 1185 mm. The mean elevation of the basin is 420 m. The bulk of the precipitation takes place within a three-month monsoon period between June and September (Biksham and Subramanian 1988).

Methodology

Figure 1 shows the general direction of flow of the Godavari River system and the location of the sampling sites all over the basin. Freshly deposited bed sediments (24 samples) from wet portions near the river banks were collected from the Godavari River

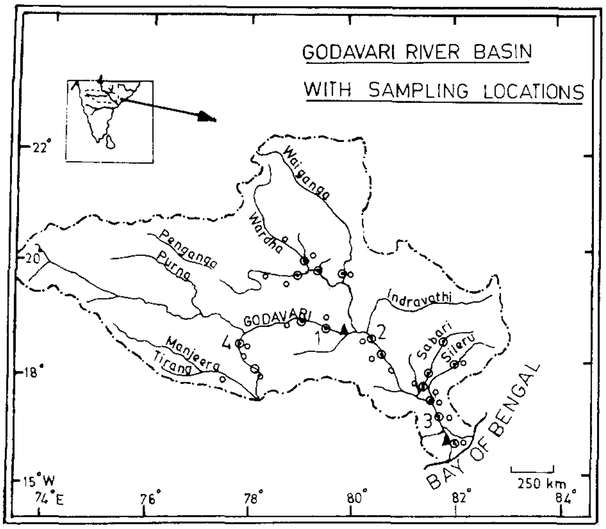

Figure 1. Map showing the Godavari River basin and sampling location. ○, bed sediment samples; ⊙, suspended sediment samples; ▲, core samples.

Table 1. Range of heavy-metal concentrations in the bed sediments of Godavari (μg/g)

Element	I.A.E.A. soil −5[a]	U.S.G.S. BCR-1[b]	Range of values in Godavari[c]
Fe	43,600	88,000 ± 2,200[d]	6,800–239,000
	(44,500 ± 1,900)	(93,700)	(60,000)
Mn	908	14,340 ± 40	102–3,620
	(852 ± 37)	(1,390)	(1,107)
Cr	28		12–408
	(28 ± 3)		(140)
Ni	10	17 ± 3	3–87
	(13)	(16)	(51)
Zn	379	131 ± 4	4–75
	(368 ± 8)	(120)	(51)
Cu	88	26 ± 5	3–262
	(77 ± 5)	(18)	(64)

[a]Based on the six sets of analysis; recommended values in parentheses.
[b]Values in parentheses refer to those recommended by Flanagan (1973).
[c]No. of samples (suspended + bed + core + fractionated sediments) = 74; No. in parentheses refers average.
[d]Standard deviation on average of three measurements.

and its important tributaries during June 1978 and May and August 1979 (Fig. 1). Of these 24 samples, 12 are from the rivers flowing through the Deccan Traps (Tertiary), six are from the rivers flowing through the granitic terrain (pre-Cambrian), and the remaining are from the main river flowing through the sedimentary terrain (Gondwana), covering a wide geological age. A similar strategy was applied for the collection of 20 suspended sediment samples (Fig. 1). Besides these, two vertical cores were also collected (Fig. 1) upstream and downstream.

Bed samples were collected by simply scooping with a plastic spade, taking care not to lose the fines, and transferred to precleaned plastic bags, sealed, and brought to the laboratory, where they were kept at 2–4°C until prepared for analysis. Suspended sediments along with the water were collected in wide-mouth polythene bottles held in the direction opposite to the river flow. The bottles were sealed and kept in the laboratory at 2–4°C. Suspended sediments usually were separated within a fortnight of collection by filtration of water through 0.45-μm membrane filters. Two vertical cores of less than 0.5 m depth penetrated manually by PVC tubes enclosed in cast-iron pipes were collected, one from midstream and another from a downstream location. Size fractions (>62 μm and 62–31 μm) of the bed sediments were separated by standard sieving methods. Fractions of 31–8 μm, 8–4 μm, and <4 μm were separated by the Attenburg cylinder method based on Stoke's law (Griffiths 1967).

The bed, core, and suspended sediments were analyzed for Si and Al by the solution technique of Shapiro and Burnock (1962). The rest of the major and minor elements were analyzed by a thin-film x-ray fluorescence (XRF) technique. Details of the thin-film XRF techniques have been reported elsewhere (Subramanian and others 1987). Size fractionated sediments were analyzed in the same way. To check the accuracy and precision of the measurements, U.S.G.S. rock standards and I.A.E.A. soil standards were analyzed this way as well. However, it should be realized that the limitations of a single season sampling only at logistically accessible locations may not provide an opportunity for extensive interpretation of the heavy-metal data presented here.

Results and Discussion

Heavy Metals in Bed and Suspended Sediments

Table 1 summarizes data (concentration of heavy metals) of the I.A.E.A. standard soil as well as U.S.G.S. standards along with the range of values for the Godavari sediments. The range of values reflects the sample-to-sample variation downstream.

Tables 2 and 3 represent the heavy metal concentration of the suspended and bed sediments in the Godavari River basin. In general the concentration of heavy metals in the suspended sediments are higher than the bed sediments in the basin. For example, suspended sediments are enriched by a factor of two to three times for Fe, two to four times for Ni, three to

Table 2. Heavy metals in the Godavari bed and suspended sediments

Location	Series	Location no.[a]	Fe	Elements (μg/g) Mn	Cr	Ni	Zn	Cu
Bed								
Upstream	1	1	45800	978	152	50	54	78
	2	1	120000	1120	329	70	67	57
	3	1	49100	903	171	53	65	38
Midstream	4	2	70300	1340	105	79	73	134
	5	2	14800	275	61	14	15	13
	6	2	40500	638	155	53	43	30
Downstream	7	3	38000	1500	110	38	30	49
	8	3	47100	1020	124	51	45	62
Tributaries								
Mangera	9	4	54000	1060	104	52	75	96
	10	4	59900	1260	99	85	71	112
	11	4	120000	1120	329	70	67	57
	12	4	78000	1147	177	69	71	88
Pranhita	13	5	239000	3620	408	87	67	262
	14	5	54700	957	125	51	57	74
	15	5	46200	1050	137	55	40	64
	16	5	6800	135	12	3	8	5
	17	5	58200	947	67	58	75	102
	18	5	56700	1200	100	61	72	100
	19	5	45600	684	148	53	47	33
Sabari	20	6	41400	697	112	41	40	50
	21	6	5700	102	30	5	4	3
	22	6	66400	1360	125	61	75	117
	23	6	60300	1180	99	62	68	108
Suspended								
Upstream	1	1	76500	1317	141	77	370	301
	2	1	75418	3660	122	75	1484	167
Midstream	3	2	16876	627	48	36	121	26
	4	2	114750	4106	265	158	783	247
	5	2	102000	1695	166	112	781	209
	6	2	62322	1214	173	102	206	162
Downstream	7	3	67085	1385	140	84	162	110
	8	3	52821	1005	112	66	188	71
	9	3	251890	4826	475	290	2650	422
Tributaries								
Manjera	10	4	73950	1444	173	101	175	168
	11	4	39100	686	85	103	112	65
Pranhita	12	5	74621	1650	162	89	166	144
	13	5	62511	2244	100	82	309	159
	14	5	82800	1404	180	107	1241	150
	15	5	26550	1133	19	31	78	76
	16	5	34633	447	54	39	60	54
Sabari	17	6	53099	507	114	79	222	54
	18	6	9736	284	19	20	28	14
	19	6	37830	484	105	62	354	54
	20	6	25424	500	80	40	76	40

[a]Sampling station numbers are shown in Figure 1.

15 times for Zn, and two to four times for Cu more than the bed sediments in the main river. In the tributaries the suspended sediments are enriched over the bed sediments by a factor of two except for certain metals like Fe and Mn, which are almost similar in concentration to the bed sediments (Table 3) because the suspension is finer and richer in multiple hydroxide coatings (Forstner and Wittmann 1981), or-

Table 3. Average heavy-metal composition of the Godavari sediments

Location	Elements (μg/g)					
	Fe	Mn	Cr	Ni	Zn	Cu
Upstream						
S[a]	75690	2490	132	76	930	234
B	71600	1000	217	58	62	55
S/B	(1.1)	(2.5)	(0.6)	(1.3)	(15)	(4.3)
Midstream						
S	111615	2895	349	205	492	214
B	41900	751	107	49	44	59
S/B	(2.6)	(3.9)	(3.3)	(4.2)	(11.2)	(3.6)
Downstream						
S	123930	2405	242	146	1000	2
B	42600	1260	121	45	38	56
S/B	(2.9)	(1.9)	(2)	(3.2)	(26)	(4)
Tributaries						
Mangera						
S	56525	1065	129	102	144	117
B	78000	1147	177	69	71	88
S/B	(0.7)	(0.93)	(0.7)	(1.5)	(2)	(1.3)
Pranhita						
S	56225	1370	103	70	371	117
B	72500	1227	142	53	52	92
S/B	(0.7)	(1.1)	(0.7)	(1.3)	(7.1)	(1.3)
Sabari						
S	31520	445	80	50	170	162
B	42800	936	96	45	49	65
S/B	(0.7)	(0.5)	(0.8)	(1)	(3.5)	(2.5)
Average						
S	76288	1784	184	113	483	149
B	60000	1064	140	52	53	73
S/B	(1.3)	(1.7)	(1.3)	(2.2)	(9.1)	(2)
Indiana ave.[b]						
B	29000	605	87	37	16	28

[a]S = suspended sediments, B = bed sediments, S/B ratio = ( ) refers to enrichment factor.

[b]Subramanian and others (1985).

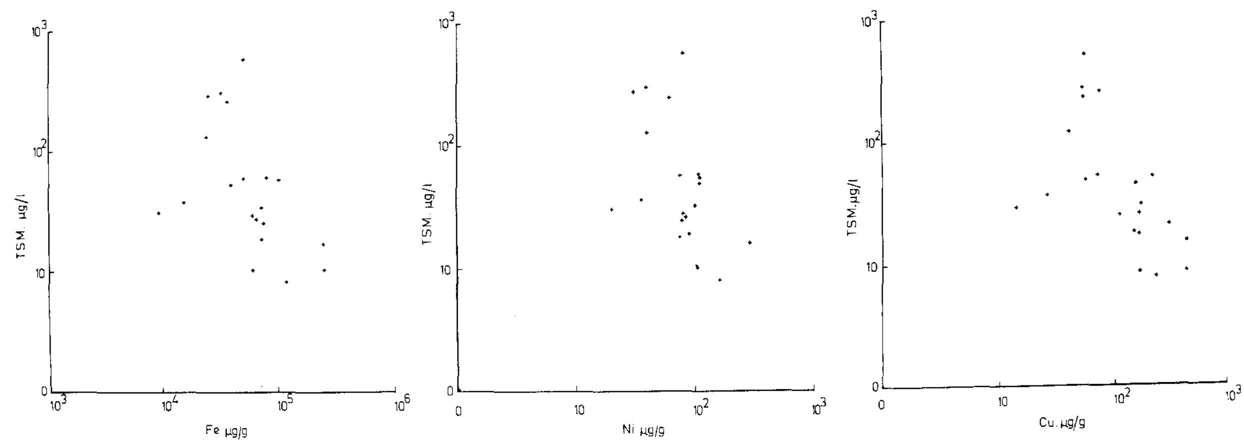

Figure 2. Scatter plot between the concentration of heavy metals and the suspended sediments. TSM = total suspended matter.

ganic and trace metals, and scavenging clays (Subramanian and others 1987). Downstream the concentration of heavy metals in suspension increases. The greater heavy-metal concentration is in the tributaries on the lower side, not in the main river, which may be due to variation in the geology of the drainage area. For example, Sabari, which drains through granitic terrains, has coarse sediments in suspension. On the other hand, Pranhita drains mainly through the Deccan Traps and has more chemically active montmorillionite clays and in turn contributes high levels of heavy-metal concentration.

Figure 2 shows the relationship of heavy metals with the suspended sediment load. Here the profile shows a negative trend between the suspended load and the concentration of heavy metals like Fe, Ni, and Cu. In the suspended sediments there is an abundance of chemically active fine-sized clays (such as montmorillionite constituting 85% of the clay fractions) (Subramanian 1980), organometal colloids, and other organic complexes, which in turn contribute metal enrichment but not mass (Fig. 2). However, in the absence of chemical fractionation studies, this is at best a speculation. The high TSM appears to have a low metal concentration due to the dominance of detrital coarse fractions (quartz and feldspar), which are generally depleted in heavy metals and hence contribute more mass but less heavy metals to TSM.

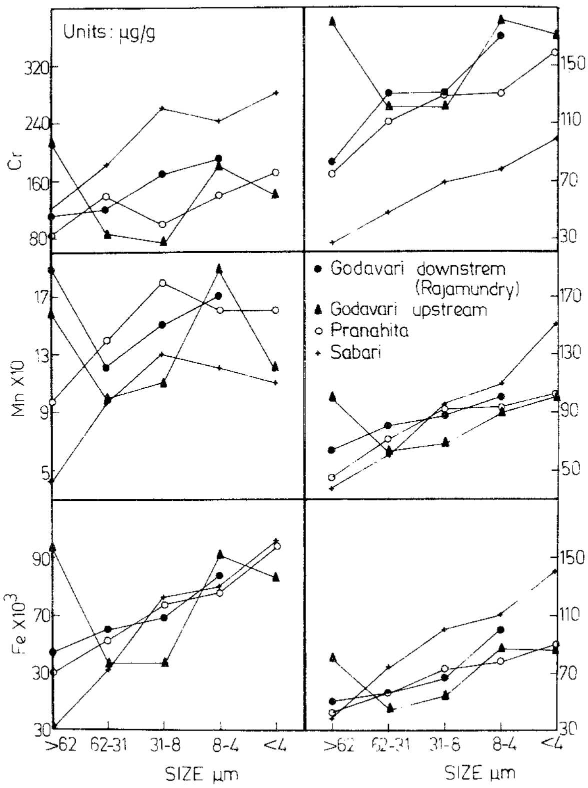

Figure 3. The distribution of heavy metals in the fractionized bed sediments.

Size Fractionation of Heavy Metals

In view of the known association of heavy metals with different particle sizes, a detailed study on the heavy-metal concentration and particle size distribution in the Godavari River sediments was attempted. The distribution of heavy metals in the grain-size spectrum of the Godavari bed sediments is shown in Figure 3 and Table 4.

The grain size significantly affects the metal data of sediments in the Godavari River. There is a general increase of metal concentration in the finer fractions (<31 µm), which is 40 percent more compared to the coarse silt and fine sand fraction. The higher concentration in the fine sediments generally is due to the increase in specific surface area and to the surface properties of clay minerals. This clearly shows the control of size over the heavy-metal concentration. Helmeke and others (1977) have pointed out that the concentration of heavy metals in the pelitic fractions reflects the man-made contamination. Hence it acts as the sink for the metals in the river sediments. Upstream, metals are enriched in both coarse and fine fractions. In the coarse fractions the presence of heavy minerals and carbonate fractions might have caused this metal enrichment (Salomons and Forstner 1984). In the other parts of the basin, an increase of metals towards the finer fractions can be observed, confirming the presence of chemically active clays as observed earlier. High concentrations of heavy metals in the finer fractions are similar to the average suspended sediments concentration (Tables 3 and 4), which in turn shows their similar source and mobility with respect to specific site location.

Since Al is an immobile element relative to the heavy metals, it is worthwhile to consider the metal/Al ratio instead of absolute values of heavy-metal concentration. The metal/Al ratio in suspended sediments shows a regular decrease downstream (Fig. 4). Thus the decreasing profile indicates the loss of mobile fractions downstream due to urbanization and estuarine processes. The profile in the bed downstream (Fig. 4) is positive with more fluctuations. This variation is due to the diluting effect caused by the tributaries; the final increase of the ratio near the estuary reflects the urban effect (addition) in the heavy-metal concentration. The metal/Al ratio in the fractionated sediments

Table 4. Heavy metals in various size fractions of the Godavari bed sediments

Location	Fraction size (μm)	Elements (μg/g)					
		Fe	Mn	Cr	Ni	Zn	Cu
Upstream	>62	95,000	1,600	220	81	100	180
(st. no. 1)	62–31	53,000	990	87	45	63	120
	31–8	53,000	1,100	75	54	69	120
	8–4	91,000	1,900	180	87	90	180
	<4	83,000	1,200	140	84	100	170
Downstream	>62	57,000	1,900	110	51	63	83
(st. no. 3)	62–31	65,000	1,200	120	56	79	130
	31–8	69,000	1,500	170	67	87	130
	8–4	87,000	1,700	190	100	100	170
Tributaries							
Pranhita	>62	50,000	970	84	42	54	74
(st. no. 5)	62–31	61,000	1,400	130	56	71	110
	31–8	74,000	1,800	98	73	93	130
	8–4	78,000	1,600	140	78	92	130
	<4	95,000	1,600	170	90	100	160
Sabari	>62	30,000	410	120	38	37	26
(st. no. 6)	62–31	51,000	970	180	74	61	47
	31–8	76,000	1,300	260	100	94	68
	8–4	80,000	1,200	240	110	110	75
	<4	95,000	1,100	260	140	150	98

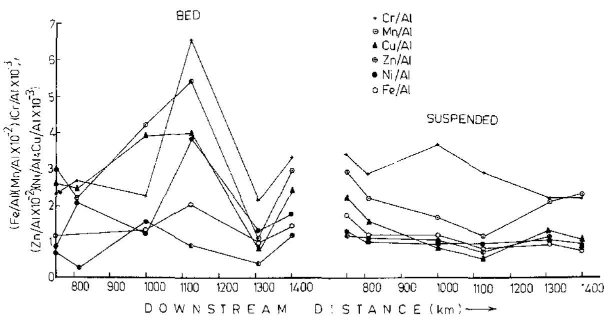

Figure 4. Downstream variation of metal/Al ratio in the bed and suspended sediments.

(Fig. 5) is similar to the one in Figure 4, hence indicating the increase of metals over the pelitic fraction and the size control over the heavy-metal concentrations with a small enhancement of the heavy metal/Al ratio over the coarse fractions as explained earlier.

Heavy Metal Distribution in Core Sediments

The man-made effects can be evaluated from the distribution of heavy metals in sediment cores. The heavy metal concentration at different depth intervals is given in Table 5 and Figure 6. There is a pronounced increase of heavy metal concentration in the surface sediments when compared to the bottom sediments, which could be due to the remobilization and deposition of heavy metals in the sedimentary layers. This profile clearly shows the increase of metal pollution during the recent decades.

Table 5 also compares the heavy-metal concentration in various locations of the Godavari River delta, the Krishna, and the Bay of Bengal. Heavy-metal concentrations in the surface sediments as well as their averages show a positive trend towards the Bay of Bengal. It shows the recent addition of heavy metals close to the delta due to the effect of urbanization (Subramanian and others 1987). Moreover, the metal/Al ratio decreases with depth (Fig. 7), suggesting the addition of metals at and/or near the surface. In the present study we noted a constant proportion of metal distribution in the two cores when compared to the reported values in the Godavari delta (Kalesha and others 1980), so the concentration of certain metals such as Zn and Cu appears to be lower. The reported values of the Bay of Bengal sediments (Sarin and others 1979) are in good agreement with our values (Table 5), but it is 5–10 times more when compared to the reported values for Krishna delta cores (Ramesh and others 1989). Godavari is thus the main contributor of heavy metals among the non-Himalayan rivers to the Bay of Bengal.

Interelement Relationship

Table 6 shows the correlation matrix of the heavy metals in the core, suspended, bed, and fractionized sediments, and some of the relationships are illus-

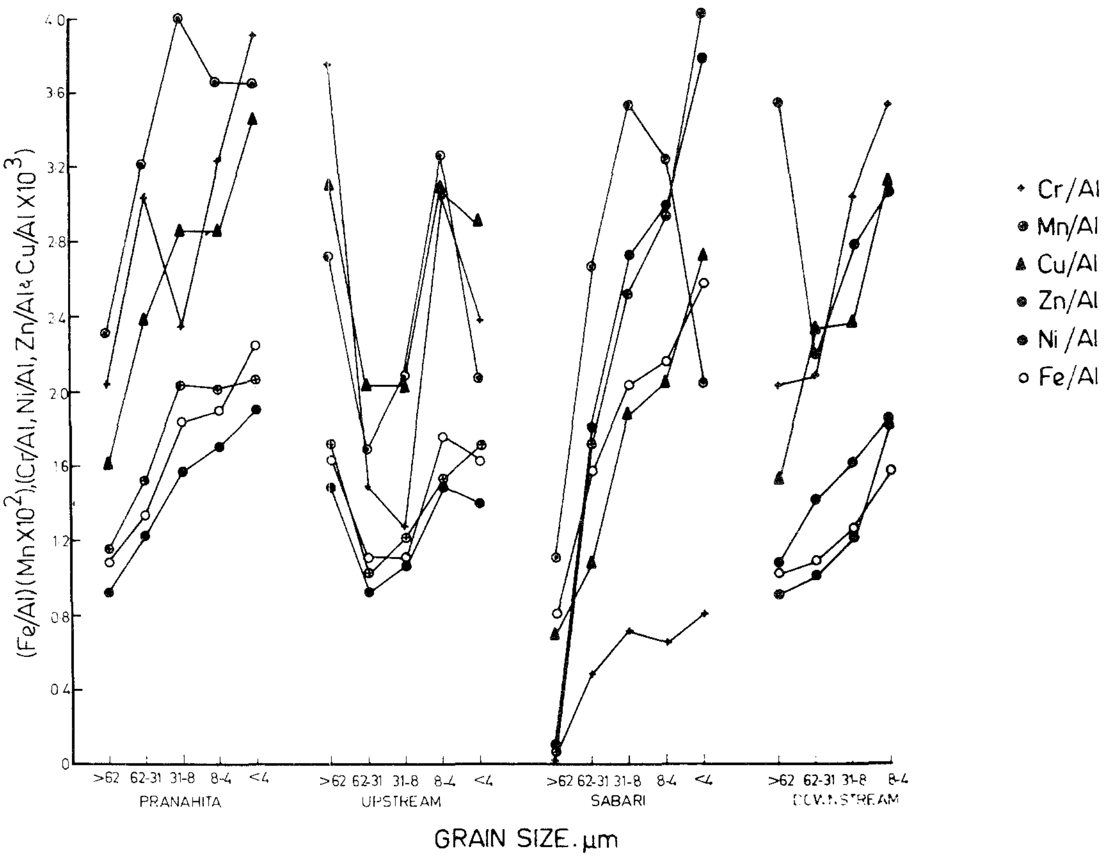

Figure 5. Variation of metal/Al ratio in the fractionized bed sediments.

Table 5. Heavy metal composition of the Godavari,[a] Krishna, and Bay of Bengal cores

Location	Depth (cm)	Elements (µg/g) Fe	Mn	Cr	Ni	Zn	Cu
Midstream	0–3	51,000	970	120	56	66	87
	3–6	60,000	1,200	160	70	76	94
	6–9	57,000	960	110	62	69	82
	9–12	43,000	750	100	44	57	69
	Average	52,750	970	123	58	67	83
Downstream	0–3	90,000	640	230	93	110	120
	3–6	76,000	840	190	79	110	130
	6–9	51,000	750	120	41	63	73
	9–12	62,000	1,100	150	64	72	84
	12–15	66,000	1,000	170	55	73	97
	15–18	53,000	1,400	110	53	65	91
	18–21	55,000	1,020	160	64	79	98
	Average	64,700	1,020	160	64	79	98
Godavari delta[b]	71,000	496	146	115	195	202	
Krishna delta (at Repalle)[c]		190	28	5	10	8	
Bay of Bengal[d]	50,000	1,017	96	89	—	53	

[a]Locations are shown in Figure 1.

[b]Kalesha and others (1980).

[c]Ramesh and others (1989).

[d]Sarin and others (1979).

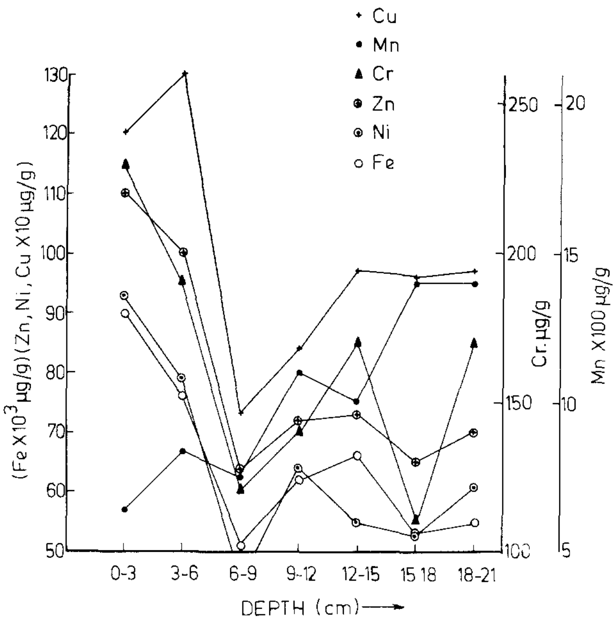

Figure 6. Vertical profile of heavy metals in the core sediments.

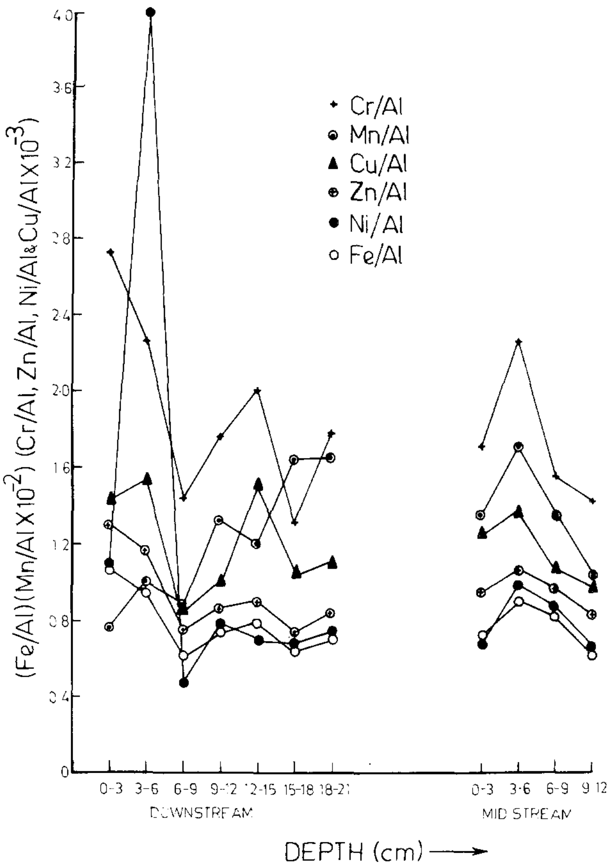

Figure 7. Vertical profile of metal/Al ratio in the core sediments.

trated in Figure 8. The excellent correlation between any two pairs of heavy metals indicates their common sink in these sediments. Several authors (Forstner and Wittmann 1981; Gibbs 1977; Singh and Subramanian 1984) have speculated on the nature of sink for heavy metals in sediments. Although the suspended sediments are richer in heavy metals than the bed sediments, the good correlation in both types points to the presence of such heavy-metal sinks such as the clay fractions, mobile fractions, organic fractions, and multiple hydroxide coatings. In the fractionated sediments for most of the heavy metals, the correlation coefficient was significant, viz., Fe–Mn: 0.62, Fe–Cr: 0.64; Fe–Zn: 0.89, respectively. While a good correlation is observed between certain metals, selective fractions based on grain size give different levels of correlation for different metals due to interaction of bed and suspended sediments and by resuspension and deposition. Thus the fractionation of heavy metals is regulated by the size–chemistry relationship.

For all the metals considered, the average heavy-metal contents of the Godavari are far in excess of the other peninsular river sediments. Based on the annual sediment load of 170 million tons in the Godavari River (Biksham and Subramanian 1988), the annual metal flux was calculated at various stations (Table 7). Based on the published values of mean annual sediment load and sediment chemistry, the average heavy-metal flux for Krishna, Cauvery (non-Himalayan), Ganges, Brahmaputra (Himalayan), Indian, and world average sediments have been computed, and those data are also presented in Table 7 for comparison. The flux rate of Himalayan rivers is high, as expected, besides this specific enrichment of heavy metals in suspended sediments in other Indian rivers already reported (Subramanian and others 1987). Variation in the fluxes indicates no uniformity primarily due to the difference in subbasin geology and varying degrees of human impact.

Conclusion

The heavy-metal concentration in the bed and suspended sediments of the Godavari vary widely. Bed sediments show an erratic variation downstream compared to the suspended and fine fractions. Suspended sediments have a higher level of these metals than do the bed sediments. The very good correlations among the elements are considered point to common sources or sinks in the river basin. The proportion of different size populations in the sediment seems to be responsible for the heavy-metal variations within the basin. The major proportion of the heavy metals is in the

Table 6. Correlation coefficient of heavy metals in the Godavari sediments

	Suspended (n = 20)					Bed (n = 24)					Size fraction (n = 19)					Core (n = 11)				
	Mn	Cr	Ni	Zn	Cu	Mn	Cr	Ni	Zn	Cu	Mn	Cr	Ni	Zn	Cu	Mn	Cr	Ni	Zn	Cu
Fe	0.91	0.90	0.91	0.69	0.93	0.87	0.89	0.71	0.53	0.80	0.62	0.64	0.62	0.89	0.71	−0.30	0.95	0.90	0.90	0.88
Mn		0.86	0.87	0.62	0.87		0.68	0.71	0.54	0.90		0.13	0.16	0.37	0.65		−0.26	−0.16	−0.36	−0.13
Cr			0.99	0.37	0.79			0.61	0.42	0.49			0.60	0.71	0.03			0.84	0.93	0.86
Ni				0.39	0.79				0.88	0.74				0.73	0.25				0.94	0.86
Zn					0.65					0.66					0.44					0.92

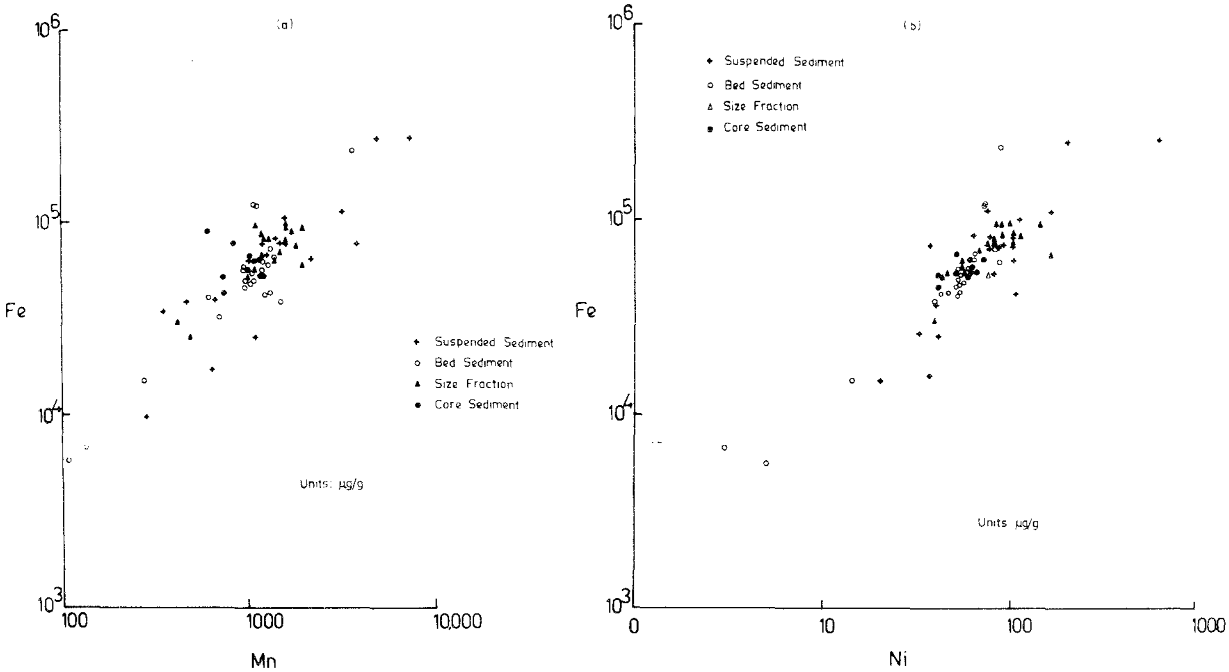

Figure 8. Scatter plot for Mn and Ni against Fe in the suspended, core, and fractionized sediments.

Table 7. Heavy metals fluxes in the suspended sediments of Godavari, major rivers of Indian subcontinent and world average

Location	Element (tons/yr)					
	Fe	Mn	Cr	Ni	Zn	Cu
Upstream	206,550	3,556	381	208	999	813
Midstream	1,127,202	29,387	4,382	2,649	2,442	1,828
Downstream	2,141,065	41,021	4,038	2,465	22,525	3,587
Tributaries						
Manjera	16,392	309	37	30	30	34
Pranhita	947,687	20,955	2,057	1,130	2,108	1,829
Sabari	63,719	609	137	95	266	65
Average	750,436	15,973	1,838	1,096	4,728	1,359
Krishna[a]	543,613	10,448	1,212	732	1,122	908
Cauvery[b]	44,020	923	107	107	355	43
Ganges[c]	29,610,000	1,135,050	86,856	45,073	604,040	82,908
Brahmaputra[c]	65,311,800	2,656,650	132,534	106,863	546,852	64,476
Indiana Ave.[b]	35,148,000	733,260	105,444	44,844	19,392	33,936
World Ave.[d]	648,240,000	14,180,252	14,180,252	1,215,450	4,726,750	1,350,500

[a]Ramesh and others (1989).
[b]Subramanian and others (1985).
[c]Subramanian and others (1987).
[d]Martin and Meybeck (1979).

pelitic fractions of the sediments and hence are available for water–sediment interaction. Urban area effects are pronounced in the sediments in the lower stretches of the river.

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