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Hydrogeochemistry, Elemental Flux, and Quality Assessment of Mine Water in the Pootkee-Balihari Mining Area, Jharia Coalfield, India

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Abstract Ninety nine mine water discharge samples were collected and analyzed for pH, electrical conductivity (EC), major cations, anions, and trace metals in the Pootkee-Balihari coal mining area of the Jharia coalfield. The mines of the area annually discharge 34.80×10^6 m^3 of mine water and 39,099 t of solute loads. The pH of the analyzed mine waters ranged from 6.97 to 8.62. EC values ranged from 711 $\mu S\ cm^{-1}$ to 1862 $\mu S\ cm^{-1}$, and reflect variations in lithology, geochemical processes, and hydrological regimes in the mines. The cation and anion chemistry indicate the general ionic abundance as: $Mg^{2+} > Ca^{2+} > Na^+ > K^+$ and $HCO_3^- > SO_4^{2-} > Cl^- > NO_3^- > F^-$, respectively. Elevated SO_4^{2-} concentrations in the Gopalichuck, Kendwadih, and Kachhi-Balihari mine waters are attributed to pyrite weathering. The water quality assessment indicated that TDS, hardness, Mg^{2+}, and SO_4^{2-} are the major parameters of concern in the study area. Except for Fe, all of the measured metals in the mine water were well within the levels recommended for drinking water. With only a few exceptions, the mine water is of good to permissible quality and suitable for irrigation.

Keywords Elemental flux · Jharia · Mine water chemistry · Mine water quality · Pootkee-Balihari

Introduction

Mining threatens the quality and quantity of surface and ground water resources in many parts of India (Choubey 1991; Gupta 1999; Khan et al. 2005; Singh 1994, 1998; Singh et al. 2007, 2010; Tiwary 2001). Mining's impacts on the natural water environment may be observed throughout the life cycle of a mine and even long after mine closure (Younger et al. 2002). The potential impacts of mining on the water environment are: (1) disruption of hydrological pathways; (2) seepage of contaminated leachates into aquifers; (3) disposal of mine water, and; (4) depression of the water table around the dewatered zone. Disposal of mine water is a worldwide problem, at both underground and opencast workings (Pulles et al. 1995). The quality of such mine water depends largely on the chemical properties of the geological materials that it came into contact with (Thompson 1980). Higher dissolved ions usually cause such waters to be unsuitable for direct discharge into river systems and can limit other potential downstream uses.

Large volumes of water can be released from aquifers during opencast and underground coal mining operations. Even a few weight percent of sulphide minerals in coal or mine waste has the potential to generate acidic conditions and create significant environmental degradation (Gladney et al. 1983). However, many coal mines generate water with near-neutral pH, frequently with elevated levels of Ca, Mg, Na, SO_4, CO_3, and HCO_3.

A long history of unscientific exploitation of the Jharia coalfield has caused environmental problems, including water resource depletion and contamination (Choubey 1991; Choubey and Sankaranarayana 1990; Sarkar et al. 2007; Singh 1990; Tiwary 2001). Surface mine development and underground mine workings below the

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piezometric level invariably changes the hydraulic gradient, affecting ground and surface water flow regimes vis-à-vis their quality and quantity in this coalfield. The quality of the discharged mine water depends on geological, hydrological, and mining conditions, which vary significantly from mine to mine (Singh et al. 2010; Younger and Wolkersdorfer 2004). We conducted a qualitative and quantitative assessment of mine water discharges from mines of the Pootkee-Balihari (P.B.) mining area in the Jharia coalfield to evaluate mine water chemistry, solute acquisition process, elemental flux, and water quality relative to domestic and irrigation uses.

Study Area

This study was confined to the P.B. mining area of the Jharia coalfield, in the eastern part of India. The Jharia coalfield (JCF) is India's largest and most extensively developed coalfield, and has been mined for more than a century. It is India's sole repository of much-needed coking coal. The Jharia coalfield is located in the Dhanbad district of Jharkhand state, occupying an area of 450 km^2 around Jharia, and is bounded by 23°37′N to 23°52′N latitudes and 86°09′E to 86°30′E longitudes (Fig. 1). The sedimentary rocks of the coalfield represent the Damuda Group of the Gondwana Supergroup, an Upper Palaeozoic-Mesozoic sequence of glaciofluviatile origin. Rocks of the Damuda Group unconformably overlie the Precambrian gneiss and schist and are pierced by igneous intrusives of Mesozoic-Tertiary age. The Gondwana sequence in the Jharia basin begins with the Talchir Formation, which is followed stratigraphically upwards by the Barakar, Barren Measures, and Raniganj Formations. The Barakars are economically the most important member of the Gondwana Group as they contain a number of thick, good quality coal seams. Two phases of deformation accompanied by igneous intrusion are believed to have occurred in this basin. The earlier (Lower Cretaceous) phase led to the intrusion of mica peridotite and the later (Palaeocene) one resulted in dolerite intrusion. The mica-peridotite occurs as dykes and sills all over the coalfield and has caused extensive devolatilization of the coal seams (Sharma and Ram 1966).

The P.B. mining area is located in the east central part of the Jharia coalfield and covers an area of 14.28 km^2 (Fig. 1). There are nine active underground coal mines in this area: (1) Gopalichuck; (2) Kendwadih; (3) Pootkee; (4) Kachhi-Balihari 5/6 pit (K.B.5/6); (5) Kachhi-Balihari 10/12 pit (K.B. 10/12); (6) South-Balihari (S.B.); (7) Pootkee-Balihari (P.B.) Project; (8) Aralgaria, and; (9) Bhagaband. The P.B. block exhibits geological characteristics that are markedly different from the generalized features of the basin described above. The P.B. mining area is mostly covered by the rocks of the Barakar Formation of the Damuda Group and Post-Gondwana igneous intrusive, apart from soil and alluvium of the Recent era, lying engulfed in the Precambrian metamorphics. The area is mostly under soil cover; the rock exposures are mainly along flowing streams. The coal-bearing Barakar Formation comprises essentially felspathic sandstones of pebbly to very fine grain sizes with colors varying from white/grey to yellowish. The other lithological units are argillaceous and carbonaceous sandstones, arenaceous shale, intercalations of shale and sandstone, carbonaceous shales, and coal

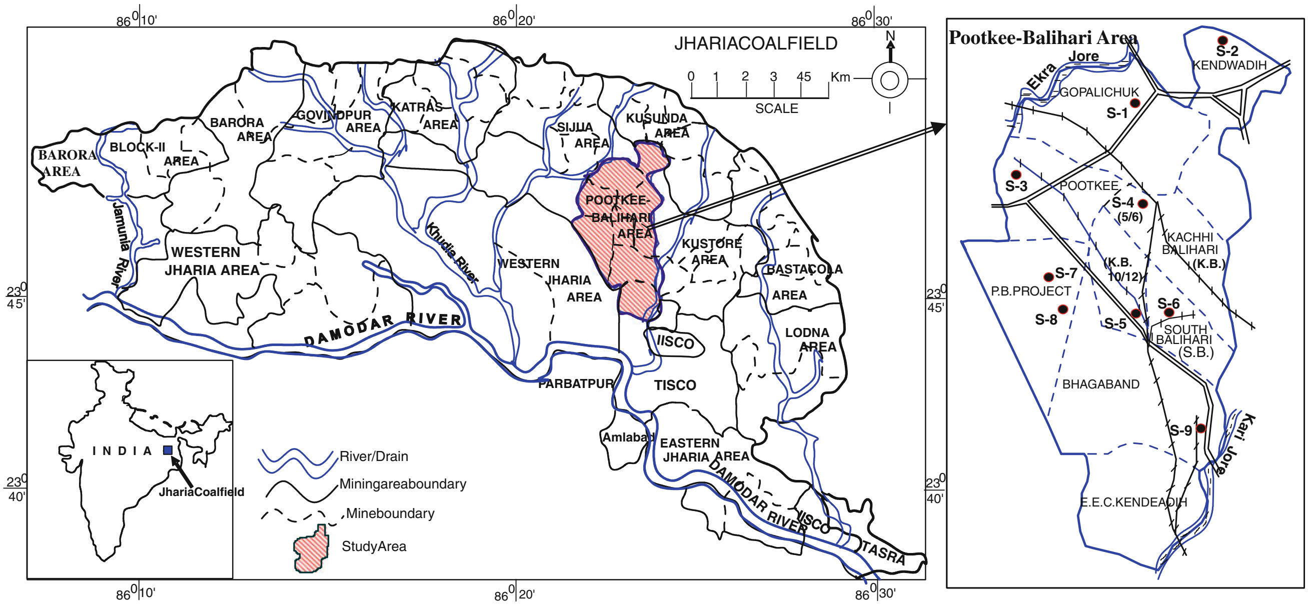

Fig. 1 Location map of the Pootkee-Balhari (P.B) mining area in Jharia coalfield, showing sampling sites

seams. The ultrabasic igneous intrusive commonly referred as 'mica-lamprophyre' rocks occur as dykes, sills, or as small intrusions, and is characterized by an abundance of ferro-magnesium minerals like biotite, hornblende, augite, and olivine. These tend to weather, producing carbonates and other alteration product like serpentine, chlorite, and kaolin (Chandra 1992; Sharma and Ram 1966).

The study area lies in the tropical region; the climate is characterized by very hot summers (up to 44°C during May–June) and cold winters (5–7°C in December–January). The average annual rainfall of the area is 1,281 mm and more than 85% of the annual rainfall occurs during the four monsoon months (June to September). The drainage pattern is mainly dendritic to sub-dentritic in nature. The P.B. area is bounded by two small streams, by Ekra jore in the northwest and by Kari jore in the southeast; the Damodar River traverses the southern part of the coal field, flowing due east for a distance of 2 km.

Materials and Methods

Ninety-nine representative mine water samples were collected from the nine underground coal mines of the P.B. mining area during 2008 and 2009 (Fig. 1). The samples were collected in 1 L pre-washed high density narrow-mouth polyethylene bottles. For trace metal analysis, 100 mL samples were acidified with HNO_3 and preserved separately. Electrical conductivity (EC) and pH values were measured in the field using a portable conductivity and pH meter. In the laboratory, the water samples were filtered through 0.45 μm Millipore membrane filters to separate suspended particles. Acid titration and molybdosilicate methods were used to determine the concentration of bicarbonate and dissolved silica, respectively, in the mine water samples (APHA.AWWA.WPCF 1995). Major anions (F^-, Cl^-, SO_4^{2-}, NO_3^-) were analyzed with an ion chromatograph (Dionex DX-120) using AS12A/AG12 columns coupled to an anion self-regenerating suppressor (ASRS) in recycle mode. Concentration of major cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) were determined using atomic absorption spectrophotometry (Varian 680-FS) in flame mode at the recommended wavelength. The analytical precision was maintained by running a known standard after every 15 samples. The overall precision (expressed as percent relative standard deviation, RSD) was below 5% for all samples. Concentration of trace metals in acidified mine water samples were determined by ICP-MS (Perkin Elmer). The accuracy of the analysis was checked by analyzing the NIST 1643b water reference standard. The precision in most cases was better than 5% RSD, with comparable accuracy.

Results and Discussion

Mine Water Chemistry

The geochemistry of the mine water samples for the different mines of the P.B. mining area are summarized in Table 1. Individual sample analyses for the same parameters and concentrations of trace metals are accessible as supplemental files (ESM, Tables 2, 3) in the on-line version of this journal.

The pH of the mine water samples ranged from 6.97 to 8.62, averaging 7.93. The EC values ranged from 711 μS cm^{-1} to 1862 μS cm^{-1}; the average EC value was 1,161 μS cm^{-1}. Total dissolved solids (TDS), which is the sum of the dissolved ion concentrations, ranged between 512 and 1,341 mg L^{-1} (avg. 836 mg L^{-1}). The spatial variation shows higher EC and TDS values for the Gopalichuck and K.B. (5/6) mine water samples and relatively low values for the S.B. and P.B. mines. No significant temporal variations in the ionic concentrations were observed during monitoring. However, large spatial variations in EC, TDS, and concentration of dissolved ions were observed in the P.B. mining area, which can be attributed to variations in lithology, geochemical processes, and the prevailing hydrological condition of the mines.

Bicarbonate (HCO_3^-) and sulphate (SO_4^{2-}) are the dominant anions in these mine waters, with minor contributions from chloride (Cl^-), fluoride (F^-), and nitrate (NO_3^-). Concentration of HCO_3^- ranged from 159 mg L^{-1} to 667 mg L^{-1}; the average HCO_3^- concentration was 472 mg L^{-1}. In equivalent units, HCO_3^- is contributing 54.7% to the total anionic (TZ^-) mass balance in the P.B. area mine waters (Fig. 2a). Concentrations of HCO_3^- exceeded sulphate concentrations and were relatively high in the Pootkee, K.B. (10/12), S.B., P.B. Project, Aralgaria, and Bhagaband mine water samples. HCO_3^- are derived mainly from soil zone CO_2, dissolution of carbonates, and reaction of silicates with carbonic acid. The soil zone in the subsurface environment contains elevated CO_2 pressure (produced by decay of organic matter and root respiration), which in turn combines with rainwater to form bicarbonate (Appelo and Postma 1993).

Sulphate in the mine water of the P.B. area ranged from 18 to 768 mg L^{-1} (avg. 284 mg L^{-1}) and accounted for 33.3% of the TZ^- (Fig. 2a). The average concentration of SO_4^{2-} was 1.4–1.7 times higher than the HCO_3^- in the mine water of the Gopalichuck, Kendwadih, and K.B. (5/6) mines. Sulphate in water is usually derived from the oxidative weathering of sulphide-bearing minerals like pyrite (FeS_2), and dissolution of gypsum ($CaSO_4 \cdot 2H_2O$) or anhydrite ($CaSO_4$). Jharia coals usually contain less than 1% sulphur (Chandra 1992). Pyrite commonly occurs as a secondary mineral in the coals and associated sediments in

Table 1 Statistical summary of measured parameters in mine water of P.B. mining area

Mine name	Stat.	pH	EC	TDS	F^-	Cl^-	HCO_3^-	SO_4^{2-}	NO_3^-	Si	Ca^{2+}	Mg^{2+}	Na^+	K^+	TH
Gopalichuck (S-1)	Min.	7.1	1,453	1,046	0.25	40.6	339	569	0.0	12.6	80.3	133.7	28.8	5.6	839
	Max.	8.5	1,773	1,277	1.61	64.4	479	767	15.4	25.0	157.8	187.6	39.8	7.3	1,082
	Avg.	7.8	1,594	1,148	0.74	49.5	436	670	2.6	18.2	123.7	154.3	32.6	6.5	944
	S.D.	0.41	107	77	0.38	6.4	42	64	4.8	4.1	20.3	16.6	3.5	0.5	77
Kendawadih (S-2)	Min.	7.0	713	513	0.41	40.4	159	107	3.3	17.2	48.9	30.0	22.0	9.5	246
	Max.	8.2	1,168	841	1.14	51.7	278	495	65.2	31.5	100.8	101.5	36.2	18.5	658
	Avg.	7.7	997	718	0.91	46.1	223	372	18.0	22.1	77.4	77.2	28.7	13.1	511
	S.D.	0.37	134	96	0.27	3.8	36	104	17.6	3.7	15.6	20.0	4.2	2.7	110
Pootkee (S-3)	Min.	7.5	1,128	812	0.32	42.7	484	162	0.0	15.2	64.5	94.4	34.2	5.2	564
	Max.	8.4	1,373	989	3.06	68.7	594	414	10.5	25.1	110.6	149.9	46.7	9.5	777
	Avg.	7.9	1,257	905	1.11	55.2	545	285	2.0	18.9	83.0	112.0	40.7	6.6	668
	S.D.	0.29	91	65	0.75	8.0	32	76	3.1	3.6	13.6	16.7	3.4	1.3	67
K.B. (5/6) (S-4)	Min.	7.30	1,557	1,121	0.27	33.7	293	568	0.0	14.8	80.3	145.3	29.1	5.3	923
	Max.	8.4	1,862	1,341	1.66	45.0	589	768	3.0	24.3	171.6	197.5	36.2	10.0	1,206
	Avg.	7.8	1,694	1,220	0.76	40.8	512	664	0.6	18.9	143.3	168.3	32.6	8.4	1,050
	S.D.	0.36	110	79	0.38	3.5	80	62	1.2	2.7	27.9	18.4	2.3	1.2	101
K.B. (10/12) (S-5)	Min.	7.5	959	690	0.38	35.2	414	110	0.0	14.4	37.8	67.7	29.8	4.4	448
	Max.	8.5	1,604	1,155	1.40	65.8	586	653	11.7	26.6	103.3	154.5	44.7	10.0	879
	Avg.	7.9	1,178	848	0.82	55.7	513	249	4.0	19.9	66.5	106.3	37.5	6.7	603
	S.D.	0.29	210	151	0.31	8.5	49	185	4.6	4.2	22.5	29.6	4.7	1.5	167
S.B. (S-6)	Min.	7.2	711	512	0.51	50.4	383	18	0.6	15.7	40.4	46.9	25.3	5.3	295
	Max.	8.4	836	602	1.32	74.3	473	76	10.7	27.6	52.1	68.8	41.2	11.9	400
	Avg.	8.0	780	562	0.84	64.8	417	50	4.5	20.9	46.3	60.2	33.0	8.9	363
	S.D.	0.41	46	33	0.25	7.2	31	18	2.5	3.4	4.3	7.1	3.8	1.7	33
P.B. Project (S-7)	Min.	7.8	721	519	0.49	47.4	400	26	0.0	15.1	29.1	55.9	32.9	6.7	326
	Max.	8.6	889	640	1.60	70.1	452	78	17.8	25.4	53.8	78.3	42.3	14.1	434
	Avg.	8.3	788	567	0.86	59.3	423	53	4.6	20.1	40.9	68.1	36.5	8.9	382
	S.D.	0.27	49	35	0.34	6.3	16	16	4.9	3.1	6.4	8.0	2.9	2.3	38
Aralgaria (S-8)	Min.	7.2	937	675	0.31	34.6	553	63	0.0	14.1	36.3	72.7	54.7	4.3	413
	Max.	8.6	1,306	940	1.60	53.6	667	134	48.3	25.3	74.5	103.6	76.9	12.0	610
	Avg.	7.9	1,105	796	0.79	42.9	614	104	8.6	17.9	58.9	89.4	67.4	5.7	515
	S.D.	0.37	332	239	0.41	10.1	119	243	9.9	3.7	37.3	39.9	12.4	2.8	246
Bhagaband (S-9)	Min.	7.6	942	678	0.52	39.0	537	79	0.0	19.3	29.7	80.4	38.6	3.4	405
	Max.	8.4	1,126	811	2.09	68.7	606	145	14.5	39.1	61.8	110.7	61.9	8.5	595
	Avg.	8.0	1,060	763	0.97	56.7	569	107	4.8	25.5	47.8	95.8	46.9	6.5	513
	S.D.	0.30	66	48	0.47	10.3	27	19	3.6	5.6	9.2	11.2	8.4	1.7	57

Unit mg L^{-1}, except pH and EC (μS cm^{-1}); *EC* Electrical conductivity, *TDS* Total dissolved solids, *TH* Total hardness

this coalfield, and the elevated concentrations of SO_4^{2-} in the mine water is attributed to pyrite weathering (Lowson et al. 1993). The low ($HCO_3/HCO_3 + SO_4$) equivalent ratio for Gopalichuck (0.34), Kendwadih (0.33), and K.B. 5/6 (0.38) mine water also suggest oxidation of sulphides as a major proton producer for further chemical reactions (Singh and Hasnain 2002; Singh et al. 2007).

Chloride concentrations in the analyzed mine water samples ranged from 33.7 to 74.3 mg L^{-1}, with an average value of 52.3 mg L^{-1}. The Cl^- concentrations did not show much spatial variation and contributes 11% to the total anionic balance (Fig. 2a). Fluoride concentrations in the analyzed mine water sample ranged from 0.25 to 3.06 mg L^{-1} (avg. 0.87 mg L^{-1}), accounting for <1.0% of the total anionic balance (Fig. 2a). Concentration of F^- exceeds WHO (1997) drinking water desirable limits of 1.2 mg L^{-1} in 5% of the mine water samples. This may be due to the weathering of fluoride-bearing minerals like biotite, muscovite, fluorite, and apatite, which occur as accessory minerals in the granites, granitic gneisses, and

Table 2 Annual mine water discharge and elemental flux estimated for different mines of the P.B. area

Mine name	Lease area (km^2)	Annual discharge ($\times 10^6$ m^3)	Annual elemental and total solute flux (Tonnes yr^{-1})									
			F^-	Cl^-	HCO_3^-	SO_4^{2-}	NO_3^-	Si	Ca^{2+}	Mg^{2+}	Na^+	K^+	Total solute
Gopalichuck	2.22	9.435	6.98	467	4,114	6,321	24.5	172	116	1,456	308	61	1,409
Pootkee	1.53	1.415	1.57	78	771	403	2.8	27	117	158	58	9	1,627
K.B. (5/6)	1.30	3.494	2.66	143	1,789	2,320	2.1	66	501	588	114	29	5,554
K.B. (10/12)	0.56	4.299	3.53	239	2,205	1,070	17.2	86	286	457	161	29	4,554
S.B. (5/7)	0.84	3.459	2.91	224	1,442	173	15.6	72	160	208	114	31	2,444
P.B. Project	2.30	5.602	4.82	332	2,370	297	25.8	113	229	381	204	50	4,007
Bhagaband	3.52	7.093	6.88	402	4,036	759	34.0	181	339	680	333	46	6,816
Total	14.28	34.80	29.3	188	16,727	1,1344	122	71	279	3,92	129	25	39,099

Table 3 Statistical summary of measured parameters in mine water, compared to prescribed limits of WHO (1997) and Indian standards (BIS 1991) for drinking water

Parameters	Minimum	Maximum	Average	WHO (1997)		BIS (1991) IS:10500	
				Maximum desirable	Highest permissible	Maximum desirable	Highest permissible
Major ions (mg L^{-1})							
pH	6.97	8.62	7.93	7.0–8.5	6.5–9.2	6.5–8.5	8.5–9.2
EC	711	1,862	1,161	750	1,500	–	–
TDS	512	1,341	836	500	1,500	500	2,000
F^-	0.25	3.06	0.87	0.6-0.9	1.5	1.0	1.5
Cl^-	33.7	74.3	52.3	250	600	250	1,000
HCO_3^-	159	667	472	200	600	200	600
SO_4^{2-}	18	768	284	200	600	200	400
NO_3^-	0.0	65.2	5.6	–	50	45	100
Silica	12.6	39.1	20.3	–	–	–	–
Ca^{2+}	29.1	171.6	76.4	75	200	75	200
Mg^{2+}	30	197.5	103.5	30	150	30	100
Na^+	22	76.9	39.5	50	200	–	–
K^+	3.4	18.5	7.9	100	200	–	–
TH	246	1,206	617	100	500	300	600
Trace Metals (μg L^{-1})							
B	17	120	45	500		1,000	5,000
Cr	4.9	14.7	9.6	50		50	No relaxation
Mn	10	279	50	500		100	300
Fe	219	838	398	300		300	1,000
Ni	1.7	24.4	9.5	20		–	–
Co	0.14	1.29	0.51	–		–	–
Cu	1.4	17.4	9.0	2,000		50	1,500
Zn	2.1	1,294	83.6	4,000		5,000	15,000
As	0.20	1.65	0.63	10		50	No relaxation
Se	0.20	5.20	1.38	10		10	No relaxation
Cd	0.01	10.0	0.46	3.0		10	No relaxation
Pb	2.3	32.6	11.27	10		50	No relaxation
Ba	21	5,515	668	700		–	–
Ag	0.07	10.04	0.86	–		–	–

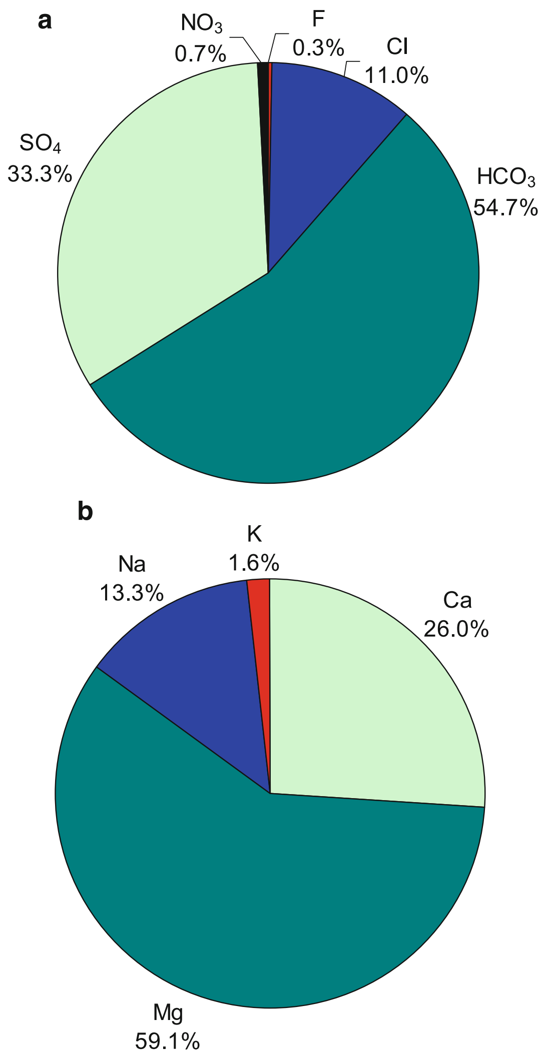

Fig. 2 Pie diagram for **a** anions and **b** cations, showing contribution of individual ions towards the total anionic (TZ^-) and cationic (TZ^+) mass balance

intrusive rocks of the area. Concentrations of nitrate in the mine water of the study were found to be low except for the Kendawadih mine water. NO_3^- concentration ranged from 0.0 to 65.2 mg L^{-1}, and the average concentration value was 5.6 mg L^{-1}, contributing <1.0% of the total anionic balance. The chief sources of nitrate in water are biological fixation, atmospheric precipitation, fertilizers, and industrial sewage (Appelo and Postma 1993).

Magnesium (Mg^{2+}) and calcium (Ca^{2+}) dominate the cation chemistry in the P.B. area mine water; the average cation concentration trend was: $Mg^{2+} > Ca^{2+} > Na^+ > K^+$. Weathering of rock-forming minerals and ion exchange processes normally control the levels of these cations in the mine water (Younger et al. 2002). Concentrations of Mg^{2+} ranged from 30.0 mg L^{-1} to 197.5 mg L^{-1} with an average value of 103.5 mg L^{-1}. On average, Mg^{2+} accounts for 59% (37–72%) of the total cations (TZ^+), in equivalent units (Fig. 2b). The spatial variation of Mg^{2+} concentration was higher in the Gopalichuck and K.B. (5/6) and lower in the mine water of the S.B. and P.B. Project mines. The presence of Ca^{2+} and Mg^{2+} makes the water hard. Concentration of Ca^{2+} in the mine waters of the P.B. mining area ranged from 29.1 mg L^{-1} to 171.6 mg L^{-1}, with an average of 76.4 mg L^{-1}, and accounts for 26% (14–38%) of the TZ^+ (Fig. 2b). High concentration of Mg^{2+} and Ca^{2+} in the waters is due to weathering of Mg-rich calcite/dolomite and Ca–Mg silicates (amphiboles, pyroxenes, olivine, and biotite). Furthermore, the high concentration of Mg^{2+}, high Mg^{2+}/Ca^{2+}, $SiO_2/(Na + K–Cl)$ and $Mg/(Ca + Mg)$ ratios in a number of the samples suggest significant contribution from weathering of ferromagnesian minerals (Hounslow 1995). The combination of high concentrations of Ca^{2+}, Mg^{2+}, HCO_3^-, and SO_4^{2-}, and the wide variation (0.28–0.96) in the $HCO_3:(HCO_3 + SO_4)$ ratio in the P.B. area mine water suggests that coupled reactions involving sulphide oxidation and carbonate (calcite and dolomite) dissolution largely control the solute acquisition processes in the study area (Pandey et al. 2001; Singh et al. 2007).

The ferromagnesian minerals are associated with the basic and ultrabasic intrusive rocks of the area (Chandra 1992; Ghose 1983). Sodium ($Na^{+)}$ and potassium (K^+) together contributed 15% to the total cationic balance (Fig. 2b). Concentrations of Na^+ ranged from 22.0 mg L^{-1} to 76.9 mg L^{-1} (avg. 39.5 mg L^{-1}) and accounts for 13% (5–29%) of the total cations (TZ^+). The spatial variation of Na^+ concentration was relatively higher in the Aralgaria and Bhagaband mines than at the other sites. K^+ is ranged between 3.4 mg L^{-1} and 18.5 mg L^{-1} (avg. 7.9 mg L^{-1}) and accounts for <2% of the total cation load. Na^+ and K^+ in the water are mainly derived from atmospheric deposition, evaporite dissolution, and silicate weathering (Berner and Berner 1987). Relatively low concentrations of Na^+ and the high $Ca + Mg:Na + K$ ratio (6.9) suggests limited contribution from weathering of sodium and potassium silicates.

Table 3 in ESM shows the concentration of 20 trace metals analysed in the 27 mine water samples collected in the months of January and May, 2009, and July, 2010. Except for iron (Fe), concentrations of all the measured metals were within the levels recommended for drinking water by the Bureau of Indian Standards (BIS 1991) and the World Health Organisation (WHO 1997). The amount of Fe ranged from 219 to 838 μg L^{-1}, exceeding the desirable limit of 300 μg L^{-1} in 66% of the mine water samples. However, it was below the maximum permissible limit of 1,000 μg L^{-1} in all of the measured samples. The amount of highly toxic contaminants, like Cd, As, Se, and Pb, were all found to be well within the prescribed limits for drinking water. Higher concentrations of barium (Ba)

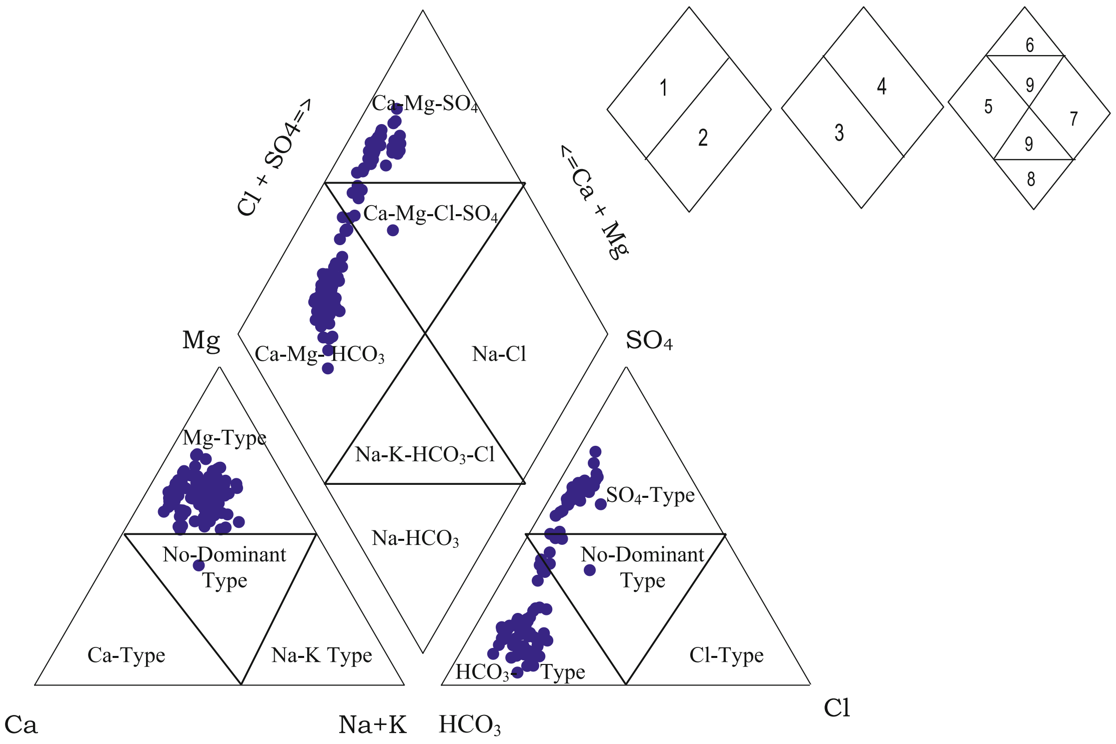

Fig. 3 Piper's trilinear diagram, showing the relationship between dissolved ions and water types (after Piper 1944)

were observed in the mine water of S.B. and P.B. Project mines, which may be attributed to local lithological sources. Barite ($BaSO_4$) is the main mineralogical source of Ba in water.

Geochemical Relationship and Water Type

A plot of the geochemical data on a Piper (1944) trilinear diagram using AquaChem software reveals that the majority of the plotted points fall in zones 1, 3, 4, 5, and 6 (Fig. 3). The points in region 1 signify the dominance of alkaline earths (Ca + Mg) over alkalies (Na + K) in the mine water of the study area. In the majority (66%) of the samples, weak acids (HCO_3) exceeds strong acids (SO_4 + Cl) and plotted points fall in zone 3. In 34% of the mine water samples, strong acids (SO_4 + Cl) exceeds weak acids (HCO_3) and plotted points fall in region 4. Plotted points of 66% samples fall in zone 5, indicating that carbonate hardness (secondary alkalinity) exceeds 50%, while in 27% of the mine water samples, non-carbonate hardness (secondary salinity) exceeds 50%, and plotted points fall in zone 6. Ca–Mg-HCO_3 and Ca–Mg-SO_4 are the two main types of water identified in the study area based on the concentration of major ions. The spatial distribution of water types in the P.B. mining area illustrated the dominance of Ca–Mg-SO_4 hydrochemical facies in the Kendwadih, Gopalichuck, K.B. (5/6) and Ca–Mg-HCO_3 facies in the Pootkee, K.B. (10/12), S.B., P.B. Project, and Bhagaband mines.

Mine Water Discharge and Elemental Fluxes

The annual mine water discharge, elemental flux, and total solute transport from each mine site has been estimated based on pumping details and discharge data provided by mining authorities and average concentrations of dissolved ions (Table 2). The mines of the Pootkee-Balihari area annually discharge about 34.8 × 10^6 m^3 of mine water into nearby waterways. The estimated annual discharge shows wide spatial variation: Pootkee discharges the least, 1.415 × 10^6 m^3 yr^{-1}, while Gopalichuck discharges 9.435 × 10^6 m^3 yr^{-1}.

The mines of the P.B. area annually delivers 39,099 tonnes (t) of solute loads and the solute delivery rate ranged from 1,627 t yr^{-1} (Pootkee) to 14,097 t yr^{-1} (Gopalichuck). The elemental flux data indicate that HCO_3^-, SO_4^{2-}, Mg^{2+}, Ca^{2+}, and Cl^- account for nearly 93% of the total solute fluxes (Fig. 4). The P.B. area mines annually deliver nearly 16,727 t of HCO_3^-, which accounts for 47.8% of the total annual solute fluxes. SO_4^{2-} constitutes 22.9% of the total annual solute fluxes, and the total sulphate transport by P.B. area mines is estimated at 11,344 t

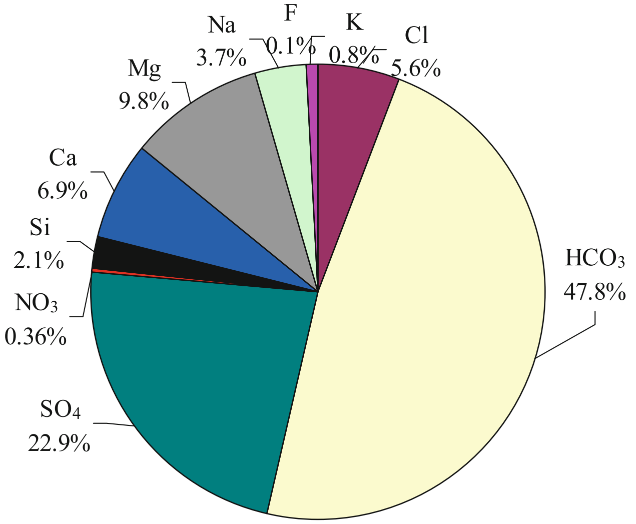

Fig. 4 Percent contribution of individual ions to the total solute flux from PB area mines

yr^{-1}. The SO_4^{2-} delivery rate is high for Gopalichuck (6,321 t yr^{-1}) and K.B. (5/6) mine (2,320 t yr^{-1}), compared to the HCO_3^- delivery rate of 4,114 and 1,789 t yr^{-1} for these two mines. Chloride constitutes 5.6% of the total solute fluxes, while F^- and NO_3^- together account only 0.5% of the total solute delivery. Mg^{2+} (9.8%), Ca^{2+} (6.9%), Na^+ (3.7%), and K^+ (0.8%) together account for 21.2% of the total annual solute fluxes; the delivery rates for these ions are estimated as 3,929, 2,799, 1,292, and 256 t yr^{-1}, respectively. The discharge of saline and high magnesium mine water in natural drains and irrigated land may affect the growth and yield of crops. A number of crops also show sensitivity to very high sulphate concentrations in irrigation water, but it is likely that this sensitivity is due to how high sulphate concentrations can limit the uptake of calcium by plants. This decrease in the uptake of calcium may be associated with relative increase in the absorption of sodium and potassium (Tiwari and Manzoor 1988).

Quality Assessment

To assess the suitability for drinking and domestic uses, the hydrochemical parameters of the mine water were compared with the prescribed specification of WHO (1997) and the Indian standard for drinking water (BIS 1991). Table 3 shows that TDS, total hardness (TH), Mg^{2+}, SO_4^{2-}, and Fe are the major objectionable parameters in the mine water of the study area. Carroll (1962) proposed four classes of water based on TDS as fresh (<1,000 mg L^{-1}), brackish (1,000–10,000 mg L^{-1}), saline (10,000–100,000 mg L^{-1}), and brine (>100,000 mg L^{-1}). By this criteria, 84% of the analyzed mine water samples fall in the fresh and 16% lie in the brackish water category. TDS exceeds the desirable limit of 500 mg L^{-1} in most of the mine water samples, indicating that the high concentrations of dissolved ions make it unsuitable for direct use for drinking purposes.

Sawyer and McCarty (1967) classified water as soft (<75 mg L^{-1}), moderately hard (75–150 mg L^{-1}), hard (150-300 mg L^{-1}), and very hard (>300 mg L^{-1}). Total hardness of the P.B. area mine water ranged from 246 to 1,206 mg L^{-1} (avg. 617 mg L^{-1}), which is hard to very hard water. The TH value exceeded the desirable limit of 300 mg L^{-1} in 56% of the samples and exceeded the maximum permissible limit of 600 mg L^{-1} in 38% of the mine water samples (BIS 1991). The spatial variation shows higher TH values for the water of the Gopalichuck, Kendwadih, and Pootkee mines and relatively lower values for the S.B. and P.B. Project mines. High TH may cause precipitation of calcium carbonate and encrustation in water supply distribution systems. Long-term consumption of extremely hard water might lead to an increased incidence of urolithiasis, anecephaly, parental mortality, some types of cancer, and cardio-vascular disorders (Agrawal and Jagetia 1997; Durvey et al. 1991).

High sulphate water has a bitter taste, while an excess of Mg may have a laxative effect. Concentration of SO_4^{2-} and Mg^{2+} exceeded the maximum permissible limit of 400 and 100 mg L^{-1} in about 30% and 41% of the mine water samples, respectively. Most of the mine water samples collected from the mines of the Gopalichuck, K.B. (5/6) and Kendwadih had high SO_4^{2-} and Mg^{2+} content and are unsuitable for direct use in drinking and domestic purposes. Sulphate causes odour and corrosion of sewers because it gets converted to hydrogen sulphide. It may also cause corrosion of metals in the distribution system, particularly in water with low alkalinity. Except for a few samples, concentrations of NO_3^- and F^- did not exceed the prescribed limit.

The suitability of water for irrigation depends on the total salt content of the water. Plants take in water from soil by osmotic pressure, so the salt content of the water affects the growth of plants, soil structure, and soil permeability (Ayers and Westcot 1985). The general criteria used for judging the suitability of water for irrigation are: (1) total salt concentration measured as electrical conductivity (EC), (2) relative proportion of sodium to other cations, expressed as sodium adsorption ratio (SAR), percent sodium (%Na), and (3) excess of carbonate over calcium and magnesium. EC and Na concentration are very important in classifying irrigation water. The salinity or salt concentration in irrigation water can be expressed as low (EC < 250 µS cm^{-1}), medium (250–750 µS cm^{-1}), high (750–2,250 µS cm^{-1}), and very high (2,250–5,000 µS cm^{-1}). High salinity in water leads to formation of saline soil and high sodium concentrations develops alkaline soil. The sodium or alkali hazard in irrigation water is expressed

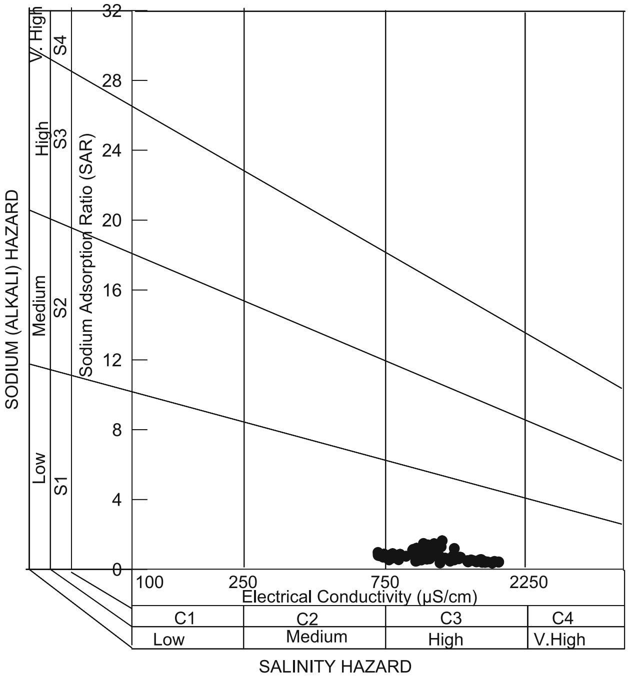

Fig. 5 U.S. salinity diagram for classification of irrigation waters (after Richards 1954)

in terms of the sodium adsorption ratio (SAR) and can be estimated by the formula $Na^+/(Ca^{2+}+Mg^{2+}/2)^{0.5}$. Irrigation waters are classified into four categories (S_1–S_4) on the basis of SAR: low (0–10), medium (10–18), high (18–26), and very high (>26) (Richards 1954). The plot of mine water data on the U.S. salinity diagram illustrate that the plotted points of majority of the samples fall in the field C_3S_1, i.e. high salinity and low alkalinity, while a few of the samples lie in the C_2S_1 zone, i.e. medium salinity and low alkalinity (Fig. 5). Medium salinity and low alkali water can be used for irrigation on almost all soils, with little danger of developing harmful levels of exchangeable Na. However, high salinity water (C_3) cannot be used on soils with restricted drainage. Even with adequate drainage, special management for salinity control may be required and plant with good salt tolerance should be selected (Karanth 1989).

Percent sodium [i.e. Na + K/(Ca + Mg + Na + K)×100] is widely used for evaluating the suitability of water quality for irrigation (Wilcox 1955). Excess sodium in irrigation water causes exchange of Na^+ in water for Ca^{2+} and Mg^{2+} in soil and produces undesirable effects on soil properties, including reductions in soil permeability. Percent sodium (%Na) in the P.B. area mine water ranged from 16.6 to 52.9% (avg. 43.6%), within the recommended value of 60% for irrigation (BIS 1991). Plotting the mine water data on a Wilcox diagram, which is based on EC and %Na, indicates that the water is good or good to permissible, suggesting that the mine water of the study area can be safely used for irrigation (Fig. 6). In addition to SAR and %Na, the excess of carbonates ($HCO_3 + CO_3$) in water over the alkaline earths (Ca + Mg) also influences the suitability of water for irrigation. This excess carbonate is denoted as ‘residual sodium carbonate’ (RSC) and computed by the equation RSC = ($CO_3 + HCO_3$) − (Ca + Mg). When the excess of carbonate concentration becomes too high, then carbonates combine with calcium and magnesium to form a solid scale, which settles out of the water (Raghunath 1987). A high value of RSC in water leads to an increase in the adsorption of sodium on soil (Eaton 1950). Irrigation waters having RSC values greater than 5 meq L^{-1} have been considered harmful to the growth of plants, while waters with RSC values above 2.5 meq L^{-1} are not suitable for irrigation purpose. In most of the analysed water samples, RSC values are below 5.0 meq L^{-1}; however, about 40% of the mine water samples, especially those collected from the P.B. Project, Aralgaria, Bhagaband, and K.B. (10/12) sites, have RSC values >2.5 meq L^{-1}, suggesting marginal suitability for irrigation uses.

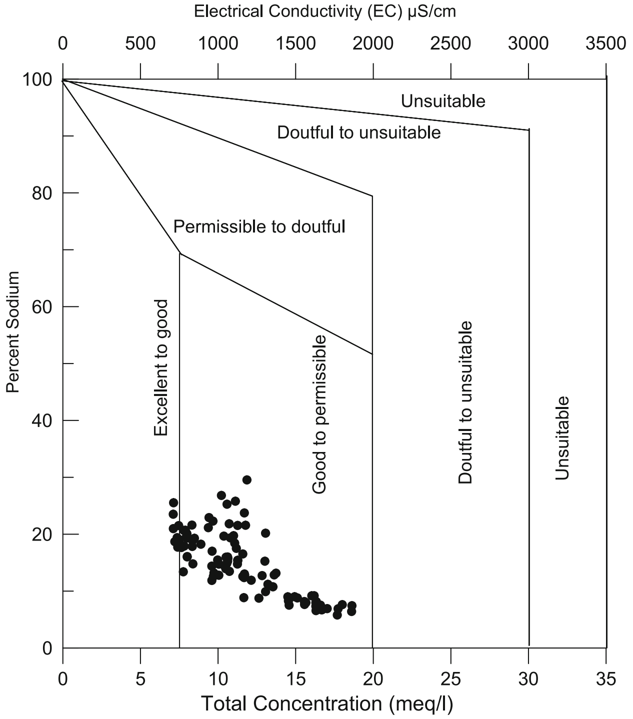

Fig. 6 Classification of irrigation water based on percent sodium and electrical conductivity (after Wilcox 1955)

Conclusions

The mine water of the P.B mining area is neutral to alkaline in nature. Ca^{2+} and Mg^{2+} are the dominant cations, while

HCO_3^- and SO_4^{2-} dominate the anionic composition. SO_4^{2-} exceeds HCO_3^- concentrations in the Gopalichuck, Kendwadih, and K.B. (5/6) mine water. Weathering of rock forming minerals and ion exchange processes are the major controlling factors for mine water chemistry. The combination of high concentrations of Ca^{2+}, Mg^{2+}, HCO_3^- and SO_4^{2-}, and wide variation in the HCO_3:(HCO_3 + SO_4) ratio suggest that coupled reactions involving sulphide oxidation and carbonate dissolution control the solute acquisition processes in the study area. Ca–Mg-HCO_3 and Ca–Mg-SO_4 are the two major identified hydrochemical facies in the mine water samples.

The mines of the P.B. mining area annually discharge about 34.80 x10^6 m^3 of mine water and 39,099 t of solute loads into nearby waterways. HCO_3^-, SO_4^{2-}, Mg^{2+}, Ca^{2+} and Cl^- account for nearly 93% of the total annual solute fluxes. TDS, hardness, Mg^{2+}, and SO_4^{2-} are the major objectionable parameters in the mine waters for domestic uses. Except for Fe, all of the measured metals in the mine water were well within the levels recommended for drinking water. The assessment of mine water for irrigation reveals that the water is good to permissible quality and can be used for irrigation with a few exceptions, where high salinity and residual sodium carbonate restrict suitability of the water for irrigation, and demands suitable water management and treatment.

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