Chemical Geology, 112 (1994) 275–291
Elsevier Science B.V., Amsterdam

[CA]

Metal contamination due to mining and milling activities at the Zawar zinc mine, Rajasthan, India

1. Contamination of stream sediments

B.G. Prusty[a], K.C. Sahu[b] and Geeta Godgul[b]
[a]*Defence Terrain Research Laboratory, Delhi 110 054, India*
[b]*Department of Earth Sciences, Indian Institute of Technology, Bombay 400 076, India*

(Received June 29, 1992; revised and accepted June 18, 1993)

ABSTRACT

Ancient base-metal mining activity at Zawar has produced widespread and persistent dispersal of metals by the Tiri river, flowing past the region. With heavy input of mine and tailing water, the river sediments are enriched with heavy metals compared to the background sediments. Samples collected from the river bed have been analysed for Pb, Zn, Cu, Cd, Fe, Mn, Ca and Mg to recognise the extent of contamination and the geochemical process of dispersion.

The river sediment is a mixture of natural erosional detritals, tailing discharges from the milling plant and hydrogenous precipitates. Besides the detrital carbonates derived from the dolomitic litho unit of the area, a significant amount of carbonate is likely to precipitate on the river bed due to influx of mine water. Correlation matrix and *R*-mode factor analyses revealed that coprecipitation of metals along with Fe-Mn-hydroxides is significant. Association of metals with the precipitated carbonates is by adsorption under alkaline to neutral pH conditions. Cu has poor association with the other heavy metals but has a strong affinity with the gross lithology of the sediments (i.e. Ca–Mg and Fe–Mn in the second factor).

The heavy-metal concentrations are extremely variable in the sediments and have been recognised by several approaches such as: (a) extraction at pH 3; (b) total dissolution of sediment samples for bulk heavy-metal analysis; and (c) sequential chemical extraction.

Geochemical partitioning of Pb, Zn, Cu and Cd into exchangeable, carbonate, organic, multiple hydroxide and lithogenic pools (operationally defined by A. Tessier) has been brought out utilising a sequential chemical extraction scheme. Nondetrital carbonates are found to be the most efficient scavengers of Pb, Zn and Cd, whereas Cu goes for organics. The results emphasize the importance of the precipitated carbonates and organics as sinks for the heavy metals, even in presence of a high concentration of multiple hydroxides.

Of all the metals, Cd appears to be the most mobile element and Zn has preferentially accumulated more in the sediments. The apparent mobility and potential bioavailability of the metals have been found to be in the order of Cd > Pb > Zn > Cu.

1. Introduction

Mining activities pose various environmental problems including disposal from mine overburden and mineral processing plants. Atmospheric fallout of milling dusts and liquid waste disposal from beneficiation plants too lead to heavy-metal contamination of river channels and groundwater. Sediments are the most favourable sink for the heavy metals in such polluted environments and readily attenuate the contaminants owing to their high sorption capacity.

Because of pollution attenuation capacity, Aston et al. (1974), Förstner (1976), and Vivian and Massie (1977) used sediment as an index to assess the water quality where there was no significant fluctuation of pH. Systematic investigation of river sediments carried out by Thornton and Webb (1975), Förstner

SSDI 0009-2541(93)E0187-X

(1976), Förstner and Wittmann (1979), and Thornton et al. (1979) in separate studies led to the detection of significant regions of heavy-metal pollution in different parts of the world. The mineralised zones and mining activities of Zawar and the associated processing plants combined have thus posed such environmental problems pertaining to heavy-metal contamination by atmospheric dust fallout and liquid waste disposal in the Tiri river flowing past the region.

The present work aims to study the dispersion pattern and estimation of extent of contamination of heavy metals in the river sediments. The study also examines the role of organics, multiple hydroxides and carbonates in the partitioning of Pb, Zn, Cu and Cd in the sediments.

2. Study area

The Tiri river, a small tributary of the Gomti river in the Udaipur district of southern Rajasthan, drains a base-metal mineralised area of Zawar and flows in E–W direction along the northern flanks of the mineralised ridge of Zawar (Fig. 1). Mining and milling activities are on the southern flank of this ridge. Within a short distance of 29 km it has several major stream inputs. The first three easterly flowing streams from the milling plant and tailing dams are the major inputs of metal contamination.

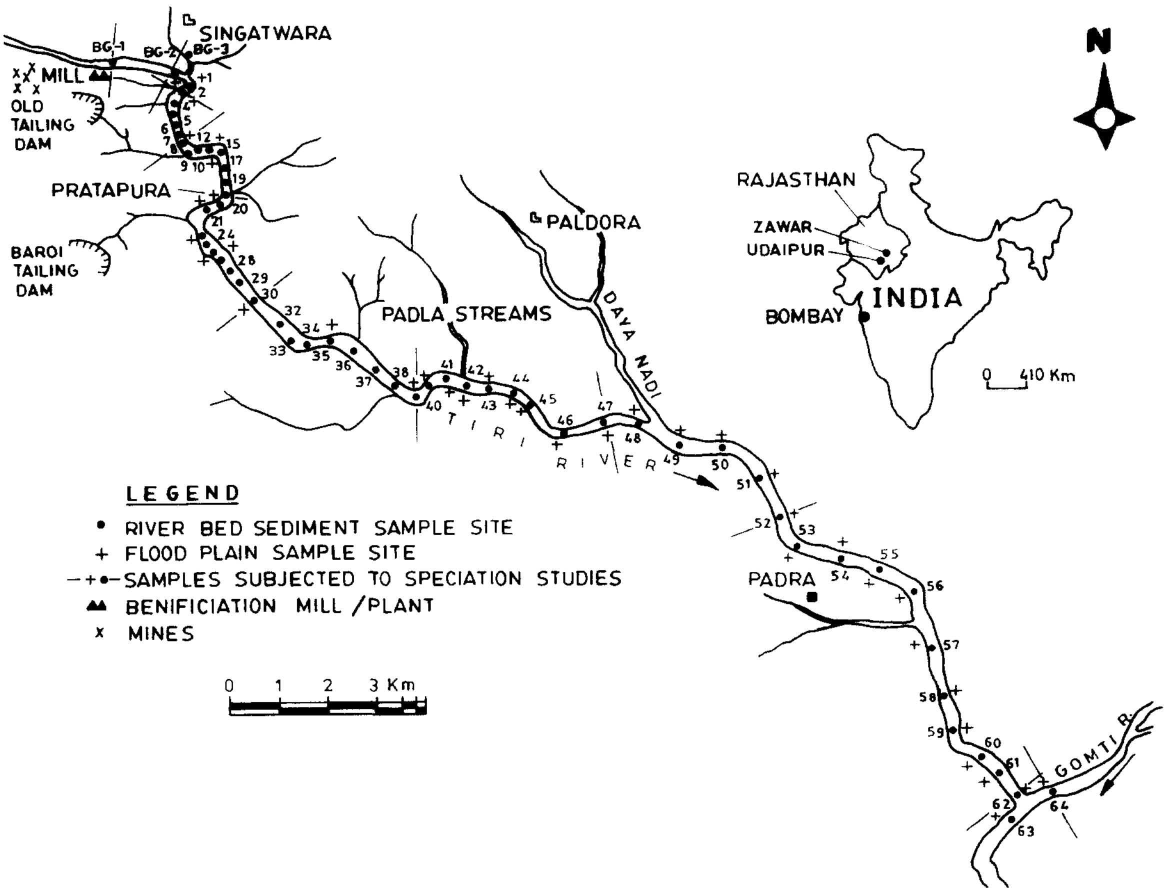

Fig. 1. Sediment and soil sampling sites along the Tiri river.

But the subsequent tributaries downstream including the Daya river are natural water inputs and cause dilution.

The area is a part of the Aravalli Supergroup characterized by undulating, steep and rugged terrain. Lithologically the hill tops are dolomite and quartzites whereas the low lying areas are of graywackes and phyllites. The Zawar region has a semi-arid climate despite an annual average rainfall of 630 mm. The rainy season is relatively short and causes flash floods in rivers and at least provides an annual cleaning by flushing out a large amount of rainwater.

Prospecting, mining and smelting of base-metal ores in the Zawar Mining Complex date back to 3000 B.C., with subsequent sporadic mining of Zn, Pb, Cd and Ag. Presently, Hindustan Zinc Ltd. is undertaking the mining activities with a production of $> 10^6$ t* of ore per annum. The ore production to milling ratio is about 100:95 but the concentrate to tailing ratio is 68:32. Hence a considerable amount of the milled material is discharged as tailing effluents. Apart from milling the ore, beneficiation is also carried out at the mine site for upgrading and separating galena and sphalerite as concentrates to meet the requirement of smelters. A major part of the mill effluents are pumped out to the tailing dams.

3. Methodology

Sediment samples were collected from 64 sites along the Tiri river starting from south of Singatwara village, the first point source of milling discharge, down to the confluence point with the Gomti river (Fig. 1). The semi-arid climate, flash flood and tailing discharges combined have deposited a mixed layer of sediment in the river bed. The sampling work was done in the December–January period by which time the mine and mill discharges have pumped a considerable amount of sediments into the river bed, replenishing the seasonal depletion of sediment. At each site, three cores from 0–10-cm depth surface sediment were taken from an area of ~ 10 m^2 and the bulked cores were stored in polythene bags. In the laboratory sediments were air dried and ground to -80# size. Two background samples were also collected from the river bed, upstream of Singatwara village.

3.1. Chemical analysis

The samples were treated for metal analysis using the following three methods:

(1) *Total dissolution of the sediments*: Complete dissolution of the samples was done using $HClO_4$–H_2SO_4–HF to estimate the total metal content (Shapiro and Brannock, 1962).

(2) *Leaching of heavy metals at pH 3*: Samples were leached at pH 3 in phthalate buffer (50 ml of 0.1 *M* $KHC_8H_4O_4$+21 ml of 0.1 *M* HNO_3+29 ml of deionized water) for 24 hr (Trefry and Meiz, 1984). A constant pH of 3 was maintained throughout the leaching period. The leached solution after centrifugation was acidified to pH 2 and preserved for metal determination.

(3) *Solid speciation*: Heavy metals present in different geochemical pools were recognised by sequential chemical extraction. The terminology of Tessier et al. (1979) and Prusty et al. (1987) will be used throughout this series of papers, even though overlap between fractions undoubtedly remains. This method is designed to differentiate among the exchangeable, carbonate, reducible (hydrous Fe/Mn-oxides), oxidisable (sulphides and organic phase) and residual fractions. Dolomite dissolves in hot HCl and so also calcite only at low pH. The detrital carbonate derived from the dolomitic country rock is less reactive than the hydrogenous precipitated carbonate. Therefore in the second step in the sequential extraction (at pH 5), detrital carbonate is not likely to contribute heavy metals into the "operationally defined" carbonate phase. The steps involved in the extraction scheme are as follows:

---

*1 t = 1 metric tonne = 10^3 kg.

Step I: Leaching with 1 *M* $MgCl_2$ at pH 7 for 1 hr with continuous agitation — Exchangeable fraction.

Step II: Residues of step I leached with 1 *M* NaOAc at pH 5 (adjusted with HOAc) for 5 hr with continuous agitation at room temperature — Carbonate-bound fraction.

Step III: Residue from step II extracted with 1 *M* $NH_2OH \cdot HCl$ in 25% (v/v) at room temperature for 6 hr and continuous agitation — Multiple hydroxide fraction.

Step IV: Residue from step III treated with 0.02 *M* HNO_3 followed by addition of 30% H_2O_2 at pH 2 and digested for 5 hr in a reflux system with occasional shaking at 85°C (Gupta and Chen, 1975). After cooling of the leachates 10 ml of 3.2 *M* NH_4OAc in 20% HNO_3 were added and the content subjected to 30-min continuous shaking — Oxidisable fraction (organic and sulphidic).

Step V: Residue of step IV was completely dissolved in $HClO_4$–HCl–HF — Lithogenic fraction or residual fraction.

The leachates obtained in each step were acidified to pH 2 and preserved in polythene bottles for further analysis.

Determinations of Pb, Zn, Cu, Cd, Fe and Mn were carried out with a double-beam atomic absorption spectrophotometer, model GBC *902*. Ca and Mg were determined by standard ethylene diaminetetraacetic acid (EDTA) technique. Concentrations of the metals are means of at least duplicate digests/leachates expressed in $\mu m\ g^{-1}$. Precision of analytical procedure including extraction and atomic absorption analysis on replicate samples were estimated against standards. The estimates of total variation at the 95% confidence level are Pb = ±5%, Zn = ±8%, Cu = ±6%, Cd = ±9%, Fe = ±8% and Mn = ±6%. Organic C was determined by wet oxidation method (Strickland and Parsons,1965). But the total organic matter present in the sediment sample was estimated by $K_2Cr_2O_7$ and H_2SO_4 treatment followed by titration against ferrous ammonium sulphate. 85% H_3PO_4 and NaF were added to the solution to remove interference of iron during titration.

The mineral constituents in the samples were identified by X-ray diffraction (XRD) technique.

4. Results

4.1. Mineralogy of sediments

The XRD pattern of the sediment samples revealed that the samples are rich in dolomite and to some extent in quartz and albite. A significant amount of hydrous oxides of Fe and Mn, e.g. todorokite, maghemite and goethite, have also been observed in the XRD analysis. Except phlogopite no clay minerals could be recognised. Although a certain amount of opaque particles is observed under the microscope, sulphide minerals could not be detected in the XRD analysis.

4.2. Contamination index and distribution of heavy metals

The hydrogenous or leachable concentration of trace metals along the lateral profile shows a variable pattern in the Tiri river sediments. Heterogeneous bed rock lithology and varied dispersion mechanisms cause variable accumulation of metal along the river course. However, metal concentrations at all sample points are found to be much higher than those of the background (Table 1).

Enrichment of any element to a higher degree is a harmful factor to the environment. The cumulative enrichment factor of elements is often more meaningful for environmental studies than that of an individual metal contaminant. Hence the number of metal concentrations (i.e. 4 or 6, see Table 1) obtained from each sample point was reduced to one parameter known as the "contamination index" (CI). The concept of CI computation is a modified version of the "pollution index" proposed by

TABLE 1

Heavy-metal analysis (pH-3 extracts) of sediments along the Tiri river (in $\mu g\ g^{-1}$)

Sample station	Distance from mill site (km)	Zn	Pb	Cu	Cd	CI(4)	Fe	Mn	CI(6)	Ca	Mg
B (avg.)		65	23	8.15	0.48	4.00	1,250	556	6.00	20,874	7,060
2	0.50	1,697	663	36.88	10.20	80.72	4,550	1,473	87.01	34,193	17,503
3	0.75	–	644	35.67	16.64	–	4,657	–	–	32,685	16,842
4	1.00	1,211	677	11.98	8.35	66.94	4,800	1,721	73.88	30,267	15,200
5	1.25	1,021	525	14.02	6.16	53.09	4,250	1,040	58.36	28,389	14,000
6	1.50	1,016	264	12.96	7.25	43.80	3,650	1,290	49.04	28,389	13,000
7	1.75	1,200	520	14.02	7.40	58.23	4,775	1,318	64.42	30,894	12,000
8	2.00	1,524	950	8.00	11.05	88.75	6,000	1,490	96.23	43,073	22,472
9	2.25	1,615	566	45.00	9.35	74.46	4,625	1,412	80.70	34,193	18,300
10	2.50	1,595	698	43.11	10.50	82.06	4,300	1,251	87.75	30,894	11,100
12	3.00	3,000	1,402	70.01	26.20	170.21	5,000	1,557	177.08	43,735	20,102
13	3.25	2,821	1,153	46.21	15.00	130.45	5,625	1,624	137.87	41,748	18,680
14	3.50	1,828	640	30.48	10.05	80.63	5,313	1,240	87.11	31,937	12,000
15	3.75	1,101	488	15.98	7.45	55.64	4,800	1,651	62.45	26,927	10,000
17	4.25	916	360	23.47	7.75	48.77	4,613	1,190	54.60	16,073	8,000
18	4.50	1,707	942	44.50	11.80	97.26	4,763	1,523	103.81	27,832	24,956
19	4.75	1,974	779	32.03	11.00	91.09	5,675	1,329	98.02	37,991	20,000
20	5.00	1,586	1,425	49.06	10.15	120.53	3,438	1,129	125.31	35,903	20,000
21	5.25	1,378	625	37.00	10.05	73.85	5,050	1,318	80.26	38,434	21,981
24	6.00	1,251	670	22.98	8.85	69.64	5,650	1,418	76.71	34,035	18,000
25	5.75	1,700	1,549	79.95	20.00	144.98	5,463	1,813	152.61	39,034	22,000
26	6.50	1,924	775	34.96	22.00	113.42	5,775	1,601	120.92	40,078	25,000
27	6.75	3,511	1,356	90.63	24.20	174.52	4,463	1,346	180.51	79,447	45,000
28	7.00	5,875	2,505	129.99	36.00	290 25	5,400	1,835	297.87	155,063	75,000
29	7.25	1,549	500	45.56	11.00	74.08	4,500	1,340	80.09	28,627	17,650
30	7.50	1,872	720	50.78	11.50	90.29	7,450	1,401	98.77	46,916	25,495
33	8.25	1,677	890	55.50	12.70	97.77	4,100	1,184	103.18	34,012	14,807
34	8.50	1,850	1,764	118.01	27.00	175.89	5,300	1,801	183.37	60,954	20,000
35	8.75	1,058	330	28.28	8.02	50.81	5,325	1,501	57.77	56,986	21,000
36	9.00	817	363	30.97	5.10	42.78	4,500	1,112	48.38	55,663	17,160
37	9.50	840	419	17.00	5.20	44.06	6,000	1,760	52.03	45,326	22,485
38	10.00	717	292	27.00	5.50	38.50	5,500	1,575	45.73	40,000	20,000
39	10.50	753	331	30.00	4.90	39.87	5,000	1,470	46.51	39,759	21,818
40	11.00	975	396	18.00	5.90	46.72	6,250	1,796	54.95	48,904	21,279
41	11.50	753	325	24.40	5.20	39.53	6,400	1,853	47.98	23,856	–
42	12.00	680	–	43.00	5.50	–	5,778	1,600	–	30,000	20,000
43	12.50	629	395	18.80	5.85	41.35	4,950	1,400	47.83	38,964	20,739
44	13.00	805	271	14.65	4.60	35.55	4,325	1,294	41.34	34,988	19,121
45	13.50	1,150	529	36.50	7.30	60.38	4,250	1,346	66.20	47,711	12,700
47	14.50	537	245	7.30	4.20	28.50	4,659	1,370	34.74	33,000	31,133
48	15.00	1,560	565	26.00	10.60	73.84	4,725	1,644	80.56	58,444	17,503
49	16.00	1,185	397	21.45	8.30	55.41	3,996	1,248	60.86	47,314	19,366
50	17.00	1,600	380	36.50	7.80	61.87	4,685	1,450	68.23	50,000	19,700
51	18.00	938	365	36.00	7.20	49.72	6,000	1,842	57.83	38,000	18,000
52	19.00	1,000	245	17.60	7.40	43.62	6,000	1,870	51.78	35,000	17,310
53	20.00	1,106	460	25.25	7.00	53.70	4,821	1,395	60.07	36,579	17,209
54	21.00	762	386	16.90	6.20	43.49	6,000	1,930	51.76	34,000	15,000
55	22.00	959	275	18.55	6.30	42.12	6,309	1,745	50.31	36,000	16,500
57	24.00	1,000	251	14.00	7.00	42.60	5,625	1,687	50.13	50,000	19,000
58	25.00	895	255	17.50	6.00	39.51	4,700	1,250	45.52	49,700	26,966
59	26.00	1,082	460	19.00	8.00	55.65	5,000	1,708	62.72	42,000	20,000
60	27.00	970	402	26.00	6.05	48.20	2,000	1,600	52.68	34,000	18,000
61	28.00	975	225	22.00	7.00	42.06	4,600	1,300	48.08	34,193	18,000
62	29.00	742	243	19.00	5.20	35.15	5,175	1,380	41.77	32,000	17,000
63	30.00	1,072	320	20.00	7.55	48.56	5,100	1,556	55.44	32,000	17,000
64	30.00	1,164	415	–	6.84	–	–	–	–	31,000	16,538

CI(4) = contamination index for Zn, Pb, Cu and Cd; CI(6) = contamination index for Zn, Pb, Cu, Fe and Mn; *B* (avg.) = average background concentrations; – = not determined.

Rang et al. (1987), where background values (B-values) are of Zawar uncontaminated sediments. Thus the level of contamination is measured with reference to the background concentration of elements. The metal concentration values were made dimensionless by dividing with average background values (B average) of Zawar uncontaminated sediments. The CI is then calculated by:

$$\mathrm{CI}=\sum_{N=1}^{n}(C_N/B_N) \qquad (1)$$

where C_N=concentration of Nth element; B=background value of Nth element; and n=number of elements (4 or 6).

High CI-values are observed near input points and marked concentration gradients are apparent along the course, reflecting preferential mobilization of hydrogenous metals by dilution. Higher CI-values at few sample sites roughly correspond to samples having higher Fe, Mn, Ca and Mg content, and are likely to be due to coprecipitation of the metals.

4.3. Metal correlation matrix and R-mode factor analysis

R-mode factor analysis was done on the normalised heavy-metal data [$\log\{c/(1-c)\}$, $0<c<1$ transformation, where c is the weight fraction]. A 8×8 matrix of simple correlation coefficient was computed from the normalised variables. Statistically significant principal components were extracted from the correlation matrix based on the inflection points or minima points of cumulative eigenvalues. Subsequently a Varimax rotation was applied. The metal correlation matrix is presented in Table 2. Table 3 summarizes the eigenvalues and the communalities that represent the proportion of variation in a given variable that is explained by a two-factor model. The factor scores of all the sample stations were determined and presented graphically in Figs. 2 and 3 with graduated circles (sizes are drawn to reflect variations in factor values). Factor analysis enables to calculate a single value for each of these groupings (Figs. 2 and 3), instead of quantitative presentation of eight separate maps for eight elements.

The total explained variance of this model is 80% at the 95% confidence level. In the present analysis, the *R* I factor is identified as Zn–Pb–Cd–Fe–Mn with a lesser but significant contribution from Cu and the *R* II factor as Ca–Mg–Cu.

4.4. Solid speciation of sediment-bound heavy metals

Once it had been established that heavy-metal pollution had affected the non-residual fractions of many of the stream sediments, a number of samples were subjected to more complex sequential leaching. Out of 64 stations only 9 samples (Nos. *3*, *8*, *20*, *30*, *39*, *47*,

TABLE 2

Correlation matrix for heavy metals of Tiri river sediments

Metals	Zn	Pb	Cd	Cu	Fe	Mn	Ca	Mg
Zn	1.00	0.91[a]	0.91[a]	0.75[a]	0.71[a]	0.65[a]	0.46	0.52[a]
Pb		1.00	0.91[a]	0.78[a]	0.63[a]	0.65[a]	0.41	0.49
Cd			1.00	0.70[a]	0.59[a]	0.71[a]	0.46	0.49
Cu				1.00	0.41	0.40	0.47	0.43
Fe					1.00	0.72[a]	0.21	0.36
Mn						1.00	0.34	0.33
C[a]							1.00	0.55[a]
Mg								1.00

[a]Significant.

TABLE 3

Factor loadings for the first two factors after Varimax rotation (pH-3 sediment extraction, $n=51$)

Metals	Factor *1*	Factor *2*	Communality
Zn	0.820	−0.483	0.905
Pb	0.810	−0.466	0.873
Cd	0.804	−0.473	0.869
Cu	0.537	−0.608	0.658
Fe	0.861	−0.056	0.745
Mn	0.841	−0.130	0.724
Ca	0.105	−0.857	0.746
Mn	0.225	−0.774	0.649
% Total variance	47.169	32.884	80.053
Cumulative % variance	47.169	80.053	
% Common variance	58.922	41.078	100.00
Eigenvalue (sum of squared factor loading)	5.107	1.062	6.169

Significant factors: factor *1*, Fe–Mn–Zn–Pb–Cd (Cu); factor *2*, Ca–Mg–Cu.

52, *62* and *64*), evenly distributed along the river course, and two background samples (B*1* and B*2*) were selected for this work. The geochemical phases dissolved in each step of the extraction sequence is operationally defined (Tessier et al., 1979; Robinson, 1985; Prusty et al., 1987) even though overlap between fractions remains and they also do not represent 100% dissolution.

In step II the Na-acetate treatment was intended to dissolve the carbonates. But some of the detrital carbonates are unlikely to dissolve by this step and it is believed to be dissolved in step IV (oxidisable or operationally defined organic phase) but more so in step V (i.e. lithogenic phase). However, it is felt that a minor portion of the detrital carbonates and total precipitated carbonates could be destroyed by the Na-acetate treatment (Presley et al., 1972). The sulphides that could not be detected by XRD, if present, would have dissolved in step IV with organics (i.e. oxidisable phase).

The analytical data on different chemical forms of Pb, Zn, Cu, Cd, Fe and Mn present in the exchangeable, carbonate, multiple hydroxide, organic and lithogenic pools are summarized in Table 4. Their relative abundance with respect to total metal content and calculated proportions of each metal in different chemical forms (deduced from Table 4) are summarized in Table 5 and Fig. 4, respectively.

The amount of a metal in any phase is dependent on the abundance of the phase in the sediment. To determine the "scavenging capacity" (SC) a phase normalisation with respect to its abundance is required. Hence the SC of a phase is determined by dividing the metal concentration of the pool by the concentration of the major element(s) which make(s) up the phase. For example, the SC of the carbonate phase for Cu is defined as:

$$\mathrm{SC}=[(\text{carbonate bound Cu in moles})/\{(\mathrm{Ca}+\mathrm{Mg})\text{ of carbonate in moles}\}]\times 100 \qquad (2)$$

The SC's of all five geochemical pools for Pb, Zn, Cu, Cd, Fe and Mn are listed in Table 6.

4.5. Metals in geochemical pools

The effectiveness of the major scavenging phase depends on the physico-chemical conditions of the depositional environment. A 10-fold increase in the SC of the organic pool and a 3–8× increase in the reducible pool are observed for all the heavy metals.

The exchangeable pool is considered to be the most mobile and bioavailable phase present in the sediments. In the Tiri river sediments most metal fractions associated with this pool are negligible. However, ~20% of non-residual Cd and 10–12% of Zn are bound to this pool.

The carbonates which are insignificant in the background sediments, become the most significant and effective scavenger in the contaminated segments. Carbonates with SC of 0.9 for Zn, 1.05 for Pb, 0.06 for Cu, 0.01 for Cd, 6.28

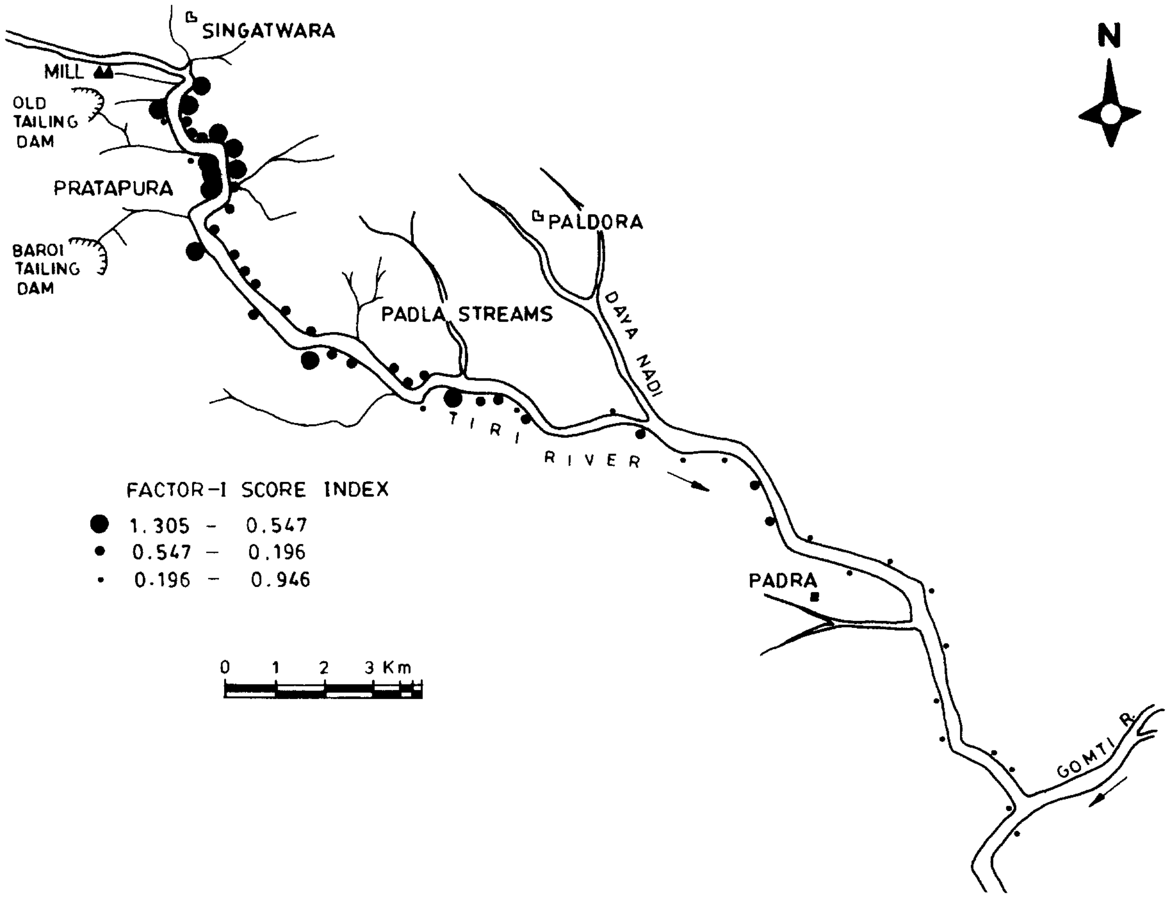

Fig. 2. Factor-I scores (Zn–Pb–Cd–Fe–Mn) of sediment heavy-metal data in standard deviation units.

for Fe and 9.29 for Mn in the background samples have been increased to 31.87 for Zn, 18.74 for Pb, 0.61 for Cu, 0.12 for Cd, 38.58 for Fe and 13.03 for Mn, respectively, at site *1* near the mill tailing discharge point. This phase accumulates ~50% of the non-lithogenic heavy metals in the polluted sediments. The organic pool has ~6–8% of the total metals present in the sediments. But the organic phase is quite significant in the uncontaminated background samples and carries ~50% of non-lithogenic Zn and ~65% of the Cu.

The reducible phase, i.e. multiple hydrous oxides of Fe and Mn, has calculated averages in μg g^{-1} (mean values, Table 4) of 70 for Zn, 88.85 for Pb, 3.01 for Cu and 1.45 for Cd, constituting 21.3% of total Zn, 45% of total Pb, 9.5% of total Cu and 18.5% of total Cd of the uncontaminated sediments, respectively. In the polluted segment the concentration of the metals in this phase increases many fold and the calculated average concentrations in μg g^{-1} are Zn = 485, Pb = 318.6, Cu = 11.24 and Cd = 3.7, constituting ~8.4% of total Zn, ~28.3% of total Pb, ~18% of total Cu and ~12.07% of total Cd, respectively. This phase is the largest scavenger for Pb and Cu next only to carbonates.

4.6. Partitioning of Zn, Pb, Cd and Cu

To bring out the competition among the three major geochemical pools, i.e. the carbonate, reducible and organic phases, for the heavy

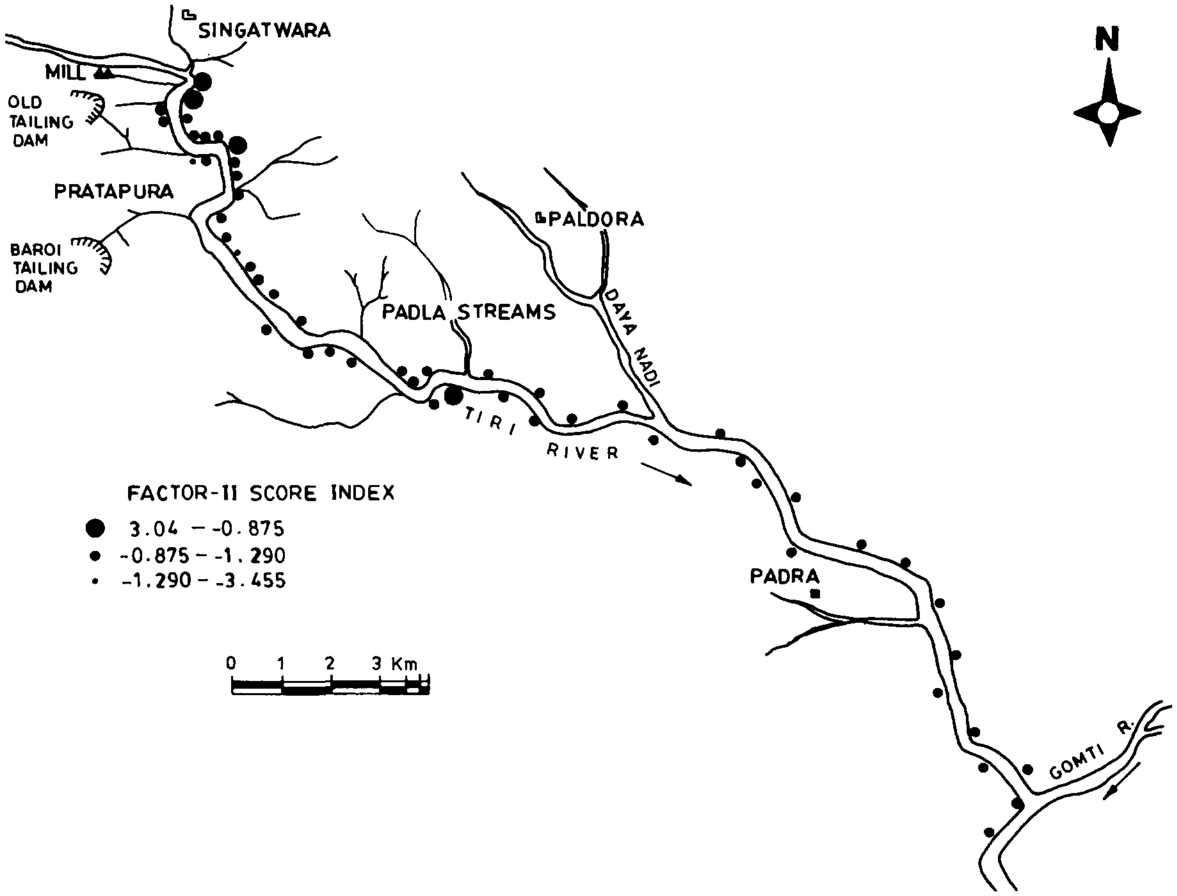

Fig. 3. Factor-II scores (Ca–Mg–Cu) of sediment heavy-metal data in standard deviation units.

metals, "competition ratios" (CR) have been calculated by taking the ratios of the SC's of a pair of the pools for the same element (Table 7). For example, CR for Cu between carbonate and reducible pools is:

$$\frac{(\text{carbonate-bound Cu})/\{(\text{Ca+Mg}) \text{ of carbonate phase}\}}{(\text{reducible Cu})/\{(\text{Fe+Mn}) \text{ of reducible phase}\}} \quad (3)$$

A value of unity for the ratio would mean that, given equal weightage of (Ca+Mg) and (Fe+Mn), Cu would partitioning equally between the two pools. Values < 1 indicate that the reducible phase competes more effectively for Cu, etc. This approach of comparison of geochemical pools assumes that the competition between any pair of pools is not significantly affected by the presence of the third pool.

4.6.1. Zinc. All nine sediment samples taken from the contaminated segment of the river for sequential extraction exhibit extremely high levels of Zn contamination. A major fraction of the metal is associated with the carbonate fraction (calculated average 26%). However, the Zn content of the carbonate pool in the background samples is meagre. At site *1*, immediately downstream the tailing discharge point, where total Zn concentration increases significantly, the apparent effectiveness of carbonates as scavengers of Zn suddenly increases by 4 times. However, the SC decreases downstream.

The organic fraction is the next most important scavenging pool for Zn, containing ~ 15% of the total metal. However, the trend of vari-

TABLE 4

Partitioning of metals into geochemical pools of sediments (in $\mu g\ g^{-1}$)

Metal Site		EEF	Carb.	Redu.	Org.	Non-litho.	Litho.	Total
Zn	B*1*	1.89	43.12	115.00	118.88	278.90	126.70	405.60
	B*2*	0.70	19.84	25.00	82.14	127.68	47.33	175.00
	3	175.00	1,640.00	412.00	263.68	2,491.00	1,154.00	3,644.40
	8	142.00	1,264.00	292.00	656.45	2,354.45	10,270.50	12,625.00
	20	112.00	2,400.00	666.60	2,103.40	5,282.00	2,562.40	7,844.40
	30	93.00	900.00	452.40	1,470.23	2,916.00	2,748.80	5,664.40
	39	6.80	1,173.00	456.00	680.00	2,316.00	2,749.00	5,064.40
	47	105.00	2,574.00	530.40	74.63	3,284.03	2,940.40	6,224.40
	52	41.60	752.00	361.40	748.17	1,903.00	3,506.00	5,409.40
	62	40.00	773.00	617.00	477.28	1,907.28	1,982.12	3,889.40
	64	48.40	1,305.40	581.00	976.76	2,911.56	1,282.84	4,194.40
Pb	B*1*	0.01	37.68	125.30	15.08	178.06	46.34	224.40
	B*2*	1.52	29.28	52.40	4.97	88.17	65.03	153.20
	3	5.28	610.75	360.00	4.92	980.95	123.05	1,104.00
	8	1.20	1,018.16	342.00	19.51	1,380.87	231.13	1,612.00
	20	11.84	1,372.00	581.00	9.88	1,974.72	60.50	2,035.00
	30	9.36	676.64	180.00	30.00	896.00	50.00	946.00
	39	0.88	668.20	309.00	19.53	987.61	149.40	1,130.00
	47	16.56	850.00	200.00	1.63	1,068.20	243.80	1,312.00
	52	1.44	450.20	250.00	8.47	710.11	49.00	759.11
	62	2.40	212.40	313.00	64.31	592.11	48.00	640.00
	64	4.64	610.00	332.60	22.51	970.00	179.50	1,149.00
Cu	B*1*	0.48	0.85	1.88	11.08	14.29	20.30	34.59
	B*2*	0.10	2.51	4.14	9.61	16.36	14.24	30.60
	3	0.65	25.96	11.96	10.15	48.72	15.10	63.80
	8	0.01	2.91	6.44	0.20	9.55	40.25	49.80
	20	0.46	28.52	14.28	4.28	47.54	86.50	134.00
	30	0.56	22.20	9.72	16.68	49.76	11.50	60.60
	39	1.58	2.44	15.96	2.95	23.00	78.27	101.20
	47	1.55	34.92	9.92	0.01	46.40	29.20	75.60
	52	0.92	4.06	10.34	2.09	17.41	27.80	45.20
	62	0.61	13.45	10.32	0.40	24.78	6.62	31.40
	64	0.90	27.24	12.20	10.76	51.10	15.90	67.00
Cd	B*1*	0.04	0.64	1.78	0.20	2.66	5.84	8.50
	B*2*	0.01	0.24	1.12	0.54	1.90	5.10	7.00
	3	3.32	5.12	3.62	4.97	17.03	7.17	24.20
	8	2.44	5.44	3.10	2.75	13.73	39.87	53.60
	20	5.04	12.56	3.14	6.75	27.50	14.50	42.00
	30	5.08	10.92	3.92	7.10	27.02	3.00	30.00
	39	0.01	10.24	3.82	5.40	19.46	10.75	30.20
	47	5.00	92.00	12.88	4.44	0.85	24.10	14.10
	52	0.68	5.56	3.12	3.96	13.32	16.00	29.30
	62	4.16	6.32	4.98	2.47	17.93	11.10	29.00
	64	4.80	9.84	3.96	3.25	21.85	4.15	26.00

EEF = easily exchangeable fraction; Carb. = carbonate fraction; Redu. = reducible fraction; Org. = organic fraction; Non-litho. = non-lithogenous fraction; Litho. = lithogenous fraction.

TABLE 5

Relative abundance of Zn, Pb, Cu and Cd in each fraction with respect to their total contents in sediments

Element	Site	% of total metal present					
		EEF	Carb.	Redu.	Org.	Non-litho.	Litho.
Zn	B*1*	0.47	10.63	28.35	29.31	68.76	31.24
	B*2*	0.40	11.34	14.29	46.94	72.96	27.05
	3	4.80	45.00	11.31	7.24	68.34	31.67
	8	1.12	10.01	2.31	5.20	18.65	81.35
	20	1.43	30.60	8.50	26.81	67.33	32.67
	30	1.64	15.89	7.99	25.96	51.48	48.53
	39	0.13	23.16	9.00	13.43	45.73	54.28
	47	1.69	41.35	8.52	1.20	52.76	47.24
	52	0.77	13.90	6.68	13.83	35.17	64.81
	62	1.03	19.87	15.86	2.27	49.04	50.96
	64	1.15	31.12	13.85	23.29	69.42	30.58
Pb	B*1*	0.01	16.80	55.84	6.72	79.35	20.65
	B*2*	1.00	19.11	34.20	3.24	57.55	42.45
	3	0.48	55.32	32.61	0.45	89.00	11.00
	8	0.07	63.16	21.22	1.21	85.66	14.34
	20	0.58	67.42	28.55	0.50	97.00	3.00
	30	0.99	71.53	19.03	3.17	94.72	5.28
	39	0.08	58.77	27.18	1.72	86.86	13.14
	47	1.26	64.79	15.24	0.12	81.42	18.58
	52	0.19	59.31	32.93	1.12	93.55	6.46
	62	0.38	33.19	48.91	10.04	92.52	7.50
	64	0.40	53.09	28.95	1.09	84.42	15.62
Cu	B*1*	1.39	2.46	5.43	32.02	41.3	58.67
	B*2*	0.33	8.20	13.53	31.41	53.46	46.54
	3	1.02	40.69	18.75	15.91	76.36	23.67
	8	0.01	5.84	12.93	0.40	19.18	80.82
	20	0.34	21.28	10.66	3.20	35.48	64.55
	30	0.92	36.63	16.04	27.52	82.11	18.98
	39	1.56	2.41	15.77	2.95	22.73	77.34
	47	2.84	46.19	13.12	.01	61.38	38.62
	52	2.17	9.58	24.39	4.93	41.06	58.94
	62	1.94	42.83	32.87	1.27	78.92	21.08
	64	1.34	40.66	18.20	16.06	76.27	23.73
Cd	B*1*	0.47	7.53	20.94	2.25	31.29	68.71
	B*2*	0.01	3.43	16.00	7.71	27.14	72.86
	3	13.72	21.16	14.96	20.54	70.38	29.62
	8	4.55	10.15	5.78	5.13	25.62	74.38
	20	12.00	29.90	7.48	16.07	65.48	34.52
	30	16.93	36.40	13.07	23.67	90.00	10.00
	39	0.01	33.91	12.65	17.88	64.44	35.55
	47	15.50	33.72	11.62	2.23	63.09	36.91
	52	2.32	18.98	10.65	13.52	45.47	54.53
	62	14.34	21.79	17.17	8.52	61.80	38.20
	64	18.46	37.85	15.23	12.50	84.05	15.96

EEF = easily exchangeable fraction; Carb. = carbonate fraction; Redu. = reducible fraction; Org. = organic fraction; Non-litho. = non-lithogenous fraction; Litho. = lithogenous fraction.

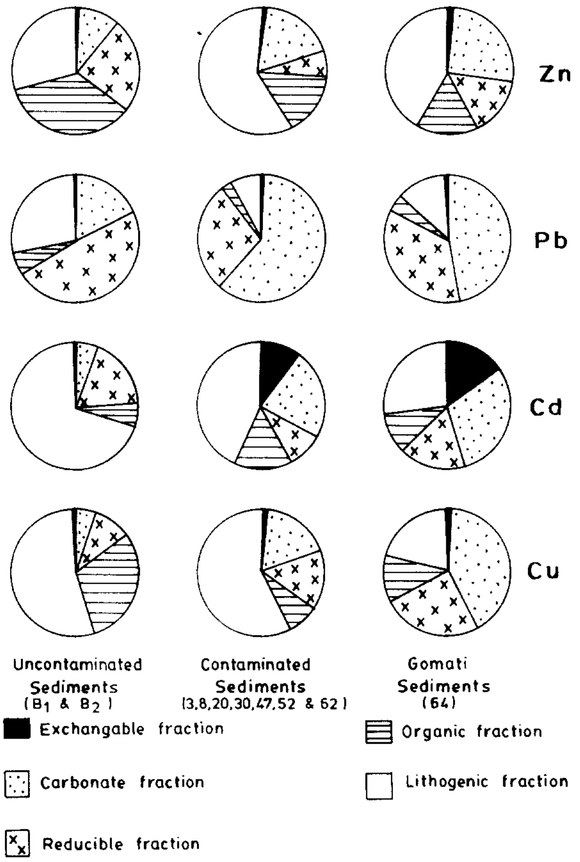

Fig. 4. Calculated proportions of Zn, Pb, Cd and Cu in each of the geochemical fractions.

ation of organic Zn as well as SC of organics for Zn are irregular. The computation of CR among pairs of geochemical pools (Table 7) reveals that carbonates can scavenge 7–10× more Zn than the multiple hydroxides and 40–165× more than the organics. Hence the order of effectiveness of scavengers in the contaminated Tiri river sediments is inferred as carbonates > reducible > organics.

4.6.2. Lead. For Pb, carbonate is the significant scavenger in the uncontaminated background samples. But its apparent effectiveness increases by 25× in the sample immediately downstream the first tailing discharge point. The concentration of Pb in the carbonates of polluted segment varies between 600 and 1372 μg g^{-1}, amounting to 61% (calculated average) of the total Pb.

The reducible pool, the second most Pb-enriched pool of Tiri sediments, contains ~20–35% of total Pb. However, its SC for Pb decreases downstream, probably due to decrease in precipitation of the multiple hydrous oxides. Pb is found to have an antipathetic association with the organic and exchangeable pools. A meagre amount ($<6\%$) is associated in both the pools combined. The lithogenic fraction also carries little Pb.

The CR's indicate that the carbonates are 5–11× more efficient in accumulating the metal than the multiple hydroxides. Between the multiple hydroxide pool and organic pool, the former is 25–88× more effective. The order of effectiveness of lead intake in the contaminated sediments is expressed as carbonates > multiple hydroxides > organics.

4.6.3. Cadmium. Results listed in Table 6 show that ~70% and ~45% of Cd is bound to the residual or lithogenic pool in the background and contaminated sediments, respectively. Downstream the mill discharge point, the non-lithogenic fraction of Cd gets enhanced in the sediment samples by 10–13×. Among the non-lithogenic fractions, the carbonates in contaminated sediments and multiple hydroxides in background sediments are the most significant pools for the metal.

A significant observation in Cd fractionation is its accumulation in the exchangeable phase (12–18% of total). The mobility and bioavailability of the metal decrease approximately in the order of extraction sequence (Hickey and Kittrick, 1984). Thus the exchangeable pool greatly decides the bioavailability of the metal (extraction of exchangeable phase is the first step in the sequential leaching). Cd may be considered as the most mobile and bioavailable element in Tiri river sediments. The multiple hydroxide and organic fractions also contain ~20% (calculated average) of the total Cd. The order of partition-

TABLE 6

Scavenging capacity of carbonate, reducible and organic pools in sediment samples

Metal	Site										
	B*1*	B*2*	*3*	*8*	*20*	*30*	*39*	*47*	*52*	*62*	*64*
Scavenging capacity [{metal/(Ca+Mg)}×100] *of carbonate pools*:											
Zn	0.95	0.86	38.71	35.83	38.42	29.18	9.91	10.73	26.24	36.53	46.13
Pb	0.83	1.27	18.74	28.86	21.96	26.73	5.65	7.86	20.38	14.07	27.15
Cu	0.02	0.11	0.61	0.08	0.46	0.72	0.02	0.11	0.14	0.64	0.96
Cd	0.01	0.01	0.12	0.15	0.2	0.35	0.09	0.13	0.19	0.3	0.35
Fe	6.09	9.47	38.58	35.28	25.16	44.75	3.09	8.54	41.35	36.8	43.77
Mn	7.04	11.54	13.07	10.91	8.67	16.85	2.08	6.88	15.76	12.18	17.16
Scavenging capacity [{metal/(Fe+Mn)}×100] *of reducible pools*:											
Zn	3.02	0.57	4.09	3.65	4.41	3.26	5.95	5.53	3.82	5.75	5.44
Pb	3.29	1.19	3.57	4.27	3.84	2.31	4.03	2.08	2.65	3.12	3.42
Cu	0.05	0.014	0.12	0.08	0.09	0.07	0.208	0.13	0.11	0.1	0.11
Cd	0.05	0.03	0.04	0.04	0.02	0.03	0.05	0.10	0.033	0.05	0.04
Scavenging capacity [{metal/org.C}×100] *of organic pools*:											
Zn	0.42	0.00	0.00	0.00	0.81	0.71	0.69	0.52	0.41	0.54	0.28
Pb	0.09	0.00	0.00	0.00	0.015	0.09	0.05	0.04	0.03	0.44	0.013
Cu	0.43	0.00	0.00	0.00	0.10	0.75	0.61	0.52	0.15	0.61	0.19
Cd	0.04	0.00	0.00	0.00	0.49	0.65	0.47	0.45	0.40	0.37	0.15
Fe	0.04	0.00	0.00	0.00	0.10	0.17	0.25	0.13	0.08	0.27	0.07
Mn	0.08	0.00	0.00	0.00	0.43	0.82	0.83	0.31	0.42	1.12	0.38

TABLE 7

"Competition ratio" among carbonate, reducible and organic pools for heavy metals in sediments

Metal	Site										
	B*1*	B*2*	*3*	*8*	*20*	*30*	*39*	*47*	*52*	*62*	*64*
(a) "Competition ratio" between carbonate and reducible pools:											
Zn	0.315	1.51	9.47	9.82	8.71	8.95	1.66	1.94	6.87	6.35	8.48
Pb	0.252	1.07	5.25	6.76	5.72	11.50	1.40	3.78	7.69	4.51	7.94
Cu	0.4	0.86	5.08	1.00	5.11	10.29	0.10	0.85	1.27	6.40	8.73
Cd	0.2	0.33	3.00	3.75	10.00	11.67	1.80	1.30	5.76	6.00	8.75
(b) "Competition ratio" between carbonate and organic pools:											
Zn	2.26	–	–	–	44.24	41.1	14.36	20.64	64.00	67.65	164.75
Pb	9.22	–	–	–	146.40	297.0	113.0	196.5	679.3	32.00	208.8
Cu	0.05	–	–	–	4.60	0.96	0.03	0.51	0.93	10.67	5.05
Cd	0.25	–	–	–	0.41	0.54	0.19	0.39	0.48	0.81	2.33
Fe	152.25	–	–	–	152.25	94.70	12.36	65.69	516.88	136.30	625.29
Mn	88.00	–	–	–	20.16	20.55	2.51	22.19	37.54	10.88	45.16
(c) "Competition ratio" between reducible and organic pools:											
Zn	7.19	–	–	–	5.44	4.59	8.62	11.06	9.32	10.65	19.43
Pb	36.56	–	–	–	25.6	25.56	80.6	52.00	88.33	7.09	26.31
Cu	0.12	–	–	–	0.90	0.09	0.34	0.25	0.73	1.67	0.58
Cd	0.63	–	–	–	0.05	0.04	0.06	0.22	0.08	0.05	0.11

– = not determined.

ing of Cd among the major pools, can be expressed as carbonates > organics > reducible pool.

4.6.4. Copper. A sizeable fraction of Cu is restricted to the lithogenic pool, amounting to 60% of the total Cu. In the background samples ~32% (calculated average) of this metal is associated with the organics and < 10% with the carbonates. However, the carbonates which are remarkably devoid of concentration of this metal in background samples become the most significant pool in the downstream contaminated region and apparently a 5–6 order of increase in this metal is noticed. While the SC of carbonates decreases with distance away from the source of contamination, that of multiple hydroxides remains almost constant throughout.

The CR computation reveals that the organic phase is the most effective scavenger in the sediments, although a major amount of the metal is associated with the carbonates, the most abundant pool of Tiri river sediments, which agrees with the observations of Paul and Pillai (1981) and Hickey and Kittrick (1984). The CR between carbonates and reducible pools also indicates that both pools compete equally for Cu. Hence the order of partitioning of Cu in Tiri river sediments is organics > carbonates = multiple hydroxides.

5. Discussion

It is apparent from the analytical data that there is considerable variation in concentrations of heavy metals within the stream sample population. However, there are a number of difficulties inherent in detailed interpretation, particularly with regard to the evaluation of concentration variation; but mining and related activities were clearly responsible for heavy-metal contamination of sediments and the aquatic environment. In the present paper a number of potential approaches for assessment of metal enrichments are attempted. The CI computation has brought out the cumulative enrichment of heavy metals and reflects the degree of enrichment of heavy metals in sediments with respect to background values. Input of natural water from the Daya river, Padla stream and other tributaries in the downstream area diluted the enhanced levels of the metals and hence the CI-values are also progressively decreased. Higher values of CI at some sample stations are considered to be due to various factors such as coprecipitation of metals with Fe-hydroxides (stations *27*, *28* and *34*) or larger concentration of organic matter (stations *45* and *47*), where activity of multiple hydroxides and carbonates seem to be insignificant.

The sediments are rich in dolomite and calcite, in which the major cations are Ca and Mg, and multiple hydroxides such as goethite, todorokite and nsutite with Fe and Mn as major cations. The above-mentioned minerals are the resultant of precipitation from the river water. While precipitation is the only source of multiple hydroxides in the river sediments, a significant amount of carbonates are detrital, derived from the country rocks and play a minor role in heavy-metal attenuation. Analysis of the metal correlation matrix (Table 2) has enabled to speculate about the mechanism behind the heavy-metal transfer. A stronger positive correlation of heavy metals with Fe and Mn in comparison to Ca and Mg indicates that the multiple hydroxides have preferential heavy-metal coprecipitation.

Zn, Pb, Cd, Fe and Mn are strongly correlatable among each other and are grouped in Factor I, indicating their source to be common. Probably the association is derived from tailing disposal and the metals were precipitated on the sediment substrate simultaneously. Thus the Factor-I loading map (Fig. 2) shows higher factor scores near the input points and the values progressively lowered downstream the river due to sediment dilution.

Factor II shows a strong loading on Ca–Mg–Cu, indicating the association of Cu with Ca and Mg (which are mostly in the form of carbonates) and the higher values of Factor II are distributed randomly (in contrast, Factor-I scores confined to the input points), that is evident in Fig. 3; hence is believed to be controlled by the gross lithology of the bedrock. Ca–Mg and Fe–Mn represent the major elements of the two above discussed groups of precipitation. Cu is poorly correlatable with Ca–Mg and not correlatable with Fe–Mn. Hence it is also believed that a third phase, organic matter, is responsible for Cu accumulation. Subsequent studies have confirmed the association of Cu with organics.

The technique of sequential chemical extraction has been applied extensively in environmental studies. Although their ability of separating heavy metals into geochemically well-defined fractions is far from perfect, nevertheless it is helpful to understand the chemical behaviour and bioavailability of metals in sediments. Minor problems arising in case of carbonate dissolution are already discussed with the results.

The results of sequential extraction do not unambiguously denote a specific mechanism behind the transfer of Cd, Cu, Pb and Zn to carbonates, multiple hydroxides and organics. Considering the presence of these elements in the five extracts of dissolution treatments, some circumstantial remarks can however be made. Cd, Pb and Zn are primarily incorporated in the carbonates of the contaminated sediments. The high percentage of Cd leached with carbonate phase is not surprising, since Cd and Ca have similar crystal ionic radii and Cd^{2+} can substitute Ca^{2+} (Span and Gaillard, 1986). Zn and Pb are also more strongly, and Cu to a limited extent, associated with the "operationally defined" carbonate phase. This is as expected from possible solubility controls of the metals where pH of the solid–water interface is found to be > 7.0 (Lindsay, 1979). Span and Gaillard (1986) also opined that in the carbonate bedrock environment with slightly alkaline pH, the heavy metals are readily attenuated to the carbonates of the sediments.

Multiple hydroxides constitute the most significant sink for heavy metals in the oxidising environment (Benjamin and Leckie, 1981), which is demonstrated in the relatively uncontaminated part of the river (pH of the water is 6.3–6.7). With the input of alkaline tailing water, the pH of the river water is increased to the range of 6.7–7.2 and consequently the metal incorporation in the multiple hydroxides also decreased. However, this phase is the largest scavenger for Pb and Cd next only to carbonates.

Organic matter normally plays a dominant role in distribution and dispersion of heavy metals in the secondary environment (Salomons and Förstner, 1984). However, in the contaminated sediments of the Tiri river none of the heavy metals except Cu is significantly accumulated in the organic fraction. The lower degree of accumulation of heavy metals with organics may be due to the fact that organo-complexing is a slow process (Paul and Pillai, 1983) and the samples are from the near-surface sediment–water interface. Moreover, competition from freshly precipitated carbonates and hydrous oxides has restricted its metal intake capacity. However, the often proposed close association of Cu and organic matter holds good in Tiri sediments. This is not surprising in light of the very high values of the formation constants of Cu-organic complexation (Tessier et al., 1980; Stumm and Morgan, 1981).

A noteworthy observation in the present fractionation study is the significant accumulation of Cd in the exchangeable phase while the other metals have only meagre adsorption. Harrison et al. (1981) and Hickey and Kittrick (1984) suggested that the mobility and bioavailability of metals decrease approximately in the order of extraction sequence. Our extraction sequence follows the order of decreasing solubility of geochemical fractions (Stover et al., 1976). Thus Cd may be considered to be the most mobile and bioavailable element in the sediment samples and the mobility sequence is proposed as Cd > Zn > Pb > Cu > Fe > Mn.

6. Conclusions

Drainage water from polymetallic sulphide deposits and mine tailing add a large amount of heavy metals into water and sediments of the Tiri river flowing past the mineralised zone of Zawar, Rajasthan. A significant amount of hydrous oxides of Fe and Mn (todorokite, goethite, birnessite, maghemite and nsutite), and carbonates are precipitated on the river bed due to influx of acid mine water and mine tailings. These precipitates are mainly responsible for enrichment of heavy metals in the sediments.

The non-lithogenic metal concentrations in the stream sediments are highly variable. Dispersion of heavy metals in sediments is closely related to the distribution of carbonates, multiple hydroxides and organics, and adsorption is found to be the most significant process of metal attenuation. The metal concentrations at all the sample points are much higher than the background and the "contamination index" values showed a marked concentration gradient. Local anomalies in the trend are observed at certain points along the channel, where heavy metals are coprecipitated with Fe-hydroxides or by incorporation in organic matter.

The coprecipitation of toxic metals with multiple hydroxides is clearly indicated from correlation matrix and *R*-mode factor analyses of sediment–metal data. Strong association of Cu with the carbonate pool is also evident from the same statistical analyses. In the polluted segments, competition from chemically reactive carbonates reduces the effectiveness of organic matter. The significant inferences drawn from metal partitioning studies are: (1) the partitioning signatures of the non-lithogenic heavy metals are different in polluted and non-polluted samples; and (2) carbonates are the most dominant sinks for heavy metals in the polluted sediments.

A major fraction of Cd is found in exchangeable form which is most mobile and easily bioavailable. With the exception of Cd and to some extent Zn the enrichment of other metals in the exchangeable pool is meagre. Cu and Zn are the only metals to have evidence of significant association with organic phase.

With the assumption that mobility and bioavailability of the metal decrease with the extraction sequence followed in this work, the apparent mobility and potential bioavailability of the metals are in the order of Cd > Pb > Zn > Cu > Fe > Mn.

Acknowledgements

This work is a part of Ph.D. thesis of the first author (B.G.P.) carried out at the Indian Institute of Technology, Bombay. The help rendered by Sri P.G. Sekar and Sri A.S. Murty in preparation of the paper is acknowledged. One of us (B.G.P.) acknowledges the Director, Defence Terrain Research Laboratory, Delhi, for granting permission to publish the work.

References

Aston, S.R., Thornton, I., Webb, J.S. and Purves, J.B., 1974. Stream sediment composition, an aid to water quality assessment. Water, Air, Soil Pollut., 3: 321–325.

Benjamin, M.M. and Leckie, J.O., 1981. Conceptual model for metal ligand–surface interaction during adsorption. Environ. Sci. Technol., 15: 1050–1056.

Elsokkary, I.H. and Lag, J., 1978. Distribution of different fractions of Cd, Pb, Zn and Cu in industrially polluted and non-polluted soils of Odda region, Norway. Acta Agric. Scand., 28: 262–268.

Förstner, U., 1976. Lake sediments as indicators of heavy metal pollut. Naturwissenschaften, 63: 465–470.

Förstner, U. and Wittmann, G.T.W., 1979. Metal Pollution in Aquatic Environment. Springer, Berlin, 486 pp.

Gupta, S.K. and Chen, K.Y., 1975. Partitioning of trace metals in selected chemical fractions on nearshore sediments. Environ. Lett., 10: 129–158.

Haque, M.A., 1987. Contamination of soil, water and vegetation by Cu, Pb and Zn ore mining and smelting at Khetri and Zawar (India). J. Geol. Soc. India, 30: 451–458.

Harrison, R.M.D., Laxen, P.H. and Wilson, S.J., 1981. Chemical association of Pb, Cd, Cu and Zn in street dust and road side soils. Environ. Sci. Technol., 15: 1378–1383.

Hickey, M.G. and Kittrick, J.A., 1984. Chemical partitioning of Cd, Cu, Ni and Zn in soils and sediments containing high level of heavy metals. J. Environ. Qual., 13: 372–376.

Kuo, S., Heilman, P.E. and Baker, A.S., 1983. Distribution and forms of Cu, Zn, Cd, Fe and Mn in soils near a Cu-smelter. Soil Sci., 135: 101–109.

Lindsay, W.L., 1979. Chemical Equilibria in Soils. Wiley, New York, N.Y.

McLaren, R.G. and Crawford, D.V., 1973. Studies on soil Cu, 1. The fractionation of Cu in soils. J. Soil Sci., 24: 172–181.

Paul, A.C. and Pillai, K.C., 1983. Trace metals in a tropical river environment — speciation and biological transfer. Water, Air, Soil Pollut., 19: 75–86.

Pillai, T.N.V., Desai, M.V.M., Mathew, E., Ganapathy, S. and Ganguly, A.K., 1971. Organic materials in the marine environment and the associated metallic elements. Curr. Sci., 40: 75–81.

Presley, J.B., Kolodny, Y., Nissenbaum, A. and Kaplan, I.R., 1972. Early diagenesis in a reducing fjord, Saanich Inlet, British Columbia, II. Trace element distribution in interstitial water and sediments. Geochim. Cosmochim Acta, 36: 1073–1090.

Prusty, B.G., 1988. Dispersion of heavy metals along Tiri river due to mining and milling activities at Zawar, Rajasthan. Ph.D. Thesis, Department of Earth Sciences, Indian Institute of Technology, Bombay (unpublished).

Prusty, B.G., Godgul, G. and Sahu, K.C., 1987. Partitioning of heavy metals in polluted Tiri river sediments due to tailing discharges from Zawar mines, Rajasthan, India. In: K.C. Sahu (Editor), Role of Earth Sciences in Environment. Indian Inst. Technol., Bombay, pp. 215–229.

Rang, M.C., Kleijn, C.E. and Schouten, C.J., 1987. Mapping of soil pollution by application of classical geomorphological and pedological field techniques. In: V. Gardiner (Editor), International Geomorphology, Part 1. Wiley, New York, N.Y., pp. 1029–1044.

Robinson, G.D., 1985. Enhancement of subtle geochemical anomalies by selective chemical extractions of metal from pebble coatings. Chem. Geol., 53: 37–51.

Salomons, W. and Förstner, U., 1984. Metals in Hydrocycles. Springer, Berlin, 349 pp.

Shapiro, D.L. and Brannock, W.W., 1962. Rapid analysis of silicates, carbonates and phosphate rocks. U.S. Geol. Surv., Bull., 1144-A.

Span, D. and Gaillard, J.F., 1986. An investigation of a procedure for determining carbonate-bound trace metals. Chem. Geol., 56: 135–141.

Stover, R.C., Sommers, L.E. and Silviera, D.J., 1976. Evaluation of metals in wastewater sludge. J. Water Pollut. Control Fed., 48: 2165–2175.

Strickland, J. and Parsons, T.R., 1965. A manual of sea water analysis. Fish. Res. Board Can. Bull., 125 pp.

Stumm, W. and Morgan, J.J., 1981. Aquatic Chemistry — An Introduction Emphasising Chemical Equilibria in Natural Water. Wiley, New York, N.Y., 2nd ed., 780 pp.

Tessier, A., Campbell, P.G.C. and Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metal. Anal. Chem., 51: 844–850.

Tessier, A., Campbell, P.G.C. and Bisson, M., 1980. Trace metal speciation in the Yamaska and St. Francois River (Quebec). Can. J. Earth Sci., 17: 90–105.

Thornton, I. and Webb, J.S., 1975. Trace elements in soils and surface waters contaminated by past metalliferous milling in parts of England. In: B.B. Hemphill (Editor), Trace Substances in Environmental Health, Vol. IX. Columbia, Mo., pp. 77–88.

Thornton, I., Watling, H. and Darracot, A., 1979. Geochemical studies in several rivers and estuaries used for oyster rearing. Sci. Total Environ., 4: 325–345.

Trefry, J.H. and Meiz, S., 1984. Selective leaching of trace metals from sediments as function of pH. Anal. Chem., 56: 745–749.

Vivian, C.M.G. and Massie, K.S., 1977. Trace metals in water and sediments of the river Tawe, South Wales, in relation to local sources. Environ. Pollut., 14: 47–61.