

Source and distribution of trace metals and nutrients in Narmada and Tapti river basins, India

Sanjay Kumar Sharma · V. Subramanian

Received: 27 March 2009 / Accepted: 5 January 2010 / Published online: 4 February 2010
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Abstract The study was designed to establish the distributions of trace metals, dissolved organic carbon, and inorganic nutrients as well as to assess the extent of anthropogenic inputs into the Narmada and Tapti rivers. Water and sediment qualities are variable in the rivers, and there are major pollution problems at certain locations, mainly associated with urban and industrial centers. The metal concentrations of samples of the aquatic compartments investigated were close to the maximum permissible concentration for the survival of aquatic life, except for higher values of Cu ($5\text{--}763\ \mu\text{g l}^{-1}$), Pb ($24\text{--}376\ \mu\text{g l}^{-1}$), Zn ($24\text{--}730\ \mu\text{g l}^{-1}$), and Cr ($70\text{--}740\ \mu\text{g l}^{-1}$) and for drinking water except for elevated concentrations of metals such as Pb, Fe ($850\text{--}2,060\ \mu\text{g l}^{-1}$), Cr, and Ni ($20\text{--}120\ \mu\text{g l}^{-1}$). In general, the concentrations of trace metals in the rivers vary down stream which may affect the “health” of the aquatic ecosystem and may also affect the health of the rural community that depends on the untreated river water directly for domestic use. The assessment of EF, I_{geo} , and PLI in the sediments reveals overall moderate pollution in the river basins.

Keywords Trace metals · Nutrients · Water and sediments · Narmada and Tapti rivers

Introduction

Trace metals have been referred to as common pollutants, which are widely distributed in the pristine river

catchments originating from natural sources and processes as chemical weathering, soil erosion, fallout of aerosols from marine, volcanic or arid soils sources (Gaillardet et al. 2003). However, the level of these metals in the environment has increased tremendously as a result of human inputs and activities (Merian 1991). For some metals, natural and anthropogenic inputs are of the same order (for example Hg and Cd), whereas for others (for example Pb) inputs due to human activities dwarf natural inputs (Clark 2001). Heavy metals discharged into a river system by natural or anthropogenic sources during their transport are distributed between the aqueous phase and sediments. Heavy metals are of high ecological significance since they are not removed from water as a result of self purification, but accumulate in reservoirs and enter the food chain (Loska and Wiechula 2003). The suspended and bed sediments of a river buffer higher metal concentrations of the water, particularly by adsorption and precipitation (Forstner and Muller 1973). Changing environmental conditions such as pH, redox potential or the presence of organic chelators in the system may render the remobilization of metals from sediments (Calmano et al. 1993). Thus, sediment quality is a widely utilized method of environmental assessment. Natural sediment formed during weathering processes might be modified markedly during transportation and deposition by chemicals of anthropogenic origin. Apparently, higher the metal concentrations in the sediments, greater the quantity of metals that could be desorbed from the sediments into the water phase by physiochemical processes (Suriya and Branica 1995). River sediments are also a major sink as well as source of nutrients. Suspended sediments play an important role in the transport of nutrients and contaminants, in water–sediment interactions influencing the river water quality and as non-point source pollutants (Martin and Meybeck 1979).

S. K. Sharma (✉) · V. Subramanian
School of Environmental Sciences, Jawaharlal Nehru University,
New Delhi 110067, India
e-mail: sanju.jnu@gmail.com

Trace metals are important in aquatic systems because of their demonstrated effects as both essential at low levels and toxic agents at higher levels for biota. Thus, the presence of these metals in the aquatic ecosystem has far-reaching implications directly to the biota and the food chain. Obviously, the chemical status of the river would have its influence on the receiving land, which might possibly reflect on the plant cultivated on such land. On the other hand, aquatic organisms may bioaccumulate and bioconcentrate environmental contaminants to more than 1,000,000 times the concentrations detected in the water column (USEPA 1995a, b). Elements like Cu, Zn, Fe, Mn, and Co, which are required for normal biochemical functions, could become toxic when present in anomalous concentrations and, according to Bowen (1966), may result in poisoning of enzyme. Interest in metals like Zn and Cu, which are required for metabolic activity in organisms, lies in the narrow “window” between their essentiality and toxicity, but others like Cd and Pb exhibit extreme toxicity even at trace levels (Iwashita and Shimamura 2003). The metal contribution from Indian rivers, which carry 20% of the global supply of sediments to the oceans, has not been properly assessed (Ramanathan et al. 1988). The metal concentrations in estuarine sediment on the West and East Coast of India have been briefly reported by Borole et al. (1982) and Subramanian et al. (1988).

Data on nutrients such as carbon (C), nitrogen (N), phosphorus (P), sulfur (S), and silica (Si) in sediments and water are rather limited in Indian rivers (Subramanian et al. 2006). The nature and flux of organic C and P in Indian rivers has been studied by few authors (Gupta et al. 1997; Ramesh et al. 1995). Study of major ions in the waters of Narmada and Tapi rivers has already been reported (Sharma and Subramanian 2008), and limited data exist on trace metal pollution in sediments of the Narmada river basin (Jain et al. 2008). The objective of this study, therefore, was to establish the nature of distribution of dissolved trace metals (Cd, Cu, Pb, Zn, Fe, Ni, Cr, Mn, and As) and nutrients such as dissolved organic carbon (DOC), dissolved inorganic nitrogen (NO_3^-), dissolved inorganic phosphorus (PO_4^{3-}), and dissolved silica (H_4SiO_4) highlighting the potential risk of their elevated concentrations on the aquatic organism and human beings. This paper also examines the trace metal pollution and nutrients concentration in sediments and their distributions.

Materials and methods

Description of the river catchments

Narmada and Tapi rivers are the two important rivers of central India, flowing into the Arabian Sea (Fig. 1).

Narmada (1,312 km) is the fifth largest river in India and largest west flowing river of Indian peninsula originating from Maikal ranges in the Shahdol district of Madhya Pradesh at Amarkantak at an elevation of 900 m. The river basin extends over an area of 89,000 km² (Alagarsamy and Zhang 2005) and lies between latitudes 21°70'N and 23°45'N and between longitudes 73°35'E and 81°51'E with a mean elevation of 760 m and crosses the state, passing swiftly through a narrow valley between the Vindhyan Range and spurs of the Satpura Range. Lying in the northern extremity of the Deccan Plateau, the basin covers a large area in the state of Madhya Pradesh and Gujarat and a comparatively smaller area in Maharashtra. The area belongs to the Humid Tropical Zone and physiographically it is divided into hilly and plain regions and dominated by black cotton soils. The normal annual rainfall for the basin works out to 1,250 mm. Nearly 90% of this is received during southwest monsoon period (June–September), out of which about 60% is received in the month of July and August.

The shorter Tapi (724 km) follows a generally parallel course to the south of the Narmada, flowing through the states of Maharashtra and Gujarat on its way into the Gulf of Cambay. The river originates near Multai in the Betul district of Madhya Pradesh at an elevation of 752 m. The river basin extends over an area of about 61,145 km² (Alagarsamy and Zhang 2005) and lies between latitudes 21°33'N and 22°01'N and between longitudes 74°30'E and 78°21'E in the northern extremity of the Deccan Plateau, like the Narmada basin. The catchment area is distributed in the states of Maharashtra, Madhya Pradesh, and a comparatively smaller area in Gujarat. The average annual rainfall is 830 mm out of which 90% falls during the southwest monsoon period.

Both these rivers are perennial; however, most of their annual discharge occurs during the southwest monsoon. With annual discharges of 47.3×10^9 and 18.9×10^9 m³, respectively (Alagarsamy and Zhang 2005), the entire region of the Narmada and Tapi river basins is subjected yearly (usually from June to September) to the monsoon, characterized by heavy rains and the consequent transport of huge quantities of particles by surficial waters into the rivers.

The upper catchments are essentially pristine forest. The middle catchments are dominated by pastoral farming and have rural population. There are mining and mineral industries discharging into the river systems in the upper reaches. Marble and coal mining activities are going on prevalently in the upper catchments of the Narmada river. In the river mouth region, heavy industries like petrochemical industries are located. Practically, there are no mining and mineral industries, except cotton and fabric industries located in the downstream of the Tapi river

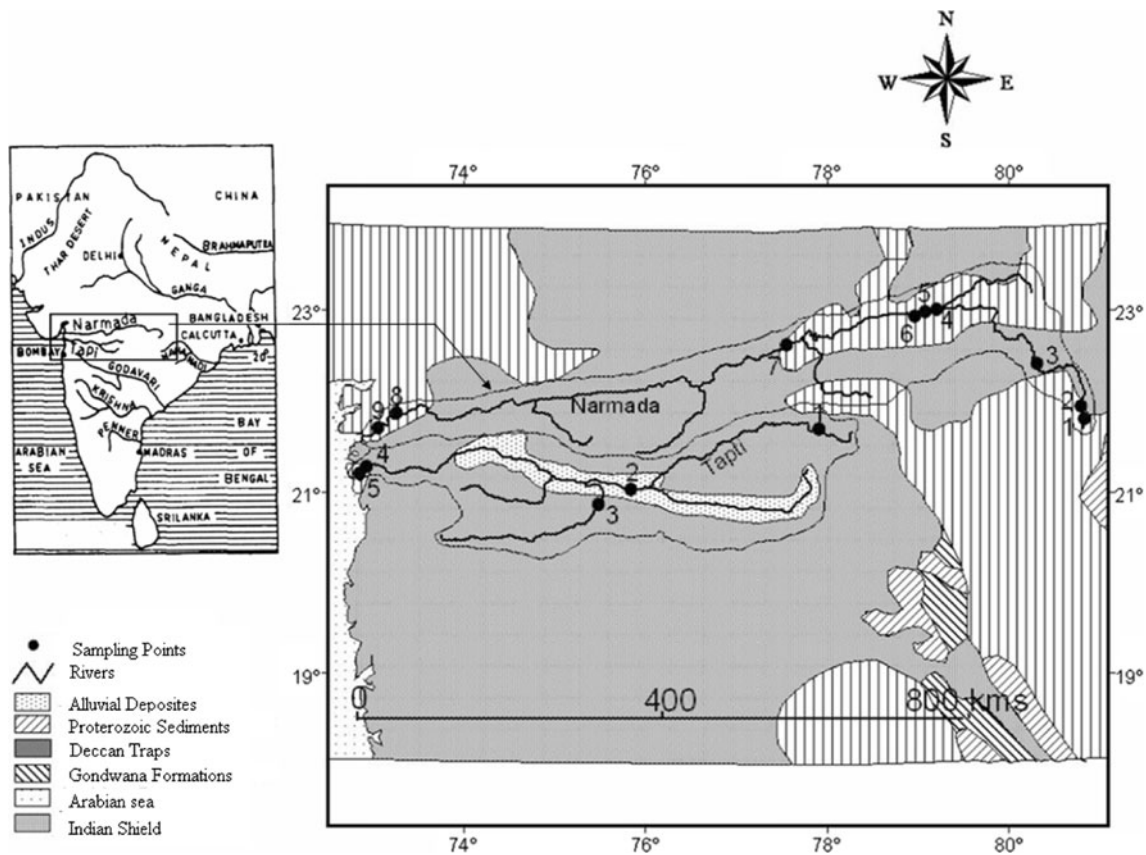


Fig. 1 The Narmada and Tapi drainage basins and the locations of sampling stations. The field circles represent main-channel stations [Narmada: 1 Amarkantak1; 2 Amarkantak2; 3 Mandla; 4 Bheraghat, 5

Guarighat; 6 Tilwaraghat (Jabalpur); 7 Hosangabad; 8 Jhaneshwar; 9 Bharuch] [Tapti: 1 Betul; 2 Bhusawal; 3 Jalgaon; 4 Kojway; 5 Gandhibagh (Surat)]

basin, whereas upstream and midstream regions are forested and agricultural. The downstream chemical composition of the river basins may also allow two constraints: namely inputs from agriculture (fertilizers) and inputs from communal sources. The former is a function of total cultivated area, whereas the latter depends on the population density. The total area under cultivation in the Narmada basin is about 44,990 km², and the population density in the basin area is 170 inhabitants/km²; out of this, in Madhya Pradesh it is 149 inhabitants/km², and it is 203 inhabitants/km², and 319 inhabitants/km² in Maharashtra and Gujarat, respectively. In the Tapi basin, the population density is 233 inhabitants/km². The population densities in these rivers are significantly lower than the Indian national population average of 324 persons/km² (CPCB 1994). In Amarkantak, the origination point of the Narmada river, the population utilizing water increases seasonally during specific periods for religious functions in the river itself. Similarly, population increases temporarily in the rivers mouth regions, i.e., Surat and Ankaleshwar. In Ankaleshwar, near Bharuch, the downstream region of the Narmada river, there are oil exploitation wells, and in the

midstream regions, particularly in and around Jabalpur, marble mining activities are prevalent.

Geology

Narmada and Tapi rivers flow through similar geological terrains. They initially flow through basaltic terrains of the Deccan Traps and then through alluvial deposits before entering the Gulf of Cambay. Though these rivers predominantly drain Deccan basalts, parts of their basins are in the Indian Shield: Vindhyan carbonates, sediments, and alluvial deposits (Dessert et al. 2001). Further, these rivers flow through areas more prone to inputs from groundwater and geothermal water. A number of hydrothermal springs have been reported along the Narmada–Tapti lineament (Minissale et al. 2000). Tectonic and flood processes constitute the most important controls on the channel morphology of the Narmada and Tapi rivers. Tapi flows initially through basaltic terrains of the Deccan Traps and then through alluvial deposits of unconsolidated fine sand, silts, and clay before opening via the Gulf of Cambay into the Arabian Sea.

The Deccan Traps are one of the largest continental flood basalt provinces formed during the Gondwanaland break-up, located at the centre-west of the Indian peninsula. The basalts of the Narmada and Tapti basins are essentially of tholeiitic composition and contain phenocrysts of altered olivine, plagioclase, clinopyroxene, opaque minerals, and altered glass (Vigier et al. 2005). Deccan lavas overlie a complex Archaean and Proterozoic basement along the southern and southeastern periphery of the province. In the northern and northeastern parts of the province, i.e., central India, they overlie diverse geological formations: the Vindhyan sedimentary basin (mid–late Proterozoic), the Gondwana sedimentary basin (Carboniferous–Jurassic, early Cretaceous), and Archaean and early Proterozoic crystalline rocks (granites, gneisses, and metasediments). In the central part, Vindhyan rocks and the Deccan Traps are present in the north of the Narmada river, and to the south, Archaean rocks are exposed and overlain by the Gondwana formations.

Sampling and chemical analysis

The water and sediment samples were collected from the prefixed stations along the waterways of the Narmada and Tapti river basins. Two sampling events (monsoon and post-monsoon) were conducted during the year 2004 in order to examine the seasonal variability of trace metals and nutrients in the Narmada–Tapti river waters. Total of nine and five sampling sites were established on Narmada and Tapti rivers, respectively. Sampling locations along the rivers are shown in Fig. 1.

The water samples were collected in polypropylene bottles treated with 10% HNO_3 and rinsed well with deionized water prior to use. Electrical conductivity (EC) and pH were measured in situ by pH-electrode and conductivity meter, respectively, during the sampling. The water samples were filtered in situ through 0.45- μm Millipore membrane filter paper. About 100 ml of filtered sample was acidified with HNO_3 to a pH ~ 2 to stabilize the dissolved metals, and rest of the portion was kept unacidified. The samples were preserved at 4°C in the laboratory for trace metal and nutrients analysis. The trace metal analysis was carried out using a Shimadzu AA-6800 Atomic Absorption Spectrometer in graphite furnace mode. The Arsenic (As) was analyzed using Shimadzu AA-6800 Atomic Absorption Spectrometer coupled with hydride generator. The Merck standards were used for the calibration for the elements analyzed, and the reproducibility of the instrument was 90–95%. Parameters such as PO_4^{3-} and NO_3^- were determined in the unacidified fractions by ion chromatography. Dissolved silica (H_4SiO_4) and DOC were determined using a Cecil spectrophotometer (model no. 594) from the unacidified water samples by the

molybdosilicate method and by the vial digestion method using a chemical oxygen demand reactor, respectively. Bed surficial sediment samples were collected with a plastic spade by scooping from the upper 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), properly mixed and powdered and were kept in cold room at 4°C. For the suspended sediment, 1 l of running water was collected in a plastic bucket at a depth of 50–100 cm from the water surface and filtered through 0.45- μm membrane filter paper, and the samples were dried. The finally ground homogenized bed sediments and suspended sediments were taken in the beaker and heated with 30% (v/v) H_2O_2 for removal of organic matter. The major and trace elements in the sediments were determined by wavelength dispersive X-ray fluorescence (WD-XRF) Spectrometry and energy dispersive X-ray fluorescence (ED-XRF) spectrometry, respectively. The Canadian soil standards (SO-1, SO-2, SO-3, and SO-4) were analyzed as unknown samples for major and trace elements, and the reproducibility was found in the range of 90–95%. Total nitrogen (TN) was determined by Kjeldahl method. Carbon and Sulfur were analyzed using ELTRA (CS-1000) Carbon–Sulfur analyzer. Before analysis, sediment samples were made free of halogens by washing with deionized water. The untreated samples were used for determining total carbon and sulfur. For removing organic fraction, samples were treated with 30% (v/v) H_2O_2 . The treated samples were used for determining inorganic fraction of carbon and sulfur. Phosphorus in sediments was determined by the method of solution A (Shapiro 1975).

Results and discussion

Dissolved trace metals and nutrients in water

The analytical results including dissolved trace metals and nutrient concentrations along the Narmada and Tapti river basins are presented in Table 1. The elemental concentrations in river waters are different during the two investigation periods; the concentrations are higher during the post-monsoon season than in the monsoon season. The spatial distributions of dissolved trace metal concentrations along the rivers are depicted in Fig. 2, which reflects their inputs. In general, the concentrations of trace metals in Narmada and Tapti rivers vary down stream from one place to another according to the land-use nature. The concentration of dissolved metals shows decreased values in the monsoon season as compared to post-monsoon season, which is perhaps due to the dilution effect of the rain fall

Table 1 Chemical composition of Narmada and Tapti river waters compared with water quality criteria for drinking water quality and protection of aquatic life

Samples ^a	pH	EC	NO ₃ ⁻	PO ₄ ³⁻	H ₄ SiO ₄	DOC	Cd	Cu	Pb	Zn	Fe	Ni	Cr	Mn	As
Narmada															
1 ^F _a	6.7	125	3.02	0.11	6.40	33.88	3	130	380	180	1,980	110	220	170	5
b	6.8	240	3.18	0.01	8.91	11.76	3	150	320	180	2,030	120	190	190	7
2 ^F _a	7.1	89	2.15	0.23	7.42	3.47	1	40	50	140	970	90	190	190	6
b	6.9	150	3.04	0.02	11.93	7.21	2	50	70	170	1,240	110	240	220	6
3 ^{F + A} _a	7.7	178	1.82	0.38	11.14	4.66	1	60	60	90	950	30	150	60	5
b	8.0	160	1.72	0.12	12.91	6.66	1	60	60	110	1,120	50	160	50	6
4 ^U _a	7.7	73	1.35	0.27	12.40	0.29	1	90	40	70	1,860	40	160	80	4
b	7.5	220	1.93	0.01	14.30	5.15	0	100	20	90	1,970	60	180	70	5
5 ^U _a	7.8	142	0.18	0.12	12.40	3.76	1	30	50	70	1,410	30	160	40	4
b	7.8	200	0.70	0.11	15.28	4.50	1	30	30	80	1,680	60	740	100	6
6 ^U _a	7.8	136	0.52	BDL	11.88	5.16	2	40	50	60	1,220	30	170	30	4
b	7.4	220	0.88	BDL	12.67	6.56	1	80	70	730	1,930	50	190	90	8
7 ^U _a	7.6	177	0.71	0.18	12.12	4.03	9	10	230	640	1,750	60	160	70	7
b	8.1	260	0.50	0.08	10.72	5.80	10	10	250	80	1,890	90	180	90	5
8 ^U _a	8.1	109	0.49	0.27	12.21	1.71	9	760	30	30	1,270	30	70	40	4
b	8.2	340	0.57	0.19	10.81	8.62	14	580	40	50	1,530	50	100	40	6
9 ^U _a	8.1	216	11.52	0.40	14.21	0.03	1	70	30	30	1,540	30	90	70	4
b	7.8	390	1.34	0.30	10.30	8.18	1	90	20	100	1,730	50	90	70	4
Tapti															
1 ^F _a	7.9	240	0.73	0.71	13.19	9.61	1	10	50	680	1,620	70	80	50	5
b	8.0	280	0.44	0.42	15.00	7.96	1	10	50	700	1,650	70	70	50	4
2 ^U _a	8.1	430	2.29	0.47	20.00	5.66	1	10	50	30	1,330	40	180	50	5
b	9.1	660	1.68	0.21	30.00	11.22	0	10	40	20	850	20	180	40	4
3 ^U _a	7.9	410	4.68	0.39	17.74	5.19	1	30	50	30	1,510	30	140	30	5
b	8.4	620	4.96	0.17	13.47	3.74	1	60	50	50	1,660	30	220	20	6
4 ^U _a	8.1	490	0.17	0.40	14.12	5.30	1	740	60	390	1,790	50	120	10	5
b	7.8	430	1.32	0.00	13.33	9.81	2	740	70	390	2,020	100	180	20	6
5 ^U _a	7.6	1,340	3.15	0.61	14.26	3.60	2	150	80	130	1,980	50	150	10	5
b	7.4	1,010	2.84	0.09	11.60	13.93	3	180	100	140	2,060	80	290	40	6
LLD							1	1	4	2	2	2	1	4	4
Water quality criteria (drinking water quality)															
India ^b							10	1,500	50	5,000	1,000	NA	50	300	50
WHO ^c							3	2,000	10	3,000	300	20	50	400	10
USA ^d							5	1,300	15	2,000	300	100	100	NA	10
Water quality criteria (protection of aquatic life)															
USA ^e							5	4	14	36	NA	145	16	NA	340

All values are in mg/L, except trace metals (µg l⁻¹), pH, and EC (µS cm⁻¹)

F forest, A agriculture, U urban, LLD lower limits of detection, BDL below detection limit

^a Seasons (a, monsoon; b, post-monsoon)

^b BIS (2003)

^c WHO (2003)

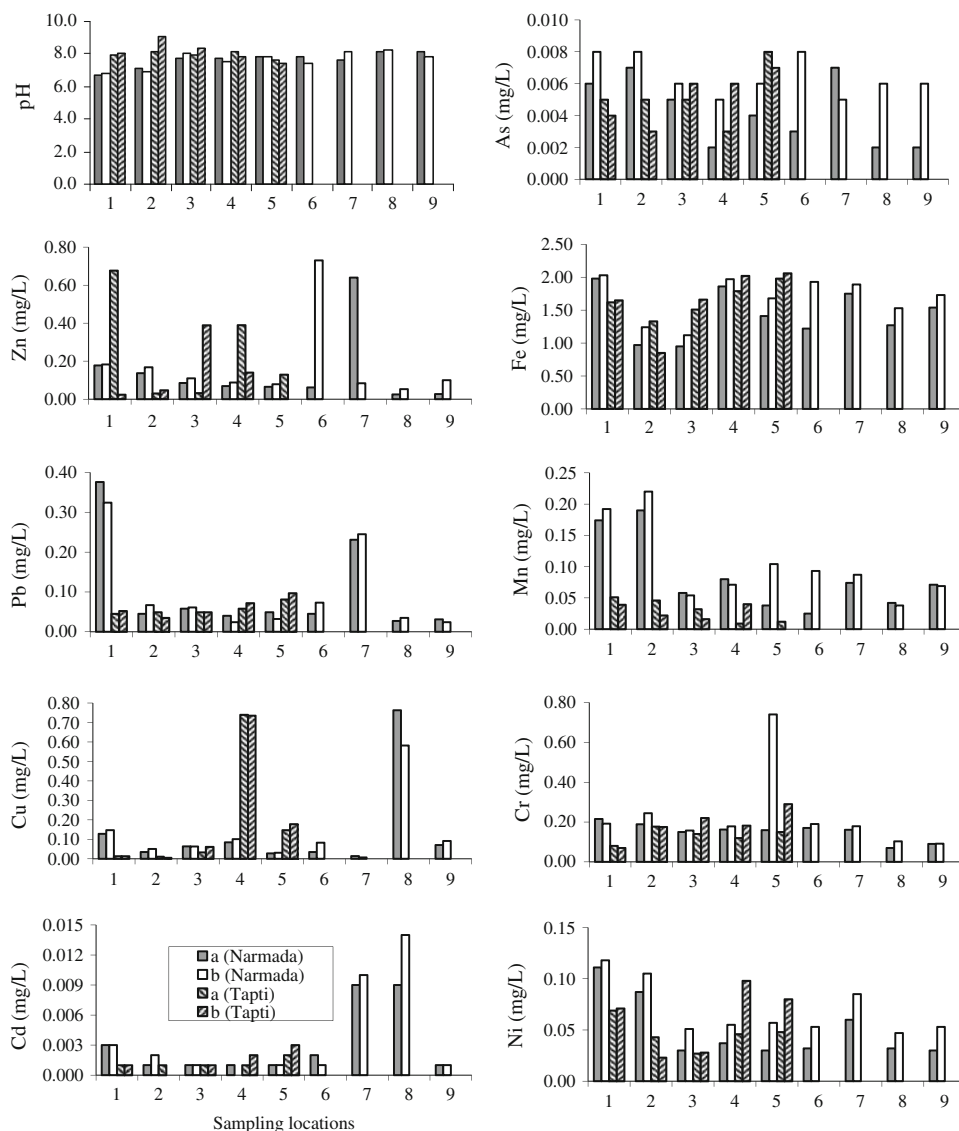
^d USEPA (2000)

^e USEPA (2001a)

and consequent increased flow of water in the basins. Thus, it is evident from the above discussion that the concentration of trace metals in water is also influenced by the

flow of water. The elevated concentrations of dissolved metals at some stations mainly the downstream sampling points (6, 7, and 8 in Narmada river; 4 and 5 in Tapti river),

Fig. 2 Distribution of dissolved trace metal concentrations for monsoon (a) and post-monsoon (b) seasons along the Narmada and Tapti river basins



except for Fe, Mn, Ni, Cr, Pb, Zn, and As which show higher values in the upper reaches also (Table 1; Fig. 2), could be attributed to the increased urbanization, industrialization, and agricultural activities in the downstream regions.

The decrease of metal concentrations with increase in pH may result from an increased adsorption when pH increases according to the surface complexation theory (Schindler and Stumm 1987) or simply based on ion solubility. Metal concentrations in the two river basins are generally low with pH more than 7.5, with few exceptions, probably limited by precipitation of the respective metal oxides. Generally, low DOC at the time of sampling reflects the low contribution of organic complexation and colloidal phases to trace metal transport. In general, metal concentrations of water samples are below or close to the maximum permitted concentration for drinking water (BIS

2003; WHO 2003; USEPA 2000), except for elevated Pb, Fe, and Cr concentrations. Ni concentration is higher than the permissible drinking water standard of WHO (2003). The dissolved concentrations of Cu, Pb, Zn, and Cr exceed the guidelines values for protection of aquatic life (USEPA 2001a).

Under natural conditions, the dissolved phosphate (PO_4^{3-}) concentration should not exceed 0.5 mg l^{-1} , as the solubility of phosphate mineral is limiting (Subramanian 1984). The average PO_4^{3-} concentrations are 0.2 and 0.3 mg l^{-1} , respectively, in Narmada and Tapti rivers, exceeding the Indian average of 0.12 mg l^{-1} (Subramanian 1984). The high concentration of PO_4^{3-} at sites 1 and 5 in Tapti river, especially in the monsoon season, is attributed to addition from anthropogenic sources, such as domestic sewage, detergent, industrial and agricultural effluents, and excessive soil phosphorus runoff. At levels higher than

0.005 mg l⁻¹, there is excessive plant growth (Sawyer et al. 1994). The NO₃⁻ concentrations vary from 0.18 to 11.52 mg l⁻¹ in Narmada river and from 0.17 to 4.96 mg l⁻¹ in Tapti river with average values of 2.0 and 2.2 mg l⁻¹, respectively, which are far below the standard drinking water quality guideline (45 mg l⁻¹) suggested by BIS and World Health Organization (WHO). Comparatively high concentration of NO₃⁻ at some of the sampling points in these rivers can be attributed to anthropogenic activities, the likely sources being NPK fertilizers, sewage, and industrial wastes which undergo biological oxidation in the water. The NO₃⁻ concentrations are typically low and less than 10 mg l⁻¹, which is the maximum contaminant level in public drinking water supply (USEPA 1976). The concentrations of DOC and H₄SiO₄ generally show increased values in post-monsoon season. Generally low DOC values (<5 mg l⁻¹) indicate a small contribution of vegetation to water chemistry. The average DOC concentrations are 6.75 and 7.60 mg l⁻¹ in the Narmada and Tapti rivers, respectively, which are higher than the world average of 4.2 mg l⁻¹ estimated by Meybeck et al. (1996) and significantly lower than measured values in humid tropical rivers such as Mekong (10–20 mg l⁻¹) (Viers et al. 1997) and 10.5 mg l⁻¹ in Congo (Seyler et al. 1995). Further, the average DOC concentrations in the Narmada and Tapti river basins exceed the DOC (2.7 mg l⁻¹) in Rio Branco (clear water) and nearly correspond to the DOC concentrations (7.7–8.6 mg l⁻¹) in Rio Solimoes (white water) but are well below the mean value (11.4 mg l⁻¹) reported in the Negro basin (black water) (Kuchler et al. 2000). These rivers are, therefore, non-organic in nature. The dissolved silica (H₄SiO₄) concentrations range from 6.4 to 16.3 mg l⁻¹ with an average of 11.6 mg l⁻¹ in Narmada river and from 11.6 to 30.0 mg l⁻¹ with an average of 16.3 mg l⁻¹ in Tapti river, which are higher than the Indian average, i.e., 7 mg l⁻¹ (Subramanian et al. 1987) and the global average concentration, i.e., 10.8 mg l⁻¹ (Meybeck et al. 1996). The high concentration of dissolved silica in the river basins reflects the contribution of weathering of silicate rocks that underlie the basins and soil erosion.

Distribution of metals, C, N, S, and P in suspended and bed sediments

The suspended and bed sediments have also been investigated in addition to water samples. The distribution of metals and nutrients (C, N, S, and P) in their different chemical forms and in suspended and bed sediments of Narmada and Tapti rivers is given in Tables 2 and 3, respectively.

The SiO₂ and Al₂O₃ contents in the Narmada and Tapti rivers show almost homogenous variation downstream, and

the same holds true in the case of Na₂O and K₂O. In Narmada river, the strong positive correlation of Na₂O and K₂O with SiO₂ ($r = 0.68$; $p = 0.05$ and $r = 0.51$; $p = 0.09$, respectively), and with Al₂O₃ ($r = 0.57$; $p = 0.08$ and $r = 0.84$; $p = 0.01$, respectively) suggest silicate as the common source rock. In general, sediments having lower silica contents show higher values of CaO. There is also considerable negative correlation of CaO and MgO with silica ($r = -0.62$; $p = 0.08$ and $r = -0.31$; $p = 0.27$, respectively) and of CaO with Al₂O₃ ($r = -0.53$; $p = 0.11$), but MgO shows poor correlation with Al₂O₃ ($r = 0.10$; $p = 0.43$). The same trend is observed in the river Tapti, where Na₂O and K₂O are strongly correlated with SiO₂ ($r = 0.98$; $p = 0.00$ and $r = 0.90$; $p = 0.01$, respectively) and also with Al₂O₃ ($r = 0.51$; $p = 0.16$ and $r = 0.56$; $p = 0.15$, respectively). CaO and MgO show negative correlation with silica ($r = -0.94$; $p = 0.02$ and $r = -0.67$; $p = 0.07$, respectively) and with Al₂O₃ ($r = -0.44$; $p = 0.19$ and $r = -0.67$; $p = 0.07$, respectively). Although at 95% confidence level, in Narmada river, Na₂O and K₂O show significant correlation with SiO₂ and Al₂O₃, respectively, whereas Na₂O, K₂O, and CaO show significant correlation with SiO₂ in Tapti river. If 80% confidence level is considered, correlation is significant in most of the cases except, MgO with SiO₂ and Al₂O₃ in Narmada river. Thus, considering the above-mentioned facts and figures, it can be inferred that carbonate also acts as a contributing source rock for the chemical composition of the Narmada and Tapti river basins. The strong correlation observed for SiO₂, Al₂O₃, Na₂O, and K₂O in the sediments suggest a similar mobility and probable transport in aluminosilicate phases.

The peninsular region is characterized by the basaltic Deccan Traps in the central part and hard rocks in the southern part. However, even in watersheds characterized by the predominance of silicate rocks, it was found that carbonate rocks present in veins and thin layers determine the basin chemistry (Quade et al. 2003). This is due to the fact that the rate of carbonate weathering dominates that of silicate weathering in a river basin (Gaillardet et al. 1999). This has been reported by Sharma and Subramanian (2008) which conclude that the chemical composition of Narmada river is more controlled by the carbonate lithology of the basin, which is present as intrusive complexes and dykes, along the minor rift zones in the Deccan Volcanic Province with neighbouring carbonate–alkaline complexes.

The degree of weathering can be quantified by chemical index of alteration (CIA) as defined by Nesbitt and Young (1982). The CIA values for average shales range from 70 to 75 which reflect the composition of muscovite, illites, and smectite minerals. In case of intensively weathered rock, CIA approaches 100. In Narmada river, this value varies from 58.1 to 70.3 with an average of 62.9, whereas it

Table 2 Chemical composition of bed and suspended sediments of Narmada and Tapi rivers compared with averages of Indian, World, Shale standard, Continental crust, and those measured in this study as local geochemical background

Oxides (%)	Narmada										Tapi					Indian average ^a	World average ^b	Shale Average ^c	Continental crust ^d	Geochemical background average ^e	LLD					
	Bed sediments					Suspended sediment					Bed sediments											Suspended sediment				
	1 ^F	3 ^F + A	4 ^U	7 ^U	8 ^U	9 ^U	Average	8 ^F	1 ^F	2 ^U	3 ^U	4 ^U	5 ^U	Average	5 ^F											
SiO ₂	59.60	56.90	54.01	59.20	57.34	49.95	56.17	55.86	52.90	49.70	48.75	56.77	49.90	51.45	50.70	50,000	94,000	80,000	82,300	76,810	8.70					
Al ₂ O ₃	14.20	13.50	13.00	13.95	13.20	13.60	13.58	13.40	14.30	14.00	13.02	17.40	16.40	15.22	16.20	29,983	48,000	47,200	35,000	49,300	1.40					
Na ₂ O	2.51	2.35	1.72	2.95	1.59	1.47	2.10	2.77	2.22	1.23	1.30	2.83	1.32	1.73	1.50	605	1,050	850.0	600.0	821	1.50					
K ₂ O	1.60	1.02	1.09	1.69	1.15	1.24	1.30	1.09	1.55	1.05	0.88	1.84	0.89	1.29	1.50	3,450	5,600	4,600	3,000	5,530	1.60					
CaO	3.50	2.32	5.65	3.85	5.15	5.72	4.37	5.80	4.23	7.40	8.36	3.31	7.40	6.40	7.70	NA	5	13.0	1.5	1.7	0.25					
MgO	3.80	2.62	3.02	1.97	2.80	3.44	2.94	3.40	3.92	5.80	6.80	2.97	3.12	4.80	6.20	NA	0.1	0.3	0.1	0.4	0.28					
ClA	65.11	70.35	60.58	62.17	62.59	61.73	63.75	58.11	64.13	59.12	55.26	68.56	63.05	61.72	60.22	NA	0.1	0.3	0.1	0.4	0.28					
Elements (mg kg ⁻¹)																										
Al	75,176	71,471	68,824	73,853	69,882	72,000	71,868	70,941	75,706	74,118	68,929	92,118	86,824	80,576	85,765	50,000	94,000	80,000	82,300	76,810	8.70					
Fe	56,700	119,700	81,550	80,010	105,700	93,800	89,577	93,100	96,600	110,600	91,770	71,400	92,400	91,128	84,000	29,983	48,000	47,200	35,000	49,300	1.40					
Mn	775	2,866	930	1,085	852	775	1,214	3,099	2,401	1,317	1,162	620	1,162	1,498	2,324	605	1,050	850.0	600.0	821	1.50					
Ti	8,400	14,040	12,840	15,000	7,260	13,800	11,890	10,800	17,400	12,120	10,560	14,400	17,400	15,180	19,200	3,450	5,600	4,600	3,000	5,530	1.60					
As	1.0	2.1	1.9	1.4	1.4	1.6	1.6	2.0	1.1	1.4	2.0	2.0	1.3	1.7	2.2	NA	5	13.0	1.5	1.7	0.25					
Cd	1.2	0.9	1.1	1.8	1.0	0.5	1.1	2.0	0.7	0.4	0.5	0.5	0.4	0.5	0.7	NA	0.1	0.3	0.1	0.4	0.28					
Cr	182.0	189.4	207.0	236.5	179.4	201.6	199.3	229.3	178.3	321.0	236.2	143.7	141.0	212.6	255.2	87	100	90.0	85.0	103.8	0.78					
Cu	203.9	158.7	100.0	269.5	212.6	188.2	188.8	275.9	373.2	396.5	339.6	319.7	250.0	326.2	278.3	28	100	45.0	25.0	97.3	0.65					
Ni	129.3	145.2	164.0	283.6	269.6	210.0	200.3	312.4	199.2	182.0	280.7	81.4	174.0	205.5	315.5	37	90	68.0	44.0	85.9	1.15					
Pb	11.4	15.7	13.7	15.8	14.3	12.5	13.9	16.4	17.8	27.3	18.9	18.5	14.5	25.0	52.8	11.2	150	20.0	17.0	9.5	1.00					
Zn	117.5	174.2	100.0	270.5	259.2	255.9	196.2	268.6	169.3	336.0	215.8	138.4	160.0	216.7	280.7	16	350	95.0	71.0	105.0	0.55					
Co	14.7	15.6	28.6	64.5	15.8	16.1	25.9	19.6	13.0	46.7	19.8	18.3	15.2	27.0	49.0	31	20	19.0	17.0	17.4	1.53					
Mo	1.7	1.3	1.1	1.1	1.3	1.4	1.3	2.5	1.7	4.8	1.1	1.9	18.0	8.9	25.8	NA	3	2.6	1.5	1.5	0.16					
Sr	100.0	617.0	216.5	138.5	907.0	1,310.0	548.2	1,779.7	176.8	509.0	2,696.1	1,842.9	368.0	1,056.3	745.2	217	150	170.0	350.0	121.0	0.24					
Ba	363.5	629.0	268.4	512.5	593.2	1,938.9	717.6	1,943.2	3,170.2	246.0	2,222.9	2,220.4	474.1	1,526.2	823.3	368	600	580.0	550.0	332.0	0.63					
V	75.1	59.2	614.3	726.4	86.5	917.6	413.2	985.5	69.6	85.2	1,023.8	1,030.3	89.7	418.9	215.0	216.6	170	130.0	107.0	67.7	0.80					
Y	BDL	65.5	BDL	BDL	49.2	15.9	43.5	BDL	BDL	79.2	BDL	197.6	72.0	142.6	221.5	NA	28	26.0	22.0	107.0	0.21					
Zr	100.0	608.0	200.0	812.2	796.0	300.0	469.4	855.7	293.1	174.0	BDL	BDL	201.0	246.6	318.2	NA	NA	160.0	190.0	107.0	0.50					
Th	2.5	2.2	4.3	2.0	2.5	3.6	2.8	3.6	2.7	BDL	3.0	4.1	3.2	3.7	5.3	9	14	12.0	10.7	1.0	0.70					
U	1.0	1.0	1.5	0.8	0.9	1.0	1.0	1.0	0.7	BDL	0.6	1.4	1.1	1.2	2.1	5.9	3	2.7	2.8	1.0	0.60					

LLD lower limits of detection, NA not available, BDL below detection limit, F forest, A agriculture, U urban

^a Subramanian et al. (1985)

^b Martin and Meybeck (1979)

^c Turekian and Wedepohl (1961), REE from Nance and Taylor (1976)

^d Taylor and McLennan (1985)

^e Present study

^f Suspended sediments

Table 3 Nutrient (C, N, and P) concentrations in bed and suspended sediments of Narmada and Tapti rivers (all parameters in mg/g, except C/N ratio)

	TC	IC	OC	TS	IS	OS	TP	TN	C/N
Narmada									
1 ^F _a	7.7	3.2	4.5	0.000	0.000	0.000	0.9	4.0	1.9
b	8.3	4.1	4.2	0.035	0.018	0.017	1.2	4.7	1.8
2 ^F _a	18.5	12.1	6.4	0.000	0.000	0.000	1.4	6.7	2.8
b	37.5	23.8	13.7	0.000	0.000	0.000	1.1	9.3	4.0
3 ^F + A _a	10.9	8.4	2.5	0.033	0.000	0.033	0.7	5.3	2.1
b	20.3	9.0	11.3	0.031	0.000	0.031	0.5	6.7	3.0
4 ^U _a	8.3	7.9	0.4	0.000	0.000	0.000	0.5	4.7	1.8
b	12.4	7.7	4.7	0.008	0.000	0.008	0.9	5.3	2.3
5 ^U _a	9.8	6.2	3.6	0.000	0.000	0.000	0.6	4.7	2.1
b	15.9	12.6	3.3	0.000	0.000	0.000	0.5	6.7	2.4
6 ^U _a	12.7	8.6	4.1	0.000	0.000	0.000	0.3	4.2	3.0
b	14.5	13.0	1.5	0.000	0.000	0.000	0.0	4.7	3.1
7 ^U _a	5.5	4.4	1.1	0.014	0.000	0.014	0.6	3.3	1.7
b	8.5	5.9	2.6	0.000	0.000	0.000	0.2	4.7	1.8
8 ^U _a	9.7	7.4	2.3	0.013	0.000	0.013	0.6	4.7	2.1
b	13.9	11.8	2.1	0.000	0.000	0.000	1.0	6.0	2.3
9 ^U _a	9.1	2.8	6.3	0.000	0.000	0.000	0.4	4.7	1.9
b	8.4	6.0	2.4	0.000	0.000	0.000	0.7	4.0	2.1
Average	13.0	8.6	4.4	0.007	0.001	0.006	0.7	5.3	2.5
8a ^a	15.7	8.1	7.5	0.000	0.000	0.000	0.9	5.7	2.8
Tapti									
1 ^F _a	32.7	13.9	18.8	0.026	0.011	0.015	0.8	8.0	4.1
b	39.4	17.8	21.6	0.033	0.026	0.007	1.0	8.3	4.7
2 ^U _a	16.5	12.0	4.5	0.015	0.000	0.015	0.7	3.3	5.0
b	18.5	13.0	5.5	0.000	0.000	0.000	1.6	4.0	4.6
3 ^U _a	15.7	11.3	4.4	0.000	0.000	0.000	0.8	2.3	6.8
b	16.8	10.7	6.1	0.000	0.000	0.000	0.5	2.7	6.2
4 ^U _a	20.1	12.8	7.3	0.075	0.000	0.075	0.7	4.7	4.3
b	25.4	19.4	6.0	0.012	0.000	0.012	1.0	5.1	5.0
5 ^U _a	30.3	18.4	11.9	0.010	0.009	0.001	0.9	5.3	5.7
b	34.6	16.2	18.4	0.000	0.000	0.000	1.1	6.7	5.2
Average	25.9	15.8	10.1	0.020	0.007	0.013	0.9	5.2	5.2
5a ^a	35.1	28.8	6.3	0.054	0.034	0.020	1.1	6.9	5.1

TC total carbon, IC inorganic carbon, OC organic carbon, TS total sulfur, IS inorganic sulfur, OS organic sulfur, TP total phosphorus, TN total nitrogen

^a Suspended sediments

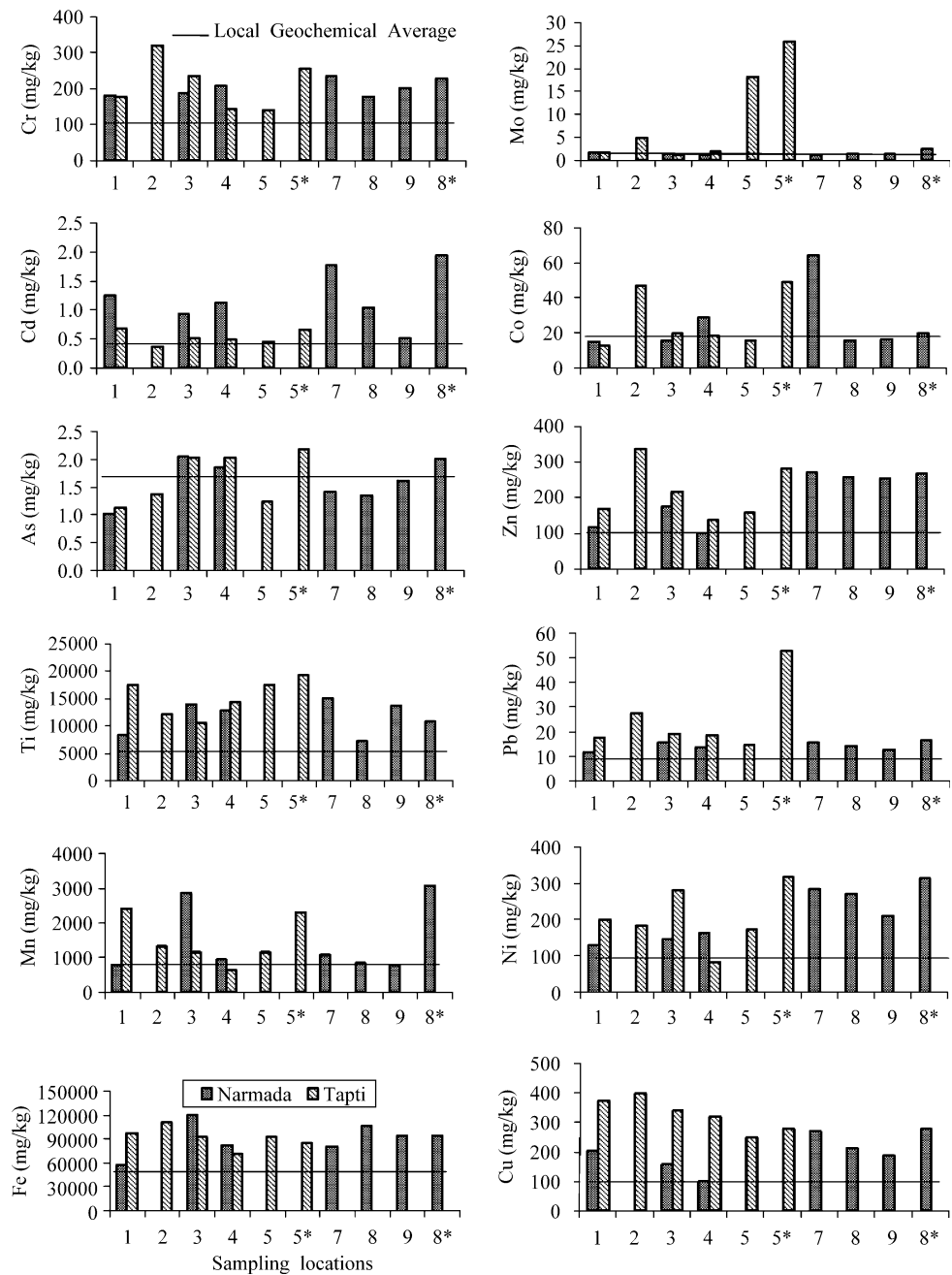
ranges from 55.3 to 68.6 with an average of 61.7 in Tapti river. These values, therefore, indicate moderate weathering taking place in these basins.

The spatial distribution of metals and nutrients can reveal the existence of natural anomalies and the presence of pollution sources in the river basin. The Indian sub-continent has high rates of chemical weathering (Subramanian 1979). Man-made dams and abrupt changes

in the basin bed topography cause resuspension of the bed sediments. The Narmada river basin except the upper reaches is dammed with 30 large, controversial dams (some are under construction), which have major impacts on hydrogeochemistry of the river. Dissolved organic matter plays an important role in controlling the concentrations of inorganic micro-elements in river waters and their non-conservative behavior during river water/sea water mixing. Flocculation of the organic and inorganic dissolved species begins as a result of chemical as well as electrostatic interactions when river water comes in contact of sea water (Sholkovitz 1978). Flocculation of dissolved organic and inorganic matter is an important removal mechanism for dissolved metals in the estuarine region. Thus, dissolved trace metal cations may be scavenged by the flocculating colloids, and the bulk of micro-elements are transferred into suspended state (Sholkovitz 1978). Hence, the little enhanced micro-elemental concentrations observed in the suspended sediments of Narmada and Tapti rivers can be attributed to the flocculation processes throughout the mixing zone. In general, the concentration of metals in bed sediments comes out to be lower than in suspended sediments which can also be attributed to the prevention of sedimentation process by water current in the monsoon season. Further, within the dry period with decreased flow rate in the river, a fraction of suspended sediment in river water is partially incorporated into the bed sediment. Most of the metal concentrations in Narmada and Tapti river sediments exceed the respective geochemical background values (in shale standard and continental crust) as well as Indian and world averages (Table 2; Fig. 3). The higher values of metals in these rivers may be attributed to geological source coupled with anthropogenic inputs from the catchments. It can be noticed from Fig. 3 that the sediments in the municipal areas (sampling stations: 3, 4, 7, 8, and 9 in Narmada river basin and 2, 3, 4, and 5 in Tapti river basin) have considerably higher concentrations for most of the metals. This characterizes the sediments as polluted due to proximity to industrial sites and municipal sewage disposal points.

The spatiotemporal distributions of total C, N, P, and S in Narmada and Tapti river sediments are shown in Fig. 4. Nutrient enrichment variations were found in sediments at different locations. The TN concentration is quite high and varies within a narrow range from 3.3 to 9.3 mg g⁻¹ with an average of 5.3 mg g⁻¹ and from 2.3 to 8.3 mg g⁻¹ with an average of 5.2 mg g⁻¹, respectively, in the two major channels, Narmada and Tapti, respectively. The variation in the TC (total carbon) content in the two basins is quite significant. It varies between 5.5 and 37.5 mg g⁻¹ (mean = 13.0 mg g⁻¹) and between 15.7 and 39.4 mg g⁻¹ (mean = 25.9 mg g⁻¹) in the two basins, respectively. In

Fig. 3 Total heavy metal concentrations in the bed and suspended sediments (*asterisk*) of Narmada and Tapti rivers



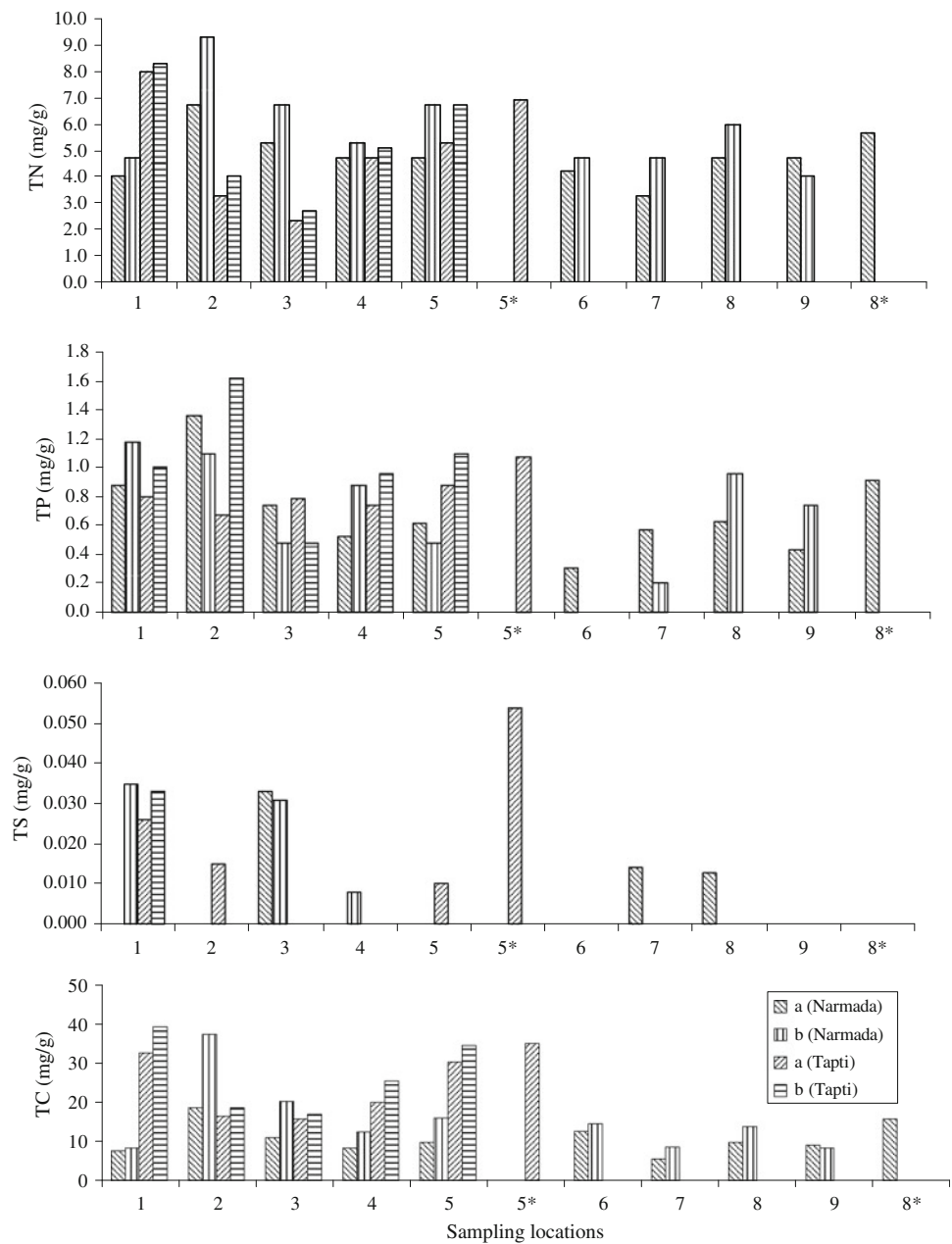
general, inorganic carbon (IC) exceeds organic carbon (OC) content indicating inorganic fertilizers applied in the agricultural lands and is washed in the river and remained unadsorbed unto the sediments as a source. The S was detected quite low or nil in the river sediments. TC and TN are strongly correlated in bed sediments of these river basins, which reflect that the concentration of TN may be regulated similar to TP by inorganic sources like fertilizers used extensively in the agricultural areas of the catchments. The C/N ratio in the Narmada and Tapti river basins ranges from 1.7 to 4.0 and from 4.1 to 6.8 with an average of 2.5 and 5.2, respectively. The TC, TN, and C/N ratio values

in these rivers are comparable to those reported by Subramanian (2008).

Metal pollution assessment

It is of primary importance to establish the natural level of metals in order to determine the extent of pollution in a river basin by metal load in sediments. A comparison of the ratio of the element concentration in particular sediment with relative concentration in the crust might indicate sources of the trace elements (Heit et al. 1980). To understand the possible sources, sediment elemental

Fig. 4 Total C, N, P, and S in bed and suspended sediments (asterisk) in monsoon (a) and post-monsoon (b) seasons



enrichment factors (SEF) were calculated according to the following equation (Kemp and Thomas 1976):

$$SEF = \frac{\frac{C_z}{Al_z} - \frac{C_b}{Al_b}}{\frac{C_b}{Al_b}}$$

where C_z is the concentration of element in sample, C_b is the background concentration of the element, Al_z is the concentration of Al in sample, and Al_b background concentration of Al.

Aluminum with a high crustal abundance is used to normalize the data as it is assumed to have had a uniform flux to the sediments during the past century, and the shale global standards are used as background values for the

corresponding elements to quantify the degree of pollution (Feely et al. 1981). The normalization of trace metals by conservative elements may reveal the imbalances due to elevated trace metal concentrations generally attributed to anthropogenic activities. An $EF = 1$ assumes a crustal source, whereas an $EF < 1$ implies natural elemental depletion. When $EF > 1$, external influences are assumed to be significant. The average EF for metals exceeds 1 except, Pb, As, Co, and Mo in Narmada river and except Mn, As, Cd, Pb, and Co in Tapi river (Table 4). The highest average EF is found for Cu with values of 2.07 and 3.22 in Narmada and Tapi rivers, respectively. This implies an additional input of these elements, perhaps from unusual geochemical enrichment or from anthropogenic

Table 4 Metal pollution assessment results of Narmada and Tapti rivers

	Fe	Mn	Ti	As	Cd	Cr	Cu	Ni	Pb	Zn	Co	Mo	PLI
Narmada													
1													
EF	0.18	-0.04	0.55	-0.39	2.09	0.79	1.14	0.54	0.22	0.14	-0.14	0.17	
I_{geo}	-0.38	-0.67	0.02	-1.34	1.01	0.24	0.48	0.01	-0.32	-0.42	-0.83	-0.39	1.29
CF	1.15	0.94	1.52	0.59	3.02	1.75	2.10	1.51	1.20	1.12	0.85	1.15	
3													
EF	1.61	2.75	1.73	0.28	1.44	0.96	0.75	0.82	0.78	0.78	-0.03	-0.10	
I_{geo}	0.69	1.22	0.76	-0.33	0.60	0.29	0.12	0.17	0.14	0.15	-0.74	-0.84	1.71
CF	2.43	3.49	2.54	1.19	2.27	1.82	1.63	1.69	1.65	1.66	0.90	0.84	
4													
EF	0.85	0.26	1.59	0.20	2.05	1.23	0.15	1.13	0.60	0.06	0.83	-0.17	
I_{geo}	0.14	-0.41	0.63	-0.48	0.86	0.42	-0.55	0.35	-0.06	-0.66	0.13	-1.02	1.45
CF	1.65	1.13	2.32	1.08	2.73	1.99	1.03	1.91	1.44	0.95	1.64	0.74	
7													
EF	0.69	0.37	1.82	-0.14	3.52	1.37	1.88	2.43	0.73	1.68	2.86	-0.24	
I_{geo}	0.11	-0.18	0.85	-0.86	1.53	0.61	0.88	1.14	0.15	0.78	1.31	-1.05	2.03
CF	1.62	1.32	2.71	0.83	4.34	2.28	2.77	3.30	1.66	2.58	3.71	0.73	
8													
EF	1.36	0.14	0.44	-0.13	1.79	0.90	1.40	2.45	0.65	1.71	0.00	-0.07	
I_{geo}	0.52	-0.53	-0.19	-0.92	0.76	0.22	0.54	1.07	0.00	0.72	-0.73	-0.83	1.55
CF	2.14	1.04	1.31	0.79	2.54	1.73	2.18	3.14	1.50	2.47	0.91	0.85	
9													
EF	1.03	0.01	1.66	0.00	0.33	1.07	1.06	1.61	0.40	1.60	-0.01	-0.02	
I_{geo}	0.34	-0.67	0.73	-0.67	-0.27	0.38	0.37	0.70	-0.19	0.70	-0.70	-0.71	1.50
CF	1.90	0.94	2.50	0.94	1.24	1.94	1.93	2.44	1.31	2.44	0.93	0.92	
8 ^a													
EF	1.04	3.09	1.11	0.27	4.15	1.39	2.07	2.94	0.86	1.77	0.22	0.83	
I_{geo}	0.33	1.33	0.38	-0.35	1.66	0.57	0.92	1.28	0.20	0.77	-0.41	0.17	2.23
CF	1.89	3.77	1.95	1.17	4.76	2.21	2.83	3.64	1.72	2.56	1.13	1.69	
Tapti													
1													
EF	0.99	1.97	2.19	-0.33	0.66	0.74	2.89	1.35	0.90	0.64	-0.24	0.12	
I_{geo}	0.39	0.96	1.07	-1.18	0.12	0.21	1.35	0.63	0.32	0.10	-1.01	-0.45	1.73
CF	1.96	2.92	3.15	0.66	1.63	1.72	3.83	2.32	1.87	1.61	0.75	1.10	
2													
EF	1.32	0.66	1.27	-0.17	-0.06	2.20	3.22	1.20	1.97	2.32	1.78	2.32	
I_{geo}	0.58	0.10	0.55	-0.91	-0.73	1.05	1.44	0.50	0.94	1.09	0.84	1.09	2.19
CF	2.24	1.60	2.19	0.80	0.90	3.09	4.07	2.12	2.87	3.20	2.68	3.20	
3													
EF	1.07	0.58	1.13	0.32	0.41	1.54	2.89	2.64	1.22	1.29	0.27	-0.19	
I_{geo}	0.31	-0.08	0.35	-0.34	-0.24	0.61	1.22	1.12	0.41	0.45	-0.40	-1.05	1.72
CF	1.86	1.42	1.91	1.19	1.27	2.28	3.49	3.27	1.99	2.06	1.14	0.73	
4													
EF	0.21	-0.37	1.17	-0.01	0.02	0.15	1.74	-0.21	0.62	0.10	-0.12	0.03	
I_{geo}	-0.05	-0.99	0.80	-0.34	-0.30	-0.10	1.13	-0.66	0.37	-0.19	-0.51	-0.27	1.40
CF	1.45	0.75	2.60	1.19	1.22	1.38	3.29	0.95	1.94	1.32	1.05	1.24	

Table 4 continued

	Fe	Mn	Ti	As	Cd	Cr	Cu	Ni	Pb	Zn	Co	Mo	PLI
5													
EF	0.66	0.25	1.78	-0.36	-0.05	0.20	1.27	0.79	0.35	0.35	-0.23	9.62	
I_{geo}	0.32	-0.08	1.07	-1.05	-0.48	-0.13	0.78	0.43	0.02	0.02	-0.78	3.00	1.80
CF	1.87	1.42	3.15	0.73	1.07	1.36	2.57	2.03	1.53	1.52	0.88	12.00	
5 ^a													
EF	0.53	1.54	2.11	0.14	0.42	1.20	1.56	2.29	3.97	1.39	1.52	14.40	
I_{geo}	0.18	0.92	1.21	-0.24	0.08	0.72	0.93	1.29	1.89	0.83	0.91	3.52	3.04
CF	1.70	2.83	3.47	1.27	1.59	2.46	2.86	3.67	5.55	2.67	2.82	17.20	

^a Suspended sediments

sources. The magnitude of input for each metal in the sediment from probable sources and/or the difference in the removal rate of each metal from the sediment may be attributed for the variability in EF values.

The geoaccumulation index (I_{geo}) introduced by Muller (1969) was also used to assess metal pollution in sediments of Narmada and Tapti rivers. It is expressed as:

$$I_{geo} = \text{Log}_2 \frac{C_n}{1.5B_n}$$

where C_n is the measured concentration of the heavy metal (n) in the <37 μm fraction of sediments, B_n is the local geochemical background value in average sediments of element n , and 1.5 is the background matrix correction factor due to lithogenic effects. Three uncontaminated surface sediments were also collected for the analysis of geochemical background values of heavy metals (B_n) from upstream of the Narmada river, where both anthropogenic and industrial activities were absent. These stations are located at almost 6–7 km downstream to origin of the river which was considered appropriate to examine the natural

abundance of heavy metals in sediments derived from weathering of Deccan basalts in the absence of anthropogenic activities. The I_{geo} consists of seven grades (0–6). The highest grade (class six) reflects 100-fold enrichment above the background values. The calculated I_{geo} indicates that the sediments of Narmada and Tapti rivers are moderately polluted with heavy metals, except As which shows I_{geo} values below zero (Tables 4, 5).

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

$$CF = \frac{\text{metal concentration in sediment}}{\text{World shale average for the metal}}$$

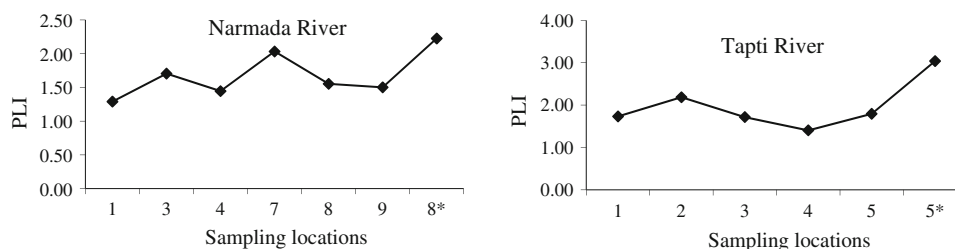
The calculated contamination factors are found to fall in the following sequences:

- Cu > Cd > Ni > Ti > Cr > Zn > Fe > Mn >
- Co > Pb > Mo > As (Narmada river)
- Cu > Mo > Ti > Ni > Cr > Zn > Fe > Mn > Cd >
- Co > Pb > As (Tapti river)

Table 5 Measure of metal pollution in sediments of Narmada and Tapti rivers

Muller (1969)			Heavy metals			
Index of geo accumulation	I_{geo} class	Sediment quality designation	Narmada river		Tapti river	
			Bed sediment	Suspended sediment	Bed sediment	Suspended sediment
5–10	6	Extremely polluted				
4–5	5	Highly polluted				
3–4	4	Moderately to highly polluted			Mo	Mo
2–3	3	Moderately polluted			–	
1–2	2	Moderately to unpolluted	Mn, Cd, Ni, Co	Mn, Cd, Ni	Ti, Cr, Cu, Ni, Zn, Mo	Ti, Ni, Pb
0–1	1	Unpolluted	Fe, Ti, Cd, Cr, Cu, Ni, Pb, Zn, Co	Fe, Ti, Cr, Cu, Pb, Zn, Mo	Fe, Mn, Ti, Cd, Cr, Cu, Ni, Pb, Zn, Co	Fe, Mn, Cd, Cr, Cu, Zn, Co
0	0	Background concentration	Fe, Mn, Ti, As, Cd, Cu, Pb, Zn, Co, Mo	As, Co	Fe, Mn, As, Cd, Cr, Ni, Zn, Co, Mo	As

Fig. 5 Pollution load index (PLI) at different sampling stations along the Narmada and Tapti rivers



To evaluate the sediment pollution severity, pollution load index (PLI) was used to find out the mutual pollution effect at different stations by different metals. PLI for a set of n polluting metals was defined as the geometric mean of the CF values for the n metals (Tomlison et al. 1980). A PLI value close to 1 indicates heavy metal loads near the background level, while values >1 indicate pollution (Cabrera et al. 1999). In Narmada river, PLI value ranges from 1.29 to 2.23 with an average of 1.68, whereas it varies between 1.40 and 3.04 with an average of 1.98 in Tapti river. The mutual pollution effect of different metals at different sampling locations in the Narmada and Tapti river basins is depicted in Fig. 5. Thus, the findings, taking into account of EF, I_{geo} , and PLI, confirm that heavy metal pollution in the two rivers under investigation is moderately serious.

Most of the toxic trace metals show considerably higher concentration at the sites 3, 4, 7, 8, and 9 of Narmada river due to influx of large volume of domestic sewage and industrial effluents from Mandla, Hoshangabad (urban area), the second largest city in the basin and major source of pollution (municipal solid waste and sewage) and Jhaneshwar (industrial town). Comparatively higher concentration is found at sampling sites 2, 3, 4, and 5 in Tapti river which may apparently be attributed to the nearby municipal and industrial activities. The upper reaches of the Narmada river basin witness several mining activities with respect to marble, limestone, and coal, whereas the midstream region passes through thick forests. The sewerage from the Jabalpur city, the largest habitat in the Narmada river basin, also drains in the river upstream region polluting the river. The downstreams of both the rivers are dominated by various kinds of industrial setups. The Narmada and Tapti rivers culminate in the Arabian Sea at Bharuch and Surat, respectively, which are the industrial towns and major source of pollution to the rivers in the coastal region.

Conclusion

Distribution characteristics of trace element concentrations and consequently the river quality in the two interesting catchments, Narmada and Tapti, are the result of combined influence of natural conditions, i.e., geological and hydro-meteorological backgrounds and human activity. Human

activities, in particular urban daily life, seem to be one of the factors influencing metal concentrations. Though human activities have not yet caused serious degradation of river water quality, some trace metal concentrations have profoundly exceeded the related standards. Dissolved metal concentrations of all water samples are below or close to the maximum permitted concentration for the protection of aquatic life (except, for Cu, Pb, Zn, and Cr) and for drinking water, except for elevated Pb, Fe, Cr, and Ni concentrations with respect to specific standards. The average PO_4^{3-} values exceed the Indian average as well as the recommended standards. But the NO_3^- concentrations are typically low except, at few sampling stations and far below the standard drinking water quality guidelines. The DOC values are higher than the world average but significantly lower than other humid tropical rivers considered for comparison. However, dissolved silica concentration exceeds Indian as well as global averages indicating silicate weathering in the basins. The CIA values indicate the moderate weathering taking place in the Narmada and Tapti rivers. Taking into account of the EF, I_{geo} , and PLI values, it can be concluded that the investigated river basins are moderately polluted with heavy metals. The higher values of metals in these 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. This study has revealed that enhanced concentrations of heavy metals are recorded near to industrial establishments or urban sewage discharge points, indicating that their concentrations have been strongly affected by anthropogenic influences. Potentially more profitable crops, like cotton, jute, rice, wheat, vegetables, sugarcane, etc., are grown in the cultivated areas of the river basins. Rice cultivation consumes lots of water; thus, contaminants can move through the food chain to human beings, affecting their health.

Thus, it is reasonable to conclude that the increased concentrations of heavy metals in the sediments of the Narmada and Tapti rivers are considerably due to direct discharge of industrial and urban wastes into the river. The distribution patterns of heavy metals in the river basins indicate that the continuous discharge of sewage and effluents into the river will continue to increase the magnitude of metal pollution in the river to intolerable limits,

and this may have severe impact on aquatic plants and other organisms in the rivers. It is, therefore, recommended that in order to check this trend, the industrial establishments and the municipal council should establish efficient waste-treatment and disposal systems.

Acknowledgments The authors would like to thank the Jawaharlal Nehru University (SKS) and University Grant Commission Project (VS), New Delhi, India for providing necessary financial support for carrying out the study. The authors are also grateful to an anonymous reviewer whose critical and constructive comments helped to improve the quality of the manuscript.

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