

Trace element chemistry of major rivers in Orissa State, India

K. O. Konhauser · M. A. Powell · W. S. Fyfe · F. J. Longstaffe · S. Tripathy

Abstract Geochemical analyses of surface waters from rivers flowing through Orissa State, India, indicated that trace element concentrations were extremely variable and consistently higher than world river average. The Brahmani River was the most solute-rich river studied, followed by the Baitarani and Mahanadi Rivers. Although all three rivers drain similar geology, the Brahmani River catchment is heavily industrialized, and water samples collected upstream and downstream from industries indicated that anthropogenic activity directly influenced its chemical composition. Samples collected from several towns, in all three river systems, did not invariably show similar patterns, with various elements having higher dissolved concentrations upstream. Because the concentration of total solids increased downstream, this implied that some components of the sewage had effectively sequestered available elements from solution and converted them to particulate material. Although the impact of pollution is clearly recognizable in water samples collected in proximity to the anthropogenic source, there are only slight elemental accumulations in the lower reaches of the Mahanadi River, with no accumulation in the Brahmani River. Apparently for these large rivers, discharged effluent becomes rapidly diluted, while complexation and sedimentation further removes trace elements from the water column. However, in the less voluminous Baitarani River, elemental enrichment near the river's mouth suggests that in this secondary

river, where dilution effects are less, the concerns over regional water quality may be more prevalent.

Key words Trace elements · Indian rivers

Introduction

In recent years, numerous papers have been published addressing the chemical composition of surface waters in river systems throughout India (i.e., Subramanian 1979; Ray and others 1984; Sarin and Krishnaswami 1984; Subramanian and others 1985, 1987; Biksham and Subramanian 1988a; Chakrapani and Subramanian 1990a). These studies have shown that river chemistry is largely controlled by regional geology, with Indian rivers collectively being alkaline and on average with about 25% more total dissolved inorganic solids (TDS) than the world river average (Subramanian 1979). These concentrations are, however, disproportionate, because some of the highest

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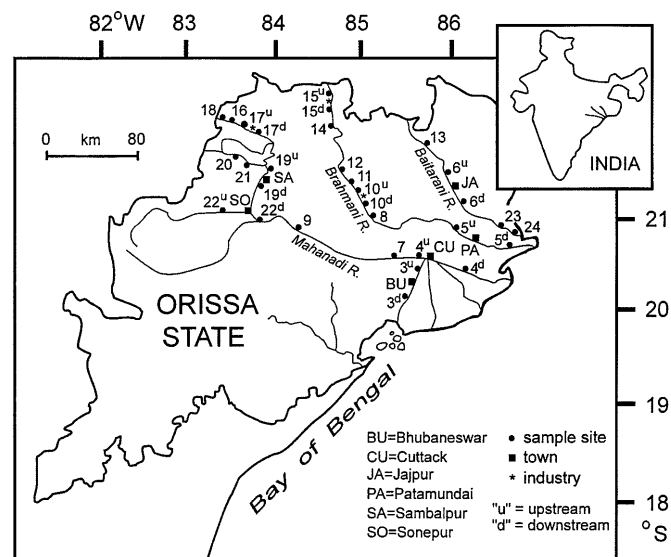


Fig. 1
Location of study areas and sample sites

Table 1
Chemical analysis of surface from Mahanadi River and tributaries (in $\mu\text{g l}^{-1}$)^a

	Site																Avg	RSD
	3D	3U	4D	4U	7	9	16	17D	17U	18	19D	19U	20	21	22D	22U		
Ag	0.29	0.22	0.28	0.27	0.18	0.30	0.13	0.25	0.13	0.60	0.13	0.10	0.09	0.29	0.12	0.13	0.22	56.2
As	3.0	1.1	1.9	0.1	0.1	0.9	0.9	1.6	0.9	0.4	0.4	0.1	0.1	0.7	1.9	1.7	1.0	82.3
B	399	360	388	324	364	380	379	445	391	373	354	364	398	383	431	386	382	7.3
Ba	44.4	38.6	64.9	39.6	71.4	92.1	25.1	32.3	25.4	38.1	30.6	37.2	28.6	39.4	44.3	47.9	43.7	40.1
Bi	0.03	0.03	0.04	0.03	0.04	0.02	0.04	0.04	0.01	0.05	0.04	0.03	0.02	0.03	0.01	0.01	0.03	40.8
Br	45	39	36	33	39	38	22	26	23	27	22	23	23	25	47	42	32	27.1
Cd	0.46	0.09	0.03	0.04	0.10	0.08	0.04	0.06	0.02	0.02	0.27	0.05	0.04	0.02	0.04	0.04	0.09	128.6
Ce	6.6	5.7	15.5	7.4	17.7	21.8	2.1	8.9	1.8	15.0	4.8	5.2	1.8	4.1	1.1	7.5	7.9	76.5
Co	1.7	1.4	4.1	1.8	5.1	14.2	0.8	1.1	0.7	1.9	1.0	1.1	0.6	0.9	0.4	2.0	2.4	134.3
Cr	9.1	7.8	13.8	8.5	15.5	30.5	5.8	7.1	6.0	7.8	7.5	8.3	6.5	7.1	5.7	9.7	9.8	60.8
Cs	0.26	0.24	0.48	0.28	0.57	0.90	0.61	0.40	0.07	0.63	0.34	0.35	0.16	0.32	0.04	0.23	0.37	59.4
Cu	10.2	4.9	6.9	5.1	9.1	17.9	2.7	4.0	2.5	4.5	4.3	5.1	3.4	4.9	4.8	5.0	5.9	61.7
Dy	0.47	0.43	1.13	0.55	1.48	3.61	0.22	0.52	0.16	0.77	0.34	0.35	0.14	0.30	0.12	0.72	0.71	117.5
Er	0.10	0.14	0.33	0.16	0.42	1.14	0.07	0.13	0.04	0.19	0.08	0.10	0.04	0.09	0.04	0.21	0.21	127.8
Eu	0.21	0.19	0.41	0.23	0.51	1.01	0.10	0.20	0.08	0.36	0.18	0.18	0.12	0.18	0.12	0.24	0.27	82.0
Ga	0.98	0.90	1.87	4.41	2.24	4.24	0.48	1.02	0.31	1.39	0.95	0.95	0.51	0.86	0.37	1.16	1.42	85.2
Gd	0.86	0.80	1.93	0.98	2.32	4.28	0.35	0.99	0.26	1.75	0.69	0.66	0.32	0.58	0.20	1.02	1.12	89.5
Ge	0.08	0.05	0.09	0.06	0.12	0.17	0.04	0.06	0.03	0.08	0.05	0.06	0.04	0.06	0.03	0.10	0.07	50.8
Hf	0.02	0.02	0.02	0.01	0.03	0.07	0.01	0.02	0.01	0.02	0.02	0.02	0.01	0.02	0.01	0.02	0.02	67.4
Ho	0.10	0.08	0.22	0.10	0.24	0.72	0.04	0.08	0.02	0.14	0.06	0.06	0.04	0.06	0.02	0.14	0.13	123.8
I	37.4	23.5	21.1	21.3	35.0	25.8	23.9	28.8	21.5	21.1	17.0	14.2	20.3	19.7	23.3	33.7	24.2	25.9
La	3.3	3.0	7.4	3.7	8.4	10.2	1.1	4.5	0.9	7.3	2.5	2.8	1.1	2.3	0.5	3.6	3.9	72.1
Li	2.7	2.5	3.7	2.6	3.9	6.9	6.3	2.7	1.1	3.3	2.7	2.7	1.7	2.4	0.8	2.4	3.0	51.7
Lu	0.02	0.04	0.06	0.02	0.08	0.23	0.01	0.02	0.01	0.03	0.02	0.02	0.01	0.02	0.01	0.03	0.04	133.6
Mn	111.8	72.6	185.1	88.2	248.3	—	52.3	62.3	57.3	94.1	44.8	45.0	25.5	35.8	19.3	94.4	96.9	63.1
Mo	0.3	0.2	0.2	0.2	0.2	0.1	0.1	0.1	0.2	0.1	0.2	0.3	0.4	0.2	0.7	0.3	0.2	61.2
Nd	3.2	2.8	7.1	3.6	8.6	12.1	1.3	4.4	0.9	6.9	2.7	2.9	1.1	2.4	0.5	3.6	4.0	76.6
Ni	6.7	6.5	10.0	7.3	11.4	19.1	3.8	5.0	4.0	5.8	8.2	6.9	4.2	6.0	3.1	7.5	7.2	52.1
P	155	68	90	89	114	146	50	89	68	90	59	87	86	79	76	97	90	30.2
Pb	3.04	2.16	4.16	2.61	5.12	6.51	1.77	2.45	0.89	3.11	2.61	2.68	1.22	1.73	0.81	2.07	2.68	54.6
Pr	0.96	0.82	2.13	1.05	2.55	3.46	0.35	1.32	0.29	2.13	0.80	0.82	0.32	0.67	0.15	1.08	1.18	76.1
Rb	7.5	5.5	13.2	6.6	14.7	35.7	5.3	6.8	2.0	10.0	5.3	6.4	3.0	4.9	2.0	8.5	8.6	90.0
Sc	0.5	0.5	0.7	0.5	0.8	1.4	0.3	0.4	0.3	0.5	0.4	0.4	0.3	0.4	0.4	0.7	0.5	50.1
Sm	0.60	0.47	1.35	0.68	1.99	2.61	0.27	0.75	0.19	1.24	0.61	0.43	0.23	0.42	0.11	0.65	0.79	84.9
Sn	3.03	2.75	2.31	2.01	1.50	1.25	0.77	0.86	0.74	0.69	0.72	1.31	0.99	0.76	0.71	0.67	1.32	57.9
Sr	81.1	78.8	85.5	79.6	91.3	94.8	42.0	57.4	53.8	54.1	63.1	69.0	64.5	67.5	119.0	121.4	76.4	28.4
Tb	0.10	0.10	0.26	0.12	0.30	0.64	0.04	0.12	0.04	0.20	0.08	0.10	0.04	0.08	0.02	0.14	0.15	99.4
Th	0.30	0.40	1.26	0.54	1.00	0.44	0.30	0.99	0.13	1.33	0.46	0.45	0.25	0.46	0.12	0.47	0.56	65.9
Ti	82.3	77.3	182.8	87.6	185.6	542.5	53.0	83.5	20.8	114.5	64.2	69.0	23.1	59.7	48.0	138.2	114.5	104.8
Tl	0.03	0.02	0.05	0.03	0.07	0.14	0.03	0.03	0.01	0.06	0.02	0.03	0.02	0.02	0.01	0.03	0.04	82.5
Tm	0.02	0.02	0.05	0.02	0.07	0.19	0.01	0.02	0.01	0.03	0.01	0.02	0.01	0.01	0.01	0.04	0.03	129.1
U	0.40	0.40	0.58	0.44	0.59	0.57	0.25	0.34	0.19	0.38	0.31	0.26	0.28	0.31	0.48	0.80	0.41	37.7
V	9.2	8.6	15.4	9.5	18.0	40.7	3.3	8.0	4.2	9.5	7.6	7.2	4.1	6.3	3.8	11.1	10.4	83.9
W	0.05	0.03	0.06	0.02	0.05	0.06	0.06	0.05	0.04	0.03	0.02	0.04	0.09	0.04	0.03	0.09	0.05	43.1
Y	2.13	1.82	4.84	2.34	6.22	16.62	0.96	1.97	0.72	3.03	1.40	1.46	0.61	1.26	0.59	3.03	3.06	124.3
Yb	0.18	0.18	0.44	0.23	0.59	1.66	0.10	0.18	0.05	0.28	0.13	0.13	0.05	0.11	0.06	0.27	0.29	131.2
Zn	17.3	8.8	14.2	9.6	16.4	28.7	6.1	8.8	4.5	9.6	6.6	15.2	5.8	8.6	5.6	9.5	11.0	54.5
Zr	0.90	0.70	0.81	0.71	1.39	1.70	0.64	1.22	0.74	0.83	0.86	1.35	0.89	0.88	0.77	0.74	0.95	31.0
pH	8.1	8.4	7.8	8.2	7.4	7.6	7.4	8.1	7.9	7.7	8.2	7.9	8.1	7.8	8.5	8.7	8.0	5.0

^a Note: — = not determined; Avg = average; RSD = relative standard deviation (standard deviation/average, in %)

elemental concentrations are found in the southern, peninsular rivers (e.g., Godavari, Krishna, Mahanadi, Narmada, Cauvery, and Tapti), compared to those northern rivers (e.g., Ganges, Brahmaputra, and Indus) draining the Himalayan Mountains (Subramanian 1979). The pen-

insular rivers, characterized by their TDS, which on average is 4 times higher than the total suspended matter (TSM), are dominated by HCO_3 , Cl, SO_4 , Ca, and Na. The bicarbonate and calcium values are indicative of intense chemical weathering in the Indian subcontinent, whereas

Table 2Chemical analyses of surface waters from Brahmani River and tributaries (in $\mu\text{g/l}^{-1}$)

	Site											RSD	10Eff ^a
	5D	5U	8	10D	10U	11	12	14	15D	15U	Avg		
Ag	0.22	0.23	0.25	0.32	0.11	0.21	0.14	0.16	0.24	0.12	0.20	30.0	0.30
As	3.3	1.3	2.2	13.2	2.1	1.5	2.1	0.9	4.7	2.2	3.4	97.9	33.8
B	377	374	459	466	394	397	447	417	419	424	418	7.0	394
Ba	54.4	41.5	67.0	176.4	85.1	40.5	41.9	42.7	84.1	63.0	69.7	53.5	287.3
Bi	0.03	0.08	0.07	1.15	0.01	0.05	0.06	0.04	0.27	0.13	0.19	165.4	3.14
Br	59	32	37	65	69	22	25	23	41	30	40	39.9	58
Cd	0.03	0.03	0.09	0.43	0.03	0.02	0.04	0.30	0.28	0.04	0.13	104.9	0.93
Ce	9.1	13.6	13.8	110.7	1.1	12.4	10.4	12.7	41.4	34.7	26.0	111.8	228.9
Co	2.3	2.7	3.0	1.7	0.5	1.8	1.7	2.1	10.7	8.5	4.5	83.3	26.7
Cr	9.5	12.9	14.1	47.5	4.9	10.0	11.0	10.3	58.8	21.8	20.1	81.7	103.3
Cs	0.41	0.63	0.56	1.05	0.04	0.66	0.59	0.59	2.87	2.59	1.00	85.8	2.31
Cu	7.7	7.8	10.0	57.6	2.6	5.3	5.7	14.9	18.6	12.5	14.3	101.3	138.5
Dy	0.74	0.94	1.06	10.63	0.08	0.81	0.73	0.74	2.42	2.23	2.04	137.7	20.93
Er	0.21	0.26	0.29	2.92	0.02	0.21	0.20	0.20	0.65	0.62	0.56	138.2	5.78
Eu	0.30	0.36	0.43	3.17	0.18	0.37	0.27	0.30	0.95	0.88	0.72	112.7	6.12
Ga	1.20	1.92	1.99	27.88	0.22	1.61	1.43	1.45	4.56	3.81	4.61	162.5	59.02
Gd	1.23	1.77	1.96	17.07	0.16	1.62	1.45	1.63	5.00	4.80	3.67	122.1	33.85
Ge	0.09	0.11	0.17	7.85	0.05	0.10	0.09	0.06	0.42	0.19	0.91	241.7	26.87
Hf	0.02	0.02	0.04	0.40	0.01	0.01	0.02	0.02	0.07	0.05	0.07	163.0	0.29
Ho	0.14	0.16	0.18	1.96	0.02	0.14	0.12	0.12	0.44	0.41	0.37	140.8	3.73
I	25.9	21.3	27.9	110.5	53.4	31.7	79.6	22.1	82.2	37.7	49.2	572.0	71.7
La	4.9	6.7	7.0	54.1	0.6	6.4	5.4	6.3	19.6	19.6	13.1	108.6	114.5
Li	2.8	3.9	4.0	19.1	3.2	3.7	3.4	3.6	14.5	12.1	7.0	76.1	49.5
Lu	0.03	0.05	0.06	0.50	0.01	0.05	0.04	0.05	0.13	0.12	0.10	125.3	1.00
Mn	151.3	106.9	120.8	348.2	20.1	68.9	74.0	110.0	457.2	355.9	181.3	74.3	414.4
Mo	0.2	0.2	0.3	52.2	0.8	0.2	0.1	0.2	1.1	0.1	5.5	267.7	77.8
Nd	4.8	6.6	7.1	59.8	0.6	6.5	5.3	6.4	19.6	20.5	13.7	114.6	122.0
Ni	7.8	9.0	9.9	41.4	3.5	7.5	7.7	7.6	24.7	20.6	14.0	75.4	85.8
P	9.1	79	114	1286	68	63	65	66	232	85	215	159.8	2179
Pb	3.15	4.15	4.84	33.54	0.75	3.31	2.93	4.26	33.19	6.46	9.66	117.8	92.42
Pr	1.39	1.99	2.09	17.20	0.17	1.92	1.62	1.87	5.90	6.15	4.03	112.5	36.35
Rb	8.6	11.5	11.2	16.7	2.9	11.4	10.1	10.5	45.6	47.3	17.6	80.2	34.9
Sc	0.5	0.6	0.7	2.5	0.3	0.5	0.5	0.5	1.2	1.2	0.9	69.6	4.6
Sm	0.84	1.32	1.22	13.22	0.09	1.11	0.98	1.09	3.70	3.59	2.72	128.9	24.12
Sn	1.78	1.66	1.53	4.12	1.26	0.79	1.07	1.20	3.31	0.81	1.75	56.8	5.36
Sr	90.3	51.6	91.8	309.6	191.5	40.7	42.7	46.9	113.4	78.3	105.7	72.6	303.4
Tb	0.16	0.22	0.24	2.21	0.02	0.18	0.16	0.20	0.64	0.57	0.46	126.6	4.53
Th	0.58	1.39	1.44	13.89	0.14	1.40	1.34	1.39	3.45	3.77	2.88	126.6	31.66
Ti	84.3	146.9	149.0	2282.5	69.2	105.9	105.8	115.7	413.5	290.8	376.4	163.0	4663.8
Tl	0.04	0.07	0.07	0.57	0.02	0.08	0.05	0.06	0.81	0.21	0.20	123.5	1.46
Tm	0.03	0.04	0.04	0.44	0.01	0.04	0.03	0.03	0.10	0.10	0.09	134.5	0.87
U	0.39	0.39	0.57	5.85	1.04	0.30	0.26	0.33	0.81	0.85	1.08	142.3	12.54
V	9.1	13.1	15.4	86.6	2.6	9.9	9.7	9.8	33.1	23.5	21.3	104.2	212.0
W	0.04	0.04	0.06	0.89	0.07	0.05	0.04	0.05	0.18	0.05	0.15	162.7	2.10
Y	3.02	3.93	4.24	44.98	0.36	3.22	2.68	3.00	10.18	9.81	8.54	139.5	87.44
Yb	0.26	0.36	0.41	3.73	0.03	0.30	0.25	0.27	0.90	0.87	0.74	133.2	7.43
Zn	11.4	10.3	29.7	52.5	5.6	9.8	9.4	15.8	73.5	24.6	24.3	83.0	132.2
Zr	0.98	0.87	1.66	22.09	0.94	0.87	1.17	1.06	2.33	1.44	3.34	178.8	11.20
pH	7.4	7.9	7.8	7.8	7.5	7.7	7.3	8.2	8.0	7.3	7.7	3.8	8.4

^a Sample 10Eff (effluent) not calculated into average or relative standard deviation

the high sulfate, chloride, and sodium values are largely due to the proximity of the sea (Subramanian and others 1987).

While these previous publications provide a general characterization of the major cation and anion concentrations of Indian waters, there are no studies, as far as we are

aware, that provide data for a wide array of trace elements. Analyses of these ions in a river system are essential for estimations of various sources influencing river chemistry and the partitioning of elements among the water column and sediment. This knowledge may be particularly relevant in some industrial regions of peninsular

Table 3
Chemical analysis of surface waters from Baitarani River and tributaries (in $\mu\text{g l}^{-1}$)

	Site						RSD
	6D	6U	13	23	24	Avg	
Ag	0.19	0.17	0.17	0.28	0.12	0.19	28.2
As	0.5	2.1	0.1	1.1	0.1	0.8	96.8
B	365	404	325	349	413	371	8.9
Ba	43.1	39.5	19.3	43.5	63.6	41.8	33.8
Bi	0.07	0.03	0.01	0.04	0.14	0.06	78.2
Br	30	39	24	95	321	102	110.5
Cd	0.04	0.03	0.02	0.04	0.06	0.04	34.9
Ce	14.6	6.9	3.0	16.6	54.9	19.2	96.6
Co	2.9	3.4	1.9	7.0	16.6	6.3	85.3
Cr	14.1	16.0	7.7	36.6	56.6	26.2	68.8
Cs	0.67	0.31	0.12	0.76	2.20	0.81	90.2
Cu	7.1	6.5	3.4	11.9	27.2	11.2	75.1
Dy	1.00	0.55	0.24	1.13	4.16	1.42	99.5
Er	0.29	0.12	0.05	0.29	1.08	0.37	100.9
Eu	0.39	0.27	0.12	0.45	1.30	0.51	81.6
Ga	1.97	1.25	0.43	2.64	6.94	2.65	85.8
Gd	1.88	1.04	0.41	2.13	7.02	2.50	93.9
Ge	0.12	0.04	0.05	0.09	0.19	0.10	55.3
Hf	0.02	0.02	0.01	0.02	0.04	0.02	44.5
Ho	0.18	0.08	0.04	0.19	0.70	0.24	100.0
I	19.6	67.4	33.4	49.0	108.5	55.6	55.6
La	7.2	3.5	1.2	8.3	25.9	9.2	95.0
Li	4.3	3.1	1.7	5.8	17.6	6.5	87.9
Lu	0.06	0.02	0.01	0.06	0.20	0.07	97.3
Mn	113.4	156.0	85.4	357.6	459.4	234.4	62.9
Mo	0.2	0.1	0.1	0.2	0.2	0.2	30.6
Nd	7.5	3.7	1.5	8.3	28.3	9.8	97.0
Ni	10.2	13.4	4.6	23.8	39.6	18.3	67.3
P	104	78	48	105	194	106	46.1
Pb	4.18	2.75	1.28	5.23	13.98	5.48	81.2
Pr	2.15	1.05	0.39	2.43	8.18	2.84	97.5
Rb	12.1	6.0	2.6	13.7	46.2	16.1	96.6
Sc	0.7	0.6	0.3	0.9	1.9	0.9	62.0
Sm	1.40	0.69	0.25	1.46	5.23	1.81	98.0
Sn	1.60	1.60	0.91	0.62	0.55	1.06	43.6
Sr	47.1	74.5	37.7	76.5	113.1	69.8	37.8
Tb	0.25	0.14	0.04	0.25	0.92	0.32	96.9
Th	1.64	0.53	0.24	1.05	4.25	1.54	93.1
Ti	150.9	32.8	25.5	92.6	268.2	114.0	78.5
Tl	0.08	0.03	0.01	0.07	0.20	0.08	84.8
Tm	0.05	0.02	0.01	0.05	0.17	0.06	95.5
U	0.40	0.29	0.08	0.34	1.06	0.43	76.3
V	13.4	10.6	5.1	19.2	48.9	19.4	79.3
W	0.04	0.10	0.3	0.18	0.04	0.08	72.7
Y	4.10	2.12	0.89	4.69	16.36	5.63	98.3
Yb	0.39	0.17	0.08	0.42	1.40	0.49	95.9
Zn	11.8	10.3	6.0	18.8	35.5	16.5	62.7
Zr	0.84	0.70	0.50	1.01	0.91	0.79	22.4
pH	7.9	8.3	7.7	7.3	7.4	7.7	5.2

India, such as Orissa State (population 31.5 million), where significant anthropogenic inputs occur from industrial, agricultural, and urban areas. Accordingly, the purpose of the current work was to complement the pre-existing studies of major element chemistry of Orissa State rivers (i.e., Subramanian 1979, 1980; Ray and others 1984;

Subramanian and others 1987; Chakrapani and Subramanian 1990a, b, 1993, 1994) by providing a more detailed geochemical study of the surface waters in three of the state's largest river systems; the Mahanadi, Brahmani and Baitarani Rivers.

Study area

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

All three river catchments are characterized by Precambrian granites, gneisses, and schists of the Eastern Ghats, with local basic intrusive and volcanic lithologies; limestones, sandstones, and shales of the Gondwanas; and recent deltaic alluvium deposits at the river mouths on the Bay of Bengal (Ray and others 1984; Chakrapani and Subramanian 1990a). It has been estimated, for example, that in the Mahanadi River basin, the lithology consists of 56% Precambrian rocks, 22% sandstone and shale of the Upper Gondwana, 17% limestone and shale of the Lower Gondwana, and 5% coastal alluvium (Chakrapani and Subramanian 1990a).

Sampling and analytical methods

Water samples were collected from the Mahanadi River, the Brahmani River and the Baitarani River, as well as several of their tributaries in October 1993. To assess anthropogenic impacts, many of the samples were collected both upstream (indicated by a U in the sample numbers) and downstream (D) from urban or industrial areas: the former include, sites 3, 4, 5, 6, 19 and 22, whereas the latter include, sites 10, 15 and 17 (Fig. 1). Site 10 was located adjacent to NALCO (National Aluminum Company), FCI (Fertilizer Corporation of India) and TTPS (Talcher Thermal Power Plant Station) on the Brahmani River at Angul; site 15 at the Rourkela Steel Plant on the Brahmani River at Rourkela; and site 17 at the Orient Paper Mill on the Ib River (a tributary of the Mahanadi) at Brajraj Nagar. Sample 10C is the collective aqueous effluent discharged by NALCO, FCI, and TTPS into the Brahmani River.

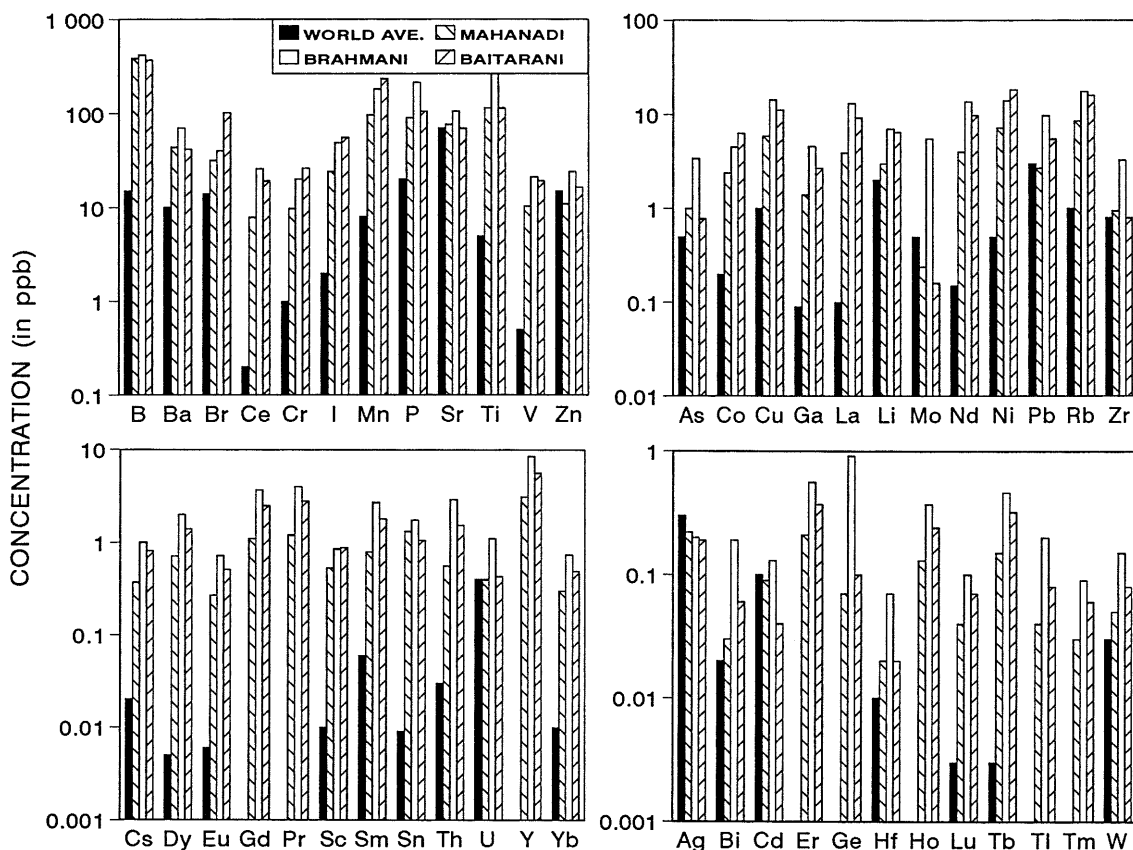


Fig. 2 Comparison of the average "dissolved" element concentrations in the surface waters of the Mahanadi, Brahmani, and Baitarani rivers with the world river average (WRA). WRA values not determined for some elements

Water samples of approximately 125 ml were collected for multielement analysis, pressure filtered through 0.2- μm Nuclepore membranes (Costar Corp.), and acidified on site with 3 ml analytical grade HNO_3 to bring the water-acid solution to a $\text{pH} < 2$. The elemental concentrations in the "dissolved" size fraction were determined by inductively coupled plasma-mass spectroscopy (ICP-MS). As a check on accuracy, Activation Laboratories (Ancaster, Canada) employed two internal standards (each run twice) and found that the errors were consistently less than 10%, while analysis of the aqueous reference standard (SLRS-2) was found to be better than $\pm 18\%$; this higher value is presumably due to the standard not being incorporated in the calibration procedure. Furthermore, analyses of duplicates suggested reproducibility typically within $\pm 15\%$.

An estimation of the organic content in the water samples was made by collecting approximately 30 ml of river water, drying in an oven at 110°C until completely evaporated, and then ashing the remaining solids in a muffled furnace at 550°C overnight. Sample weights were then compared between preashing and postashing to determine loss on ignition values (predominantly organics, with some volatile metals). Similarly, the concentration of total solids (dissolved and particulate materials) could be determined from the preashing weight.

Surface water chemistry

The concentrations of 48 trace elements in river water (dissolved size fraction) are given for several sample sites in the Mahanadi River and tributaries (Table 1), the Brahmani River and tributaries (Table 2), and the Baitarani River (Table 3); pH values for individual sample sites are also provided. Concentrations for Au, Be, Hg, In, Ir, Nb, Os, Pd, Pt, Re, Rh, Ru, Sb, Se, Ta, and Te were all below the detection limit for ICP-MS and therefore are not listed in Tables 1-3.

The large relative standard deviation values (1σ) shown in Tables 1-3 indicate that there is significant variability among the individual sampling sites in all three river basins: the greatest variability is in the surface waters of the Brahmani, followed by the Mahanadi and Baitarani rivers, respectively. The wide range of concentrations most likely represents different point-source inputs, since chemical weathering of granites and sedimentary rocks (throughout the river's catchment) are unlikely to provide such large spatial fluctuations in trace element content. Additionally, we are dealing with extremely low concentrations (in ppb); hence, some variability through analytical error can also be expected.

As shown in previous studies of river systems (Stallard and Edmond 1983), the chemical composition of surface waters is primarily determined by the geological source and erosional regime. Because all three rivers drain simi-

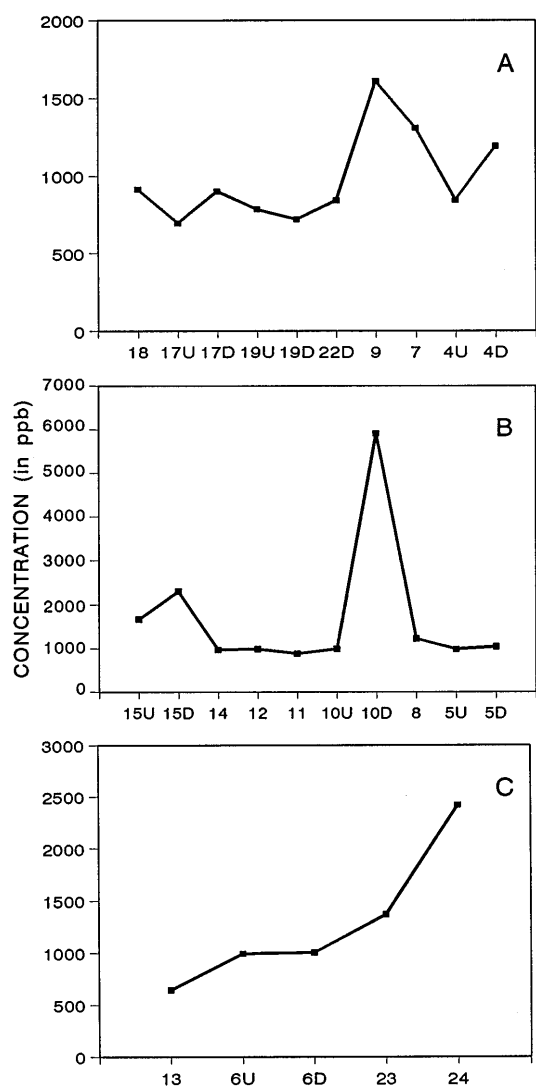


Fig. 3

Comparison of total trace element content in the surface waters from various sample sites (upstream to downstream) in A: the Mahanadi River; B: the Brahmani River; and C: the Baitarani River

lar geological terrains, it might be expected that the dissolved element concentrations should also be similar. While this assumption was shown to be valid for major cations and anions (Subramanian and others 1987), the trace element concentrations for all three rivers differed extensively. The disparity in concentrations sometimes approached (or exceeded) one order of magnitude, with the highest concentrations typically belonging to the surface waters of the Brahmani River (Fig. 2). Of the 48 trace elements displayed, the Brahmani River had the highest concentration for all, except Br, Co, Cr, I, Mn, Ni, and Sc, which were higher in the Baitarani River, and Ag, which was higher in the Mahanadi River. Furthermore, compared to the world river average, all elements, with the exception of Ag, were found in excess in the Brahmani River. In the Baitarani and Mahanadi rivers, most

elements were also found in higher concentrations, with the exception of Ag, Cd, Mo, and Zr for the Baitarani and Ag, Cd, Mo, Pb, and Zn for the Mahanadi.

To determine whether trace elements accumulated from the upper reaches (Precambrian Shield) to the lower reaches (coastal alluvium) of each river system, the total concentrations of all 48 elements were compared at several sampling sites along the course (upstream to downstream) of the Mahanadi River (Fig. 3A), the Brahmani River (Fig. 3B), and the Baitarani River (Fig. 3C). In the Mahanadi River basin, there was a slight overall trend to increased trace element concentrations downstream. Most significant was the consistent increase immediately downstream from either urban or industrial areas. The large increase at site 9 suggests a high elemental input into the stream; however, we are not aware of any anthropogenic source at this locality. In the Brahmani River, there was no obvious elemental accumulation downstream. The only pattern seen was the dramatic increase in total dissolved elements directly downstream from the discharge of industrial effluent at Angul. In the Baitarani River, however, elemental accumulation downstream was more pronounced, with the trend largely due to the solute-rich waters collected at sample sites 23 and 24.

A similar analysis was made between waters collected upstream and downstream of various towns (Fig. 4). It was surprising to find that the concentrations (for 29 elements, including rare earth elements (Ree's) averaged together) were frequently higher in the former sampling location. Taking into account the maximum potential error in accuracy (18%), these include: site 5 (Cs, Ti, and Th); site 6 (Sr, W, I, and As); site 19 (Mo, Zr, Sn, W, and Zn); and site 22 (U, Zn, Cr, Sc, Ni, Pb, Ti, V, Li, W, Th, Rb, Mn, Co, Ree's, and Cs). When the elements were grouped according to their placement in the periodic table (i.e., alkali and alkaline earths, transition metals, actinides, and others), there appeared to be a similar plotting of actinides, alkaline earths, and alkali metals. The transition metals showed no such pattern, with some metals being enriched, while others showed significant depletion. More interestingly, these metals did not even correlate when their valences were compared. For example, Cu, Ni, and Zn have 2+ charges in solution as the dominant ions (Moore and Ramamoorthy 1983), but they seldom behaved in accordance.

The concentrations of total solids (TS) were calculated upstream and downstream of several towns (Table 4). For sites 3, 4, 19, and 22, TS increased downstream of the urban areas, presumably due to the addition of sewage. For some sampling sites (4 and 19), the effluent appears to have been comprised predominantly of inorganic components, since the inorganic-to-organic ratio increased. This correlates well with the observed increases in trace element concentrations downstream (Fig. 4). For other sites (3 and 22), the concentration of organics increased substantially downstream of the towns, indicating the organic-rich nature of the effluent. In sampling site 5, the concentration of total solids actually decreased downstream. This apparent loss appears to come at the ex-

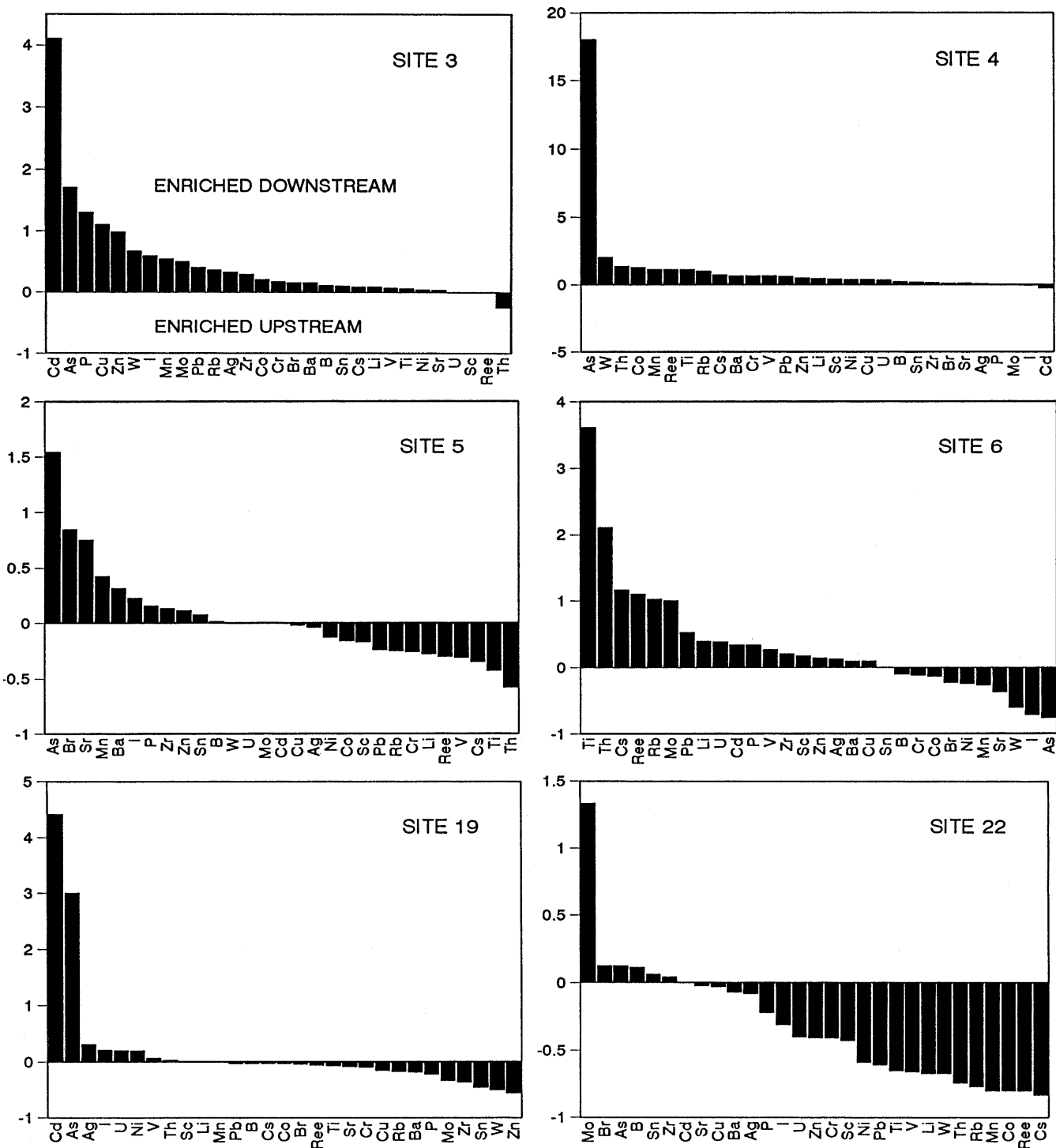


Fig. 4 Comparison of trace element concentrations in the surface waters from various sample sites, both upstream and downstream of urban areas. The axis indicates the factor by which trace elements are enriched in either location

pense of the inorganic components, since the levels of organic material in the surface waters were higher downstream.

In Fig. 5, a comparison is made between concentrations of trace elements upstream and downstream of industry. Correcting for possible analytical error, only Mo was depleted downstream for site 17; all other metals were consistently enriched downstream. At site 10, every element was found in significantly higher concentrations, with differences often greater than one order of magnitude. At

Table 4Concentration of total solids (dissolved and particulate) in surface waters (in mg l⁻¹)

	Site									
	3U	3D	4U	4D	5U	5D	19U	19D	22U	22D
Total solids	256.3	302.8	272.6	437.9	418.0	312.0	240.8	257.1	249.6	275.2
Inorganic	158.9	151.4	139.1	262.7	288.4	137.3	106.0	125.9	127.3	132.1
Organic	97.4	151.4	133.5	175.2	129.6	174.7	134.8	131.2	122.3	143.1
% inorganic	62	50	51	60	69	44	44	49	51	48
% organic	38	50	49	40	31	56	56	51	49	52

this location we were able to sample the aqueous effluent that was discharged by the three main industries located there. Table 2 shows that this effluent is clearly responsible for the variation in composition between upstream and downstream localities.

Conclusions

In any river system, an understanding of the concentrations, and fate, of trace elements is of profound importance in addressing their impact on the regional environment. The surface waters of the Mahanadi, Brahmani, and Baitarani rivers were shown to have extremely variable trace element concentrations, consistently higher than the world river average. This contradicts the prevailing thought that Indian rivers have low heavy-metal concentrations compared to world mean values (Biksham and Subramanian 1988b). While some elemental enrichment may stem from the complex geological terrains of Orissa State (Chakrapani and Subramanian 1990a), it is unlikely that weathering of metallogenic terrains is significant in affecting river chemistry all along the river's course. For example, the concentration of trace elements in the upper stretches of the river, which drain crystalline rock, do not generally exceed the concentration of the same elements in the lower stretches of the river, which drain coastal alluvium. If any pattern has arisen, it is that element concentrations tend to increase downstream. This is particularly evident in the Baitarani River, where the concentrations near the river's mouth are most elevated, suggesting that either the elements are actually being concentrated, through additive or evaporative processes, or that the sites further downstream (i.e., 23 and 24) have higher elemental inputs. In either case, this argues against significant input of trace elements through chemical weathering of shield lithologies alone.

A more likely explanation for the high and variable concentrations, and the subtle to dramatic downstream increases, is anthropogenic inputs: industrial pollution, domestic sewage, and agricultural runoff. In a recent survey of the total industrial pollution in Orissa, it was estimated that industrial wastewater constitutes by volume about 33% of the total wastewater, with the remaining

67% coming from the domestic sector and nonpoint sources (Sene-Johansen 1995).

The impact of pollution on river chemistry is most evident in the Brahmani River, where high elemental concentrations correspond to the presence of heavily industrialized areas (Sene-Johansen 1995). This contrasts with the Mahanadi catchment, with minor industrialization and lower dissolved element concentrations. In the Brahmani River, site 10 exemplifies the influence of anthropogenic activity. This location marks the discharge point of industrial effluent from NALCO, FCI, and TTPS into the river. The pollutants emitted from NALCO consist of fluorides and fly ash, both released as by-products during smelting of the aluminum hydroxide precursor. The waste materials generated from the refinery are typically flushed with water into an ash pond; however, these ponds frequently overflow (especially after heavy rains) and the ash slurry pollutes the river. The ash content of the coal is very high, with a wide array of trace metals enriched several orders of magnitude over their original content in the coal (Tazaki and others 1989). In addition to NALCO, the FCI plant manufactures urea and is coal-based. The various pollutants generated from the process are nitrogen compounds, cyanide, chromium, and other suspended solids. TTPS also operates using coal, with the main source of pollutants derived from the solid wastes in the form of fly ash and bottom ash. The common practice is also to dispose of the ash into settling ponds, which periodically overflow. The end result of all three industries is a collective discharge of effluent, in which the concentrations of most elements are enriched over 10 times the upstream values.

Sample site 15 (Rourkela Steel Plant) and sample site 17 (Orient Paper Mill) shows similar patterns of element enrichment downstream. The operation in Rourkela comprises a large integrated steel plant, along with a coke plant, foundry, sintering plant, captive power plant, nitric acid plant, a sulfuric acid plant, and a fertilizer plant. Discharge of the waste products of the raw iron ore and fertilizer manufacturing both result in pollution of the local waters. The paper mill at Brajraj Nagar is regarded as a highly water-polluting industry because of the extensive use of chemicals (Sene-Johansen 1995). The Orient Paper Mill produces its own caustic soda, and mercury, which is used in its manufacturing, is often detected in the ef-

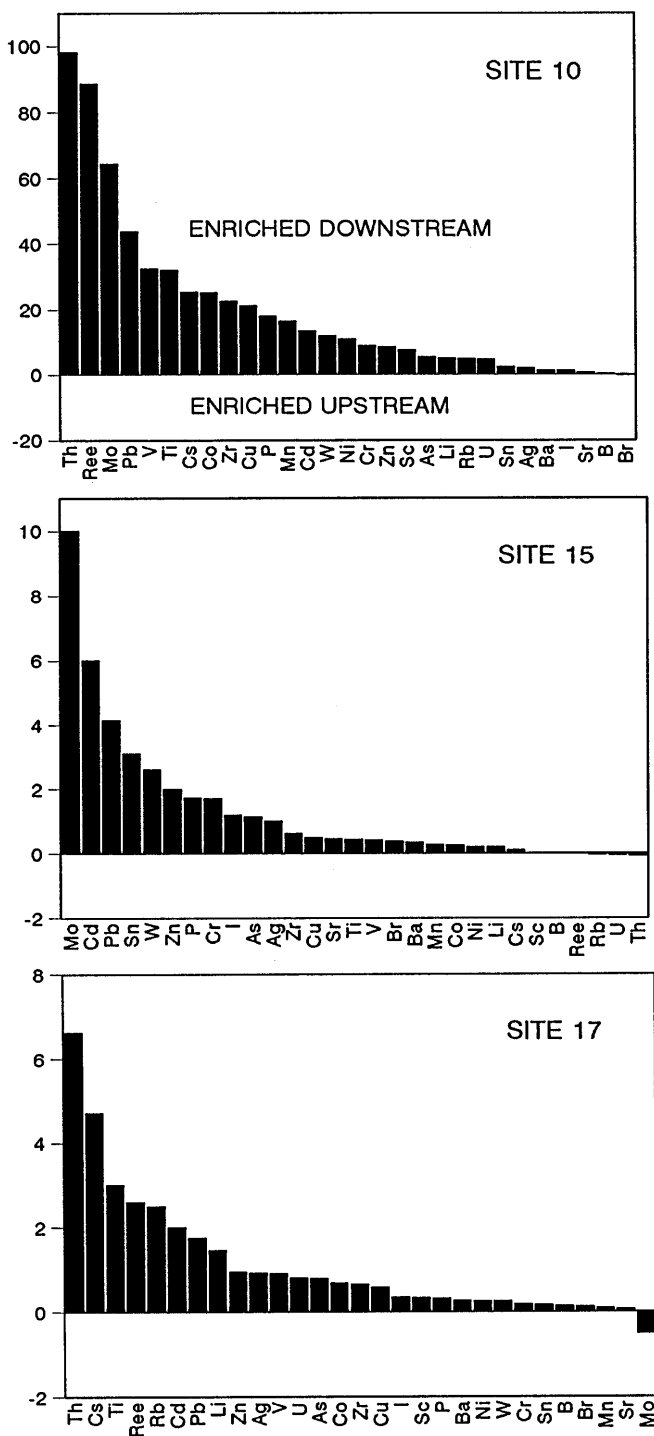


Fig. 5 Comparison of trace element concentrations in the surface waters from various sample sites, both upstream and downstream of industry

fluent. In addition, the wastewater contains high levels of suspended solids, both organic and inorganic. The other two major sources of pollution, domestic sewage and agricultural runoff, also affect river chemistry. Because none of the towns in Orissa have proper sewage,

open drains carry the wastewater directly into the river system. In addition, there is no organized garbage or domestic waste disposal, and hence it is dumped directly into local rivers. Although there has not been any direct measurement of the sewage from any city in Orissa, it is not difficult to imagine that it must exert a major influence on river chemistry. The effects of sewage input can be observed in the commonly higher elemental concentrations (in surface waters) for sampling sites located downstream from urban areas. In some locations, where higher concentrations were found upstream of the towns, complexation by some components of the sewage may have effectively sequestered available elements from solution and converted them to particulate material. The resultant metal salts, hydroxides, and organometallic complexes can then either remain in suspension or flocculate into the bottom sediment, as is shown by the high metal concentrations in the bottom sediment directly downstream from the towns (unpublished data).

Although the use of fertilizers and pesticides in the state is low, high concentrations of phosphorus in all three rivers (compared to the world river average) can also be partially attributed to both its use and the runoff from livestock manure. However, because agricultural activity is widespread, and a nonpoint source of contaminants to a river system, it is extremely difficult to determine where the pollutants are entering the river.

Overall, the results from this study indicate that major Indian rivers, such as the Mahanadi and Brahmani, as well as secondary rivers, such as the Baitarani, carry substantial amounts of trace elements in solution, with all three rivers being extremely solute-rich compared to the world river average. Anthropogenic activity clearly controls their chemical composition. Although the impact of pollution is readily recognizable in local samples, there does not appear to be a significant accumulation of elements in the lower stretches of the Mahanadi or Brahmani rivers. Subsequently, high elemental inputs at one particular site tend not to be clearly recognizable many kilometers downstream. Apparently, for these large rivers, discharged effluent becomes rapidly diluted, while complexation and sedimentation of soluble elements may further result in their depletion from the water column, in proximity to the anthropogenic source. In the latter case, these elements build up in the bottom sediment. This is not, however, the pattern in the less voluminous Baitarani River. Element enrichment near the river's mouth indicate that in this secondary river, where dilution effects are less, the concerns over regional water quality may be considerably more prevalent.

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