Fluvial geochemistry of Subarnarekha River basin, India

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The fluvial geochemistry of the Subarnarekha River and its major tributaries has been studied on a seasonal basis in order to assess the geochemical processes that explain the water composition and estimate solute fluxes. The analytical results show the mildly acidic to alkaline nature of the Subarnarekha River water and the dominance of Ca^{2+} and Na^{+} in cationic and HCO_3^{-} and Cl^{-} in anionic composition. Minimum ionic concentration during the monsoon and maximum concentration in the pre-monsoon seasons reflect concentrating effects due to decrease in the river discharge and increase in the base flow contribution during the pre-monsoon and dilution effects of atmospheric precipitation in the monsoon season. The solute acquisition processes are mainly controlled by weathering of rocks, with minor contribution from marine and anthropogenic sources. Higher contribution of alkaline earth ($\text{Ca}^{2+} + \text{Mg}^{2+}$) to the total cations (TZ^{+}) and high $(\text{Na}^{+} + \text{K}^{+})/\text{Cl}^{-}$, $(\text{Na}^{+} + \text{K}^{+})/\text{TZ}^{+}$, $\text{HCO}_3^{-}/(\text{SO}_4^{2-} + \text{Cl}^{-})$ and low $(\text{Ca}^{2+} + \text{Mg}^{2+})/(\text{Na}^{+} + \text{K}^{+})$ equivalent ratios suggest that the Subarnarekha River water is under the combined influence of carbonate and silicate weathering. The river water is undersaturated with respect to dolomite and calcite during the post-monsoon and monsoon seasons and oversaturated in the pre-monsoon season. The pH–log H_4SiO_4 stability diagram demonstrates that the water chemistry is in equilibrium with the kaolinite. The Subarnarekha River annually delivered 1.477×10^6 ton of dissolved loads to the Bay of Bengal, with an estimated chemical denudation rate of $77 \text{ ton km}^{-2} \text{ yr}^{-1}$. Sodium adsorption ratio, residual sodium carbonate and per cent sodium values placed the studied river water in the ‘excellent to good quality’ category and it can be safely used for irrigation.

Keywords. Subarnarekha River basin; weathering; solute acquisition; dissolved flux; saturation index; water quality.

1. Introduction

Water is the most essential natural resource for sustaining all forms of life, food production, economic development and general well-being. Water is also one of the most manageable natural resources as it can be diverted, transported, stored and recycled. India accounts for 2.4% of the global

land and 4% of the world water resources, but it has to support 16% of the world’s human and 20% of livestock populations (Kumar *et al.* 2005). Rivers are the major source of fresh water for agricultural and industrial usage. River processes form a major link in the geochemical cycle and the hydro-chemical study of river basins reveals the nature of weathering at a basin scale and helps

in understanding the exogenic cycling of elements in the continent–river–ocean system. Nearly 90% of the natural weathered as well as man-made materials that are transported in both dissolved and particulate phases are delivered to the oceans by rivers (Meybeck 1987, 2003). The quantification of the major-ion composition of river water has broad implications in assessing the hydrogeological characteristics; weathering processes, water quality type and rainfall chemistry (Drever 1988; Gaillardet *et al.* 1999; Brennan and Lowenstein 2002). In addition, information on river water chemistry is essential to assess the water quality for domestic, agricultural and industrial uses and useful in environmental impact assessment and pollution control. India is gifted with a river system comprising more than 20 major rivers with several smaller river basins and its tributaries. Many of these rivers are perennial and some of them are seasonal (Rao 1975). The rivers of India drain a total area of about $3.1 \times 10^6 \text{ km}^2$ and annually discharge 1650 km^3 of water, accounting for 4.5% of the global river discharge (Krishnaswami and Singh 2005). The hydrological cycle in most of the Indian river basins is being modified quantitatively and qualitatively as a result of developmental activities such as construction of dams and reservoirs; land use change; indiscriminate disposal of anthropogenic, industrial and mining wastes; unplanned application of agrochemicals and discharges of improperly treated sewage/industrial effluents (Chakrapani and Subramanian 1990; Ramanathan *et al.* 1994; Singh and Hasnain 1999; Subramanian 2000).

Previous studies have revealed the major-ion chemistry of some of the world's large- and medium-sized river systems including the Amazon (Gibbs 1972; Stallard and Edmond 1983, 1987; Gaillardet *et al.* 1997), Orinoco (Nemeth *et al.* 1982), Mackenzie (Reeder *et al.* 1972), Mississippi (Presley *et al.* 1980), Mekong (Carbonnel and Meybeck 1975), Changjiang and Huanghe (Hu *et al.* 1982; Zhang *et al.* 1990, 1995; Chen *et al.* 2002), Ganges–Brahmaputra (Abbas and Subramanian 1984; Sarin *et al.* 1989; Galy and France-Lanord 1999), Godavari (Biksham and Subramanian 1988; Jha *et al.* 2009), Krishna (Ramesh and Subramanian 1988; Das *et al.* 2005), Cauvery (Ramanathan *et al.* 1994; Pattanaik *et al.* 2013), Mahanadi (Chakrapani and Subramanian 1990); Damodar (Singh and Hasnain 1999) and Mahi (Sharma *et al.* 2012). These extensive studies not only reported the signatures of river systems

responding to natural processes, such as atmospheric precipitation and chemical weathering, but also detected the significant signatures responding to human activities. The chemical composition of river water is determined by several factors such as relief and altitude of the catchment, tectono-climatic setup, rainfall quantity and quality, bedrock geology, soil and vegetation cover, biological and anthropogenic activities in the drainage basin (Berner and Berner 1987; Stallard and Edmond 1987; Rajamani *et al.* 2009). In comparison to large rivers, the smaller rivers invariably flow in less diverse geological terrains, having limited tectono-climatic variations and the effect of human interventions could be better constrained in a smaller river basin. The present study deals with the fluvial geochemistry of the Subarnarekha River basin – a moderate size rain-fed river of eastern India flowing through India's important mining and industrial belt. This study aims to characterise the major-ion chemistry and evaluates weathering and solute acquisition processes and anthropogenic influences on the surface water quality of the Subarnarekha River. This study also envisages the seasonal and downstream compositional changes, dissolved fluxes and suitability of surface water resources for irrigation uses.

2. Subarnarekha River basin

The Subarnarekha is a moderate sized river basin, extending over $19,296 \text{ km}^2$ and covering 0.6% of the geographical area of India. The total annual yield of water flowing within the basins is in the order of 7940 million m^3 (CBPCWP 1986). It is a rain-fed river that rises from a series of contact springs located near the Nagri village ($23^\circ 18' \text{N}$, $85^\circ 11' \text{E}$) at an elevation of 740 m on the Ranchi Plateau in Chhota Nagpur highland (figure 1). The Subarnarekha empties its enormous volume of water and sediment load into the Bay of Bengal after its 395 km long journey from its source at Nagri village to its mouth near Kirtania port ($21^\circ 33' 18'' \text{N}$, $87^\circ 23' 31'' \text{E}$). Out of its total length of 395 km, 269 km are in Jharkhand, 64 km in West Bengal and 62 km in Odisha states. The Subarnarekha is a very important river to satisfy the irrigation, industrial and municipal water demands of these three states. Ruru, Kanchi, Karkari, Kharkai and Dulung are the major tributaries of the Subarnarekha River.

Figure 1. Location map of Subarnarekha River basin showing sampling locations, major mines, minerals and industrial zones.

The major part of the Subarnarekha basin lies on the Indian Shield, where the ancient Precambrian igneous and metamorphic rocks are exposed. In the lower reaches of the basin, the younger geological formation such as Tertiary Gravels, Pleistocene Alluvium and Recent Alluvium are exposed. Pelitic schist, calc-magnesium metasediments, ortho-amphibolites, tonalite-trondhjemite, banded iron formation, mafic lavas, phyllites, shales, metapellites, quartzites, soda-granites, granitic-gneiss, dolerite dyke swarms and gravels are the major litho units associated with the geological formations of the basin. The Subarnarekha basin is rich in mineral resources mainly comprising ores of metals such as copper, iron, uranium, chromium, gold, and vanadium and non-metals such as kyanite, asbestos, barytes, apatite, china clay, talc, limestone, dolomite and building stones (figure 1). The basin is studded with a large number of mineral-based industries and mines

both working and abandoned with the attendant problems of environmental hazard. Heavy Engineering Corporation (HEC), Usha Martin Industries, Steel Authority of India (SAIL), Hindalco Industries Ltd., Tata Steel and Iron Company, Hindustan Copper Ltd. (HCL) and Uranium Corporation of India (UCIL) are the major industrial units in the basin.

The Subarnarekha basin is dominated by humid tropical climate with hot summers and mild winters. The mean monthly temperature varies from 40.5°C in May to 9.0°C in December. The mean annual rainfall in the basin is ~1400 mm. The rainfall distribution is not uniform and 85–95% of the annual precipitation and about 82% of the total annual flow actually occurs over only four wet months (June–September), while in the remaining part of the year, the Subarnarekha River and its tributaries run almost dry. Agricultural land accounts for 62% of the total basin area

Table 1. Chemical composition of surface water of Subarnarekha River and its major tributaries.

Site code	Site name/tributary	pH	EC ($\mu\text{S cm}^{-1}$)	TDS (mg l^{-1})	F^{-} (μM)	Cl^{-} (μM)	HCO_3^{-} (μM)	SO_4^{2-} (μM)	NO_3^{-} (μM)	Silica (μM)
Subarnarekha main channel										
1 a	Nagri	6.26	116	87	12	274	533	22	154	187
b		6.33	138	99	16	305	590	25	189	232
c		6.20	90	71	9	97	464	11	124	210
2 a	Namkum	7.20	570	427	18	1260	3623	149	186	392
b		7.57	1000	645	27	3179	5229	256	4	198
c		7.08	408	305	23	1175	1934	154	420	292
3 a	Tatisilwai	6.72	499	404	13	1817	2547	142	529	362
b		7.38	1220	847	23	5802	5016	196	963	387
c		6.95	431	309	22	1533	1770	155	404	298
4 a	Hundru	7.91	183	157	19	229	1443	68	17	280
b		8.00	265	212	22	865	1557	95	9	312
c		7.85	167	136	17	327	1213	61	9	210
5 a	Muri	7.72	216	176	16	284	1600	96	28	284
b		7.93	762	599	65	1424	5000	629	38	323
c		8.15	190	129	22	555	902	97	36	135
6 a	Chandil	8.25	165	135	18	133	1229	56	10	320
b		7.69	177	154	31	177	1439	52	12	280
c		8.09	119	95	23	97	820	52	17	228
7 a	Barabinda	7.98	162	140	21	131	1311	55	34	293
b		8.19	190	162	28	170	1500	48	30	315
c		7.62	125	100	22	92	852	57	27	230
8 a	Kanderbera	7.97	154	134	55	141	1229	62	10	252
b		8.54	185	154	28	167	1500	44	2	243
c		8.08	143	118	21	101	1066	70	22	228
9 a	Janshedpur (Sonari)	7.72	290	254	17	281	2459	131	28	343
b		7.31	221	187	22	272	1744	86	11	288
c		7.79	190	162	19	168	1475	91	28	256
10 a	Janshedpur (Mango)	7.62	249	206	18	258	1956	93	23	355
b		7.53	216	190	20	279	1744	67	37	315
c		7.82	209	156	20	211	1311	113	59	256
11 a	Galudih	7.80	395	340	37	581	2295	729	17	332
b		7.51	259	208	46	486	1672	151	37	278
c		7.94	163	138	24	150	1229	79	46	213
12 a	Moosabani U/S	8.17	293	246	26	316	2131	273	25	258
b		8.73	305	244	48	587	1744	347	1	302
c		7.84	261	193	23	236	1311	423	52	218

13 a	Moosabani D/S	8.14	313	262	21	312	2377	265	26	248
b		7.51	297	227	48	574	1639	279	1	315
c		7.78	186	150	23	223	1279	90	81	224
14 a	Shyamsunderpur	8.39	249	210	39	301	1885	184	25	257
b		7.79	293	249	45	535	2016	240	34	280
c		7.72	174	143	23	164	1246	92	50	229
15 a	Baharagora	8.02	238	209	19	275	1836	182	17	293
b		7.65	285	223	52	558	1621	247	19	315
c		8.11	165	137	22	188	1180	85	46	229
16 a	Gopiballavpur	7.92	227	201	33	253	1803	152	14	303
b		8.38	279	236	49	552	1852	229	18	290
c		8.00	168	137	22	131	1229	82	24	233
17 a	Mahapal	7.60	304	275	17	259	2852	92	4	280
b		8.02	283	227	44	531	1805	206	14	287
c		7.78	176	139	24	161	1262	64	22	235
18 a	Sonakaniya	7.91	219	189	18	218	1718	121	7	340
b		8.93	249	198	45	480	1500	190	7	303
c		8.03	158	131	25	128	1213	70	16	221
19 a	Rajghat	7.83	229	197	16	236	1803	126	23	321
b		8.66	246	221	44	406	1885	184	34	307
c		8.20	156	139	23	127	1279	74	16	249
Tributaries										
20 a	Kanchi	7.74	165	140	15	122	1311	40	11	327
b		7.89	207	177	23	248	1623	57	14	305
c		7.77	148	118	20	346	869	58	18	270
21 a	Kharkari	7.83	198	174	14	384	1475	82	18	307
b		8.02	294	256	15	550	2361	70	20	342
c		7.65	186	163	16	344	1410	55	35	263
22 a	Kharkhai	7.87	319	280	23	307	2705	146	46	338
b		8.65	566	453	28	1408	3449	376	197	375
c		7.73	231	197	18	234	1770	128	36	263
23 a	Garra	7.60	504	410	43	700	2623	943	23	326
b		7.70	803	585	57	2202	1621	2172	37	372
c		7.87	291	229	24	283	1836	336	19	254
24 a	Sankh	7.80	253	219	34	118	2192	86	2	377
b		8.77	315	247	48	518	1787	325	18	318
c		7.97	175	141	19	85	1295	73	13	305

Table 1. (Continued.)

Site code	Site name/tributary	Ca ²⁺ (μM)	Mg ²⁺ (μM)	Na ⁺ (μM)	K ⁺ (μM)	SAR (meq)	%Na	RSC (meq)	TZ ⁻ (meq)	TZ ⁺ (meq)	NICB (%)
Subarnarekha main channel											
1 a	Nagri	188	102	406	54	0.76	44.3	-0.05	1.02	1.04	1.1
b		203	118	441	58	0.78	43.7	-0.05	1.15	1.14	-0.4
c		178	91	244	53	0.47	35.6	-0.07	0.72	0.79	5.0
2 a	Namkum	1347	342	1687	278	1.30	36.8	0.24	5.38	5.34	-0.4
b		1746	541	3230	492	2.14	44.9	0.65	8.95	8.29	-3.8
c		1025	293	1208	268	1.05	35.9	-0.70	3.86	4.11	3.2
3 a	Tatisilwai	1537	330	1601	239	1.17	33.0	-1.19	5.19	5.57	3.6
b		3229	576	3209	419	1.65	32.3	-2.59	12.20	11.24	-4.1
c		1111	284	1233	209	1.04	34.1	-1.02	4.04	4.23	2.3
4 a	Hundru	440	214	449	66	0.56	28.2	0.13	1.84	1.82	-0.6
b		672	232	910	114	0.96	36.1	-0.25	2.64	2.83	3.4
c		384	170	371	69	0.50	28.4	0.10	1.69	1.55	-4.3
5 a	Muri	475	204	578	76	0.70	32.5	0.24	2.12	2.01	-2.6
b		420	301	5713	127	6.73	80.2	3.55	7.78	7.28	-3.3
c		297	171	615	107	0.90	43.6	-0.04	1.71	1.66	-1.5
6 a	Chandil	381	172	365	45	0.49	27.0	0.12	1.50	1.52	0.5
b		482	200	472	42	0.57	27.4	0.07	1.76	1.88	3.2
c		272	129	273	31	0.43	27.5	0.02	1.06	1.11	2.1
7 a	Barabinda	378	174	391	46	0.53	28.4	0.20	1.61	1.54	-2.1
b		520	213	448	46	0.52	25.2	0.03	1.82	1.96	3.6
c		319	137	259	37	0.38	24.5	-0.06	1.11	1.21	4.5
8 a	Kanderbera	395	189	393	45	0.51	27.3	0.06	1.56	1.61	1.5
b		509	205	418	44	0.49	24.4	0.07	1.78	1.89	2.8
c		384	185	262	31	0.35	20.5	-0.08	1.35	1.43	2.9
9 a	Jamshedpur (Sonari)	758	403	725	58	0.67	25.2	0.13	3.05	3.11	0.9
b		591	247	548	61	0.60	26.7	0.06	2.22	2.28	1.4
c		472	300	495	48	0.56	26.0	-0.07	1.87	2.09	5.4
10 a	Jamshedpur (Mango)	557	268	623	62	0.69	29.3	0.30	2.44	2.34	-2.2
b		599	246	595	55	0.65	27.8	0.05	2.21	2.34	2.7
c		462	282	467	61	0.54	26.2	-0.18	1.83	2.01	4.8
11 a	Galudih	1050	626	1176	79	0.91	27.2	-1.07	4.39	4.61	2.4
b		652	248	782	117	0.82	33.3	-0.13	2.54	2.70	2.9
c		501	182	327	58	0.40	22.0	-0.14	1.61	1.75	4.3
12 a	Moosabani U/S	816	406	679	76	0.61	23.6	-0.32	3.04	3.20	2.5
b		769	300	947	127	0.92	33.4	-0.40	3.07	3.21	2.2
c		661	301	470	80	0.48	22.2	-0.62	2.47	2.47	0.1

13 a	Moosabani D/S	885	423	635	90	0.56	21.7	-0.25	3.27	3.34	1.1
b		750	289	805	123	0.79	30.9	-0.44	2.82	3.01	3.2
c		546	192	359	47	0.42	21.6	-0.20	1.79	1.88	2.7
14 a	Shyamsunderpur	631	255	631	77	0.67	28.5	0.11	2.62	2.48	-2.7
b		777	310	879	137	0.84	31.8	-0.16	3.11	3.19	1.3
c		519	177	342	52	0.41	22.0	-0.15	1.67	1.79	3.4
15 a	Baharagora	616	391	585	71	0.58	24.6	-0.18	2.51	2.67	3.0
b		654	293	886	145	0.91	35.3	-0.28	2.74	2.92	3.1
c		489	202	324	22	0.39	20.0	-0.21	1.61	1.73	3.7
16 a	Gopiballavpur	594	376	551	59	0.56	23.9	-0.14	2.41	2.55	2.9
b		714	295	923	139	0.92	34.5	-0.17	2.93	3.08	2.5
c		504	182	323	29	0.39	20.4	-0.15	1.57	1.72	4.6
17 a	Mahapal	836	552	735	49	0.62	22.0	0.07	3.32	3.56	3.5
b		670	308	896	127	0.91	34.4	-0.16	2.81	2.98	3.0
c		490	212	331	44	0.39	21.1	-0.14	1.60	1.78	5.3
18 a	Sonakaniya	559	342	481	51	0.51	22.8	-0.09	2.20	2.33	2.9
b		593	277	752	107	0.81	33.1	-0.25	2.41	2.60	3.8
c		439	190	330	40	0.42	22.7	-0.05	1.52	1.63	3.4
19 a	Rajghat	536	362	537	65	0.57	25.1	0.00	2.33	2.40	1.4
b		614	284	779	90	0.82	32.6	0.09	2.74	2.66	-1.4
c		484	201	327	42	0.40	21.2	-0.09	1.59	1.74	4.4

Tributaries

20 a	Kanchi	377	191	478	10	0.63	30.0	0.17	1.54	1.62	2.7
b		482	210	750	51	0.90	36.7	0.24	2.02	2.19	3.9
c		337	166	452	44	0.64	33.0	-0.14	1.37	1.50	4.7
21 a	Kharkari	454	370	584	54	0.64	27.9	-0.18	2.05	2.29	5.3
b		761	428	851	77	0.78	28.1	-0.02	3.09	3.31	3.4
c		504	314	513	46	0.57	25.5	-0.23	1.91	2.20	6.8
22 a	Kharkhai	908	529	644	59	0.54	19.6	-0.18	3.37	3.58	2.9
b		1394	540	1889	219	1.36	35.3	-0.43	5.83	5.98	1.2
c		748	282	484	42	0.48	20.3	-0.29	2.31	2.59	5.5
23 a	Garra	1567	711	1279	79	0.85	23.0	-1.94	5.28	5.91	5.7
b		2306	478	2665	220	1.60	34.1	-3.95	8.26	8.45	1.2
c		816	374	624	46	0.57	22.0	-0.55	2.83	3.05	3.6
24 a	Sankh	696	490	369	36	0.34	14.6	-0.19	2.52	2.78	4.9
b		816	359	942	99	0.87	30.7	-0.57	3.02	3.39	5.8
c		470	258	271	29	0.32	17.1	-0.17	1.56	1.76	6.0

Units: Concentrations are in $\mu\text{M l}^{-1}$, except pH, EC ($\mu\text{S cm}^{-1}$), TDS (mg l^{-1}), TZ^+ (meq l^{-1}), TZ^- (meq l^{-1}) and NICB (%).

EC, electrical conductivity; TDS, total dissolved solids; TZ^+ , total cations; TZ^- , total anions; NICB, normalised inorganic charge balance; a, post-monsoon (September 2011); b, pre-monsoon (May 2012); c, monsoon (July 2012).

and nearly 31% of the area is devoted to forests. A number of dams/reservoirs (Getasuld, Hatia, Chandil, Galudih) have been constructed on the Subarnarekha and its tributaries mainly for the purpose of electricity generation, flood control and irrigation.

3. Methodology

Seventy-two water samples were collected from 24 sites along the Subarnarekha River and its major tributaries during the post-monsoon (September 2011), pre-monsoon (May 2012) and monsoon (July 2012) seasons (figure 1). The sampling seasons were selected according to the hydrological regime in the basin. The samples were mostly collected from the middle of the river, either from the bridge or with the help of a boat to avoid local heterogeneity and possible human influence near the river banks. Water samples were collected in the pre-washed narrow mouth 1-l high-density polyethylene bottles. Electrical conductivity (EC) and pH values were measured in the field using a portable conductivity and pH meter after recalibration with the standard buffer solutions. The water samples were filtered through 0.45 μm Millipore membrane filter to separate the suspended particulates. The concentration of bicarbonate (HCO_3^-) and dissolved silica (SiO_2) were determined by acid titration and molybdosilicate methods, respectively (APHA 1998). The concentration of major F^- , Cl^- , SO_4^{2-} and NO_3^- were analysed by Dionex ion chromatograph (DX-120) using anions AS12A/AG12 columns. The major cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) were determined by atomic absorption spectrophotometer (Varian 680 FS) in flame mode. Three replicates were run for each sample and the instrument was recalibrated after every 15 samples analysis. An overall precision, expressed as per cent relative standard deviation, was obtained below 5% for the entire samples. Total cations (TZ^+) and anions (TZ^-) are coupled by the relation $\text{TZ}^+ = 0.947 \times \text{TZ}^- \pm 0.237$ with a correlation coefficient of 0.989 and the normalised inorganic charge balance (NICB) is within $\pm 10\%$ (table 1). USGS hydrogeochemical software (PHREEQC) is used for the estimation of saturation index values of carbonate mineral phases (Parkhurst and Appelo 1999). Aquachem and Grapher software of Waterloo Hydrologic have been used for Piper diagram and other graphical presentation.

Water quality parameters such as sodium adsorption ratio (SAR), per cent sodium (%Na) and residual sodium carbonate (RSC) were computed to assess the suitability of the Subarnarekha River basin water for irrigation by the following equations:

$$\text{SAR} = \text{Na}^+ / \sqrt{(\text{Ca}^{2+} + \text{Mg}^{2+}) / 2}, \quad (1)$$

$$\% \text{Na} = \text{Na} + \text{K} / (\text{Ca} + \text{Mg} + \text{Na} + \text{K}) \times 100, \quad (2)$$

$$\text{RSC} = (\text{CO}_3^{2-} + \text{HCO}_3^-) - (\text{Ca}^{2+} + \text{Mg}^{2+}). \quad (3)$$

(All ionic concentrations used for the calculation are expressed in meq l^{-1} .)

4. Results and discussion

4.1 Fluvial geochemistry

The analytical results of surface water samples of the Subarnarekha River and its major tributaries during the post-monsoon, pre-monsoon and monsoon seasons are given in table 1. Table 2 shows the range and average concentration of the measured parameters and ionic ratios in the Subarnarekha River water during the post-monsoon, pre-monsoon and monsoon seasons.

The pH of the Subarnarekha River water varied from 6.20 (mildly acidic) to 8.93 (alkaline), with most samples falling within a range of 7.0–8.0. The pH was slightly higher during the lean flow pre-monsoon (avg. 7.95) period as compared to the high flow regimes of monsoon (7.74) and post-monsoon (7.75). The water was slightly acidic in nature at the Nagri site, which might be due to comparatively more organic loading near the origin site of the Subarnarekha River. EC varied from 116 to 570 $\mu\text{S cm}^{-1}$ in post-monsoon, 138 to 1220 $\mu\text{S cm}^{-1}$ in pre-monsoon and 90 to 431 $\mu\text{S cm}^{-1}$ during the monsoon season. On an average, the lowest EC is observed during the monsoon (196 $\mu\text{S cm}^{-1}$) and the highest in the pre-monsoon (377 $\mu\text{S cm}^{-1}$), while the post-monsoon season is characterised by an intermediate value (271 $\mu\text{S cm}^{-1}$). Total dissolved solids (TDS) in the Subarnarekha basin water ranged from 71 to 847 mg l^{-1} with an average concentration value of 225 mg l^{-1} . The low TDS value is observed near the river origin site at Nagri village and it increases randomly at the downstream sites. Like EC, TDS concentration was relatively higher

Table 2. Range and average concentration of measured parameters and major-ion ratios in Subarnarekha River basin water for post-monsoon, pre-monsoon and monsoon seasons.

Parameters	Average ($n = 72$)		Post-monsoon ($n = 24$)		Pre-monsoon ($n = 24$)		Monsoon ($n = 24$)	
	Range	Average $\pm$ Std. dev.	Range	Average $\pm$ Std. dev.	Range	Average $\pm$ Std. dev.	Range	Average $\pm$ Std. dev.
pH	6.20–8.93	7.81 $\pm$ 0.51	6.26–8.39	7.75 $\pm$ 0.46	6.33–8.93	7.95 $\pm$ 0.6	6.20–8.22	7.74 $\pm$ 0.44
EC ($\mu\text{S cm}^{-1}$)	90–1220	282 $\pm$ 195	116–570	271 $\pm$ 117	138–1220	377 $\pm$ 282	90–431	196 $\pm$ 81
TDS (mg l^{-1})	71–847	225 $\pm$ 136	87–427	228 $\pm$ 91	99–847	292 $\pm$ 190	71–309	156 $\pm$ 57
F ⁻ (μM)	9–65	27 $\pm$ 13	12–55	23 $\pm$ 11	15–65	36 $\pm$ 14	9–25	21 $\pm$ 3
Cl ⁻ (μM)	85–5802	536 $\pm$ 822	118–1817	383 $\pm$ 389	167–5802	928 $\pm$ 1254	85–1533	298 $\pm$ 347
HCO ₃ ⁻ (μM)	464–5229	1792 $\pm$ 904	533–3623	1956 $\pm$ 667	590–5229	2162 $\pm$ 1222	464–1934	1259 $\pm$ 343
SO ₄ ²⁻ (μM)	11–2172	187 $\pm$ 285	22–943	179 $\pm$ 214	25–2172	274 $\pm$ 428	11–423	107 $\pm$ 91
NO ₃ ⁻ (μM)	0.81–963	65 $\pm$ 143	2.40–529	53 $\pm$ 110	0.81–963	73 $\pm$ 196	8.5–420	67 $\pm$ 109
SiO ₂ (μM)	135–392	283 $\pm$ 52	187–392	307 $\pm$ 47	198–387	303 $\pm$ 43	135–305	239 $\pm$ 35
Ca ²⁺ (μM)	178–3229	699 $\pm$ 476	188–1567	708 $\pm$ 363	203–3229	872 $\pm$ 673	178–1111	517 $\pm$ 221
Mg ²⁺ (μM)	91–711	294 $\pm$ 130	102–711	351 $\pm$ 154	118–576	312 $\pm$ 118	91–374	220 $\pm$ 70
Na ⁺ (μM)	200–5713	808 $\pm$ 831	365–1687	691 $\pm$ 368	418–5713	1280 $\pm$ 1246	200–1233	453 $\pm$ 261
K ⁺ (μM)	10–492	92 $\pm$ 84	10–278	76 $\pm$ 59	42–492	135 $\pm$ 110	22–268	64 $\pm$ 57
TZ ⁻ (meq)	0.72–12.20	2.79 $\pm$ 1.94	1.02–5.38	2.77 $\pm$ 1.22	1.15–12.20	3.75 $\pm$ 2.77	0.72–4.04	1.86 $\pm$ 0.77
TZ ⁺ (meq)	0.79–11.24	2.88 $\pm$ 1.85	1.04–5.91	2.88 $\pm$ 1.33	1.14–11.24	3.78 $\pm$ 2.53	0.78–4.23	1.99 $\pm$ 0.82
NICB (%)	-4.3–6.83	2.20 $\pm$ 2.58	-2.71–5.69	1.60 $\pm$ 2.41	-4.09–5.77	1.73 $\pm$ 2.57	-4.30–6.83	3.27 $\pm$ 2.57
Ionic ratios								
Na ⁺ + K ⁺ /Cl ⁻	0.63–4.10	2.26 $\pm$ 0.72	1.01–4.0	2.46 $\pm$ 0.66	0.63–4.10	2.02 $\pm$ 0.75	0.94–3.55	2.31 $\pm$ 0.71
*Ca ²⁺ /Na ⁺	0.07–1.88	1.03 $\pm$ 0.33	0.46–1.88	1.04 $\pm$ 0.27	0.07–1.22	0.82 $\pm$ 0.24	0.48–1.73	1.23 $\pm$ 0.33
*Mg ²⁺ /Na ⁺	0.05–1.33	0.47 $\pm$ 0.20	0.20–1.33	0.55 $\pm$ 0.23	0.05–0.56	0.33 $\pm$ 0.11	0.23–0.95	0.54 $\pm$ 0.16
*HCO ₃ ⁻ /Na ⁺	0.61–5.94	2.78 $\pm$ 0.96	1.31–5.94	3.08 $\pm$ 0.94	0.61–4.59	2.13 $\pm$ 0.73	1.44–4.78	3.12 $\pm$ 0.87
(Ca ²⁺ + Mg ²⁺)/HCO ₃ ⁻	0.29–3.43	1.12 $\pm$ 0.39	0.84–1.74	1.06 $\pm$ 0.22	0.29–3.43	1.15 $\pm$ 0.53	0.91–1.57	1.15 $\pm$ 0.80
(Ca ²⁺ + Mg ²⁺)/TZ ⁺	0.20–0.85	0.71 $\pm$ 0.09	0.56–0.85	0.73 $\pm$ 0.06	0.20–0.76	0.65 $\pm$ 0.11	0.56–0.83	0.75 $\pm$ 0.06
(Ca ²⁺ + Mg ²⁺)/Na ⁺ + K ⁺	0.25–5.85	2.69 $\pm$ 0.91	1.26–5.85	2.89 $\pm$ 0.90	0.25–3.09	2.05 $\pm$ 0.60	1.30–4.86	3.13 $\pm$ 0.86
(Na ⁺ + K ⁺)/TZ ⁺	0.15–0.80	0.29 $\pm$ 0.09	0.15–0.44	0.27 $\pm$ 0.06	0.24–0.80	0.35 $\pm$ 0.11	0.17–0.44	0.25 $\pm$ 0.06
*HCO ₃ ⁻ /SiO ₂	2.21–26.46	6.29 $\pm$ 3.17	2.85–10.19	6.32 $\pm$ 1.89	2.55–26.46	7.27 $\pm$ 4.90	2.21–7.22	5.26 $\pm$ 1.18
Ca ²⁺ /SO ₄ ²⁻	0.67–16.90	5.94 $\pm$ 3.13	1.44–10.85	5.80 $\pm$ 2.51	0.67–16.50	5.88 $\pm$ 4.01	1.56–16.90	6.14 $\pm$ 2.80

Ionic ratio in equivalent unit, except *molar ratio.

in the pre-monsoon (292 mg l^{-1}) as compared to the post-monsoon (228 mg l^{-1}) and monsoon (156 mg l^{-1}) seasons. Seasonal variation of EC and TDS values indicates an increase in ionic concentrations during the pre-monsoon season, probably due to excessive evaporation and/or contribution from the groundwater in the summer months and dilution effects of atmospheric precipitation in the monsoon season. The elevated temperature in the hot summer months increases water evaporation and causes a reduction in river flow, resulting in an enhancement in solute concentration. Spatial variations in ionic concentration show a sharp increase at the Namkum–Tatisilwai–Muri industrial zone (sites 2, 3 and 5) and for the Garra tributary (T-4). Namkum, Tatisilwai and Muri are under the influence of industrial activities. Huge quantities of industrial and urban effluents are discharged into the Kharkai and the main Subarnarekha River at these locations. Tributary Garra receives highly polluted water and effluents with high sulphate contents and has high concentration of total suspended and dissolved solids mainly in the Jaduguda–Ghatsila mining complex areas.

HCO_3^- , Ca^{2+} , Na^+ and dissolved silica account for >75% of the total dissolved loads and dominate the major-ion chemistry of the Subarnarekha River water. The HCO_3^- was the most dominant anion in the surface water of the Subarnarekha River followed by Cl^- , SO_4^{2-} , NO_3^- and F^- . The major anions constitute 65% of the TDS. The plot of the analytical data on anion diagram relating HCO_3^- , Cl^- and SO_4^{2-} shows the clustering of plotted points near the HCO_3^- apex with a secondary trend towards Cl^- and SO_4^{2-} (figure 2a). Bicarbonate concentration ranged from 464 to $5229 \mu\text{M}$ with an average value of $1792 \mu\text{M}$ and it contributed 69% (20–87%) to the total anionic (TZ^-) charge balance in equivalent unit. Bicarbonate in river water is mainly contributed from the dissolution of atmospheric CO_2 and weathering of carbonates and/or silicate minerals by the carbonic acid. The CO_2 in the subsurface environment is mainly originated from the decomposition of organic matter, which in turn combines with rainwater to form bicarbonates.

Chloride (Cl^-) concentration in the analysed water samples of the Subarnarekha River ranged from 85 to $5802 \mu\text{M}$ (avg. $536 \mu\text{M}$) and it accounts for 16% of the total anionic charge (TZ^-). Except halite, most of the rock types contain very low

Figure 2. (a) Ternary anion diagram relating HCO_3^- , SO_4^{2-} and Cl^- and (b) ternary cation diagram relating Ca^{2+} , Mg^{2+} and $(\text{Na} + \text{K})^+$.

concentration of chloride and it is believed that the major portion of Cl^- in water is primarily derived from either the atmospheric source or the sea water (Berner and Berner 1987). Leaching of salt and saline residues in the soil, municipal, industrial, animal wastes and usage of fertiliser also plays a vital role as the source of chloride (Appelo and Postma 1996; Singh *et al.* 2008). Large spatial variations and increased chloride concentrations at sites W-2, W-3 and W-23 may be attributed to anthropogenic sources. The concentration of SO_4^{2-} and NO_3^- in the surface water of the Subarnarekha River basin was found in the range of 11–2172 and $0.81\text{--}963 \mu\text{M}$ and it accounted for 12% and 2.3% of the total anionic charge (TZ^-) balance, respectively. Relatively the higher concentration of nitrate at Namkum (W-2) and Tatisilwai (W-3) sites indicates the anthropogenic contribution from

Figure 3. Average concentration of measured parameters in Subarnarekha basin water.

the leaching of fertiliser from agricultural fields. The concentration of F^- varied from 9 to $65 \mu M$ (avg. $27 \mu M$) and on an average it contributed 1.2% to the total anions (TZ^-).

Ca^{2+} , Mg^{2+} , Na^+ and K^+ together constitute 25% of the TDS. Calcium was the most dominant cation in the water of the Subarnarekha River, contributing 49% of the total cations (TZ^+) followed by Na^+ (26%), Mg^{2+} (22%) and K^+ (3%). The calcium concentration ranged from 178 to $3229 \mu M$, while the concentration of Na^+ varied from 200 to $5713 \mu M$. The concentration of Mg^{2+} and K^+ ranged from 91 to 711 and 10 to $492 \mu M$, respectively, with an average value of 294 and $92 \mu M$. Ca^{2+} and Mg^{2+} together account for about 71% of the total cationic charge balance in the equivalent unit. The cation concentration in the Subarnarekha basin water generally followed the decreasing order of $Ca^{2+} > Na^+ > Mg^{2+} > K^+$ with some minor exceptional samples, where Na^+ concentration was found to be higher than the Ca^{2+} or Mg^{2+} exceeding the Na^+ concentration. The plot of the analytical data on cation diagram relating Ca^{2+} , Mg^{2+} and $(Na^+ + K^+)$ shows that the plotted points of the water samples fall either in the 'calcium' or in 'no dominant' zone (figure 2b). Dissolved silica (SiO_2) concentration in the Subarnarekha River water varied from 187 to $392 \mu M$ during the post-monsoon, 198 to $387 \mu M$ in the pre-monsoon and 135 to $305 \mu M$ in the monsoon (table 2). On average,

the dissolved silica accounted for 9% (2–19%) of the TDS and it exceeds the chloride and sulphate concentrations at many sites. The average concentration of dissolved silica ($283 \mu M$) in the studied river water is higher than the average global ($200 \mu M$) and Indian ($117 \mu M$) rivers (Ramanathan *et al.* 1994). The higher concentration of dissolved silica in the Subarnarekha River reflects the important contribution from the weathering of silicate rocks. The average HCO_3^-/SiO_2 molar ratio for the Subarnarekha and its tributaries vary between 2 and 26 (avg. 6.3); however, in a majority of samples it ranges between 5 and 10, indicating the combined influence of carbonate and silicate weathering (Hounsflow 1995). The high HCO_3^-/SiO_2 ratio (>10) in some water samples can result from the supply of alkalinity from carbonates, salt affected soils and/or anthropogenic sources. No specific trend has been observed in the downstream variation of dissolved ionic concentrations. In general, the temporal variation of average concentration of major ions on the river basin scale follows a decreasing order of pre-monsoon > post-monsoon > monsoon (figure 3).

The trilinear Piper plot (Piper 1944) for the Subarnarekha River water reveals the dominance of alkaline earth ($Ca^{2+} + Mg^{2+}$) metals over alkalis ($Na^+ + K^+$) and weak acid (HCO_3^-) over strong acids ($SO_4^{2-} + Cl^-$). The plotted points of majority of samples fall in the field 5, signifying the carbonate hardness (secondary salinity)

Figure 4. Piper trilinear diagram showing the hydrogeochemical character of river water and hydrochemical facies (after Piper 1953).

that exceeds 50% (figure 4). Only five water samples fall in the field 9, indicating water of an intermediate (mixed) chemical character having no one cation–anion pair exceeding 50%. Ca–HCO₃ and Ca–Mg–HCO₃–Cl are identified as the dominant hydrogeochemical facies in the surface water of the Subarnarekha River basin.

The average chemical composition of the Subarnarekha River basin water along with some other Indian Rivers and the world and Indian averages is summarised in table 3. The TDS content of the Subarnarekha basin water is higher than that of the Indus, Brahmaputra, Godavari, Damodar and the Indian and world average rivers, but it is lower as compared to the Krishna, Cauvery, Narmada, Tapti, Mahi and Gomti rivers and comparable to Mahanadi, Son and Ganges averages. Like other Indian rivers, the Subarnarekha has high alkalinity, indicating the extent of mixing with HCO₃-rich groundwater and atmospherically regulated PCO₂-water reactions, which may further enhance the carbonate alkalinity. Potassium concentrations do not show much variation in

the Subarnarekha water as in the other river basins, suggesting conservative behaviour of this element. Berner and Berner (1987) reported that only 15% of the river transport of potassium is in the dissolved form. The low concentration of dissolved K in water may be attributed to the resistance of potassium bearing minerals (orthoclase, microcline) against weathering. Potassium is commonly fixed in specific clay minerals, after being released during the primary weathering reactions and therefore does not behave in the same way as the other weathering derived ions (Stott and Burt 1997). The higher contributions of dissolved silica, Na⁺ and SO₄²⁻ to the TDS in comparison to the other river basins may be attributed to silicate weathering and inputs from the sulphide weathering and anthropogenic sources in the drainage basin.

4.2 Weathering and solute acquisition processes

Chemical load in the river basin is considered to be a reflection of its watershed and flood-plains and processes occurring in the tributaries

Table 3. Average composition of Subarnarekha basin water in comparison to other major Indian River basins.

Rivers	Drainage area	Discharge MCM	HCO ₃	Cl	SO ₄	H ₄ SiO ₄	Ca	Mg	Na	K	TDS	References
Subarnarekha	19,296	7940	109	19	18	17	28	7	19	3.6	225	Present study
Damodar	25,820	12,210	94	11	21	22	15	9	16	4.0	191	Singh and Hasnain (1999)
Krishna	258,948	62,800	178	38	49	24	29	8	30	2.4	360	Ramesh and Subramanian (1988)
Cauvery	87,900	20,950	135	20	13	23	21	9	43	4.0	272	Ramanathan <i>et al.</i> (1994)
Godavari	312,812	118,000	105	17	8	10	22	5	12	3.0	181	Biksham and Subramanian (1988)
Mahanadi	141,589	66,640	122	23	3	17	24	13	14	8.3	224	Chakrapani and Subramanian (1990)
Indus	321,289	79,500	64	9	15	5	27	1	1	2.1	122	Subramanian (1983)
Narmada	98,795	54,600	225	20	5	9	14	20	27	2.0	322	Subramanian (1983)
Tapti	65,145	17,982	150	65	1	16	19	22	48	3.0	322	Subramanian (1983)
Mahi	34,841	11,800	246	38	19	21	31	17	55	2.7	436	Sharma <i>et al.</i> (2012)
Gomti	30,437	7390	262	9	15	14	29	18	27	4.8	380	Gupta and Subramanian (1994)
Son	71,250	22,420	125	18	10	18	29	8	14	3	227	Maharana <i>et al.</i> (2015)
Ganges	861,404	468,700	128	10	11	18	25	8	11	3.0	214	Subramanian (1983)
Brahmaputra	258,008	627,000	38	15	10	7	29	7.4	12	2.5	148	Subramanian (1983)
Indian avg.	3,287,782	1,858,100	74	15	13	7	30	7	12	3.0	159	Subramanian (1983)
World avg.	—	—	62	4	9	12	16	4	4.4	1.5	115	Sarin <i>et al.</i> (1989)

Units: mg l⁻¹. TDS: total dissolved solids; MCM: million m³.

(Richey *et al.* 1990). Berner and Berner (1996) identified three possible sources of dissolved salt into the inland waters as (i) sea salt carried in the atmosphere and deposited on the land; (ii) weathering reaction taking place in the drainage basin and (iii) anthropogenic input. The proportions of contribution from these sources vary in space and time, resulting in seasonal and downstream variations in the chemical composition within the river basin. The atmospheric contribution to the dissolved salt in the inland water has been discussed by various authors (Stallard and Edmond 1983; Sarin *et al.* 1989; Berner and Berner 1996). The input of chloride concentration through precipitation is generally used as a parameter for evaluating the atmospheric contribution. This is because of the fact that Cl⁻ is regarded as a conservative element as it reacts very little with other ions, does not form complexes and also does not participate in the biogeochemical cycling, except in small basins where biota plays a dominant role (Viers *et al.* 2001). The atmospheric contribution to the dissolved salts in the aquatic water can be assessed by comparing the chemical composition with the local rainwater chemistry or by taking the ratios of elements to Cl⁻ (Sarin *et al.* 1989; Pandey *et al.* 1994; Singh *et al.* 2005). The average Na⁺/Cl⁻ (2.03) and K⁺/Cl⁻ (0.23) ratios in the surface water of the Subarnarekha River were found to be higher as compared to marine aerosols (Na⁺/Cl⁻ = 0.85 and K⁺/Cl⁻ = 0.0176). This indicates a limited contribution from the atmospheric precipitation and suggests that high proportions of dissolved ions in this water are derived from the weathering of rock-forming minerals and anthropogenic sources. The plot of geochemical data on Gibbs's diagram (Gibbs 1970) that represents the ratio of (Na⁺ + K⁺)/(Na⁺ + K⁺ + Ca²⁺) and Cl⁻/(Cl⁻ + HCO₃⁻) as a function of TDS also indicates the dominance of weathering of rocks as a major controlling factor to determine the surface water chemistry of the Subarnarekha basin (figure 5).

Weathering of different parent rocks (e.g., carbonates, silicates and evaporites) yields different combinations of dissolved cations and anions in the water (Drever 1988; Berner and Berner 1996). For instance, calcium and magnesium in the river water are mainly derived from the weathering of carbonate and silicate minerals and evaporite dissolution. Silicate weathering along with evaporite dissolution and atmospheric precipitation are the major sources of sodium and potassium in the river water.

Figure 5. Gibbs's diagram representing the ratio of (a) $\text{Na}+\text{K}/(\text{Na}+\text{K}+\text{Ca})$ and (b) $\text{Cl}/(\text{Cl}+\text{HCO}_3)$ as a function of TDS (after Gibbs 1970).

Dissolved silica is exclusively derived from the weathering of silicates. The plot of $(\text{Ca}^{2+} + \text{Mg}^{2+})$ vs. $(\text{HCO}_3^- + \text{SO}_4^{2-})$ will be close to 1:1 line if the dissolution of calcite, dolomite and gypsum is the dominant reaction in a system. Figure 6(a) shows that plotted points of the majority of the Subarnarekha water samples fall below the theoretical 1:1 trend line in the variation diagram relating $(\text{Ca}^{2+} + \text{Mg}^{2+})$ to $(\text{HCO}_3^- + \text{SO}_4^{2-})$. The excess of $(\text{HCO}_3^- + \text{SO}_4^{2-})$ over $(\text{Ca}^{2+} + \text{Mg}^{2+})$ suggests contribution from the non-carbonate source and demanding that the required portion of $(\text{HCO}_3^- + \text{SO}_4^{2-})$ to be balanced by the alkalis $(\text{Na}^+ + \text{K}^+)$. $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{HCO}_3^-$ ratio demarcates the maximum portion of bicarbonate that can be derived from the carbonate weathering (Stallard and Edmond 1983). The variation diagram between $(\text{Ca}^{2+} + \text{Mg}^{2+})$ and HCO_3^- for the Subarnarekha basin water shows that in the majority of samples $(\text{Ca}^{2+} + \text{Mg}^{2+})$ the contents are in excess of alkalinity and the magnitude of excess being larger for the tributaries (figure 6b). The excess of $(\text{Ca}^{2+} + \text{Mg}^{2+})$ over bicarbonate in these waters indicates some extra source of Ca^{2+} and Mg^{2+} and excess part of the positive charges is balanced by other anions such as SO_4^{2-} and/or Cl^- . The data plot along the equiline on $(\text{Ca}^{2+} + \text{Mg}^{2+})$ vs. TZ^+ at lower concentration range suggests a significant contribution of Ca^{2+} and Mg^{2+} to the total cations. Deviations of plotted points from 1:1 equiline at higher concentration especially during the pre-monsoon indicate

the increasing contribution of alkalis $(\text{Na}^+ + \text{K}^+)$ to the total cations with increasing ionic concentrations (figure 6c).

The concentrations of $(\text{Na}^+ + \text{K}^+)$ in the analysed water samples are significantly in excess over chloride and high $(\text{Na}^+ + \text{K}^+)/\text{Cl}^-$ ratio i.e., 2.26 suggests non-atmospheric source of alkalis which might be derived from silicates weathering (figure 6d). $(\text{Na}^+ + \text{K}^+)/\text{TZ}^+$ and $(\text{Ca}^{2+} + \text{Mg}^{2+})/(\text{Na}^+ + \text{K}^+)$ ratios can be used as an index to assess the contribution of cations through silicate weathering (Stallard and Edmond 1983; Sarin *et al.* 1989). The plot of $(\text{Na}^+ + \text{K}^+)$ vs. TZ^+ shows the deviation of plotted points from the 1:1 equiline and the $(\text{Na}^+ + \text{K}^+)/\text{TZ}^+$ ratio varies between 0.15 and 0.80 (figure 6e). The $(\text{Ca}^{2+} + \text{Mg}^{2+})/(\text{Na}^+ + \text{K}^+)$ molar abundance ratio in the silicates of upper crust is generally 1.0 (Taylor and McLennan 1985). The average $(\text{Ca}^{2+} + \text{Mg}^{2+})/(\text{Na}^+ + \text{K}^+)$ ratio in the Subarnarekha River water is 2.7, comparable to the world (2.2) and Indian (2.5) river water averages (figure 6f). The observed low $(\text{Ca}^{2+} + \text{Mg}^{2+})/(\text{Na}^+ + \text{K}^+)$ ratio, i.e., 2.7 and higher $(\text{Na}^+ + \text{K}^+)/\text{TZ}^+$, i.e., 0.29 ratio in the analysed waters suggest that the chemical composition of the Subarnarekha River is under the combined influence of carbonate and silicate weathering (Sarin *et al.* 1989; Singh *et al.* 2005).

Small rivers draining only carbonates are characterised by higher calcium and magnesium concentrations and have high $\text{Ca}^{2+}/\text{Na}^+$, i.e., 50;

Figure 6. Scatter plot between (a) Ca+Mg vs. $\text{HCO}_3 + \text{SO}_4$, (b) Ca+Mg vs. HCO_3 , (c) Ca+Mg vs. total cations, (d) Na+K vs. Cl, (e) Na+K vs. total cations and (f) Ca+Mg vs. Na+K.

$\text{Mg}^{2+}/\text{Na}^+$, i.e., 10; and $\text{HCO}_3^-/\text{Na}^+$, i.e., 120 ratios (Gaillardet *et al.* 1999). The dissolved loads of water draining silicate terrains is expected to have a low $\text{Ca}^{2+}/\text{Na}^+$ molar ratio because of higher solubility of Na^+ relative to Ca^{2+} . The molar ratios of $\text{Ca}^{2+}/\text{Na}^+ = 0.35 \pm 0.15$, $\text{Mg}^{2+}/\text{Na}^+ = 0.24 \pm 0.12$, $\text{HCO}_3^-/\text{Na}^+ = 2 \pm 1$ are assigned for the silicate end member. The observed molar ratios of $\text{Ca}^{2+}/\text{Na}^+$ (1.04), $\text{Mg}^{2+}/\text{Na}^+$ (0.48) and

$\text{HCO}_3^-/\text{Na}^+$ (2.78) in the Subarnarekha River waters are much lower than those of the waters draining carbonate lithology and higher than that drain silicate rocks, indicating that the solute chemistry of the Subarnarekha River is essentially controlled by two-component mixing from the dissolution of silicates and carbonates. The plots of $\text{HCO}_3^-/\text{Na}^+$ vs. $\text{Ca}^{2+}/\text{Na}^+$ and $\text{Ca}^{2+}/\text{Na}^+$ vs. $\text{Mg}^{2+}/\text{Na}^+$ relating carbonate and silicate end

Figure 7. Mixing diagrams using sodium normalised ratio of (a) $\text{Mg}^{2+}/\text{Na}^+$ vs. $\text{Ca}^{2+}/\text{Na}^+$ and (b) $\text{HCO}_3^-/\text{Na}^+$ vs. $\text{Ca}^{2+}/\text{Na}^+$ relating carbonate and silicate end members (after Gaillardet *et al.* 1999).

members show the dominance of silicate weathering over the carbonate dissolution in solute acquisition processes in the Subarnarekha River basin (figure 7).

4.3 Saturation index and water mineral equilibrium

The saturation index (SI) of the studied water with respect to calcite (SI_c) and dolomite (SI_d) was estimated using the USGS hydrogeochemical

software PHREEQC (Parkhurst and Appelo 1999) in order to investigate the level to which the natural water has equilibrated with the carbonate mineral phases. PHREEQC is a widely used modelling code that employs various approaches and thermodynamic databases for solving solution–solid–gas equilibria (Lecomte *et al.* 2005; Binet *et al.* 2009; Tiwari and Singh 2014). The saturation index of a particular mineral phase can be defined as $\text{SI} = \log_{10}(\text{IAP}/K_{sp})$, where IAP is the ion activity product of the solution and K_{sp} is the solubility product at a given temperature (Garrels and Mackenzie 1967). A positive saturation index specifies that the water is being supersaturated with respect to a particular mineral phase and therefore incapable of dissolving more of the mineral and the mineral phase in equilibrium precipitate under suitable physico-chemical condition. Undersaturation condition is denoted by a negative index and suggests the dissolution of mineral phase, while neutral SI denotes the equilibrium state with the mineral phase. The plot of saturation index of calcite (SI_c) vs. dolomite (SI_d) demonstrates that most of the post-monsoon and monsoon water samples are undersaturated with respect to dolomite and calcite, while water is supersaturated with respect to both during the pre-monsoon (figure 8). The supersaturation condition in pre-monsoon may be attributed to evaporation effects during the lean water level period of summer season which causes the preferential extraction of Ca by precipitation (Hardie and Eugster 1970). The undersaturation condition represents water that has come from an environment where rock matrices contain insufficient calcite and dolomite or where Ca and Mg exist in other forms. Undersaturated waters are capable to dissolve calcite and/or dolomite when it comes in contact with source rocks.

The clay mineral assemblages, which would be consistent with the natural water chemistry, can be established through thermodynamic data (Garrels and Christ 1965). The thermodynamic stability relationships of the Subarnarekha River water are plotted in the silicate systems: (a) $\text{Na}_2\text{O}-\text{Al}_2-\text{SiO}_2-\text{H}_2\text{O}$, (b) $\text{K}_2\text{O}-\text{Al}_2-\text{SiO}_2-\text{H}_2\text{O}$, (c) $\text{CaO}-\text{Al}_2-\text{SiO}_2-\text{H}_2\text{O}$ and (d) $\text{MgO}-\text{Al}_2-\text{SiO}_2-\text{H}_2\text{O}$ at 25°C to predict the possible clay mineral assemblages which would be in equilibrium with the river water chemistry (figure 9). The pH–log H_4SiO_4 stability diagram demonstrates that the majority of data points fall in the range of kaolinite stability field except some

Figure 8. Relationship between saturation indices of calcite (SI_c) and dolomite (SI_d).

pre-monsoon samples which fall in the chlorite and Ca-feldspar zones in $MgO-Al_2-SiO_2-H_2O$ and in $CaO-Al_2-SiO_2-H_2O$ system. The enrichment of Mg and Ca in the water during pre-monsoon may explain it (Das and Dhiman 2003). Water-mineral equilibria imply that the Subarnarekha River water chemistry is in equilibrium with the kaolinite. Stability in the kaolinite field suggests that the CO_2 -enriched water reacts with silicate minerals contained in the host rock, particularly in plagioclase feldspar and converted into allophone-hallosite-kaolinite. The reactive water leached out Ca, Mg, Na and HCO_3 from the host silicates and results in a more silica-rich clay minerals by the reaction:

4.4 Dissolved fluxes and chemical denudation rate

The Subarnarekha River shows enormous spatial and temporal variations in the water discharge. Figure 10 shows the variation in water discharge

for the monsoon and non-monsoon seasons at five locations. About 69–98% of the annual water discharge from the river occurs during the monsoon (June–September) and 2–31% in the lean flow period of non-monsoon (October–May). The annual dissolved fluxes and chemical denudation rates of the Subarnarekha River at various locations and its major tributaries were calculated by using the average TDS, catchment area and annual water discharge (table 4). The Subarnarekha River annually transported 0.179×10^6 ton of dissolved chemical loads to the Muri site and the estimated chemical denudation rate of the catchment at this site was $135 \text{ ton km}^{-2} \text{ yr}^{-1}$. The dissolved load and water discharge increase unsystematically at downstream sites and the annual solute fluxes at Ghatsila and Rajghat sites were estimated to be in the range of 1.585×10^6 – 1.477×10^6 ton, respectively. Kharkai, the largest Subarnarekha tributary, annually delivered 1.023×10^6 ton of dissolved loads to the Subarnarekha River at Adityapur. The annual solute fluxes of the other tributaries such as Sankh (0.016×10^6 ton), Garra (0.082×10^6 ton), Kanchi (0.109×10^3 ton) and Karkari (0.188×10^3 ton) were low as compared to the Kharkai (1.023×10^6 ton). The chemical

Figure 9. Mineral stability diagrams for the silicate system: (a) $\text{Na}_2\text{O}-\text{Al}_2-\text{SiO}_2-\text{H}_2\text{O}$; (b) $\text{K}_2\text{O}-\text{Al}_2-\text{SiO}_2-\text{H}_2\text{O}$; (c) $\text{CaO}-\text{Al}_2-\text{SiO}_2-\text{H}_2\text{O}$; (d) $\text{MgO}-\text{Al}_2-\text{SiO}_2-\text{H}_2\text{O}$ (after Garrels and Christ 1965).

denudation rates of the Kharkai, Garra, Karkari and Kanchi catchments were estimated to be in the range of 176, 169, 119 and 105 $\text{ton km}^{-2} \text{yr}^{-1}$, respectively.

4.5 Water quality assessment for irrigation uses

EC and Na are the most important parameters for determining the suitability of water for irrigation uses. High salt concentrations in the irrigation water affect the soil structure, permeability and aeration, which indirectly affect the plant growth. Irrigation water can be classified into low ($\text{EC} \leq 250 \mu\text{S cm}^{-1}$), medium ($250-750 \mu\text{S cm}^{-1}$), high ($750-2250 \mu\text{S cm}^{-1}$) and

Figure 10. Seasonal variations in water discharge of the Subarnarekha and Kharkai rivers at different sites.

Table 4. Average annual solute fluxes and chemical denudation rate of the Subarnarekha and its tributaries.

River/tributary	Site/tributaries name	Area (km ²)	Discharge (million m ³)	TDS (mg l ⁻¹)	Solute flux (×10 ⁶)(ton yr ⁻¹)	Chemical denudation rate (ton km ⁻² yr ⁻¹)
Subarnarekha	Muri	1330	596	301	0.179	135
	Adityapur	6309	2831	310	0.878	139
	Jamshedpur	12,649	6593	201	1.325	105
	Ghatsila	14,176	6950	228	1.585	112
	Baharagora	—	4974	190	0.945	—
	Rajghat	19,296	7940	186	1.477	77
Tributaries	Kanchi	1036	750	145	0.109	105
	Karkari	1575	950	198	0.188	119
	Kharkai	5825	3300	310	1.023	176
	Garra	483	200	408	0.082	169
	Sankh	196	80	202	0.016	82

very high (2250–5000 $\mu\text{S cm}^{-1}$) salinity classes based on the total concentration of soluble salts in water (USSL 1954). The excess sodium in water produces undesirable effects on soil properties and reduces its permeability. High salt concentration in water results in the formation of saline soil, whereas a high sodium concentration leads to the development of alkaline soil. The alkali hazard in the use of water for irrigation is expressed in terms of sodium absorption ratio (SAR) and determined by the absolute and relative concentration of cations. On the basis of SAR value, water can be classified as low ($\text{SAR} < 6$), medium (6–12), high (12–18) and very high (> 18) alkali water.

The calculated value of SAR in the surface water of the Subarnarekha River basin ranges from 0.32 to 6.73 (avg. 0.79). The plotted data of the majority of water samples on the US salinity diagram fall in the category of C1S1 and C2S1, i.e., low-to-medium salinity and low alkali water (figure 11). Such water can be used for irrigation in most of the soil and crops with little danger of development of exchangeable sodium and salinity. Four water samples of the pre-monsoon season fall in the zones of C3S1 and C3S2 indicating high salinity and low-to-medium alkali hazard. High saline waters are not suitable to irrigate the agricultural fields with restricted drainage and it requires special management for salinity control. For utilisation of such water, soil must be permeable, drainage must be adequate and irrigation water must be applied in excess to provide considerable leaching.

%Na in water is a parameter computed to evaluate the suitability of water for irrigation use. %Na denotes the relative proportions of alkali

Figure 11. US salinity diagram for classification of irrigation waters (USSL 1954).

to the total cations. The role of sodium in the classification of irrigation water was emphasised because of the fact that sodium reacts with soil and affects its physical condition and soil structure including the formation of crusts and reduction in soil aeration, infiltration rate and soil permeability. Maximum %Na of 60% is recommended for irrigation water. %Na in the analysed river water ranges between 15 and 44% in the post-monsoon, 24 and 80% in the pre-monsoon and 17 and 44% in the monsoon seasons. The plot of analytical data on Wilcox (1955) diagram relating EC and %Na placed the Subarnarekha River water under

Figure 12. Plot of %Na vs. EC (after Wilcox 1955).

excellent to good and good to permissible categories for irrigation uses (figure 12).

The relative abundance of alkaline earths ($\text{Ca}^{2+} + \text{Mg}^{2+}$) with respect to bicarbonate and carbonate also influences the suitability of water for irrigation uses. The excess of carbonates ($\text{CO}_3^{2-} + \text{HCO}_3^-$) over alkaline earths ($\text{Ca}^{2+} + \text{Mg}^{2+}$) in irrigation water may cause the complete precipitation of Ca and Mg as carbonates (Karanth 1989). The water with high RSC has high pH and land irrigated with such water becomes infertile owing to the deposition of sodium carbonate (Eaton 1950). Irrigation waters having RSC values $>5 \text{ meq l}^{-1}$ have been considered harmful to the growth of plants, while waters with RSC values above 2.5 meq l^{-1} are unsuitable for irrigation. A RSC value between 1.25 and 2.5 meq l^{-1} is considered as the marginal quality and value $<1.25 \text{ meq l}^{-1}$ as the safe limit for irrigation. The calculated RSC values in most of the analysed water samples are $<2.5 \text{ meq l}^{-1}$, suggesting marginal to safe quality of the Subarnarekha River water for irrigation use (table 1).

5. Conclusion

The hydro-geochemical study of the Subarnarekha River basin has been carried out to evaluate the

major-ion chemistry, solute acquisition processes, dissolved fluxes and suitability of river water for irrigation uses. The analytical result shows that the Subarnarekha water is alkaline in nature like other major Indian rivers. Ca^{2+} and Na^+ were the dominant cations, while HCO_3^- and Cl^- dominate in the anion chemistry of the Subarnarekha River water. Seasonality in the ionic concentration is related to the rainfall dilution and river flow regime. Increase in TDS and ionic concentrations during the pre-monsoon season may be attributed to enhancement in groundwater contribution during the low flow regime of summer months. The Subarnarekha River water chemistry is largely controlled by weathering of rocks with minor contribution from the atmospheric and anthropogenic sources. The high concentration of HCO_3^- and ($\text{Ca}^{2+} + \text{Mg}^{2+}$) and observed $\text{Ca}^{2+}/\text{Na}^+$, $\text{Mg}^{2+}/\text{Na}^+$, $\text{HCO}_3^-/\text{Na}^+$ and $\text{HCO}_3^-/\text{SiO}_2$ ratios suggest that the major-ion chemistry of the Subarnarekha River is essentially controlled by two-component mixing from the dissolution of silicates and carbonates. The high concentration of dissolved silica, low ratio of $(\text{Ca}^{2+} + \text{Mg}^{2+})/(\text{Na}^+ + \text{K}^+)$ and high $(\text{Na}^+ + \text{K}^+)/\text{TZ}^+$ ratio suggest significant contribution of dissolved ions from the silicate weathering. The water chemistry is largely undersaturated with respect to calcite and dolomite; however, most of the pre-monsoon water samples are supersaturated with respect to both. The supersaturation condition in pre-monsoon may be attributed to evaporation effects during the lean water level period which causes preferential extraction of Ca by precipitation. The chemical behaviour of the river water in the silicate systems demonstrates kaolinite as the possible mineral that is in equilibrium with the water. The Subarnarekha River annually delivered 1.477×10^6 ton of dissolved loads to the Bay of Bengal and the estimated chemical denudation rate of the catchment is $77 \text{ ton km}^{-2} \text{ yr}^{-1}$. The annual solute fluxes of the tributaries varied from a minimum of 0.016×10^6 ton (Sankh) to a maximum of 1.023×10^6 ton (Kharkai). The calculated parameters of SAR, %Na and RSC show that the Subarnarekha River water is of the 'excellent to good' category for irrigation and can be used to irrigate all soils for tolerant, semi-tolerant and sensitive crops.

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