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ORIGINAL ARTICLE

Source and distribution of metals in bed sediments of Subarnarekha River, India

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Abstract The study was taken up to establish the distributions of metals as well as to assess the extent of anthropogenic inputs into the Subarnarekha River. Bed sediments were collected; analyzed for metals; and assessed with the index of geo-accumulation (I_{geo}), enrichment factor (EF) value, concentration factor (CF) and pollution load index (PLI). Metals in the sediment were variable in the river and there are major pollution problems at certain locations. The average concentrations of Fe, Cu, Cr, Pb, Mn, Ni, Zn, Co and Ba in mg/kg was found to be 30,802 ± 11,563, 69 ± 57, 111 ± 74, 75 ± 61, 842 ± 335, 42 ± 22, 100 ± 39, 15 ± 4 and 698 ± 435, respectively. The I_{geo}, EF, CF and PLI indices showed that the contamination of Pb and Cu was more serious than that of Ni, Zn, Co and Ba, whereas the presence of Fe, Mn and Cr might be primarily from natural sources. The contamination of the sediments with metals at few locations is attributed to mining, industries and other anthropogenic causes. Principal component analysis was employed to better comprehend the controlling factors of sediment quality. The statistical analysis of inter-metallic relationship revealed the high degree of correlation among the metals indicated their identical behaviour during transport. PCA outcome of three factors together explained 83.8 % of the variance with >1 initial eigenvalue indicated both innate and anthropogenic activities are contributing factors as source of metal profusion in Subarnarekha River basin.The overall study reveals moderately serious pollution in the river basin principally in some locations under the anthropogenic influences.

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Introduction

Sediments are ecologically important components of the aquatic habitat, which play a significant role in maintaining the trophic status of any water body (Singh et al. 1997). Sediments can be sensitive indicators for monitoring contaminants in aquatic environments. Metal contamination in aquatic environments has received a good amount of attention due to toxicity, persistence in the environment and subsequent accumulation in aquatic habitats. The occurrence of elevated levels of trace metals especially in the sediments can be a good indication of man-induced pollution and high levels of heavy metals can often be attributed to anthropogenic influences, rather than natural enrichment of the sediment by geological weathering (Lord and Thompson 1988; Davies et al. 1991; Binning and Baird 2001; Eja et al. 2003). Sediments near urban areas commonly contain high levels of contaminants (Lamberson et al. 1992; Cook and Wells 1996) which constitute a major environmental problem faced by many anthropogenically impacted aquatic environments (Magalhaes et al. 2007). Sediments in rivers not only play important roles at influencing the pollution, but also record the history of their pollution.

Sediments act as both carrier and sources of contaminants in aquatic environment (Walling et al. 2003; Shuhaimi 2008). Sediments contaminated with metals and other pollutants may be pollution sources to overlying waters and benthic food chains for years to come (Lyman et al. 1987). Heavy metal residues in contaminated sediments may accumulate in microorganisms, such as aquatic flora and fauna, which in turn, may enter into the food chain and eventually result in human health problems (Cook et al. 1990; Deniseger et al. 1990). Metals may become concentrated up the food chain (Eja et al. 2003), leading to enhanced levels in liver and muscle tissues of fishes (Eja et al. 2003), aquatic bryophytes (Mouvet et al. 1993) and aquatic biota (Ramos et al. 1999). Therefore, several regulations were described for limiting the concentrations of some of metals in waters and soils. The concentration of trace elements in river sediments is an important indicator of environmental contamination (Narin et al. 1997; Soylak et al. 1999, 2002a; Alagarsamy 2006). There are a great number of studies on trace element concentration of sediments and soil (Narin and Soylak 1999; Tuzen 2003; Dalman et al. 2006; Capilla et al. 2006; Arslan and Gizir 2006; Soylak et al. 2002b; Soylak and Yilmaz 2006).

Chemical leaching of bedrocks, water drainage basins and runoff from banks are the primary sources for the lithogenic contribution of metals. Discharge of urban and industrial waste water, combustion of fossil fuels, mining and smelting operations, processing and manufacturing industries, waste disposal including dumping, etc. are primary anthropogenic sources of pollution (Pardo et al. 1990; Klavins et al. 2000; Yu et al. 2001; Chukwujindu et al. 2007). Fertilizers and pesticides used in farming and forestry and the effects of transportation combustion and stormwater runoff from roads also may contribute to heavy metal contamination (Friberg et al. 1986). Pollutants released to surface water can accumulate to harmful levels in sediments by forming stable complexes with inorganic and organic compounds (Nienke and Lee 1982; Moore and Ramamoorthy 1984).

There is a growing concern over the use of River Subarnarekha by resident along the river banks and the fauna and flora of the ecosystem. The Subarnarekha flows through India's most industrialized areas known for ore mining, steel production, power generation, cement production and other related activities. Mining of Copper, Uranium and other metals leads to inflow of metals in the river. Also, industrial activity, particularly the iron and steel industries of the basin has also been a major contributor of certain metals to the water and sediments of the river. Moreover, the basin sustains several major cities and towns such as Jamshedpur, Ranchi, Muri, Ghatsila, etc. Also earlier, a study by Upadhyay et al. (2006) reported the concentration of Cu, Pb, Zn and Cd in the bed sediments at 4 locations of the basin which opined moderate to high pollution with respect to Cu, Zn and Pb. In view to the above facts, this study is aimed at assessing the quality of sediment from River Subarnarekha. The concentrations of nine metals (iron, copper, chromium, lead, manganese, nickel, zinc, cobalt and barium) in Subarnarekha River sediments collected in post-monsoon at 21 locations along a 400-km reach of the river between its origin to mouth is reported.

Materials and methods

Description of the study area

The study is carried out in Subarnarekha River which flows through the East Singhbhum district, which is one of India's important industrialized areas known for ore mining, steel production, power generation, cement production and other related activities. The Subarnarekha River is the 8th river of India by its flow (12.37 billion m^3/year) and length. The River Subarnarekha is a rain fed river originating near Nagri village (23°18′02″N, 85°11′04″E) in the Ranchi district runs through several major cities and towns such as Ranchi, Muri, Jamshedpur, Ghatsila, Bahragora, etc. covering a distance of about 400 km. It finally joins the Bay of Bengal at Kirtania port (21°33′18″N, 87°23′31″E) in Orissa. Before falling in the Bay of Bengal, the river flows through Ranchi, Saraikela and East Singhbhum districts of Jharkhand, West Midnapore district of West Bengal and Balasore district of Orissa. Of its total length 269 km are in Jharkhand and 64 km in West Bengal and 62 in Orissa. The Subarnarekha basin covers an area of 19,300 km^2. This area is nearly 0.6 % of the total national river basin area and yields 0.4 % of the country's total surface water resources. Its important tributaries include the Raru, Karkari, Kharkai and Sankh Rivers.

The Subarnarekha River flows over the Precambrian terrain of the Singhbhum craton in eastern India. The rocks are of an iron ore series and the primary rock types are schist and quartzite. The major part of the basin lies on the Indian Shield where ancient Precambrian igneous and metamorphic rocks are exposed. It is only in the lower reaches of the basin, southeast of Ghatsila, that the younger geological formations, namely, tertiary gravels, Pleistocene alluvium and recent alluvium are exposed. A wide range of age is represented in the geological formations in parts of the basin: from 3.8 billion-year-old older metamorphic groups of rocks (including tonalite-gneiss) in parts of Mayurbhanj district to the most recent deltaic alluvium which is actively advancing towards the sea at the mouth of the river. The Subarnarekha basin is rich in mineral resources which are varied comprising ores of copper, iron, uranium, chromium, gold, vanadium, limestone, dolomite, kyanite, asbestos, barites, apatite, china clay, talc, etc. (Naha and Ghosh 1960; Saha 1973; Sarkar 1982).

Sample collection

The bed sediment samples were collected from 21 locations along the entire stretch of the Subarnarekha River from its origin to mouth. The geological map of the Subarnarekha River basin with the sampling stations are given in Fig. 1. Bed surficial sediment samples were collected with a plastic spade by scooping from the upper

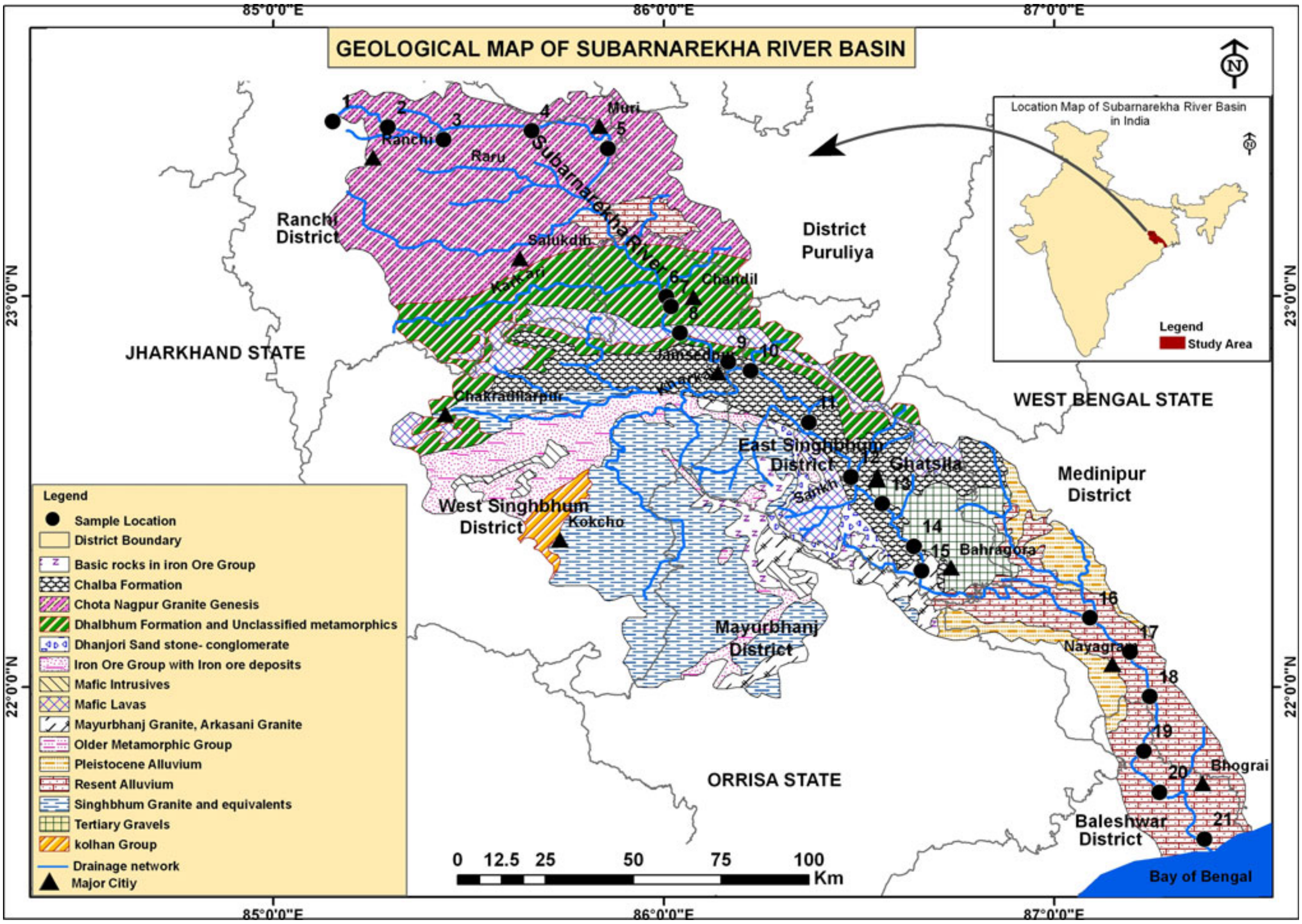

Fig. 1 The geological map of Subarnarekha River basin and the locations of sampling stations {1 Nagri, 2 Namkom, 3 Tatisilwai, 4 Hundru, 5 Muri, 6 Chandil, 7 Barabinda, 8 Kanderbera, 9 Tatanagar (Sonari), 10 Tatanagar (Mango), 11 Galudih, 12 Mosabani (u/s Sankh), 13 Mosabani (d/s Sankh), 14 Shyamsunderpur, 15 Baharagora, 16 Gopiballavpur, 17 Mahapal, 18 Sonakaniya, 19 Jaleswar, 20 Pontai, 21 Kirtania}

3–5 cm of river bed representing contemporary deposits at a water depth of about 50 cm. Then the sediments were packed and sealed in polyethylene bags and brought to the laboratory, where they were dried at room temperature (25–30 °C). Dried samples were sieved through 2 mm sieve to be separated from pebbles and conglomerates. Then the samples were freed from shells and visible shell fragments. After that, samples were mixed well by Coning and Quartering method and about 100 g of the sample was taken. The samples were transferred into a porcelain dish and dried in an oven at 110° C for 24 h. The samples are then powdered in a dry mortar-pestle and sieved through standard sieve of 200 mesh size (75 microns). Subsequently, the samples are preserved for the digestion and further analysis of metals.

Laboratory analysis

Collected samples was taken and subjected to digestion in microwave by the method 3,052 as given by U.S. EPA (1996). This is a total digestion method with different combination of acids applicable to most matrices. 0.25 ± 0.001 g of sample was taken in inert polymeric microwave vessels. Then 0.5 ml of double distilled water was added to improve the solubility of the minerals and prevent temperature spikes due to exothermic reactions. Subsequently, 4.5 ml HNO_3, 2 ml HF, 1 ml HCl and 0.5 ml H_2O_2 were added. The vessels were sealed and then heated in microwave system (Anton Paar). After cooling, the samples were filtered through Qualitative Whatman filter paper (no. 1; pore size 11 μm) and the volume was made up to 50 ml by adding 2 % (v/v) nitric acid. Aliquots were preserved for the analysis of metals. All the chemicals used were of AR grade (Merck, Darmstadt, Germany). Concentration of Fe, Cu, Cr, Pb, Mn, Ni, Zn, Co and Ba were analyzed using inductively coupled plasma mass spectrometer (Perkin Elmer ELAN DRC-e). The isotopes measured for Fe, Cu, Cr, Pb, Mn, Ni, Zn, Co and Ba were 57, 63, 52, 208, 55, 60, 66, 59 and 138, respectively. A calibration blank and an independent calibration verification standard was analyzed every 15 samples to confirm the calibration status of the ICP-MS. Matrix interference (blank) was <1 % for all elements. Recovery rates of metals spiked in sediments ranged from 88 to 110 %. Triplicates of sample analysis yielded relative percent differences of <5 %.

Validation methodology

The method of analysis was validated using NIST-1646a standard reference material (Estuarine sediment), supplied by the National Institute of Standards and Technology (NIST), USA. The accuracy and precision were checked by analyzing the certified reference material under the same conditions. The % of recovery varied from 87.3 to 112 (Table 1).

Principal component analysis/factor analysis (PCA/FA)

Principal component analysis (PCA) is a powerful pattern recognition tool that attempts to explain the variance of a large dataset of intercorrelated variables with a smaller set of independent variables (Simeonov et al. 2003). PCA technique extracts the eigenvalues and eigenvectors from the covariance matrix of original variables. The principal components (PC) are the uncorrelated (orthogonal) variables obtained by multiplying the original correlated variables with the eigenvector, which is a list of coefficients (loadings or weightings). Thus, the PCs are weighted linear combinations of the original variables. PC provides information on the most meaningful parameters, which describe the whole data set while affording data reduction with a minimum loss of original information (Hair et al. 1995; Sharma 1996; Vega et al. 1998). Factor analysis further reduces the contribution of less significant variables obtained from PCA and the new group of variables obtained from PCA and the new group of variables known as varifactors (VF) is extracted through rotating the axis defined by PCA (Vega et al. 1998; Wunderlin et al. 2001). FA further reduces the contribution of less significant variables obtained from PCA and the new group of variables obtained from PCA and the new group of variables known as VF is extracted through rotating the axis defined by PCA.

Table 1 Metal concentration in standard reference material (Estuarine sediment NIST-1646a)

Element	Certified concentration (mg/kg)	Observed concentration (mg/kg)	Recovery (%)
Fe	20,080	20,932 ± 41	104
Cu	10.01	11.2 ± 0.7	112
Cr	40.90	38.17 ± 1.2	93.3
Pb	11.7	11.07 ± 0.62	94.6
Mn	234.5	210.8 ± 12.3	89.9
Ni	23.0	21.74 ± 1.1	94.5
Zn	48.90	42.69 ± 1.4	87.3
Co	5.0	4.77 ± 0.31	95.4
Ba	210.0	194.9 ± 10.6	92.8

Calculation of enrichment factor, geo-accumulation index and pollution load index

In order to assess the influence of metals in the study area, the enrichment factor (EF) was calculated for each metal in the soil using the formula:

$$\mathrm{EF} = (C_X/C_{\mathrm{Fe}})_s / (C_X/C_{\mathrm{Fe}})_c$$

where C_X and C_{Fe} refer to the concentration of element X and Fe in the soil (s) and earth's crust (c), respectively. Iron is used here as reference element. Metal concentrations were normalized to the textural characteristic of sediments with respect to Fe. Iron was selected because it is a major sorbent phase for trace metals, and is a quasi-conservative tracer of the natural metal-bearing phases in fluvial and coastal sediments (Schiff and Weisberg 1999; Turner and Millward 2000). A five-category ranking system is used in this paper to denote the degree of anthropogenic contamination. $EF < 2$ states deficiency to minimal contamination, $EF = 2$–5 moderate contamination, $EF = 5$–20 significant contamination, $EF = 20$–40 very high contamination, and $EF > 40$ extremely high contamination (Sutherland 2000; Kartal et al. 2006).

A quantitative measure of the extent of pollution in the study area was calculated from the metals' concentration in the soil using the method of Muller (1979), which is known as the index of geo-accumulation (I_{geo}).

$$I_{\mathrm{geo}} = log_2(C_n/1.5\,B_n)$$

where C_n is the measured concentration of the metal 'n' in the soil and B_n is the geochemical background value in fossil argillaceous sediments (average shale).

Pollution load index (Tomlison et al. 1980) has been calculated to determine the pollution load of sediments. PLI is represented as geometric mean of CF value of n number of metals estimated at contaminated site. The index is based on the concentration factor (CF) of each metal present in the soil or sediment

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots\ldots\ldots \times CF_n)^{1/n}$$

where n is the number of metals and CF is the contamination factor.

To quantify the magnitude of pollution by different metals, contamination factor (CF) is used (Salomons and Forstner 1984). It is expressed as:

$$\mathrm{CF} = \text{Metal concentration in sediment} / \text{World shale average for sediment}$$

Pollution load index provides a simple, comparative means for assessing the level of metal pollution and classified as no pollution (*PLI* <1), moderate pollution ($1 < PLI < 2$), heavy pollution ($2 < PLI < 3$), and extremely heavy pollution ($3 < PLI$).

Results

The detailed results of metals in the bed sediments of Subarnarekha River are shown in Table 2. Considering all the sampling locations, the average concentrations of Fe, Cu, Cr, Pb, Mn, Ni, Zn, Co and Ba in mg/kg was found to be 30,800 ± 11,560, 69 ± 57, 111 ± 74, 75 ± 61, 842 ± 335, 42 ± 22, 100 ± 39, 15 ± 4 and 698 ± 435, respectively. The maximum of Fe, Cr and Mn was found at Kanderbera while the maximum concentration of Cu, Ni and Co was noticed at Mosabani (U/S of Sankhnalla). Pb and Zn were found to be highest at Tatisilwai and Ba at Muri. To assess the level of pollution, enrichment factor, geo-accumulation index (I_{geo}) and PLI were calculated. The EF ranged from 0.80 to 17.68 for Cu, 0.72 to 3.27 for Cr, 1.43 to 24.69 for Pb, 0.57 to 2.16 for Mn, 0.42 to 4.14 for Ni, 1.13 to 3.37 for Zn, 0.66 to 1.78 for Co and 0.48 to 6.92 for Ba (Table 3). The I_{geo} values varied from −2.65 to 3.19 thus falling in the I_{geo} class of 0 to 4 (Table 4, Fig 2). The average PLI value was calculated to be 1.01 with a range from 0.57 to 1.35 (Table 5). Table 6 gives reported concentration range of metals in bed sediments in different river basins by various researchers. It can be seen from the table that the concentrations of the metals are in accordance to other studies.

Table 2 Concentration of metals (mg/kg) in bed sediment with respect to different locations of Subarnarekha river basin

Code	Location	Fe	Cu	Cr	Pb	Mn	Ni	Zn	Co	Ba
1	Nagri	50,350	38.5	165.6	87.0	517.0	33.4	148.1	13.3	584.2
2	Namkom	26,705	41.0	71.8	203.0	600.8	23.8	168.0	18.3	1,528.6
3	Tatisilwai	26,090	38.5	57.7	273.0	866.7	19.4	177.0	13.9	1,126.9
4	Hundru	30,870	27.2	42.3	106.0	882.2	18.6	115.9	12.6	516.3
5	Muri	19,645	33.8	36.0	123.0	696.4	16.2	78.9	12.0	1,669.9
6	Chandil	40,170	57.9	102.9	93.0	964.9	40.6	116.5	14.4	778.2
7	Barabinda	44,070	63.9	123.2	83.0	1,139.4	45.5	126.4	15.6	644.3
8	Kanderbera	51,680	48.8	322.7	46.7	1,606.5	74.2	117.1	15.9	411.9
9	Tatanagar, Sonari	26,440	36.0	67.4	63.2	1,027.9	33.0	78.5	16.0	1,161.0
10	Tatanagar, Mango	24,765	44.4	70.6	65.0	693.9	27.7	82.1	13.5	1,253.6
11	Galudih	32,820	79.6	198.4	43.6	1,113.1	77.5	76.1	23.5	439.5
12	Mosabani u/s Sankh	15,440	260.3	55.0	55.8	427.3	92.0	89.3	25.3	259.7
13	Mosabani d/s Sankh	17,680	168.5	53.6	48.1	466.7	36.9	53.6	11.4	968.7
14	Shyamsunderpur	32,605	134.3	126.4	44.0	891.6	68.7	83.6	18.5	519.3
15	Baharagora	28,065	107.2	104.3	46.4	680.4	78.9	77.9	19.6	503.4
16	Gopiballavpur	16,150	57.7	50.3	48.3	387.9	30.1	49.8	10.4	778.4
17	Mahapal	21,870	43.2	94.0	37.6	597.0	39.2	59.5	12.0	582.1
18	Sonakaniya	50,100	52.2	163.7	30.3	1,554.0	37.8	159.6	14.8	284.4
19	Jaleswar	43,765	55.1	249.8	31.3	1,114.2	47.6	118.3	14.4	257.6
20	Pontai	26,670	27.8	100.1	23.5	842.6	24.2	78.2	8.7	190.8
21	Kirtania	20,900	25.7	75.0	26.1	605.3	25.3	52.2	8.6	192.2
	Indian average[a]	29,983	28	87	11.2	605	37	16	31	368
	World average[b]	48,000	100	100	150	1,050	90	350	20	600
	Shale average[c]	47,200	45	90	20	850	68	95	19	580

[a] Subramanian et al. 1985

[b] Martin and Meybeck 1979

[c] Turekian and Wedepohl 1961

Table 3 Enrichment factor of metals in the Subarnarekha River bed sediments

Code	Location	Fe	Cu	Cr	Pb	Mn	Ni	Zn	Co	Ba
1	Nagri	1.00	0.80	1.72	4.08	0.57	0.46	1.46	0.66	0.94
2	Namkom	1.00	1.61	1.41	17.94	1.25	0.62	3.13	1.71	4.66
3	Tatisilwai	1.00	1.55	1.16	24.69	1.84	0.52	3.37	1.32	3.52
4	Hundru	1.00	0.92	0.72	8.10	1.59	0.42	1.86	1.02	1.36
5	Muri	1.00	1.80	0.96	14.78	1.97	0.57	2.00	1.52	6.92
6	Chandil	1.00	1.51	1.34	5.46	1.33	0.70	1.44	0.89	1.58
7	Barabinda	1.00	1.52	1.47	4.44	1.44	0.72	1.42	0.88	1.19
8	Kanderbera	1.00	0.99	3.27	2.13	1.73	1.00	1.13	0.76	0.65
9	Tatanagar, Sonari	1.00	1.43	1.34	5.65	2.16	0.87	1.48	1.50	3.57
10	Tatanagar, Mango	1.00	1.88	1.49	6.20	1.56	0.78	1.65	1.35	4.12
11	Galudih	1.00	2.54	3.17	3.14	1.88	1.64	1.15	1.78	1.09
12	Mosabani u/s Sankh	1.00	17.68	1.87	8.53	1.54	4.14	2.87	4.07	1.37
13	Mosabani d/s Sankh	1.00	9.97	1.59	6.42	1.47	1.45	1.50	1.60	4.46
14	Shyamsunderpur	1.00	4.32	2.03	3.18	1.52	1.46	1.27	1.41	1.30
15	Baharagora	1.00	4.01	1.95	3.90	1.35	1.95	1.38	1.74	1.46
16	Gopiballavpur	1.00	3.75	1.63	7.06	1.33	1.29	1.53	1.60	3.92
17	Mahapal	1.00	2.07	2.26	4.05	1.52	1.24	1.35	1.36	2.17
18	Sonakaniya	1.00	1.09	1.71	1.43	1.72	0.52	1.58	0.74	0.46
19	Jaleswar	1.00	1.32	2.99	1.69	1.41	0.76	1.34	0.82	0.48
20	Pontai	1.00	1.09	1.97	2.08	1.75	0.63	1.46	0.81	0.58
21	Kirtania	1.00	1.29	1.88	2.95	1.61	0.84	1.24	1.02	0.75

Table 4 Geo-accumulation index of metals in the Subarnarekha river sediments

I_{geo} value	I_{geo} class	Sediment quality (Muller 1979)	Metals
>5	6 (>64 fold increase)	Extremely polluted	
4–5	5	Highly polluted to very highly polluted	
3-4	4 (25 fold increase)	Highly polluted	Pb
2–3	3	Moderately polluted to highly polluted	Pb
1–2	2 (five-fold increase)	Moderately polluted	Cu, Cr, Pb
0–1	1 (double the background value)	Unpolluted to moderately polluted	Cu, Cr, Pb, Mn, Zn, Ba
<0	0	Background concentration	Fe, Cu, Cr, Pb, Mn, Ni, Zn, Co, Ba

Discussion

Metals in bed sediments

The increased concentration of Fe, Mn and Cr at Kanderbera may be attributed to geogenic sources. This is the only location which falls in the basic igneous rock layer. The river flows through the basic igneous rock layer from north to southeast for about 2 km and basic igneous rocks are known to be rich in Ferromagnesium (Hiss 1960; Maitre 2002; Pidwirny 2006). Also, Mn and Cr are also known to be associated with weathering of mafic rocks (Gough et al. 1989; Gasser and Dahlgren 1994). Mosabani is known for its viable grades of Cu with extensive mining of Cu in the area. This can be the source of enhancement of Cu, Ni and Co in the location. Namkom, Tatisilwai and Muri are associated with large scale industrial activities including manufacturing of paints and batteries. Also the locations are under heavy vehicular load. These anthropogenic activities are known to be associated with augmentation of Pb, Zn and Ba (Bonnevie et al. 1994; Kennedy and Gadd 2000; Al-Masri et al. 2002).

A number of significant correlations have been obtained in the study (Table 7) like Fe with Cr, Mn and Zn; Cu with Ni and Co; Cr with Mn and Co; Pb with Ni and Ba; Mn with Co; Ni with Co. Overall the divergent results indicated that the significant correlation was not always correlated with the common sources. In other words, the single correlation analysis is not enough for the metal source identification; it should be conducted together with other analysis tools.

Table 5 Contamination factor of metals in the Subarnarekha River sediments

Code	Location	Fe	Cu	Cr	Pb	Mn	Ni	Zn	Co	Ba	PLI
1	Nagri	1.07	0.85	1.84	4.35	0.61	0.49	1.56	0.70	1.01	1.10
2	Namkom	0.57	0.91	0.80	10.15	0.71	0.35	1.77	0.97	2.64	1.19
3	Tatisilwai	0.55	0.86	0.64	13.65	1.02	0.29	1.86	0.73	1.94	1.14
4	Hundru	0.65	0.61	0.47	5.30	1.04	0.27	1.22	0.67	0.89	0.84
5	Muri	0.42	0.75	0.40	6.15	0.82	0.24	0.83	0.63	2.88	0.85
6	Chandil	0.85	1.29	1.14	4.65	1.14	0.60	1.23	0.76	1.34	1.19
7	Barabinda	0.93	1.42	1.37	4.15	1.34	0.67	1.33	0.82	1.11	1.26
8	Kanderbera	1.09	1.08	3.59	2.33	1.89	1.09	1.23	0.84	0.71	1.35
9	Tatanagar, Sonari	0.56	0.80	0.75	3.16	1.21	0.49	0.83	0.84	2.00	0.98
10	Tatanagar, Mango	0.52	0.99	0.78	3.25	0.82	0.41	0.86	0.71	2.16	0.94
11	Galudih	0.70	1.77	2.20	2.18	1.31	1.14	0.80	1.24	0.76	1.23
12	Mosabani u/s Sankh	0.33	5.78	0.61	2.79	0.50	1.35	0.94	1.33	0.45	1.02
13	Mosabani d/s Sankh	0.37	3.74	0.60	2.40	0.55	0.54	0.56	0.60	1.67	0.89
14	Shyamsunderpur	0.69	2.99	1.40	2.20	1.05	1.01	0.88	0.98	0.90	1.20
15	Baharagora	0.59	2.38	1.16	2.32	0.80	1.16	0.82	1.03	0.87	1.11
16	Gopiballavpur	0.34	1.28	0.56	2.42	0.46	0.44	0.52	0.55	1.34	0.71
17	Mahapal	0.46	0.96	1.04	1.88	0.70	0.58	0.63	0.63	1.00	0.80
18	Sonakaniya	1.06	1.16	1.82	1.51	1.83	0.56	1.68	0.78	0.49	1.09
19	Jaleswar	0.93	1.22	2.78	1.56	1.31	0.70	1.25	0.76	0.44	1.07
20	Pontai	0.57	0.62	1.11	1.18	0.99	0.36	0.82	0.46	0.33	0.65
21	Kirtania	0.44	0.57	0.83	1.31	0.71	0.37	0.55	0.45	0.33	0.57

Principal component analysis (PCA)

Inter-element correlation was studied in the sediment and the results of PCA are provided in the Table 8. PCA was adopted to assist the interpretation of elemental data. This powerful method allows identifying the different groups of metals that correlate and thus can be considered as having a similar behaviour and common origin (Tahri et al. 2005). The number of significant principal components is selected on the basis of Kaiser criterion with eigenvalue higher than 1 (Kaiser 1960).

The PCA of sediment of Subarnarekha basin shows that the variables are correlated to three principal components in which 83.81 % of the total variance is justified. The number of significant principal components is selected on the basis of Kaiser criterion with eigenvalue higher than 1 (Kaiser 1960). According to this criterion, only first three principal components are retained because the subsequent eigenvalues are less than 1. After Varimax rotation, three components (factors) are extracted. These components are related to the sources of the elements.

The first factor seems to be associated to the earth's crust and the geological formation of the area. The first component with 40.94 % of variance comprises of Fe, Mn, Cr, Zn and Co with high loadings.

The second component (PC2) contributes Cu, Ni and Co at 28.02 %. This factor may be attributed to the mining activities of the area. Extensive Cu mining is associated with the area and may have lead to the concentration of Cu, Ni and Co. Ni and Co have been studied to be associated with Cu mining and smelting (Lantzy and Mackenzie 1979; Nriagu 1989; Barceloux 1999; Ikenaka et al. 2010).

The third component (PC3) explains 14.86 % of variance of our result and is associated with Pb, Zn and Ba. This component seems to be arisen from anthropogenic sources; like the industrial wastes and vehicular pollution. Ba is reported to be associated with many industries like manufacture of alloys, paints, soaps, paper, rubber, glass, ceramics, television picture tubes, brick and tile refractories, plastics stabilizers, fireworks and in lubricating additives. Pb is also known to be caused by anthropogenic activities like industrial uses, waste incineration, coal burning, etc. (Cheng and Hu 2010). Zinc compounds and dust were used principally by the agriculture, chemical, paint, and rubber industries. Zinc is used in a wide variety of materials including galvanizing on iron products, in alloys, in rubber, glazes, enamels, paper and glass (Belliles 1978).

All the three metals are also identified to be allied with vehicular pollution. Barium is present in fuel additives and in fillers, which are used in the brake linings (in the form of barite) and tyres of vehicles (Hopke et al. 1980; Kennedy and Gadd 2000). Pb is one

Table 6 Comparison of metals (mg kg^{-1}) in bed sediment with other studies

Location	Fe	Cu	Cr	Pb	Mn	Ni	Zn	Co	Ba	Reference
Narmada River, India	89,577	188.8	199.3	13.9	1,214	200.3	196.2	25.9	717.6	Sharma (2010)
Tapti River, India	91,128	326.2	212.6	25.0	1,498	205.5	216.7	27.0	1,526.2	Sharma (2010)
Kor river, South west Iran	–	6.5–34.7	40–128	3.1–11.1	–	40–152.5	14.1–59.7	–	–	Sheykhi and Moore (2012)
Xi River, China	–	258.1–1791.5	90.6–516	126.9–1405.8	–	70.5–174.5	503–4929	12.2–21.9	–	Lin et al. (2012)
Cauvery River, India	11,144	11.2	389	4.3	1,763.3	27.7	93.1	1.9	–	Raju et al. (2012)
Buriganga River, Bangladesh	–	231	610	476	–	125	836	33	–	Mohiuddin et al. (2010)
Brahmani River, India	–	12.3	76	11.2	–	28.2	19.7	15.1	–	Rath et al. (2009)
Tapacura River, Brazil	550–32,606	0.96–57.3	0.04–5.9	<0.01–1.31	13.5–157.6	0.06–6.53	4.03–55.2	–	–	Aprile and Bouvy (2008)
Swartkops River, South Africa	–	9.5	11.9	24.7	119.4	–	45.0	–	–	Binning and Baird (2001)
Ohio River, USA	29,800	40.1	43.4	55.6	1,570	51.5	369	–	137	Youger and Mitsch (1989)
Damodar River, India	246.3–3,243.5	–	–	22.6–204.4	57.3–345.9	–	–	–	–	Banerjee and Gupta (2012)
Nandira River, India	–	15.5	214	12.9	–	55.4	51.1	25.3	–	Rath et al. (2009)
ALmendares river, Cuba	–	158	144	93	–	–	262	11.7	–	Olivares-Rieumont et al. (2005)
Subarnarekha River, India	30,800	69	111	75	842	42	100	15	698	Present study

metal of concern for emissions from vehicles (Howard and Sova 1993; Soylak et al. 2002b; Soylak and Turkoglu 1999). Lead is also used for batteries, fuel tanks, solder, seals, bearings, and wheel weights (Sander et al. 2000; Lohse et al. 2001; USDI 2003). Lead also comes from the wear of tyres since Pb oxide is used as filler materials in some overseas makes of tyres (Sharheen 1975). As Zn is used as a vulcanization agent in vehicle tyres (Alloway 1990) and the higher wearing rate at the high temperature in the area may contribute to the high Zn content in the soil (Davis et al. 2001). Zn is also used as minor additive to gasoline and various auto-lubricants and released during combustion and spillage (Ipeaiyeda and Dawodu 2008).

Contamination and toxicity assessment of metals in bed sediments

Enrichment factor analysis indicates the moderate to high contamination of the metals in the Subarnarekha basin (Table 3). The EF ranged from 0.80 to 17.68 for Cu, 0.72 to 3.27 for Cr, 1.43 to 24.69 for Pb, 0.57 to 2.16 for Mn, 0.42 to 4.14 for Ni, 1.13 to 3.37 for Zn, 0.66 to 1.78 for Co and 0.48 to 6.92 for Ba. Of all the metals, enrichment factor indicates highest contamination with respect to Pb (EF 1.43–24.69). The EF shows Cu and Ba to be in minimal to moderate polluted stage except in two locations where the pollution is significant. Zn, Mn, Co, Ni and Cr are found to be at minimal contaminated stage except few locations where moderate contamination is encountered. The contamination of the metals at few locations is attributed to mining, industries and other anthropogenic causes as depicted by PCA.

The geo-accumulation index proposed by Muller (1969) for the quantification of metal accumulation in sediments consists of seven classes (0 to 6), indicating various degrees of enrichment above the background values ranging from unpolluted to very highly polluted sediment quality (Table 4). Variations of the calculated I_{geo} values, based on background value of sediments in the Subarnarekha River, are presented in Fig. 2. The I_{geo} values indicated that at some of the locations all the studied metals falls in the I_{geo} class 0 which represents an unpolluted status of the sediment. I_{geo} values for Pb have been found to be highest and between <0 and 3.19; thus falling under the I_{geo} class of 0 to 4 i.e. unpolluted to highly polluted status. Cu, Cr and Pb at some locations fall in the I_{geo} class 2 with a five-fold increase in concentration thus indicating moderate pollution.

To quantify the magnitude of pollution by different metals, contamination factor (CF) is used. The calculated contamination factors are found to fall in the following sequences (Table 5):

Table 7 Pearson correlation matrix between different metals in the sediment of Subarnarekha river ($n = 21$)

	Fe	Cu	Cr	Pb	Mn	Ni	Zn	Co	Ba
Fe	1.000	−0.220	0.785*	−0.011	0.749*	0.169	0.687*	0.432**	−0.335
Cu		1.000	−0.051	−0.255	−0.213	0.772*	−0.124	0.616*	−0.289
Cr			1.000	−0.306	0.703*	0.475**	0.318	0.497**	−0.475
Pb				1.000	−0.100	−0.462	0.573*	−0.030	0.581*
Mn					1.000	0.200	0.499*	0.527*	−0.272
Ni						1.000	−0.106	0.707*	−0.484
Zn							1.000	0.207	−0.017
Co								1.000	−0.047
Ba									1.000

*Correlation significant at the 0.01 level (two tailed)

**Correlation significant at the 0.05 level (two tailed)

Table 8 Principal component loadings (varimax normalized) for the metals in the bed sediment of Subarnarekha River

Elements	PC1	PC2	PC3
Fe	0.946	-2.326×10^{-2}	-5.462×10^{-2}
Cu	−0.267	0.867	−0.137
Cr	0.833	0.216	−0.351
Pb	5.547×10^{-2}	−0.149	0.938
Mn	0.880	2.307×10^{-2}	−0.104
Ni	0.176	0.906	−0.368
Zn	0.704	-3.598×10^{-2}	0.519
Co	0.534	0.713	9.648×10^{-2}
Ba	−0.304	−0.165	0.756
Eigenvalues	3.684	2.522	1.337
% Total variance	40.935	28.024	14.855
Cumulative variance	40.935	68.959	83.814

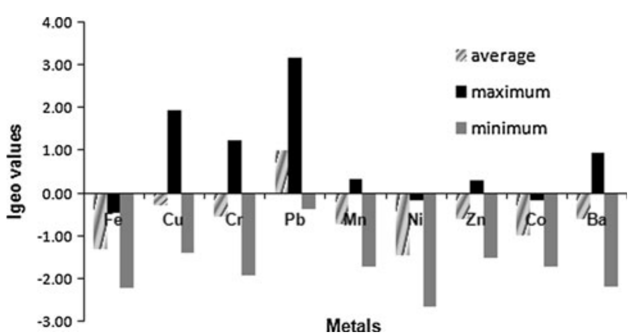

Fig. 2 I_{geo} values (maximum, minimum, average) of the metals in the study area

$$Pb > Cu > Cr > Ba > Zn > Mn > Co > Fe > Ni$$

To evaluate the sediment pollution severity, PLI was used to find out the mutual pollution effect at different stations by different metals. A PLI value close to 1 indicates metal loads near the background level, while values >1 indicate pollution (Cabrera et al. 1999). In Subarnarekha River, PLI value ranges from 0.57 to 1.35 with an average of 1.01. The mutual pollution effect of different metals at different sampling locations in the river basin is depicted in Fig. 3. Thus, the findings, taking into account of EF, I_{geo}, and PLI, confirm that metal pollution in the Subarnarekha River is moderately serious. A previous study by Upadhyay et al. (2006) in the Subarnarekha River basin also suggested similar results. Though the study was confined to only 4 locations in the East Singhbhum district and 4 metals (Cu, Pb, Zn and Cd), the results confirmed moderate to high pollution for Zn and moderate pollution in case of Pb and Zn. However, the present study suggests that the metal pollution in the sediments of Subarnarekha River have increased with the passing years.

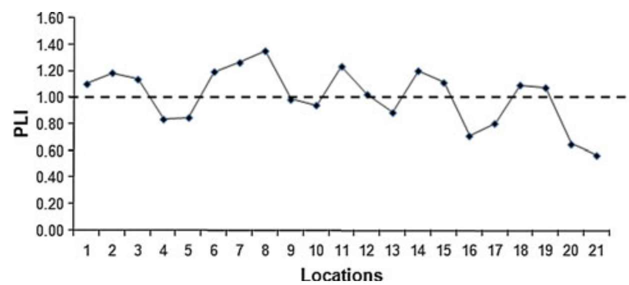

Fig. 3 Pollution load index (PLI) at different sampling stations along the Subarnarekha River basin

Most of the toxic trace metals show considerably higher concentration at the sites under the influence of anthropogenic activities in the Subarnarekha Basin. Influx of large volume of domestic sewage and industrial effluents from the urban settlements, mining activities, vehicular pollution are the major sources of metal pollution. The upper reaches of the Subarnarekha river basin is dominated by various kinds of industrial setups while mid stream witness several mining activities with respect to copper, uranium, etc. The sewerage from the Ranchi, Muri, Jamshedpur, Ghatsila, Jaleswar cities also drains in the river polluting the river.

Conclusions

Distribution characteristics of metal concentrations and consequently the sediment quality of the Subarnarekha River basin is the result of combined influence of natural conditions, i.e. geological backgrounds and human activity. Taking into account of the EF, I_{geo} and PLI values, it can be concluded that the investigated river basin is moderately to highly polluted with metals. In general, the contamination of Pb and Cu was more serious than that of Ni, Zn, Co and Ba, whereas the presence of Fe, Mn and Cr might be primarily from natural sources. The higher values of metals in the rivers imply additional inputs from unusual geochemical enrichment, which in turn may be attributed to the geological sources coupled with anthropogenic inputs from the catchments. PCA outcome of three factors together explained 83.8 % of the variance with >1 initial eigenvalue also indicated both innate and anthropogenic activities are contributing factors as source of metal profusion in Subarnarekha river basin. This study has revealed that enhanced concentrations of metals are recorded near to industrial and mining establishments indicating that their concentrations have been strongly affected by anthropogenic influences. Thus, it is reasonable to conclude that the increased concentrations of metals in the sediments of the Subarnarekha river is considerably due to direct discharge of industrial, urban and mining wastes into the river. Overall, the toxic trace elements in the sediment of the Subarnarekha River, especially for Pb and Cu, pose a high potential for severe impact on aquatic plants and other organisms and could act as secondary sources of pollution in the overlying water column. The results of this study indicate that monitoring and immediate managerial measures must be taken to avoid further potentially toxic metal pollution of river sediments. Continuous monitoring and further studies of the area are recommended to ascertain long-term effects. Further investigation is also recommended for seasonal variability of toxic metals in the study area along with isotopic tracing of the metals.

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