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Trace element geochemistry of river sediment, Orissa State, India

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Abstract

Geochemical analyses of bottom sediment from rivers flowing through Orissa State, India indicated that trace element concentrations were extremely variable, and commonly higher than crustal abundance. The highest elemental concentrations were associated with the Brahmani River, followed by the Baitarani and Mahanadi Rivers. Although all three rivers drain similar geology, the Brahmani River catchment is heavily industrialized, and sediment collected downstream from industry confirms that anthropogenic activity influenced its chemical composition. A similar pattern was observed in sediments collected downstream from towns in the Mahanadi and Baitarani catchments. In both examples, the clay size fraction was shown to be the most highly reactive component of the sediments. Comparisons between metal concentrations from the upper to lower stretches of the three river systems indicated no net accumulation downstream. Apparently, trace elements discharged into the river system tend to be short-lived in the water column, rapidly settling out or becoming adsorbed into the bottom sediment. Although for much of the year, the trace metals may remain locally incorporated as bottom sediment, during monsoonal episodes, where bedload transport can be significant, the effects of pollution may expand over regional distances. © 1997 Elsevier Science B.V.

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1. Introduction

In any river system, an understanding of the concentration, and fate, of trace elements is extremely important in addressing their impact on the regional environment. The ultimate sink for elements in solution is the bottom sediment (Hart, 1982). Once deposited, these solids are subject to bedload transport downstream where they eventually may be discharged into the oceans. Bedload transport can often be appreciable, and in the

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Brahmaputra River, for example, sand waves during the monsoon can migrate downstream by as much as 600 m per day (Coleman, 1969), corresponding to 10^6–10^7 t of daily bedload (Milliman and Meade, 1983).

In a study of sediment cores from the Bay of Bengal, Sarin et al. (1979) determined that the bulk of the marine sediments were derived from weathering of the Himalayan Mountains, and transported to the oceans by the Ganges and Brahmaputra Rivers; these two rivers contribute in excess of 80% of the allochthonous sediments (Subramanian, 1979). In contrast, the major southern Peninsular rivers (i.e. Krishna, Narmada, Tapati, Cauveri, Godavari and Mahanadi) drain low-relief topography, and hence, contribute disproportionally low levels of sediment to the Bay of Bengal (Subramanian et al., 1987). However, the sediment from these rivers contain a greater component of smectitic clays (compared to the illitic and kaolinitic clays in northern rivers), and therefore, can bind and accumulate significant amounts of metals (Subramanian et al., 1987). This behavior has been documented in the bottom sediments of several Peninsular rivers, which contain higher trace metal concentrations (e.g. V, Mn, Co, Cu, Zn, and Ba) than their northern counterparts with enrichments associated with the fine sediment size-fractions (Subramanian et al., 1985).

In previous studies of river sediment in Peninsular India, Chakrapani and Subramanian (1990a) and Ramesh et al. (1990) observed that trace metal concentrations varied considerably within the basin. Ramesh et al. (1990) attributed this variation, in part, to human influence, and as we have previously shown with trace element concentrations in surface waters (Konhauser et al., 1997), pollution is particularly relevant in some regions of Peninsular India, such as Orissa State (population 31.5 million), where anthropogenic inputs occur from industrial, agricultural and urban areas. Accordingly, the purpose of the current work is to provide a more detailed geochemical study of bottom sediments (with concentrations for 30 trace elements) in three of the state's largest river systems; the Mahanadi, Brahmani and Baitarani Rivers.

2. Study area

Studies were conducted throughout the State of Orissa, located on the eastern coast of India, adjacent to the Bay of Bengal. The State is characterized by a tropical climate, and is drained by several major river systems, including the Mahanadi, Brahmani, and Baitarani Rivers (Fig. 1). The Mahanadi River is the largest of the three, flowing east and draining into the Bay of Bengal. The basin extends over an area of approximately 141 600 km^2, has a total length of 851 km, and has a peak discharge of 44 740 $m^3\ s^{-1}$. The Brahmani River is the next largest river in Orissa, with a drainage area of 39 035 km^2, a length of 800 km, and a peak discharge of 22 640 $m^3\ s^{-1}$. The Baitarani River has a drainage basin of only 8 570 km^2, a length of 365 km, and a peak discharge of 14 150 $m^3\ s^{-1}$.

All three river catchments are characterized by Precambrian granites, gneisses and schists of the Eastern Ghats, with local basic intrusive and volcanic lithologies; limestones, sandstones, and shales of the Gondwanas; and recent deltaic alluvium deposits at the river mouths on the Bay of Bengal (Chakrapani and Subramanian, 1990a). It has been estimated, for example, that in the Mahanadi River basin, the lithology consists

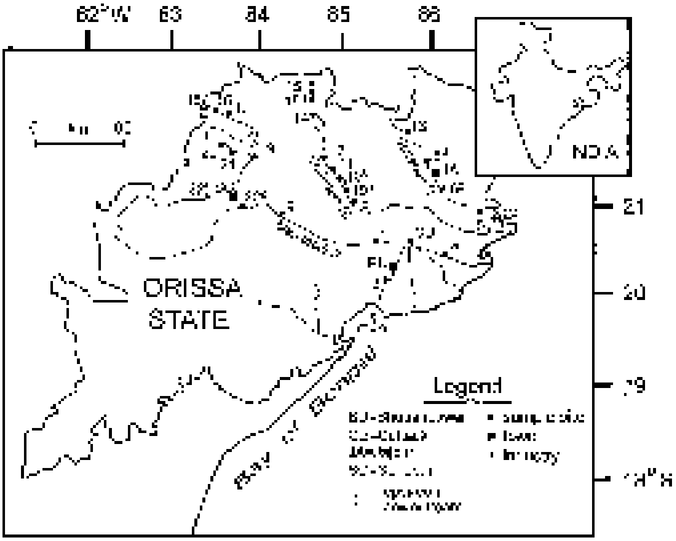

Fig. 1. Location of study areas and sample sites.

of 56% Precambrian rocks, 22% sandstone and shale of the Upper Gondwana, 17% limestone and shale of the Lower Gondwana, and 5% coastal alluvium (Chakrapani and Subramanian, 1990a). Orissa State also comprises some highly mineralized terrains that host significant iron, coal, bauxite, lead, and copper deposits (Chakrapani and Subramanian, 1993). In total, Orissa contributes about 18% of the explored mineral resources in India (Sene-Johansen, 1995).

3. Methodology

Sediment samples were collected from the Mahanadi River, the Brahmani River and the Baitarani River, as well as several of their tributaries, one month after the monsoon season ended (in October 1993). To assess anthropogenic impacts, some samples were collected both upstream (indicated by a ‘‘U’’ in the sample numbers) and downstream (‘‘D’’) from urban or industrial areas: the former include, sites 6 and 22, whereas the latter include, sites 10 and 15 (Fig. 1). Site 10 was located adjacent to NALCO (National Aluminum Company), FCI (Fertilizer Corporation of India) and TTPS (Talcher Thermal Power Plant Station) on the Brahmani River at Angul; site 15 was located near the Rourkela Steel Plant on the Brahmani River at Rourkela.

Sediment samples (approximately 250 g) were collected, by hand, at the surface of the river bottom (near-shore) and stored wet in plastic bags until returned to the laboratory. Prior to chemical analysis, samples were air dried for one week, dried in an oven at 110°C for 24 hours, and subsequently ground for 50 s in a tungsten carbide mill. Most elemental concentrations were determined, by Bondar Clegg Services, Ottawa using inductively coupled plasma: atomic emission spectroscopy (ICP-AES) after samples were digested in a sequence of HF, HNO_3, $HClO_4$ and HCl. Rare earth elements were analyzed by instrumental neutron activation analysis (INAA) on the solid, homogenized samples. Reference standard (G2; USGS granite standard) was analyzed, in addition to several duplicate samples. Accuracy for both ICP-AES and INAA was within ±9% of accepted amounts for any elements; precision for both methods was within ±5%. In addition, results for several internal standards demonstrated accuracy and reproducibility consistently better than the values for the external standards.

To analyze the different sediment size-fractions, unmilled samples were disaggregated with an agate mortar and pestle, and dispersed in distilled water using an ultrasonic probe. The resulting supernatant was decanted into a settling column and size fractions larger than 20 μm, of 2–20 μm and smaller than 2 μm were removed by settling according to Stokes Law. These separates were then dried in a pre-heated oven. All size fractions were analyzed by ICP-AES.

The mineralogy of all sediment samples (bulk and clay size-fraction) were determined by X-ray diffraction (XRD) using a Rigaku rotating anode diffractometer (Co K $\propto$ radiation). The scans were carried out at 160 kV and 45 mA, from 2 to 82,° two theta at a rate of 10° per min. Sample preparation involved packing the milled sediments into Al sample-holders, so as to obtain a random particle orientation. In addition, subsamples weighing approximately 40 mg each of the less-than-2 μm material were dispersed in 2 ml deionized water, pipetted onto a glass slide to obtain a preferred orientation of particles, and analyzed by XRD.

4. Results

The average concentrations for 30 elements in the bottom sediments of the Mahanadi, Brahmani and Baitarani Rivers are given in Fig. 2. In each river, large relative standard deviation values (from: 4 to 85% in the Mahanadi; 23 to 101% in the Brahmani; 23 to 120% in the Baitarani) were calculated, indicating that significant variability existed amongst individual sampling sites. The wide range of concentrations (from site to site) likely represents different point-source inputs, since chemical weathering of granites and sedimentary rocks throughout the river's catchment is unlikely to provide such large spatial fluctuations in trace-element content.

Because the chemical composition of river sediment is primarily determined by the geological source and erosional regime, it might be expected that elemental concentrations for all three rivers should be comparable. However, trace element concentrations differed greatly. The highest concentrations typically belong to the sediment of the Brahmani River, with the exceptions of Ba, Hf, Mo, Rb and Sr which were highest in the Mahanadi and Co, Cr and Ni which were highest in the Baitarani River. These results correlate well with earlier data on surface water chemistry (Konhauser et al., 1997) which showed that the Brahmani River consistently had higher dissolved elemental concentrations than either the Mahanadi or Baitarani Rivers.

Sediments from all three river basins commonly have higher elemental concentrations than crustal abundances, including Ag, As, Ba, Ce, Cs, Hf, La, Li, Lu, Mo, Nb, Pb, Rb, Sb, Sm, Ta, Th, U and Zr. Furthermore, in comparison to the trace element concentrations

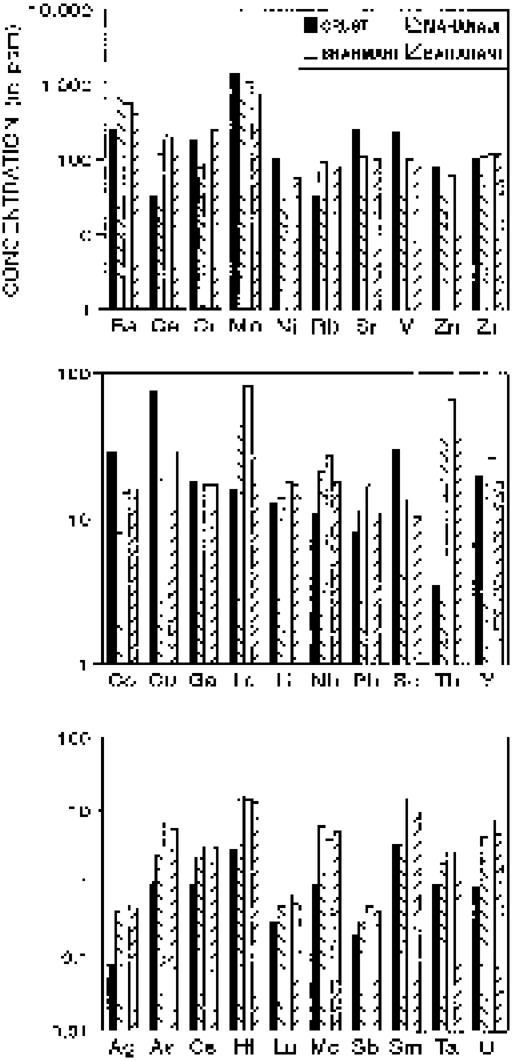

Fig. 2. Comparison of trace element concentrations in bottom sediments of the Mahanadi, Brahmani, and Baitarani Rivers with crustal abundance. Crustal abundance values from Taylor and McLennan (1985).

determined for other peninsular rivers (Biksham and Subramanian, 1988), the elemental concentrations of the Brahmani bottom sediments are in excess of Rb, Ba, Pb, Th and U; the Baitarani has higher Rb and Th; and the Mahanadi is higher in Rb, Ba and Th. Similarly, in contrast to major northern rivers, such as the Ganges and Brahmaputra, the Brahmani River has higher concentrations of Mn, Cu, Zn, Ba, Th and U; the Baitarani River has higher Mn, Ni, Cu, Ba and Th; and the Mahanadi River has higher Mn and Ba (Biksham and Subramanian, 1988).

Table 1
Mineralogy of sediments in study area Mahanadi River and tributaries

Site	3	4	7	9	16	17	18	19	22D	22U
Quartz	m	m	m	m	m	m	m	m	m	m
Feldspars	mn	mn	mn	mn	mn	t	mn	mn	mn	mn
Hematite								t		
Ilmenite	t					mn	t		t	t
Magnetite										
Anatase	t	t	t	t	mn	t	mn	mn	mn	mn
Dolomite	t	t	t		t		t		t	
Kaolinite		t	t		mn	t	t			t
Illite	t	t		t	mn		t	t	mn	
Smectite			t			t	t	t		

m = major constituent; mn = minor constituent; t = trace constituent.

Sediments from all three river systems have a relatively simple mineralogy, dominated by quartz, with minor amounts of feldspars and Fe-oxides and Ti-oxides, and trace amounts of dolomite and various clay minerals. In general, all sediments contain similar clay mineral assemblages; predominantly kaolinite and illite, with lesser amounts of smectite (Tables 1–3). Although most sediment is comprised of grains between 1 and 25 μm in size (Chakrapani and Subramanian, 1994), our chemical analyses of various size-fractions from all three river systems, indicated that a high proportion of the trace element content resided in the clay material (less than 2 μm) (Fig. 3). This fraction includes clay minerals, fine-grained Fe- and Mn-oxides, Fe- and Mn-hydroxide coatings on finely dispersed particles, and organic matter (Förstner, 1982). Not surprisingly, the lowest trace metal concentrations were associated with the largest size-fractions, consisting of crystalline materials, principally quartz. This pattern of enrichment is expected since some clays have high cation-exchange capacities (Grim, 1968), iron and manganese oxides are capable of binding transition metals either onto their surfaces (Schwertmann and Fitzpatrick, 1992) or through co-precipitation as metal coatings (Jenne, 1968), and organic matter has

Table 2
Mineralogy of sediments in study area Brahmani River and tributaries

Site	5	8	10D	10U	11	12	14	15D	15U
Quartz	m	m	m	m	m	m	m	m	m
Feldspars	mn	mn	mn	t	mn	mn	mn	m	m
Hematite			t	mn		t	t	mn	t
Ilmenite	t							t	t
Magnetite						t	t	mn	t
Anatase	t				t	t	t	t	t
Dolomite			t	t			t	t	
Kaolinite	t	mn		t	t	t	t	t	t
Illite	t	mn				t	t	t	t
Smectite		MN		t		t		t	t

m = major constituent; mn = minor constituent; t = trace constituent.

Table 3
Mineralogy and sediments in study area Baitarani River and tributaries

Site	6D	6U	13	23	24
Quartz	m	m	m	m	m
Feldspars	mn	mn	mn	mn	mn
Hematite	t	t	mn		
Ilmenite					t
Magnetite			t		
Anatase	t	t		t	t
Dolomite				t	t
Kaolinite	t	t	t	t	t
Illite	t			t	t
Smectite					t

m = major constituent; mn = minor constituent; t = trace constituent.

naturally anionic surfaces (in solution at circumneutral pH) capable of binding cationic species (Guy and Chakrabarti, 1976).

Because reworking of the sediments produces finer-grained sediments downstream (Chakrapani and Subramanian, 1994), it might be expected that elemental accumulations should exist at the downstream sites. To determine whether trace elements accumulated from the upper reaches (Precambrian Shield) to the lower reaches (coastal alluvium) of each river system, the total concentration of all 30 elements were compared at several sampling sites along the course (upstream to downstream) of the Mahanadi, Brahmani, and Baitarani Rivers (Fig. 4). In the Mahanadi River basin, there was a slight overall trend to decreased trace element concentrations downstream. Most significant was the dramatic decrease in metal concentrations downstream from sites 17 and 7, and the immediate increase downstream from Sonepur (site 22D). The large increase at site 9 suggests a high elemental input into the stream; however, we are not aware of any unique trace element source at this locality. In the Brahmani River, there does not appear to be an obvious pattern of elemental accumulation or depletion downstream. The only pattern to arise was the significant increase in total elemental concentration directly downstream from the discharge of industrial effluent at Angul (site 10) and Rourkela (site 15), and the unexpected rise at site 11. In the Baitarani River, however, elemental accumulation downstream was more pronounced, with the trend largely due to the extreme increase immediately below the town of Jajpur (site 6), and the sustained high elemental values at sample sites 23 and 24.

A consistent observation amongst all three rivers was the fluctuation in elemental concentrations throughout the river courses. This behavior corresponded to earlier findings by Subramanian et al. (1985), Chakrapani and Subramanian (1990a) and Ramesh et al. (1990) who showed variability in the sediment from the Ganges, Mahanadi and Krishna Rivers, respectively. Ramesh et al. (1990) attributed this variability to: 1) change in relative contribution of sediments draining different geological formations; 2) sorting of size fractions during transport processes; and 3) human influences, such as point-source industrial inputs. The influence of anthropogenic activity is examined in greater detail in

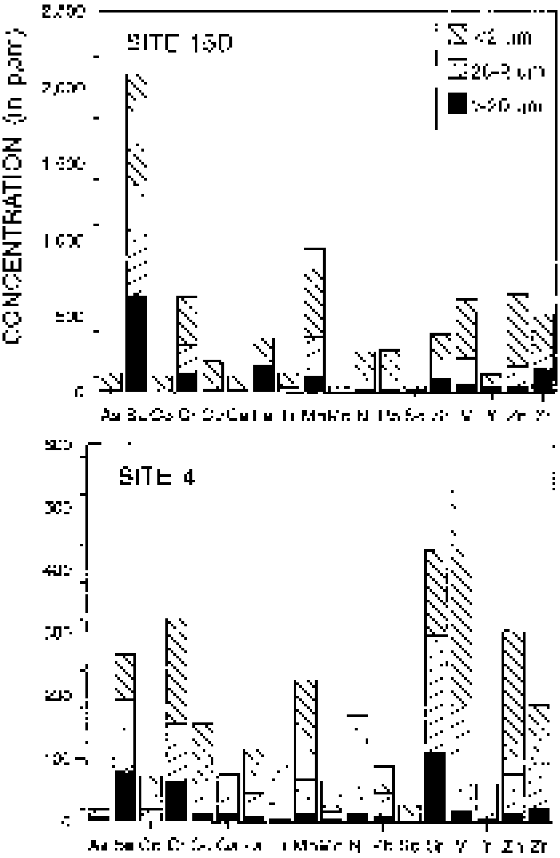

Fig. 3. Chemical analysis of sediment size fractions from site 15D (Brahmani River) and site 4 (Mahanadi River).

Fig. 5. At sites 10 and 15, almost all elements were enriched in samples collected downstream from industrial complexes. Given the maximal error in accuracy (9%), the only elements showing enrichment upstream were Sb, Ag, Co and As at site 10 and Sr, Ga, Rb, Li and Cs at site 15. Samples collected downstream from towns showed similar patterns. At site 6, every trace element, except Sr, was enriched downstream, while at site 22, all elements except Zr, Th, As, Hf and U were enriched downstream. Collectively these results confirm that sites downstream from anthropogenic activity are overwhelmingly dominated by downstream enrichment.

5. Discussion

Chemical analyses of bottom sediment from the Brahmani, Mahanadi and Baitarani Rivers indicated trace element concentrations that commonly exceeded crustal abundance. This observation is consistent with earlier views that some peninsular Indian rivers have

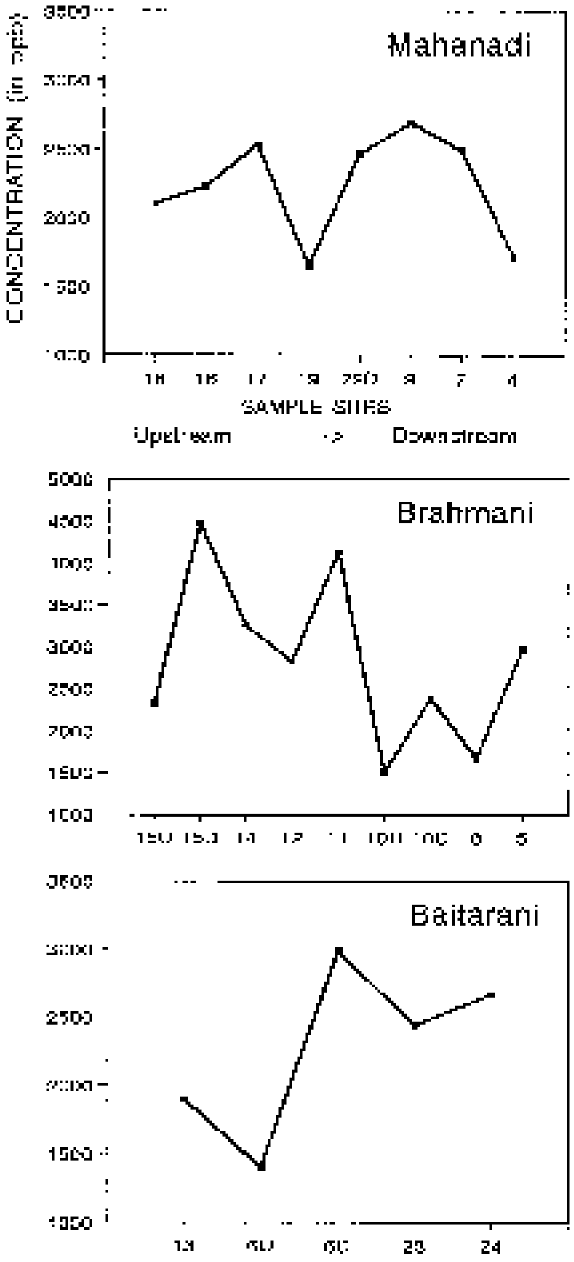

Fig. 4. Comparison of total trace element content (30 elements) in sediments from various sample sites (upstream to downstream) in the Mahanadi, Brahmani, and Baitarani Rivers.

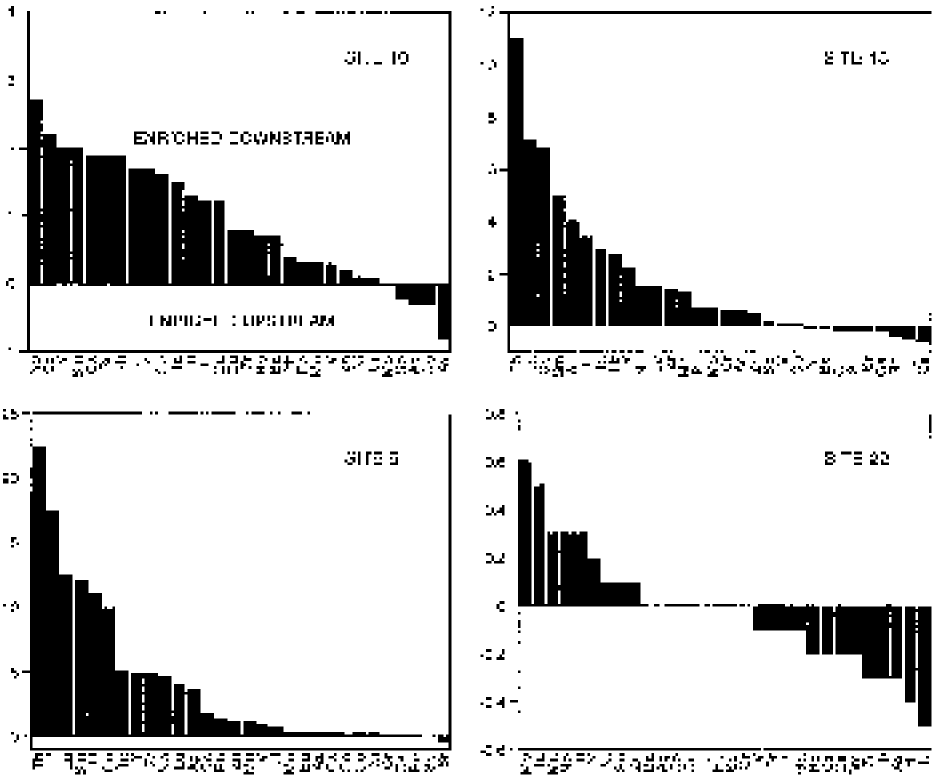

Fig. 5. Comparison of trace element concentrations in the surface waters from various sample sites, both upstream and downstream of industry (sites 10 and 15) and urban areas (sites 6 and 22). *Y*-axis indicates the factor by which trace elements are enriched in either location.

high trace metal concentrations compared to other major world rivers (Biksham and Subramanian, 1988; Chakrapani and Subramanian, 1990a). These rivers drain highly mineralized terrains, yet the variable concentration throughout the river courses, and the lack of correlation between inland (shield) and more coastal (alluvium) sites, imply that weathering is not the only source of metals to the river system.

In a recent survey of the total industrial pollution in Orissa, it was estimated that industrial wastewater constitutes by volume about 33% of the total wastewater, with the remaining 67% coming from the domestic sector and non-point sources (Sene-Johansen, 1995). In the Brahmani River, site 10 exemplifies the influence of anthropogenic activity. This location marks the discharge point of industrial effluent from NALCO, FCI and TTPS into the river. The pollutants emitted from NALCO consist of fluorides and fly ash, both released as by-products during smelting of the aluminum hydroxide precursor. The waste materials generated from the refinery typically are flushed with water into an ash pond, where after heavy rains, these ponds overflow and the ash slurry invariably pollutes the river. The ash content of the coal is very high, and the ash contains a wide array of trace metals enriched by several orders of magnitude over their original content in the coal

(Tazaki et al., 1989). In addition to NALCO, the FCI factory manufactures urea and is fuelled by coal. Pollutants generated from the process include nitrogen-compounds, cyanide, chromium and other suspended solids. TTPS also operates using coal, with the main source of pollutants being solid wastes in the form of fly ash and bottom ash. Common practice is to dispose of the ash in settling ponds, which periodically overflow. The operation in Rourkela (sample site 15) comprises a large integrated steel plant, along with a coke plant, foundry, sintering plant, captive power plant, nitric acid plant, sulfuric acid plant, and fertilizer plant. Discharge of waste products from these manufacturing activities results in pollution of the local waters, and hence the bottom sediments.

Another major sources of pollution, domestic sewage, can also be observed from the sediment samples. Because none of the towns in Orissa have proper sewage systems, open drains carry the waste water directly into the river system. In addition, there is no organized garbage or domestic waste disposal, and hence it is dumped directly into local rivers. Although there has not been any direct measurement of the sewage from any city in Orissa, it is not difficult to imagine that it must exert a major influence on river chemistry. The effects of sewage outflow, and the concomitant high elemental composition, was observed in the surface waters (Konhauser et al., 1997) and bottom sediment for sampling sites located downstream from urban areas. The mechanisms by which trace elements are taken up by the sediments include, (1) adsorption to clays, metal oxides/hydroxides and organic matter, (2) biological uptake, and (3) physical accumulation of metal-enriched particulate material by sedimentation and entrainment (Hart, 1982). The actual partitioning of trace elements amongst these substrates, however, has not been the focus of this study.

6. Conclusions

The effects of pollution are clearly observed in local samples, yet there does not appear to be a net accumulation of trace elements downstream. Apparently, trace elements discharged into the river system tend to be short-lived in the water column, rapidly settling out or becoming adsorbed into the bottom sediment. However, during monsoonal episodes, which have been determined to be the most dominating factor controlling the flow of Indian rivers (Ray et al., 1984), bedload transport can be significant. Hence it is possible that locally concentrated polluted sediment could become regionally distributed. For example, the sediment load carried during September in the Mahanadi River had been estimated to range from 18 to 74% of the annual load (Chakrapani and Subramanian, 1990b), with much of the sediment transported significant distances downstream. Accordingly, the patterns of element enrichment observed downstream from anthropogenic sources may only represent those metals accumulated since the last peak flow.

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