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Use of sequential leaching, mineralogy, morphology and multivariate statistical technique for quantifying metal pollution in highly polluted aquatic sediments—A case study: Brahmani and Nandira Rivers, India

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ABSTRACT

The particle size distribution, geochemical composition and sequential leaching of metals (Fe, Mn, Ni, Cu, Co, Cr, Pb, Zn and Cd) are carried out in core sediments (<88 μm) from the Brahmani and Nandira Rivers, India. To confirm the contamination of downstream sediments by fly ash, mineralogical and morphological characterizations were carried out. High environmental risk of Co, Pb and Ni is due to their higher availability in exchangeable fraction. The metals like Zn, Cu and Mn represent an appreciable portion in the carbonate phase. Metals such as Zn, Pb, Cd, Co and Ni are associated with reducible phase may be due to adsorption. The organic bound Cu, Zn, and Pb seem to be second dominant fraction among non-lithogenous in Nandira sediments. Factor analysis data reveals that textural parameters, Fe–Mn oxy/hydroxides, organic precipitation and coal fly ash disposals, are individually responsible for the enrichment of heavy metals. The relationships among the stations are highlighted by cluster analysis to identify the contamination levels.

1. Introduction

Sediments transported by rivers, by and large, are the erosional products of the rock types exposed in the basin. River sediments provide a major sink for heavy metals in the aquatic environment by various physico-chemical processes such as precipitation, adsorption and chelation. The contribution of heavy metals depends on a variety of factors such as basin geology, physiography, chemical reactivity, lithology, mineralogy, hydrology, vegetation, land-use pattern and biological productivity. Besides the natural processes, additional influx of the solid wastes into the river sediments from the industrial activities and mining practices causes enrichment of heavy metals. The amount of influx of the waste material into the river system varies depending upon the intensity of these activities. Determination of total metal content in sediments provides important information about pollution level if the background concentration is known. However, to understand the mobilization of heavy metals and assess the bioavailability, the total concentration is not enough [1]. Therefore, it is vital to perform chemical partitioning studies of heavy metals in the sediments to accurately assess the toxic potential. The rivers Brahmani and Nandira, not only obtain sediments from natural sources but also receive enormous amounts of solid wastes from industrial activities in Angul-Talcher area, Orissa. Hence, an attempt has been made to study the heavy metals in the sediments of these rivers.

In India about 65% of total electricity is generated through the use of coal as fuel. Indian coal contains up to 55% ash and its combustion results in large amount of residual coal fly ash [2]. Presently about 110 million tones of coal-ash is generated in India [3] and by the year 2012 this is predicted to increase to 170 million tons per annum [4]. The physical and chemical properties of this industrial waste in general are quite variable as they are influenced by coal source, particle size, type of coal burning processes and degree of weathering. Coal fly ash is a mixture of metallic oxides, silicates and other inorganic particulate matter along with unburnt carbon. Apart from this, it also contains many trace metals. The leachability of these trace metals to surface waters is quite important. Trace metals, though present as a relatively small fraction in coal fly ash are of special interest due to their cumulative build up, long life, high toxicity to man, plants and animals through air, water and soil intake [5]. Ash contamination poses a serious threat to

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environment. Untrapped and air borne coal fly ash can get deposited over a vast surface of land water basins damaging and intoxicating the flora as well as contaminating the aquatic systems [6]. Since the rivers of our study area are carrying a substantial amount of coal fly ash from the thermal plants, the study has been extended to estimate the contribution of trace metals due to contamination of the same.

The risk assessment code (RAC) demonstrates that the metals in sediments are bound with different strengths to different fractions. The RAC assesses the availability of metals in solution by applying a scale to the percentage of sediments that can reduce metals in the exchangeable and carbonate fractions. With the aim of achieving a broder assessment of Brahmani and Nandira metal pollution in terms of ecological risk, a quantitative approach has been made.

2. Background

2.1. Geographical settings

The area under study is bound by 20°49′ and 21°6′N latitudes and 85°5′ and 85°26′E longitudes (Fig. 1). The river Brahmani along with its tributaries forms the major drainage in the area. This basin lies in an Indian shield, which constitutes pre-cambrian rocks such as granites, granite gneisses, quatzites, schists, amphibolites, pegmatites, khondalites and charnockites and gondwana rocks like shale, sandstone and coal, specifically in and around Talcher. The soil of the area varies from rich red loamy to gravelly detritus with a small patch of laterite. The elevation of the land surface ranges from 60 to 200 m above mean sea level [7]. The area enjoys a subtropical monsoon climate with an average annual rainfall of 1421 mm. The temperature varies from 6 to 46° C [8].

2.2. Anthropogenic setup of the basin

Availability of raw materials, perennial water supply from Brahmani–Nandira, ease of transport and free market conditions led to rapid growth of industrialisation in the study area. Intensive industrialisation and mining activity in the industrial belt of Angul-Talcher leading to solid and liquid waste disposal have created environmental problems pertaining to heavy metal contamination of Nandira River and ultimately that of Brahmani. The area is quickly emerging as a big source of coal and thermal power in the country. The major industries existing in the area include three power plants; Talcher Thermal Power Station (TTPS), National Thermal Power Corporation (NTPC), NALCO Captive Power Plant (CPP); a Fertilizer plant (FCI); NALCO smelter; and a Chemical plant (Orichem). In addition, coal mines and other mining activities are also predominant. Besides, there are 35 small-scale industries near existing major industries. The major plants along with their products, raw materials used and potential of liquid waste generated and volume coal fly ash generated are given in Table 1 [9].

The indiscriminate disposal of effluents due to industrial activities has completely unbalanced the pristine river environment, which has been silted due to large deposits of suspended solids.

2.3. Literature review

There are reports on coal fly ash characterization [2] of dissolved and particulate heavy metals in water [10] and fluoride in groundwater [8] and trace element distribution of river sediments of Orissa including the Brahmani River [7]. No study has been carried out so far to assess the behaviour and characteristics of heavy metals in the sediments of the Brahmani and Nandira Rivers using mineralogical, morphological, sequential leaching technique as well as statistical interpretation. The quantification of metal pollution through different indices like enrichment ratio, geo-accumulation index and pollution load index were determined in Brahmani and Nandira sediments Rath et al. [11]. But in the present study geochemical fractionation of metals in the said river sediments was determined and their potential ecological risk to the aquatic system was assessed using risk assessment code. RAC is a technique to evaluate metal bioavailability in aquatic system on a semi quantitative approach. A comparative chart is given in Table 2 [12–14,1,15–17] for the different methods adopted for quantifying metal pollution by different authors.

2.4. Objectives

The objectives of the study are to establish the provenance, distribution pattern of major and minor elements, association of metals in different geochemical phases, mineralogical and morphological characteristics of sediments and coal fly ash for identifying the sources. Further, the multivariate approach (factor and cluster) has been applied to understand the geochemical processes and to evaluate the responses occurring in the environment.

3. Materials and methods

3.1. Sample collection and analytical methods

The monitoring network and sampling strategy were designed to cover a wide range of determinants at key sites, which reasonably represent the sediment quality of the river systems accounting for tributary and inputs from industrial drains that have impact on downstream sediment quality. Under the sediment quality-monitoring Programme of the Brahmani River, samples from thirteen locations of Brahmani River (B1–B6) and Nandira River (N1–N7) were collected as shown in Fig. 1. Samples were collected at 0–20 cm depths manually by inserting a PVC tube (5 cm diameter) into the riverbed and removing it slowly. The core sediments were divided into 0–10 cm and 10–20 cm depth intervals for analysis. The sediment samples were homogenized and air-dried at room temperature. A portion of the sample was taken for textural analysis (Sand, Silt and Clay percentages).

Concentrations of metals like Al, Ti, Fe, Mn, Co, Cu, Cr, Ni, Pb, Zn, Cd and Hg were analyzed in bulk sediments. Powdered samples were digested in triplicate, in 100 ml Teflon beakers followed by addition of 2 ml $HClO_4$, 12 ml HF and 8 ml HNO_3. The concentration of metals was determined by AAS (Varian, Model Spectra 20+) in flame mode and that of Hg was determined in flameless mode with background correction. For Hg, sediments were digested for 2 h with aquaregia (HNO_3:3HCl) to which 5% $KMnO_4$ and potassium persulphate solutions were added [18]. All the samples were analyzed in triplicate with blanks similarly treated for metal analysis. The precision and accuracy of the methods were systematically and routinely checked by analyzing USGS reference samples like GXR (soil), where the precision (coefficient of variation of five replicate analysis) was 3% for Cu, Cr and Fe and 4% for Pb, Cd, Co, Ni, Mn and Zn.

Trace metals (Fe, Mn, Co, Cu, Cr, Ni, Pb, Zn, Cd) were sequentially extracted from <88 μm (-200ASTM) fraction of sediments of Brahmani and Nandira Rivers following the method proposed by Tessier et al. [19] into five phases operationally defined as exchangeable (F_1), carbonate (F_2), Fe–Mn hydroxide (F_3), organic (F_4) and residual (F_5). The <88 μm fraction contains fine sand, silt, and clay which are

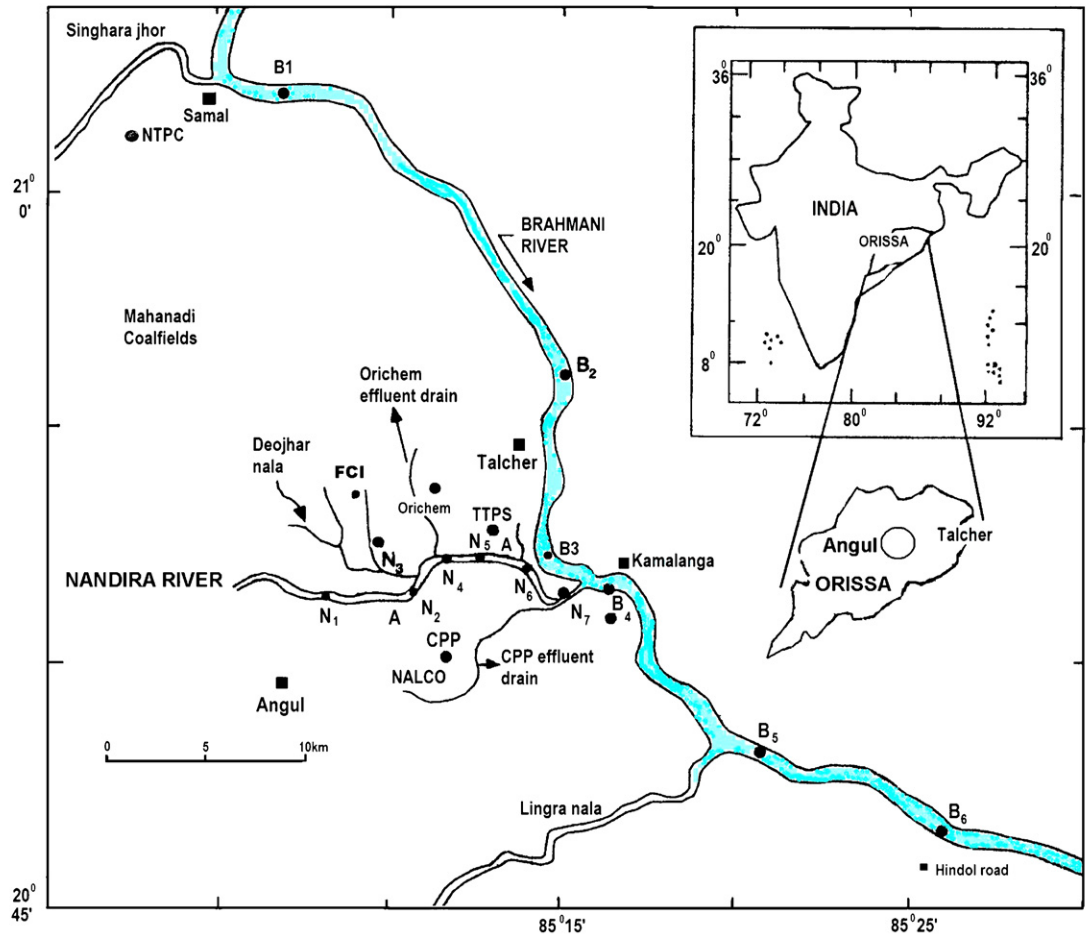

Fig. 1. Map showing sampling locations.

highly responsible for retaining heavy metals in aquatic sediments [20,21]. The detailed scheme is as follows:

1. Exchangeable fraction (1 M $MgCl_2$, pH 7.0).
2. Carbonate bound fraction (1 M NaOAc adjusted to pH 5.0 with acetic acid.
3. Fe–Mn oxide bound fraction (reducible phase) (0.04 M $NH_2OH{\cdot}HCl$ in 25% (v/v) HOAc at 96 °C).
4. Organic bound (oxidized phase) (5 ml of 30% H_2O_2 and 0.02 M HNO_3 3 ml of 30% H_2O_2 at 85 °C).
5. Residual fraction (total digestion with a concentrated mixture of $HNO_3/HClO_4/HF$).

Table 1

The details of major plants along with their products, raw materials used and potential of solid/liquid waste generated (Source: Orissa Pollution Control Board)

Plant	Product	Raw materials used	Water consumption (m^3/day)	Waste water generated (m^3/day)	Volume of coal fly ash generated (tons/day)
FCI, Talcher	1. Urea, 2. Ammonia	Coal Lime stone Methanol Alum Sulphuric acid Caustic soda Hydrated lime	44,882	17,224	720
NALCO, CPP	840 MW	Coal Fuel oil	91,067	74,094	6,048
TTPS, Talcher	500 MW	Coal Fuel oil Lime	32,840	25,980	3,427
Orichem Ltd., Talcher	1. Sodium dichromate, 2. Chromic acid, 3.Yellow sodium sulphate	Ash Chrome ore Lime stone Sulphuric acid Coal Fuel oil	140	40	–

Table 2
A comparative statement of different methods used for determination of metal toxicity level in assessing environmental risk and their consequences

Sl. no.	Method adoption	Environmental consequences
1	Enrichment ratio (ER) = (Metal/'Al' or 'Fe') sample/(Metal/'Al' or 'Fe') Earth's crust (Sinex and Helz [12])	Enrichment of metal with respect to background, country/world average), where ER >1 is enrichment
2	Geo-accumulation index (I geo) = $\log_2 \{C_n/1.5B_n\}$ where C_n = concentration of element 'n' B_n = geological background metal concentration of source rock average in precivilised period (Muller [13])	Quantification of metal accumulation which compare the present status with precivilised background value I geo >0 is polluted
3	Pollution load index (PLI) = $[\mathrm{Cf}_1 \times \mathrm{Cf}_2 \ldots x\ \mathrm{Cf}_j x \ldots \mathrm{Cf}_n]^{1/n}$ where Cf_j = contamination factor of metal 'j' with respect to world rock average, n = number of metal (Tomlinson et al. [14])	Pollution status of a site or region considering all metal concentrations PLI >1 is polluted
4	Alumino-sillicate normalization factor = metal/aluminum concentration (Salmons and Forstner [1])	It is useful in environmental studies concerning the determination of human contribution in metal enrichment in aquatic sediments
5	Bio concentration factor (BCF) = metal concentration in benthos as bioindicator/bioavalibility metal in sediments, i.e. in exchangeable fraction (Soto-Jimenez and Paez-Osuna [15])	Metal bioavalibilty in normal pH condition, high environmental risk determination
6	Bio production index (BPI) = $\Sigma E_r = \Sigma \mathrm{Tr}_i \times \mathrm{Cf}_i$ E_r = potential ecological risk, Tr_i = the toxic response factor for a given metal Cf_i = contamination factor (a ratio between pre-industrial record and present metal concentration value) (Hakanson [16])	This is based on the assumption that the sensitivity of the aquatic system depend oh its productivity. BPI < 150 = low ecological risk 150 < BPI < 600 = moderate ecological risk BPI > 600 = very high ecological risk
7	Risk assessment code (RAC) = metal concentration in (exchangeable + carbonate) phase (Perin et al. [17]), *Present method*	Quantification of metal bioavalibility

Metal concentrations such as Fe, Mn, Co, Cu, Cr, Ni, Pb, Zn and Cd in each leachets were analyzed using AAS. The precision and accuracy of the methods were systematically and routinely checked as per the procedure followed in metal analysis of bulk samples.

The estimation of organic matters and $CaCO_3$ were carried out adopting Walkley and Black [22] and Hutchinson and Mclennan [23] methods, respectively. For determination of total phosphorous, the samples were digested following procedure recommended by Rochford [24] and estimated by single solution method [25]. The analytical data quality was ensured through careful standardization, procedural blank measurements, spiked and triplicate samples.

3.2. Data treatment and multivariate statistical methods

Multivariate analysis of the river sediment quality data set was performed through cluster and factor analysis techniques [26–28]. The above statistical analyses were applied on experimental data standardized through z-scale transformation in order to avoid miss classification due to wide differences in data dimensionality [29]. Further more, the standardization procedure eliminates the influence of different units of measurements and renders the data dimensionless.

Varimax roated factor analysis was performed on correlation matrix of rearranged data for two different rivers. The variance/covariance and factor loadings of the variables with eigen values were computed. The data on heavy metal concentration, grain size fraction along with organic matter, $CaCO_3$ and total phosphorous in sediments of the study area was processed using SPSS-10.0 statistical software. Rotation of the axis defined by factor analysis produced a new set of factors, each one involving primarily a sub-set of the original variables with a little overlap as possible, so that the original variables were divided into groups. The factor analysis of the present data set further sorted by the contribution of less significant variables (<0.4 factor score). A varimax rotation (raw) of the different varifactors of eigen value greater than 1, were further cleaned up by this technique and in varifactors original variables participated more clearly. Liu et al. [29] classified the factor loading as “strong”, “moderate” and “weak” corresponding to absolute loading values of >0.75, 0.75–0.50 and 0.50–0.40, respectively.

Factor and cluster analyses were combined to assess the degree of contamination, determination of chemical processes and to trace the diffusion paths. Hierachial agglomerative clustering was performed on data normalized to zero mean and unit variance using squared Euclidean distances as the measure of similarity [30]. Wards method was selected because it possesses a small space distorting effect, uses more information on cluster contents than other methods [31] and has been proven to be an extremely powerful grouping mechanism [32].

4. Results and discussion

4.1. Metals in sediments

The heavy metal concentrations in sediments of different locations are given in Table 3. It shows that the sediments contain appreciable amounts of metals, their range of concentrations (μg/g) are: Al (20,500–92,400), Fe (8400–36,500), Ti (1800–8400), Mn (115–1272), Cu (4.4–36.9), Ni (10.6–94.4), Co (8.1–41.1), Pb (2.4–24.7), Zn (9.1–75.6), Cr (48.2–360.9), Cd (0.62–3.32) and Hg (0.03–2.62) for both layers of the sediments.

While comparing concentrations of metals in the top (0–10 cm) and bottom sediments (10–20 cm), it is found that in most of the stations Ni, Cd, Hg, Cu, Co, Pb and Zn for Nandira and Cr, Mn, Cu, Ni, Pb and Zn for Brahmani River are bottom enriched. On the other hand, the rest of the metals do not show any specific layer enrichment. The total average metal concentrations except Cd in Nandira sediments are much higher than that of the Brahmani. Linear regression analysis was carried out between fine sediment fractions with metal content along with organic matter and total phosphorous (Fig. 2). It is observed that organic matter is having a good correlation ship with finer fraction (R^2 = 0.871) of the sediment. The metals like Pb, Cd, Cr, Hg, Cu, Zn, and Co having R^2 values (0.324–0.575) showed moderate positive relationship with the finer fractions.

The average chemical composition of the surface sediments of Nandira and Brahmani Rivers is compared with Indian River average, World average, as well as the surface sediments of other rivers flowing in the Indian sub-continent (Table 4). Nandira sediments have 218% more Zn, 142% more Cr, 86% more Ni, 38% more Mn than the Indian River average, reflecting high anthropogenic contribution by industrial activity.

4.2. Metals in coal fly ash

Chemical composition as well as textural analysis of pond ash and coal fly ash from ESPs (electrostatic precipitators) has been

Table 3
Distribution of heavy metals (μg/g) in the sediments of Nandira and Brahmani Rivers

Stations	Al	Fe	Ti	Mn	Cu	Ni	Co	Pb	Zn	Cr	Cd	Hg
N1T	30,100	19,000	2,700	216	10.2	31.9	20.2	8.9	12.6	63.3	0.62	0.29
N2T	37,900	29,500	3,400	783	14.2	30.3	29.4	9.7	18.8	140.3	0.64	0.18
N3T	43,700	22,600	6,400	629	11.8	47.3	21.7	12.6	54.1	143.1	0.69	0.19
N4T	56,200	34,800	7,600	1,272	18.2	72.9	29.9	12.9	75.6	360.4	2.27	0.44
N5T	52,300	21,000	3,500	1,029	14.5	77.1	23.8	10.6	67.5	264.8	1.45	0.43
N6T	74,400	36,500	7,400	1,173	17.0	65.5	24.0	12.0	56.4	196.5	1.94	1.92
N7T	54,300	28,300	4,100	807	22.8	62.9	28.2	23.3	72.5	330.4	2.57	2.01
Average	49,843	27,386	5,014	844	15.5	55.4	25.3	12.9	51.1	214.1	1.45	0.78
N1B	45,000	21,000	4,600	355	13.7	20.4	12.3	8.4	14.4	48.2	0.94	0.13
N2B	40,900	30,600	5,500	823	12.3	34.5	30.5	10.5	22.5	133.4	0.66	0.20
N3B	49,400	23,400	4,300	678	14.0	48.3	25.3	13.2	65.2	160.7	1.40	0.26
N4B	40,000	30,900	3,200	1,213	10.9	87.0	21.2	9.8	62.2	256.4	2.26	0.52
N5B	50,400	17,600	5,600	744	17.5	93.7	26.7	14.0	65.2	316.6	1.70	0.45
N6B	60,200	36,400	6,600	959	17.2	66.4	26.5	14.3	60.2	180.3	2.19	2.25
N7B	67,500	32,200	8,400	1,054	34.9	94.4	41.1	24.7	75.2	360.9	3.32	2.62
Average	50,486	27,443	5,457	832	17.2	63.5	26.2	13.6	52.1	208.1	1.78	0.92
B1T	47,600	17,800	3,000	192	6.6	14.1	9.1	2.4	10.9	51.6	1.86	0.06
B2T	41,800	8,400	2,200	184	6.2	10.6	13.9	8.8	9.3	53.8	2.08	0.07
B3T	43,200	12,600	3,100	159	14.9	17.9	18.7	8.1	11.3	62.4	1.25	0.07
B4T	84,600	28,700	2,600	345	24.3	72.4	19.1	18.8	46.5	147.6	2.66	0.44
B5T	25,200	12,600	3,000	205	4.4	32.7	8.7	16.1	19.8	93.3	2.60	0.16
B6T	21,600	28,100	4,700	185	17.1	21.3	21.3	13.2	20.2	47.0	1.97	0.09
Average	44,000	18,033	3,100	212	12.3	28.2	15.1	11.2	19.7	76.0	2.07	0.15
B1B	30,800	18,500	3,000	208	7.8	12.1	11.4	6.0	9.1	65.6	2.00	0.03
B2B	81,000	12,200	1,800	196	11.5	13.3	13.7	10.7	10.2	54.5	1.44	0.09
B3B	37,000	12,400	3,500	208	16.2	19.2	14.3	9.1	27.2	67.5	1.95	0.12
B4B	92,400	29,400	5,400	416	36.9	75.5	20.0	20.0	48.4	150.6	2.58	0.28
B5B	20,500	10,600	2,900	240	14.1	34.2	17.4	10.6	24.4	95.8	1.77	0.18
B6B	27,700	17,400	3,800	115	7.2	23.9	12.9	12.3	19.8	52.1	2.13	0.07
Average	48,233	16,750	3,400	231	15.6	29.7	15.0	11.5	23.2	81.0	1.98	0.13

Note: T; top, B; bottom.

carried out for both the thermal plants in the study area as heavy metal contamination occurs in the sediments of the Brahmani and Nandira Rivers due to anthropogenic activities. Pond ash collected from ash ponds and ESP coal fly ash of both the Thermal plants have been analyzed for concentrations of heavy metals like: Fe, Mn, Co, Ni, Cu, Zn, Cr, Pb, Cd, Hg and the data is incorporated in Table 5. Metal concentrations (except Fe and Mn) in TTPS pond ash as well as ESP coal fly ash are comparatively higher than that of NALCO. After mixing of TTPS coal fly ash, the concentrations of Pb, Cu, Ni, Zn and Cd increase significantly in comparison to upstream stations. This implies that most of the metals of Nandira sediments are contributed by coal fly ash of thermal plants. A comparison of the present study with the reported Indian average [33] has been provided in Table 5. The comparison readily shows that the concentrations of Mn, Co, Pb and Cr in the ESP coal fly ash of study area are higher than Indian average.

Table 4
Comparison of average metal composition (μg/g) of the Brahmani and Nandira River bed sediments with others of India and World in addition Indian average, World average and source rock average

River	Al	Fe	Ti	Mn	Cu	Ni	Co	Pb	Zn	Cr	Cd	Hg
Ganga [49]	46,600	21,600	3000.00	400	21	20	–	25	46	52	–	–
Godavari [50]	47,800	60,300	8000.00	1,060	73	52	–	13	53	126	–	–
Krishna [49]	33,800	42,300	5300.00	1,040	49	30	–	9	31	68	–	–
Cavery [51]	48,700	17,600	3000.00	319	12	30	–	10	26	129	–	–
Mahanadi [52]	62,200	56,100	–	2,020	57	9	–	60	125	15	–	–
Gomati [49]	44,300	21,600	–	554	104	–	–	–	–	–	–	–
Narmada [53]	28,900	31,400	4,000	514	40	23	–	5	50	–	–	–
Tapti [53]	44,400	10,900	21,100	1,300	126	60	–	5	118	–	–	–
Damodar [54]	50,000	14,900	3,200	390	27	11	–	-	39	22	–	–
Illinois, USA [56]	–	–	–	–	19	–	–	28	81	–	2.00	-
Toyohira, Japan [57]	–	–	–	–	22	–	–	24	152	–	0.20	-
Genesse, USA [58]	–	–	–	–	18	–	–	40	69	–	–	–
Tigris, Turkey [59]	–	–	–	–	729	66.4	32	–	369	–	–	–
Brahmani	47,800	17,400	3,300	221	14	29	15	11	21	78	2.02	–
Nandira	50,200	27,400	5,200	838	16	59	26	13	52	211	1.54	–
Indian average [53]	50,000	29,000	3,500	605	28	37	31	11	16	87	–	–
World average [55]	94,000	48,000	4,200	1,050	100	90	20	150	350	100	1	–
Surf. Rock [55]	69,300	35,900	3,800	720	32	49	19	20	129	97	0.13	0.18

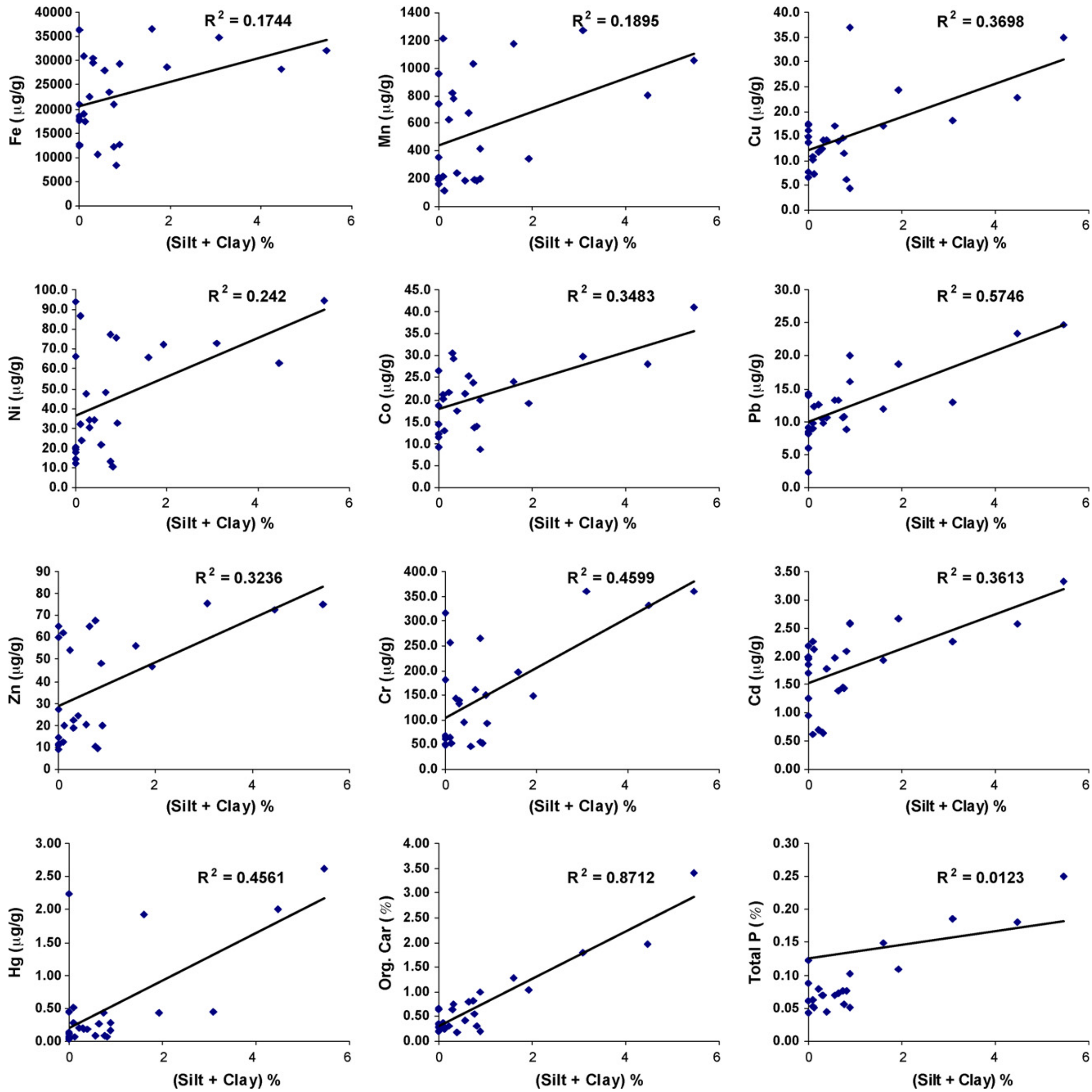

Fig. 2. Linear regression analysis of metal content verses finer fraction of the sediments.

4.3. Mineralogy and morphology of coal fly ash

It has been observed that concentration of heavy metals in sediment samples of Nandira downstream stations is quite high. As coal fly ash from ash pond overflow mixes with downstream stations, it is most probably the potential contributor of heavy metals into the sediments. To confirm the contamination of downstream sediments by coal fly ash, mineralogical and morphological characterization of Nandira and Brahmani sediments were carried out by X-RD and Optical microscopy, respectively. The pond ash of NALCO and TTPS contains quartz, mullite, magnetite and hematite as major mineral phases (Fig. 3a). The pond ash of the above two locations also contains cenospheres, opaque minerals and carbon particles. Morphological features of pond ash of NALCO and TTPS are given in Fig. 4(a and b). Mineralogically the sediments of downstream stations contain quartz, hematite, magnetite, iron, mullite and sillimanite as major mineral phases (Fig. 3b). The sediments contain cenospheres (Fig. 4c–e) and also mullite phases mostly coming from coal fly ash.

4.4. Textural characteristics

From the average value of different size fraction and weight percentages (Table 6) it is observed that medium sand (0.50–0.25 mm) dominates both the river sediments followed by coarse sand (1.00–0.50 mm). The upstream stations of Nandira and Brahmani River are courser and contain gravels. Clay content is very less (<1%) in all most all the sediment samples except N7, which is only 2.45%. More than 5% silt was found at stations N7 and B4. This may be due to mixing of finer fractions of coal fly ash samples.

Table 5
Metal concentrations (μg/g) in the fly ash samples (both pond ash and ESP ash) of two different thermal power plants (10 samples each)

Metals	NALCO						TTPS						Indian coal fly ash (average) [25]
	Pond ash			Coal fly ash			Pond ash			Coal fly ash			
	Minimum–maximum	Mean	Standard deviation	Minimum–maximum	Mean	Standard deviation	Minimum–maximum	Mean	Standard deviation	Minimum–maximum	Mean	Standard deviation	
Fe	32,000–38,000	36,000	2,514	30,145–33,789	31,658	1,261	19,000–22,000	21,000	1,546	23,245–25,789	24,721	1,652	NA
Mn	198–205	202	2.91	252–267	260.6	4.2	141–145	143	1.98	184–214	197.1	10.0	38.9
Cu	50–62	55	5.41	95.7–110.2	101.88	5.0	91–103	97	5.27	92.6–112	101.2	6.2	100
Ni	98–110	104	5.65	102.6–117.2	108.55	5.1	148–154	151.35	2.73	147.2–164.2	158.4	5.5	150
Co	18.7–24.2	21	2.45	35.9–39.1	37.43	1.2	31–37	33.98	3.05	44.6–48.7	46.5	1.4	23.6
Pb	80.7–95.2	86	6.53	91.3–97.5	94.48	1.7	101–112	106.3	5.55	96.3–112.4	104.4	5.4	35
Zn	150–160	156	4.54	155.4–164.1	161.05	2.7	171–175	173	2.05	192.4–206.4	200.9	4.5	NA
Cr	198–210	206	5.31	235.1–247.1	242.43	3.7	311–323	316	5.56	310.4–328.1	319.5	5.4	120
Cd	3.8–4.5	4.2	0.3	4.1–4.8	4.43	0.2	6.3–9.2	7.8	1.29	7.24–8.10	7.8	0.3	NA
Hg	1.96–2.95	2.34	4.27	2.84–3.52	3.243	0.3	10.20–12.00	11.0	6.25	10.5–14.3	12.8	1.1	NA

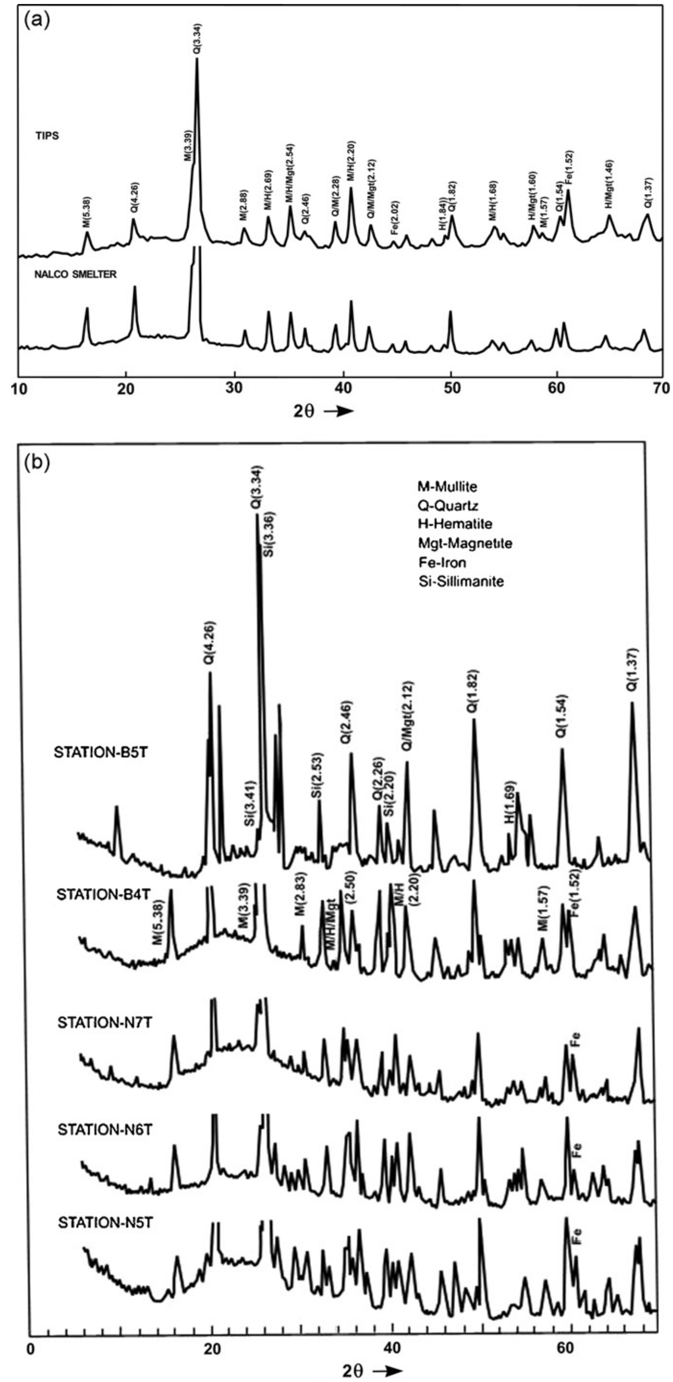

Fig. 3. (a) X-ray difractograms of pond ash samples from NALCO and TTPS showing mineral phases. (b) X-ray difractograms of some selective stations of Brahmani and Nandira Rivers showing mineral phases.

4.5. *Organic matter*

The organic matter in the sediments of Brahmani and Nandira Rivers ranges from 0.17% and 3.40% with an average value of 0.42% and 1.00%, respectively (Table 6). The highest organic matter, 3.40%, is seen at station N7 of Nandira River. The organic matter concentration in the downstream decreases but remains on the higher side compared to the average until station B4 for Brahmani, which is the confluence point of Nandira. From that point downwards, the dilution of Brahmani River sediment results in lowering the concentrations. It can thus be very well observed that the major

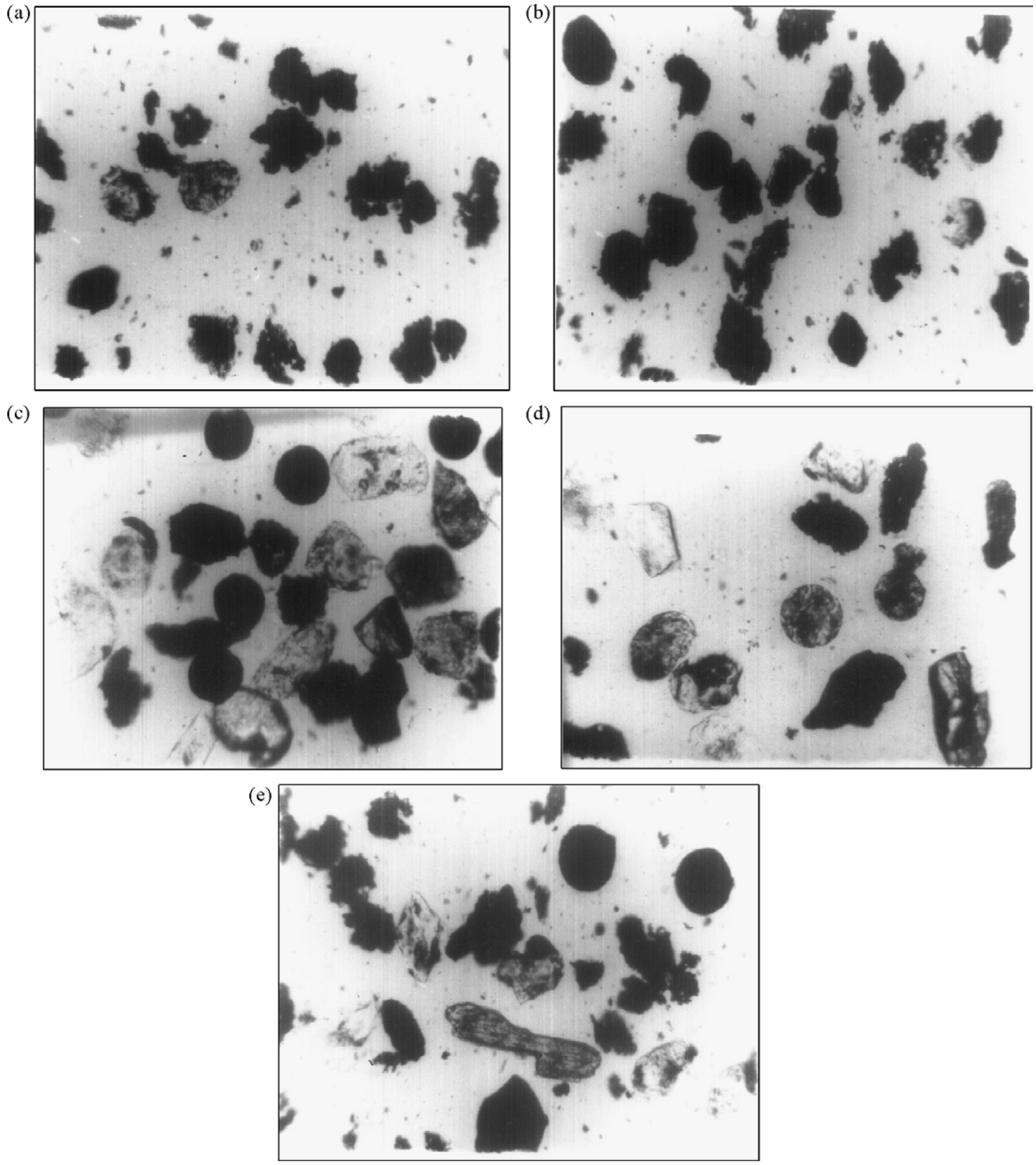

Fig. 4. (a) Morphological features of pond ash samples from NALCO (25×) (b) Morphological features of pond ash samples from TTPS (25×) (c) Morphological features of sediment from station N6 (25×) (d) Morphological features of sediment from station N7 (25×) (e) Morphological features of pond ash samples from B4 (25×).

contribution of organic matter is due to the discharge of coal fly ash into the riverbed.

4.6. Sequential leaching of heavy metals

The average heavy metal content in various geochemical phases of Brahmani upstream, downstream and Nandira River sediments are shown in Fig. 5. The total metal concentration of the chemical partitioning data is slightly less than that of the sum of individual phases, which is mainly due to the loss of metal through washing and processing at the time of analysis. The importance of individual phases and their association with heavy metals are discussed below.

4.6.1. Exchangeable phase

The sequence of leaching of heavy metals by 1M $MgCl_2$ in the Nandira, Brahmani upstream and downstream sediments is Co > Pb > Ni > Mn > Cr > Cu > Cd > Zn > Fe, Ni > Co > Mn > Pb > Cu > Zn > Cr > Fe > Cd and Ni > Co > Pb > Mn > Cu > Cr > Cd > Zn > Fe, respectively. The low concentration of some of the metal ions in exchangeable fraction suggests poor availability of the metals in the sediments, which can be attributed to high pH. Higher availability of Mn compared to the Fe in this fraction can be explained by the redox condition of the sediment. Under low redox condition, Mn is more available than Fe as the latter is controlled by pH [34]. Again according to Rankama and Sahama [35], in comparison to Mn, Fe-compound formed during weathering is readily soluble and less stable. The stations N6 and N7 of the Nandira River and the confluence point of the Nandira–Brahmani (B4) are having high exchangeable Ni, Pb and Co. This fraction is having high environmental risk among non-lithogenous phases due to greater potential for mobility into surface water which threat to pollution with respect to Co, Pb, Ni and to some extent Cu in the study area.

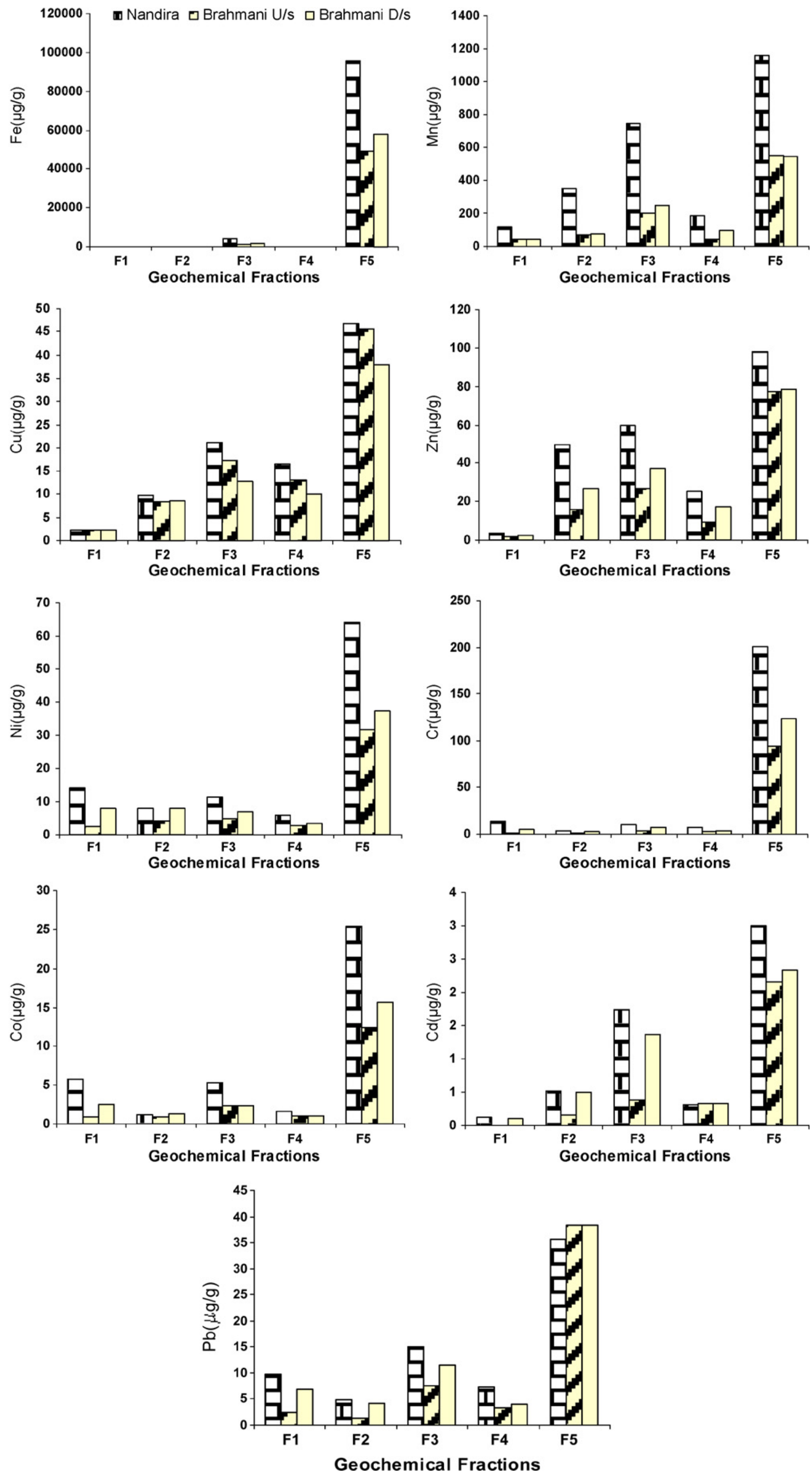

Fig. 5. Average metal content in different geochemical fractions in Nandira, Brahmani upstream and downstream stations.

Table 6
Distribution of grain size parameters, organic matter, calcium carbonate, and total phosphorous (%) in the sediments of Nandira and Brahmani Rivers

Stations	Soil texture										Soil type	Chemical parameters		
	Gv	Vcs	Cs	Ms	Fs	Vfs	Csilt	Msilt	Fsilt	Clay		OM	CaCO3	Total P
N1T	32.30	26.43	16.90	21.28	2.57	0.31	0.12	0.09	0.00	0.00	Sandy gravel	0.32	2.27	0.05
N2T	19.25	30.85	20.36	21.56	6.18	1.25	0.24	0.10	0.10	0.11	Gravely sand	0.75	1.90	0.07
N3T	0.40	6.12	16.90	68.27	6.65	1.03	0.40	0.14	0.05	0.04	Sandy	0.30	1.74	0.08
N4T	22.69	25.94	17.19	16.55	7.06	5.99	1.50	0.90	0.90	1.28	Gravely sand	1.80	2.01	0.19
N5T	0.14	5.05	10.61	61.92	19.41	1.52	0.60	0.30	0.25	0.20	Sandy	0.82	2.46	0.08
N6T	2.49	15.54	21.71	50.94	6.05	0.90	0.77	0.50	0.60	0.50	Sandy	1.29	2.43	0.15
N7T	1.08	4.61	16.01	59.74	10.02	2.38	1.70	2.30	1.10	1.06	Sandy	1.96	1.32	0.18
N1B	25.16	30.53	22.79	20.80	0.62	0.10	0.00	0.00	0.00	0.00	Gravely sand	0.29	2.65	0.34
N2B	28.32	27.44	17.56	20.32	4.82	0.99	0.20	0.20	0.10	0.00	Gravely sand	0.63	1.93	0.07
N3B	17.38	13.74	14.76	46.63	6.06	0.38	0.40	0.30	0.10	0.25	Gravely sand	0.79	1.95	0.07
N4B	20.94	32.24	26.11	19.12	0.96	0.30	0.23	0.10	0.00	0.00	Gravely sand	0.39	2.30	0.06
N5B	0.44	7.46	16.42	63.24	11.68	0.51	0.25	0.00	0.00	0.00	Sandy	0.67	2.74	0.12
N6B	5.38	17.07	22.29	45.82	8.21	1.01	0.23	0.00	0.00	0.00	Sandy	0.63	2.14	0.09
N7B	1.25	5.50	25.20	43.20	13.70	4.25	1.45	1.60	1.40	2.45	Sandy	3.40	1.28	0.25
B1T	27.07	27.20	18.65	25.86	1.03	0.16	0.03	0.00	0.00	0.00	Gravely sand	0.35	1.67	0.06
B2T	0.56	0.05	0.28	43.31	45.93	8.26	0.80	0.20	0.20	0.41	Sandy	0.31	0.92	0.08
B3T	0.20	3.12	7.81	79.57	9.01	0.23	0.06	0.00	0.00	0.00	Sandy	0.28	1.41	0.48
B4T	0.25	4.82	8.39	31.48	22.67	26.31	4.15	0.60	0.40	0.93	Sandy	1.03	1.38	0.11
B5T	0.67	14.95	36.00	43.27	3.35	0.43	0.43	0.40	0.30	0.20	Sandy	0.21	1.56	0.05
B6T	0.00	5.33	56.61	10.38	23.94	2.98	0.20	0.17	0.14	0.25	Sandy	0.41	0.98	0.07
B1B	9.45	32.92	28.46	28.40	0.71	0.07	0.00	0.00	0.00	0.00	Sandy	0.20	1.82	0.04
B2B	0.09	0.08	0.56	45.20	41.12	10.94	1.25	0.60	0.16	0.00	Sandy	0.55	1.05	0.06
B3B	0.26	3.54	5.22	78.32	9.31	0.28	0.07	0.00	0.00	0.00	Sandy	0.35	1.18	0.56
B4B	1.40	9.09	6.23	47.67	30.89	3.59	0.25	0.12	0.36	0.40	Sandy	0.99	1.40	0.10
B5B	0.08	11.88	42.79	43.62	0.68	0.36	0.20	0.20	0.10	0.10	Sandy	0.17	1.65	0.04
B6B	0.05	2.01	14.32	75.25	7.12	0.91	0.22	0.12	0.00	0.00	Sandy	0.24	1.31	0.05

4.6.2. Carbonate phase

The sequence of leaching of metals by 1M NaOAc (pH 5.0) in the Nandira, Brahmani upstream and downstream sediments is Zn > Mn > Cu > Cd > Ni > Pb > Co > Cr > Fe, Zn > Cu > Ni > Mn > Cd > Co > Pb > Cr > Fe and Zn > Cu > Ni > Cd > Mn > Pb > Co > Cr > Fe, respectively. In this fraction, Fe and Cr concentrations remain low as compared to the total concentration. The metals like Zn, Cu and Mn represent an appreciable portion of the total metal content most likely due to similarity in their ionic radii to that of calcium [20,21,36,37]. The contributions of carbonate Zn and Pb are high in Nandira sediments in comparison with Brahmani.

4.6.3. Fe–Mn hydroxide or reducible phase

The sequence of leaching in 0.04 M $NH_2OH{\cdot}HCl$ with 25% HOAc in the Nandira, Brahmani upstream and downstream sediments is Mn > Cd > Zn > Cu > Pb > Co > Ni > Fe > Cr, Mn > Zn > Cu > Co > Pb > Cd > Ni > Cr > Fe and, Cd > Mn > Zn > Cu > Pb > Ni > Co > Cr > Fe, respectively. Relatively higher concentration of Mn in this phase is related to the colloids of Mn transported at higher pH [38]. Fe–Mn oxides act as efficient scavenger for the metals such as Zn, Pb, Cd, Co, and Ni. The association of the above metals in this phase may be due to adsorption into colloids of Fe–Mn.

4.6.4. Organic phase

The average metal concentrations in Brahmani upstream stations is <7% except Cd (11%). The high average of Cu (14%), Zn and Mn (10%) were found in Brahmani downstream stations. However, relatively higher concentrations of Cu (17%), Zn (11%) and Pb (10%) are found in Nandira sediments which are very close to the data in the sediment of Suoael River, Brazil [39] and river Nile, Egypt [40] and Yamaska and Saint Francois River, Canada [19]. The contribution of metal in this fraction follows the order Cu > Zn > Pb > Mn > Ni > Cd > Co > Cr > Fe for the Nandira River sediments, whereas in the case of Brahmani upstream and downstream, the order is Cu > Cd > Zn > Pb > Ni > Co > Mn > Cr > Fe and Cu > Zn > Mn > Pb > Cd > Ni > Co > Cr > Fe, respectively.

4.6.5. Residual phase

The metal concentrations in this inert fraction are higher than any of preceding extraction, which represents normally more than 40% of the total concentration in the present study. A major portion of Fe and Cr are found to be associated with this phase represents detrital origin, while Zn and Pb are having slightly less contribution towards this phase. The contribution of metal in this fraction follows the order Fe > Cr > Co > Ni > Cd > Pb > Mn > Zn for the Nandira River sediments, whereas in the case of Brahmani upstream and downstream, the order is Fe > Cr > Pb > Cd > Co > Ni > Mn > Zn and Fe > Cr > Co > Pb > Ni > Mn > Cu > Zn > Cd, respectively.

4.7. Ecological risk assessment

By studying the distribution of the metals between the different phases, their bioavailability and toxicity can be ascertained. The fractions introduced by man's activity include the adsorptive and exchangeable and bound to carbonates which are considered to be weakly bound and may equilibrate with aqueous phase thus becoming more rapidly bioavailable [41]. It is evident from the results of the fractionation studies that the metals in the sediments are bound to different fractions with different strengths. The strength values can, therefore, give a clear indication of sediment reactivity, which in turn assess the risk connected with the presence of metals in an aquatic environment [42]. Jain [42] in metal fractionation study of Yamuna River sediments (India) discussed RAC and found 30–50% of lead and cadmium in exchangeable fraction indicating high risk. This criterion, risk assessment code as given in Table 7 indicates that sediment, which can release in exchangeable and carbonate fractions, less than 1% of the total metal will be considered safe for the environment. On the contrary, sediment releasing in the same fraction more than 50% of the total metal has to be considered highly dangerous and can easily enter the food chain [17].

Table 7
Criteria for risk assessment code (RAC)

Risk	Metals in carbonate and exchangeable fraction (%)
No risk	<1
Low risk	1–10
Medium risk	11–30
High risk	31–50
Very high risk	>50

The RAC values of metals at different stations are plotted for Brahmani and Nandira separately are shown in Fig. 6(a and b), respectively. Fe always remains associated with exchangeable and carbonate phases by <1% of the total and therefore included in the no risk category. In case of Brahmani except Cr most of the metals are showing low to medium risk in downstream stations of Nandira Brahmani confluence. In case of Nandira N6 and N7 stations are showing high environment risk with respect to Zn and Pb. Other metals except Cr are showing low to medium risk at most of the stations.

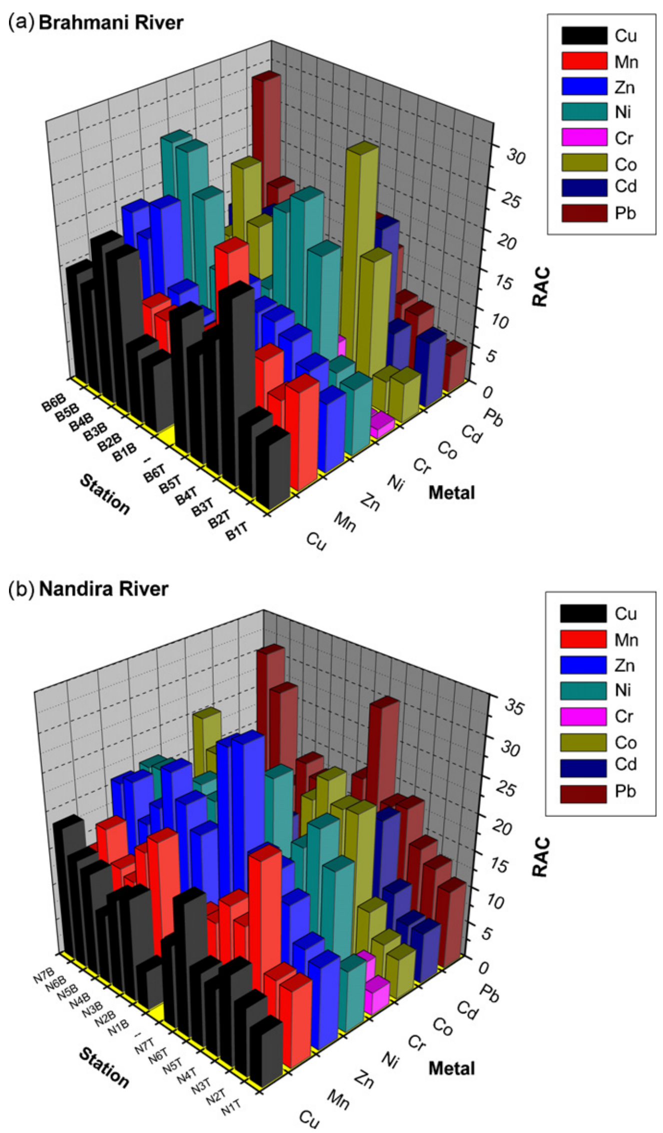

Fig. 6. (a) RAC values of metals at different stations (top and bottom) in Brahmani River. (b) RAC values of metals at different stations (top and bottom) in Nandira River.

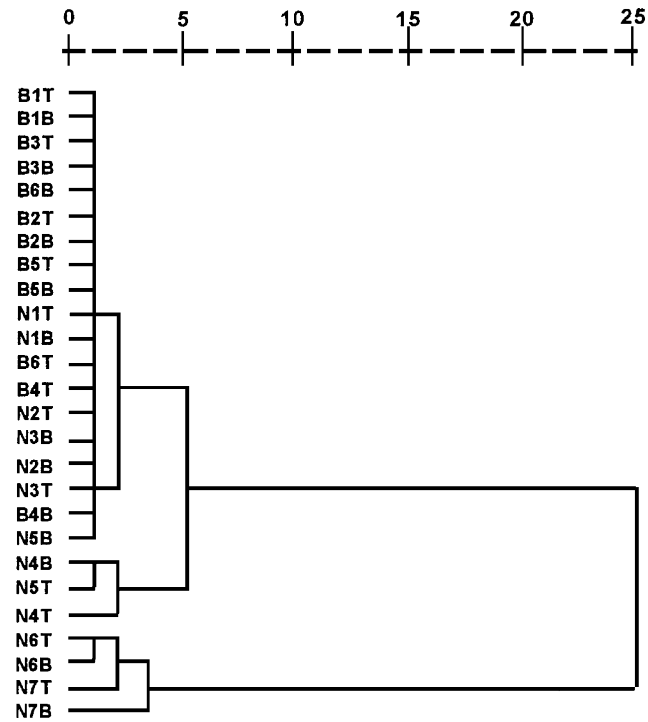

Fig. 7. Dendogram showing relationship among sampling sites along Brahmani and Nandira Rivers.

4.8. Statistical analyses

4.8.1. Cluster analysis

The relationship among stations obtained through cluster analysis synthesized by the dendogram plots (distance cluster combine) is shown in Fig. 7. This gives indication to assess the level of contamination. The dendogram shows a sequence in the association, displaying the information as degree of contamination of heavy metals between stations. From a look at the dendogram plot, the status of the pollution is broadly categorized into three major groups, i.e. less, moderately, and highly contaminated sediments.

The first group, association of stations B1, B2, B3, B5, B6 and N1 at a slightly lower significance level may be regarded as less contaminated indicating high lithogenic contribution. Similarly the stations like N2, N3, N5B and B4B as well as stations N4 and N5T were detected as a moderately contaminated group. Stations like N7 and N6 are considered at a higher significance level of contamination.

4.8.2. Factor analysis

To understand the effect of natural and anthropogenic flux, which is responsible for enrichment of the heavy metals and their movement in riverine sediments, factor analysis with rotation has been carried out to clarify the relationship between heavy metals, total phosphorous, grain size classes, organic matters and $CaCO_3$(%) in the sediments of the Nandira and Brahmani River for 26 cases. The results of factor analysis for six factors are given in Table 8, with values greater than 0.50, considering their significant influence towards the geochemical processes [21]. Six principal components (PC) or factors (eigen value greater than unity) explaining 85.7% of the variance or information contained in the original data set was retained, which is sufficient to give a good idea of the data structure.

A varimax rotation of PCs was used to clarify the above picture as it achieves a simpler and more meaningful representation of the underlying factors by decreasing the contribution to factors of vari-

Table 8
R-mode factor loading of 27 variables according to the varimax method for data set of Brahmani and Nandira Rivers

Variable	Varifactor-1	Varifactor-2	Varifactor-3	Varifactor-4	Varifactor-5	Varifactor-6
Fine silt	0.896					
Med. silt	0.890					
Clay	0.887					
Gravel			−0.930			
Very coarse sand			−0.864			
Med. sand			0.793			0.506
Very fine sand				0.881		
Coarse silt	0.546			0.716		
Fine sand			0.407	0.708		
Coarse sand				0.584		−0.690
Cd	0.631		0.439			
Pb	0.629					
Hg	0.570	0.467				
Ni		0.872				
Zn		0.867				
Cr	0.480	0.840				
Co	0.429	0.651				
Cu	0.420				0.635	
Mn		0.869				
Al				0.700	0.475	
Ti					0.673	
Fe		0.669			0.572	
OM	0.801	0.425				
$CaCO_3$		0.662	−0.400			
TP						0.802
Eigen value	10.15	4.77	2.2	1.94	1.31	1.06
Percent of variance	40.6	19.1	8.8	7.8	5.3	4.2

ables with minor significance and increasing the more significant one [43,44].

Varifactor-1 represents 40.6% of the total variance, which is found to be strongly associated with fine silt, medium silt, coarse silt and clay with organic matter and toxic metals ions like Pb, Cd and Hg. Textural parameters are playing an important role for distribution of organic matter as well as toxic metal ions like Pb, Cd, Hg along with Cr, Co and Cu. Sahu and Mukherjee [45] observed that clay acts as a sink for Pb, Cd, Hg, etc. derived from industrial wastes and fine grained sediments also control the levels of metals in the sediment–water system due to their greater cation capacity promoting the adsorption of positively charged metal ions.

Varifactor-2 contributes 19.1% of total variance and is strongly associated with Ni, Mn, Zn, Cr, Fe, Co with $CaCO_3$ and organic matter. Fe–Mn oxides/hydroxides seem to play an important role in scavenging heavy metals like Ni, Zn, Cu, Co and Cr [19,46]. Most of these metals dissociate into the solution by various industrial effluents and subsequently become precipitated and adsorbed by finer particles. However, the possibility of carbonaceous precipitation and/or organic matter contribution cannot be overruled. Organic matters not only solubilise the metal species by complexing the metal ions but also take out the metal ions from the solution [47]. Thus, in this factor Fe–Mn oxy-hydroxide, organic precipitation is responsible for enrichment of metal ions in the sediments.

Varifactor-3 contributes 8.8% of total variance grain size factor, where gravel, very coarse sand, $CaCO_3$% are inversely proportional to medium sand, fine sand and Cd concentration. This indicates that two different sources, i.e. terrigenous and anthropogenic (coal fly ash) are responsible for $CaCO_3$ and Cd accumulation in the river sediments.

In varifactor-4, Al is positively correlated with very fine sand (125–62.5 μm), fine sand (250–125 μm), and coarse silt (62.5–31 μm) size fraction. Coal fly ash primarily consists of aluminous-silicate matrix. Buchhlotz and Landsberger [48] reported that the concentration of metal ions of coal fly ash is 80% in the size fraction of 20–106 μm. In this present work, it is observed that highest concentration of Al is in 31–125 μm size range.

Varifactor-5 (5.3% of variance) is associated with Al, Ti, Fe, and Cu and can be interpreted as heavy mineral contribution. Heavy minerals like Sillimanite, Mullite, Rutile, Magnetite, and Hematite, etc. mainly contribute the above metals. Varifactor-6 (4.2% of the total variance) is contributed by total phosphorous. This single loading may be considered as an independent source to sediments of the study area.

5. Conclusion

The present study reveals that there is considerable variation in the concentration of heavy metals in Brahmani upstream, downstream as well as Nandira River sediments. This variation may be due to the change in magnitude of industrial/mining waste and sewage being added to river stretch at different locations. The average concentration of Zn, Cr, Ni and Mn determined in the present river sediments are found to be much higher than the Indian River average. However, the average concentration of most of the metals except Cd is found to be lower than the World river average as well as World surface rock. Most of the trace metals such as Pb, Zn, Ni, Co and Cu in the sediments are associated in most mobile fractions (carbonate and exchangeable bound) are posing a medium to high environmental risk and thus exert a potential hazard for the aquatic environment. According to risk assessment code, N6 and N7 stations are showing high environment risk with respect to Zn and Pb and can pose bioavailability to the aquatic fauna community. The mineralogical–morphological characteristics of Nandira and Brahmani downstream stations confirm the contamination of metal content coal fly ash samples generated from the thermal plants.

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